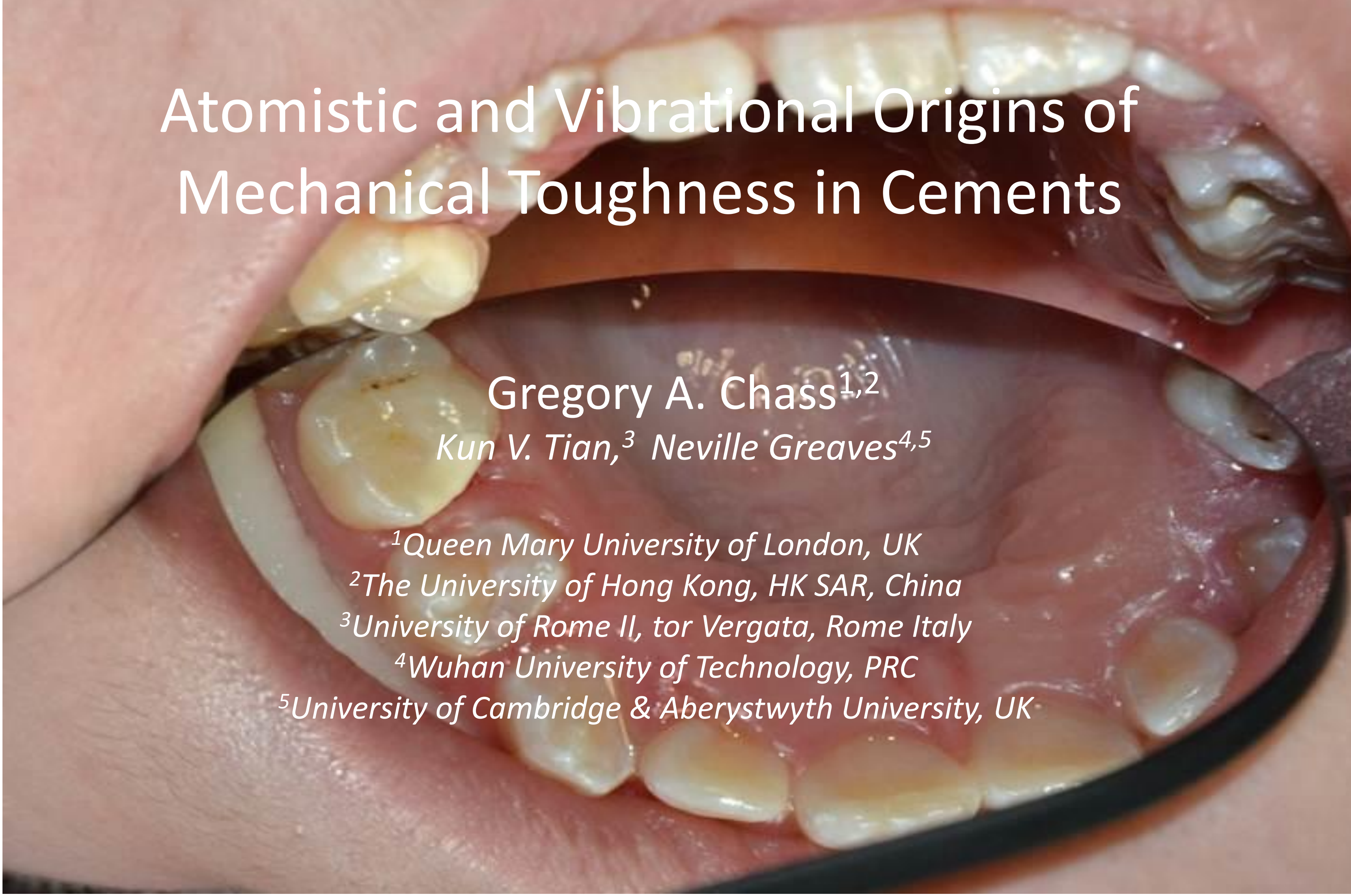


Atomistic and Vibrational Origins of Mechanical Toughness in Cements

Gregory A. Chass[1,2]

Kun V. Tian,[3] Neville Greaves[4,5]

[1]Queen Mary University of London, UK
[2]The University of Hong Kong, HK SAR, China
[3]University of Rome II, tor Vergata, Rome Italy
[4]Wuhan University of Technology, PRC
[5]University of Cambridge & Aberystwyth University, UK

Overview

- Motivations & Project Background
- Results - Cementation Profiles
- Impact & Transferability
- Summary & Conclusions

Motivations

Personal Motivations

田坤
Tian Kun ‘TK’
(Clinical Dentist)

Neville Greaves (Glass Physicist)

Project Motivations

Cementation and ductility

Tradition and Health

Growing need for Non-specialists in facilities science

REF-2014 & REF-2022 Motivations

<u>ENGINEERING AN IMPACT CASE</u>

- Embettering lives
- Transforming industry
- Functional Research

Tarjan Glass Company HU, (1893)

