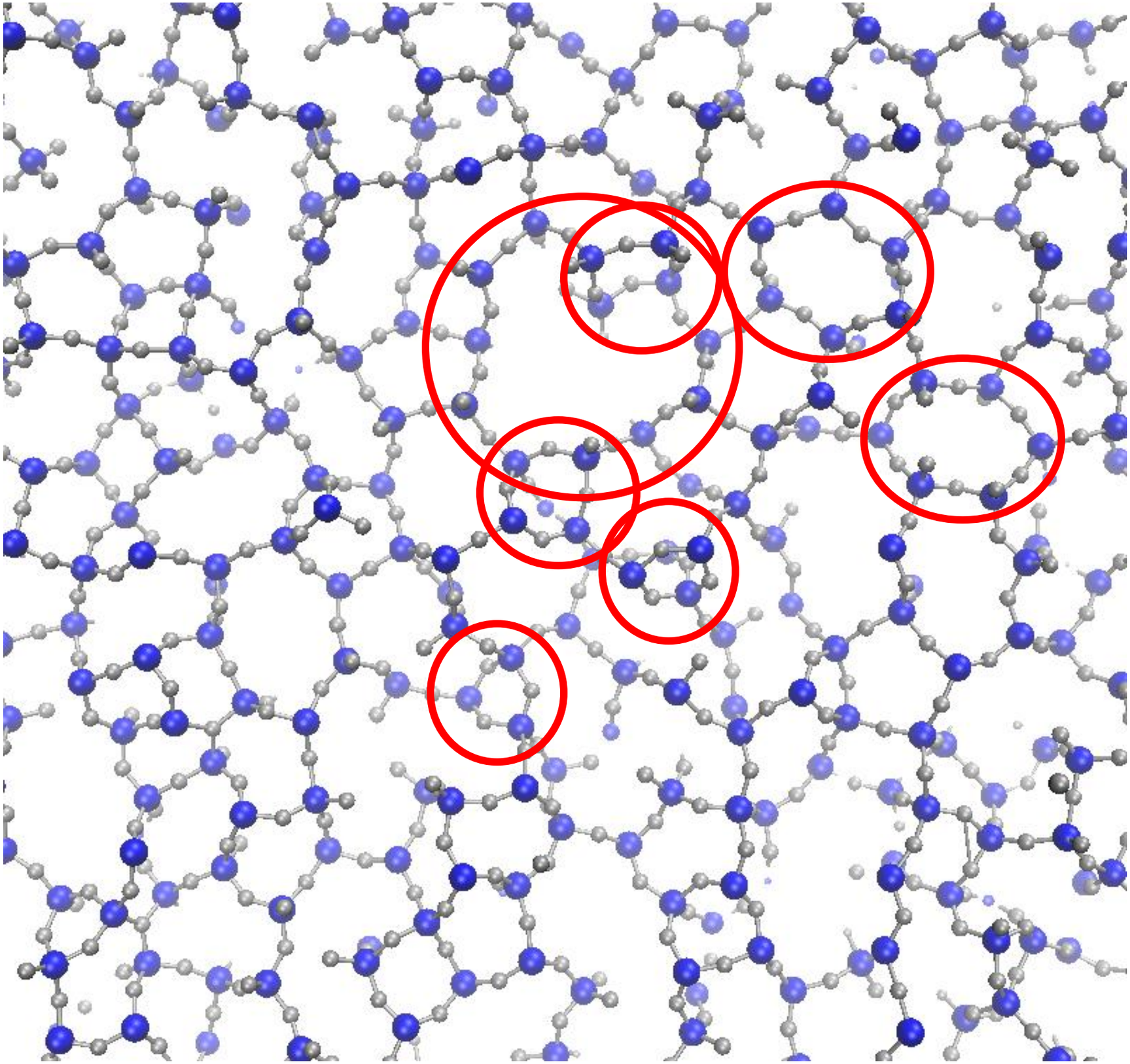
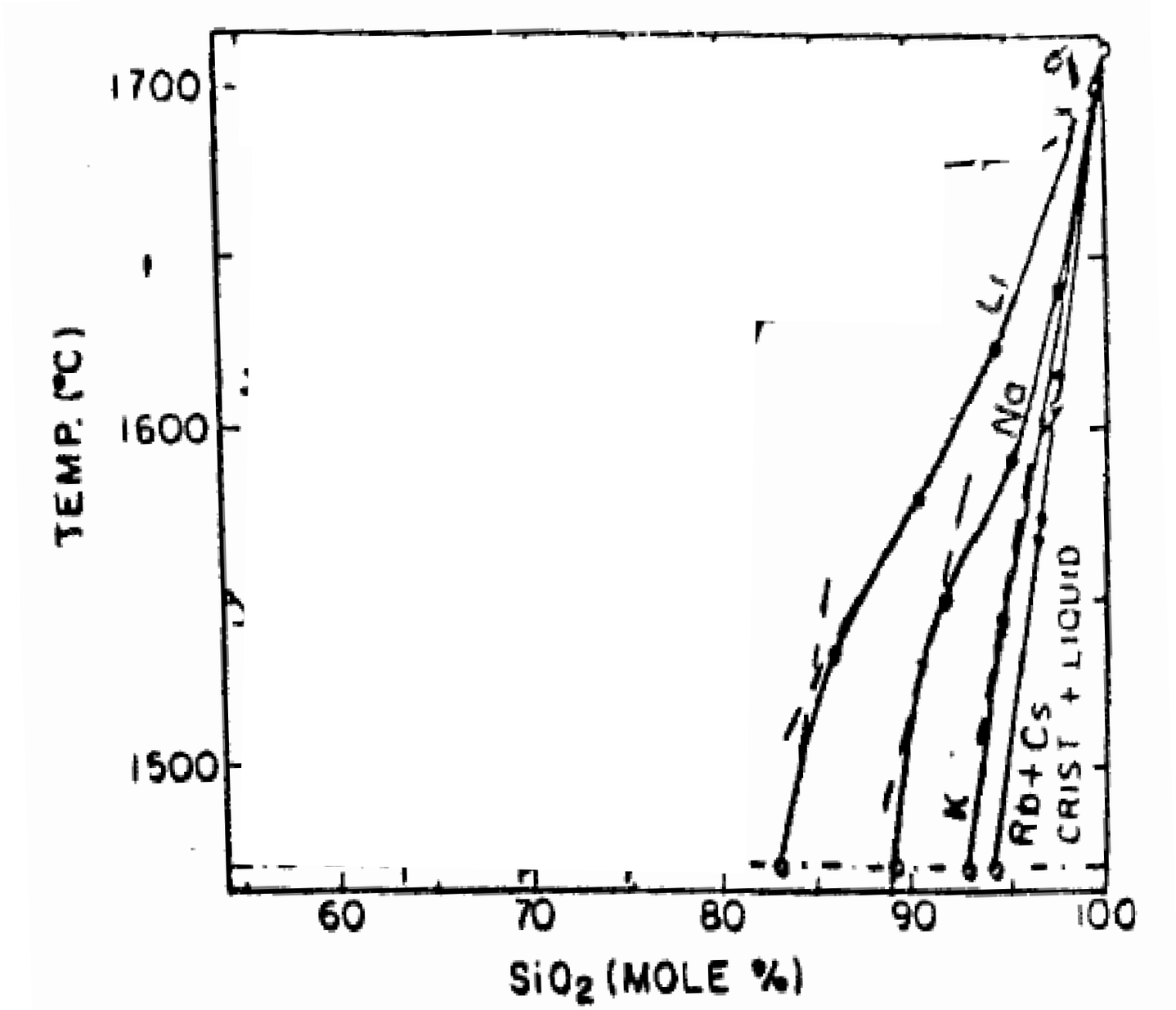
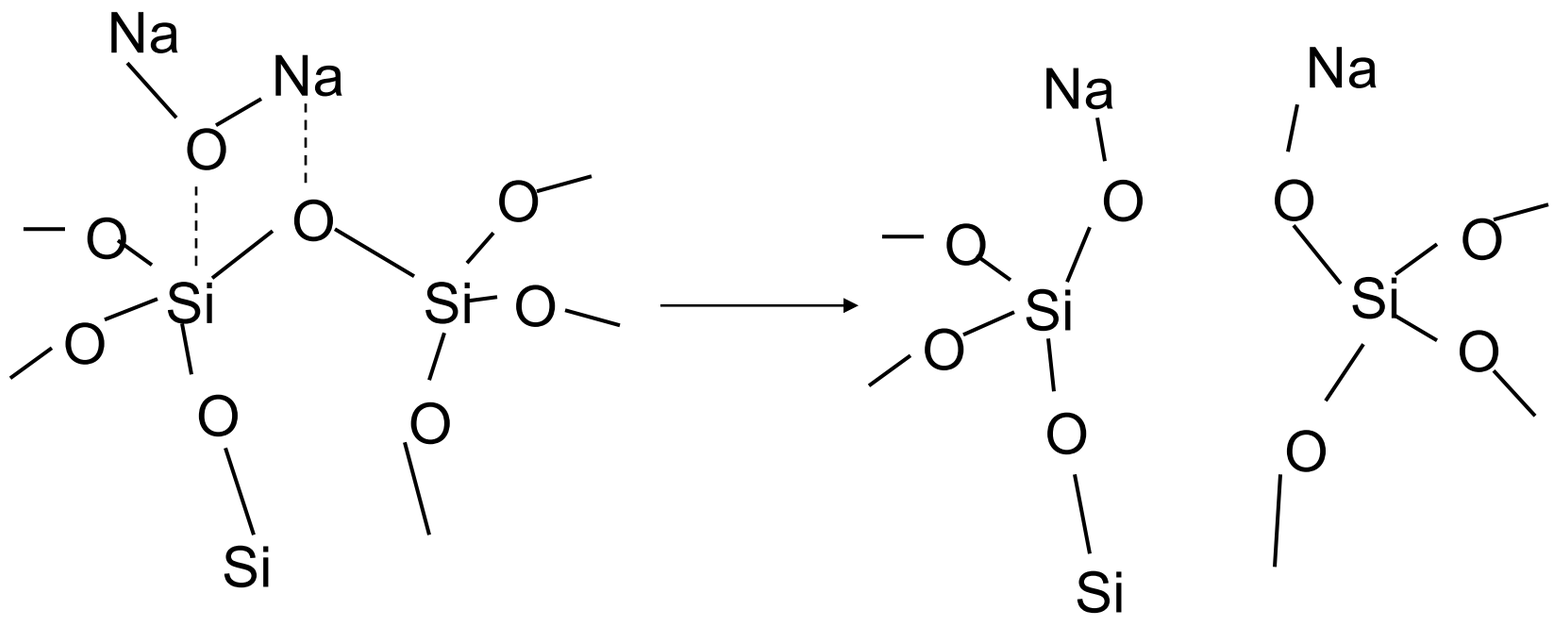


