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Electronic Supplementary Information

The steps of thermal treatment of Na-magadiite: a computational study by ab initio DFT calculations.

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With the Quantum-ESPRESSO computational package, the NMR calculations were done by the GIPAW method. The calculated chemical shielding (σ_{iso}) of reference standards were compared with their respective experimental chemical shifts (Table S1). The equations obtained by linear regression (Figure S1) were used to obtain the spectra of ^{29}Si nucleus (Figure S4) with a Lorentzian distribution and broadening of 120 MHz. The thermodynamic potentials of Figure S2 and the vibrational modes of Table S5 were performed using DFPT. The simulated XRD of Figure S4 were plotted using the Mercury program, with an FHWM = 1.0º at 2θ. Theoretical and experimental assignments of mainly peaks of XRD were written in Table S2 and Table S3, respectively. The PBE-D3 were used to compare the electronic energies (Table S4) and ΔGº/ΔHº (Figure S3) with PBE. Atomic positions and cell parameters of all PEB-optimized models were provided in Table S6.

Table S1) Experimental and theoretical NMR parameters of reference systems of known structure for ^{29} Si and ^{23}Na nuclei.

^{29}Si			^{23}Na		
Compound	**Calculated σ_{iso}**	**Experimental δ_{iso} (ppm)**	**Compound**	**Calculated σ_{iso}**	**Experimental δ_{iso} (ppm)**
α-$Na_2Si_2O_5$	447.0	-94.2[a]	α-$Na_2Si_2O_5$	531.4	17.3[a]; 17.4[d]
β-$Na_2Si_2O_5$	439.4	-86.3[a]	β-$Na_2Si_2O_5$	534.6	14.9[a] ; 20.4[d]
	439.2	-88.2[a]		542.9	7.6[a] ; 8.3[d]
Kaolinite	442.9	-91.7[b]	NaCl	543.2	6.6[e]

	443.5	-94.2[b]			
Talc	449.7	-97.0[c]	$Na_3P_3O_9$	555.7	-5.6[d]

[a]Ref. 1, [b]Ref. 2, [c]Ref. 3, [d]Ref. 4, [e]Ref. 5

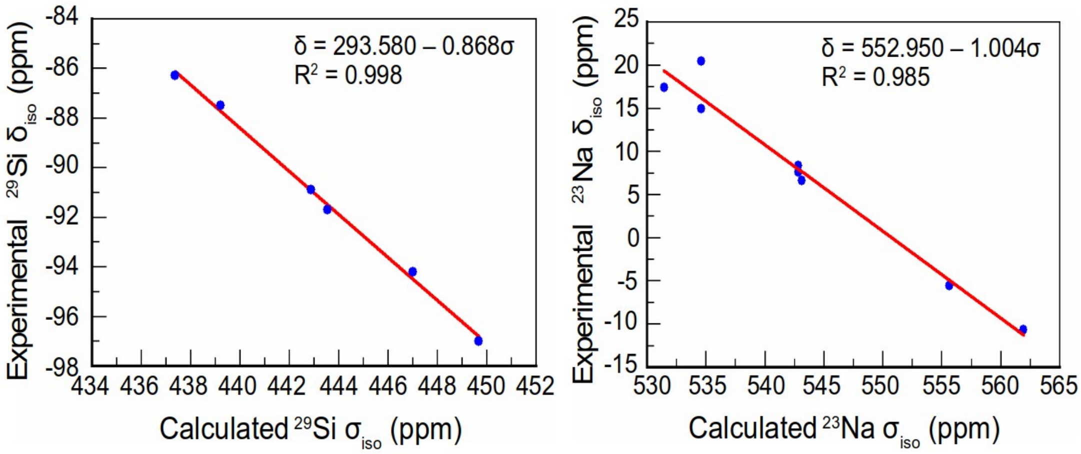

Figure S1) Correlation between experimental isotropic chemical shift δ_{iso} and calculated isotropic chemical shielding σ_{iso} for ^{29}Si and ^{23}Na nuclei.

