Otto Schott Institute of Materials Research
Lessingstr. 12 (AWZ), 07743 Jena
delia.brauer@uni-jena.de
www.brauergroup.uni-jena.de

FRIEDRICH-SCHILLER-
UNIVERSITÄT
JENA

Paving the Way for the Bioactivity of Glass

Delia S. Brauer

Photo: Jens Meyer, Uni Jena

JENA LICHTSTADT.

CITY OF LIGHT

JENA

GLASSTADT.

CITY OF GLASS

Jena & Glass

FRIEDRICH-SCHILLER-
UNIVERSITÄT
JENA

Portraits: Wikimedia Commons

Jena & Glass

Jena & Glass & Biomaterials

Interface reactions between machinable bioactive glass-ceramics and bone

W. Höland, W. Vogel, and K. Naumann
Friedrich-Schiller-University Jena, Otto-Schott-Institute, Department of Chemistry, Jena, DDR

J. Gummel
Humboldt University, Orthopedic Clinic, Department of Medicine (Charité) Berlin, DDR

A new biomaterial for bone substitution, a "machinable bioactive glass-ceramic" has been developed. The material contains two main crystal phases, mica and apatite, and is therefore machinable and bioactive. It has the advantage to be workable by the surgeon, if necessary, during operation. The preparation method of this glass-ceramic is described. Different types of the material can be produced in dependence of the composition, nucleation, and crystallization of the basic glass. *In vivo* and *in vitro* investigations showed a characteristic solubility of the material. A Ca-phosphate-rich interface layer with apatite crystals (from the basic glass-ceramic) and a thickness of about 5–10 μm grows as solid-state reaction between glass-ceramic and bone. This interface reaction is interpreted as a chemical process which includes a slight solubility of the glass-ceramic and a solid state reaction between the stable apatite crystals in the glass-ceramic and the bone.

Journal of Biomedical Materials Research, Vol. 19, 303–312 (1985)

CCC 0021-9304/85/030303-10$04.00

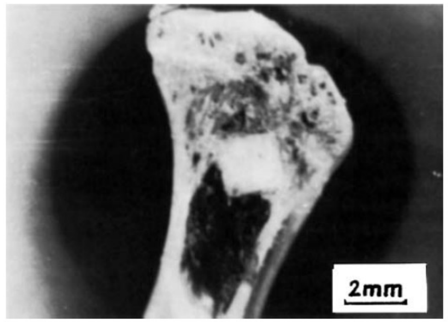


Figure 5. Transverse section of a machinable bioactive glass-ceramic implant (2 × 2 × 2 mm) in a tibia of the guinea pig.

Bioactive Glasses ?

What is Special about Bioactive Glass?

FRIEDRICH-SCHILLER-
UNIVERSITÄT
JENA

25TH International Congress on Glass (ICG2019)
Hosted By ACerS Glass & Optical Materials Division 100 years

Session 2: Glass in Healthcare (TC04)
Julian Jones, Imperial College London, UK,
julian.r.jones@imperial.ac.uk
Delia Brauer, Friedrich-Schiller-Universität Jena, Germany,
delia.brauer@uni-jena.de
Qiang Fu, Corning Inc., USA, fuq2@corning.com

PNCS-ESG 2018
15th International Conference on the Physics of Non-Crystalline Solids & 14th European Society of Glass Conference
9 - 13 July 2018 - Saint Malo

BIOGLASSES 1
Session Chair: Robert HILL
Room: LAMENNAIS 1&2

BIOGLASSES 3
Session Chair: Delia BRAUER
Room: VAUBAN

Session S2: *Glasses in Healthcare*
Aldo R. Boccaccini, Friedrich-Alexander-University, Erlangen
Delia S. Brauer, Friedrich-Schiller-University, OSIM, Jena

2024 GLASS & OPTICAL MATERIALS DIVISION ANNUAL MEETING
The American Ceramic Society ceramics.org
Welcome to Fabulous Las Vegas Nevada
ceramics.org/gomd24 | MAY 19 – 23, 2024

Session 1: Glasses, Glass-Ceramics, and Glass-Based Biomaterials
ORGANIZERS:
Delia Brauer, University of Jena, Germany
Leena Hupa, Åbo Akademi, Finland

Joint Meeting of
DGG / ČSS / SSS

92nd Annual Meeting of
German Society of Glass Technology (DGG)

in conjunction with the

Annual Meetings of
the Czech Glass Society (ČSS)
and the Slovak Glass Society (SSS)

Bayreuth, Germany
28 – 30 May 2018

2023 GLASS & OPTICAL MATERIALS DIVISION ANNUAL MEETING (GOMD 2023)

—WEDNESDAY—

S2: Glass and Interactions with Its Environment: Fundamentals and Applications

Session 1: Glasses, glass-ceramics and glass-based biomaterials
Room: Royal C
Session Chairs: Delia Brauer, Friedrich-Schiller-Universität; Jamieson Christie, Loughborough University
9:20 AM
(GOMD-S2-056-2023) Unravelling the structural role of ...

11:40 AM
(GOMD-S2-062-2023) Developing reactive potentials to understand the dissolution of phosphate glass
Z. Fallah[1]; J. K. Christie*[1]
1. Loughborough University, Department of Materials, United Kingdom

12:00 PM
(GOMD-S2-063-2023) Use of glass from smartphone touch screen for radiological accident dosimetry by EPR spectroscopy
M. Mobasher[2]; N. Ollier*[1]; F. Trompier[2]
1. CEA, France
2. IRSN, France

Soda-Lime Silicate Glass

ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Biomaterials 24 (2003) 1349–1356

Biomaterials

www.elsevier.com/locate/biomaterials

A comparative study between in vivo bone ingrowth and in vitro apatite formation on Na_2O–CaO–SiO_2 glasses

Shunsuke Fujibayashi[a,*], Masashi Neo[a], Hyun-Min Kim[b], Tadashi Kokubo[b], Takashi Nakamura[a]

[a] *Department of Orthopaedic Surgery, Graduate School of Medicine, Kyoto University, Kawahara-Cho 54, Sakyo-ku, Kyoto 6068507, Japan*

[b] *Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Japan*

Received 5 September 2002; accepted 15 October 2002

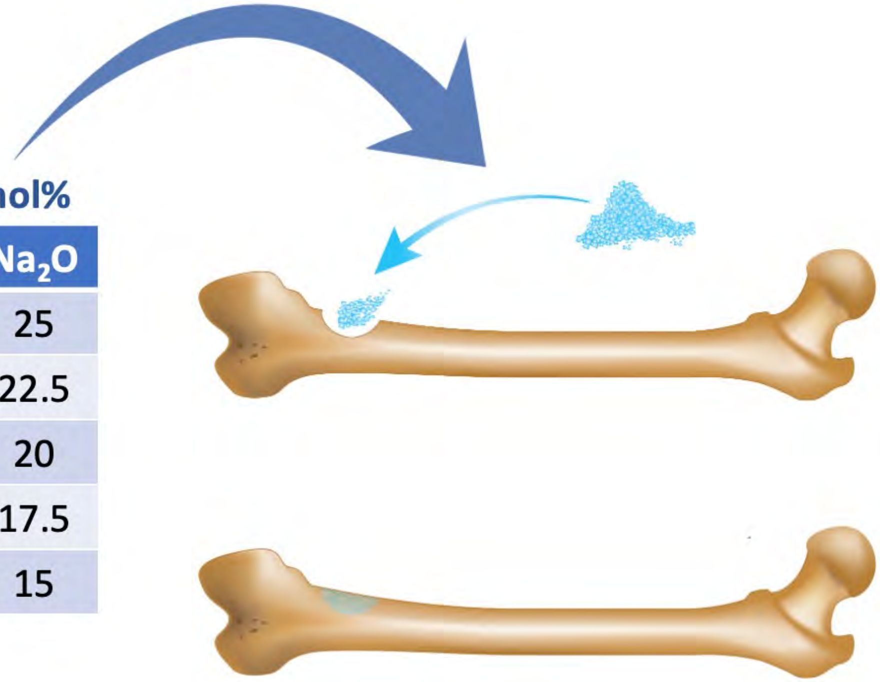
Table 1
Compositions of glasses

Glass	Composition/mol%		
	Na_2O	CaO	SiO_2
A	25.0	25.0	50.0
B	22.5	22.5	55.0
C	20.0	20.0	60.0
D	17.5	17.5	65.0
E	15.0	15.0	70.0

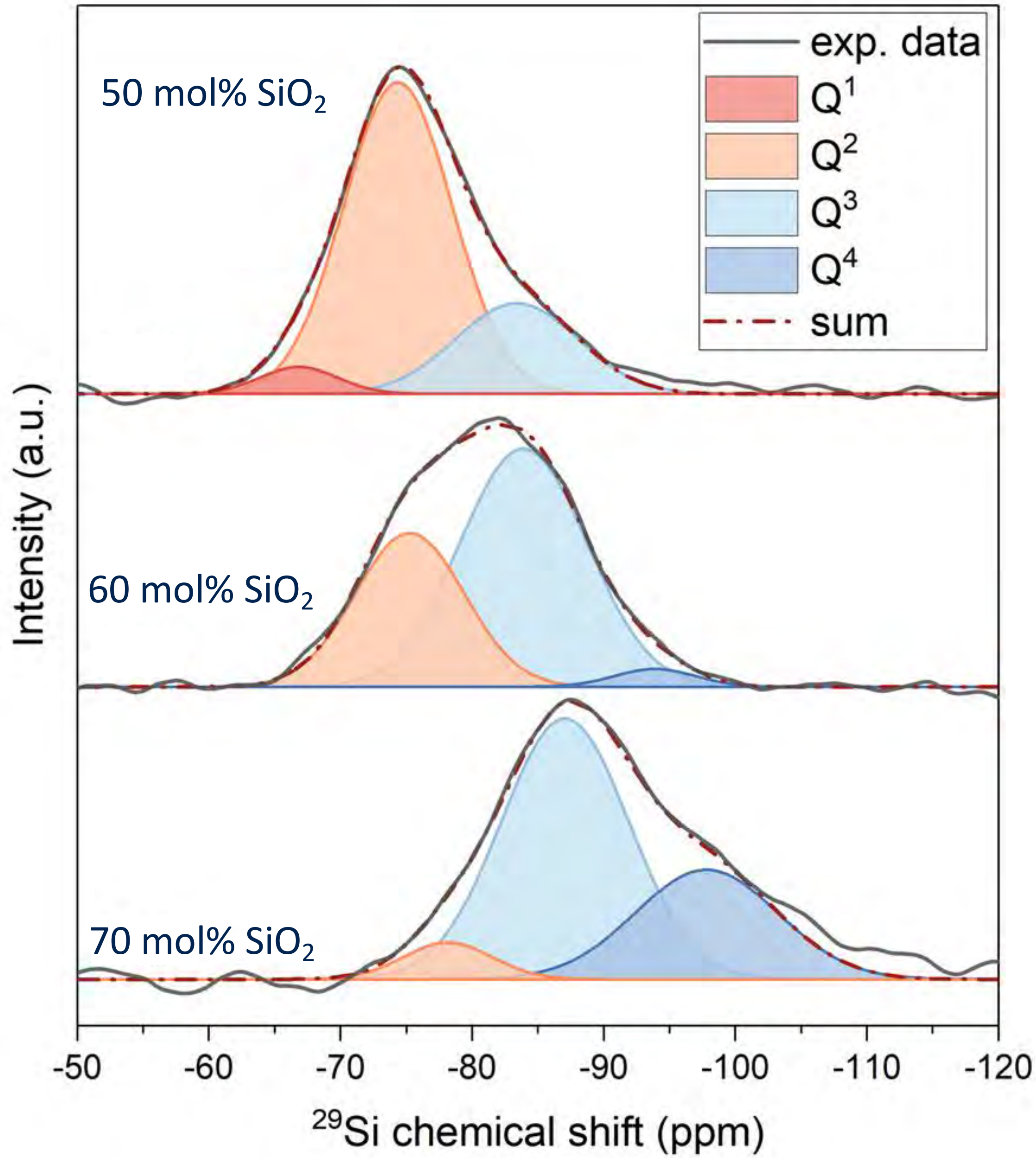
Soda-Lime Silicate Glass

Glass Composition in mol%

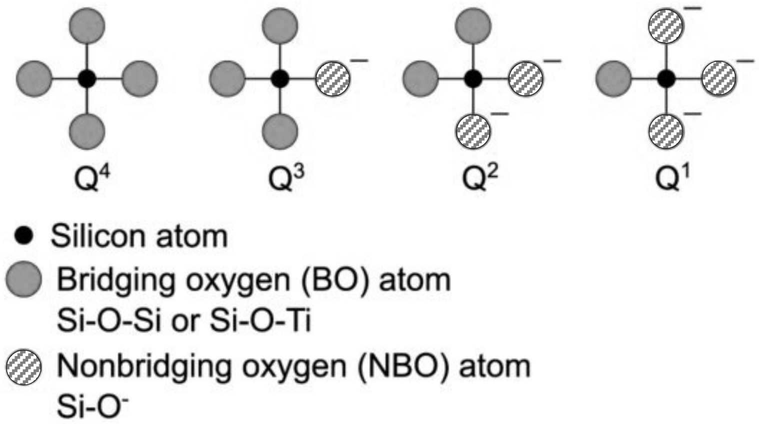
Glass	SiO_2	CaO	Na_2O
Si50	50	25	25
Si55	55	22.5	22.5
Si60	60	20	20
Si65	65	17.5	17.5
Si70	70	15	15



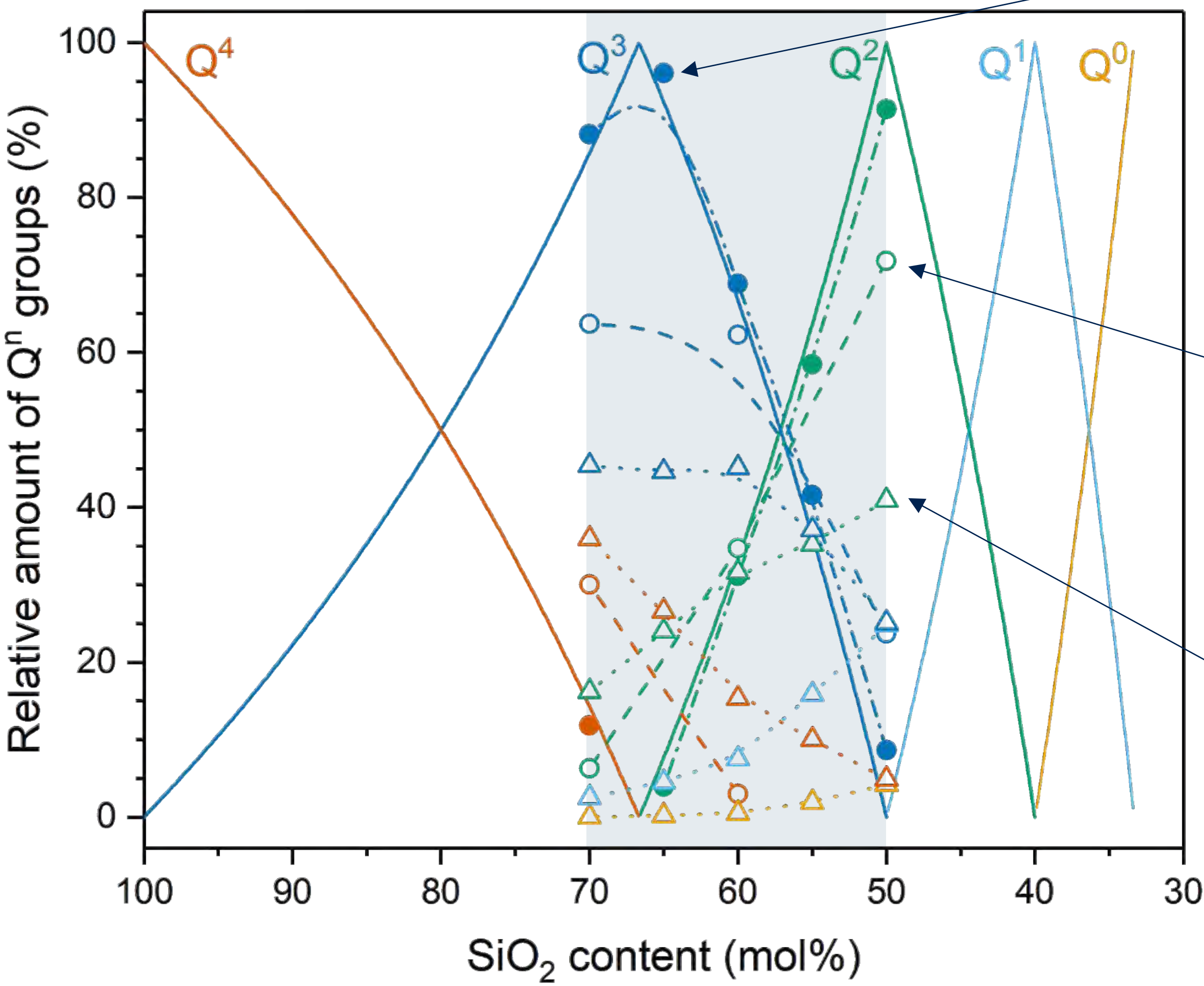
Solid-State ^{29}Si MAS NMR



Q^n groups:



