Supplementary Material

Title: **Benchmarking DFT approximations for studying apatites**

1 Initial Co-ordinates

This section contains the initial coordinates [1] for Hydroxyapatite (HAP), Fluorapatite (FAP) and Chlorapatite (ClAP) along with their cell parameters, which have been used in our study.

1.1 Initial Coordinates of Hydroxyapatite (HAP)

ATOMIC_POSITIONS {angstrom}

Ca	4.708347	2.718311	0.009899
Ca	4.708253	2.718311	3.427351
Ca	0.000047	5.436704	3.447149
Ca	0.000000	5.436622	6.864601
Ca	8.191500	2.014778	1.718625
Ca	2.357399	0.053578	1.718625
Ca	2.350901	8.101436	5.155875
Ca	1.132299	2.068356	5.155875
Ca	3.576001	6.086658	1.718625
Ca	−3.483200	6.140237	5.155875
P	1.593948	3.251078	1.718625
P	−2.689758	5.149076	1.718625
P	7.398058	3.005938	5.155875
P	3.612490	0.245140	5.155875
P	1.095810	7.909875	1.718625
P	3.114352	4.903937	5.155875
O	3.018491	2.682184	1.718625
O	5.521894	4.199833	1.718625
O	−0.813594	3.955182	5.155875
O	−0.876215	6.882017	5.155875
O	5.584515	1.272998	1.718625
O	1.689809	5.472830	5.155875
O	1.613534	4.787809	1.718625
O	−1.368703	4.363748	1.718625
O	6.077003	3.791266	5.155875
O	4.953132	0.996543	5.155875
O	−0.244832	7.158472	1.718625
O	3.094766	3.367206	5.155875
O	0.812182	2.801248	0.483277
O	−2.688439	6.051021	2.953973
O	7.396739	2.103994	3.920527
O	2.832042	0.697254	6.391223
O	1.876258	7.457761	0.483277
O	0.812182	2.801248	2.953973
O	3.896118	5.353767	3.920527
O	7.396739	2.103994	6.391223

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O      −2.688439    6.051021    0.483277
O       1.876258    7.457761    2.953973
O       2.832042    0.697254    3.920527
O       3.896118    5.353767    6.391223
O       0.000000    0.000000    2.076786
O       0.000000    0.000000    5.514036
H       0.000000    0.000000    3.162270
H       0.000000    0.000000    6.599520

CELL_PARAMETERS {angstrom}
   9.416600    0.000000    0.000000
  −4.708300    8.155015    0.000000
   0.000000    0.000000    6.874500
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1.2 Initial Coordinates of Fluorapatite (FAP)

```
ATOMIC_POSITIONS (angstrom)
Ca      4.698697    2.712740    0.006878
Ca      4.698603    2.712740    3.432222
Ca      0.000047    5.425561    3.445978
Ca     −0.000000    5.425479    6.871322
Ca      8.192049    1.971666    1.719550
Ca      2.310138    0.057945    1.719550
Ca      2.388512    8.080356    5.158650
Ca      1.104888    2.029611    5.158650
Ca      3.593762    6.108690    1.719550
Ca     −3.493399    6.166634    5.158650
P       1.594722    3.243113    1.719550
P      −2.687393    5.135675    1.719550
P       7.386043    3.002626    5.158650
P       3.605979    0.240487    5.158650
P       1.092671    7.897814    1.719550
P       3.103928    4.895188    5.158650
O       3.018883    2.663666    1.719550
O       5.496011    4.192039    1.719550
O      −0.797361    3.946262    5.158650
O      −0.882406    6.855704    5.158650
O       5.581056    1.282596    1.719550
O       1.679767    5.474635    5.158650
O       1.625263    4.781252    1.719550
O      −1.370596    4.340156    1.719550
O       6.069246    3.798145    5.158650
O       4.953317    0.983107    5.158650
O      −0.254667    7.155194    1.719550
O       3.073387    3.357049    5.158650
O       0.812397    2.784113    0.484913
O      −2.693736    6.042688    2.954187
O       7.392386    2.095612    3.924013
O       2.817311    0.688500    6.393287
O       1.881339    7.449800    0.484913
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O       0.812397    2.784113    2.954187
O       3.886253    5.354188    3.924013
O       7.392386    2.095612    6.393287
O      -2.693736    6.042688    0.484913
O       1.881339    7.449800    2.954187
O       2.817311    0.688500    3.924013
O       3.886253    5.354188    6.393287
F       0.000000    0.000000    1.719550
F       0.000000    0.000000    5.158650

CELL_PARAMETERS {angstrom}
   9.397300    0.000000    0.000000
  -4.698650    8.138301    0.000000
   0.000000    0.000000    6.878200
```

1.3 Initial Coordinates of Chlorapatite (ClAP)

```
ATOMIC_POSITIONS {angstrom}
Ca      4.796502        2.769259        0.020972
Ca      -0.000002       5.538523        3.409122
Ca      -0.000002       5.538523        6.755328
Ca      4.796502        2.769259        3.367178
Ca      -1.159652       2.135769        1.694075
Ca      3.526694        6.235607        1.694075
Ca      -2.367043       8.244181        1.694075
Ca      5.956152        6.172013        5.082225
Ca      1.269806        2.072175        5.082225
Ca      7.163543        0.063601        5.082225
P       1.650138        3.393257        1.694075
P       1.032790        8.040212        1.694075
P       -2.682926       5.182095        1.694075
P       3.146362        4.914525        5.082225
P       3.763710        0.267570        5.082225
P       7.479426        3.125687        5.082225
O       3.095766        2.844666        1.694075
O       5.581574        1.258683        1.694075
O       5.712162        4.204442        1.694075
O       1.700734        5.463116        5.082225
O       -0.785074       7.049098        5.082225
O       -0.915662       4.103340        5.082225
O       1.633718        4.957823        1.694075
O       -0.313961       7.243720        1.694075
O       -1.319765       4.414027        1.694075
O       3.162782        3.349958        5.082225
O       5.110461        1.064062        5.082225
O       6.116265        3.893755        5.082225
O       0.852387        2.936037        0.441343
O       1.827622        7.577952        0.441342
O       -2.680010       6.101574        0.441342
O       3.944113        5.371745        3.829493
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O       2.968878        0.729830        3.829492
O       7.476510        2.206208        3.829492
O       3.944113        5.371745        6.334957
O       2.968878        0.729830        6.334958
O       7.476510        2.206208        6.334958
O       0.852387        2.936037        2.946807
O       1.827622        7.577952        2.946808
O      -2.680010        6.101574        2.946808
Cl      0.000000        0.000000        0.000000
Cl      0.000000        0.000000        3.388150

CELL_PARAMETERS {angstrom}
   9.593000     0.000000     0.000000
  -4.796500     8.307782     0.000000
   0.000000     0.000000     6.776300
```

2 Exchange-correlation Functional/Pseudopotential/Basis set/

Tables S1 and S2 offer a comprehensive summary of the various pseudopotentials and basis sets we have employed, along with their respective sources. For the rest of this document, we have used the acronyms GTH-D and GTH-T for representing the analytical GTH pseudopotential with DZVP and TZVP basis sets, respectively. Grimme's D3 corrections used are with zero damping.

Table S1: Combination of XCs , Pseudopotentials, and basis sets used in this work.

	Planewave basis			GPW basis	
Functional	**USPP**	**ONCV**	**PAW**	**GTH-D**	**GTH-T**
LDA	✓	✓	✓		
PW91	✓	✓	✓		
PBE	✓	✓	✓	✓	✓
PBEsol	✓	✓	✓	✓	✓
PBE-D3	✓	✓	✓		
PBEsol-D3	✓	✓	✓		
optB88-vdW	✓	✓	✓		
optB88			✓		
optB86b-vdW	✓	✓	✓		
optB86b			✓		
PBE-vdW-DF3	✓	✓	✓		
PBEsol-vdW-DF3	✓	✓	✓		
r^2SCAN				✓	✓
r^2SCAN-D3					✓
HSE06				✓	
HSE06-D3				✓	

Table S2: Source of the utilized pseudopotentials

Basis Set	PP	Source
Plane wave	USPP	[2, 3] Ca.pbe-spn-rrkjus_psl.1.0.0.UPF, Other elements: *.pbe-n-rrkjus_psl.1.0.0.UPF, Ca.pbesol-spn-rrkjus_psl.0.2.3.UPF, Other elements: *.pbesol-n-rrkjus_psl.0.1.UPF
	PAW	Pseudo Dojo (JTH v1.1) [4]
	ONCV	Pseudo Dojo (ONCVPSP v0.5) [4]
GPW	GTH	[5]

3 Predicted Lattice Parameetrs

In this section, we provide the numerical values of the lattice parameters obtained for the three apatites (see tables S3-S5) for different exchange-correlation functionals, pseudopotentials, and bases. We also provide, for each apatite, the deviation from experimentally reported lattice parameters.