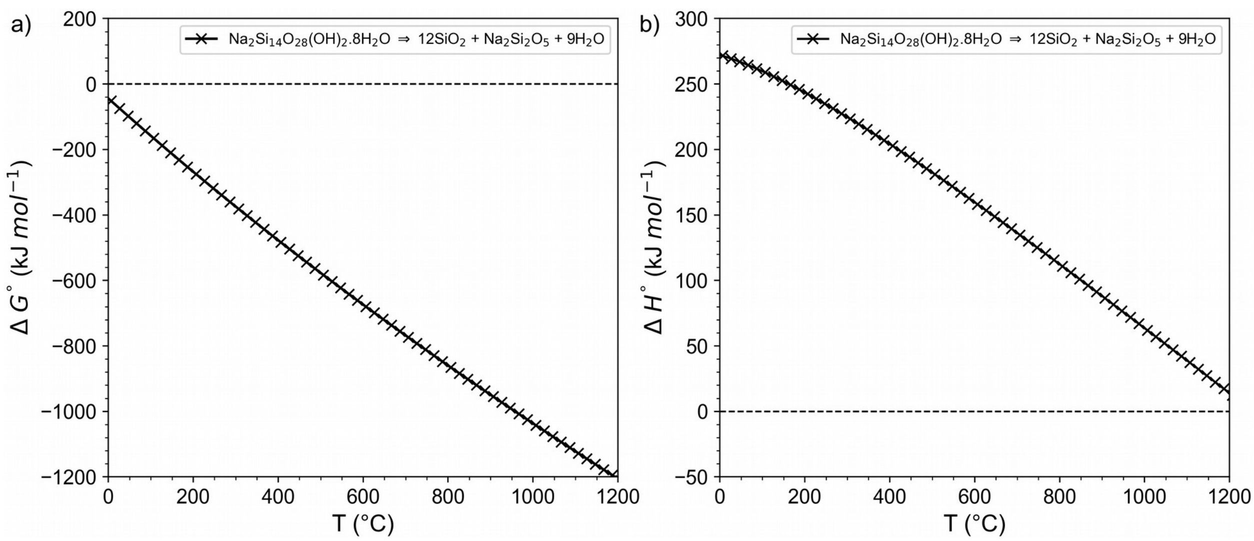

Figure S2) a) Gibbs free energy and b) Enthalpy of the final decomposition of Na-magadiite as a function of temperature.

Table S2) Assignments (h k l) of main XRD peaks of Na-magadiites.

2 θ	**$Na_2Si_{14}O_{28}(OH)_2.8\ H_2O$**	**$Na_2Si_{14}O_{28}(OH)_2.4\ H_2O$**	**$Na_2Si_{14}O_{28}(OH)_2$**
$d_{(0\,0\,2)}$	5.72°	5.93°	5.98°
$d_{(0\,0\,4)}$	11.44°	11.87°	11.97°
$d_{(0\,0\,6)}$	17.25°	17.84°	18.00°
$d_{(0\,0\,7)}$	20.05°	20.85°	21.03°
$d_{(0\,0\,8)}$	23.04°	23.82°	24.08°
$d_{(0\,0\,9)}$	26.07°	26.90°	27.15°

$d_{(0\ 0\ 10)}$	28.87º	29.97º	30.22º
$d_{(1\ 0\ 4)}$	12.88º	12.90º	12.90º
$d_{(1\ 0\ 6)}$	15.78º	15.98º	16.02º
$d_{(1\ 0\ 7)}$	17.75º	18.10º	18.14º
$d_{(1\ 0\ 8)}$	19.96º	20.41º	20.50º
$d_{(1\ 0\ 9)}$	22.37º	22.90º	23.03º
$d_{(1\ 0\ 10)}$	24.92º	25.52º	25.67º
$d_{(1\ 0\ 11)}$	27.57º	28.23º	28.41º
$d_{(1\ 0\ 12)}$	30.32º	31.03º	31.24º

Table S3) Experimental assignments (h k l) of main peaks of high-temperature in situ XRD of Na-magadiites.[f]

Temperature	2θ
273 K	5.68º, 24.96º, 26.01°, 27.35°, 28.26º
573 K	6.24º, 25.79°, 26.90°
673 K	7.60º, 26.2°

[f] Ref. 6

Dehydration Steps:

$Na_2Si_{14}O_{28}(OH)_2.8H_2O \rightarrow Na_2Si_{14}O_{28}(OH)_2.4H_2O + 4\ H_2O$ (R1)

$Na_2Si_{14}O_{28}(OH)_2.4H_2O \rightarrow Na_2Si_{14}O_{28}(OH)_2 + 4\ H_2O$ (R2)

Table S4) PBE and PBE-D3 electronic desorption energies of dehydration steps of Na-magadiite.