Background

Optimising Tooth & Bone Replacements

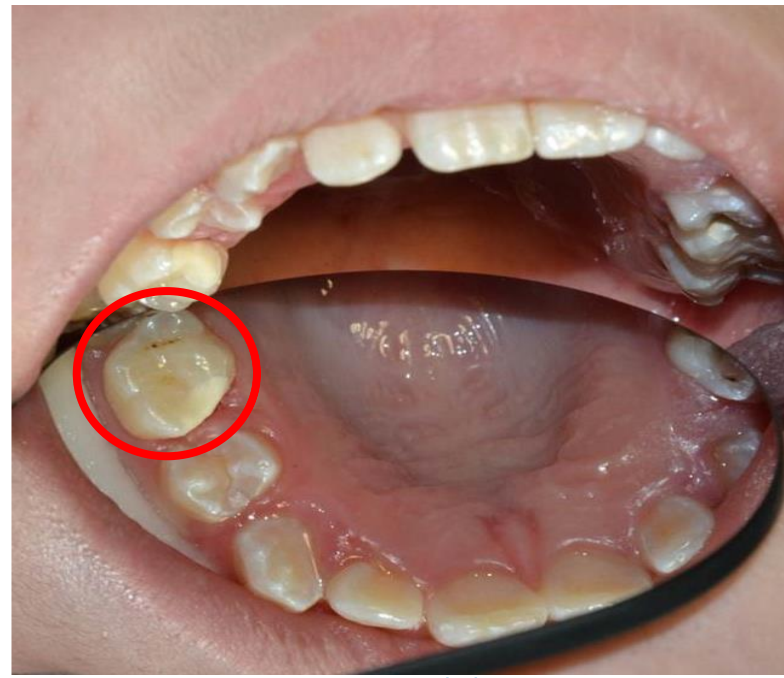
~1g / filling
= 125 T / yr

Toxicity of dental materials

125 million amalgam fillings carried out annually in Europe
GICs are the least toxic over time

mercury amalgam
release Hg

resin composite
release methacrylate



<u>no toxicity</u>
glass ionomer cement (GIC)

Wilson, A. D. & Kent, B. E. A new translucent cement for dentistry. The glass ionomer cement. *Br. Dent. J.* 15, 133–135 (1972).

<u>EU Commission report</u>:

• GIC material of choice to replace Hg-amalgams

• Richest countries using Hg the most (established industry)

• Restricted use due to resistance & lacking knowledge

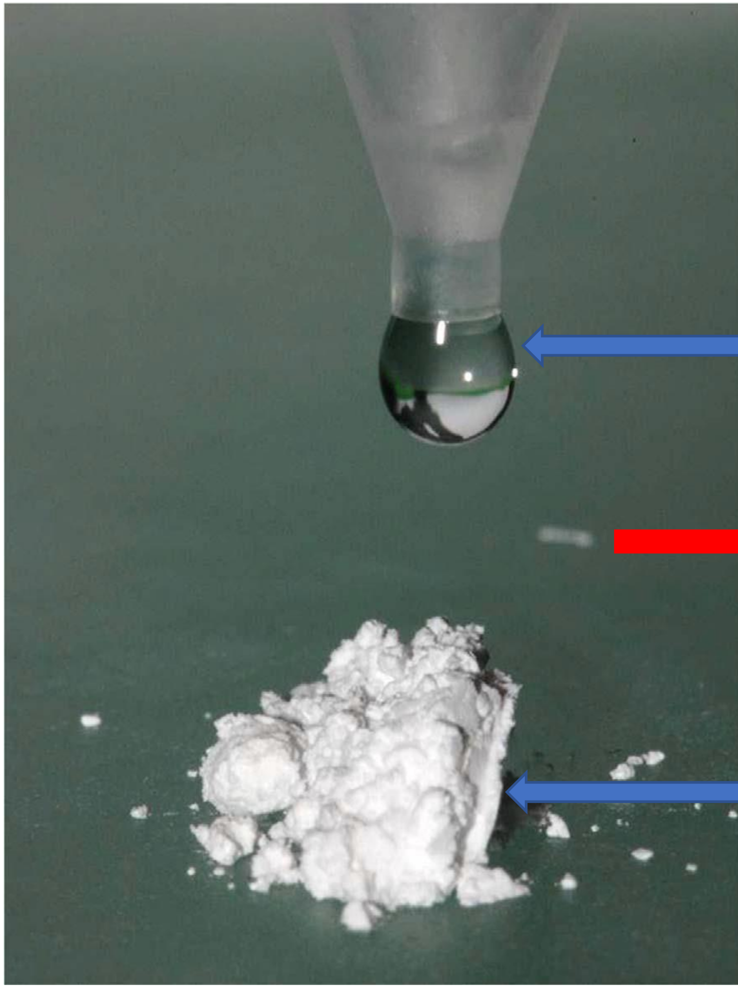
• Growth of R&D market size to top 5b €/yr by 2025


Study on the potential for reducing mercury pollution from dental amalgam and batteries

