SUPPLEMENTARY DATA

Table S1*: Bond length and bond strength of some selected A-O bonds (A = Si, Al, B, Be, P). Difference of electronegativity (χ_O - χ_A) between O and A in the Pauling scale.*

A-O bond	Bond length (Å)	Bond strength (kJ/mol)	χ_O - χ_A (Pauling scale)
Si-O	1.63	452	1.5
Al-O	1.62	502	1.8
B-O	1.36	536	1.4
Be-O	1.33	437	1.8
P-O	1.63	335	1.2

Table S2*. Structural classification of silicates. Structural features of each class are given, together with the corresponding stoichiometry (Si:O ratio) and Q_n nomenclature.*

Class	Structural features	Si-O ratio	Q_n nomenclature
Nesosilicates (N)	*Isolated* tetrahedra:SiO_4^{4-}	1:4	Q_0
Sorosilicates (S)	*Isolated* pairs of tetrahedra sharing one oxygen: $Si_2O_7^{6-}$	2:7	Q_1
Cyclosilicates (C)	*Ring* silicates	1:3	Q_2
Inosilicates (I)	Single *chains* of tetrahedra or Double *chains* of tetrahedra	1:3 (single) 4:11 (double)	Q_2 (single) Q_2 and Q_3 (double)
Phyllosilicates (P)	*Sheet* silicates	2:5	Q_3
Tektosilicates (T)	*3D framework* of tetrahedra	1:2	Q_4

Table S3: *Total energies per Si atom (in Hartrees) of some selected $Si_xO_yF_z$ clusters at T = 0 K and without inclusion of the zero-point energy, computed at the DFT/B3LYP/def2-TZVPD level of theory from the optimized geometries.*

Q_n coordination type	Cluster	Total energy per Si atom (Hartrees)
Q_2	$Si_3O_3F_6$	-564.812
	$Si_4O_4F_8$	-564.815
	$Si_6O_6F_{12}$	-564.816
Q_3	$Si_4O_6F_4$	-502.522
	$Si_8O_{12}F_8$	-502.540

Geometry of the clusters considered in the study, after optimization at the DFT/B3LYP/def2-TZVPD level of theory (Cartesian coordinates given in Å).

SiF_4

Si	0.00000000	0.00000000	0.00000000
F	0.90508900	0.90508900	0.90508900
F	-0.90508900	-0.90508900	0.90508900
F	-0.90508900	0.90508900	-0.90508900
F	0.90508900	-0.90508900	-0.90508900

Si_2OF_6

O	0.00000000	-0.00138800	0.10967300
Si	1.59604900	-0.00005000	0.01013200
Si	-1.59604600	-0.00022700	0.01014200
F	-2.12925400	1.47050400	-0.13001200
F	-2.21291800	-0.64091300	1.30425100
F	-2.06595600	-0.82931200	-1.23882500
F	2.12941400	-1.46672900	-0.16690700
F	2.21274700	0.60788900	1.32002700
F	2.06596200	0.86022600	-1.21756000

$Si_3O_2F_8$

Si	-1.03173900	-0.00422700	0.00000000
O	-0.11125300	-0.02698300	1.31241700
O	-0.11125300	-0.02698300	-1.31241700
Si	0.48958700	-0.00285600	2.79417100
Si	0.48958700	-0.00285600	-2.79417100
F	1.53264600	-1.16507300	-2.96254600
F	-0.64982000	-0.18627100	-3.86069600
F	1.21321900	1.36600500	-3.06040800
F	-1.98517300	-1.25671500	0.00000000
F	-1.92736800	1.29082300	0.00000000
F	-0.64982000	-0.18627100	3.86069600
F	1.21321900	1.36600500	3.06040800
F	1.53264600	-1.16507300	2.96254600

$Si_4O_3F_{10}$

Si	1.30922100	1.12411700	-0.29240500
Si	-1.21775000	-0.81143700	-0.47859300
Si	4.02005500	-0.40700700	0.33782400
Si	-4.12598700	0.14628000	0.37512000
O	-0.04398900	0.27332100	-0.38564700
O	2.55708200	0.17719600	0.05843600
O	-2.59508200	-0.18624700	0.05408100
F	-4.24438400	0.75674400	1.81733100
F	-5.00451900	-1.15478400	0.30299500
F	-4.68261300	1.18878100	-0.66026300
F	-1.38832200	-1.28057100	-1.97211100
F	-0.84226800	-2.07234700	0.38755300
F	1.56479800	1.85274900	-1.66422000
F	1.15170000	2.22456600	0.82236000
F	4.21595100	-1.74848500	-0.45568000
F	5.12444800	0.61516400	-0.11583100
F	4.20058200	-0.69754000	1.87095400