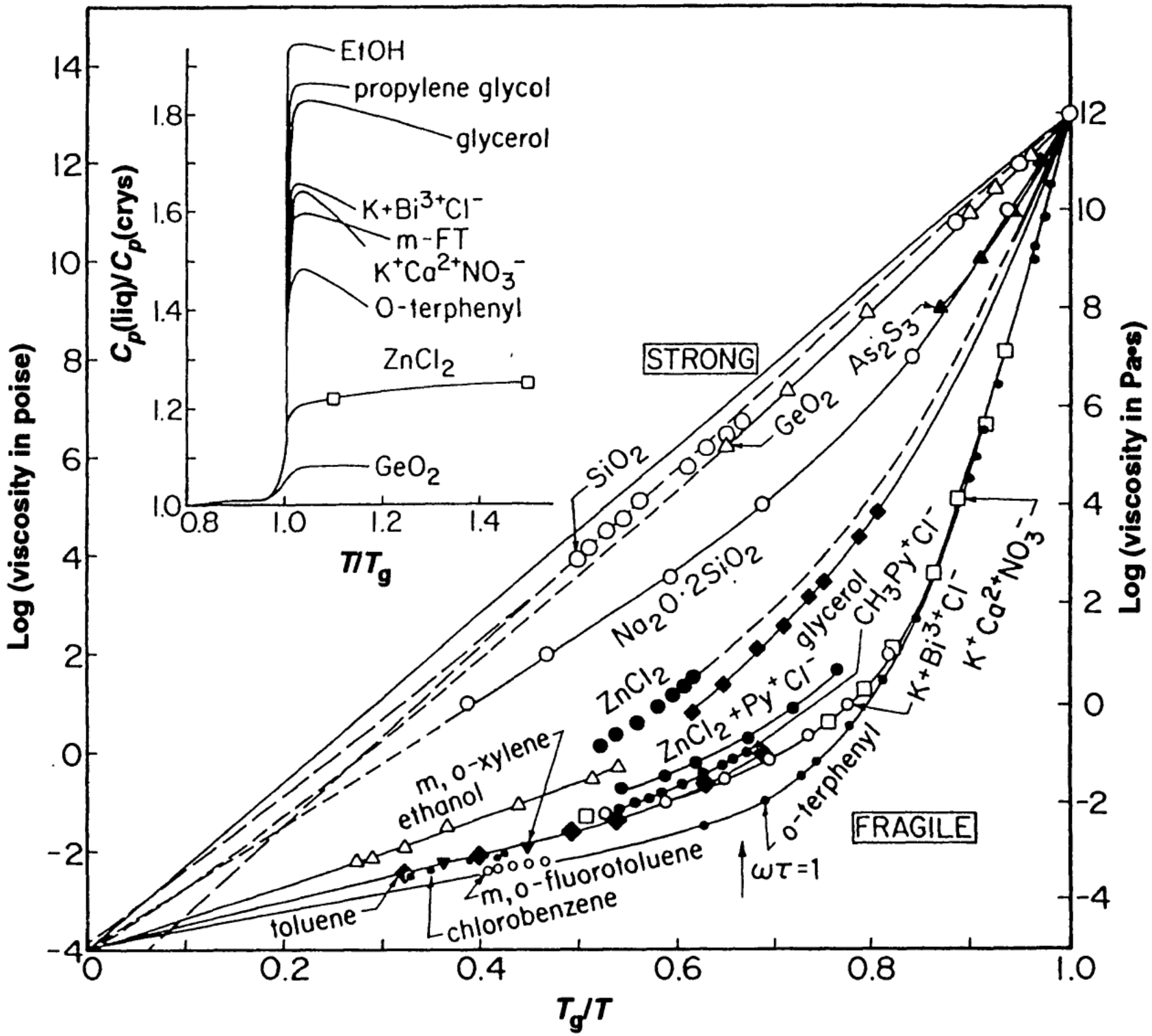
RUTGERS



If the addition of R2O (alkali metal oxides) to silica cause the formation of NBO, and [Li] = [Cs], then the same number of NBO are formed, but the effect is much greater in the latter than the former. What is happening?

Alkali Additions
RUPTURE OF NETWORK STRUCTURE




Log (viscosity in poise)
Log (viscosity in Pa·s)
T_g/T
STRONG
FRAGILE
SiO_2
GeO_2
As_2S_3
$Na_2O{\cdot}2SiO_2$
$ZnCl_2$
$ZnCl_2+Py^+Cl^-$
glycerol
$CH_3Py^+Cl^-$
$K^+Bi^{3+}Cl^-$
$K^+Ca^{2+}NO_3^-$
o-terphenyl
m, o-xylene
ethanol
m, o-fluorotoluene
chlorobenzene
toluene
$\omega\tau=1$
$C_p(liq)/C_p(crys)$
T/T_g
EtOH
propylene glycol
glycerol
$K+Bi^{3+}Cl^-$
m-FT
$K^+Ca^{2+}NO_3^-$
O-terphenyl
$ZnCl_2$
GeO_2

RUTGERS

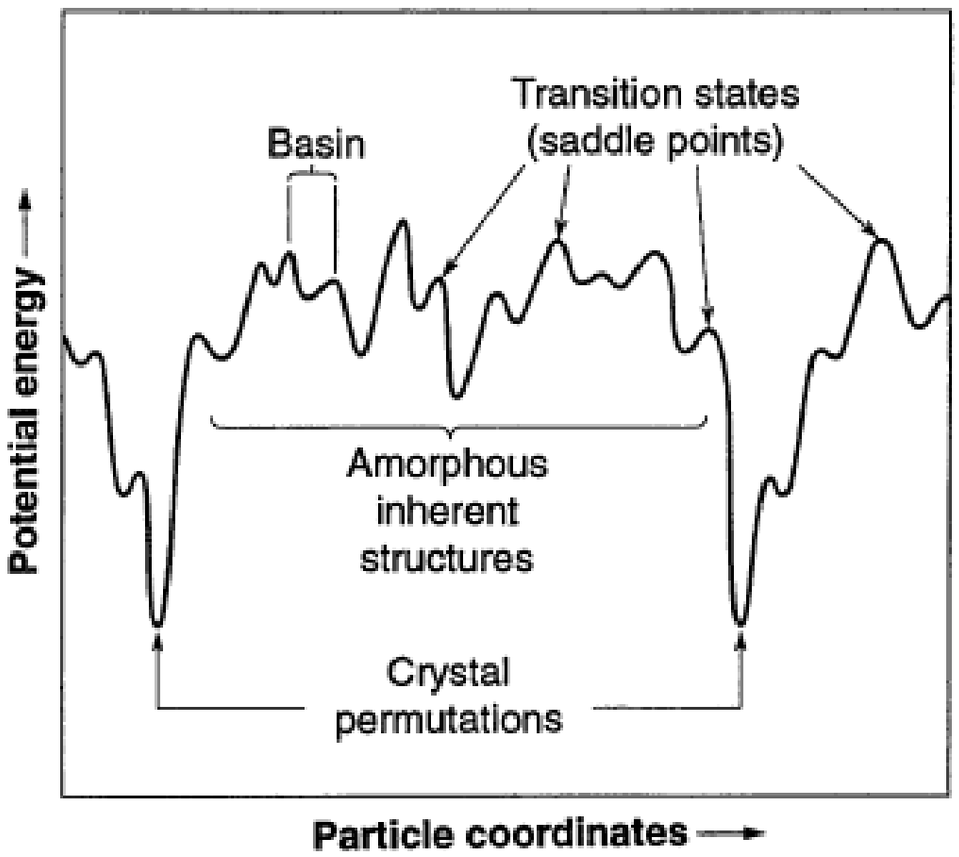


Fig. 1. Schematic diagram of the potential energy hypersurface in the multidimensional configuration space for a many-particle system.

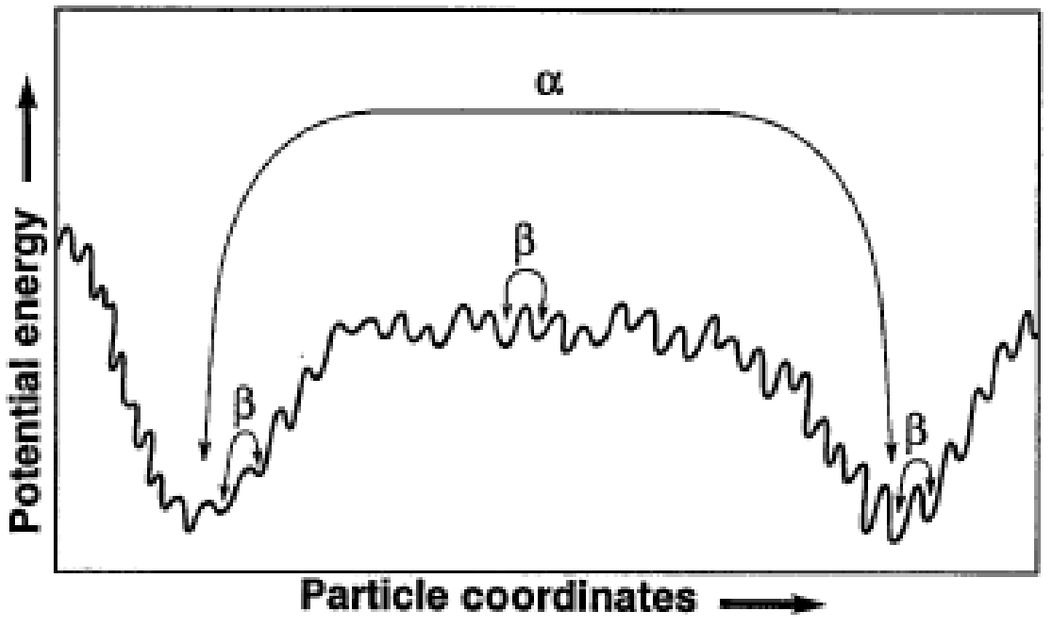


Fig. 4. Two-scale potential energy topography characteristic of regions of configuration space explored by fragile glass formers near T_g. The elementary interbasin transitions are associated with β relaxations, and large distance intercrater transitions are associated with α relaxations.