Structure



compositional analysis

^{29}Si MAS NMR

MD simulation

Network Connectivity (NC)

Definition:

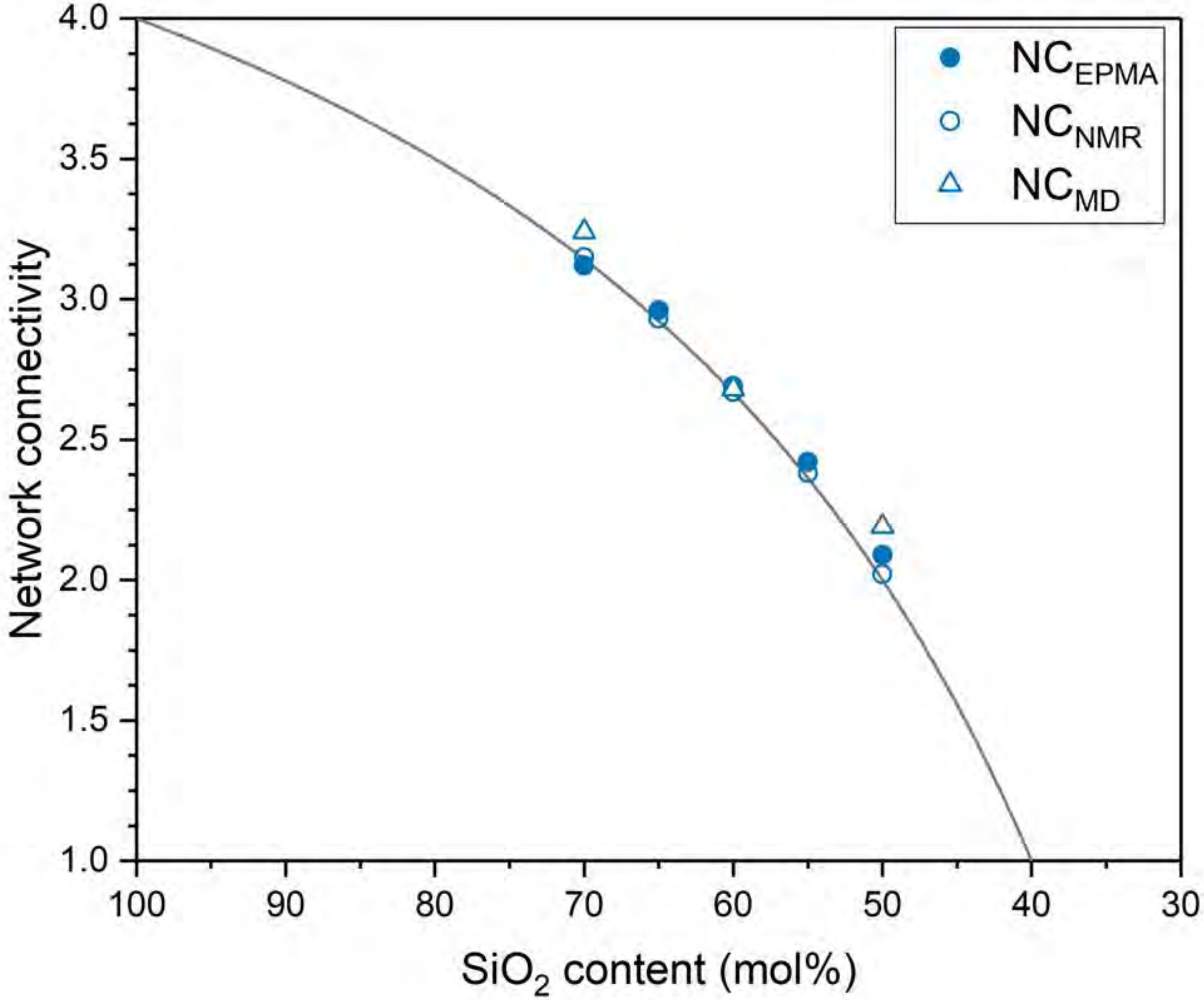
Average number of bridging oxygen atoms per network forming element (Si).

Calculation from composition in mol%:

$$NC = \frac{4 * SiO_2 - 2 * (CaO + Na_2O + SrO + K_2O + \ldots)}{SiO_2}$$

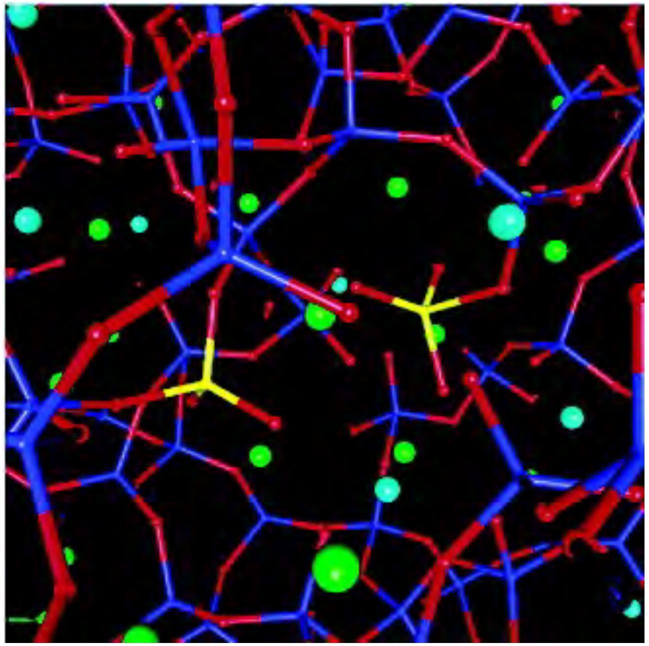
NC gives a single parameter describing the average degree of silicate network polymerisation.

Network Connectivity

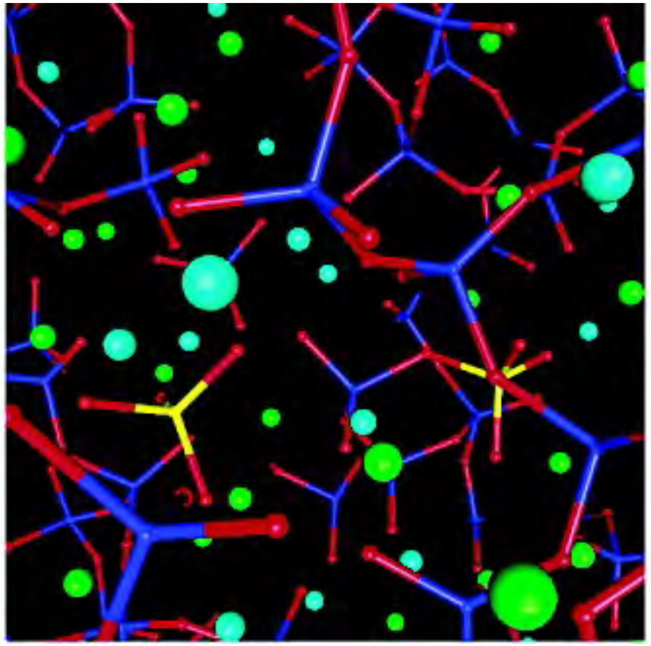


MD Simulations

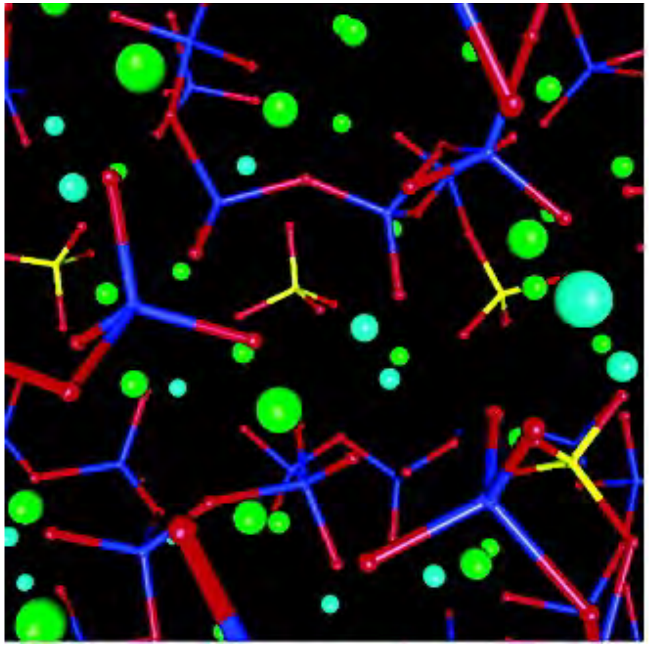
O Si P Ca Na



66.9mol% SiO_2
NC = 3.33



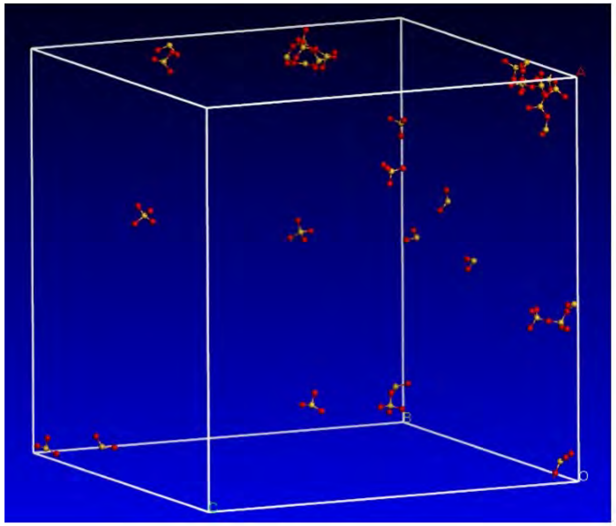
56.5mol% SiO_2
NC = 2.83



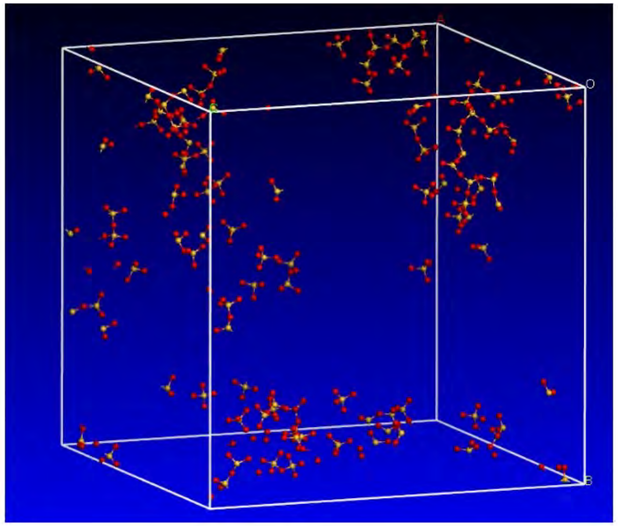
46.1mol% SiO_2
NC = 2.11
Bioglass 45S5

Tilocca et al., Chem. Mater. 19 (2007) 95-103

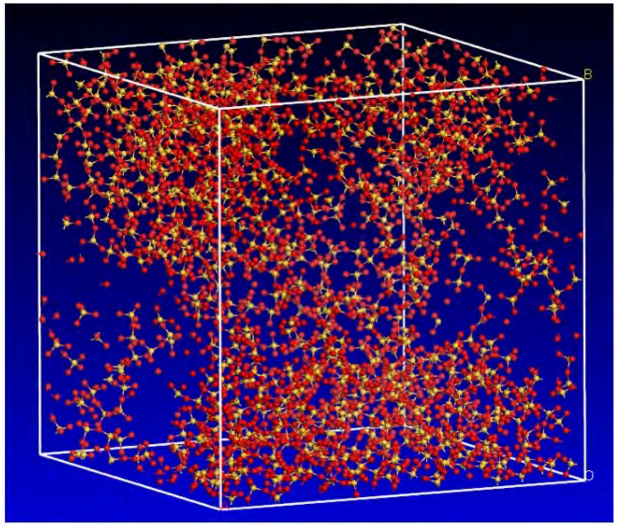
MD Simulations



70 mol% SiO_2
NC = 3.14



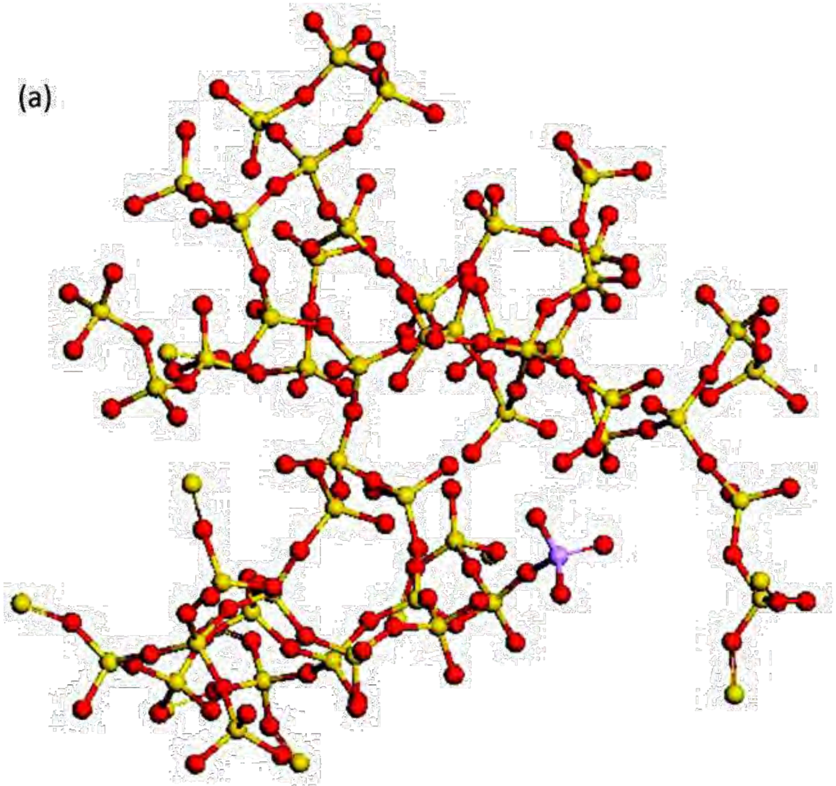
60 mol% SiO_2
NC = 2.67



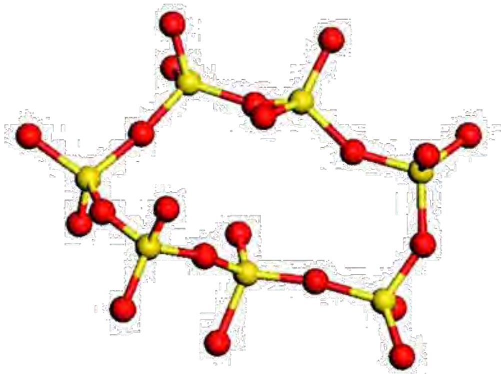
50 mol% SiO_2
NC = 2.00

MD Simulations

(a)



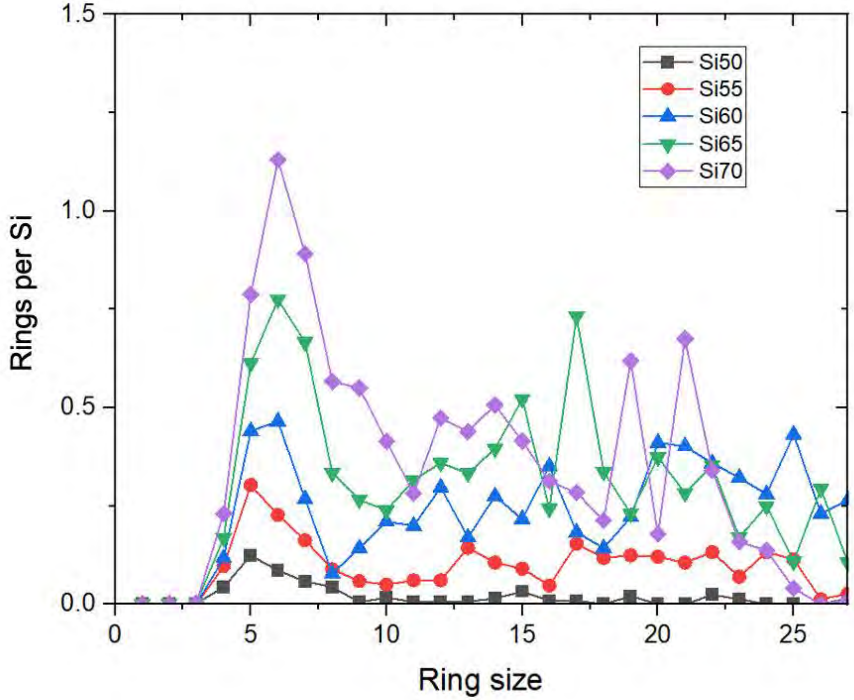
(b)