Final report

European Commission – DG ENV
11 July 2012

Glass Ionomer Cements (GICs)



Chemistry of GICs

develops at the ‘hybrid’ interface between glass particles and polymer

40% aqueous solution of poly(acrylic) acid (PAA)

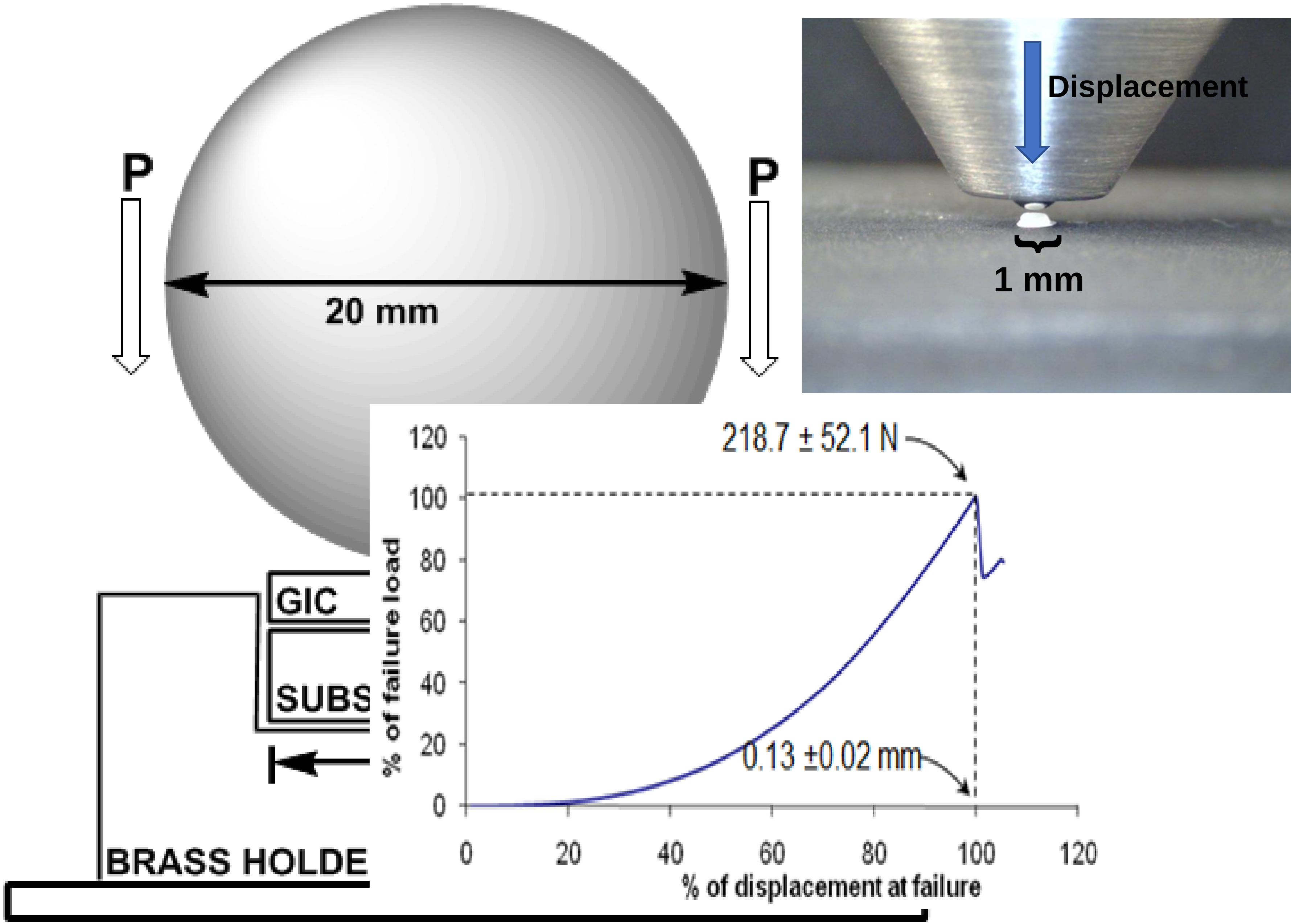
- gel formation at glass surface
- release of Ca^{2+} and Al^{3+} from the glass
- polyacrylic acid molecules crosslink chelating with Al^{3+}
- polyalkenoate salt gelation promotes further reaction