Stillinger, Science 267 (1995)

RUTGERS

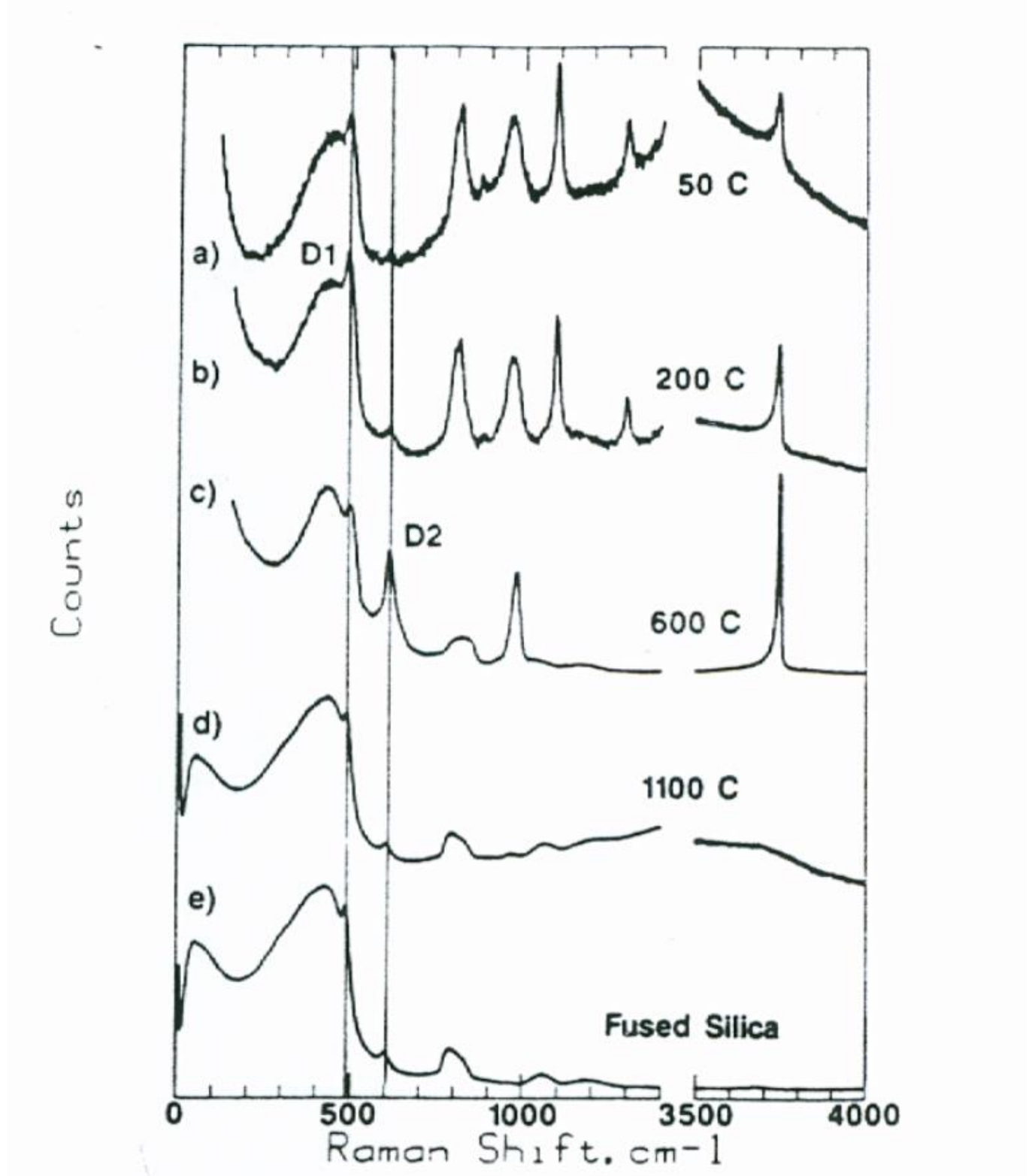
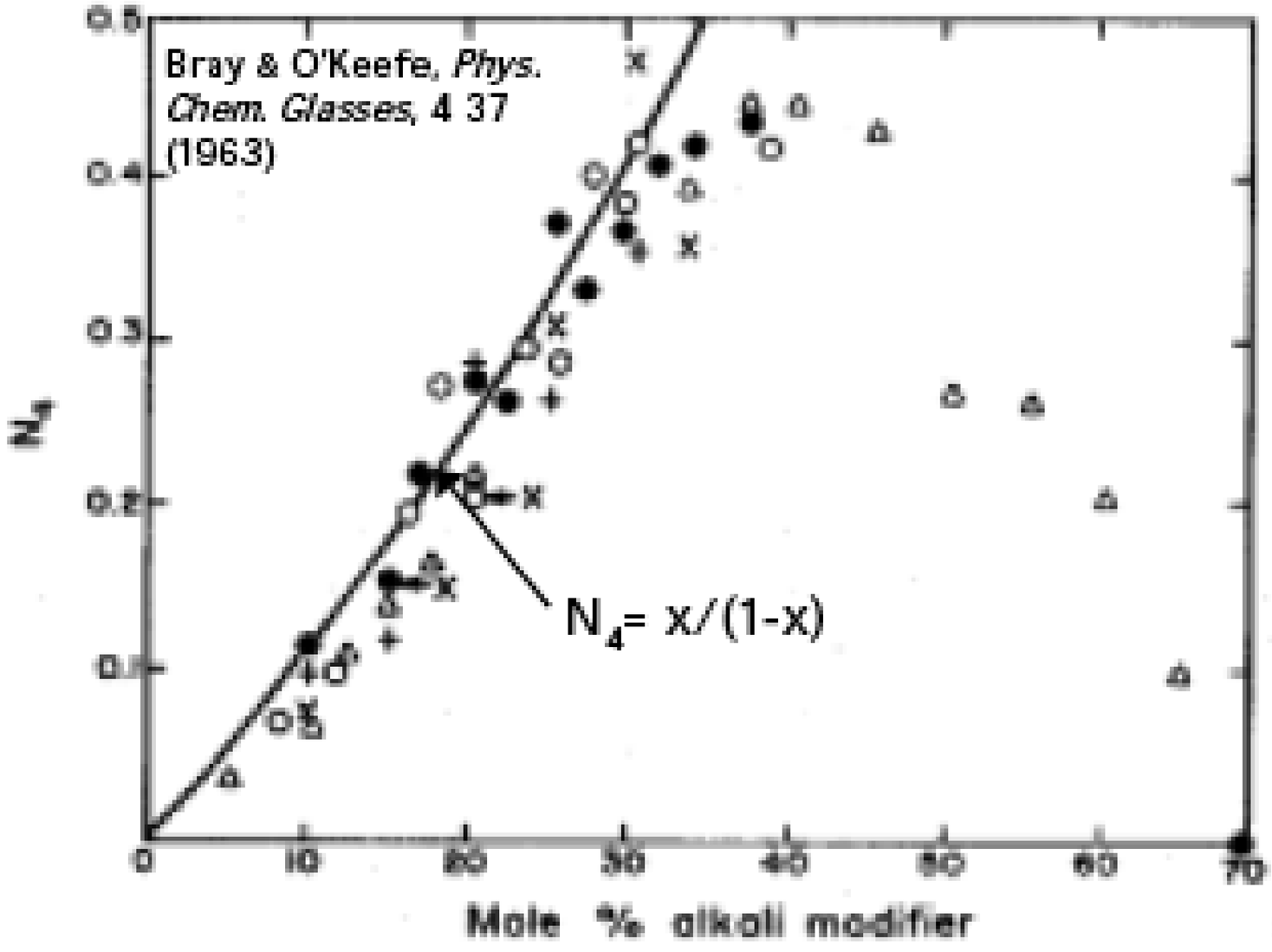


Fig. 1. Raman spectra of SiO_2 gels dried at 50 °C, heated to 200 or 600 °C, or fully consolidated at 1100 °C.

Bray's Quantitative NMR Results for N_4



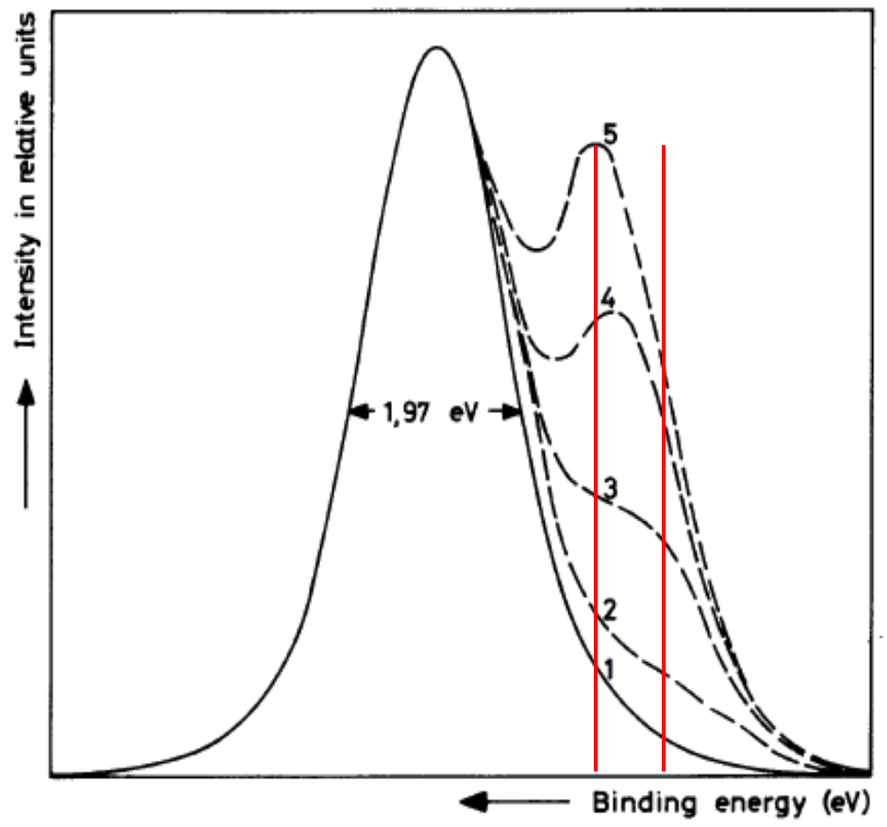
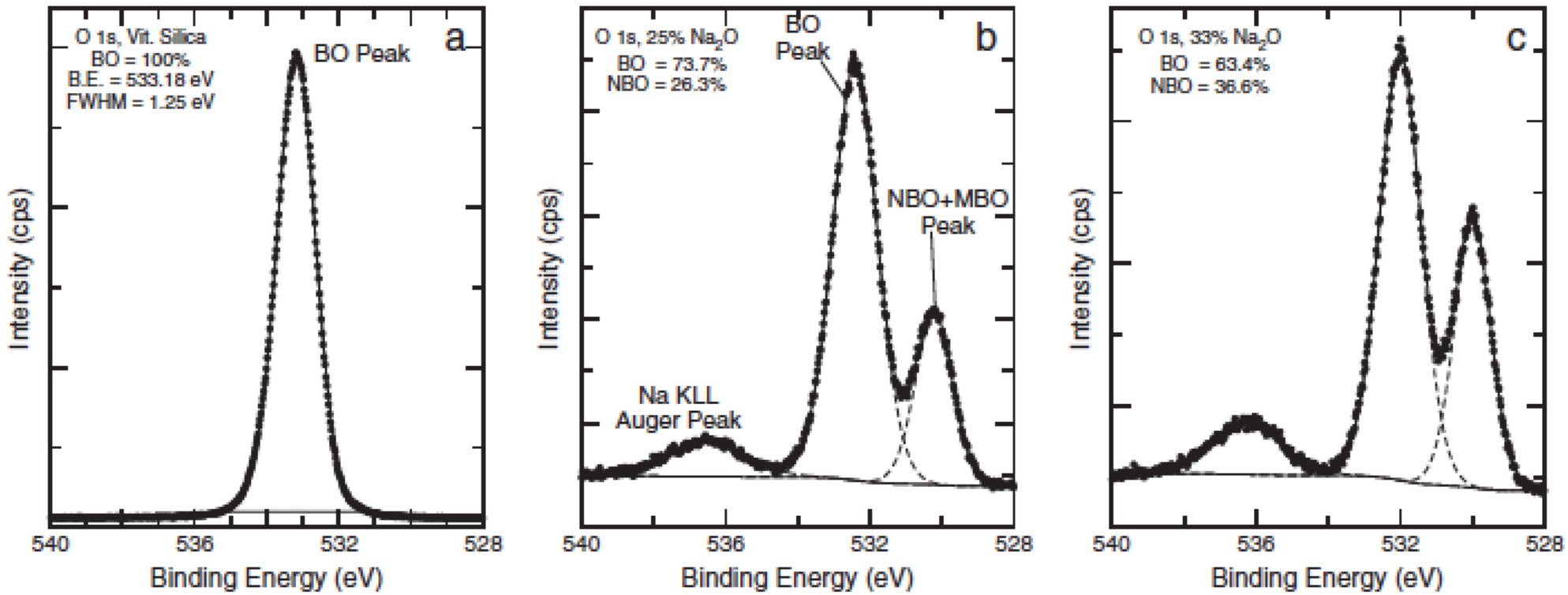


