MECHANISM OF INITIAL STEP OF GERMANOSILICATE FORMATION IN SOLUTION

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SUPPORTING INFORMATION

S1a./Selected distances (Å) and angles (degree) for the stationary points along the reaction path to form GeO-Ge (reaction between $Ge(OH)_3O^-$ and $Ge(OH)_4$, see figure 1) with the explicit AIMD approach (average on the trajectory associated to each point) and for the cluster calculation in an implicit solvent model (COSMO). Structure labels are presented in scheme 1.

Distances and angles	R		TS1		I		TS2		P	
	AIMD	*COSMO*	AIMD	*COSMO*	AIMD	*COSMO*	AIMD	*COSMO*	AIMD	*COSMO*
d(Ge1-O3)	1.72 ± 0.03	*1.70*	1.73 ± 0.04	*1.72*	1.73 ± 0.04	*1.76*	1.77 ± 0.04	*1.80*	1.78 ± 0.04	*1.78*
d(Ge2-O3) (rc1)	3.8 ± 0.2	*3.56*	2.40	*2.76*	1.96 ± 0.08	*1.93*	1.85 ± 0.05	*1.81*	1.82 ± 0.05	*1.83*
d(Ge2-O4) (rc2)	1.77 ± 0.05	*1.79*	1.83 ± 0.05	*1.81*	1.92 ± 0.06	*1.90*	2.50	*2.71*	4.1 ± 0.4	*3.38*
d(Ge1-Ge2)	4.7 ± 0.2	*3.84*	3.6 ± 0.1	*3.65*	3.4 ± 0.1	*3.20*	3.22 ± 0.09	*3.03*	3.2 ± 0.08	*3.25*
a(Ge1-O3-Ge2)	113 ± 7	*86.16*	123 ± 6	*106.58*	139 ± 7	*120.25*	126 ± 6	*114.12*	127 ± 6	*128.82*
a(O3-Ge2-O5)	103 ± 14	*89.83*	84 ± 4	*80.32*	90 ± 4	*89.12*	98 ± 4	*103.77*	101 ± 5	*116.68*
a(O3-Ge2-O4)	135 ± 7	*153.87*	172 ± 4	*170.48*	172 ± 4	*179.58*	172 ± 4	*158.36*	135 ± 15	*124.53*

S1b./ Selected distances (Å) and angles (degree) for the stationary points along the reaction path to form the SiO-Ge (reaction between $Si\text{-}OH)_3O^-$ and $Ge(OH)_4$, see figure 2) with the explicit AIMD approach (average on the trajectory associated to each point) and for the cluster calculation in an implicit solvent model (COSMO). Structure labels are presented in scheme 1.

Distances and angles	R		TS1		I		TS2		P	
	AIMD	*COSMO*	AIMD	*COSMO*	AIMD	*COSMO*	AIMD	*COSMO*	AIMD	*COSMO*
d(Si1-O3)	1.61 ± 0.03	*1.65*	1.60 ± 0.03	*1.60*	1.62 ± 0.03	*1.64*	1.64 ± 0.04	*1.66*	1.65 ± 0.04	*1.65*
d(Ge2-O3) (rc1)	3.72 ± 0.2	*3.61*	2.50	*2.73*	2.0 ± 0.1	*1.92*	1.83 ± 0.05	*1.80*	1.81 ± 0.05	*1.82*
d(Ge2-O4) (rc2)	1.79 ± 0.04	*1.81*	1.81 ± 0.04	*1.81*	1.89 ± 0.05	*1.90*	2.50	*2.72*	3.8 ± 0.2	*3.38*
d(Si1-Ge2)	4.6 ± 0.2	*3.83*	3.7 ± 0.1	*3.61*	3.29 ± 0.1	*3.15*	3.18 ± 0.08	*2.98*	3.18 ± 0.08	*3.18*
a(Si1-O3-Ge2)	113 ± 9	*84.75*	127 ± 6	*110.24*	130 ± 6	*124.17*	133 ± 7	*118.68*	135 ± 7	*132.77*
a(O3-Ge2-O5)	104 ± 13	*84.91*	84 ± 4	*81.11*	90 ± 4	*88.70*	97 ± 4	*103.53*	100 ± 4	*117.49*
a(O3-Ge2-O4)	103 ± 12	*163.71*	172 ± 4	*171.60*	173 ± 3	*179.48*	171 ± 5	*157.46*	141 ± 8	*125.30*

S1c./ Selected distances (Å) and angles (degree) for the stationary points along the reaction to form the GeO-Si (reaction between $Ge(OH)_3O^-$ and $Si(OH)_4$, see figure 3) with the explicit AIMD approach (average on the trajectory associated to each point) and for the cluster calculation in an implicit solvent model (COSMO). Structure labels are presented in scheme 1.