Reaction - Calculation	Energy (kcal/mol)	Energy (kJ/mol)
R1 - PBE	46.518	194.446
R1 - PBE-D3	67.601	282.572
R2 - PBE	69.972	292.485
R2 - PBE-D3	94.556	395.243

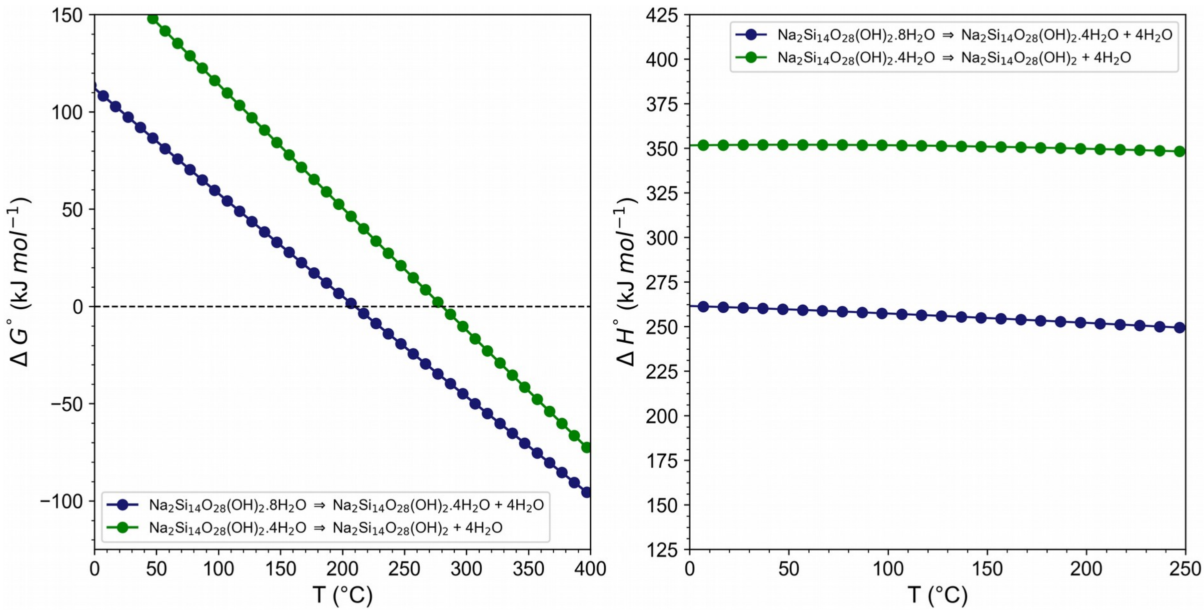

Figure S3) Gibbs free energy and Enthalpy of the dehydration reactions of Na-magadiite as a function of temperature using PBE-D3.

