

## Supporting Information:

### Evidence for Atomic Mixing via Multiple Intermediates during the Dynamic Interconversion of Silicate Oligomers in Solution ,

Kim E. Jelfs, Edwin Flikkema and Stefan T. Bromley

#### Global Optimisations:

The global optimisations of all oligomers used a three step approach. Firstly, a few high temperature (e.g. 8000-12000K) and reasonably short (50000 steps) basin hopping (BH) runs were employed using a relatively disordered (although not chemically unfeasible) starting structures. From a selection (as structurally diverse as possible) of low energy structures resulting from these calculations a number of longer BH runs (typically 1 million steps) at moderate temperatures 2000-4000K were then employed. The best oligomers from these runs were then used to seed low temperature BH runs which aims to explore the local potential energy landscape of each low energy candidate from the long BH runs. The geometries of the best (i.e. lowest energy) 10-15 oligomers for each composition considered were then energy minimized using DFT. These energy minimized structures were then used for the subsequent calculations of the free energies of solution.

#### Solvation calculations:

In the alkaline solution conditions used in the experiment by Schüth *et al.* the D4Rs have one of their eight protons missing (this is presumably also true, although not explicitly demonstrated, for any Si<sub>16</sub>-based intermediate species). The necessary compensation of this single excess charge is provided by cationic species in solution (e.g. tetramethylammonium cation (TMA<sup>+</sup>), protons) which are strongly attracted to the O<sup>-</sup> site. The resulting dynamic neutral complex is that which describes most fully the discrete microscopic chemical nature of the solute, independent of its solvating environment. In our study we employ protons as our neutralizing cations resulting in neutral hydroxylated oligomers. Although TMA<sup>+</sup> cations species are thought to play an active role in promoting D4R stability, we also find that the solvated (SiO<sub>2</sub>)<sub>8</sub>(H<sub>2</sub>O)<sub>4</sub> D4R species has the lowest free energy of solution of any such oligomer we could find in our global optimization searches, consistent with what is found in experiment. In contrast, if we assume that the silicate oligomers are artificially isolated from any charge compensating cations (i.e. are bare isolated charged species in solution) we find that other silicate oligomers become more stable. This change in oligomer stability of bare charged species is mainly due to: (i) unpredictable increases in solvation energy dependent on

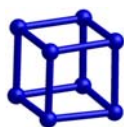
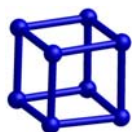
the location of the O<sup>-</sup> centre on the oligomer and, (ii) increased tendency for intra-molecular H-bonding between the O<sup>-</sup> centre and OH groups. The use of neutral hydroxylated oligomers, although not reproducing the full steric effects of the larger TMA<sup>+</sup>, does inhibit these two unwanted effects in an effective way. We should note that the neutralizing effect of cations on silicate oligomer solvation energies has been quantitatively shown by previous calculations showing that sodium cations weaken the interaction of a deprotonated silica dimer with water to an extent that it is comparable to that between the neutral dimer and water.<sup>1</sup>

The solvation of the hydroxylated neutral silicate oligomers was taken into account using the Polarizable Continuum Model (PCM – see ref 19 main article). For treating small charged silica species, especially when calculating reaction barriers, it is also known to be important to additionally include a short range solvation shell of explicit water molecules (see for example ref 8 main article) to the bare PCM treatment. When considering only the solvation free energy of isolated neutral oligomers with increasing size, however, it is known that the solvation energies per Si atom rapidly reduce and progressively appear to approach a limiting average value (ref 18 main article). For the hydroxylated silica monomer we calculate the solvation free energy to be 14.3 kJ/mol/Si using PCM, which underestimates the value given when also using an explicit solvent shell by ~14.8 kJ/mol/Si. Comparing this with the PCM solvation energy of 17.5 kJ/mol/Si for the D4R the corresponding underestimation is ~2 kJ/mol/Si showing that the PCM value is already much closer to the explicit solvent value for this size. For the significantly larger Si<sub>16</sub>-based oligomers in our study this underestimation is likely to be even less (see values below). Further, considering that we do not aim to provide absolute energies but only relative energies, any small absolute errors are likely to be similar in each solvation calculation thus largely cancelling out.