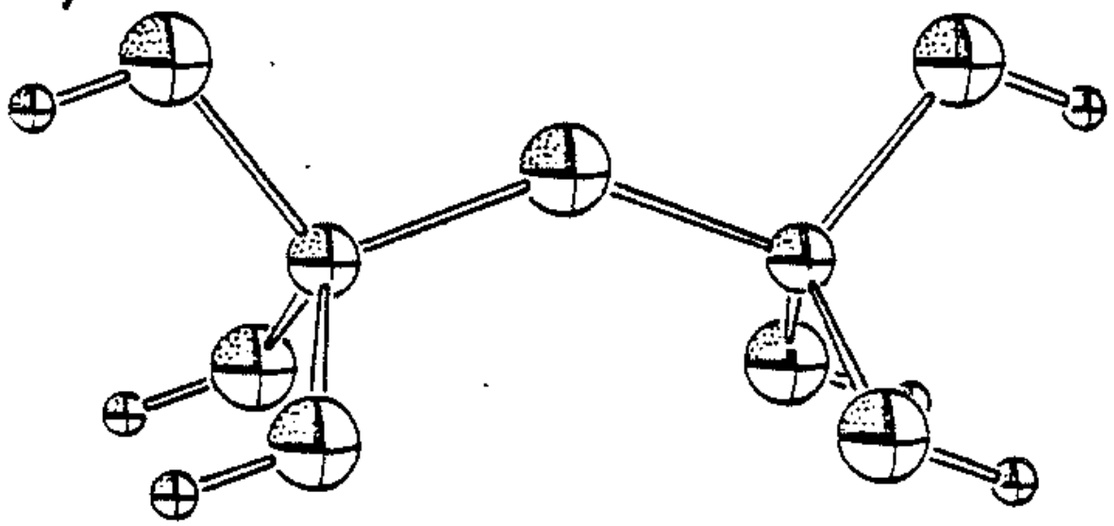
Fig. 2. O 1s-spectra of silica glasses and sodium silicate glasses.
1: Suprasil W, Suprasil, Infrasil
2: 9 wt.-% Na_2O
3: 20 wt.-% Na_2O
4: 30 wt.-% Na_2O
5: 40 wt.-% Na_2O

Na additions in XPS spectra show change in NBO concentration and even peak location.

RUTGERS

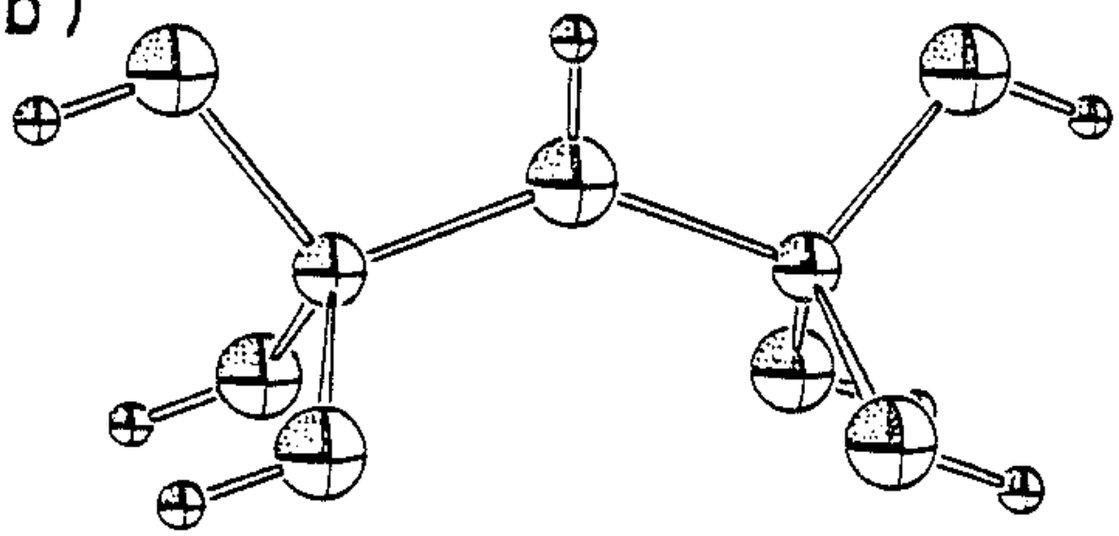

a
O 1s, Vit. Silica
BO = 100%
B.E. = 533.18 eV
FWHM = 1.25 eV
BO Peak
b
O 1s, 25% Na2O
BO = 73.7%
NBO = 26.3%
BO Peak
NBO+MBO Peak
Na KLL Auger Peak
c
O 1s, 33% Na2O
BO = 63.4%
NBO = 36.6%
d
O 1s, 40% Na2O
BO = 54.4%
NBO = 45.6%
e
O 1s, 50% Na2O
BO = 42.1%
NBO = 57.9%
f
O 1s, 55% Na2O
BO = 32.3%
NBO = 67.7%
Intensity (cps)
Binding Energy (eV)
540
536
532
528

(a)

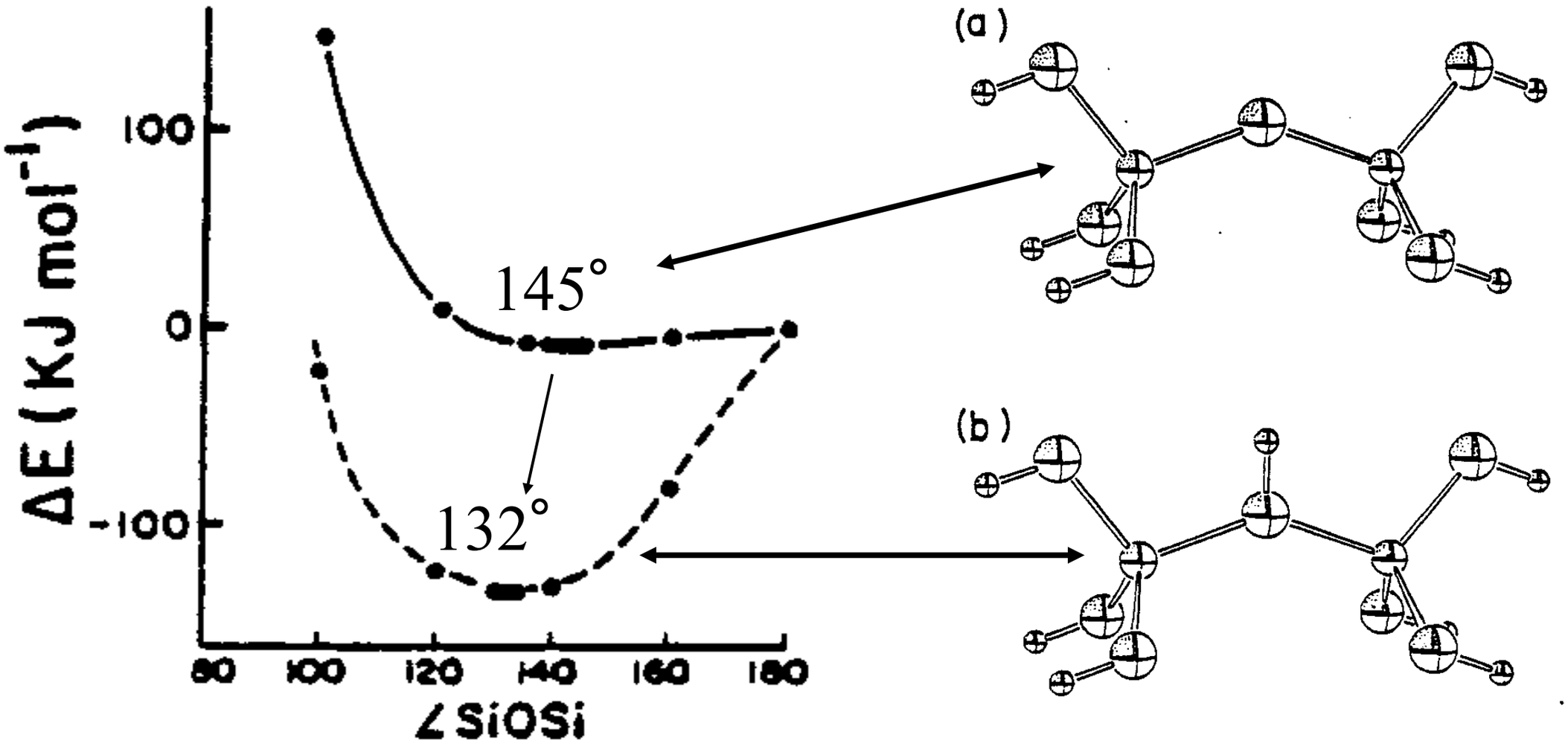


$H_6Si_2O_7$

(b)