Table S3: Predicted lattice parameters of HAP (in Å) along with their percentage deviations (Δ) and root mean squared error (RMSE) with respect to the experimental results [1].

HAP						
XC Functional	Pseudopotential	a	$\Delta a(\%)$	c	$\Delta c(\%)$	RMSE
NA	EXPT	9.41	NA	6.87	NA	NA
LDA	USPP	9.26	-1.59	6.75	-1.75	0.14
LDA	ONCV	9.24	-1.81	6.74	-1.89	0.15
LDA	PAW	9.25	-1.70	6.75	-1.75	0.14
PW91	USPP	9.55	1.49	6.87	0.00	0.10
PBE	USPP	9.58	1.81	6.89	0.29	0.12
PBE	ONCV	9.56	1.59	6.89	0.29	0.11
PBE	PAW	9.57	1.70	6.89	0.29	0.11
PBE	GTH-D	9.54	1.38	6.97	1.46	0.12
PBE	GTH-T	9.54	1.38	6.95	1.16	0.11
PBEsol	USPP	9.40	-0.11	6.82	-0.73	0.04
PBEsol	ONCV	9.39	-0.21	6.82	-0.73	0.04
PBEsol	PAW	9.40	-0.11	6.83	-0.58	0.03
PBEsol	GTH-D	9.40	-0.11	6.91	0.58	0.03
PBEsol	GTH-T	9.39	-0.21	6.89	0.29	0.02
PBE-D3	USPP	9.54	1.41	6.87	-0.02	0.09
PBE-D3	ONCV	9.52	1.17	6.86	-0.15	0.08
PBE-D3	PAW	9.53	1.28	6.86	-0.15	0.09
PBEsol-D3	USPP	9.36	-0.53	6.80	-1.01	0.06
PBEsol-D3	ONCV	9.36	-0.53	6.81	-0.87	0.06
PBEsol-D3	PAW	9.36	-0.53	6.81	-0.87	0.06
optB88-vdW	USPP	9.47	0.64	6.87	0.00	0.04
optB88-vdW	ONCV	9.45	0.43	6.87	0.00	0.03
optB88-vdW	PAW	9.41	0.00	6.88	0.15	0.01
optB88	PAW	9.47	0.64	6.84	-0.44	0.05
optB86b-vdW	USPP	9.46	0.53	6.87	0.00	0.04
optB86b-vdW	ONCV	9.46	0.53	6.87	0.00	0.04
optB86b-vdW	PAW	9.43	0.21	6.87	0.00	0.01
optB86b	PAW	9.44	0.32	6.84	-0.44	0.03
PBE-vdW-DF3	USPP	9.35	-0.64	6.84	-0.44	0.05
PBE-vdW-DF3	ONCV	9.33	-0.85	6.83	-0.58	0.06
PBE-vdW-DF3	PAW	9.34	-0.74	6.84	-0.44	0.05
PBEsol-vdW-DF3	USPP	9.32	-0.96	6.83	-0.58	0.07
PBEsol-vdW-DF3	ONCV	9.18	-2.44	6.76	-1.60	0.18
PBEsol-vdW-DF3	PAW	9.19	-2.34	6.77	-1.46	0.17
r^2SCAN	GTH-D	9.42	0.11	6.91	0.58	0.03
r^2SCAN	GTH-T	9.41	0.00	6.90	0.44	0.02
r^2SCAN-D3	GTH-T	9.38	-0.32	6.88	0.15	0.02
HSE06	GTH-D	9.50	0.95	6.90	0.43	0.06
HSE06-D3	GTH-D	9.47	0.64	6.89	0.29	0.04

Table S4: Predicted lattice parameters of FAP (in Å) along with their percentage deviations (Δ) and root mean squared error (RMSE) with respect to the experimental results [1].

FAP						
XC Functional	Pseudopotential	a	$\Delta a(\%)$	c	$\Delta c(\%)$	RMSE
	EXPT	9.39	-	6.87	-	-
LDA	USPP	9.20	-2.01	6.76	-1.59	0.15
LDA	ONCV	9.18	-2.21	6.75	-1.74	0.17
LDA	PAW	9.20	-2.05	6.76	-1.59	0.16
PW91	USPP	9.49	1.06	6.89	0.35	0.07
PBE	USPP	9.51	1.28	6.90	0.44	0.09
PBE	ONCV	9.49	1.06	6.90	0.44	0.07
PBE	PAW	9.50	1.17	6.91	0.58	0.08
PBE	GTH-D	9.49	1.06	6.97	1.46	0.10
PBE	GTH-T	9.48	0.96	6.96	1.31	0.09
PBEsol	USPP	9.34	-0.53	6.83	-0.58	0.05
PBEsol	ONCV	9.33	-0.64	6.83	-0.58	0.05
PBEsol	PAW	9.34	-0.53	6.84	-0.44	0.04
PBEsol	GTH-D	9.36	-0.32	6.90	0.44	0.03
PBEsol	GTH-T	9.35	-0.43	6.92	0.73	0.05
PBE-D3	USPP	9.46	0.79	6.88	0.16	0.05
PBE-D3	ONCV	9.39	0.02	6.86	-0.20	0.01
PBE-D3	PAW	9.45	0.69	6.88	0.12	0.05
PBEsol-D3	USPP	9.30	-0.96	6.81	-0.89	0.08
PBEsol-D3	ONCV	9.25	-1.52	6.79	-1.10	0.11
PBEsol-D3	PAW	9.31	-0.89	6.82	-0.75	0.07
optB88-vdW	USPP	9.41	0.26	6.88	0.15	0.02
optB88-vdW	ONCV	9.40	0.06	6.87	0.04	0.00
optB88-vdW	PAW	9.40	0.06	6.87	0.04	0.01
optB88	PAW	9.40	0.11	6.86	-0.15	0.01
optB86b-vdW	USPP	9.41	0.26	6.88	0.15	0.02
optB86b-vdW	ONCV	9.37	-0.22	6.87	-0.06	0.01
optB86b-vdW	PAW	9.37	-0.18	6.87	-0.04	0.01
optB86b	PAW	9.38	-0.11	6.85	-0.29	
PBE-vdW-DF3	USPP	9.30	-0.93	6.85	-0.33	0.06
PBE-vdW-DF3	ONCV	9.24	-1.65	6.81	-0.80	0.12
PBE-vdW-DF3	PAW	9.29	-1.08	6.84	-0.44	0.07
PBEsol-vdW-DF3	USPP	9.27	-1.24	6.83	-0.58	0.09
PBEsol-vdW-DF3	ONCV	9.09	-3.17	6.74	-1.85	0.23
PBEsol-vdW-DF3	PAW	9.14	-2.63	6.77	-1.48	0.19
r^2SCAN	GTH-D	9.37	-0.21	6.92	0.73	0.04
r^2SCAN	GTH-T	9.36	-0.32	6.91	0.58	0.04
r^2SCAN-D3	GTH-T	9.33	-0.64	6.90	0.44	0.05
HSE06	GTH-D	9.45	0.63	6.89	0.29	0.04
HSE06-D3	GTH-D	9.42	0.32	6.88	0.15	0.02

Table S5: Predicted lattice parameters of ClAP (in Å) along with their percentage deviations (Δ) and root mean squared error (RMSE) with respect to the experimental results [1].