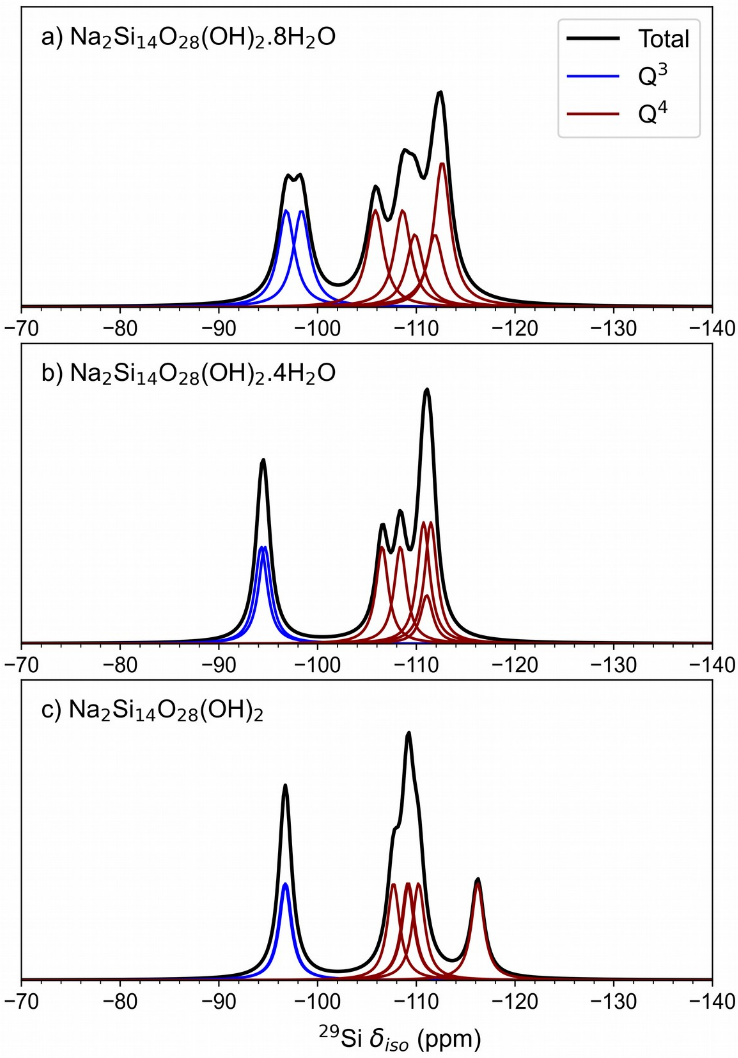

Figure S4) Simulated ^{29}Si NMR spectra of a) $Na_2Si_{14}O_{28}(OH)_2$. 8 H_2O b) $Na_2Si_{14}O_{28}(OH)_2$. 4 H_2O, and c) $Na_2Si_{14}O_{28}(OH)_2$.

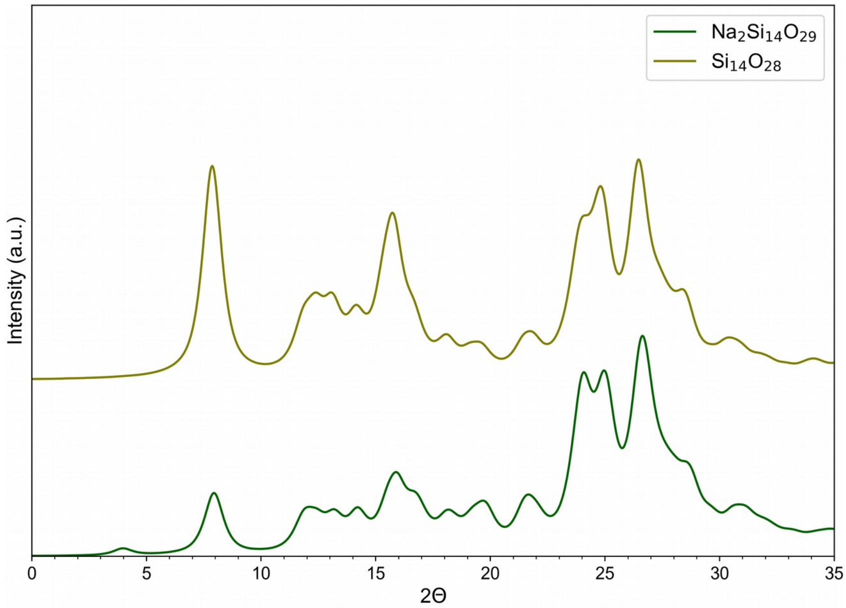

Figure S5) Simulated XRD patterns of intermediate models of Na-magadiites.

Table S5) Assignments of the main calculated vibrational modes of Na-magadiites.