(glass polyalkenoate cements)

sodium-calcium- phosphor-fluoro-alumino-silicate glass

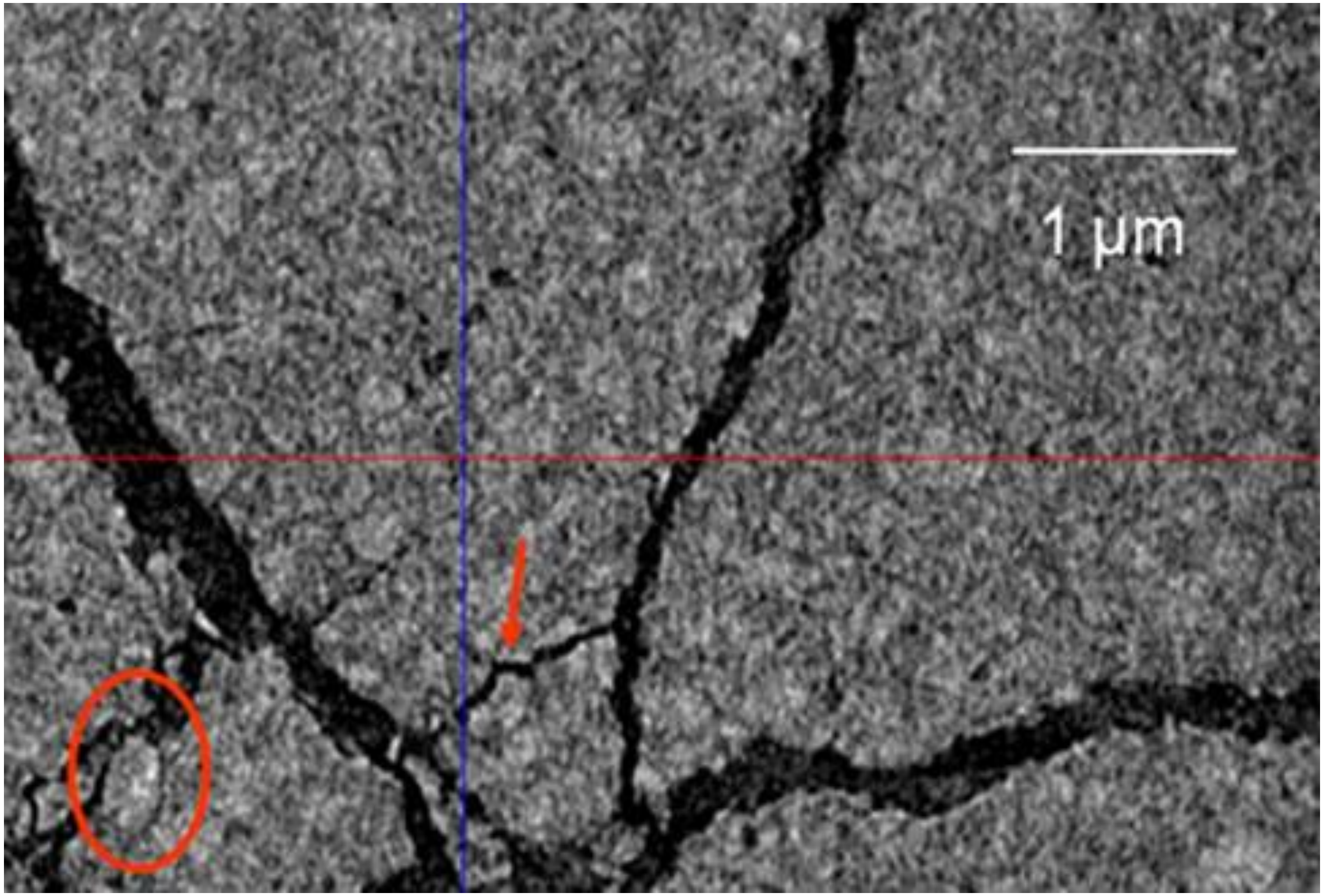
$Na_{6.3}Ca_{6.6}P_{6.2}Al_{16.9}Si_{11.8}O_{32.5}F_{\cancel{19.7}}$

The Problem - Brittlenss



Microcracking in GICs along glass-polymer interface

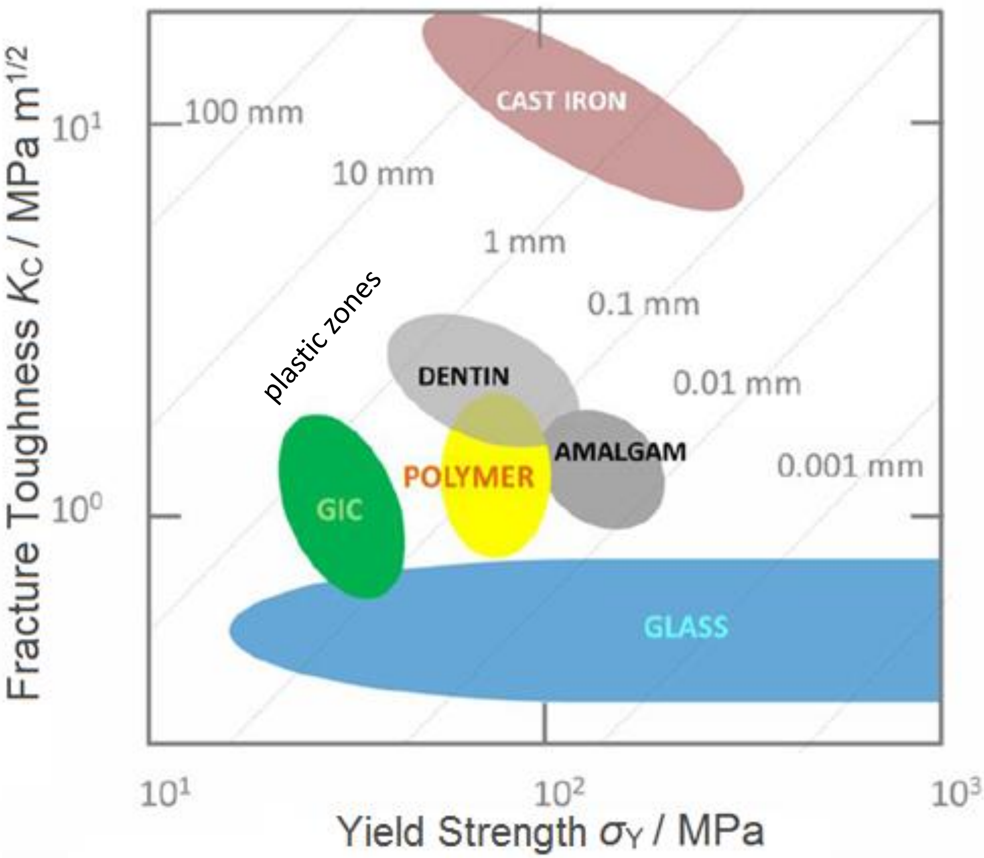
X-ray Microtomography, following Hertzian indentation

