Figure S1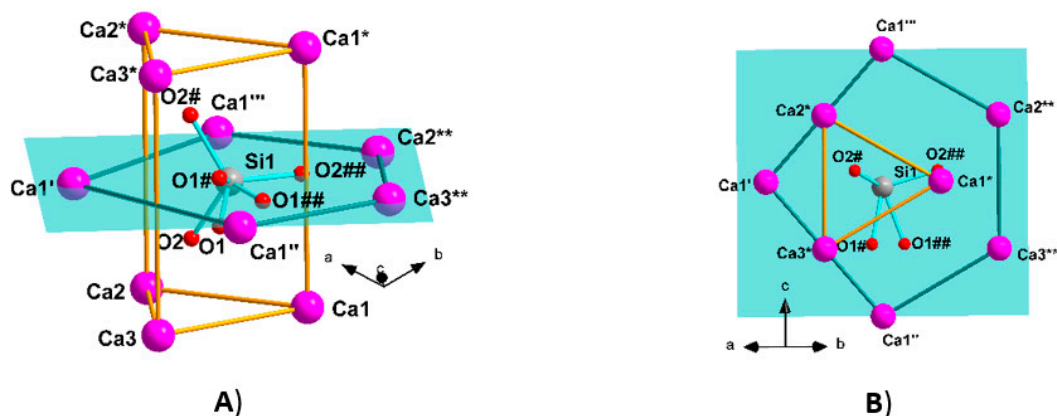. Presentation of the trigonal prism and the atoms at the equator plane for the α-C2S trigonal polymorph: **A)** depicts the top and **B)** the bottom view. Symmetry codes: ('): 1+x,y,z; (''):1+x-y,1-z,-z; ('''):1+x-y,1-y,1-z; (*):1+x,1+y,1-z; (**): x,1+y,z; (#): 1-y,1+x-y,z; (##): -x+y,1-y,z.
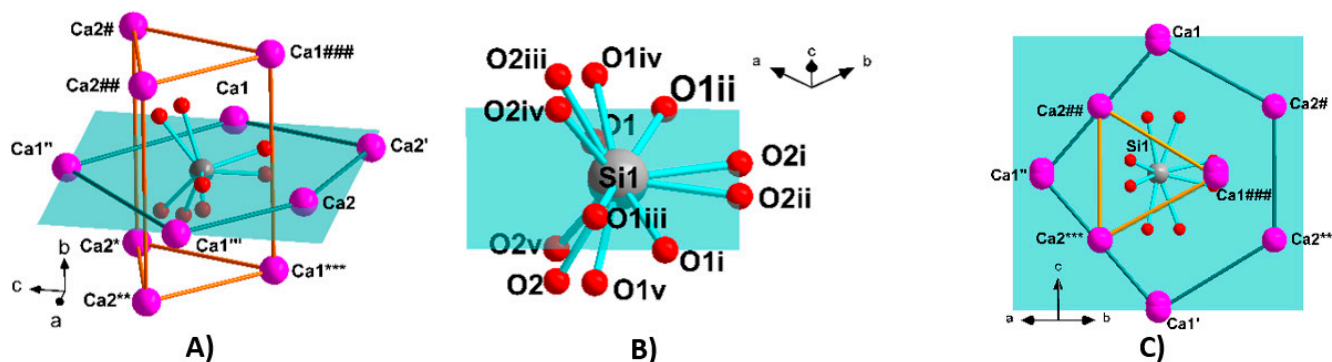

Figure S2. Presentation of the trigonal prism and the atoms at the equator plane for the α-C2S hexagonal polymorph: **A)** depicts the top and **C)** the bottom view; **B)** presents the oxygen sites for the SiO4-4 anion. Symmetry codes: ('): x,y-1+z; (''):1+x-y,x,-0.5+z; ('''):x-y,x,0.5+z; (*):x-y,x,0.5+z; (**):x,1+y,z; (***):1+x,1+y,z; (#): x-y.1+y,0.5+z; (##):1+x-y,1+y,0.5+y; (###): 1+x-y,1+x,-0.5+z.