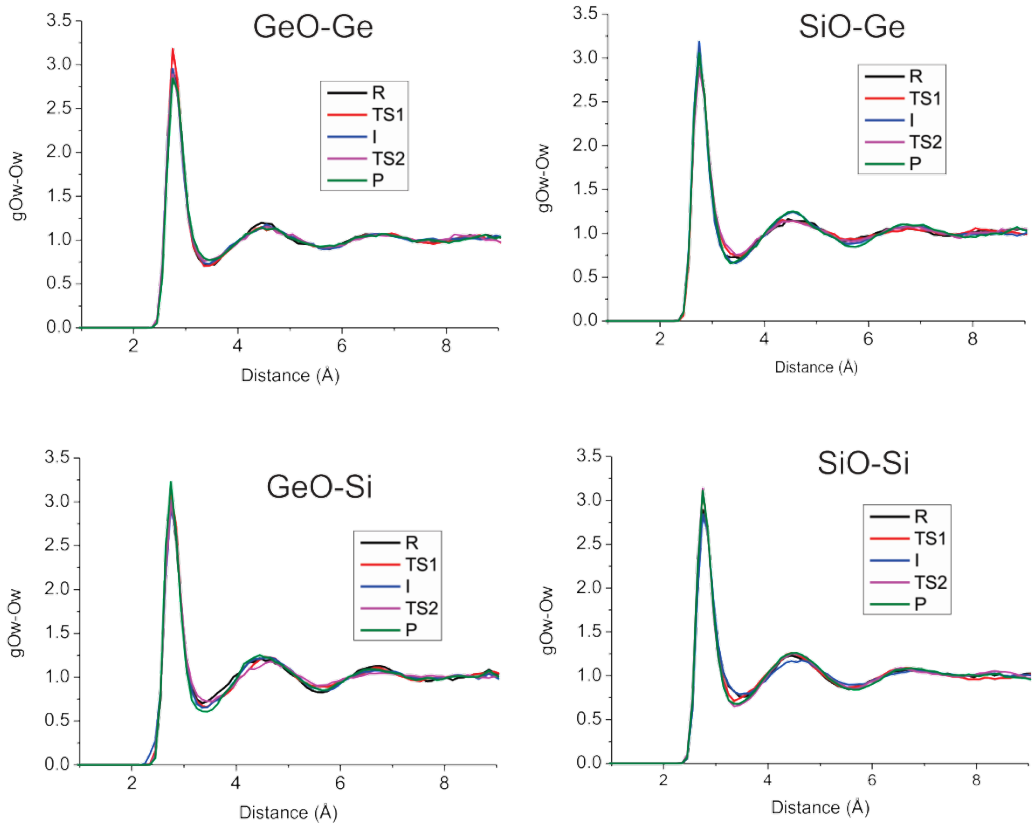
Distances and angles	R		TS1		I		TS2		P	
	AIMD	*COSMO*	AIMD	*COSMO*	AIMD	*COSMO*	AIMD	*COSMO*	AIMD	*COSMO*
d(Ge1-O3)	1.76 ± 0.04	*1.78*	1.73 ± 0.04	*1.72*	1.73 ± 0.03	*1.76*	1.73 ± 0.04	*1.79*	1.75 ± 0.04	*1.78*
d(Si2-O3) (rc1)	3.74 ± 0.2	*3.67*	2.40	*2.53*	1.84 ± 0.07	*1.81*	1.72 ± 0.04	*1.70*	1.68 ± 0.04	*1.70*
d(Si2-O4) (rc2)	1.67 ± 0.04	*1.68*	1.70 ± 0.04	*1.70*	1.80 ± 0.06	*1.79*	2.50	*2.51*	3.8 ± 0.2	*3.82*
d(Ge1-Si2)	4.6 ± 0.2	*3.80*	3.69 ± 0.09	*3.56*	3.29 ± 0.08	*3.14*	3.24 ± 0.08	*3.00*	3.19 ± 0.09	*3.10*
a(Ge1-O3-Si2)	108 ± 8	*80.38*	126 ± 6	*112.53*	134 ± 7	*123.13*	140 ± 8	*118.75*	137 ± 7	*125.50*
a(O3-Si2-O5)	91 ± 9	*88.00*	84 ± 4	*81.17*	92 ± 4	*89.34*	97 ± 4	*102.24*	108 ± 5	*109.79*
a(O3-Si2-O4)	143 ± 11	*156.31*	172 ± 4	*173.54*	174 ± 3	*178.27*	170 ± 4	*167.34*	109 ± 14	*140.46*