ClAP						
XC Functional	Pseudopotential	a	$\Delta a(\%)$	c	$\Delta c(\%)$	RMSE
	EXPT	9.59	-	6.77	-	-
LDA	USPP	9.52	-0.70	6.57	-3.00	0.15
LDA	ONCV	9.50	-0.90	6.56	-3.13	0.16
LDA	PAW	9.51	-0.83	6.56	-3.10	0.15
PW91	USPP	9.86	2.86	6.68	-1.28	0.20
PBE	USPP	9.89	3.13	6.69	-1.18	0.22
PBE	ONCV	9.86	2.82	6.69	-1.18	0.20
PBE	PAW	9.87	2.92	6.70	-1.03	0.20
PBE	GTH-D	9.82	2.40	6.79	0.30	0.16
PBE	GTH-T	9.83	2.50	6.76	-0.15	0.17
PBEsol	USPP	9.69	1.04	6.62	-2.22	0.13
PBEsol	ONCV	9.86	0.94	6.63	-2.07	0.12
PBEsol	PAW	9.69	1.04	6.63	-2.07	0.12
PBEsol	GTH-D	9.64	0.52	6.73	-0.59	0.03
PBEsol	GTH-T	9.64	0.52	6.71	-0.88	0.03
PBE-D3	USPP	9.85	2.67	6.67	-1.45	0.19
PBE-D3	ONCV	9.82	2.41	6.66	-1.55	0.18
PBE-D3	PAW	9.83	2.50	6.67	-1.49	0.18
PBEsol-D3	USPP	9.66	0.72	6.60	-2.47	0.13
PBEsol-D3	ONCV	9.65	0.61	6.61	-2.39	0.12
PBEsol-D3	PAW	9.66	0.71	6.61	-2.33	0.12
optB88-vdW	USPP	9.73	1.44	6.69	-1.17	0.11
optB88-vdW	ONCV	9.72	1.33	6.69	-1.20	0.11
optB88-vdW	PAW	9.73	1.44	6.69	-1.22	0.11
optB88	PAW	9.77	1.88	6.64	-1.92	0.16
optB86b-vdW	USPP	9.74	1.56	6.69	-1.15	0.12
optB86b-vdW	ONCV	9.68	0.99	6.68	-1.29	0.09
optB86b-vdW	PAW	9.74	1.56	6.69	-1.15	0.12
optB86b	PAW	9.74	1.56	6.64	-1.92	0.14
PBE-vdW-DF3	USPP	9.59	-0.05	6.68	-1.38	0.07
PBE-vdW-DF3	ONCV	9.56	-0.30	6.67	-1.48	0.07
PBE-vdW-DF3	PAW	9.57	-0.20	6.68	-1.39	0.07
PBEsol-vdW-DF3	USPP	9.55	-0.40	6.66	-1.56	0.08
PBEsol-vdW-DF3	ONCV	9.37	-2.30	6.62	-2.20	0.19
PBEsol-vdW-DF3	PAW	9.38	-2.19	6.63	-2.12	0.18
r^2SCAN	GTH-D	9.67	0.83	6.75	-0.30	0.06
r^2SCAN	GTH-T	9.67	0.83	6.73	-0.59	0.06
r^2SCAN-D3	GTH-T	9.62	0.31	6.72	-0.74	0.04
HSE06	GTH-D	9.70	1.14	6.80	0.44	0.08
HSE06-D3	GTH-D	9.67	0.83	6.78	0.15	0.06

4 Predicted Distances / Bond Lengths

In this section, we provide the numerical values of the distances / bond lengths between some important pair of atoms / ions due to the different exchange-correlation functionals and pseudopotentials. These results may be seen in tables S6-S8. The experimental data reported in these tables is measured directly from the cif files.

Table S6: Predicted distances / bond lengths (in Å) of Ca_I-Ca_I, $\langle Ca_I\text{-}O\rangle$, $\langle Ca_{II}\text{-}O\rangle$, $\langle P\text{-}O\rangle$ and OH-OH in HAP. The distances / bonds enclosed within angular brackets ($\langle \ldots \rangle$) denote the average quantities performed over all O atoms (O_I through O_{III}). In the table, the numbers in parenthesis represent the percentage deviation with respect to the experimental data, measured directly from the cif file given by [1] The difference in the % deviation despite similar values of bond lengths occurs due to rounding-off.

HAP						
		Ca_I-Ca_I	$\langle Ca_I\text{-}O\rangle$	$\langle Ca_{II}\text{-}O\rangle$	$\langle P\text{-}O\rangle$	OH-OH
	EXPT	3.42(0.00)	2.55(0.00)	2.52(0.00)	1.56(0.00)	3.44(0.00)
LDA	USPP	3.36(-1.73)	2.49(-2.34)	2.42(-4.20)	1.54(-1.28)	3.38(-1.76)
LDA	ONCV	3.35(-1.85)	2.49(-2.49)	2.41(-4.37)	1.54(-1.28)	3.37(-1.91)
LDA	PAW	3.36(-1.71)	2.49(-2.35)	2.42(-4.24)	1.54(-1.28)	3.38(-1.76)
PBE	USPP	3.42(0.12)	2.57(0.89)	2.54(0.48)	1.57(0.64)	3.45(0.27)
PBE	ONCV	3.42(0.06)	2.57(0.73)	2.53(0.22)	1.56(0.00)	3.44(0.15)
PBE	PAW	3.42(0.11)	2.57(0.82)	2.53(0.32)	1.56(0.00)	3.44(0.22)
PBE	GTH-D	3.42(-0.02)	2.57(0.64)	2.53(0.14)	1.56(0.00)	3.44(0.09)
PBE	GTH-T	3.42(0.05)	2.57(0.73)	2.53(0.23)	1.55(-0.64)	3.44(0.16)
PBEsol	USPP	3.40(-0.46)	2.54(-0.68)	2.47(-1.99)	1.55(-0.64)	3.42(-0.56)
PBEsol	ONCV	3.40(-0.66)	2.53(-0.94)	2.47(-2.26)	1.57(0.64)	3.41(-0.75)
PBEsol	PAW	3.40(-0.60)	2.53(-0.85)	2.47(-2.18)	1.56(0.00)	3.41(-0.68)
PBEsol	GTH-D	3.39(-0.73)	2.53(-1.03)	2.47(-2.36)	1.56(0.00)	3.41(-0.82)
PBEsol	GTH-T	3.39(-0.66)	2.53(-0.94)	2.47(-2.26)	1.55(-0.64)	3.41(-0.75)
PBE-D3	USPP	3.41(-0.24)	2.56(0.43)	2.52(-0.23)	1.55(-0.64)	3.43(-0.09)
PBE-D3	ONCV	3.41(-0.31)	2.56(0.26)	2.51(-0.50)	1.55(-0.64)	3.43(-0.21)
PBE-D3	PAW	3.41(-0.25)	2.56(0.36)	2.51(-0.40)	1.57(0.64)	3.43(-0.14)
PBEsol-D3	USPP	3.39(-0.93)	2.52(-1.25)	2.46(-2.74)	1.56(0.00)	3.40(-1.02)
PBEsol-D3	ONCV	3.39(-0.84)	2.52(-1.27)	2.45(-2.81)	1.56(0.00)	3.40(-0.98)
PBEsol-D3	PAW	3.39(-0.78)	2.52(-1.18)	2.46(-2.74)	1.57(0.64)	3.41(-0.91)
optB88-vdW	USPP	3.39(-0.75)	2.48(-2.90)	2.39(-5.24)	1.56(0.00)	3.39(-1.29)
optB88-vdW	ONCV	3.39(-0.92)	2.49(-2.39)	2.41(-4.65)	1.56(0.00)	3.39(-1.27)
optB88-vdW	PAW	3.39(-0.85)	2.49(-2.30)	2.41(-4.56)	1.56(0.00)	3.40(-1.20)
optB88	PAW	3.46 (1.17)	2.45 (-3.92)	2.41 (-4.37)	1.56 (0.00)	3.42 (-0.58)
optB86b-vdW	USPP	3.42(0.06)	2.54(-0.46)	2.47(-2.17)	1.56(0.00)	3.43(-0.16)
optB86b-vdW	ONCV	3.42(0.02)	2.54(-0.51)	2.47(-2.22)	1.56(0.00)	3.43(-0.20)
optB86b-vdW	PAW	3.42(0.05)	2.54(-0.43)	2.47(-2.12)	1.55(-0.64)	3.43(-0.13)
optB86b	PAW	3.45 (0.88)	2.44 (-4.31)	2.40 (-4.76)	1.56 (0.00)	3.42 (-0.58)
PBE-vdW-DF3	USPP	3.39(-0.82)	2.48(-2.92)	2.39(-5.22)	1.55(-0.64)	3.39(-1.37)
PBE-vdW-DF3	ONCV	3.38(-0.96)	2.47(-3.09)	2.39(-5.40)	1.55(-0.64)	3.39(-1.50)
PBE-vdW-DF3	PAW	3.39(-0.89)	2.48(-3.01)	2.39(-5.31)	1.55(-0.64)	3.39(-1.44)
PBEsol-vdW-DF3	USPP	3.38(-1.14)	2.48(-2.97)	2.39(-5.29)	1.55(-0.64)	3.38(-1.57)
PBEsol-vdW-DF3	ONCV	3.38(-1.18)	2.48(-3.01)	2.39(-5.32)	1.57(0.64)	3.38(-1.62)
PBEsol-vdW-DF3	PAW	3.38(-1.10)	2.48(-2.92)	2.39(-5.25)	1.56(0.00)	3.38(-1.53)
r^2SCAN	GTH-D	3.42(0.12)	2.54(-0.34)	2.47(-2.03)	1.56(0.00)	3.44(-0.06)
r^2SCAN	GTH-T	3.42(-0.02)	2.54(-0.52)	2.47(-2.21)	1.56(0.00)	3.43(-0.20)
r^2SCAN-D3	GTH-T	3.41(-0.29)	2.45(-3.92)	2.42(-3.97)	1.55(-0.64)	3.42(-0.58)
HSE06	GTH-D	3.44(0.58)	2.47(-3.14)	2.39(-5.16)	1.54(-1.28)	3.45(0.29)
HSE06-D3	GTH-D	3.44(0.58)	2.46(-3.53)	2.41(-4.37)	1.54(-1.28)	3.44(-0.58)

Table S7: Predicted distances / bond lengths (in Å) of Ca_I-Ca_I, $\langle Ca_I\text{-}O\rangle$, $\langle Ca_{II}\text{-}O\rangle$, $\langle P\text{-}O\rangle$ and F-F in FAP. The distances / bonds enclosed within angular brackets ($\langle \ldots \rangle$) denote the average quantities performed over all O atoms (O_I through O_{III}). In the table, the numbers in parenthesis represent the percentage deviation with respect to the experimental data, measured directly from the cif file given by [1].