$H_7Si_2O_7$

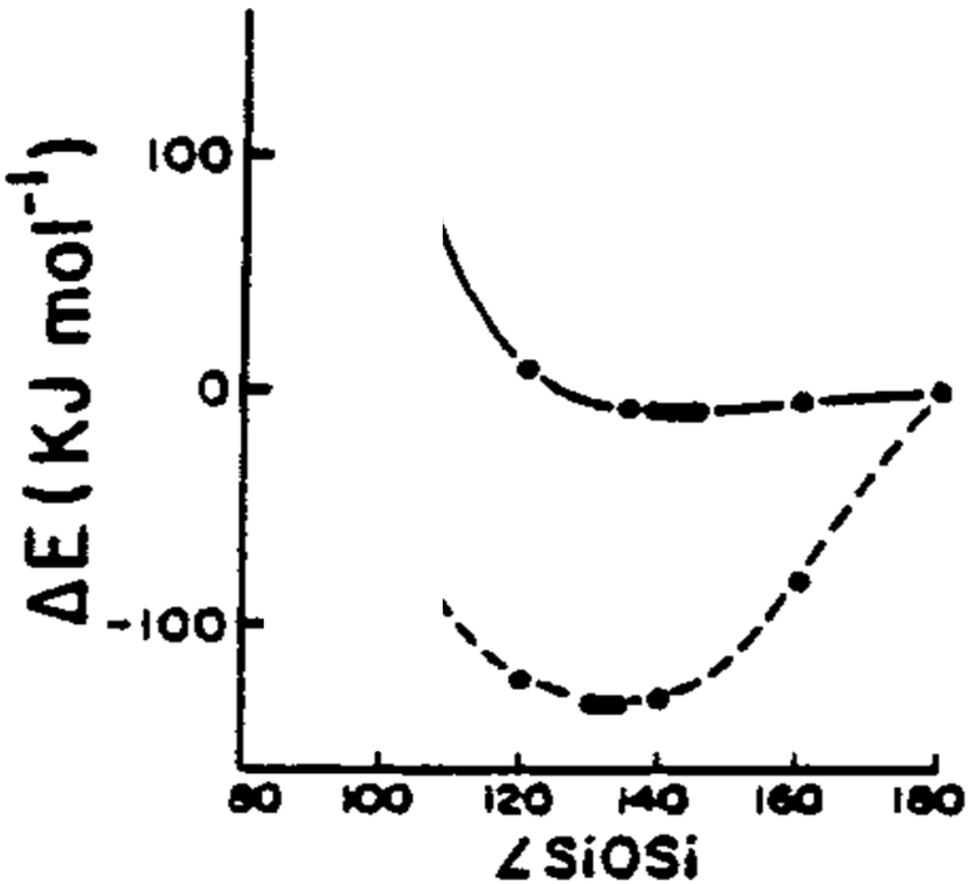


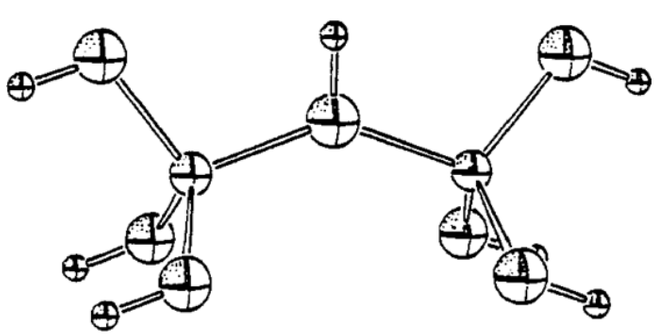
Geisinger, Gibbs, Navrotsky PhysChemMiner 11(1985)266
Van Heusden et al, IEEE Trans. Nucl. Sci. 46 (1999) 1562

RUTGERS

Energy vs. Angle

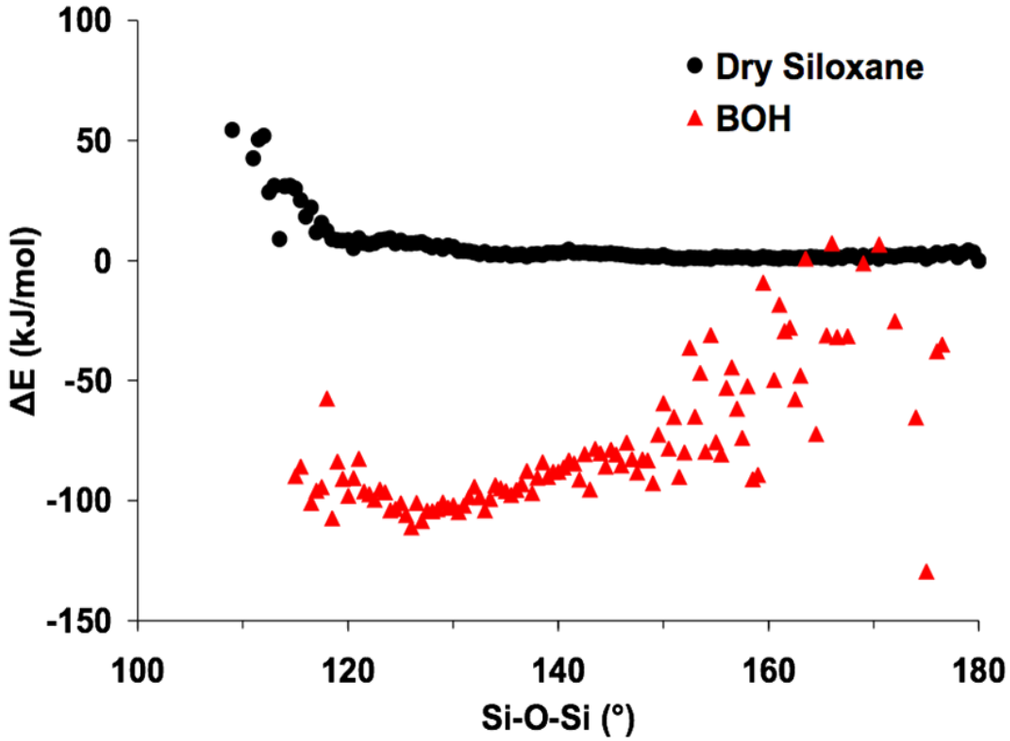
Molecular Orbital (QM)

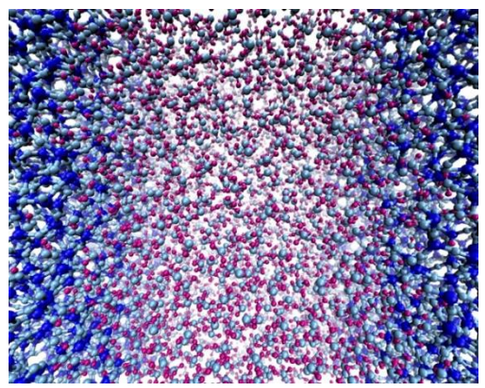




Geisinger et al., Phys. Chem. Miner. 11 (1985) 266.
Van Heusdan et al. IEEE Nucl. Sci, 46(1999)1562