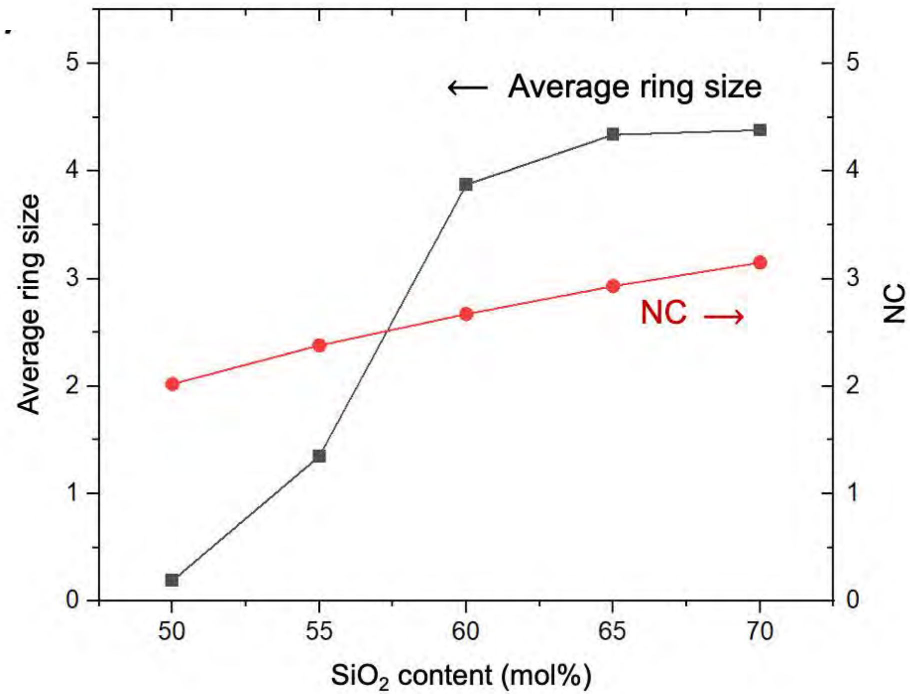


small silicate fragments
+ rings in bioactive glasses

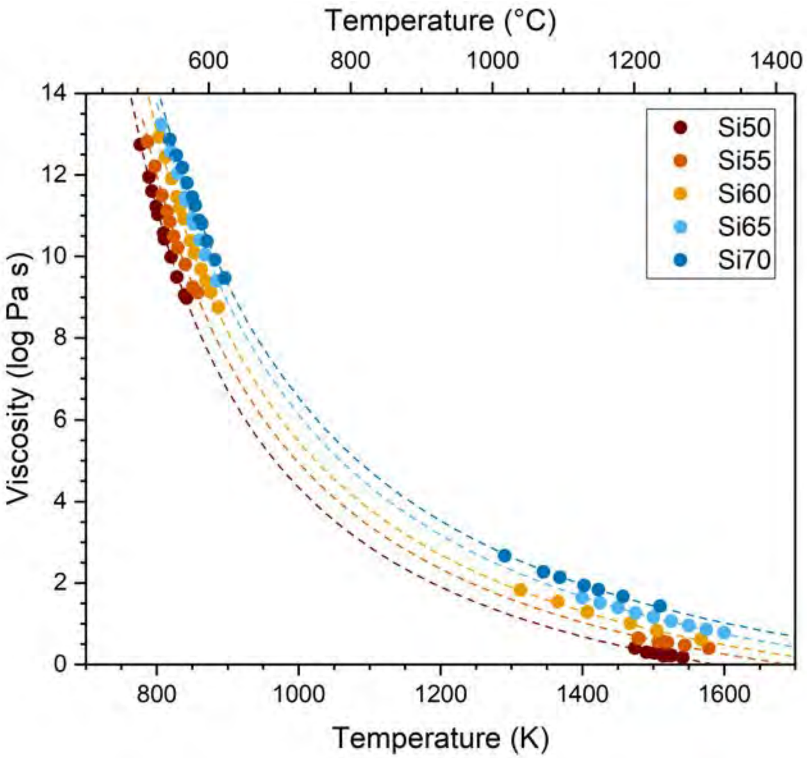
Xiang & Du, Chem Mater 23 (2011) 2703

MD Simulations

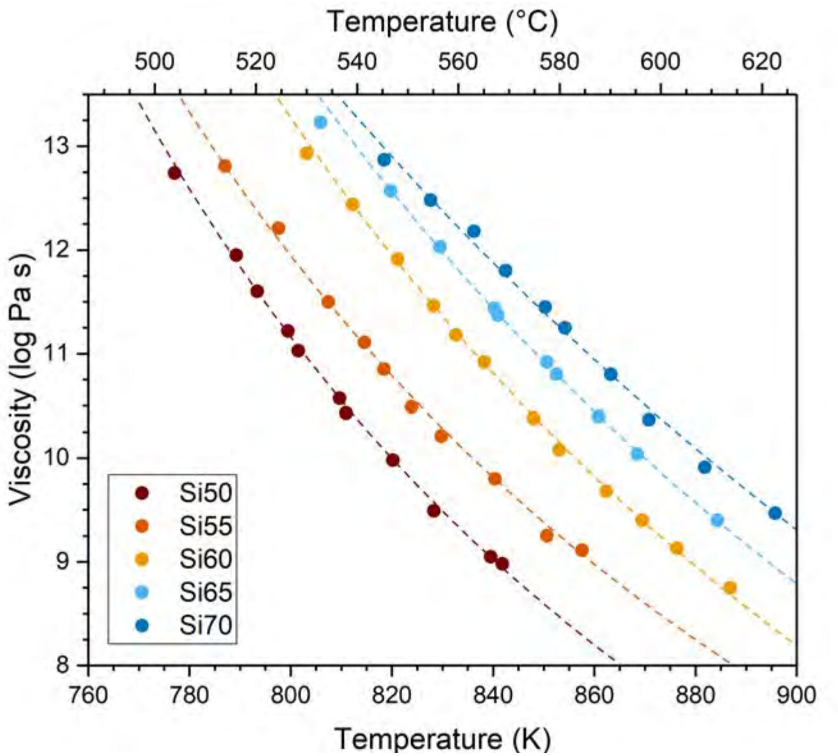




Viscosity

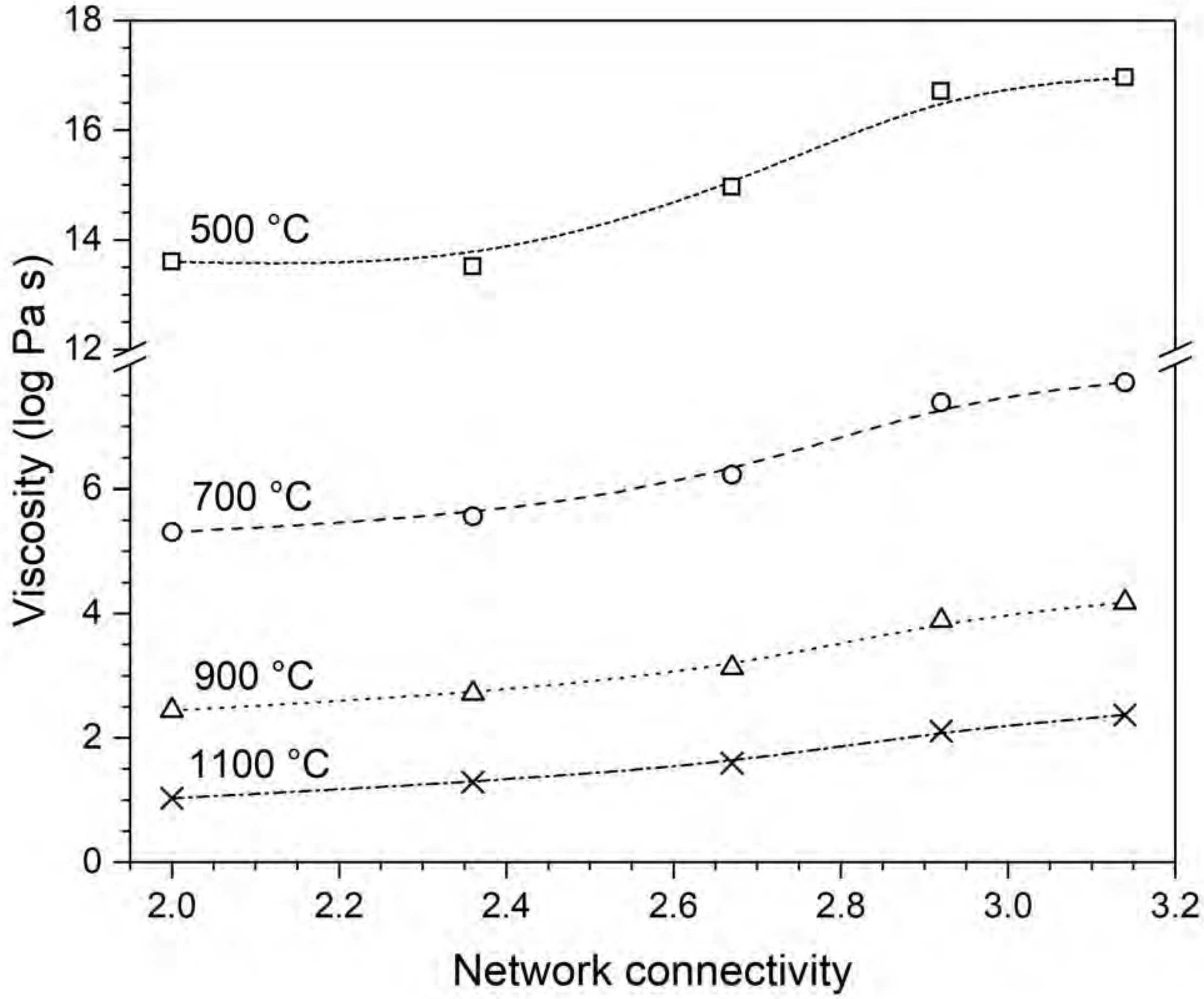


Adam Gibbs fitting



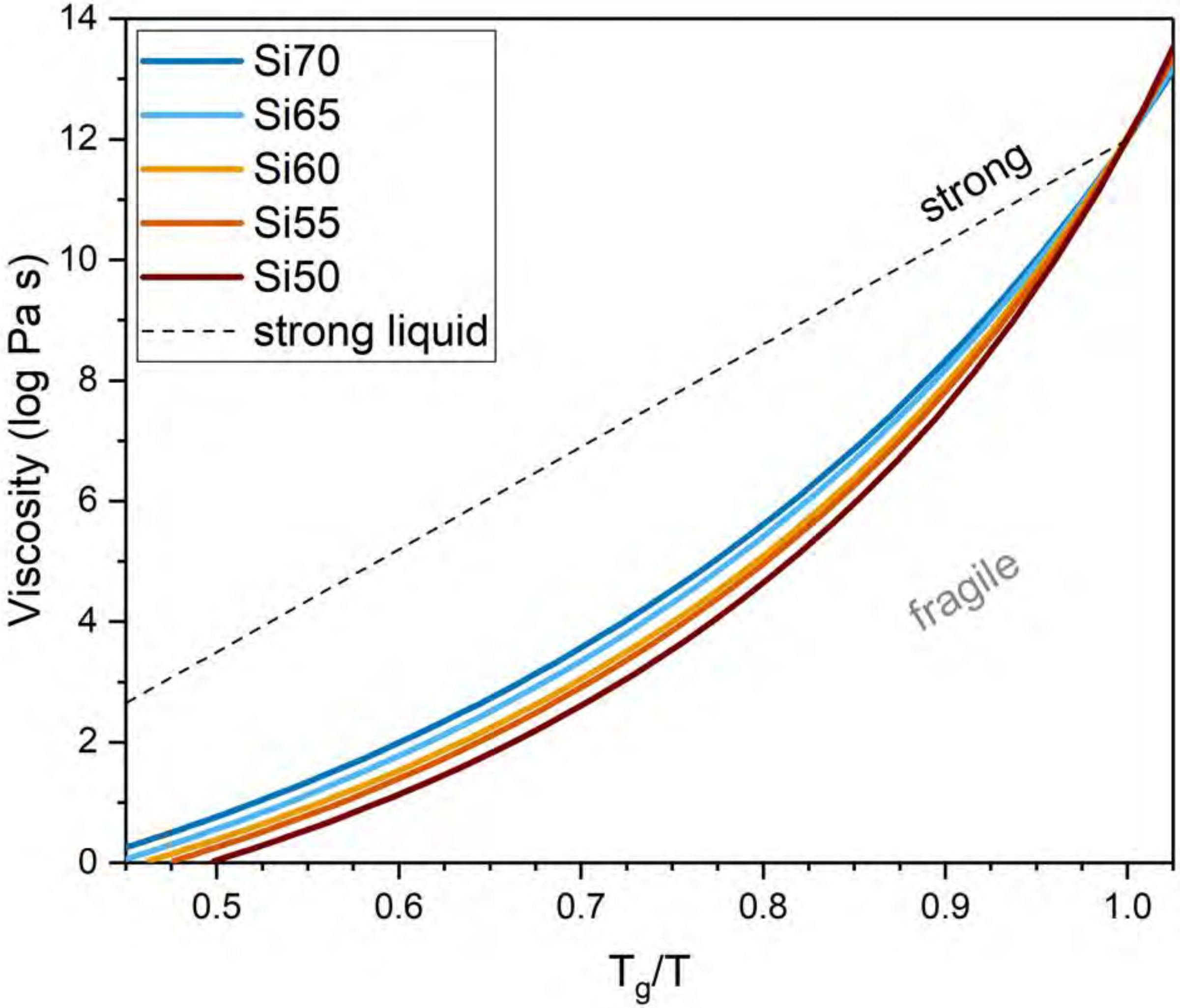
Vogel Fulcher Tammann fitting

Viscosity



Viscosity (log Pa s)
18
16
14
12
6
4
2
0
500 °C
700 °C
900 °C
1100 °C
2.0
2.2
2.4
2.6
2.8
3.0
3.2
Network connectivity

Fragility


Si70
Si65
Si60
Si55
Si50
strong liquid
strong
fragile
Viscosity (log Pa s)
T_g/T
0
2
4
6
8
10
12
14
0.5
0.6
0.7
0.8
0.9
1.0

More Details…

WEDNESDAY 15th APRIL

LUMIERE

BASIC GLASS SCIENCE - 5

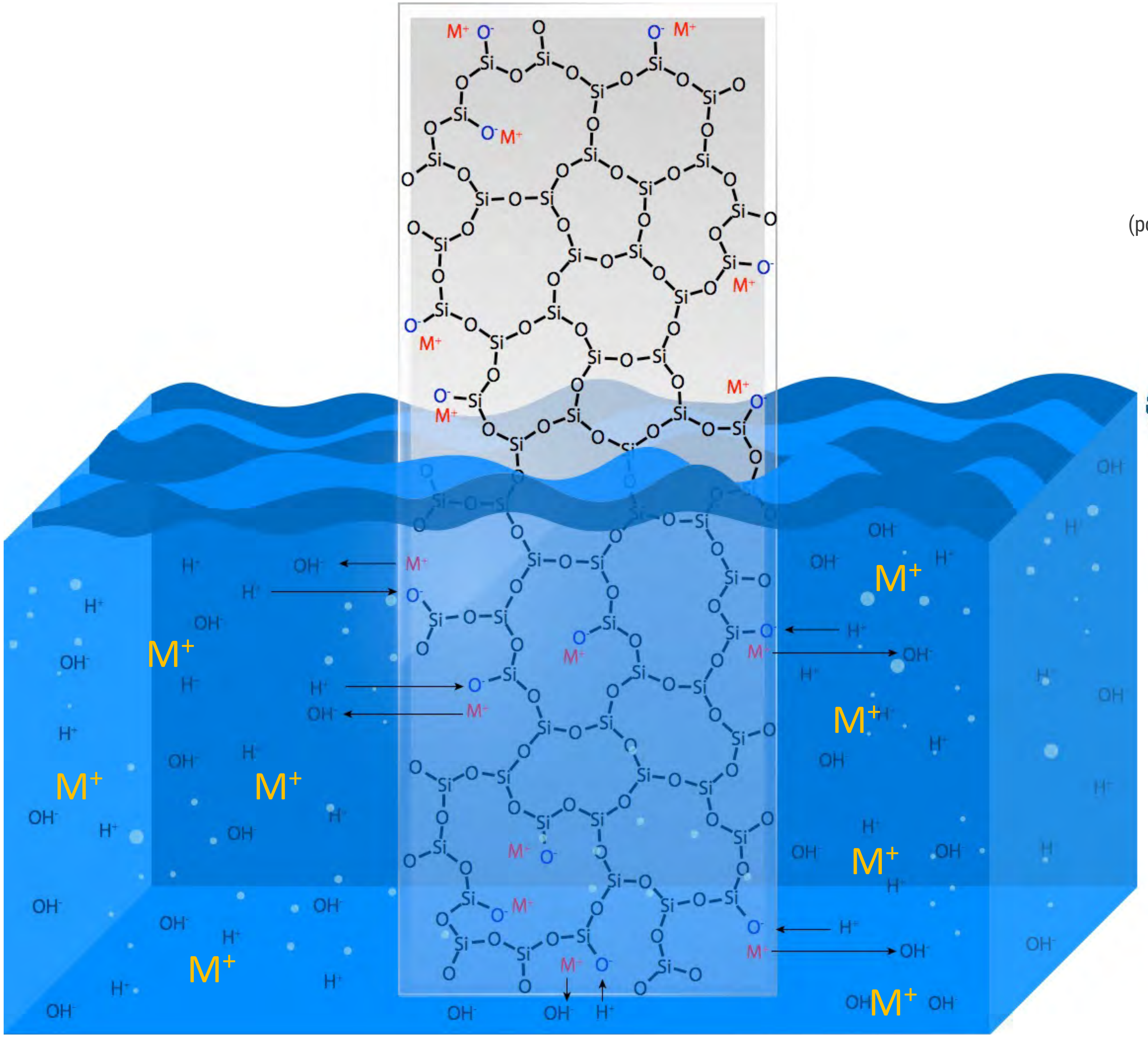
Session Chair: Katia BUROV

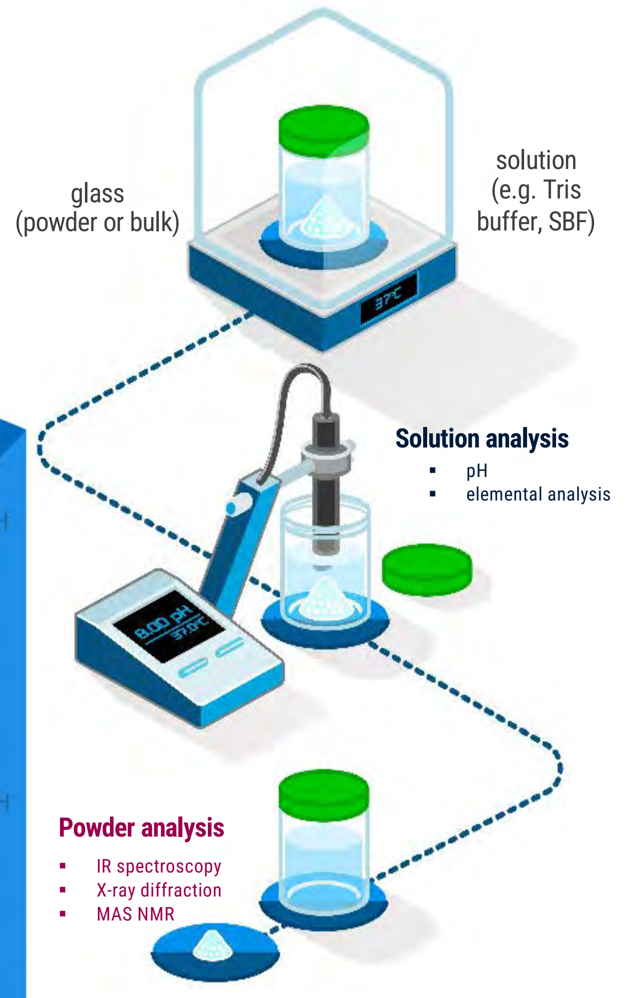
9:30 › **Invited:** **M. Ono,** *Tohoku University*
Effective thermal strengthening of glass by enhanced configurational entropy at its supercooled state