Figure S3. Presentation of the trigonal prism and the atoms at the equator plane for the α'_H-C$_2$S polymorph: **A)** depicts the top and **C)** the bottom view; **B)** presents the oxygen sites for the SiO$_4^{-4}$ anion. Symmetry codes: ('): -0.5+x,0.5-y,0.5-z; (''): 0.5+x,0.5-y,1.5-z; ('''):1+x,y,z; (*): 1.5-x,0.5+y,0.5+z; (**):2-x,-0.5+y,1-z; (***):1-x,-0.5+y,1-z; (#): 1.5-x,1.5-y,0.5-z; (##):2-x,0.5-y,1-z; (###):1-x,1-y,1-z

Figure S4. Presentation of the trigonal prism and the atoms at the equator plane for the α'_L-C$_2$S polymorph: **A)** depicts the top and **C)** the bottom view; **B)** presents the oxygen sites for the SiO$_4^{-4}$ anion. Symmetry codes: ('):-0.5+x,0.5-y,0.5-z; (''):0.5+x,0.5-y,1.5-z; ('''):1+x,y,z; (*):1.5-x,-0.5+y,0.5+z; (**): 2-x,-0.5+y,1-z; (***): 1-x,-0.5+y,1-z; (#):1.5-x,1.5-y,0.5-z; (##);2-x,0.5+y,1-z; (###):1-x,1-y,1-z.