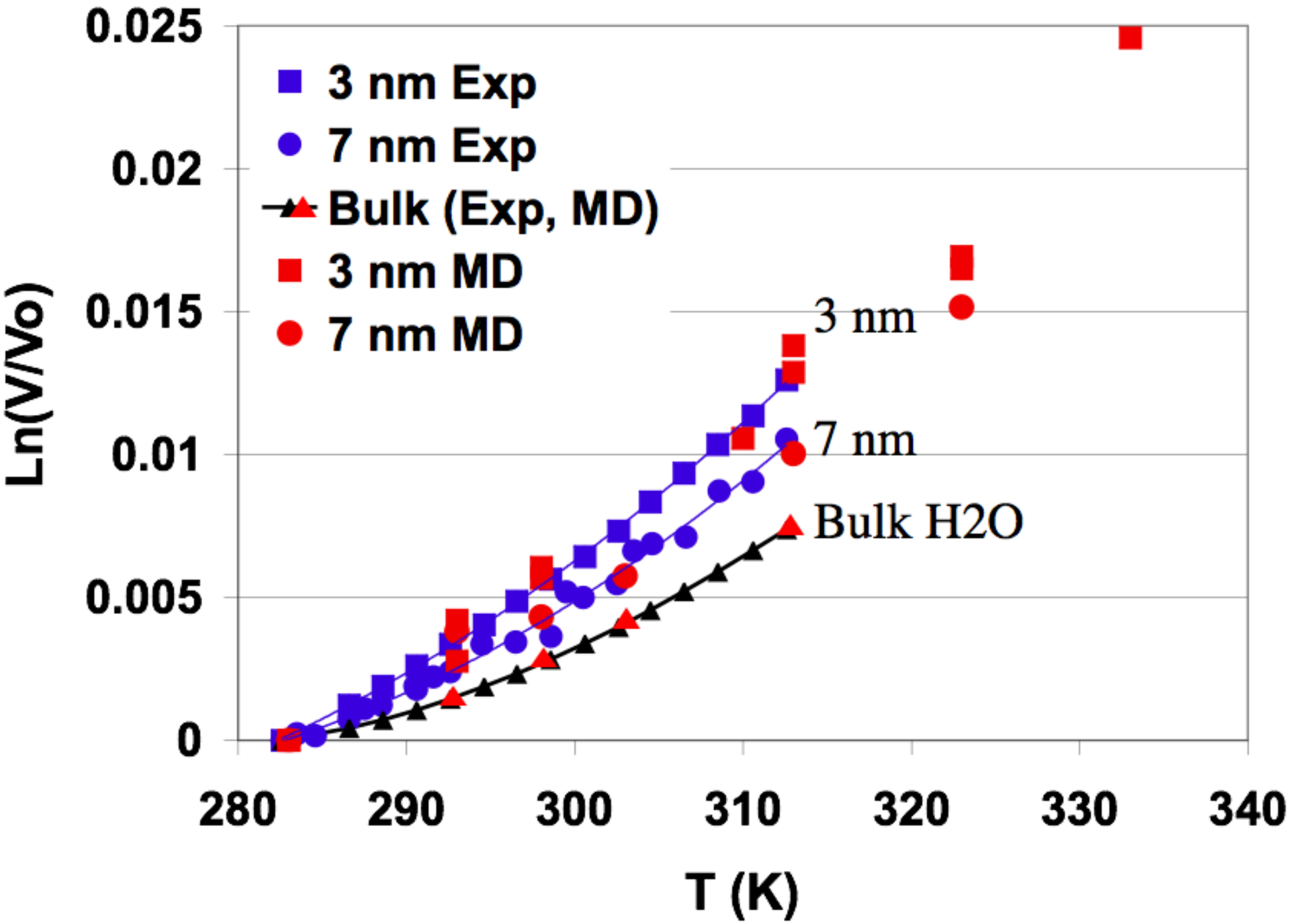
Our MD





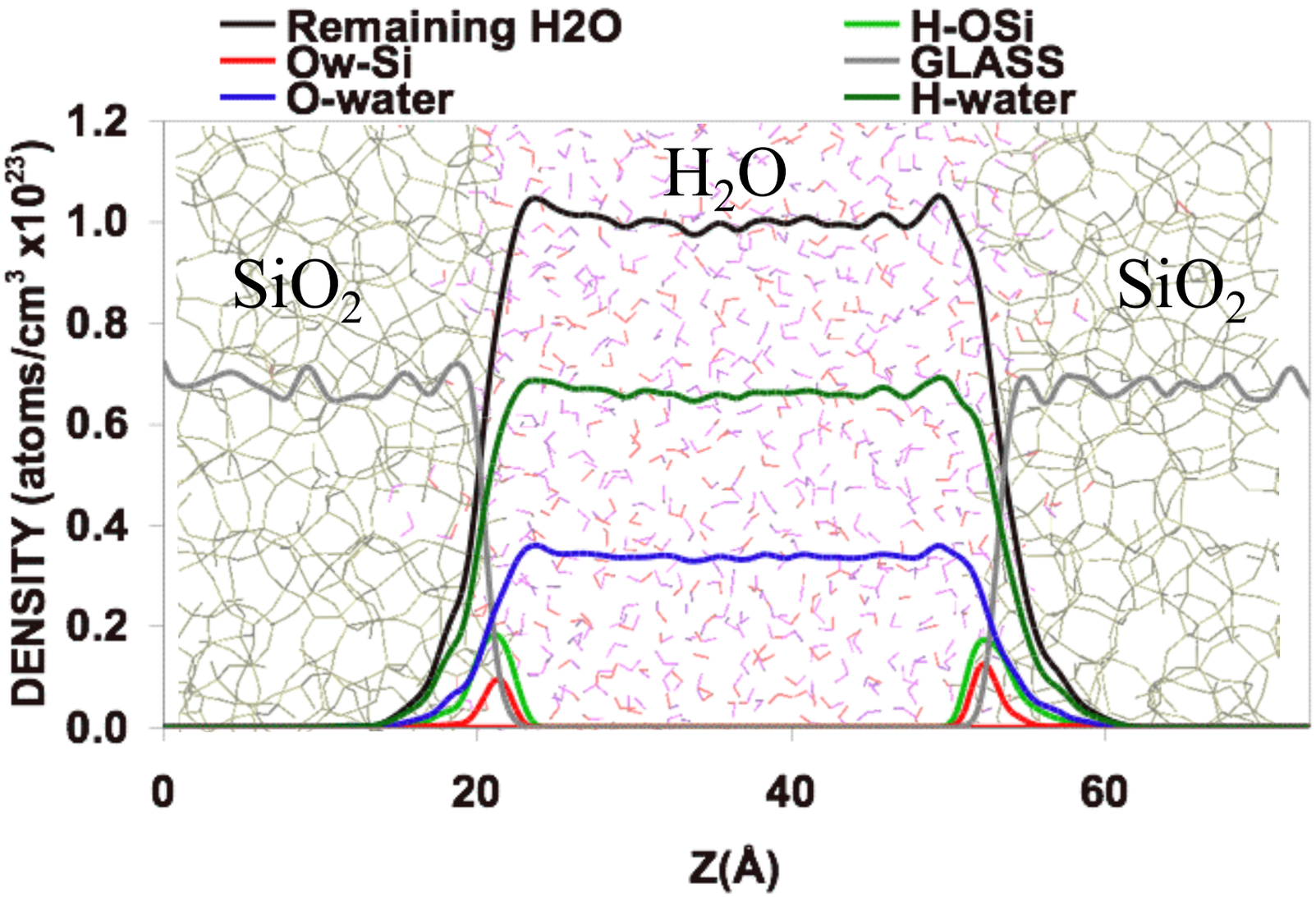
RUTGERS

MD Simulations: Constant Pressure (1 atm) at different Temperatures



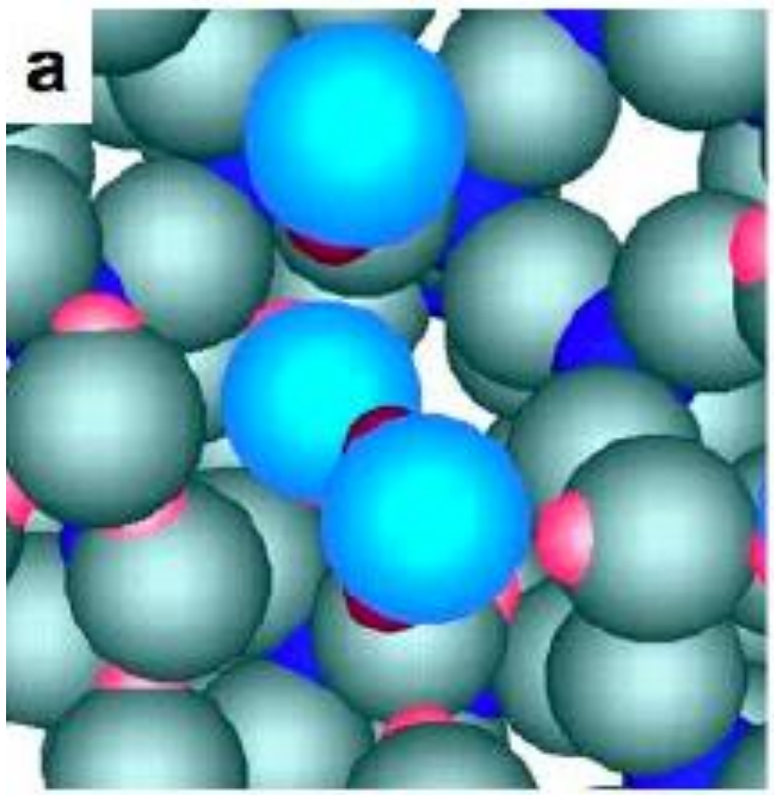
Garofalini et al ChemPhysChem2008
Xu et al Langmuir 2009.

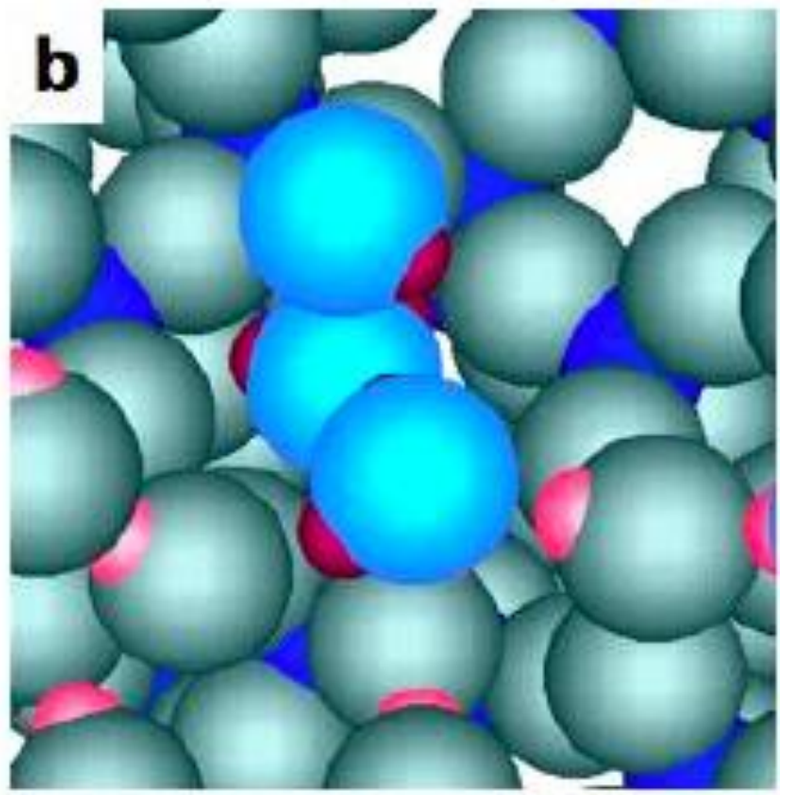
RUTGERS

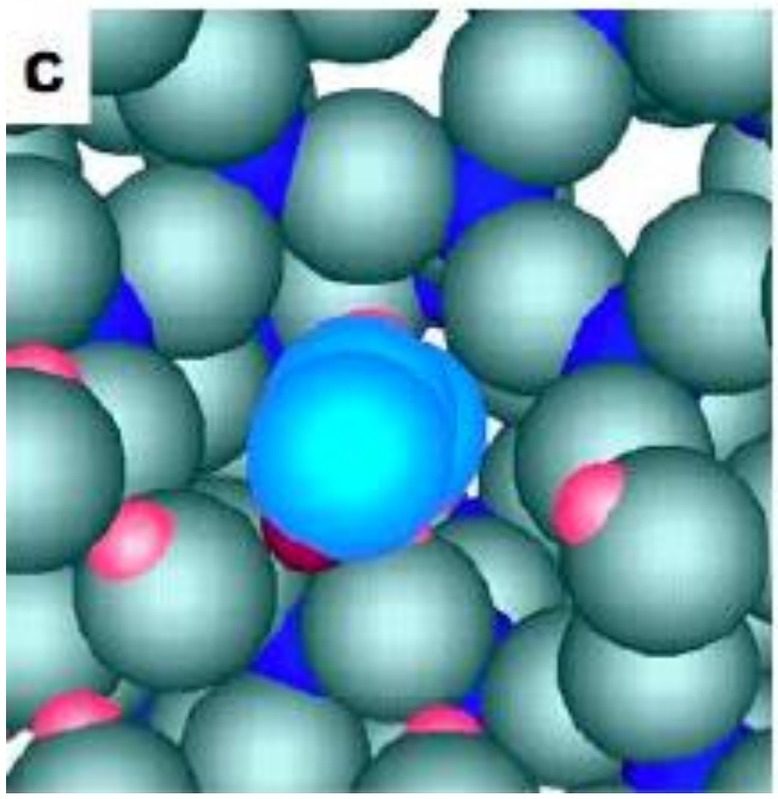


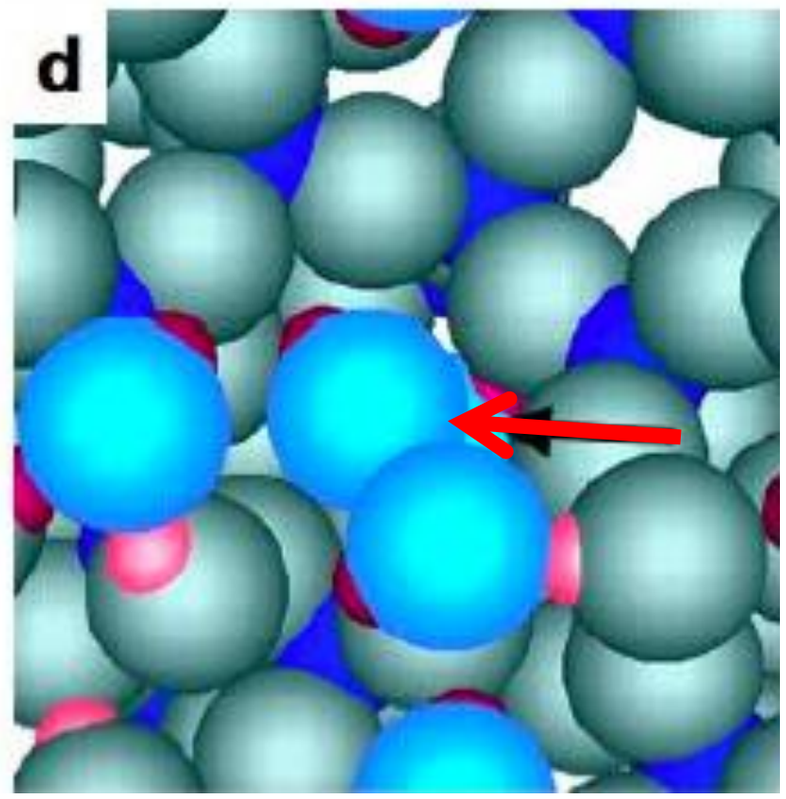
Garofalini et al ChemPhysChem 9 (2008), Xu et al Langmuir (2009).