Assignments	**$Na_2Si_{14}O_{28}(OH)_2.8\ H_2O$**	**$Na_2Si_{14}O_{28}(OH)_2.4\ H_2O$**
$\nu_a(H_2O)$	3714, 3566, 3607, 3590, 3386	3397, 3234
$\nu_s(H_2O)$	3492, 3476, 3343, 3175, 3153	3274, 2983
$\delta_{sc}\ (H_2O)$	1640, 1620, 1590	1645
δ(SiO-H)	1384, 1252	1385, 1249
ν(Si-O-Si)	1213, 1165, 1112, 1084, 1057	1215, 1166, 1107, 1072, 1029
ν_a(O-Si-O)	1002	998
ν_a(Si-OH)	969	965
$\delta_{tw}\ H_2O$ + ν_s(O-Si-O)	836, 802, 763, 699	929, 882, 804, 763, 687
$\delta_{tw}\ H_2O$ + $\delta(O\text{-}Si\text{-}O)_{2\text{-rings}}$	635, 575, 557, 503, 535, 459, 422	658, 639, 558, 549, 441, 419
Assignments	**$Na_2Si_{14}O_{28}(OH)_2$**	**$Na_2Si_{14}O_{29}$**
δ(SiO-H)	1285	-
ν(Si-O-Si)	1211, 1148, 1126, 1077,	1191, 1145, 1067
ν_a(O-Si-O)	1046	1000
ν_a(Si-OH)	983	-
ν_s(O-Si-O)	939, 876, 773, 750, 685	992, 943, 819, 769, 712, 659
$\delta(O\text{-}Si\text{-}O)_{2\text{-rings}}$	586, 553, 450, 442, 416	580, 499, 453, 439, 412

Table S6) PBE-optimized cell parameters and atomic positions of magadiites.

$Na_2Si_{14}O_{28}(OH)_2.4H_2O$

Cell Parameters

-5.266530486	5.068935471	-0.004838970
5.265672746	5.068513541	-0.004525869
-21.063285505	5.041104111	29.789175225

Atomic positions (cartesian x y z in Å)

Si	-1.160124976	2.307569514	0.135032263	O	-8.274976945	11.540173049	11.450483551
Si	-4.620193682	3.777784446	1.988112014	O	-11.358597776	5.222966292	12.219725453
Si	-0.153506025	4.361835935	2.355907805	O	-9.728248985	3.662051154	13.644461836
Si	2.355565692	6.272964521	2.284463500	O	-13.235626999	5.789115879	14.014201935
Si	-2.663188673	6.180432446	1.924133226	O	-10.199370190	5.591615849	15.411721021
Si	-6.180221439	5.059752787	4.304921867	O	-11.774634464	7.707017639	13.026834978
Si	-4.162676548	7.480662615	4.247014092	O	-10.194201335	9.428618986	14.155541468
Si	-6.790096283	4.936536758	10.422668614	O	-8.279121028	9.137708614	15.965704297
Si	-3.527688256	7.574051775	10.356833905	O	-9.266521426	7.113193122	17.429058003
Si	-9.046256730	4.825476285	14.557001793	O	-11.784627549	7.314057823	16.535147654
Si	-8.030597737	6.885049624	12.343615099	O	-10.984288348	5.214724247	17.930785867
Si	-5.515431568	8.781088889	12.392118458	O	-13.142024304	3.893881235	18.631000267
Si	-12.490833206	6.297234396	12.678315934	O	-15.315322426	6.598706768	18.571635869
Si	-10.539532421	8.712435135	12.741475591	O	-12.828708644	6.412761147	19.507636117
Si	-10.544553684	6.314827136	16.822204584	O	-13.231332696	9.245645934	15.548528575
Si	-12.058530036	5.023753959	19.147953228	O	-9.732581874	11.359295488	15.924432692
Si	-8.030557240	8.142731283	17.219352840	O	-11.360071033	9.795271357	17.350623470
Si	-14.066056858	7.452141090	19.207832254	O	-11.964158282	12.366567952	16.851813187
Si	-9.044454817	10.201694150	15.009047755	O	-13.551310349	8.551432379	18.103190466
Si	-12.495357628	8.726516830	16.885429106	O	-14.577349887	8.162351056	20.554637385
Si	-10.785842558	11.307146976	17.172166320	O	-12.788840832	9.076021702	22.300769146
Si	-14.694064828	7.537541744	25.325596427	O	-16.567314301	9.606692551	20.495146354
Si	-20.417365526	6.167554837	27.590982933	O	-15.426523763	11.604512355	22.180965197
Si	-18.708072086	8.740568860	27.287760887	O	-15.810780556	6.253819150	22.141334663
Si	-16.713554535	9.957354317	25.268516592	O	-13.919283163	7.073760557	23.975494406
Si	-23.725992339	8.835439998	27.648245726	O	-18.453094157	8.779971930	22.326862597
Si	-21.215469203	10.654359116	27.217408916	O	-15.465358453	8.928706583	24.976735721
Si	-22.223929746	12.707007273	29.437685101	O	-17.218622976	10.668016856	23.919758121
Na	-10.361101037	6.114461844	7.627928841	O	-16.220320224	11.059001741	26.380376250
Na	-2.460226833	3.578290082	7.035406679	O	-17.958496009	9.091520658	25.897219192
Na	-10.365097473	8.915211408	21.944692642	O	-18.905617514	12.782429412	26.558115164
Na	-18.261260901	6.381285513	22.538260029	O	-21.044182559	11.461631817	25.804858959
O	3.393878512	6.215254364	1.024253792	O	-19.893134649	9.797360613	27.590541684
O	1.170191394	5.216512093	1.982177590	O	-17.668969301	8.797925336	28.547490694
O	-0.396019588	3.350904056	1.114287829	O	-22.464927692	9.639687463	27.011761644
O	0.017244739	3.553954217	3.768032051	O	-21.455663693	11.665773801	28.459328136
O	-1.401036428	5.378893572	2.562356946	O	-19.281036299	7.228064963	27.109879627
O	-2.292094326	6.868927961	0.503569748	O	-23.354293779	8.143524228	29.066819759
O	-0.082271745	8.319798178	0.645211633	O	-21.141598619	6.695603387	28.930873809
O	-0.420477004	9.023685373	3.192059174	O	-19.708411513	4.754565604	27.940492361
O	-3.110078438	7.303640699	3.007451330	H	-18.301247147	11.474100206	23.998960756
O	-2.158984815	0.854365617	3.678966145	H	-15.672556461	8.951669801	20.470219765
O	-3.483798316	2.716546997	2.467011006	H	-5.133649164	6.080833581	9.096115545
O	-3.910705616	5.190250544	1.638210372	H	-7.765402997	3.549087729	5.573059656