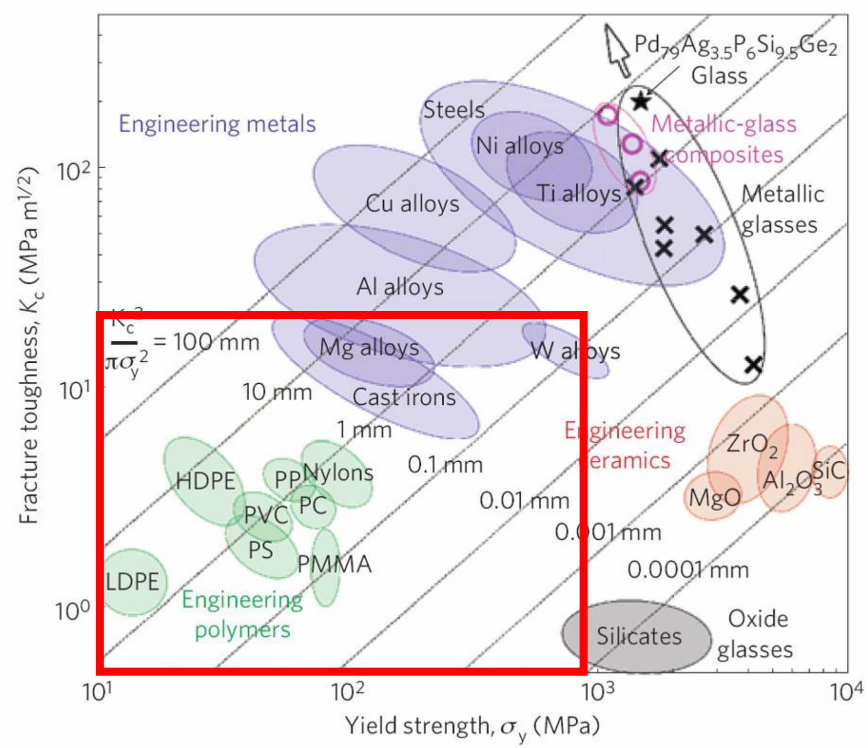


K V Tian, G. A Chass et. al., Qualitative assessment of microstructure and Hertzian indentation failure in biocompatible glass ionomer cements J Mater Sci: Mater Med (2012) 23:677–685