FAP						
		Ca_I-Ca_I	$\langle Ca_I\text{-}O\rangle$	$\langle Ca_{II}\text{-}O\rangle$	$\langle P\text{-}O\rangle$	F-F
	EXPT	3.43(0.00)	2.55(0.00)	2.52(0.00)	1.53(0.00)	3.44(0.00)
LDA	USPP	3.37(-1.66)	2.49(-2.19)	2.46(-2.38)	1.54(0.65)	3.38(-1.71)
LDA	ONCV	3.36(-1.78)	2.49(-2.34)	2.46(-2.56)	1.53(0.00)	3.38(-1.86)
LDA	PAW	3.37(-1.63)	2.49(-2.20)	2.46(-2.42)	1.54(0.65)	3.38(-1.71)
PBE	USPP	3.43(0.03)	2.57(0.88)	2.56(1.73)	1.56(1.96)	3.45(0.26)
PBE	ONCV	3.43(0.28)	2.57(0.84)	2.56(1.42)	1.55(1.31)	3.45(0.35)
PBE	PAW	3.44(0.38)	2.57(0.95)	2.56(1.51)	1.55(1.31)	3.45(0.43)
PBE	GTH-D	3.44(0.34)	2.57(0.90)	2.56(1.46)	1.56(1.96)	3.45(0.39)
PBE	GTH-T	3.44(0.30)	2.57(0.85)	2.56(1.41)	1.56(1.96)	3.45(0.35)
PBEsol	USPP	3.40(-0.63)	2.53(-0.78)	2.50(-0.60)	1.55(1.31)	3.42(-0.69)
PBEsol	ONCV	3.41(-0.55)	2.53(-0.80)	2.50(-0.70)	1.54(0.65)	3.42(-0.65)
PBEsol	PAW	3.41(-0.48)	2.53(-0.70)	2.50(-0.63)	1.55(1.31)	3.42(-0.57)
PBEsol	GTH-D	3.41(-0.45)	2.53(-0.65)	2.51(-0.58)	1.56(1.96)	3.42(-0.53)
PBEsol	GTH-T	3.41(-0.41)	2.54(-0.60)	2.51(-0.52)	1.55(1.31)	3.42(-0.50)
PBE-D3	USPP	3.42(-0.06)	2.56(0.46)	2.54(0.94)	1.56(1.96)	3.44(0.04)
PBE-D3	ONCV	3.42(-0.28)	2.55(-0.13)	2.52(-0.03)	1.55(1.31)	3.43(-0.32)
PBE-D3	PAW	3.42(-0.08)	2.56(0.43)	2.54(0.86)	1.55(1.31)	3.44(0.00)
PBEsol-D3	USPP	3.39(-0.90)	2.52(-1.19)	2.49(-1.17)	1.55(1.31)	3.40(-1.01)
PBEsol-D3	ONCV	3.39(-1.00)	2.51(-1.62)	2.47(-1.87)	1.54(0.65)	3.40(-1.22)
PBEsol-D3	PAW	3.40(-0.75)	2.52(-1.08)	2.49(-1.09)	1.55(1.31)	3.41(-0.87)
optB88-vdW	USPP	3.42(-0.10)	2.55(-0.22)	2.51(-0.22)	1.56(1.96)	3.43(-0.18)
optB88-vdW	ONCV	3.43(0.00)	2.55(-0.08)	2.52(-0.08)	1.55(1.31)	3.44(-0.08)
optB88-vdW	PAW	3.43(0.00)	2.55(-0.04)	2.52(-0.01)	1.55(1.31)	3.44(-0.05)
optB88	PAW	3.41(-0.58)	2.43 (-3.57)	2.38 (-6.67)	1.55(1.31)	3.42 (-0.58)
optB86b-vdW	USPP	3.42(-0.03)	2.54(-0.41)	2.51(-0.44)	1.56(1.96)	3.43(-0.22)
optB86b-vdW	ONCV	3.43(0.01)	2.54(-0.37)	2.51(-0.39)	1.55(1.31)	3.43(-0.18)
optB86b-vdW	PAW	3.43(0.01)	2.54(-0.37)	2.51(-0.40)	1.55(1.31)	3.43(-0.20)
optB86b	PAW	3.41(-0.58)	2.44(-4.31)	2.38(-6.67)	1.54(0.65)	3.43(-0.58)
PBE-vdW-DF3	USPP	3.40(-0.87)	2.48(-2.76)	2.44(-3.20)	1.56(1.96)	3.39(-1.39)
PBE-vdW-DF3	ONCV	3.39(-1.02)	2.48(-2.89)	2.44(-3.32)	1.55(1.31)	3.39(-1.56)
PBE-vdW-DF3	PAW	3.39(-1.02)	2.48(-2.84)	2.44(-3.23)	1.55(1.31)	3.39(-1.52)
PBEsol-vdW-DF3	USPP	3.38(-1.27)	2.48(-2.91)	2.44(-3.35)	1.54(0.65)	3.38(-1.70)
PBEsol-vdW-DF3	ONCV	3.37(-1.48)	2.47(-3.26)	2.42(-3.79)	1.54(0.65)	3.37(-1.97)
PBEsol-vdW-DF3	PAW	3.39(-1.17)	2.48(-2.78)	2.44(-3.21)	1.54(0.65)	3.38(-1.60)
r^2SCAN	GTH-D	3.42(-0.05)	2.54(-0.45)	2.51(-0.48)	1.55(1.31)	3.43(-0.26)
r^2SCAN	GTH-T	3.39(-0.93)	2.48(-2.85)	2.44(-3.28)	1.55(1.31)	3.39(-1.46)
r^2SCAN-D3	GTH-T	3.45(0.58)	2.41(-5.49)	2.39(-5.16)	1.54(0.65)	3.4(-1.16)
HSE06	GTH-D	3.43(0.00)	2.44(-4.31)	2.38(-5.56)	1.55(1.31)	3.37(-2.03)
HSE06-D3	GTH-D	3.34(0.00)	2.45(-3.92)	2.42(-3.97)	1.54(0.65)	3.36(-2.33)

Table S8: Predicted distances / bond lengths (in Å) of Ca_I-Ca_I, $\langle Ca_I\text{-}O\rangle$, $\langle Ca_{II}\text{-}O\rangle$, $\langle P\text{-}O\rangle$ and Cl-Cl in ClAP. The distances / bonds enclosed within angular brackets ($\langle \ldots \rangle$) denote the average quantities performed over all O atoms (O_I through O_{III}). The numbers in parenthesis give the percentage deviation with respect to the experimental data, measured directly from the cif file given by [1]. The difference in the percentage deviation despite similar values of bond lengths occurs due to rounding-off.