10:00 › **G. Macrelli,** *SiMathModels*
Kinetics issues of ion exchange in silicate glasses

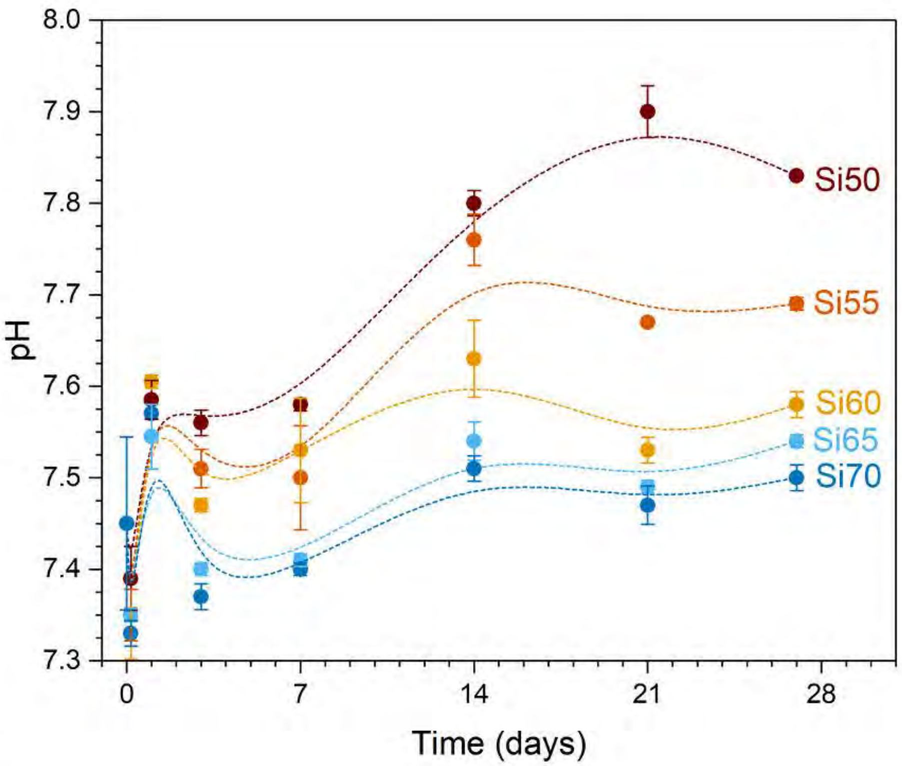
10:15 › **Z. Jin,** *Friedrich Schiller University Jena*
From windows to bioactive glass: structure, viscosity and crystallization of soda lime silicate glasses

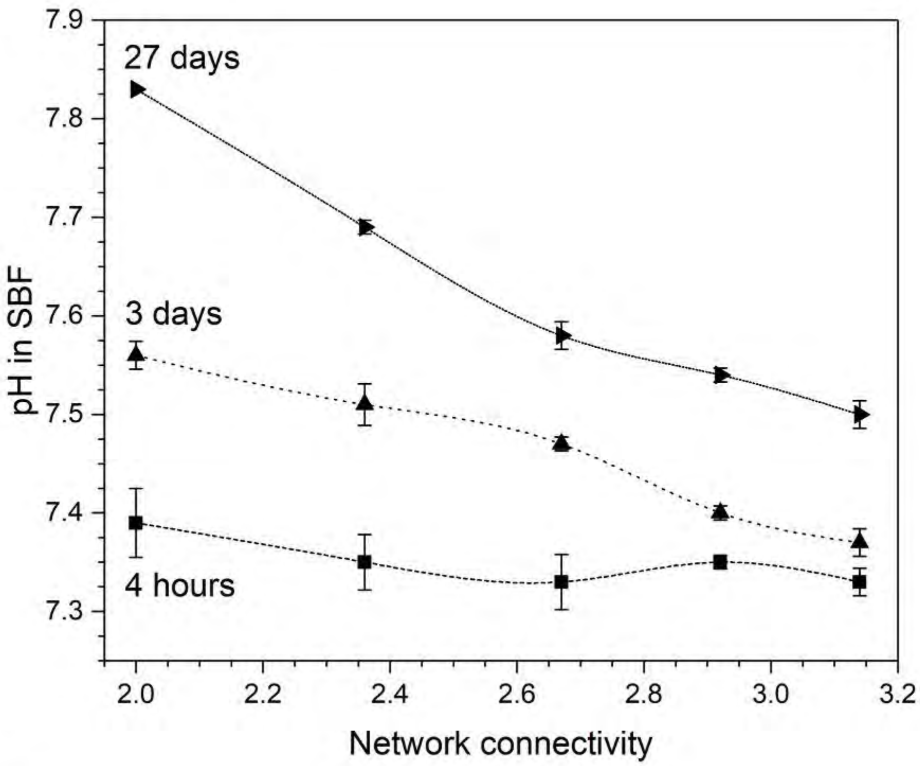
Reactions with Water





pH Changes in Solution

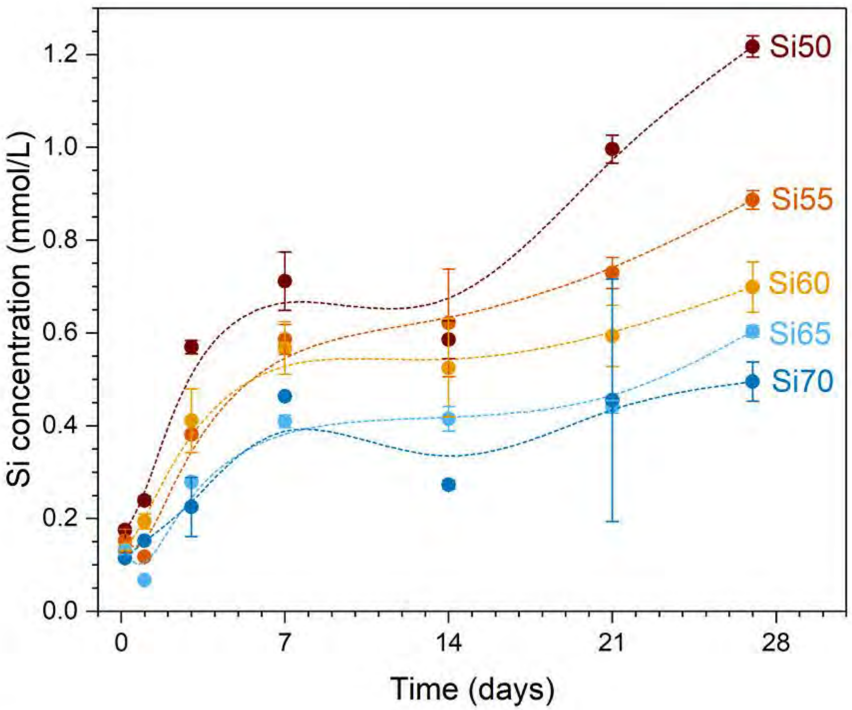


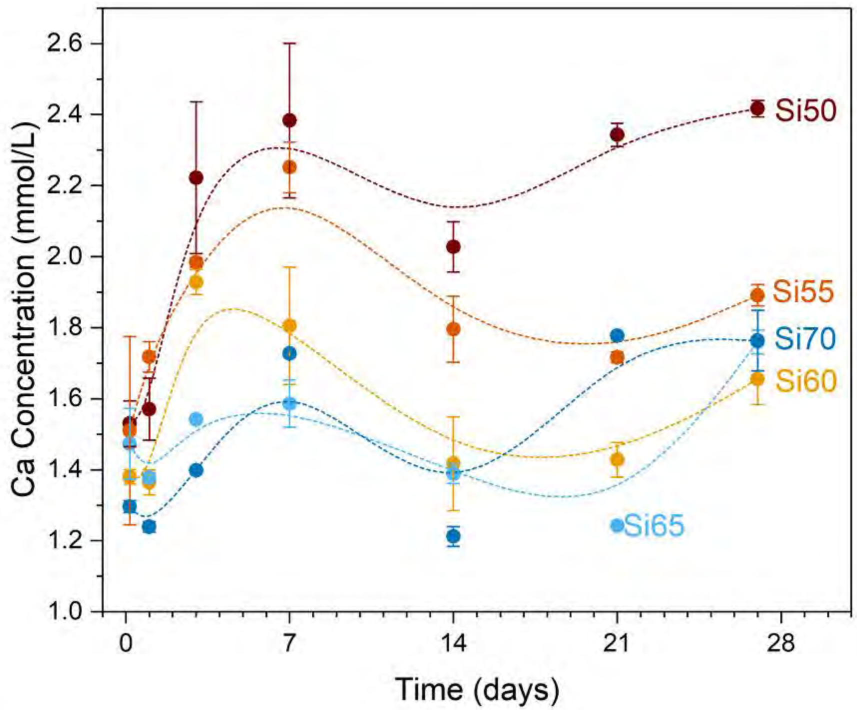


Immersion in simulated body fluid (pH 7.4, 37°C)

pH Changes in Solution

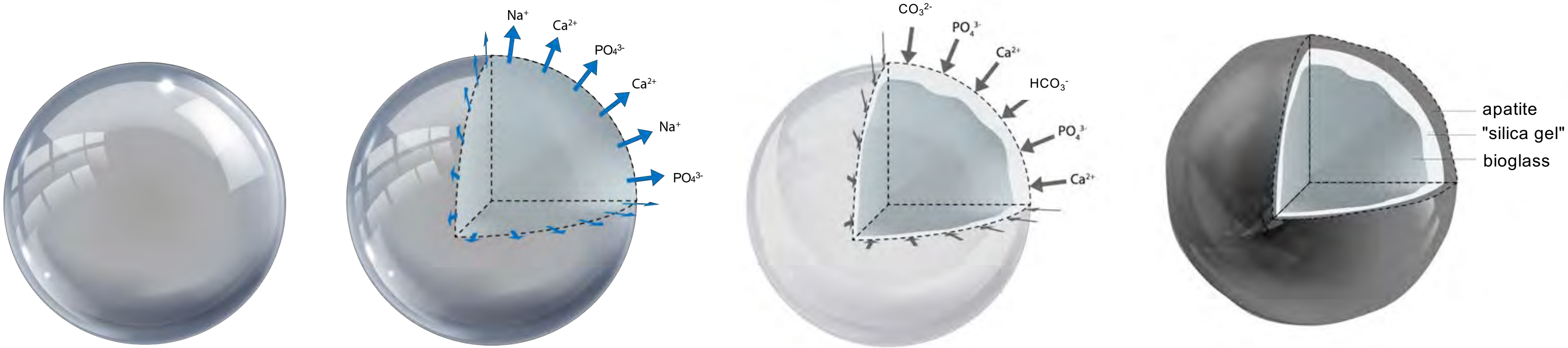
FRIEDRICH-SCHILLER-UNIVERSITÄT JENA



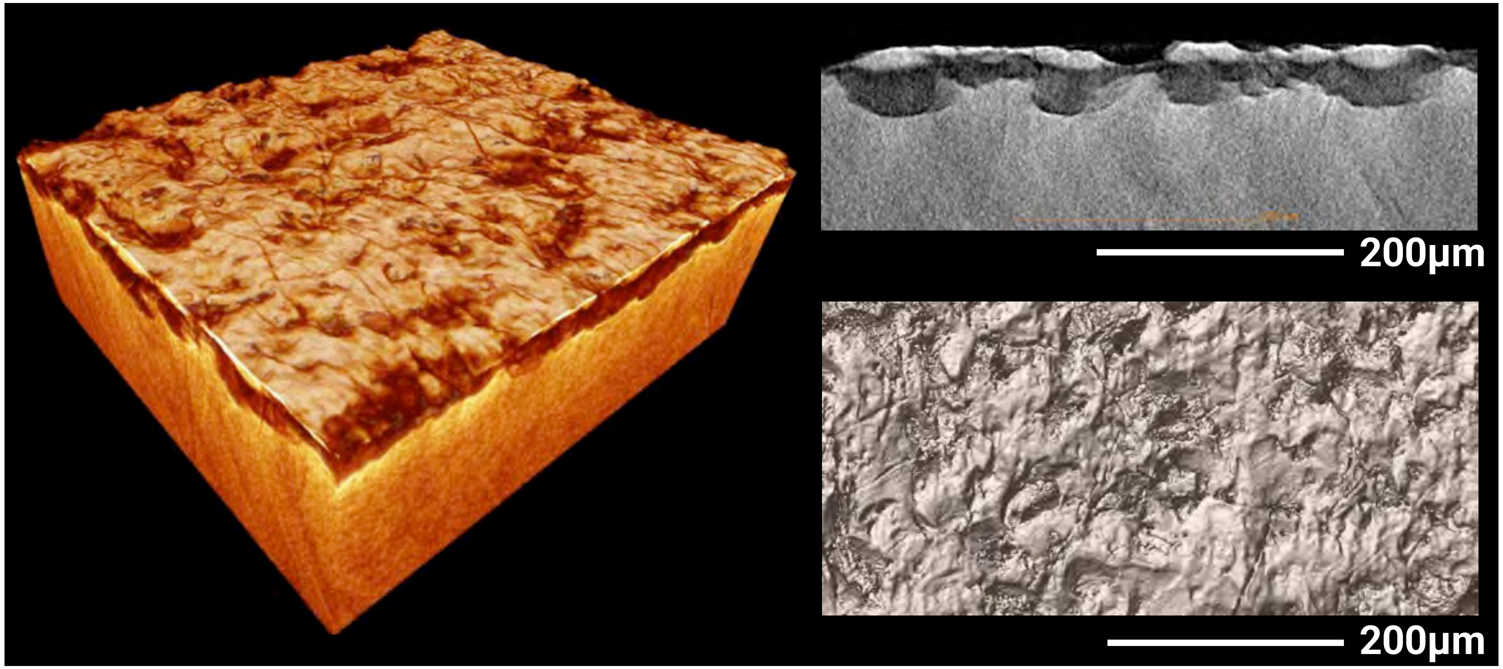


Immersion in simulated body fluid (pH 7.4, 37°C)