Toughness and Strength of Dental Materials

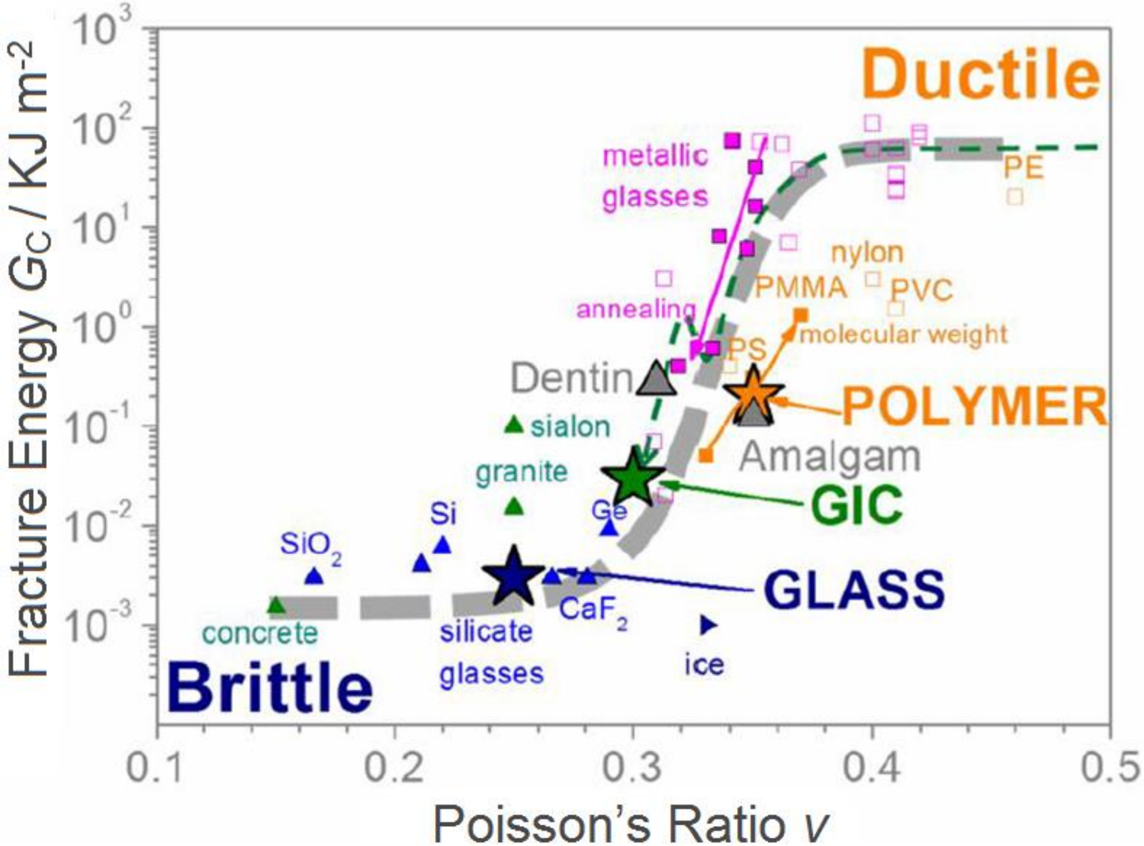
Currently GICs are mechanically weaker than dentin

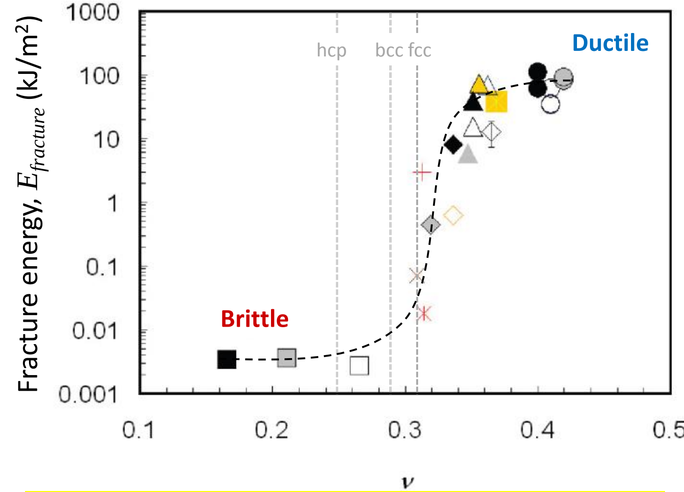




Brittle – Ductile Transition and Poisson's ratio

GIC sets more brittle than dentin





Poisson's Ratio and Modern Materials
Greaves GN, Greer AL, Lakes RS and Rouxel T
Nature Materials 10, 823-837 (2011).