ClAP						
		Ca_I-Ca_I	$\langle Ca_I\text{-}O\rangle$	$\langle Ca_{II}\text{-}O\rangle$	$\langle P\text{-}O\rangle$	Cl-Cl
	EXPT	3.27(0.00)	2.56(0.00)	2.90(0.00)	1.57(0.00)	3.34(0.00)
LDA	USPP	3.23(-1.45)	2.47(-3.33)	2.84(-2.13)	1.55(-1.27)	3.28(-1.82)
LDA	ONCV	3.22(-1.57)	2.47(-3.46)	2.84(-2.29)	1.54(-1.91)	3.28(-1.94)
LDA	PAW	3.23(-1.42)	2.47(-3.34)	2.84(-2.13)	1.55(-1.27)	3.28(-1.80)
PBE	USPP	3.27(0.00)	2.56(0.13)	2.90(-0.01)	1.57(0.00)	3.35(0.30)
PBE	ONCV	3.28(0.20)	2.56(-0.01)	2.90(-0.07)	1.57(0.00)	3.35(0.08)
PBE	PAW	3.28(0.25)	2.56(0.06)	2.90(0.01)	1.57(0.00)	3.35(0.14)
PBE	GTH-D	3.29(0.32)	2.56(0.15)	2.91(0.09)	1.57(0.00)	3.35(0.21)
PBE	GTH-T	3.29(0.39)	2.56(0.25)	2.91(0.17)	1.57(0.00)	3.35(0.28)
PBEsol	USPP	3.25(-0.76)	2.51(-1.79)	2.87(-1.20)	1.56(-0.64)	3.31(-1.00)
PBEsol	ONCV	3.25(-0.64)	2.51(-1.79)	2.87(-1.20)	1.56(-0.64)	3.31(-0.92)
PBEsol	PAW	3.26(-0.59)	2.51(-1.72)	2.87(-1.11)	1.56(-0.64)	3.32(-0.86)
PBEsol	GTH-D	3.26(-0.52)	2.51(-1.63)	2.87(-1.03)	1.57(0.00)	3.32(-0.79)
PBEsol	GTH-T	3.26(-0.45)	2.52(-1.54)	2.88(-0.95)	1.57(0.00)	3.32(-0.72)
PBE-D3	USPP	3.27(-0.22)	2.54(-0.41)	2.90(-0.27)	1.57(0.00)	3.34(-0.24)
PBE-D3	ONCV	3.26(-0.30)	2.54(-0.54)	2.89(-0.45)	1.57(0.00)	3.33(-0.35)
PBE-D3	PAW	3.27(-0.25)	2.54(-0.47)	2.89(-0.36)	1.57(0.00)	3.33(-0.29)
PBEsol-D3	USPP	3.24(-1.03)	2.50(-2.17)	2.86(-1.48)	1.56(-0.64)	3.30(-1.28)
PBEsol-D3	ONCV	3.25(-0.90)	2.50(-2.17)	2.86(-1.49)	1.56(-0.64)	3.30(-1.21)
PBEsol-D3	PAW	3.25(-0.86)	2.50(-2.10)	2.86(-1.40)	1.56(-0.64)	3.31(-1.14)
optB88-vdW	USPP	3.29(0.48)	2.53(-1.17)	2.90(-0.21)	1.57(0.00)	3.35(0.03)
optB88-vdW	ONCV	3.29(0.48)	2.53(-1.16)	2.89(-0.31)	1.57(0.00)	3.34(0.00)
optB88-vdW	PAW	3.29(0.55)	2.53(-1.07)	2.90(-0.23)	1.57(0.00)	3.35(0.07)
optB88	PAW	3.29(0.61)	2.52(-1.56)	2.82(-2.76)	1.55(-1.27)	3.32(-0.60)
optB86b-vdW	USPP	3.29(0.48)	2.53(-1.09)	2.90(-0.18)	1.57(0.00)	3.35(0.05)
optB86b-vdW	ONCV	3.29(0.50)	2.52(-1.43)	2.89(-0.50)	1.56(-0.64)	3.34(-0.09)
optB86b-vdW	PAW	3.29(0.50)	2.52(-1.38)	2.89(-0.41)	1.57(0.00)	3.34(-0.06)
optB86b	PAW	3.27(-0.61)	2.53(-1.17)	2.84(-2.07)	1.55(-1.27)	3.33(-0.30)
PBE-vdW-DF3	USPP	3.29(0.42)	2.52(-1.47)	2.89(-0.49)	1.57(0.00)	3.34(-0.13)
PBE-vdW-DF3	ONCV	3.30(0.63)	2.50(-2.34)	2.88(-0.89)	1.56(-0.64)	3.33(-0.28)
PBE-vdW-DF3	PAW	3.30(0.67)	2.50(-2.29)	2.88(-0.85)	1.56(-0.64)	3.34(-0.24)
PBEsol-vdW-DF3	USPP	3.29(0.52)	2.49(-2.39)	2.87(-0.97)	1.56(-0.64)	3.33(-0.36)
PBEsol-vdW-DF3	ONCV	3.28(0.22)	2.45(-3.95)	2.85(-1.80)	1.55(-1.27)	3.31(-1.01)
PBEsol-vdW-DF3	PAW	3.29(0.35)	2.46(-3.78)	2.85(-1.65)	1.56(-0.64)	3.31(-0.88)
r^2SCAN	GTH-D	3.29(0.48)	2.46(-3.62)	2.86(-1.51)	1.57(0.00)	3.32(-0.76)
r^2SCAN	GTH-T	3.29(0.61)	2.47(-3.45)	2.86(-1.36)	1.57(0.00)	3.32(-0.63)
r^2SCAN-D3	GTH-T	3.32(1.52)	2.39(-3.45)	2.86(-1.36)	1.57(0.00)	3.32(-0.63)
HSE06	GTH-D	3.37(3.05)	2.44(-4.69)	2.87(-1.03)	1.55(-1.27)	3.39(1.50)
HSE06-D3	GTH-D	3.34(2.14)	2.49(-2.73)	2.88(-0.69)	1.57(0.00)	3.33(-0.30)

5 Predicted Elastic Constants

In this section, we provide the numerical values of the five elastic constants obtained for the three apatites (see tables S9-S11) for different exchange-correlation functionals, pseudopotentials, and bases. Except for ClAP, for which experimental data is not available, the deviations from the experimentally reported elastic constants are also reported.

Table S9: Elastic constants of HAP (in GPa) along with the total root mean squared error (RMSE) with respect to the available experimental data [6]. The numbers in parenthesis denote the percentage deviation of the corresponding elastic constant with respect to the experimentally reported data.