S1d./ Selected distances (Å) and angles (degree) for the stationary points along the reaction to form the SiO-Si (reaction between $Si(OH)_3O^-$ and $Si(OH)_4$, see figure 4) with the explicit AIMD approach (average on the trajectory associated to each point) and for the cluster calculation in an implicit solvent model (COSMO). Structure labels are presented in scheme 1.

Distances and angles	R		TS1		I		TS2		P	
	AIMD	*COSMO*	AIMD	*COSMO*	AIMD	*COSMO*	AIMD	*COSMO*	AIMD	*COSMO*
d(Si1-O3)	1.60 ± 0.03	*1.65*	1.61 ± 0.03	*1.60*	1.61 ± 0.03	*1.63*	1.68 ± 0.04	*1.65*	1.65 ± 0.04	*1.66*
d(Si2-O3) (rc1)	3.82 ± 0.15	*3.58*	2.40	*2.51*	1.69 ± 0.04	*1.81*	1.68 ± 0.04	*1.69*	1.69 ± 0.04	*1.70*
d(Si2-O4) (rc2)	1.65 ± 0.04	*1.68*	1.71 ± 0.04	*1.70*	1.80 ± 0.05	*1.79*	2.50	*2.52*	3.7 ± 0.2	*3.39*
d(Si1-Si2)	5.1 ± 0.2	*3.79*	3.64 ± 0.06	*3.51*	3.31 ± 0.07	*3.09*	3.13 ± 0.09	*2.97*	3.05 ± 0.09	*2.91*
a(Si1-O3-Si2)	140 ± 12	*84.46*	130 ± 4	*115.62*	155 ± 12	*127.68*	141 ± 11	*124.84*	132 ± 9	*120.16*
a(O3-Si2-O5)	85 ± 8	*88.44*	86 ± 4	*81.14*	92 ± 3	*88.84*	104 ± 4	*102.04*	104 ± 4	*111.32*
a(O3-Si2-O4)	134 ± 7	*157.00*	172 ± 4	*173.96*	174 ± 3	*179.4*	172 ± 4	*167.01*	100 ± 9	*130.47*

S2./ Radial distribution function of water oxygen $g_{(Ow\text{-}Ow)}$ in the stationary states of the reaction forming gemano-silicate.

Structure	R	TS1	I	TS2	P
			GeO-Ge		
max	*2.93*	*3.19*	*2.96*	*2.90*	*2.85*
min	*0.72*	*0.70*	*0.73*	*0.76*	*0.77*
			SiO-Ge		
max	*3.06*	*3.09*	*3.20*	*2.90*	*3.06*
min	*0.71*	*0.75*	*0.66*	*0.76*	*0.66*
			GeO-Si		
max	*3.03*	*3.09*	*2.95*	*3.03*	*3.24*
min	*0.70*	*0.66*	*0.65*	*0.72*	*0.61*
			SiO-Si		
max	*2.90*	*3.13*	*2.85*	*3.15*	*3.12*
min	*0.76*	*0.71*	*0.79*	*0.65*	*0.68*



Peaks having the largest surface (higher max and lower min values of gOw-Ow) indicate a more structured water around germano-silicate.

S3./ Root means square displacement (RMSD) of water.