Reactions in Body Fluids



3D view

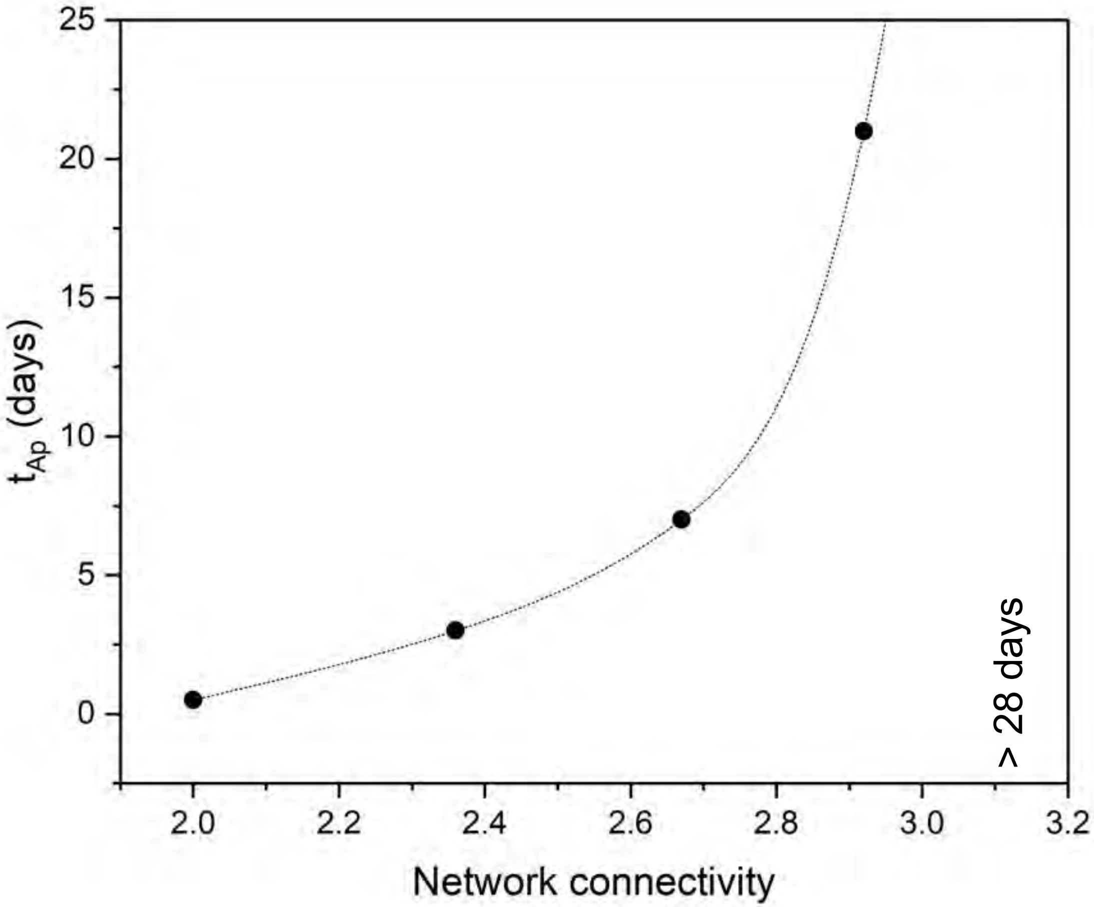


cross section

top view

Visualisation of surface layers formed on a bioactive glass by X-ray 3D microscopy

In Vitro Apatite Formation

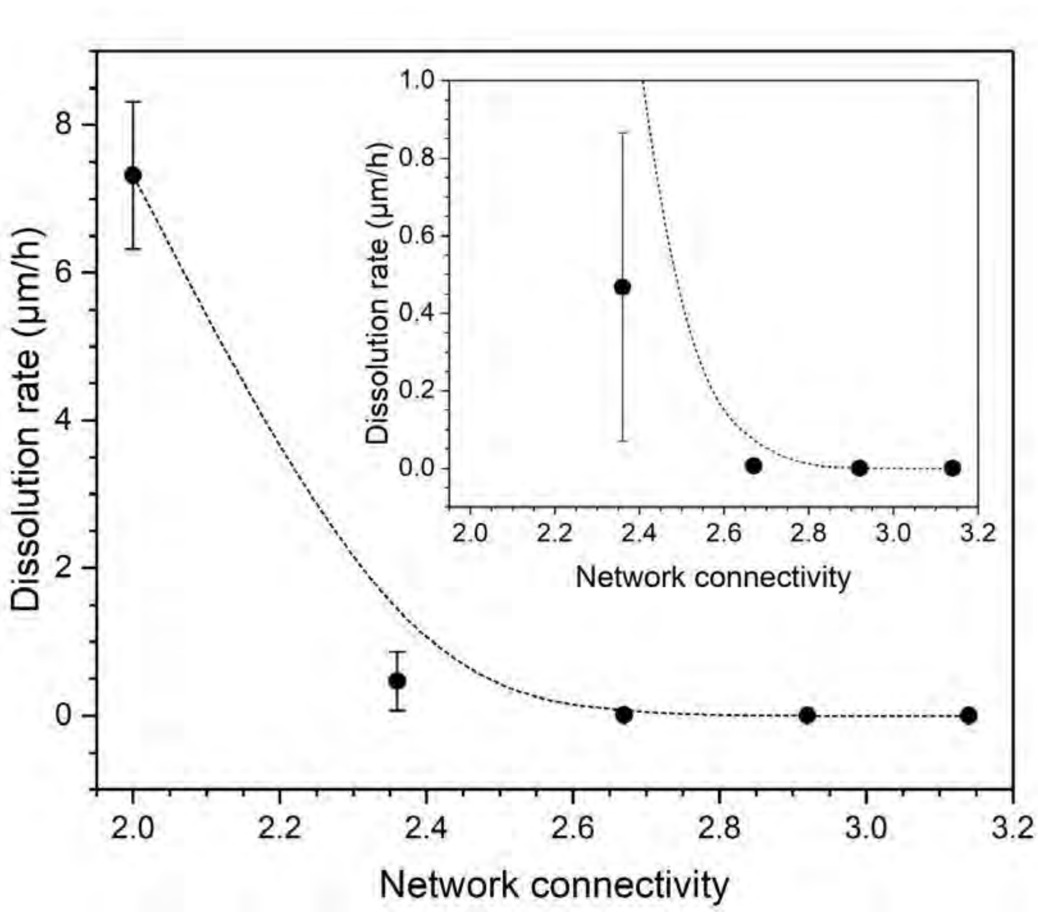


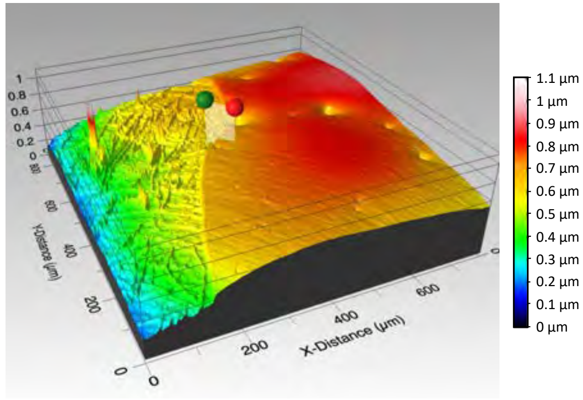
First time point of apatite detection during immersion in simulated body fluid

after: Fujibayashi et al., Biomaterials 24 (2003) 1349–1356

Dissolution under Dilute Conditions

FRIEDRICH-SCHILLER-UNIVERSITÄT JENA





Dissolution in Tris-HCl buffer solution (0.06M, pH 7.4, 37°C);
ASTM C1926: Measurement of glass dissolution rate using stirred dilute reactor conditions on monolithic samples

Soda-Lime Silicate Glass

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Biomaterials

ELSEVIER

Biomaterials 24 (2003) 1349–1356

www.elsevier.com/locate/biomaterials

A comparative study between in vivo bone ingrowth and in vitro apatite formation on Na_2O–CaO–SiO_2 glasses

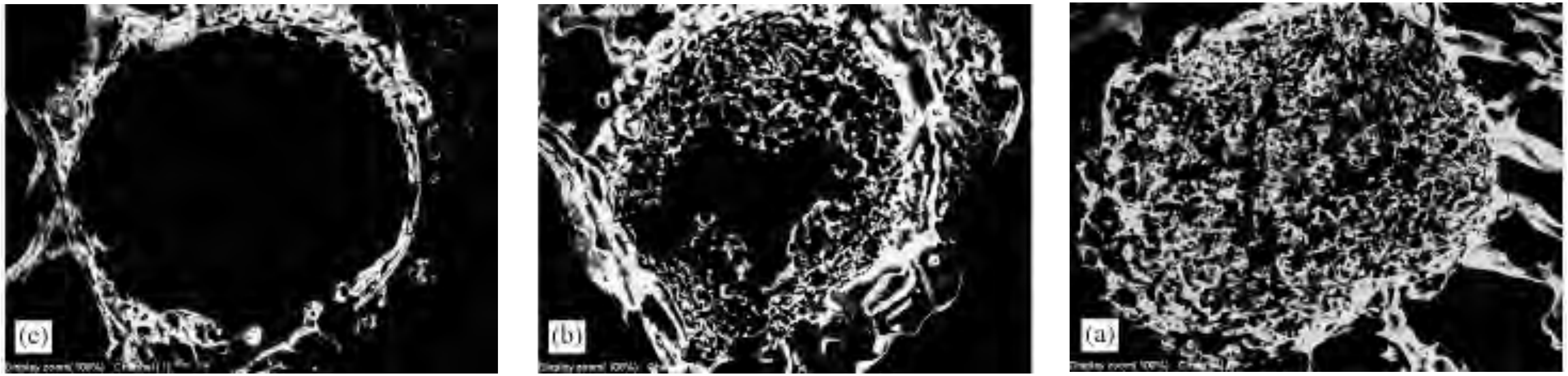
Shunsuke Fujibayashi[a,*], Masashi Neo[a], Hyun-Min Kim[b], Tadashi Kokubo[b], Takashi Nakamura[a]

[a] *Department of Orthopaedic Surgery, Graduate School of Medicine, Kyoto University, Kawahara-Cho 54, Sakyo-ku, Kyoto 6068507, Japan*

[b] *Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Japan*

Received 5 September 2002; accepted 15 October 2002

In Vivo Bone Formation

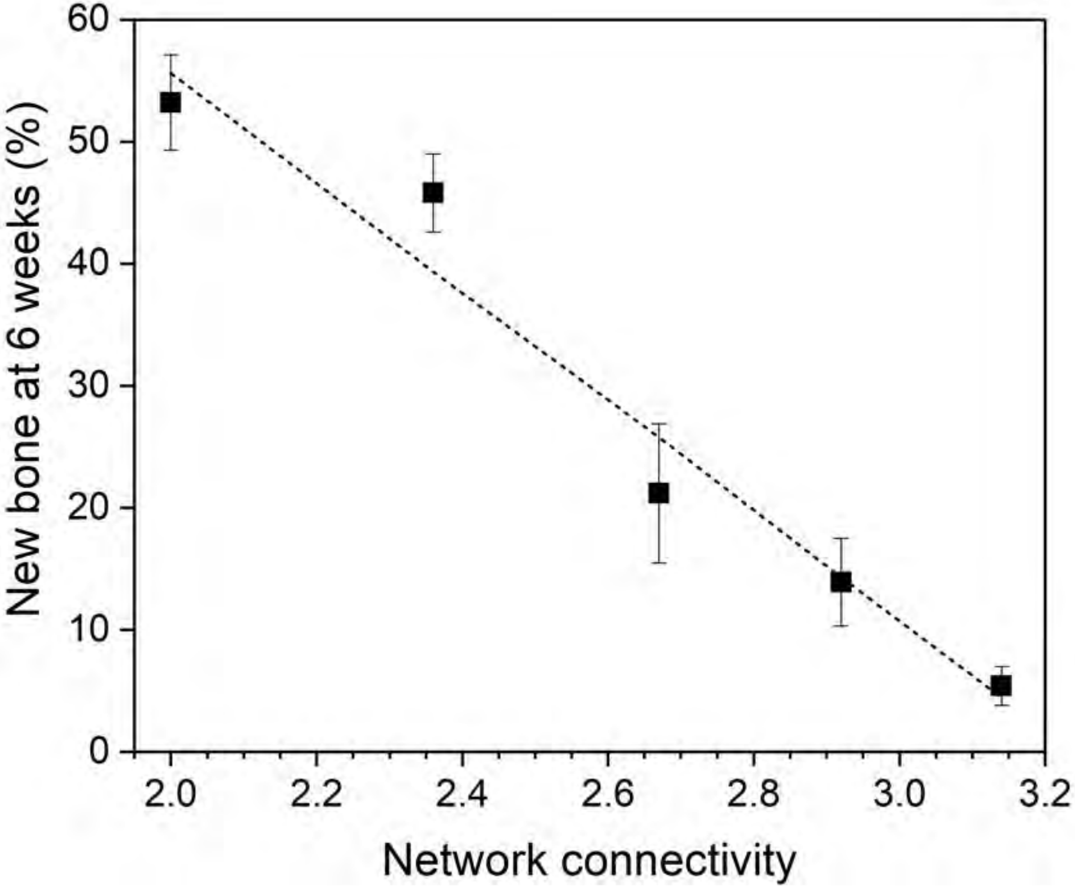


70mol% SiO_2	60mol% SiO_2	50mol% SiO_2
NC = 3.14	NC = 2.67	NC = 2.00

Granules of SiO_2-CaO-Na_2O glasses implanted into defect in the femur (thigh bone) of rabbits.
Fluorescent calcein staining; imaging by confocal laser scanning microscopy. Time: 6 weeks

Fujibayashi et al., Biomaterials 24 (2003) 1349–1356

In Vivo Bone Formation



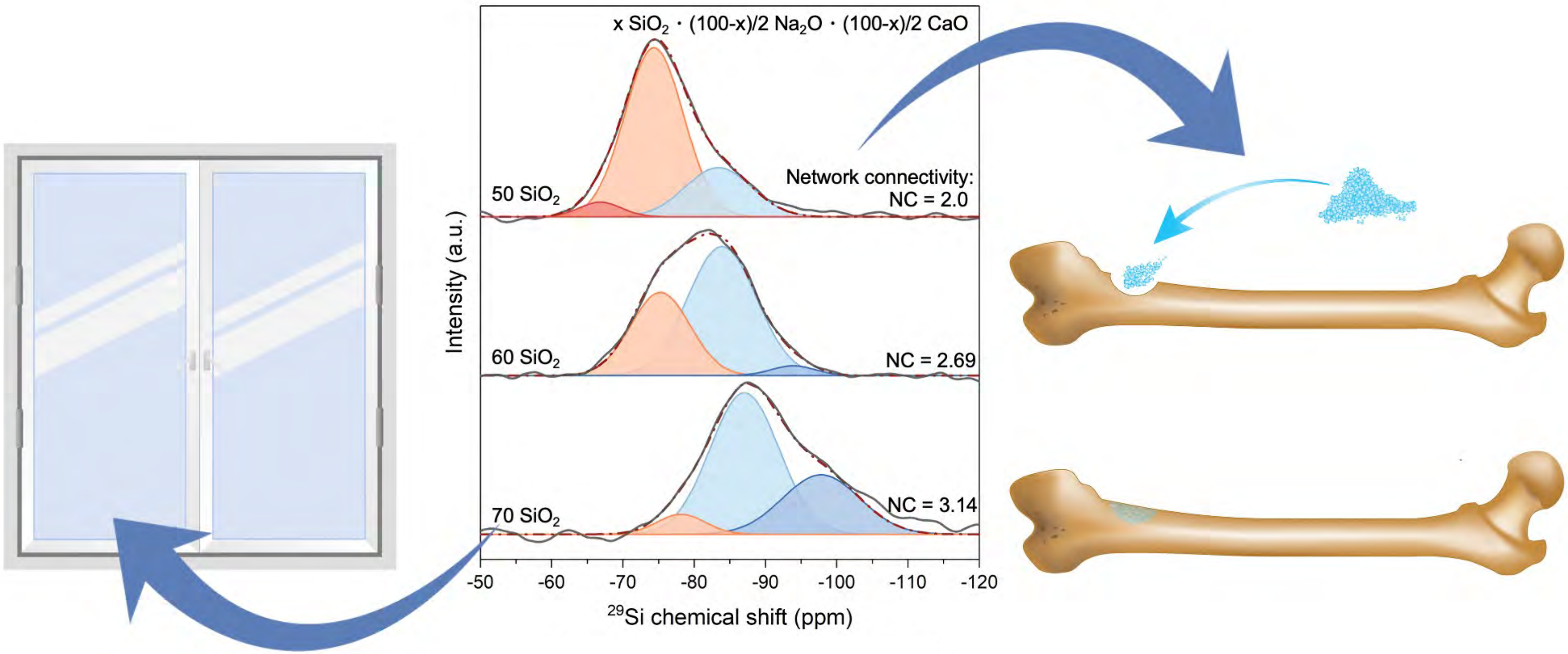
Newly formed bone after implantation of granules of SiO_2-CaO-Na_2O glasses into defect in the femur (thigh bone) of rabbits. Time: 6 weeks

after: Fujibayashi et al., Biomaterials 24 (2003) 1349–1356

Soda-Lime Silicate Glasses

…become bioactive

- if we reduce the silica content
- thereby reducing the silicate network polymerisation



Bioactive Glasses

Bioactive Glasses

Three very well-known compositions (in mol%)

Glass	SiO_2	P_2O_5	CaO	Na_2O	MgO	K_2O	NC
45S5 #	46.1	2.6	26.9	24.4	-	-	2.12
S53P4 $	53.9	1.7	21.8	22.6	-	-	2.54
13-93	54.6	1.7	22.1	6.0	7.7	7.9	2.59