$Si_3O_3F_6$

Si	0.00000000	1.48207500	-0.85567600
Si	0.00000000	-1.48207500	-0.85567600
Si	0.00000000	0.00000000	1.71135200
O	0.00000000	0.00000000	-1.51922500
O	0.00000000	-1.31568700	0.75961300
O	0.00000000	1.31568700	0.75961300
F	-1.26923000	-2.28468000	-1.31906100
F	1.26923000	-2.28468000	-1.31906100
F	1.26923000	0.00000000	2.63812100
F	-1.26923000	0.00000000	2.63812100
F	-1.26923000	2.28468000	-1.31906100
F	1.26923000	2.28468000	-1.31906100

$Si_4O_4F_8$

Si	2.10843900	0.73764900	0.00000800
O	1.69242700	-0.81497200	-0.00075400
O	0.81472500	1.69188700	-0.00102600
Si	0.73776900	-2.10838300	0.00033500
Si	-0.73776900	2.10838300	-0.00033500
O	-0.81472500	-1.69188700	0.00102600
O	-1.69242700	0.81497200	0.00075300
Si	-2.10843900	-0.73764900	-0.00000800
F	-1.04188800	2.98070500	1.27264800
F	-1.04429600	2.98181000	-1.27180700
F	-2.98146300	-1.04286200	1.27223400
F	-2.98104900	-1.04368900	-1.27216900
F	2.98104900	1.04368800	1.27216900
F	2.98146300	1.04286200	-1.27223400
F	1.04429600	-2.98180900	1.27180800
F	1.04188800	-2.98070600	-1.27264700

$Si_6O_6F_{12}$

Si	0.00128600	0.06541000	-3.22765800
Si	-0.00128600	-0.06541000	3.22765800
Si	2.66299700	0.07158300	1.49153900
Si	-2.66299700	-0.07158300	-1.49153900
Si	-2.75188900	0.37211800	1.65617900
Si	2.75188900	-0.37211800	-1.65617900
O	1.38069600	-0.22587800	-2.46921700
O	-1.38069600	0.22587800	2.46921700
O	1.22448900	-0.00009500	2.19515600
O	-1.22448900	0.00009500	-2.19515600
O	-2.49720800	0.13407400	0.08999400
O	2.49720800	-0.13407400	-0.08999400
F	0.05478000	1.49191800	-3.89247000
F	-0.20327700	-0.99865800	-4.36920100
F	-3.60731600	1.04116900	-2.08312300
F	-3.32290600	-1.47278700	-1.77650000
F	-3.33982600	1.81465500	1.88341100
F	-3.80100400	-0.67283400	2.19125500
F	-0.05478000	-1.49191800	3.89247000
F	0.20327700	0.99865800	4.36920100
F	3.32290600	1.47278700	1.77650000
F	3.60731600	-1.04116900	2.08312300
F	3.33982600	-1.81465500	-1.88341100
F	3.80100400	0.67283400	-2.19125500

$Si_4O_6F_4$

Si	0.85198900	1.29469000	-0.71240700
Si	0.87529200	-0.58677500	1.34114900
Si	-0.19419100	-1.25075900	-1.14339400
Si	-1.53317800	0.54294400	0.51474500
O	1.63206000	0.66903800	0.59427700
O	0.62159300	0.04139900	-1.75333800
O	-0.64342800	1.73621700	-0.18682600
O	0.64347500	-1.73621600	0.18694500
O	-1.63185200	-0.66881900	-0.59413100
O	-0.62149200	-0.04163000	1.75350200
F	-0.37265400	-2.39649600	-2.19110900
F	1.63288700	2.48051700	-1.36553600
F	1.67719300	-1.12488400	2.56995300
F	-2.93760400	1.04071700	0.98616700

$Si_8O_{12}F_8$

Si	0.00000000	0.00000000	0.00000000
O	0.00000000	0.00000000	1.61751000
O	1.51917700	0.00000000	-0.55521900
Si	0.42876600	-0.76563900	2.97632900
Si	2.94292200	-0.76506800	-0.62012700
O	2.03742400	-0.92429700	3.04133700
O	3.55702000	-0.92369300	0.86789500
Si	3.37149400	-1.53027300	2.35588300
F	3.93627800	0.08526300	-1.49001700
F	4.61543200	-1.12803000	3.22617700
F	-0.72569900	1.29691200	-0.50790000
F	-0.04716400	0.08383500	4.20855400
Si	-0.88593500	-2.90868100	-0.62086400
Si	-0.45736300	-3.67388600	2.35514700
Si	2.48555900	-4.43895400	1.73502000
Si	2.05679300	-3.67331500	-1.24131000
O	-1.07146100	-3.51526100	0.86712500
O	-0.27649200	-2.21998000	3.04086800
O	-0.79403600	-1.29500400	-0.55578900
O	0.96638200	-4.43895400	2.29023900
O	0.44813500	-3.51465800	-1.30631700
O	2.48555900	-4.43895400	0.11751000
F	2.53272400	-4.52278900	-2.47353400
F	-1.45071800	-4.52421700	3.22503700
F	-2.12987200	-3.31092400	-1.49115700
O	2.76205200	-2.21897400	-1.30584800
O	3.27959500	-3.14395000	2.29080900
F	3.21125800	-5.73586600	2.24292000