HAP							
XC Functional	Pseudo-potential	C_{11} (%)	C_{12} (%)	C_{13} (%)	C_{33} (%)	C_{44} (%)	RMSE
	EXPT	137.0	42.5	54.9	172.0	39.6	-
LDA	USPP	160.0 (16.8)	54.0 (27.1)	79.2 (44.3)	213.0 (23.8)	34.6 (-12.6)	24.3
LDA	ONCV	159.0 (16.1)	52.4 (23.3)	78.0 (42.1)	212.4 (23.5)	34.4 (-13.1)	23.6
LDA	PAW	158.4 (15.6)	51.8 (21.9)	78.0 (42.1)	211.4 (22.9)	36.0 (-9.1)	23.0
PW91	USPP	121.6 (-11.2)	33.2 (-21.9)	68.8 (25.3)	168.4 (-2.1)	37.2 (-6.1)	10.4
PBE	USPP	130.3 (-4.9)	47.1 (10.8)	65.7 (19.7)	174.7 (1.6)	48.7 (23.0)	7.4
PBE	ONCV	119.4 (-12.9)	32.0 (-24.7)	65.5 (19.3)	164.5 (-4.4)	23.2 (-41.4)	13.1
PBE	PAW	119.0 (-13.1)	31.8 (-25.2)	65.4 (19.1)	163.7 (-4.8)	44.7 (12.9)	11.4
PBE	GTH-D	130.9 (-4.5)	38.3 (-9.9)	58.0 (5.6)	164.2 (-4.5)	34.8 (-12.2)	5.5
PBE	GTH-T	129.8 (-5.2)	37.3 (-12.1)	58.9 (7.2)	164.3 (-4.5)	37.7 (-4.7)	5.6
PBEsol	USPP	136.5 (-0.4)	39.9 (-6.1)	70.5 (28.4)	182.7 (6.2)	35.8 (-9.6)	8.7
PBEsol	ONCV	137.5 (0.3)	40.3 (-5.1)	69.7 (26.9)	184.0 (6.9)	36.3 (-8.3)	10.6
PBEsol	PAW	136.4 (-0.4)	40.5 (-4.7)	70.1 (27.7)	183.6 (6.7)	37.5 (-5.3)	8.7
PBEsol	GTH-D	145.8 (6.4)	46.7 (10.0)	62.1 (13.1)	182.6 (6.1)	35.1 (-11.5)	7.5
PBEsol	GTH-T	145.1 (5.9)	45.7 (7.5)	62.7 (14.1)	182.8 (6.3)	34.4 (-13.2)	7.5
PBE-D3	USPP	125.4 (-8.5)	42.3 (-0.5)	61.4 (11.8)	169.0 (-1.7)	35.2 (-11.1)	6.4
PBE-D3	ONCV	124.4 (-9.2)	36.6 (-13.9)	65.4 (19.1)	172.4 (0.2)	56.4 (42.4)	10.8
PBE-D3	PAW	119.8 (-12.6)	32.0 (-24.7)	68.4 (24.6)	169.0 (-1.7)	36.0 (-9.1)	11.1
PBEsol-D3	USPP	134.0 (-2.2)	35.1 (-17.1)	68.5 (24.8)	180.4 (4.9	32.3 (-18.4)	19.6
PBEsol-D3	ONCV	145.2 (6.0)	41.6 (-2.1)	69.0 (25.7)	188.8 (9.8)	48.8 (23.2)	11.3
PBEsol-D3	PAW	138.8 (1.3)	42.4 (-0.2)	71.6 (30.4)	187.2 (8.8)	30.8 (-22.2)	10.9
optB88-vdW	USPP	144.4 (5.4)	43.8 (3.1)	66.8 (21.7)	185.6 (7.9)	47.6 (20.2)	9.5
optB88-vdW	ONCV	142.0 (3.7)	43.6 (2.6)	67.8 (23.5)	186.8 (8.6)	37.0 (-6.6)	9.2
optB88-vdW	PAW	142.0 (3.7)	55.0 (29.4)	66.4 (21.0)	182.6 (6.2)	42.8 (8.1)	9.3
optB88	PAW	103.8 (-24.2)	37.8 (-11.1)	70.4 (28.2)	179.2 (4.2)	35.6 (-10.1)	16.9
optB86b-vdW	USPP	144.8 (5.7)	46.0 (8.2)	68.0 (23.9)	187.6 (9.1)	35.2 (-11.1)	10.1
optB86b-vdW	ONCV	142.2 (3.8)	43.6 (2.6)	67.8 (23.5)	186.2 (8.3)	37.4 (-5.6)	9.0
optB86b-vdW	PAW	141.6 (3.4)	43.8 (3.1)	68.0 (23.9)	186.0 (8.1)	41.2 (4.0)	8.9
optB86b	PAW	103.8 (-24.2)	38 (-10.6)	72.8 (32.6)	181 (5.2)	36.6 (-7.6)	17.5
PBE-vdW-DF3	USPP	151.2 (10.4)	50.8 (19.5)	70.6 (28.6)	197.2 (14.7)	36.8 (-7.1)	15.2
PBE-vdW-DF3	ONCV	152.6 (11.4)	51.4 (20.9)	70.6 (28.6)	198.0 (15.1)	38.0 (-4.0)	15.8
PBE-vdW-DF3	PAW	150.8 (10.1)	49.2 (15.8)	72.4 (31.9)	197.8 (15.0)	37.0 (-6.5)	15.5
PBEsol-vdW-DF3	USPP	153.2 (11.8)	51.4 (20.9)	70.8 (29.0)	199.2 (15.8)	38.8 (-2.0)	16.3
PBEsol-vdW-DF3	ONCV	184.6 (34.7)	71.8 (68.9)	77.4 (41.0)	234.4 (36.3)	54.0 (36.4)	39.3
PBEsol-vdW-DF3	PAW	167.6 (22.3)	59.6 (40.2)	74.4 (35.5)	215.2 (25.1)	38.8 (-2.0)	26.4
r^2SCAN	GTH-D	162.7 (18.8)	46.1 (8.5)	62.3 (13.5)	196.6 (14.3)	56.4 (42.3)	18.0
r^2SCAN	GTH-T	162.7 (18.8)	46.4 (9.2)	63.8 (16.3)	188.5 (9.6)	52.3 (32.0)	15.4
r^2SCAN-D3	GTH-T	156.1 (13.9)	47.9 (12.7)	72.5 (32.0)	200.8 (16.7)	52.6 (32.8)	18.5
HSE06	GTH-D	178.7 (30.5)	44.7(5.3)	63.5 (15.7)	222.4 (29.3)	63.5 (60.5)	31.4
HSE06-D3	GTH-D	126.6 (-7.5)	48.7(14.5)	55.1 (0.3)	212.6 (23.2)	51.0 (28.8)	19.4

Table S10: Predicted elastic constants of FAP (in GPa) along with the total root mean squared error (RMSE) in relation to the available experimental findings [7]. The numbers in parenthesis denote the percentage deviation of the corresponding elastic constant with respect to the experimentally reported data.

FAP							
XC Functional	Pseudo-potential	C_{11} (%)	C_{12} (%)	C_{13} (%)	C_{33} (%)	C_{44} (%)	RMSE
	EXPT	143.4	44.5	57.5	180.5	41.5	
LDA	USPP	164.0(14.4)	55.8(25.4)	74.0(28.7)	200.5(11.1)	38.0(-8.4)	15.7
LDA	ONCV	165.6(15.5)	56.4(26.7)	74.4(29.4)	212.8(17.9)	47.2(13.7)	20.0
LDA	PAW	166.2(15.9)	58.2(30.8)	74.8(30.1)	215.2(19.2)	24.9(-40.0)	22.3
PW91	USPP	126.0(-12.1)	34.8(-21.8)	63.4(10.3)	169.4(-6.1)	22.6(-45.5)	13.5
PBE	USPP	126.1(-12.1)	35.3(-20.7)	63.4(10.3)	166.7(-7.6)	30.3(-27.0)	12.1
PBE	ONCV	128.5(-10.4)	37.1(-16.6)	66.2(15.1)	166.7(-7.6)	27.8(-33.0)	12.1
PBE	PAW	127.6(-11.0)	36.9(-17.1)	62.6(8.9)	166.6(-7.7)	25.0(-39.8)	12.6
PBE	GTH-D	137.4(-4.2)	41.9(-5.8)	56.0(-2.6)	164.0(-9.1)	23.8(-42.7)	11.2
PBE	GTH-T	136.5(-4.8)	40.8(-8.3)	56.6(-1.6)	164.6(-8.8)	22.2(-46.5)	11.7
PBEsol	USPP	146.9(2.4)	46.5(4.5)	67.5(17.4)	186.8(3.5)	29.3(-29.4)	7.8
PBEsol	ONCV	145.5(1.5)	45.2(1.6)	67.0(16.5)	177.2(-1.8)	22.2(-46.5)	9.8
PBEsol	PAW	147.7(3.0)	51.2(15.1)	65.6(14.1)	186.0(3.0)	20.2(-51.3)	11.1
PBEsol	GTH-D	152.6(6.4)	49.3(10.8)	60.3(4.9)	183.9(1.9)	23.3(-43.9)	9.6
PBEsol	GTH-T	152.3(6.2)	48.3(8.5)	60.6(5.4)	194.2(7.6)	22.7(-45.3)	11.4
PBE-D3	USPP	130.2(-9.2)	42.0(-5.6)	65.0(13.0)	187.0(3.6)	22.3(-46.2)	11.3
PBE-D3	ONCV	139.2(-2.9)	44.4(-0.2)	64.4(12.0)	185.2(2.6)	46.8(12.8)	4.8
PBE-D3	PAW	124.0(-13.5)	33.2(-25.4)	59.6(3.7)	173.0(-4.2)	17.4(-58.1)	15.1
PBEsol-D3	USPP	150.0(4.6)	42.4(-27.1)	69.0(-7.7)	182.0(-15.4)	30.0(-21.2)	7.2
PBEsol-D3	ONCV	155.0(8.1)	53.4(20.0)	71.8(24.9)	202.2(12.0)	49.6(19.5)	13.8
PBEsol-D3	PAW	147.0(2.5)	47.2(6.1)	68.2(18.6)	191.2(5.9)	19.6(-52.8)	12.1
optB88-vdW	USPP	158.4(10.5)	54.4(22.2)	68.6(19.3)	199.4(10.5)	28.6(-31.1)	13.9
optB88-vdW	ONCV	149.6(4.3)	48.0(7.9)	66.0(14.8)	188.6(4.5)	14.8(-64.3)	13.4
optB88-vdW	PAW	148.8(3.8)	47.8(7.4)	66.4(15.5)	189.0(4.7)	16.4(-60.5)	12.8
optB88	PAW	138.4(-3.5)	42.0(-5.6)	66.2(15.1)	181.0(0.3)	9.6(-76.7)	15.0
optB86b-vdW	USPP	160.0(11.6)	55.2(24.0)	68.6(19.3)	201.4(11.6)	32.8(-21.0)	14.3
optB86b-vdW	ONCV	149.2(4.0)	47.6(7.0)	65.2(13.4)	188.6(4.5)	37.2(-10.4)	6.1
optB86b-vdW	PAW	150.2(4.7)	48.6(9.2)	66.0(14.8)	190.4(5.5)	20.6(-50.4)	11.6
optB86b	PAW	138.6(-3.3)	41.8(-6.0)	65.4(13.7)	179.8(-0.3)	25.6(-38.3)	8.3
PBE-vdW-DF3	USPP	147.8(3.1)	47.0(5.6)	66.0(14.8)	187.8(4.0)	9.6(-76.9)	15.3
PBE-vdW-DF3	ONCV	168.4(17.4)	60.4(35.7)	71.2(23.8)	211.6(17.2)	29.4(-29.2)	20.9
PBE-vdW-DF3	PAW	160.2(11.7)	55.4(24.5)	68.4(19.0)	200.8(11.2)	30.4(-26.7)	14.5
PBEsol-vdW-DF3	USPP	147.0(2.5)	47.4(6.5)	64.8(12.7)	188.0(4.2)	11.0(-73.5)	14.6
PBEsol-vdW-DF3	ONCV	175.6(22.5)	69.4(56.0)	76.6(33.2)	221.2(22.5)	65.2(57.1)	29.1
PBEsol-vdW-DF3	PAW	177.2(23.6)	65.4(47.0)	74.8(30.1)	224.2(24.2)	37.2(-10.4)	27.6
r^{2}SCAN	GTH-D	143.4(0.0)	57.9(30.1)	76.1(32.3)	192.8(6.8)	43.0(3.6)	11.7
r^{2}SCAN	GTH-T	141.8(-1.1)	55.7(25.2)	57.5(0.0)	197.1(9.2)	52.0(25.3)	10.1
r^{2}SCAN-D3	GTH-T	165.9 (15.7)	51.0 (14.6)	67.0 (16.5)	204.5 (13.3)	46.1 (11.0)	15.7
HSE06	GTH-D	167.0 (16.4)	45.4(2.1)	81.0 (40.9)	224.4 (24.3)	62.8 (51.4)	26.5
HSE06-D3	GTH-D	186.1 (29.7)	47.5(6.7)	63.1 (9.7)	226.7 (25.6)	52.8 (27.2)	28.7