After the system is corrected for translation and rotation, RMSD is calculated by the equation below

$$RMSD(\mathrm{Ow}) = \sqrt{\frac{\sum_{i=1}^{N} (r_i(t) - r_i(t=0))^2}{N}}$$

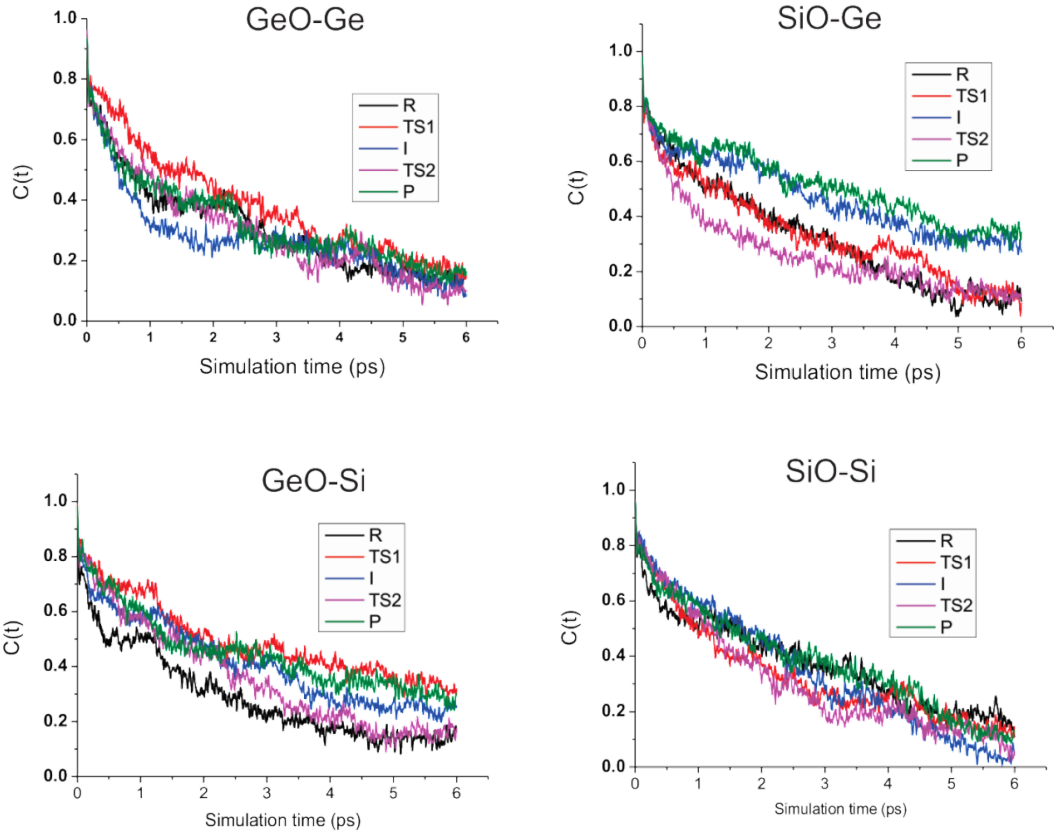
Where N is the number of water molecules, $r_i(t)$ is the coordinates of water at time t.

Structure	GeO-Ge	SiO-Ge	GeO-Si	SiO-Si
R	2.8	**3.4**	2.8	2.2
TS1	2.9	3.0	**2.3**	2.0
I	2.7	**2.0**	2.8	2.1
TS2	**3.0**	2.7	**3.3**	**1.8**
P	**2.6**	2.8	2.5	**2.3**

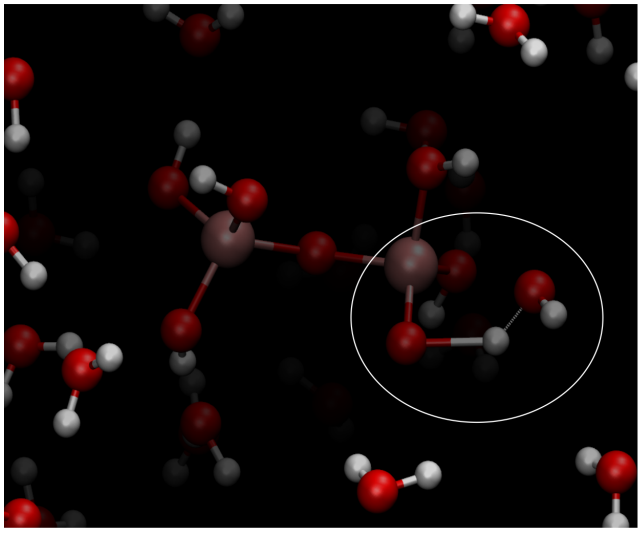
S4./ Time correlation function of the orientation of water OH groups.