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<sup>1</sup> I M. J. Mora-Fonz, C. R. A. Catlow, D. W. Lewis, *Phys. Chem. Chem. Phys.* 2008 10, 6571.

Selected oligomer properties:

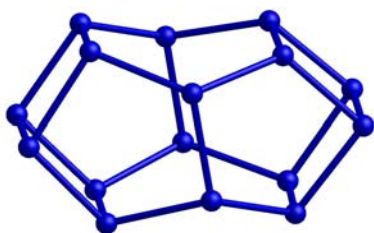


Name:  $2 \times \text{D4R}$

Formula:  $2 \times \text{Si}_8\text{O}_{16}(\text{H}_2\text{O})_4$

Free energy of solvation (kJ/mol/Si) : 17.5

Total free energies reported below are given with respect to that of  $2 \times \text{D4R}$ :

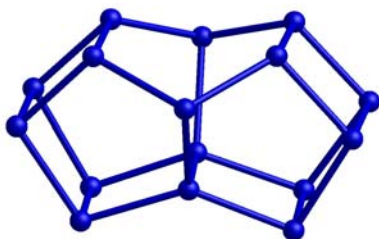


Name: S2

Formula:  $\text{Si}_{16}\text{O}_{32}(\text{H}_2\text{O})_{16}$

Free energy of solvation (kJ/mol/Si): 13.8

Relative total free energy (kJ/mol) : 35

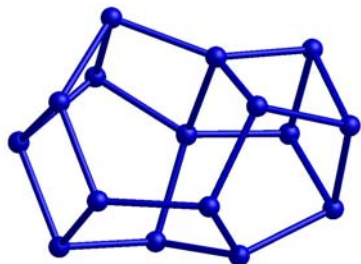


Name: S3

Formula:  $\text{Si}_{16}\text{O}_{32}(\text{H}_2\text{O})_{14}$

Free energy of solvation (kJ/mol/Si): 12.9

Relative total free energy (kJ/mol) : -9

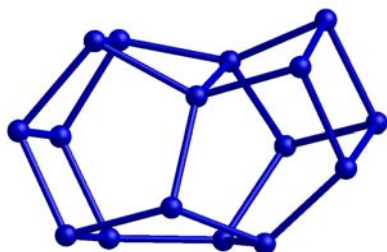


Name: S4

Formula:  $\text{Si}_{16}\text{O}_{32}(\text{H}_2\text{O})_{14}$

Free energy of solvation (kJ/mol/Si): 13.5

Relative total free energy (kJ/mol) : 0

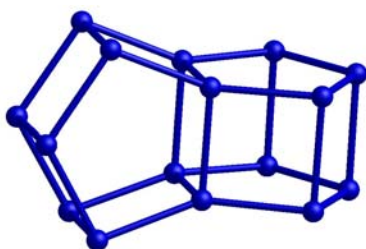


Name: S5

Formula:  $\text{Si}_{16}\text{O}_{32}(\text{H}_2\text{O})_{14}$

Free energy of solvation (kJ/mol/Si): 13.0

Relative total free energy (kJ/mol) : 6

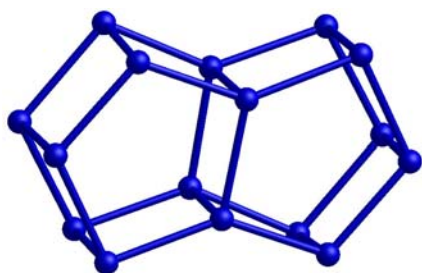


Name: S6

Formula:  $\text{Si}_{16}\text{O}_{32}(\text{H}_2\text{O})_{12}$

Free energy of solvation (kJ/mol/Si): 12.6

Relative total free energy (kJ/mol) : -28



Name: S7

Formula:  $\text{Si}_{16}\text{O}_{32}(\text{H}_2\text{O})_{12}$

Free energy of solvation (kJ/mol/Si): 12.1

Relative total free energy (kJ/mol) : -5