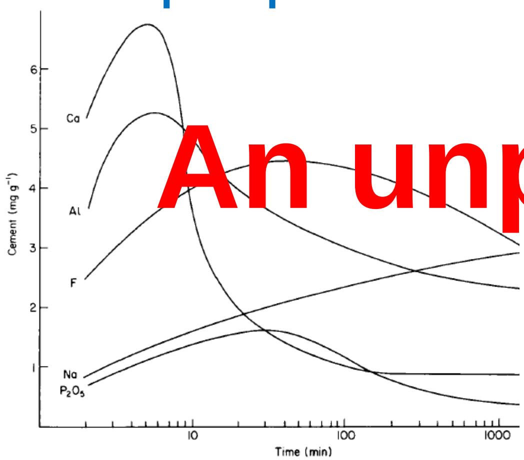
Cementation Profiles of GIC cements

Ion (Ca^{2+}, Al^{3+}) precipitation

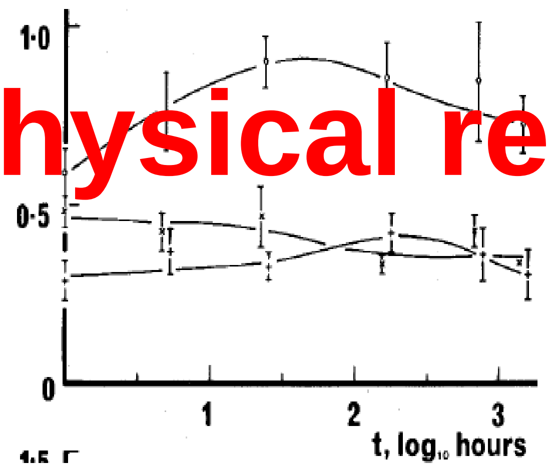
Fracture toughness

Al(6) : Al(5+4) Ratios by NMR

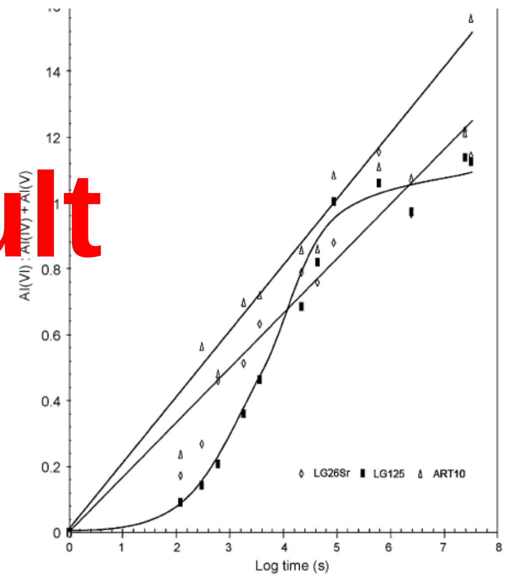
An unphysical result



H.J.Prosser, *J.Chem. Biotechnol*, **1979**



C.H.Loyd, *Dent.Mater*, **1987**



N. Zainuddin, Dent.Mater, **2009**

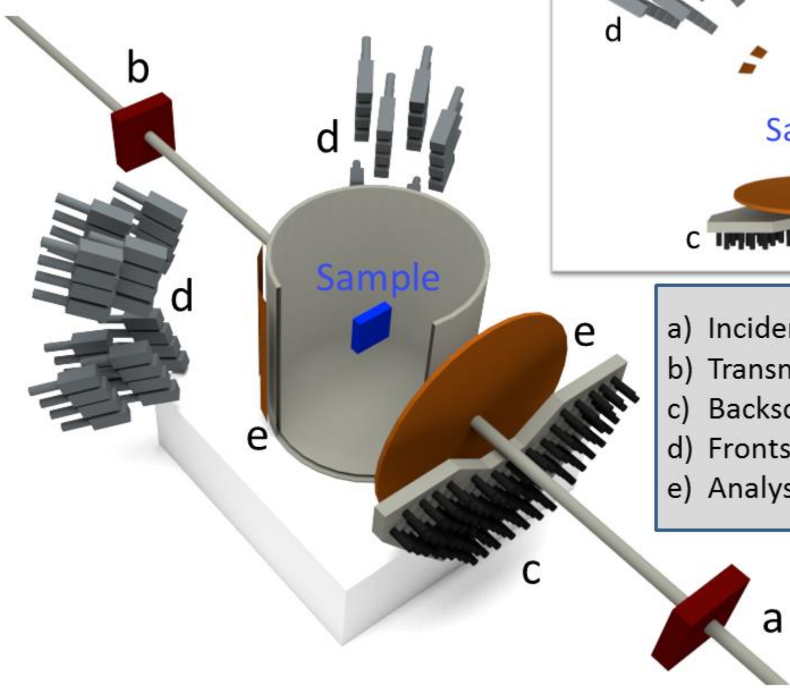
Time

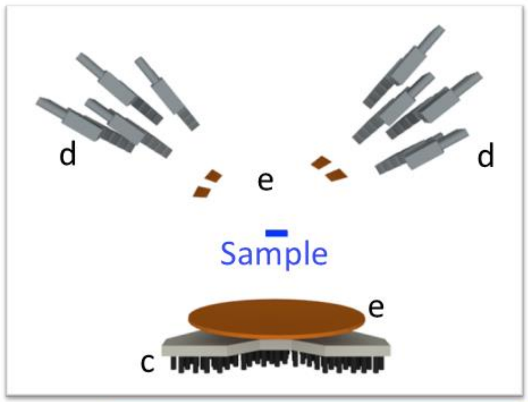
In-situ NCS Cementation Profiles

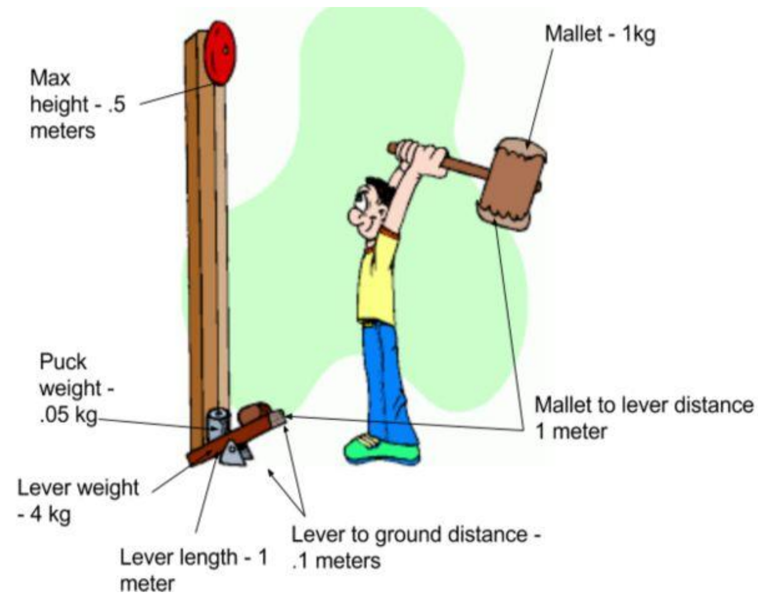
nature COMMUNICATIONS

Atomic and vibrational origins of mechanical toughness in bioactive cement during setting