45S5: Bioglass
$ S53P4: BonAlive

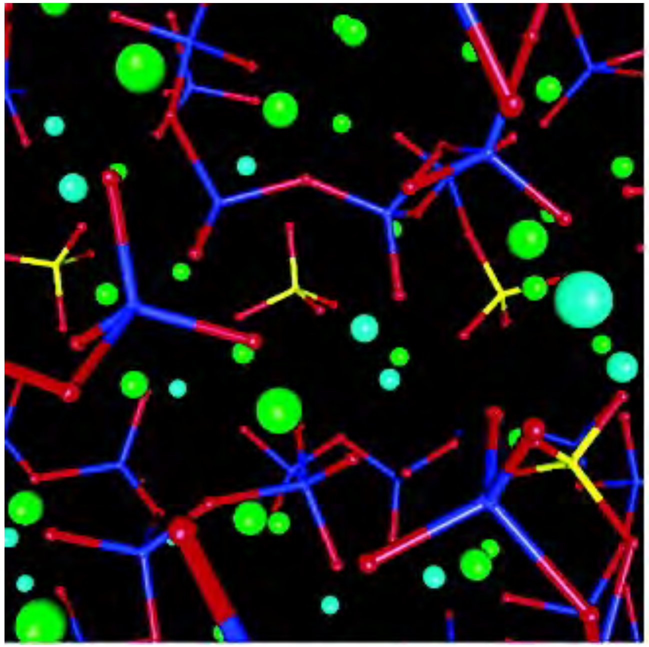
Network connectivity calculation:

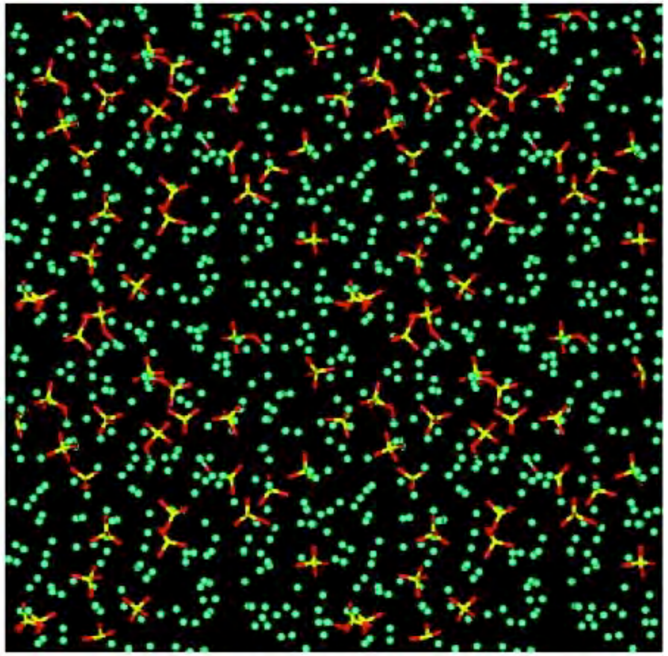
$$NC = \frac{4^* \, SiO_2 - 2^* \, (CaO+Na_2O+SrO+K_2O+\ldots) + 6^* \, P_2O_5}{SiO_2}$$

MD Simulations

Bioglass 45S5

46.14 SiO_2, 24.36 Na_2O, 26.93 CaO, 2.57 P_2O_5 (in mol%)



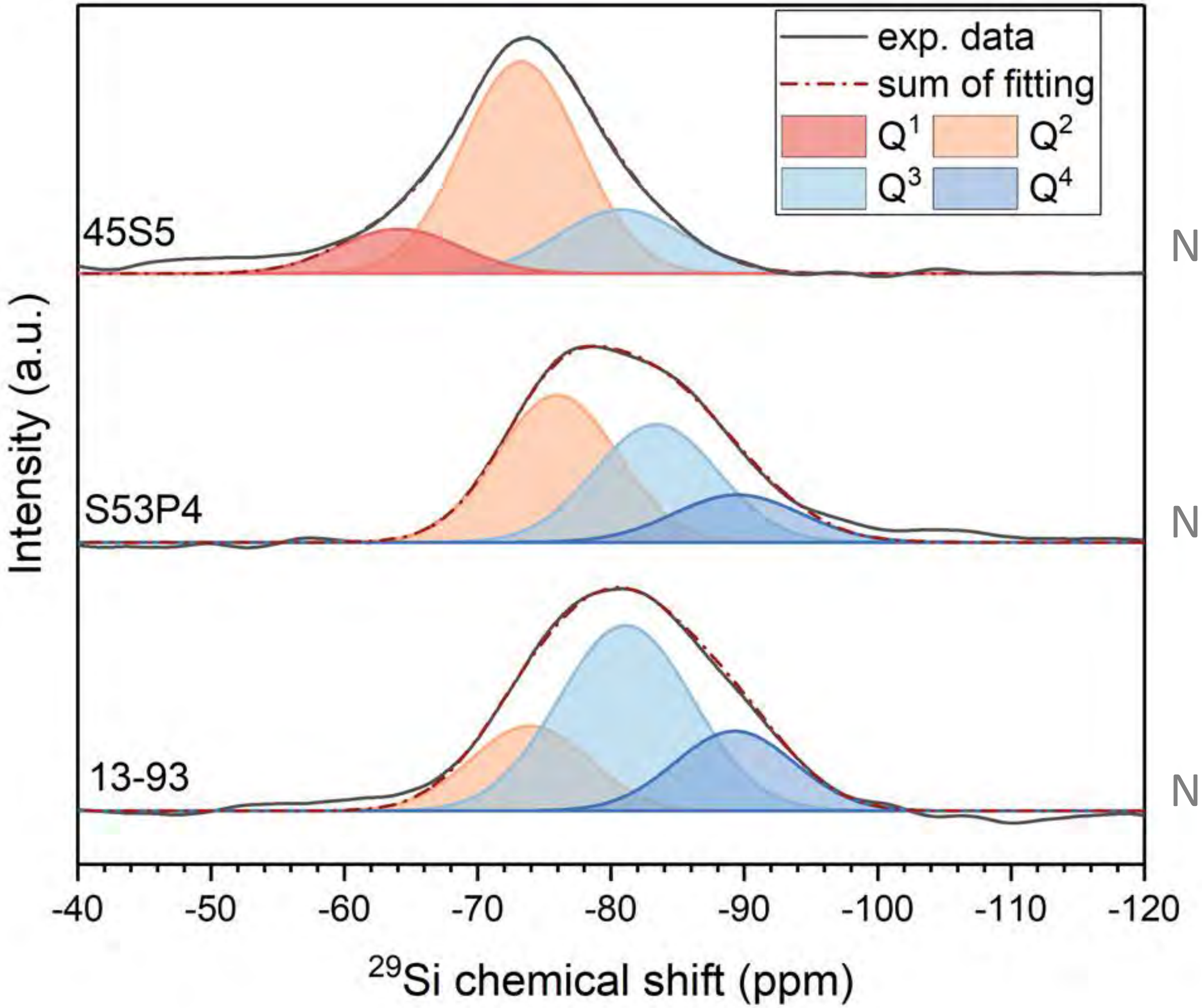


Tilocca et al., Chem. Mater. 19 (2007) 95-103

Tilocca & Cormack, J Phys Chem B 111 (2007) 14256-14264

Structure

Structural analysis:
solid-state
^{29}Si MAS NMR



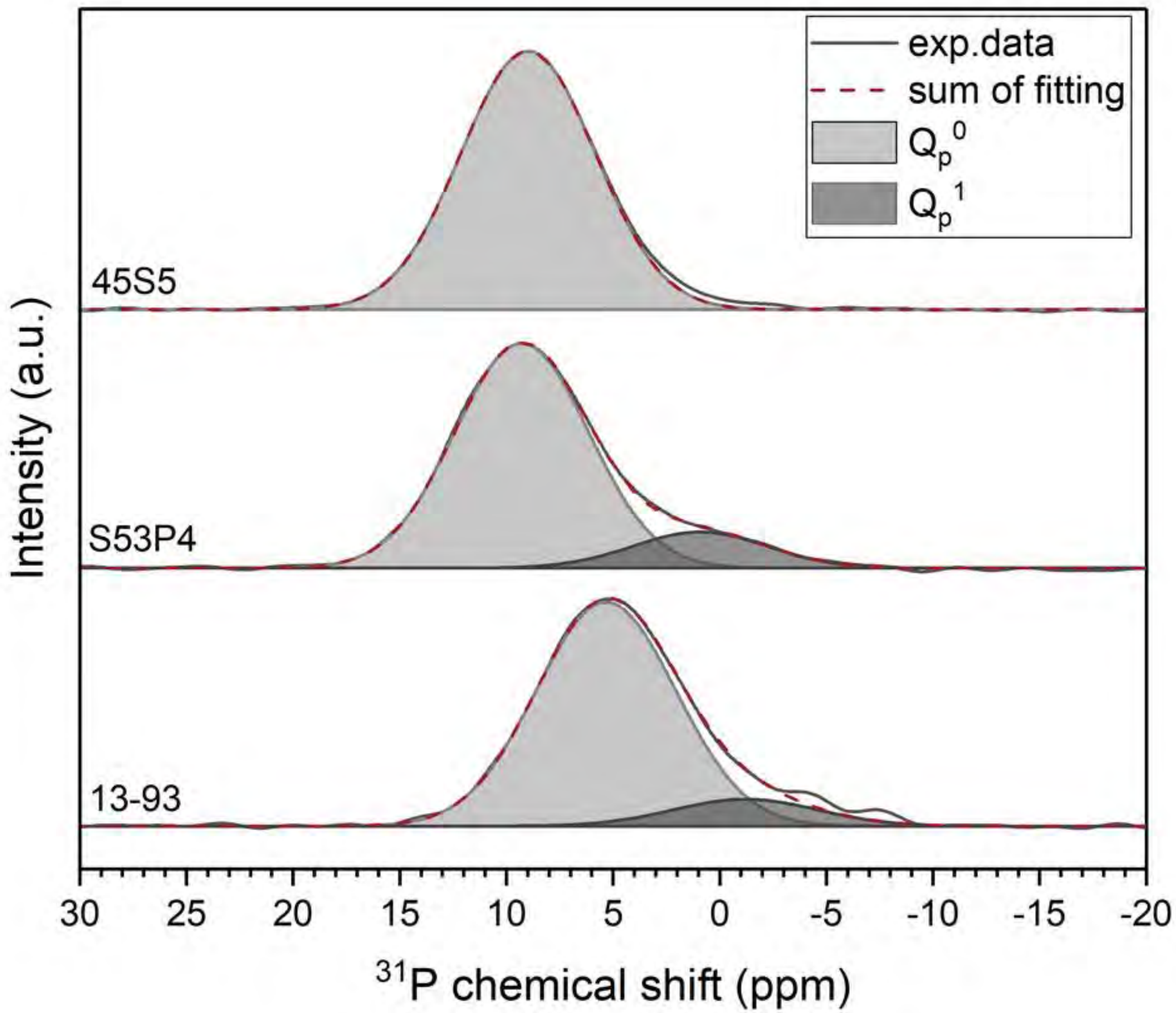
NC = 2.11

NC = 2.54

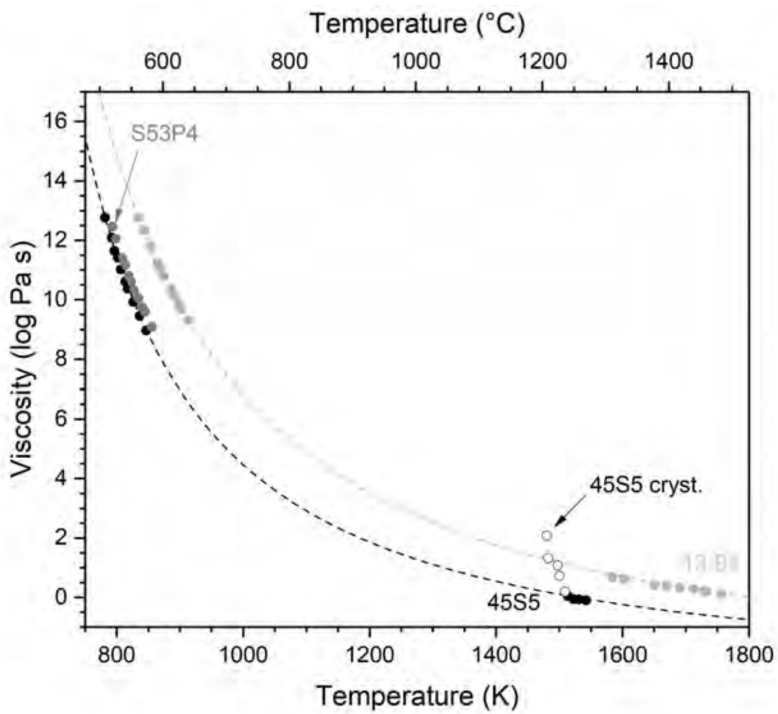
NC = 2.59

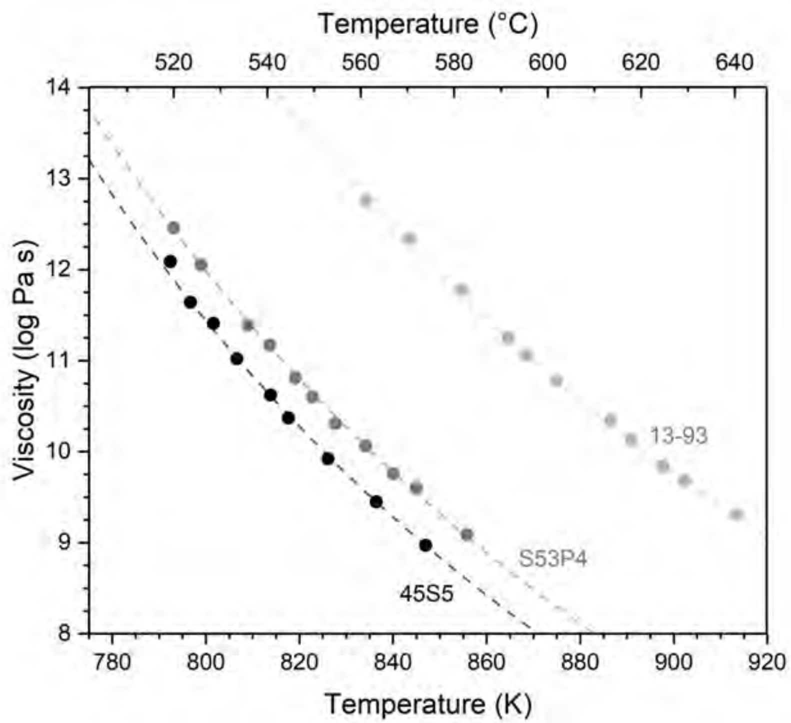
Structure

Structural analysis:
solid-state
^{31}P MAS NMR

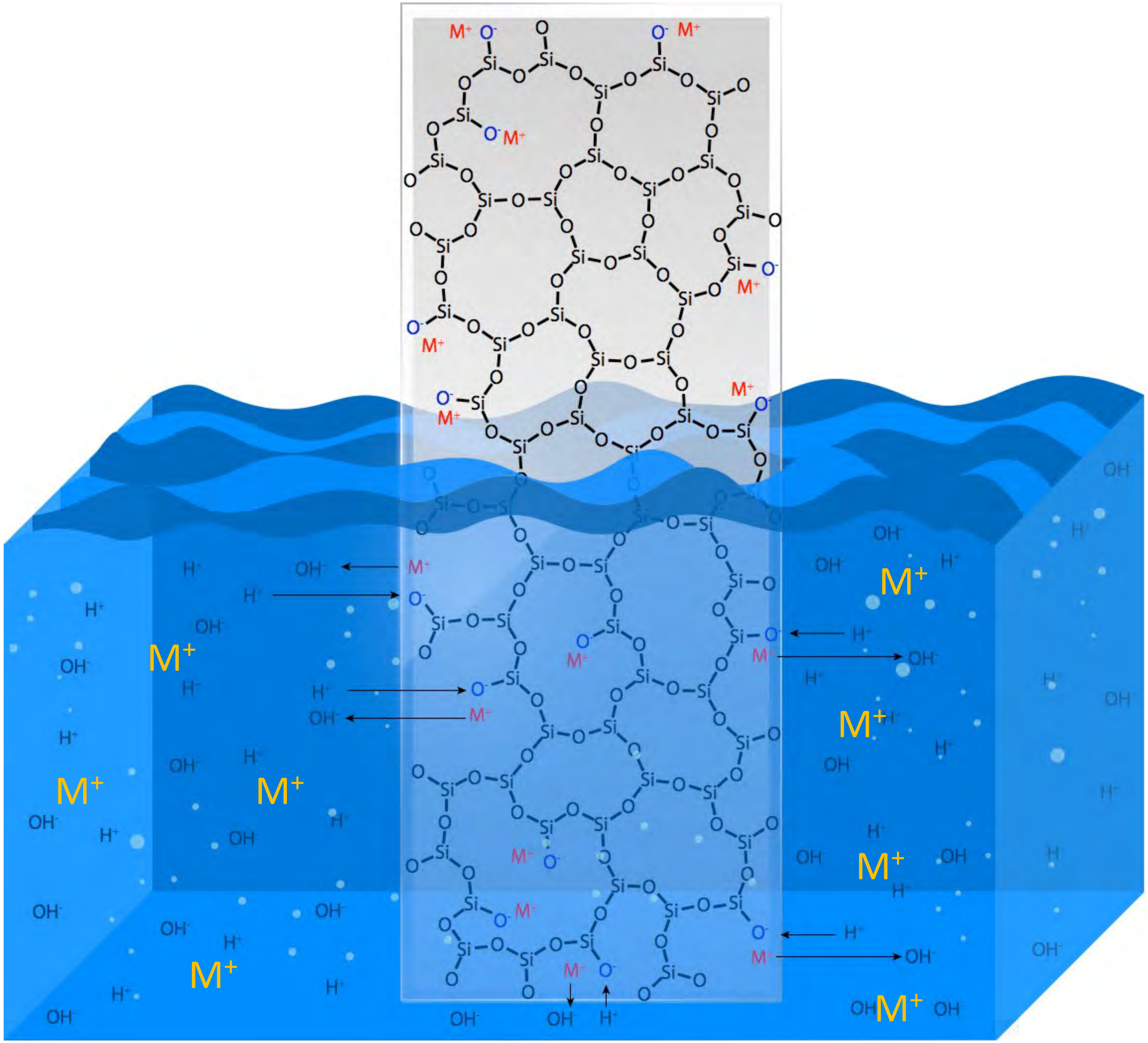


Viscosity


Temperature (°C)
600
800
1000
1200
1400
16
14
12
10
8
6
4
2
0
S53P4
45S5 cryst.
45S5
Viscosity (log Pa s)
800
1000
1200
1400
1600
1800
Temperature (K)