Table S11: Predicted elastic constants of ClAP (in GPa). A comparison could not be made between the DFT results and experimental data due to the lack of latter in literature.

ClAP						
XC Functional	Pseudopotential	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}
LDA	USPP	112.0	29.0	56.0	186.0	42.0
LDA	ONCV	126.0	30.0	78.6	200.4	48.0
LDA	PAW	126.8	31.0	78.2	200.4	48.2
PW91	USPP	111.5	28.0	75.0	195.0	45.0
PBE	USPP	110.7	30.5	55.4	160.4	37.8
PBE	ONCV	108.3	29.3	54.8	158.8	38.0
PBE	PAW	109.2	29.9	54.9	183.3	37.9
PBE	GTH-D	106.1	24.3	56.9	158.7	38.9
PBE	GTH-T	104.7	22.8	56.7	157.4	39.0
PBEsol	USPP	115.7	29.4	64.3	180.7	42.6
PBEsol	ONCV	115.3	29.0	64.2	176.7	42.4
PBEsol	PAW	115.1	29.3	64.9	170.5	43.1
PBEsol	GTH-D	116.9	25.9	65.8	175.5	43.7
PBEsol	GTH-T	113.9	23.4	66.4	184.1	43.9
PBE-D3	USPP	111.0	33.0	52.0	159.0	38.8
PBE-D3	ONCV	125.2	37.0	51.8	163.6	38.0
PBE-D3	PAW	112.8	31.2	57.0	163.0	39.0
PBEsol-D3	USPP	115.0	35.0	56.0	176.0	41.0
PBEsol-D3	ONCV	130.2	37.4	60.8	179.0	44.8
PBEsol-D3	PAW	117.2	29.0	66.4	178.8	42.6
optB88-vdW	USPP	117.4	44.0	68.6	178.6	43.6
optB88-vdW	ONCV	118.0	29.4	67.8	191.4	43.6
optB88-vdW	PAW	118.2	31.8	67.6	178.2	43.2
optB88	PAW	113.2	30.8	60.4	178.0	41.0
optB86b-vdW	USPP	114.2	42.0	63.0	174.0	42.0
optB86b-vdW	ONCV	118.0	28.8	67.6	180.4	43.6
optB86b-vdW	PAW	116.8	28.6	67.6	177.4	43.6
optB86b	PAW	113.8	30.4	61.6	170.8	41.4
PBE-vdW-DF3	USPP	123.4	29.6	74.6	182.2	45.6
PBE-vdW-DF3	ONCV	138.0	37.2	74.2	189.2	48.0
PBE-vdW-DF3	PAW	125.2	30.4	74.2	189.6	45.2
PBEsol-vdW-DF3	USPP	125.0	29.6	74.8	190.2	46.4
PBEsol-vdW-DF3	ONCV	151.6	42.8	77.8	212.2	53.6
PBEsol-vdW-DF3	PAW	142.6	36.6	82.8	212.4	51.2
r^2SCAN	GTH-D	138.2	30.6	61.8	188.7	52.9
r^2SCAN	GTH-T	125.4	26.2	63.1	191.7	52.7
r^2SCAN-D3	GTH-T	126.6	22.3	73.6	195.0	54.3
HSE06	GTH-D	161.5	45.0	47.0	178.22	56.7
HSE06-D3	GTH-D	136.4	40.0	38.8	188.0	57.1

6 DFT Simulations of Aluminum

The SCF convergence criterion was set to $\epsilon_{\text{SCF}} = 10^{-6}$ Ha, ensuring accurate electronic structure calculations. The force and pressure convergence criteria were set to 10^{-4} Ha/Bohr and 0.1 Kbar, respectively. A high plane-wave cutoff of 1500 Ry and a relative cutoff of 100 Ry were used to ensure well-converged total energy and stress tensor calculations. The initial cell dimensions were set to $a = b = c = 4.0389$ Å, corresponding to a cubic symmetry. The atomic positions in fractional coordinates are:

Al 0.0000.0000.000
Al 0.5000.5000.000
Al 0.5000.0000.500
Al 0.0000.5000.500

Table S12: Predicted elastic constants of cubic Al in GPa. The numbers in parenthesis denote the percentage deviation of the corresponding elastic constant with respect to the experimentally reported data. GTH potentials are taken from [5].

Material	XC	Pseudopotential	C_{11}(%)	C_{12} (%)	C_{44} (%)	RMSE
Al	Expt.[8]	-	106.8	60.7	28.2	-
	PBE-Sol	GTH-T	140.0(31.0)	50.5(-16.8)	29.1(3.1)	20.0
	R2SCAN	GTH-T	130.7(22.3)	71.2(17.2)	23.2(-17.7)	15.3

7 Predicted Bulk Modulus

In this section, we provide the numerical values of the bulk modulus obtained for the three apatites (see table S13) for different exchange-correlation functionals, pseudopotentials, and bases. Except for ClAP, for which experimental data is not available, the deviations from the experimentally reported bulk modulus are also reported.

Table S13: Calculated Bulk Modulus (in GPa) from Voigt-Reuss-Hill approximation. The numbers in parenthesis (ΔB) represents the percentage deviation of B from the experimental data [6].