Figure S5. Presentation of the trigonal prism and the atoms at the equator plane for the β-C$_2$S trigonal polymorph: **A)** depicts the top and **B)** the bottom view. Symmetry codes: ('):x, 1+y,z; (''):05-x,0.5+y,0.5-z; ('''):0.5-x,-0.5+y,0.5-z; (*):1-x,2-y,1-z; (**):-x,2-y,1-z; (***):0.5+x,1.5-y,-0.5+z; (#): -0.5+x,1.5-y,-0.5+z; (##):1-x,1-y,1-z; (###):-x,1-y,1-z.
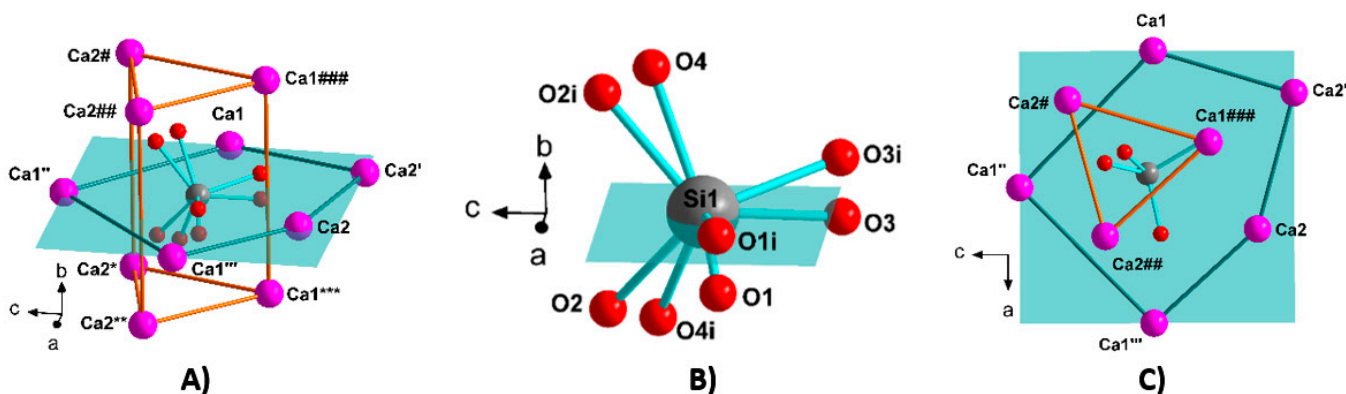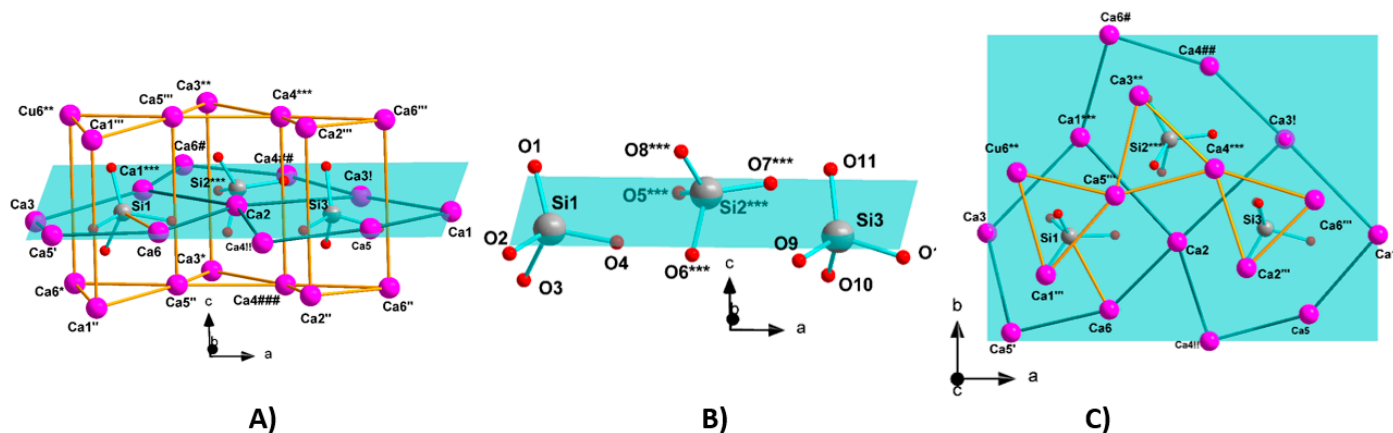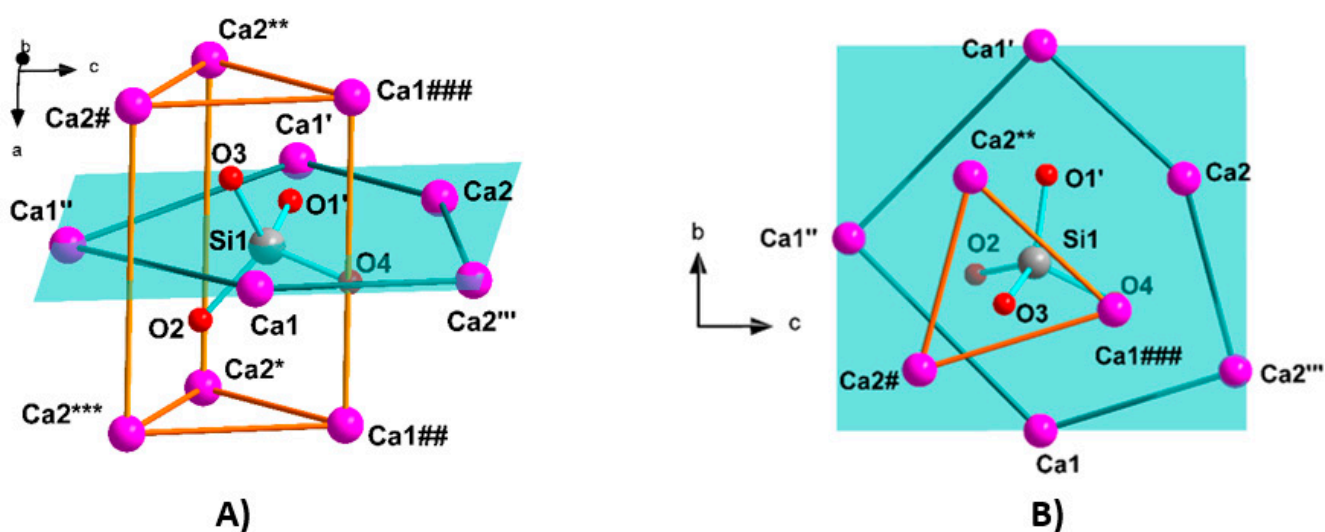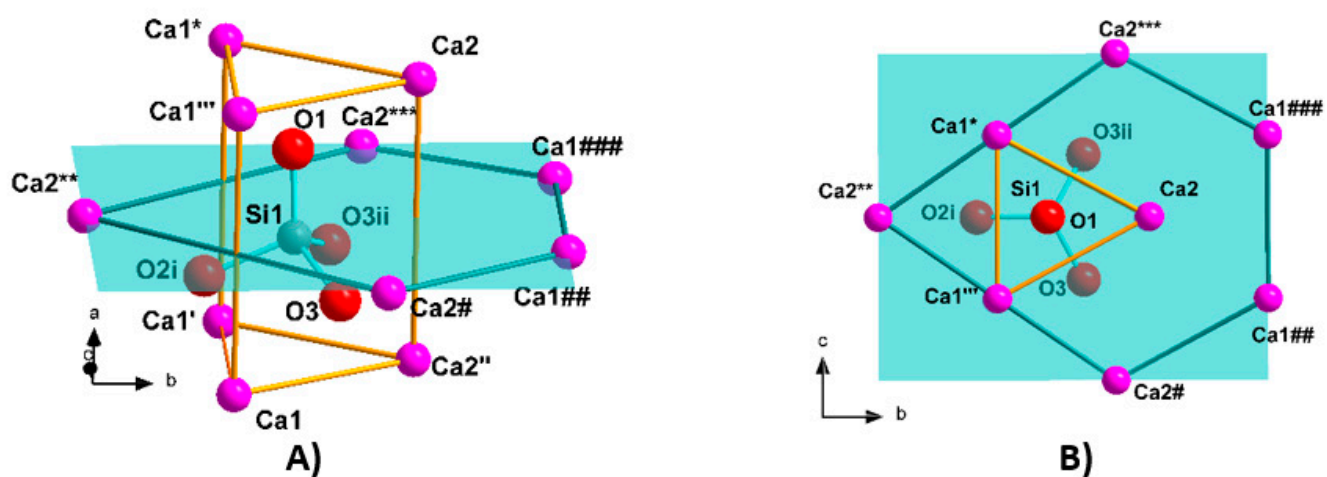
Figure S6. Presentation of the trigonal prism and the atoms at the equator plane for the γ-C₂S polymorph: **A)** depicts the top and **B)** the bottom view. Symmetry codes: ('):-x,-y,0.5+z; (''):-1+x,y,z; ('''):1+x,y,z; (*):1-x,-y,0.5+z; (**):1.5-x,-0.5+y,0.5-z; (***):-0.5+x,0.5-y,1-z; (#): -0.5+x,0.5-y,-z; (##):0.5+x,0.5-y,-z; (###): 0.5-x,0.5-y,0.5-z.