O	-4.932424297	6.088514582	4.596976628	H	-16.057220060	11.304394867	22.916411071
O	-3.387208651	7.948054719	5.594911346	H	-15.735116035	11.007632660	21.452480017
O	-2.251581237	5.950744552	7.267011595	H	-13.096389023	8.474939412	23.026563180
O	-6.686310105	4.351135301	5.654671171	H	-13.422715724	8.782307349	21.564336122
O	-4.889670199	3.424013822	7.394634256	H	-15.467632246	6.894311602	21.452054831
O	-5.276093520	8.778287611	7.427705648	H	-15.171031420	6.465373569	22.877861142
O	-4.042355940	6.866766541	9.009544114	H	-18.104471204	9.417366855	23.017357071
O	-7.917821581	6.248581518	7.243416320	H	-17.817227862	8.994249543	21.587484446
O	-6.030736989	5.424500302	9.072725315	H	-7.280056965	6.035240972	7.981706248
O	-7.557618011	3.546309256	10.060903138	H	-7.572849518	5.608357760	6.554219489
O	-5.720125465	4.747144496	11.644138460	H	-5.198414693	4.023413006	8.121166342
O	-7.877259258	6.063846695	10.937439169	H	-2.560740229	6.551546725	6.541454165
O	-4.776590489	8.423713941	10.998014556	H	-5.521827975	3.720241979	6.659189488
O	-6.692248796	7.719687238	12.710997262	H	-2.885902821	6.243883610	8.002934991
O	-9.258640672	7.923285697	12.127401421	H	-4.932825964	8.137288038	8.116274192
O	-8.291791836	5.894363675	13.597583478	H	-4.638068435	8.564978674	6.690164601

$Na_2Si_{14}O_{28}(OH)_2$

Cell Parameters

-5.314466762	5.055087165	-0.004764813
5.314642326	5.055824132	-0.004631321
-21.259515955	5.023053079	29.538307014

Atomic positions (cartesian x y z in Å)