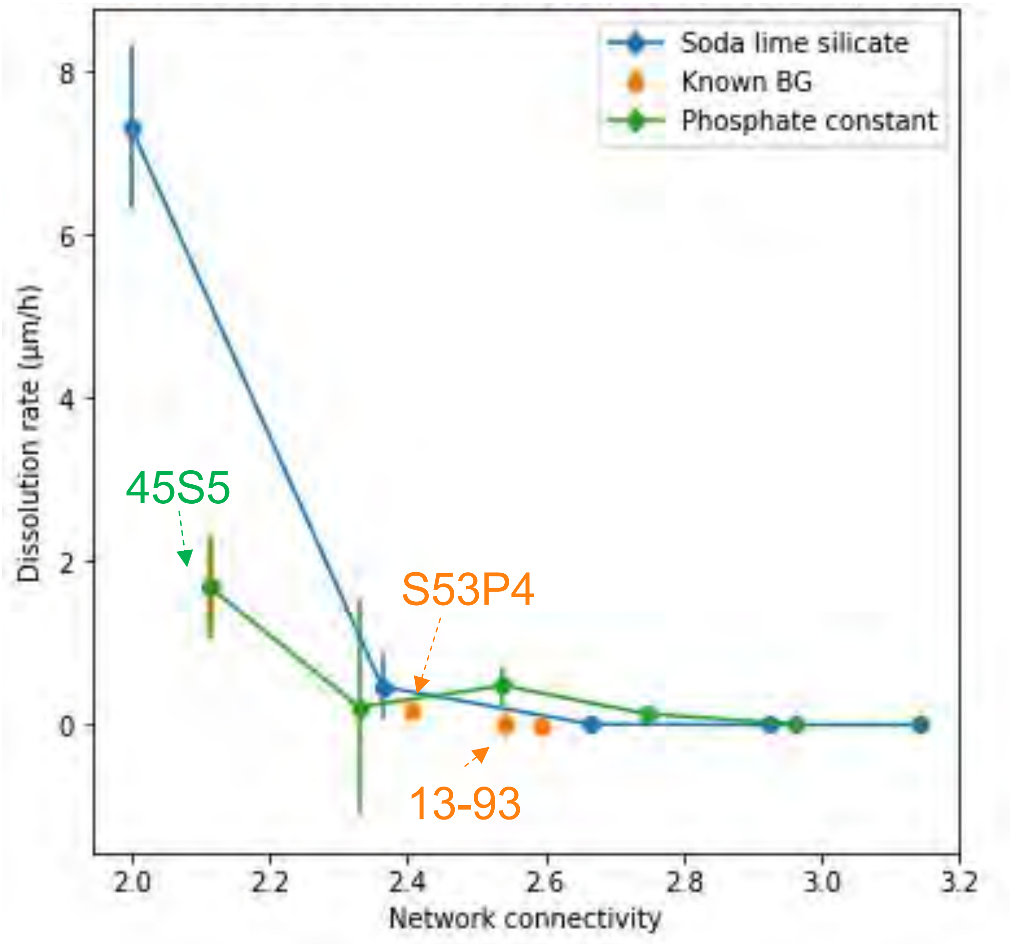

Temperature (°C)
520
540
560
580
600
620
640
14
13
12
11
10
9
8
13-93
S53P4
45S5
Viscosity (log Pa s)
780
800
820
840
860
880
900
920
Temperature (K)

Reactions with Water



Bioactive Glasses

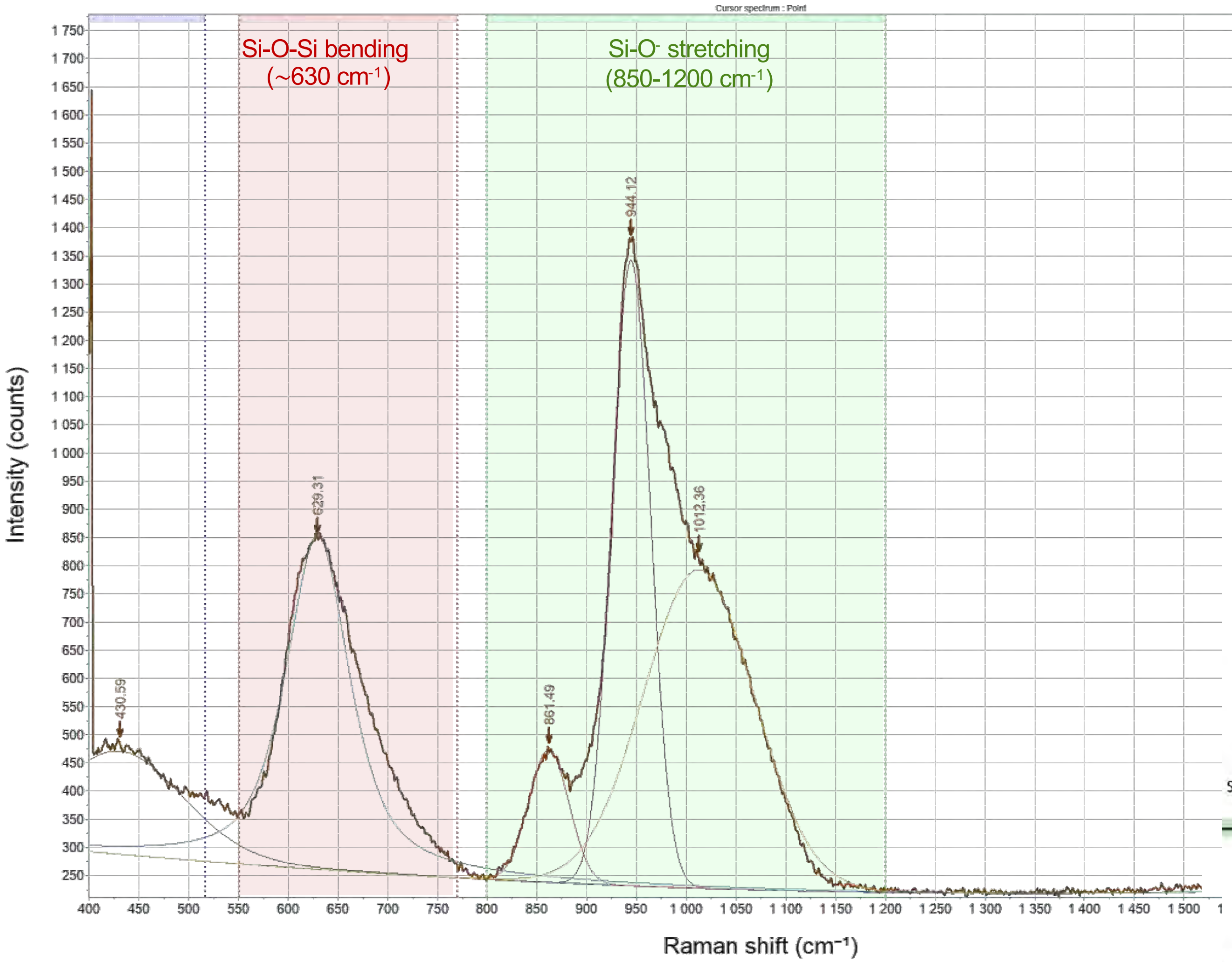
FRIEDRICH-SCHILLER-
UNIVERSITÄT
JENA

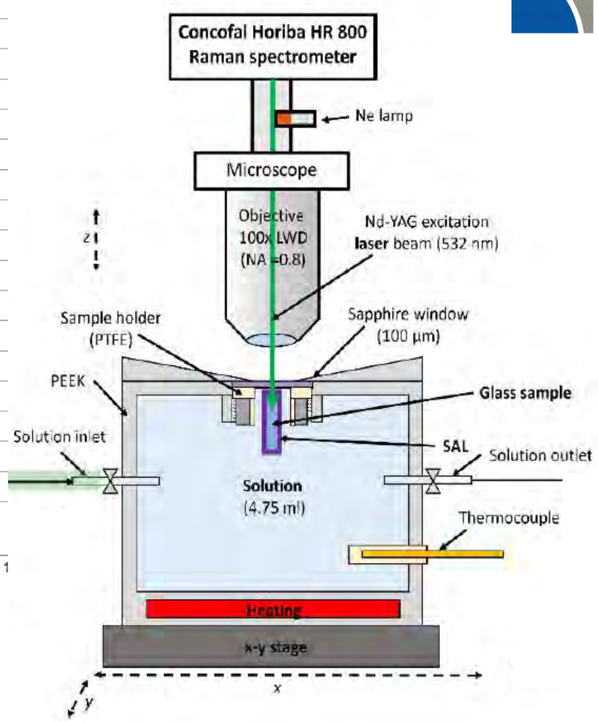


Dissolution rate as a function of network connectivity

Dissolution in Tris-HCl buffer solution (0.06M, pH 7.4, 37°C);
ASTM C1926: Measurement of glass dissolution rate using stirred dilute reactor conditions on monolithic samples