Parameter	α-C2S Tri	α-C2S-Hex	α'H-C2S	α'L-C2S (Si1)	α'L-C2S Si(2***)	α'L-C2S (Si3)	β-C2S	γ-C2S

Table-S1. Geometric parameters of trigonal prisms

Parameter	α-C2S Tri	α-C2S-Hex	α'H-C2S	α'L-C2S (Si1)	α'L-C2S Si(2***)	α'L-C2S (Si3)	β-C2S	γ-C2S
Si-A1	3.752	3.682	3.915	3.262	3.839	2.814	3.830	2.968
Si-A2	3.616	3.682	3.386	4.047	3.600	3.910	3.461	2.968
Si-A3	3.198	3.195	3.299	3.475	3.508	3.335	3.126	3.034
<Si-A1,2,3>	3.522	3.429	3.533	3.595	3.649	3.353	3.472	2.990
Si-A4	3.616	3.682	3.386	3.140	3.915	3.542	3.973	3.535
Si-A5	3.752	3.682	3.915	3.940	3.104	3.877	3.205	3.353
Si-A6	3.198	3.195	3.299	3.530	3.201	3.502	3.277	3.513
<Si-A4,5,6>	3.522	3.429	3.533	3.537	3.407	3.640	3.485	3.467
Si-B1	3.198	3.195	3.245	3.433	3.558	3.16	3.287	3.581
Si-B2	3.782	3.570	3.099	3.728	3.074	3.889	3.812	3.658
Si-B3	3.751	3.682	4.226	2.891	4.167	3.331	3.042	4.834
Si-B4	3.616	3.682	3.198	3.898	2.892	4.34	4.009	4.834
Si-B5	3.544	3.756	3.778	2.856	3.999	3.099	2.965	3.658
Si-A1,2,3	2.766	2.766	2.824	2.801	2.824	2.985	2.537	2.196
Si-A4,5,6	2.766	2.766	2.762	2.801	2.762	2.576	3.006	2.884
equat.- A1,2,3	2.766	2.766	2.801	2.737	2.960	2.738	2.783	2.548
equat.- A4,5,6	2.766	2.766	2.801	2.846	2.615	2.850	2.705	2.534
h/<l>	1.507	1.507	1.555	1.554	1.561	1.585	1.572	1.444

Footnote: Si-A1, Si-A2, Si-A3, Si-A4, Si-A5, Si-A6, Si-B1, Si-B2, Si-B3, Si-B4 and Si-B5 are distances to the corresponding calcium cation; <Si-A1,2,3> and <Si-A4,5,6> are the average distances of Si atoms from the corresponding calcium cations belonging to the bottom and top base, respectively. Si-A1,2,3; Si-A4,5,6; equat.- A1,2,3 and equat.- A4,5,6 are distances of Si cations and B1, …, B5 equator plane from the plane defined by the calcium atoms at the bottom (A1,2,3) and top (A4,5,6) bases of the trigonal prism; h is the height of the prism and <l> is the average length of the triangular bases. All lengths in the table are in Å. The coding of distances refers to Figure 7 of the main text.