Si	-1.082598	2.265460	0.003438	O	-6.193477	5.730060	9.030764
Si	-4.472018	3.751393	2.062540	O	-7.613128	3.665550	9.758903
Si	0.024812	4.365251	2.081640	O	-5.568259	4.550219	11.304390
Si	2.563005	6.174289	2.254856	O	-7.861371	5.897619	11.167610
Si	-2.507667	6.191897	1.972762	O	-4.688409	8.256947	10.892017
Si	-6.125270	5.036241	4.413058	O	-6.461838	7.562997	12.742757
Si	-4.189097	7.525707	4.216576	O	-9.001852	8.029682	12.178094
Si	-6.806125	4.972442	10.334172	O	-8.293276	6.027225	13.803650
Si	-3.425027	7.538727	10.135319	O	-8.028625	11.569896	11.192183
Si	-9.018679	4.782250	14.560525	O	-11.351175	5.079970	12.098632
Si	-7.902759	6.871449	12.476013	O	-9.548238	3.688622	13.480636
Si	-5.364539	8.675282	12.300299	O	-13.266663	5.855927	13.784536
Si	-12.398350	6.256521	12.485381	O	-10.282576	5.357173	15.420724
Si	-10.430500	8.697984	12.567847	O	-11.564313	7.590947	12.882609
Si	-10.442057	6.286322	16.749624	O	-10.276245	9.627355	13.897265
Si	-12.125017	4.958426	18.991035	O	-8.286752	8.968555	15.520131
Si	-7.909728	8.115432	16.846134	O	-9.018869	6.965796	17.137146
Si	-14.058843	7.449548	19.183746	O	-11.584316	7.385322	16.436575
Si	-9.016624	10.208984	14.759892	O	-10.887714	5.375676	18.017731
Si	-12.402902	8.728635	16.835999	O	-13.179937	4.028068	18.163012
Si	-10.683245	11.362288	17.015268	O	-15.321168	6.729628	18.426449
Si	-14.820663	7.453699	25.102850	O	-12.930809	6.267455	19.563065
Si	-20.416838	6.171840	27.262251	O	-13.267598	9.140009	15.537841
Si	-18.697180	8.805812	27.066265	O	-9.554685	11.301635	15.836662
Si	-16.755461	9.943492	24.907887	O	-11.343517	9.895525	17.221022
Si	-23.768339	8.785504	27.346806	O	-11.788635	12.467688	16.576944
Si	-21.237452	10.614381	27.235912	O	-13.349121	8.478353	18.125320
Si	-22.343164	12.714238	29.316767	O	-14.518280	8.121009	20.554649
Na	-13.000786	8.284673	7.475731	O	-16.825735	9.261620	20.292435
Na	-5.031955	5.766967	7.064307	O	-14.200015	6.704940	23.798233

Na	-13.010025	6.689108	21.842365	O	-15.623254	8.764764	24.530281
Na	-20.971972	4.169904	22.261337	O	-17.206703	10.621617	23.537731
O	3.696833	6.232356	1.081050	O	-16.053333	10.969417	25.974026
O	1.461372	5.065703	1.815262	O	-18.021648	9.220807	25.656311
O	-6.575562	4.358394	5.783657	O	-18.904531	12.923923	26.081062
O	-3.883897	6.863755	8.765881	O	-21.194899	11.577082	25.919100
O	-0.351512	3.508357	0.758088	O	-19.800667	9.914208	27.501740
O	0.067440	3.402252	3.398300	O	-17.565222	8.750284	28.242208
O	-1.084071	5.516641	2.367036	O	-22.345985	9.462587	26.950998
O	-2.345950	7.114534	0.639928	O	-21.613813	11.472088	28.559139
O	-0.018450	8.391895	0.758739	O	-19.360796	7.339303	26.868696
O	-0.108878	9.067618	3.340954	O	-23.604759	7.864477	28.680614
O	-2.958320	7.107431	3.235522	O	-21.278425	6.586042	28.561371
O	-2.078635	0.702079	3.670433	O	-19.594053	4.831739	27.663172
O	-3.417298	2.583636	2.458510	H	-18.624187	11.243728	23.901758
O	-3.647025	5.089911	1.660515	H	-15.935219	8.746158	20.185482
O	-4.994414	6.216479	4.789193	H	-5.300502	6.241432	9.138235
O	-3.569320	8.274224	5.522146	H	-7.995320	3.736927	5.418473