$Si_5O_6F_8$

Si	-0.00048100	0.00007500	-0.00040200
Si	-0.00011100	0.00047400	5.57048300
Si	2.85441600	0.00007500	0.78650600
Si	0.76765300	-0.71138700	2.78504000
O	1.59743200	0.18402200	-0.22539300
O	-0.24766600	-0.44465500	1.54027800
O	2.27733600	-0.44465500	2.23625500
O	0.42455400	0.28073300	4.02980300
F	3.84084800	-1.09202700	0.23452600
F	-0.56480500	-1.09202700	-0.97982400
F	3.65499800	1.34711900	0.90878800
F	-0.75065500	1.34711900	-0.30556200
O	-0.06212600	-1.60679600	5.79547300
O	0.61638900	-2.23697200	3.33382500
Si	0.21678800	-2.84617200	4.78357500
F	1.04596000	0.64613900	6.54990400
F	-1.40025700	0.64613900	5.87564200
F	-1.06554000	-3.74678100	4.66129200
F	1.38067700	-3.74678100	5.33555400

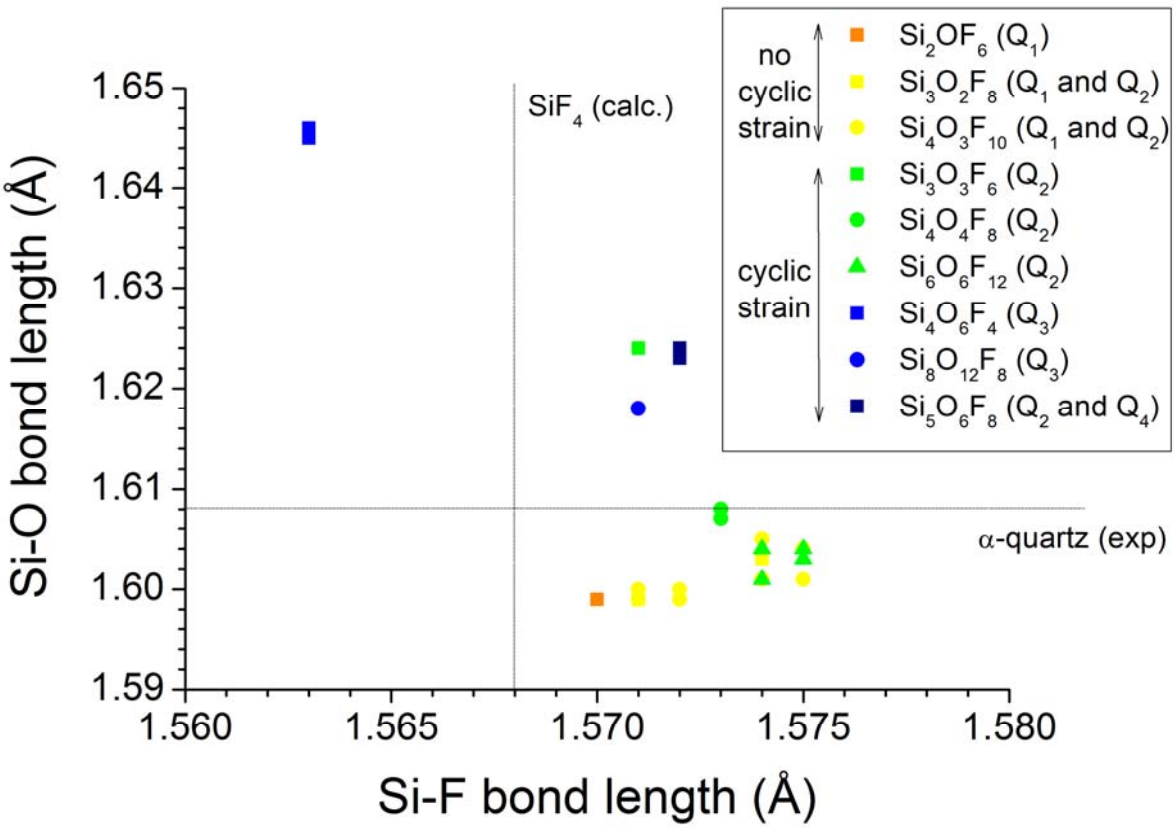

Figure S1. *Correlation between Si-O and Si-F bond lengths in the structural models for silicates sketched in Figure 2.*