Table S2. Crystallographic parameters for all studied structures.

Parameters for 8B2 prototype structure.

Formula Unit	$InNi_2$				
ICDD #	640098				
Crystal system	hexagonal				
Space Group	$P6_3/mmc$				
Cell parameters	a=4.265 Å and c=5.163 Å				
Cell volume/Z	81.33 Å³/2				
Atom	Wyck.	S.O.F.	x/a	y/b	z/c
In1	2c	1	1/3	2/3	1/4
Ni1	2a	1	0	0	0
Ni2	2d	1	1/3	2/3	0.75
Reference	[31]				

Parameters for C23 prototype structure.

Formula Unit	$CaSi_2$				
ICDD #	158275				
Crystal system	Orthorhombic				
Space Group	$Pnma$				
Cell parameters	a=7.691 Å, b=4.8174 Å and c=9.0477 Å				
	335.2 Å³/4				
Atom	Wyck.	S.O.F.	x/a	y/b	z/c
Ca1	4c	1	0.5207	0.2500	0.6759
Ca2	4c	1	0.6545	0.2500	0.0730
Si1	4c	1	0.2552	0.2500	0.1072
Reference	[32]				

Parameters for α_{Tr}-C$_2$S

Formula Unit	Ca$_2$SiO$_4$ (tr)				
ICDD #	82999				
Crystal system	Trigonal				
Space Group	*P*-3*m*1				
Cell parameters	a=5.532 Å and c=7.327 Å				
Cell volume/Z	V = 194.2 Å^3/Z=2				
Atom	**Wyck.**	**S.O.F.**	**x/a**	**y/b**	**z/c**
Ca1	2d	1	-1/3	1/3	0.2523
Ca2	1b	1	0	0	1/2
Ca3	1a	1	0	0	0
Si1	2d	1	1/3	2/3	0.2314
O1	6i	0.3333	0.2714	0.5430	0.0176
O2	6i	1	0.1749	0.3498	0.2928
Reference	[4]				

Parameters for α_{H}-C$_2$S

Formula sum	Ca$_2$SiO$_4$ (α_H)				
ICDD #	82998				
Crystal system	Hexagonal				
Space Group	*P*6$_3$/*mmc*				
Cell parameters	a=5.532 Å and c=7.327 Å				
Cell volume/Z	V=194.2 Å^3/Z=2				
Atom	**Wyck.**	**S.O.F.**	**x/a**	**y/b**	**z/c**
Ca1	4f	0.5	1/3	2/3	0.7373
Ca2	2a	1	0	0	1
Si1	2c	1	1/3	2/3	1/4
O1	12k	0.333	0.2721	0.5442	0.4595
O2	12k	0.333	0.1741	0.3482	0.2018
Reference	[4]				

Parameters for α′H-C2S

Formula Unit	Ca2SiO4 (α'_H)				
ICDD #	82997				
Crystal system	Orthorhombic				
Space Group	*Pnma*				
Cell parameters	a=6.871 Å, b= 5.601 Å and c=9.556 Å				
Cell volume/Z	V = 367.8 Å³/Z=4				
Atom	Wyck.	S.O.F.	x/a	y/b	z/c
Ca1	8d	0.5	0.3326	1/4	0.5732
Ca2	8d	0.5	0.9879	1/4	0.2989
Si1	4c	1	0.7831	1/4	0.5891
O1	8d	0.5	1.0050	0.1919	0.5545
O2	8d	0.5	0.7436	0.0308	0.7016
O3	8d	0.5	0.6658	0.1901	0.4449
O4	8d	0.5	0.7041	0.5030	0.6495
Reference	[4]				