$Na_2Si_{14}O_{29}$

Cell Parameters

7.510334046	0.006206116	-0.089103441
-0.292784635	7.505957148	-0.127558618
15.592102648	-10.620994149	22.237724440

Atomic positions (cartesian x y z in Å)

Si	2.768720	0.575270	0.369690	O	9.597120	2.588280	7.440820
Si	6.181310	-0.503540	2.003180	O	10.948600	1.263810	9.282770
Si	3.523320	3.114920	2.231900	O	12.612910	-0.557550	8.253090
Si	2.906480	6.046590	2.329120	O	10.448910	-1.253730	9.691100
Si	6.482790	2.617250	1.790200	O	14.435451	3.103710	7.454690
Si	7.262590	0.102230	4.621290	O	12.280950	-4.048350	8.373140
Si	8.718170	2.625250	3.939940	O	10.183001	-3.890570	10.038980
Si	8.690650	-0.949360	7.148020	O	14.128380	-4.943500	10.130660
Si	8.372290	3.517030	6.885720	O	11.754049	-2.449120	11.607330
Si	10.357511	-2.447480	10.779090	O	14.152430	-2.440120	9.342620
Si	11.058800	-0.216520	8.609430	O	13.954781	-0.076950	10.509810
Si	10.593710	2.747860	8.725900	O	12.833140	1.528340	12.232270
Si	13.834750	-3.961260	8.876989	O	12.307731	-0.766420	13.616461
Si	14.002800	-0.843270	9.072880	O	14.164370	-2.434920	12.647110
Si	12.586880	-2.258540	12.983001	O	12.099140	-3.397270	14.025090
Si	12.698999	-4.407030	15.166730	O	12.188169	-5.950710	14.839820
Si	11.852100	0.769460	13.277781	O	16.629780	-5.565820	14.522141
Si	15.912870	-4.214560	15.110351	O	14.319530	-4.489710	15.029790
Si	14.027360	1.426110	11.134521	O	16.584509	-2.189790	11.641900
Si	15.693480	-2.013760	12.984200	O	15.463650	1.655080	11.871060
Si	16.335739	0.991290	13.079400	O	15.721910	-0.462670	13.503640
Si	13.202120	-3.180380	17.692261	O	17.864408	0.785370	12.558300
Si	16.123411	-9.513841	20.398710	O	16.303928	-2.930670	14.176730
Si	16.741850	-6.427290	20.035000	O	12.181760	-3.945080	16.609280
Si	15.925250	-4.247300	18.128860	O	14.313499	-4.350320	18.092129
Si	20.484030	-9.752500	20.492491	O	16.469349	-3.917730	16.597380
Si	19.733810	-6.736140	19.911341	O	16.389231	-2.950820	19.024090
Si	21.954700	-5.798610	21.826641	O	16.539820	-5.693910	18.560850

O	1.986370	6.882460	1.219760	O	19.780430	-2.899210	18.921030
O	3.190720	4.561740	1.611470	O	19.738890	-6.693450	18.344501
O	3.125300	1.930710	1.218770	O	18.245739	-6.379820	20.558020
O	2.788290	2.864210	3.703210	O	15.841610	-5.612420	21.100779
O	5.126670	3.029070	2.645760	O	20.087179	-8.206651	20.570459
O	6.490380	3.378190	0.370170	O	20.745150	-5.736230	20.767740
O	6.274780	5.996050	0.685680	O	16.203560	-7.981660	19.766081
O	6.737050	6.604230	3.215870	O	19.652571	-10.488770	21.696630
O	7.733770	3.101950	2.737530	O	17.092911	-9.639740	21.664499
O	2.739530	-1.561540	3.955270	O	14.603530	-9.931240	20.764980
O	4.613200	-0.563370	2.378430	O	7.848270	-0.898850	5.802950
O	6.560060	1.025490	1.548040	Na	12.609260	-0.121240	16.545010
O	8.595901	1.049660	4.290610	O	13.893190	-1.905090	17.011669
O	8.200380	3.438260	5.284190	Na	15.924350	-1.033500	17.350222
O	9.005079	-2.498410	7.517690	Na	3.820690	0.122380	4.898840
O	7.785870	-0.291130	8.356589	O	5.978270	0.940840	5.046730
O	10.189060	-0.246930	7.211640	Na	5.635490	3.139300	4.948230

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