RUTGERS









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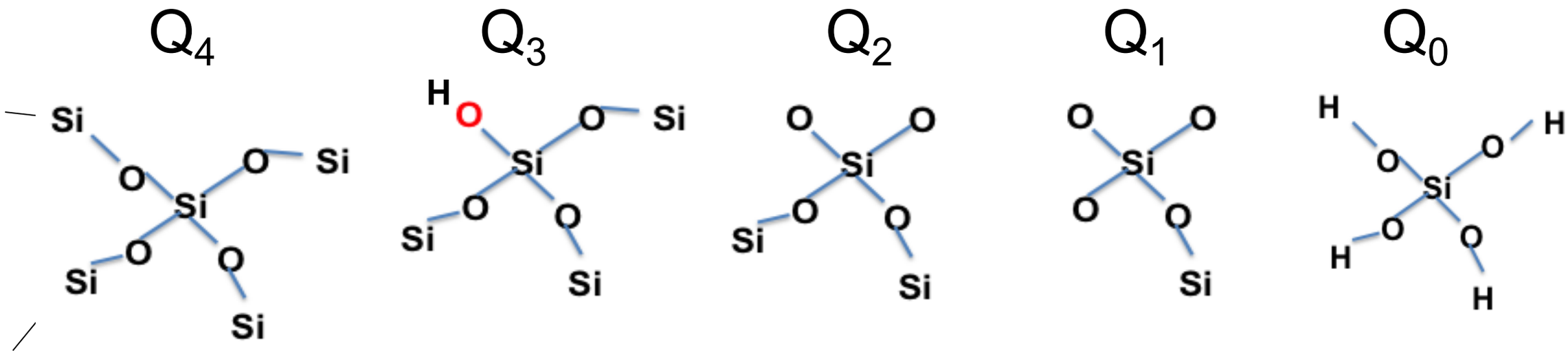
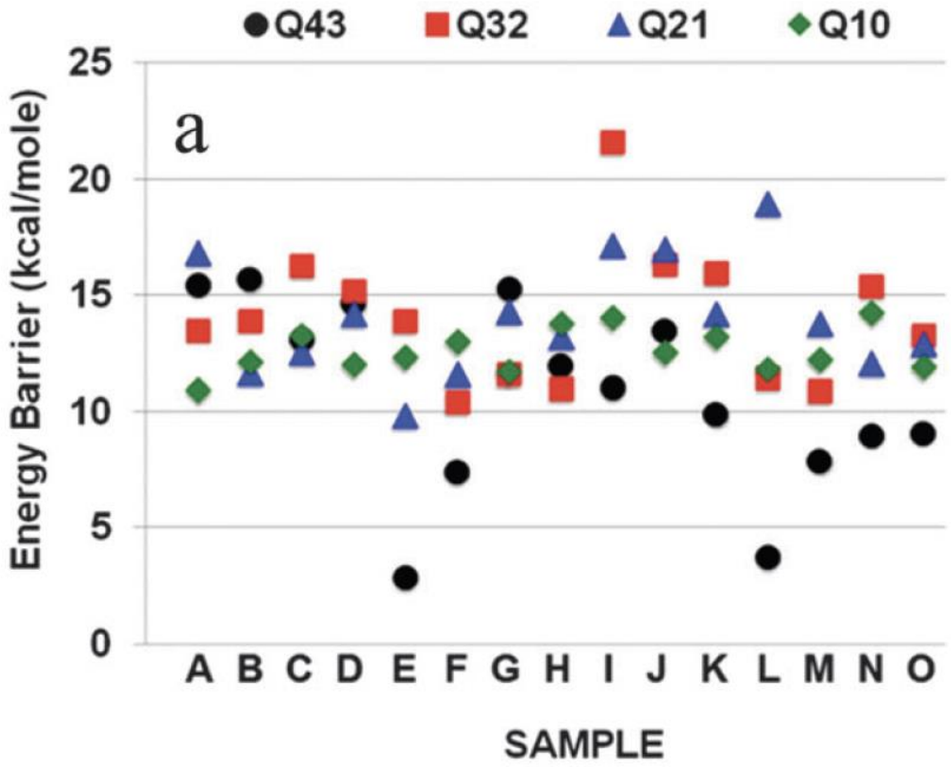


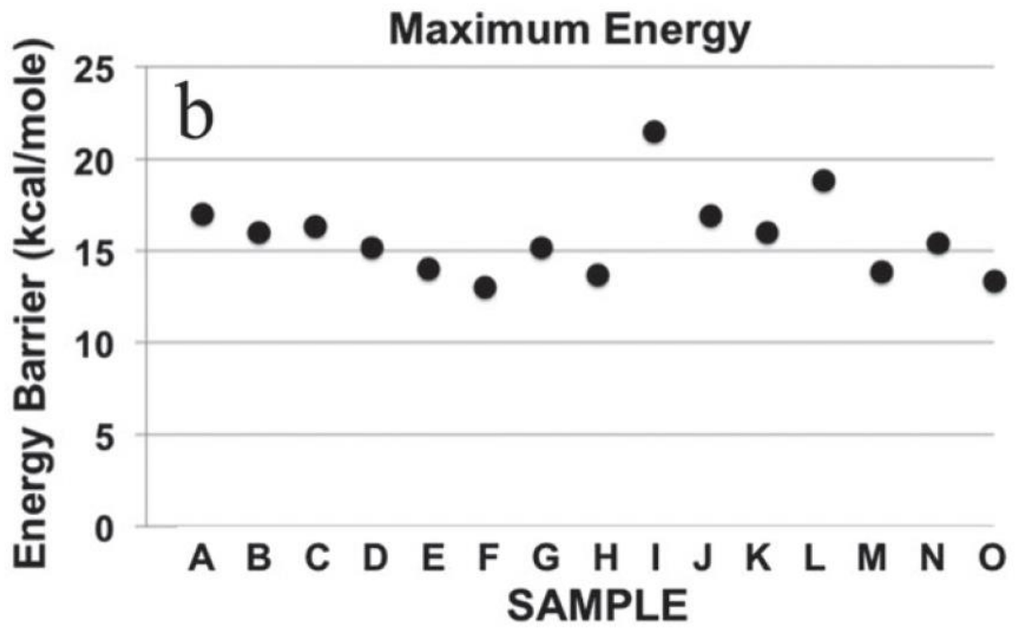
	MD SIMULATIONS	EXPERIMENTS	AB-INITIO
ENERGY	15-24 kcal/mole*	14-24 kcal/mole	18-39 kcal/mole

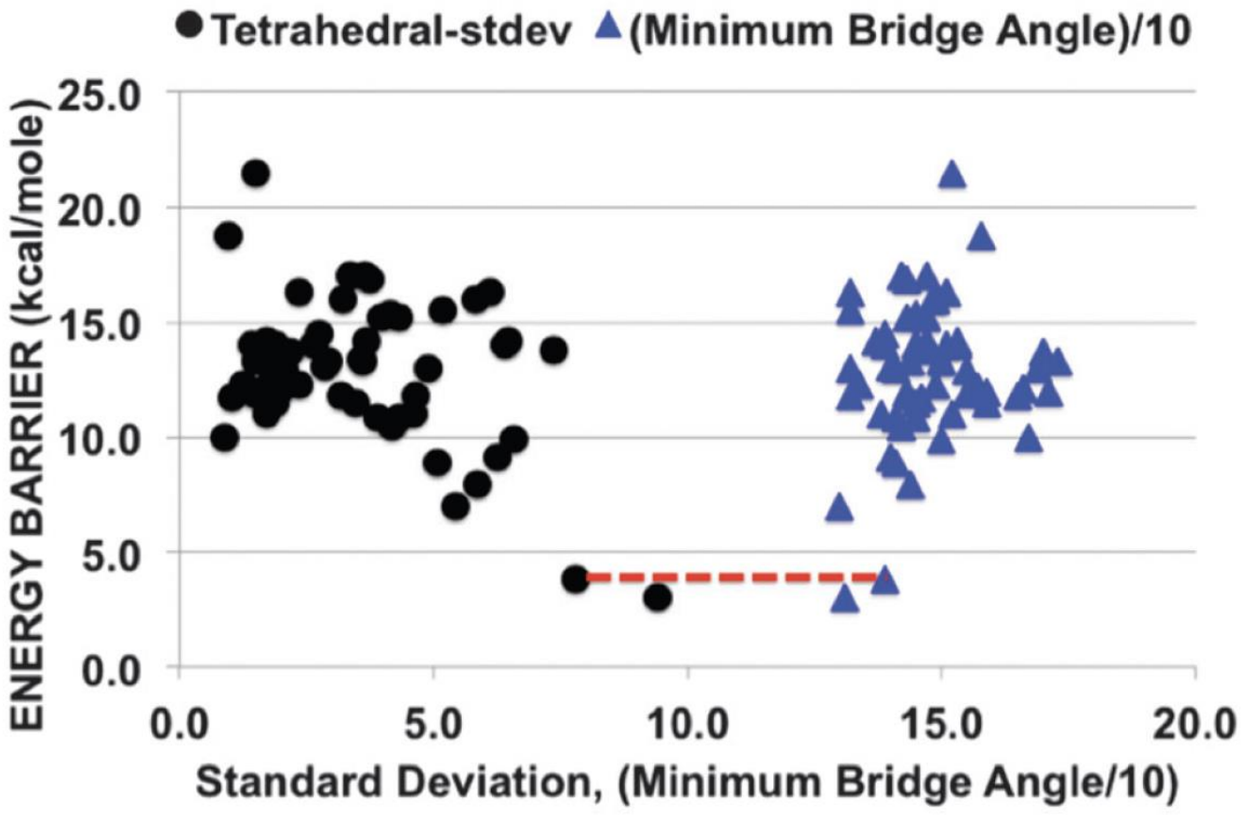
*MD: Kagan, Lockwood, Garofalini PhysChemChemPhys, 16 (2014) 9294 (15 kcal/mole)
Ablaza, Fox, DeGuzman, Garofalini PCCP (to be published)

Xiao & Lasaga (1994);
Pelmenschikov (2000,2001);
Crisenti & Kubicki (2006);
Icenhower and Dove GGA 2000

RUTGERS


Q43
Q32
Q21
Q10
a
Energy Barrier (kcal/mole)
25
20
15
10
5
0
A B C D E F G H I J K L M N O
SAMPLE


Maximum Energy
b
Energy Barrier (kcal/mole)
25
20
15
10
5
0
A B C D E F G H I J K L M N O
SAMPLE


Tetrahedral-stdev
(Minimum Bridge Angle)/10
ENERGY BARRIER (kcal/mole)
25.0
20.0
15.0
10.0
5.0
0.0
0.0
5.0
10.0
15.0
20.0
Standard Deviation, (Minimum Bridge Angle/10)