Parameters for α′L-C2S

Formula Unit	Ca2SiO4 (α'_L)				
ICDD #	82996				
Crystal system	Orthorhombic				
Space Group	*Pna2₁*				
Cell parameters	a=20.527 Å, b=9.496 Å and c=5.590 Å				
Cell volume/Z	V = 1089.6 Å³/Z=12				
Atom	Wyck.	S.O.F.	x/a	y/b	z/c
Ca1	4a	1	0.7787	0.0726	0.7465
Ca2	4a	1	0.4417	0.0469	0.8011
Ca3	4a	1	0.1225	0.0794	0.7025
Ca4	4a	1	0.9958	0.8137	0.7228
Ca5	4a	1	0.6627	0.7836	0.7652
Ca6	4a	1	0.3275	0.8001	0.7453
Si1	4a	1	0.2607	0.0680	0.7590

Si2	4a	1	0.9284	0.0805	0.7557
Si3	4a	1	0.5896	0.0959	0.727
O1	4a	1	0.7585	0.8504	0.4906
O2	4a	1	0.7716	0.8674	0.053
O3	4a	1	0.7811	0.0640	0.2141
O4	4a	1	0.6628	0.9287	0.2032
O5	4a	1	0.6080	0.4332	0.1838
O6	4a	1	0.5845	0.6998	0.0427
O7	4a	1	0.4988	0.5610	0.2906
O8	4a	1	0.5969	0.6734	0.4786
O9	4a	1	0.9500	0.4462	0.1919
O10	4a	1	0.9252	0.6903	0.1270
O11	4a	1	0.9213	0.6881	0.4724
O12	4a	1	0.8344	0.5495	0.1618
Reference	[4]				

Parameters for β-C2S

Formula Unit	Ca2SiO4 (β)				
ICDD #	81096				
Crystal system	Monoclinic				
Space Group	*P*21/*n*				
Cell parameters	a=5.512 Å, b=6.758 Å, c=9.314 Å and β= 94.581°				
Cell volume/Z	V = 345.8 Å³/Z=4				
Atom	Wyck.	S.O.F.	x/a	y/b	z/c
Ca1	4e	1	0.2276	0.3435	0.4304
Ca2	4e	1	0.2203	0.9979	0.7018
Si1	4e	1	0.2680	0.7806	0.4193
O1	4e	1	0.2195	0.0077	0.4424
O2	4e	1	0.4753	0.7496	0.3083
O3	4e	1	0.0158	0.6728	0.3619
O4	4e	1	0.3431	0.6757	0.5718
Reference	[3]				

Parameters for γ-C2S

Formula Unit	Ca2SiO4 (γ)				
ICDD #	82994				
Crystal system	Orthorhombic				
Space Group	*Pbnm*				
Cell parameters	a= 5.076 Å, b=11.214 Å and c=6.758 Å				
Cell volume/Z	V = 384.7 Å3/Z =4				
Atom	Wyck.	S.O.F.	x/a	y/b	z/c
Ca1	4a	1	0	0	1
Ca2	4c	1	0.9924	0.2822	0.2500
Si1	4c	1	0.4293	0.0950	0.2500
O1	4c	1	0.7489	0.0932	0.2500
O2	4c	1	0.2996	0.9624	0.2500
O3	8d	1	0.2991	0.1623	0.0561
Reference	[4]				

Table S3. Transformation matrices of the unit cell axes which relate the cell axes of each belite polymorph with the hexagonal axes of the α-C$_2$S polymorph.

$(a',b',c')=(a,b,c)P$	Transformation matrix P
a'_H-C$_2$S: $(a_{\alpha'H}, b_{\alpha'H}, c_{\alpha'H})=(a_{\alpha H}, b_{\alpha H}, c_{\alpha H})\ P$	$\begin{pmatrix} 0 & 1 & -1 \\ 0 & 1 & 1 \\ 1 & 0 & 0 \end{pmatrix}$
a'_L-C$_2$S: $(a_{\alpha'L}, b_{\alpha'L}, c_{\alpha'L})=(a_{\alpha H}, b_{\alpha H}, c_{\alpha H})\ P$	$\begin{pmatrix} 0 & -1 & -1 \\ 0 & 1 & -1 \\ 3 & 0 & 0 \end{pmatrix}$
a'_γ-C$_2$S: $(a_\gamma, b_\gamma, c_\gamma)=(a_{\alpha H}, b_{\alpha H}, c_{\alpha H})\ P$	$\begin{pmatrix} -1 & 0 & -1 \\ -1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$
a'_β-C$_2$S: $(a_\beta, b_\beta, c_\beta)=(a_{\alpha H}, b_{\alpha H}, c_{\alpha H})\ P$	$\begin{pmatrix} 1 & -1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$