XC Functional	Pseudopotential	HAP	FAP	ClAP
		B (ΔB)	B (ΔB)	B
Expt.		89.0	94.0	–
LDA	USPP	104.3 (17.2)	82.0(-12.7)	85.2
LDA	ONCV	103.1 (15.9)	104.7 (11.4)	84.9
LDA	PAW	102.7 (15.4)	105.7 (12.4)	85.5
PW91	USPP	80.2 (-9.9)	80.4 (-14.5)	71.0
PBE	USPP	86.4 (-3.0)	80.4 (-14.5)	71.3
PBE	ONCV	77.9 (-12.5)	82.6 (-12.1)	69.9
PBE	PAW	77.6 (-12.8)	81.0 (-13.8)	71.9
PBE	GTH-D	80.4 (-9.6)	82.3 (-12.5)	68.2
PBE	GTH-T	80.2 (-9.9)	82.1 (-12.7)	67.2
PBEsol	USPP	88.3 (-0.8)	92.4 (-1.8)	76.5
PBEsol	ONCV	88.5 (-0.5)	90.7 (-3.5)	75.9
PBEsol	PAW	88.4 (-0.7)	93.0 (-1.0)	75.8
PBEsol	GTH-D	89.7 (0.8)	91.5 (-2.7)	75.8
PBEsol	GTH-T	89.4 (0.5)	92.1 (-2.0)	74.5
PBE-D3	USPP	81.6 (-8.3)	85.4 (-9.0)	70.8
PBE-D3	ONCV	81.3 (-8.6)	88.4 (-6.0)	76.1
PBE-D3	PAW	79.2 (-11.1)	78.3 (-16.8)	86.0
PBEsol-D3	USPP	85.3 (-4.1)	92.2 (-1.91)	75.0
PBEsol-D3	ONCV	91.2 (2.5)	99.2 (5.6)	82.1
PBEsol-D3	PAW	90.4 (1.6)	93.2 (-0.9)	77.3
optB88-vdW	USPP	90.6 (1.8)	98.9 (5.2)	82.9
optB88-vdW	ONCV	90.3 (1.5)	93.0 (-1.0)	78.8
optB88-vdW	PAW	92.6 (4.0)	93.0 (-1.1)	78.9
optB88	PAW	76.7(-13.8)	87.8(-6.6)	74.7
optB86b-vdW	USPP	91.9 (3.2)	99.7 (6.1)	84.0
optB86b-vdW	ONCV	90.3 (1.5)	92.5 (-1.6)	77.9
optB86b-vdW	PAW	90.3 (1.4)	93.5 (-0.5)	77.3
optB86b	PAW	77.4(-13.0)	87.4(-7.0)	74.7
PBE-vdW-DF3	USPP	96.7 (8.6)	92.2 (-1.9)	81.9
PBE-vdW-DF3	ONCV	97.3 (9.3)	105.1 (11.8)	89.6
PBE-vdW-DF3	PAW	96.8 (8.8)	99.7 (6.1)	83.2
PBEsol-vdW-DF3	USPP	97.6 (9.6)	91.7 (-2.5)	83.0
PBEsol-vdW-DF3	ONCV	116.6 (31.0)	112.3 (19.4)	98.1
PBEsol-vdW-DF3	PAW	106.3 (19.4)	111.2 (18.3)	94.7
r^2SCAN	GTH-D	95.2 (6.9)	98.2 (4.4)	83.5
r^2SCAN	GTH-T	95.1 (6.9)	90.4 (-3.9)	78.8
r^2SCAN-D3	GTH-T	98.1 (10.2)	99.7(6.0)	80.9
HSE06	GTH-D	101.5 (14.0)	105.3(12.0)	86.4
HSE06-D3	GTH-D	84.5 (-5.05)	104.3(10.9)	76.6

8 Density of States

In this section, the total density of states for the three apatites are plotted. Note that all combinations of exchange-correlation functionals and pseudopotentials are not plotted to prevent clutter and improve the understanding of the figures.

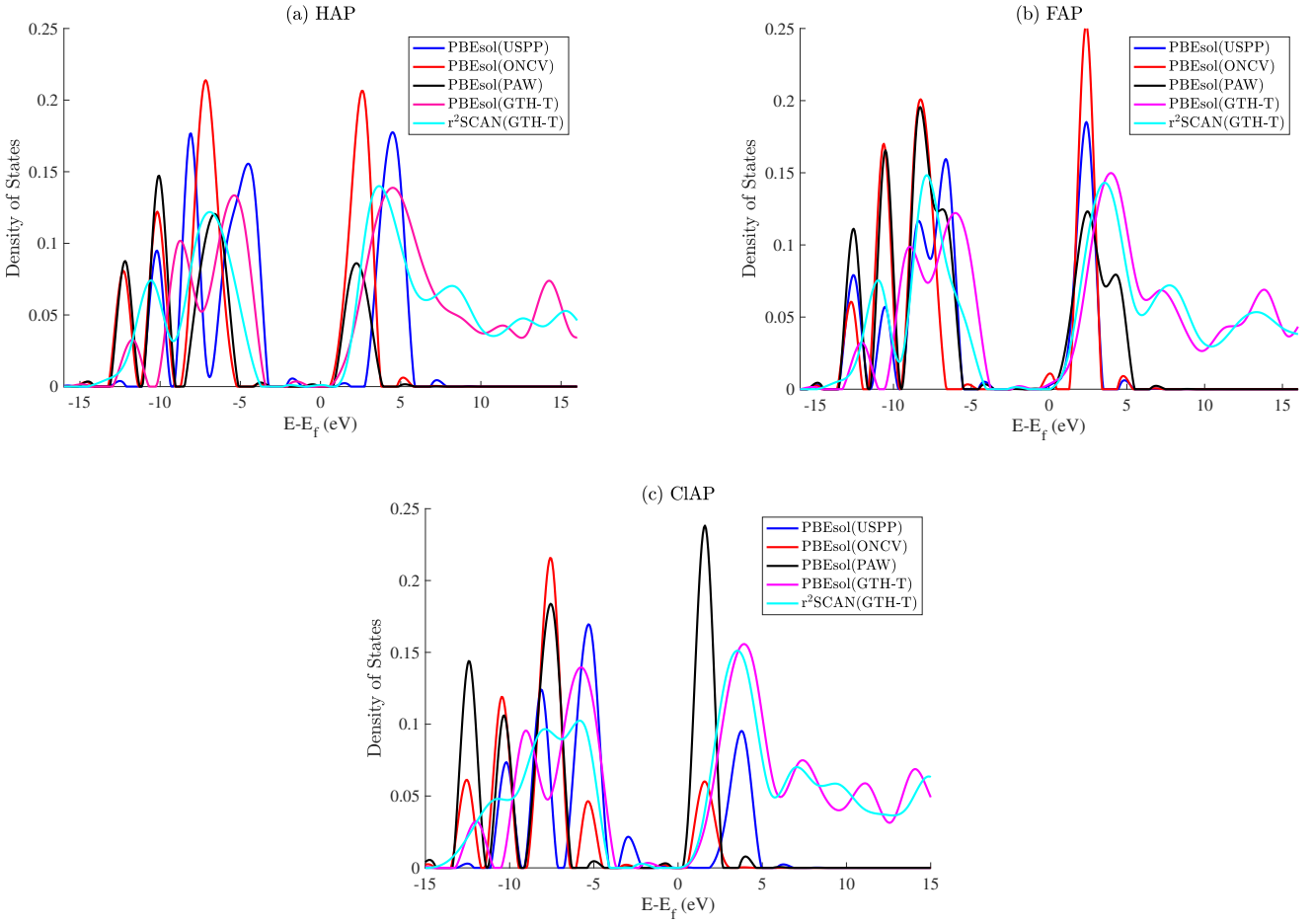

Figure S1: Total density of states of apatites: (a) HAP, (b) FAP and (c) ClAP.

9 Predicted Band Gap

In this section, we provide the numerical values of the band gap (see table S14) for the three apatites.

Table S14: Predicted band gap of apatites (in eV).

XC Functional	Pseudopotential	Band Gap		
		HAP	FAP	ClAP
LDA	USPP	5.35	5.77	5.51
LDA	ONCV	5.42	5.85	5.57
LDA	PAW	5.35	5.77	5.51
PW91	USPP	5.29	5.58	5.48
PBE	USPP	5.21	5.56	5.35
PBE	ONCV	5.29	5.61	5.37
PBE	PAW	5.23	5.58	5.33
PBE	GTH-D	5.17	5.51	5.03
PBE	GTH-T	5.14	5.44	5.32
PBEsol	USPP	5.23	5.67	5.41
PBEsol	ONCV	5.33	5.71	5.40
PBEsol	PAW	5.27	5.67	5.40
PBEsol	GTH-D	5.18	5.54	5.17
PBEsol	GTH-T	5.16	5.48	5.03
PBE-D3	USPP	5.39	5.64	5.42
PBE-D3	ONCV	5.33	5.74	5.44
PBE-D3	PAW	5.28	5.62	5.41
PBEsol-D3	USPP	5.38	5.80	5.42
PBEsol-D3	ONCV	5.36	5.81	5.49
PBEsol-D3	PAW	5.31	5.69	5.45
optB88-vdW	USPP	5.29	5.63	5.43
optB88-vdW	ONCV	5.34	5.68	5.46
optB88-vdW	PAW	5.43	5.67	5.45
optB88	PAW	5.22	5.55	5.35
optB86b-vdW	USPP	5.30	5.63	5.42
optB86b-vdW	ONCV	5.35	5.70	5.47
optB86b-vdW	PAW	5.32	5.69	5.45
optB86b	PAW	5.22	5.55	5.34
PBE-vdW-DF3	USPP	5.16	5.53	5.29
PBE-vdW-DF3	ONCV	5.23	5.68	5.35
PBE-vdW-DF3	PAW	5.17	5.56	5.30
PBEsol-vdW-DF3	USPP	5.28	5.67	5.40
PBEsol-vdW-DF3	ONCV	5.24	5.76	5.38
PBEsol-vdW-DF3	PAW	5.18	5.64	5.33
r^2SCAN	GTH-D	6.12	6.14	6.27
r^2SCAN	GTH-T	5.99	6.35	6.31
r^2SCAN-D3	GTH-T	6.04	6.51	6.26
HSE06	GTH-D	7.47	7.79	7.63
HSE06-D3	GTH-D	7.50	7.85	7.66

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