The time correlation of the hydroxyl groups of water is calculated by the equation $(t) = \langle P_2.\overrightarrow{u(OH_0)}.\overrightarrow{u(OH_t)}\rangle$, where *P2* is the second order Legendre polynomial and $u_{OH}(t)$ is the orientation of the water OH bond at time *t*. The relaxation time τ, a time-integration of *C(t)*, is an indication of the water re-orientation speed. A small relaxation time indicates a fast water re-orientation. In the figure below, we only consider the last 6ps of simulation.

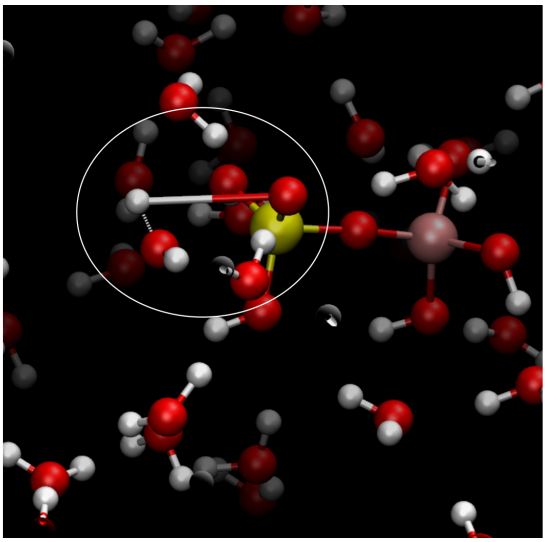
Correlation time (ps)	GeO-Ge	SiO-Ge	GeO-Si	SiO-Si
R	*1.84*	*1.94*	**1.74**	2.23
TS1	***2.28***	*2.03*	**2.94**	1.99
I	***1.65***	*2.83*	2.46	2.07
TS2	*1.80*	***1.62***	2.15	**1.85**
P	*1.95*	***3.06***	2.69	**2.28**



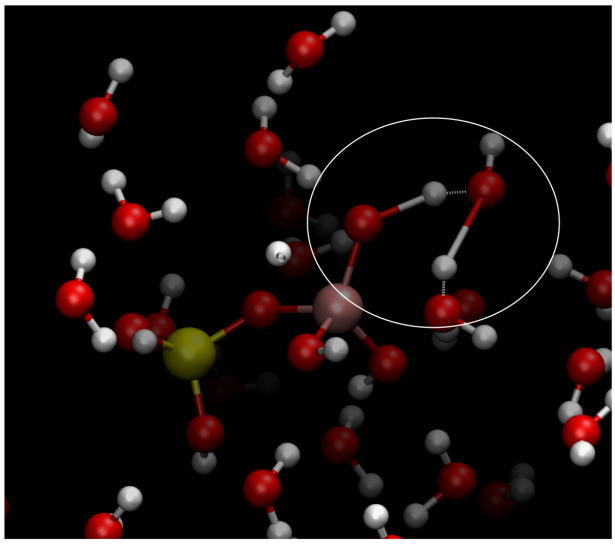
S5./ Internal and external proton transfer mechanism of the water removal step. The elongated OH bond indicate where H is transferred from.



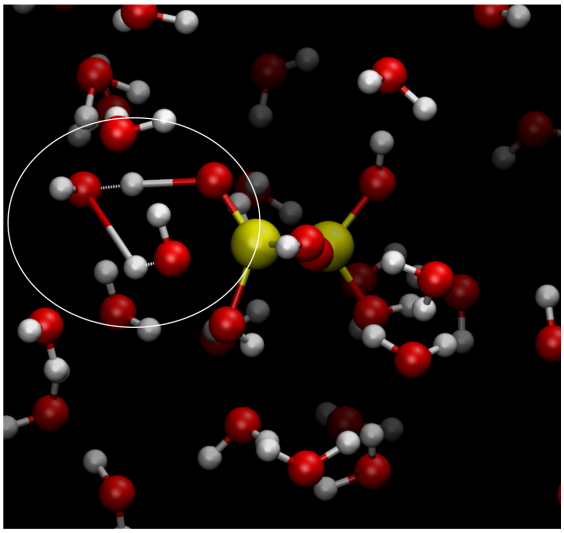
GeO-Ge direct H transfer



GeO-Si direct H transfer



SiO-Ge water assisted H transfer



SiO-Si water assisted H transfer