RUTGERS

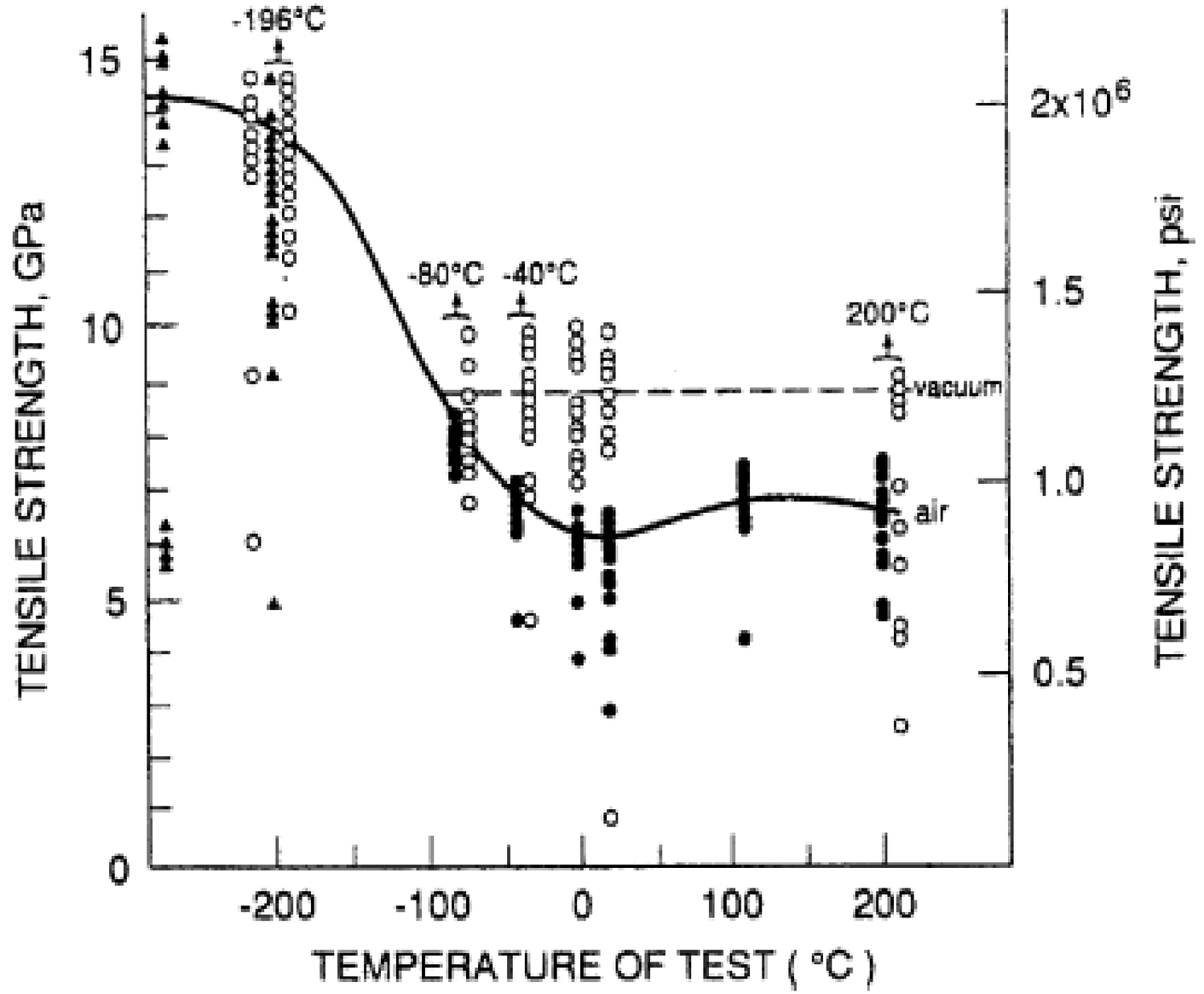
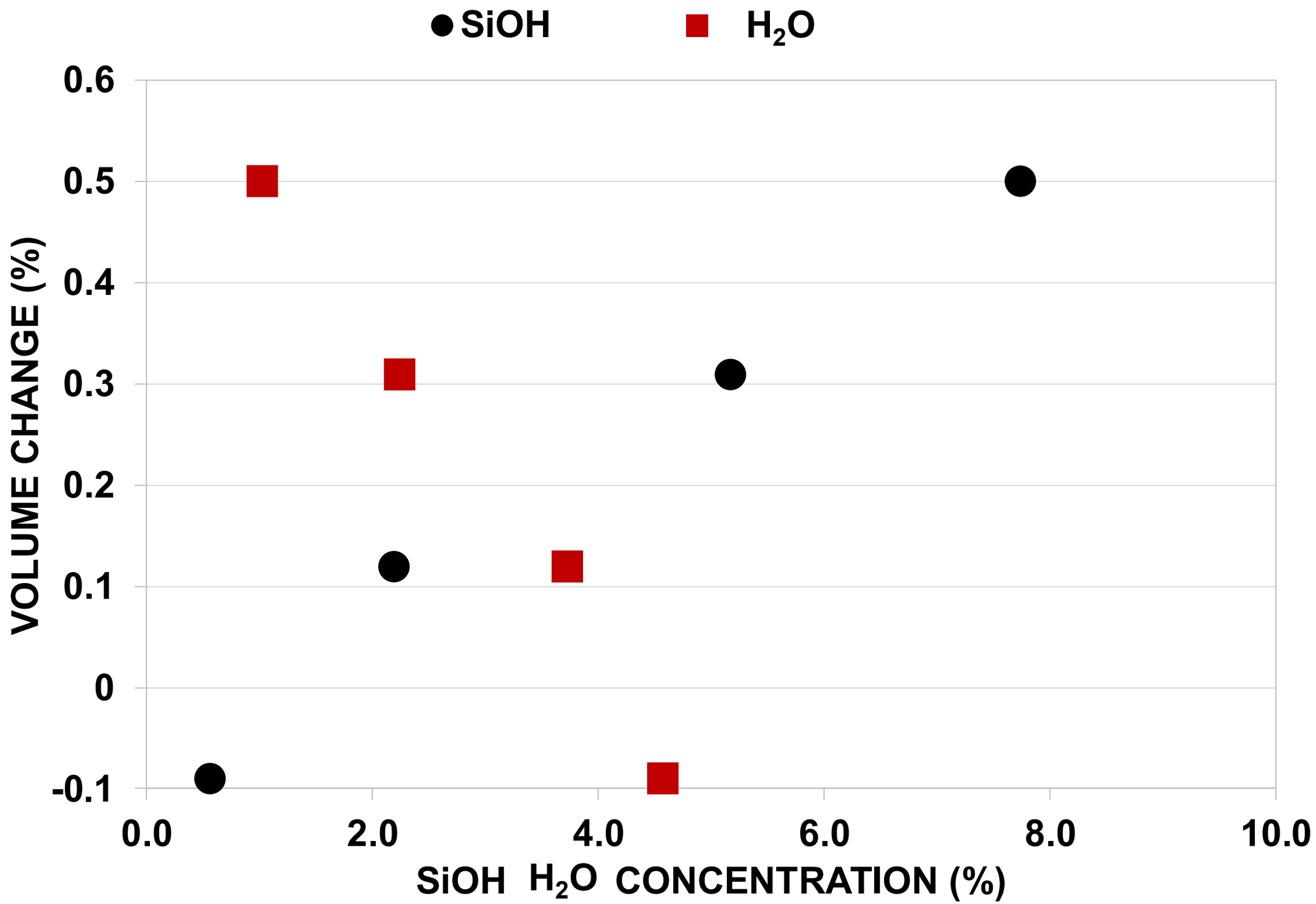


Fig. 1. Strengths of silica fibers as a function of temperature. Fibers tested in liquid helium or liquid nitrogen (filled triangles), fibers tested in vacuum (open circles), and fibers tested in air (filled circles) (from [18]).

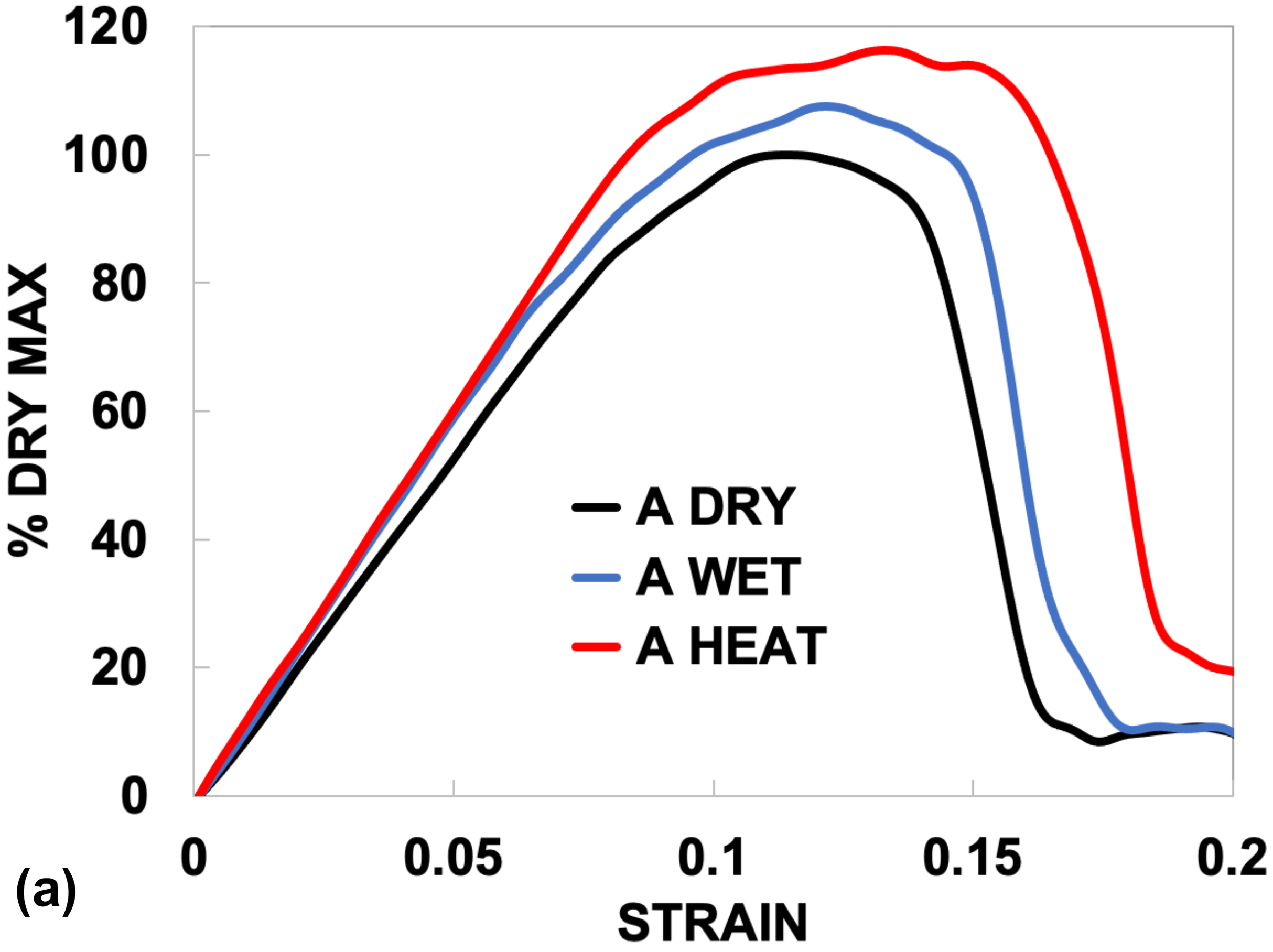
Kurkjian et al. JNCS 2003

RUTGERS



Garofalini et al, JAmCeramSoc(2019)

RUTGERS


120
100
80
60
40
20
0
% DRY MAX
0
0.05
0.1
0.15
0.2
STRAIN
A DRY
A WET
A HEAT

(a)