In situ Raman spectroscopy

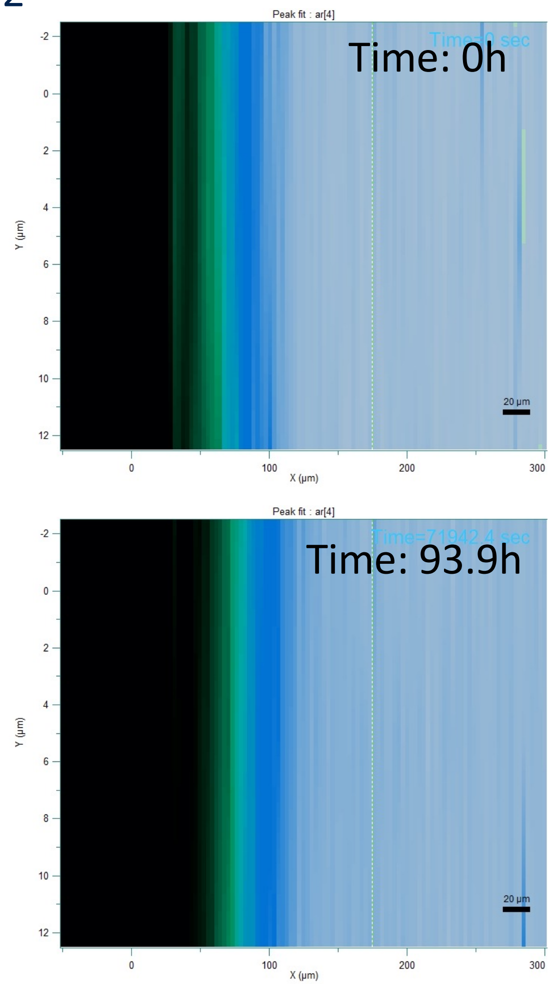


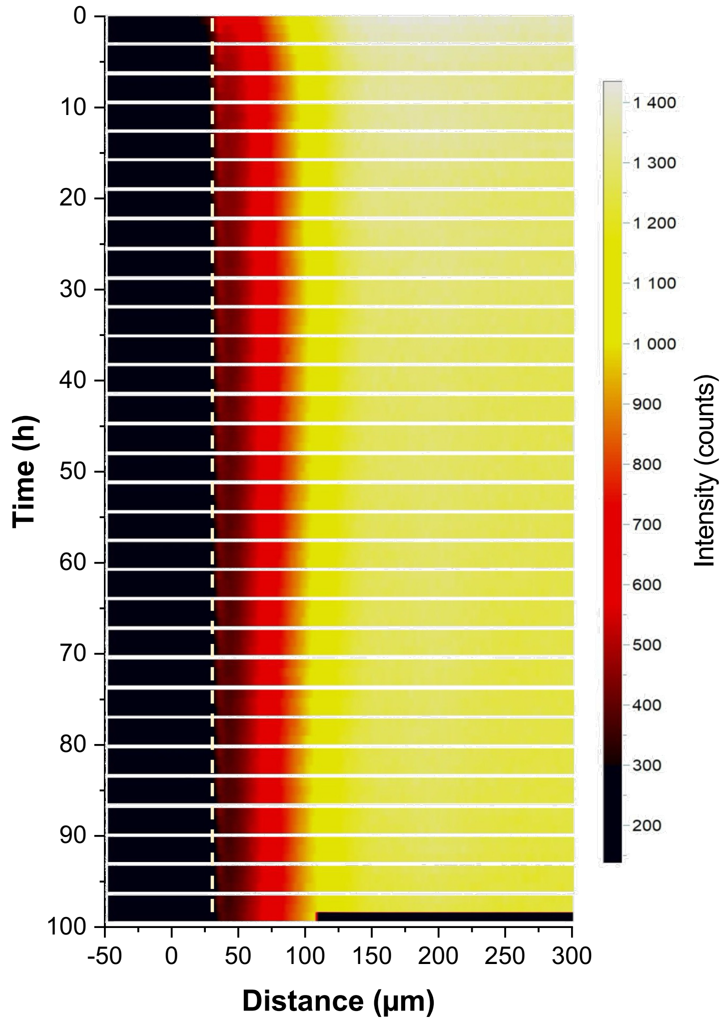


M. Fritzsche, PhD thesis, 2022, Universität Bonn

In situ Raman spectroscopy

Bioglass 45S5
in DI H_2O

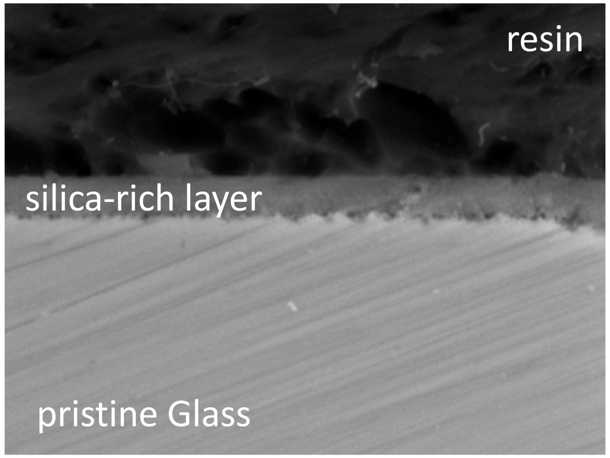




In situ Raman spectroscopy

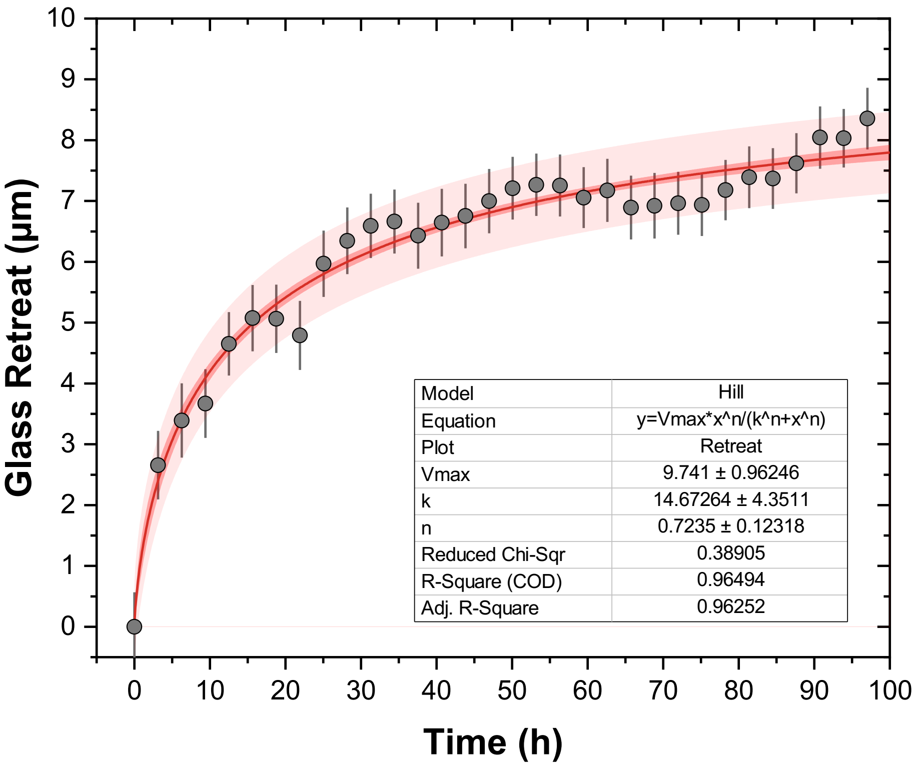
FRIEDRICH-SCHILLER-UNIVERSITÄT JENA

Bioglass 45S5
in DI H_2O

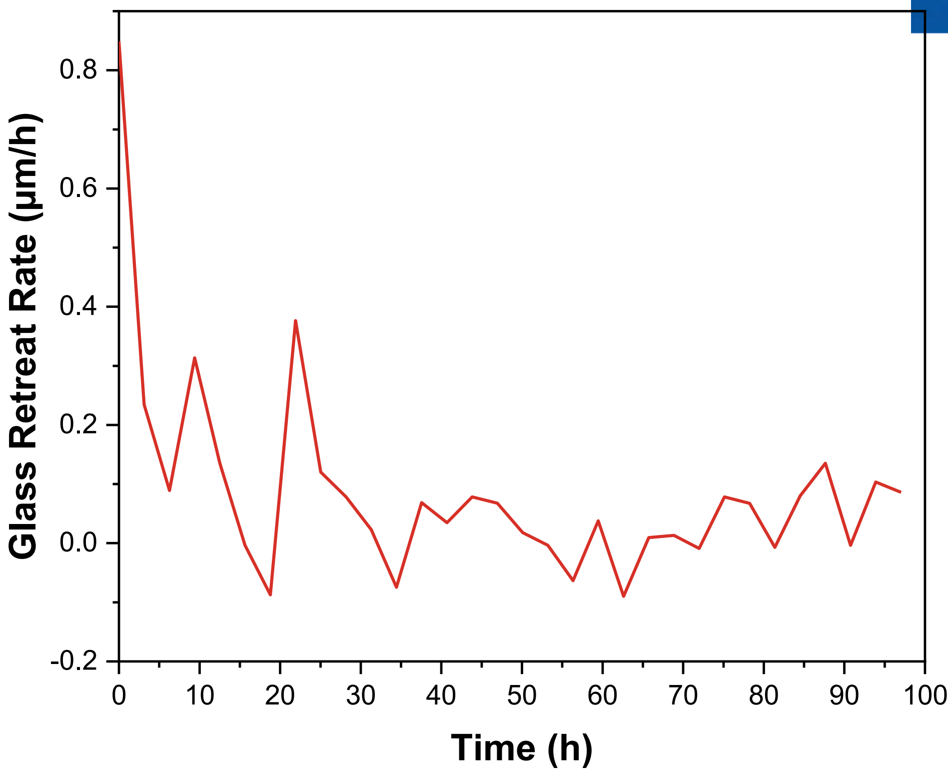


SEM @ about 3 weeks

UNIVERSITÄT BONN



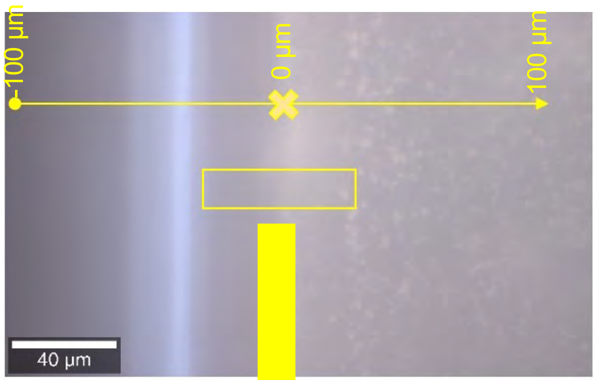
Model	Hill
Equation	y=Vmax*x^n/(k^n+x^n)
Plot	Retreat
Vmax	9.741 ± 0.96246
k	14.67264 ± 4.3511
n	0.7235 ± 0.12318
Reduced Chi-Sqr	0.38905
R-Square (COD)	0.96494
Adj. R-Square	0.96252

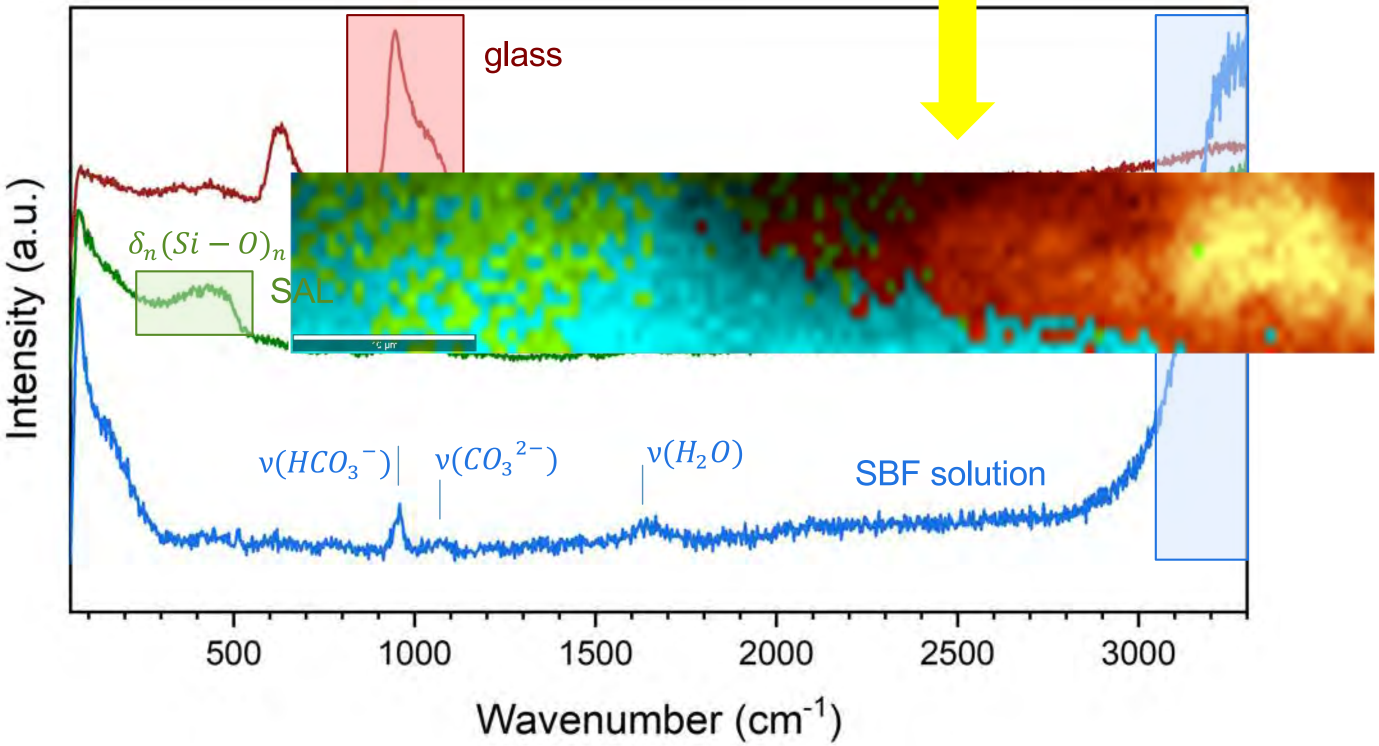


In situ Raman spectroscopy

FRIEDRICH-SCHILLER-UNIVERSITÄT JENA

in simulated body fluid
at 7 days,
preliminary study



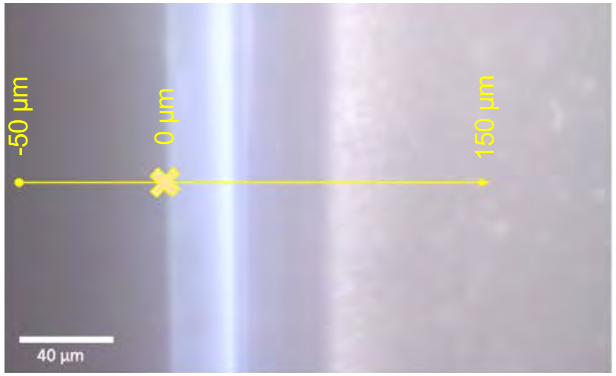


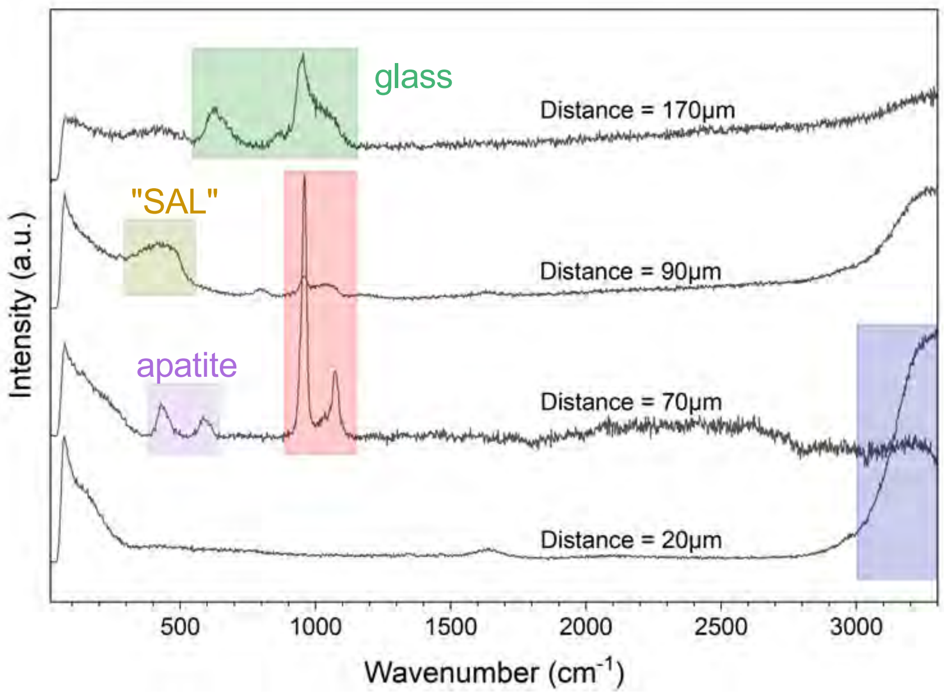
glass
SAL
SBF solution

scan: 60 µm x 10 µm

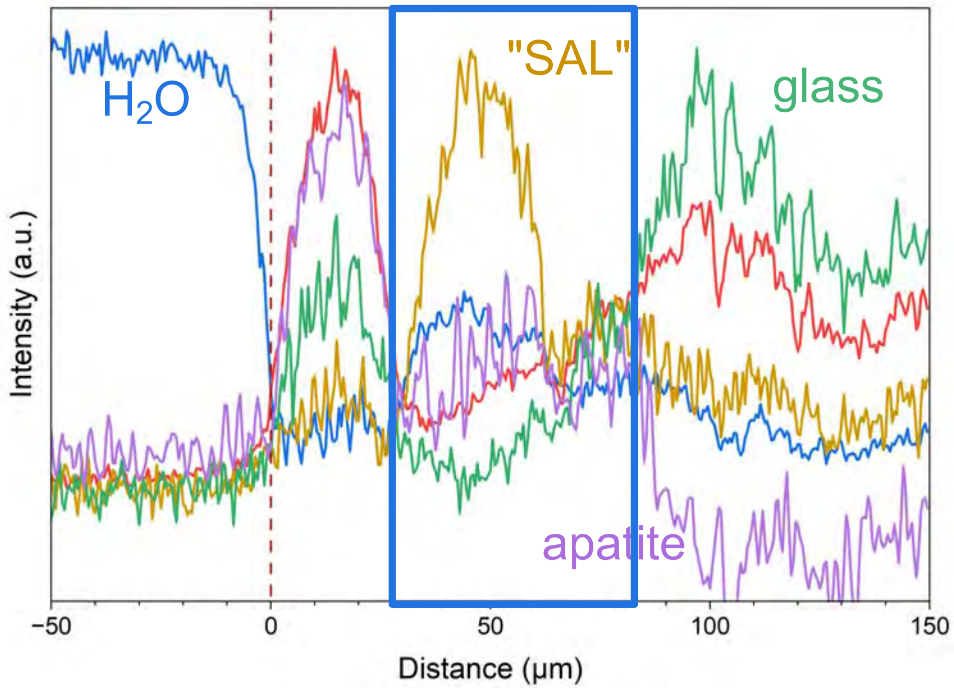
In situ Raman spectroscopy

in simulated body fluid
at 21 days,
preliminary study





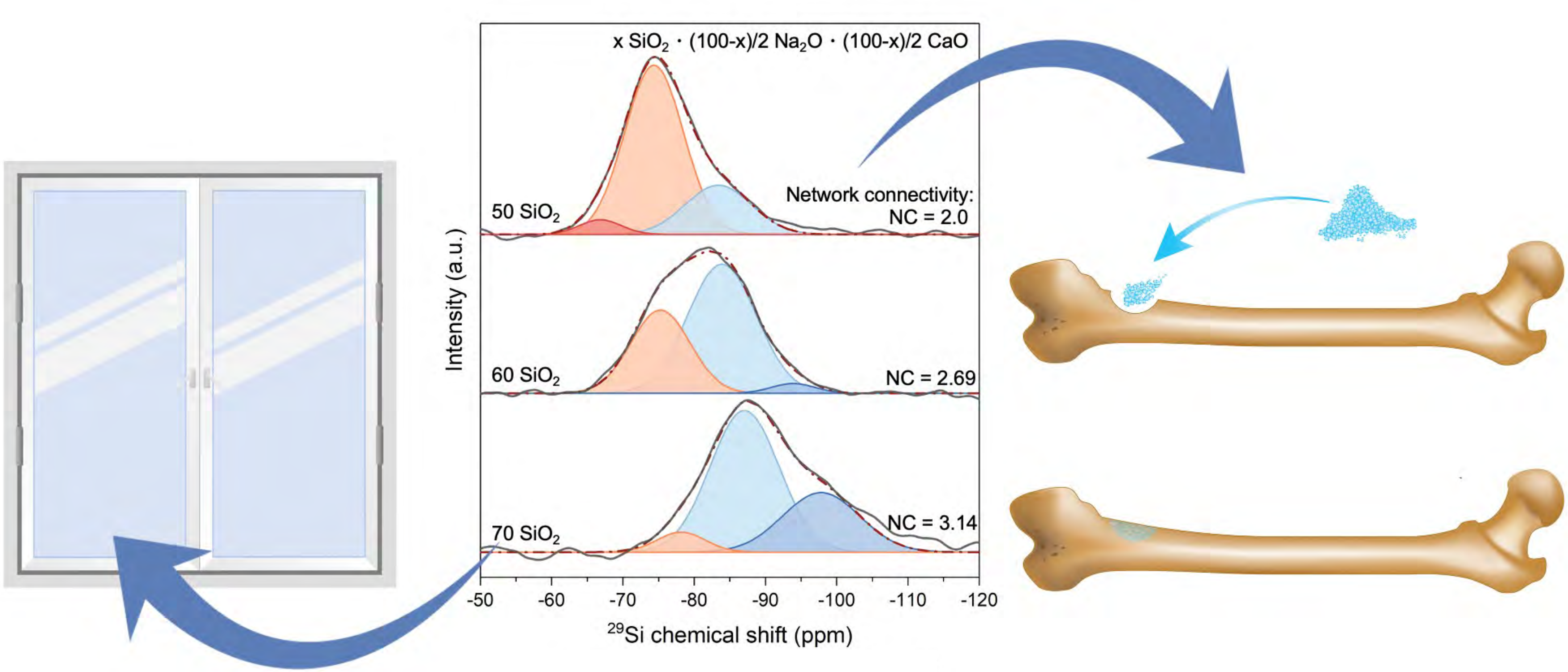
Raman spectra at various positions



Intensity of selected signal over distance

Conclusions

- Bioactive glasses are "special" in their application
- Structure & property-wise, they are soda-lime silicate glasses with low silicate content
- Inclusion of phosphate helps to adjust certain properties but does not change them fundamentally



Jena & Glass

Otto Schott

FRIEDRICH-SCHILLER-UNIVERSITÄT JENA

Ernst Abbe

FRIEDRICH-SCHILLER-UNIVERSITÄT JENA

Carl Zeiss

Carl & Delia

A big THANK YOU to:

…you for your attention

Daniel Neuville, Scott Kroeker, Jincheng Du, Stéphane Gin, Thorsten Geisler-Wierwille, Andrea de Camargo, Britt Wildemann, Georg Matziolis, Victoria Horbert, Juliana Martíns-Schalinski, Bettina Löffler, John McCloy, Leena Hupa, Leo van Wüllen, Hana Kaňková, Izabela Radecka, Diana Horkavcová, Aldo Boccaccini, Toshihiro Kasuga, Jérémy Soulié, Thorsten Schäfer,…

Carl Zeiss Stiftung

materials microbes microenvironments

DFG

DAAD Deutscher Akademischer Austausch Dienst German Academic Exchange Service

Japan Society for the Promotion of Science · Founded 1932 ·