Vesuvio



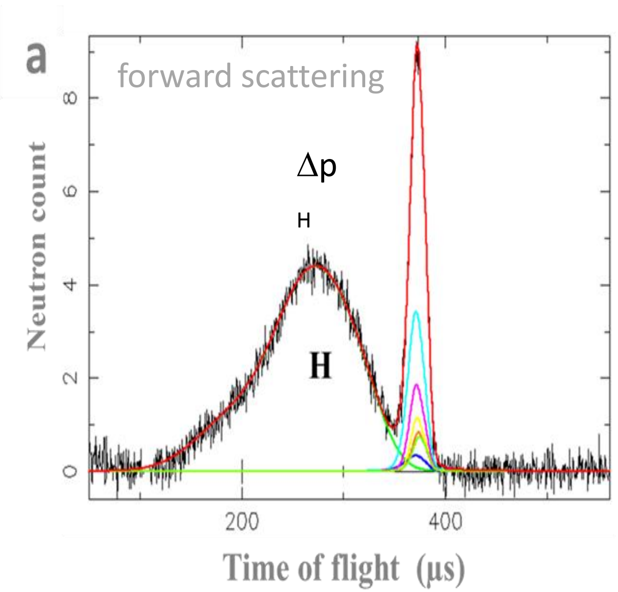


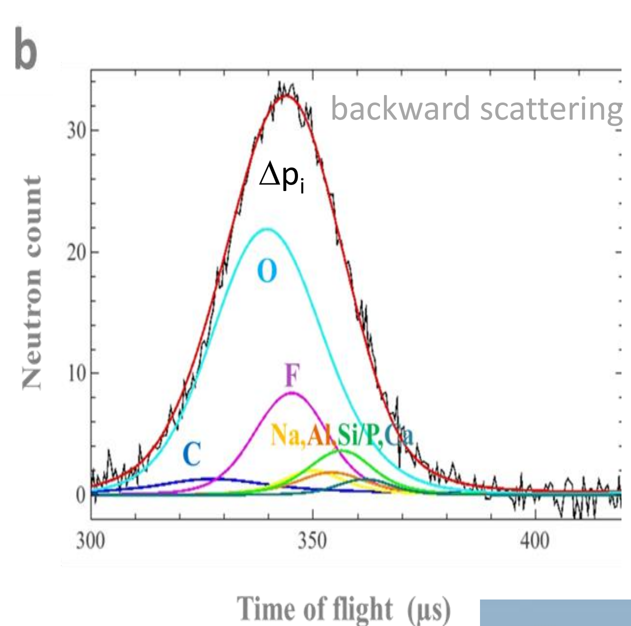


a) Incident monitor
b) Transmitted monitor
c) Backscattering detectors
d) Frontscattering detectors
e) Analyser Gold foils

Atomic and vibrational origins of mechanical toughness in bio-cement during setting
Tian KV, Chass GA and Greaves GN
Nature Communications **6** 8631 pp 1-10 (2015) **|** DOI: 10.1038/ncomms9631

Vesuvio – Neutron Compton Scattering





- Δp_i measures atomic cohesion

For multicomponent systems approximate average NCS width

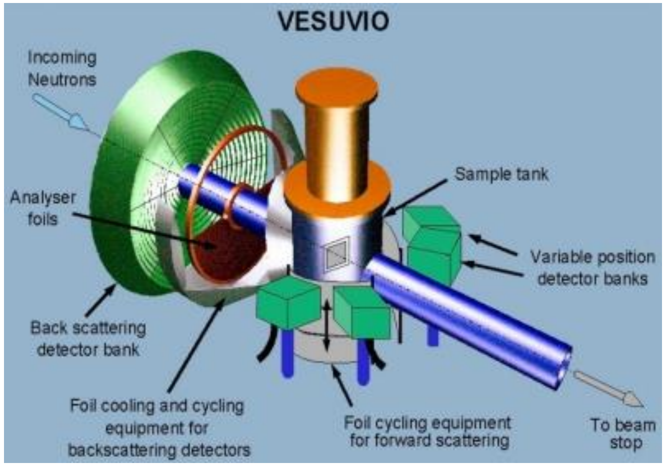
$$\Delta p = \sum_i c_i \Delta p_i$$

VESUVIO NCS Spectrometer (RAL)

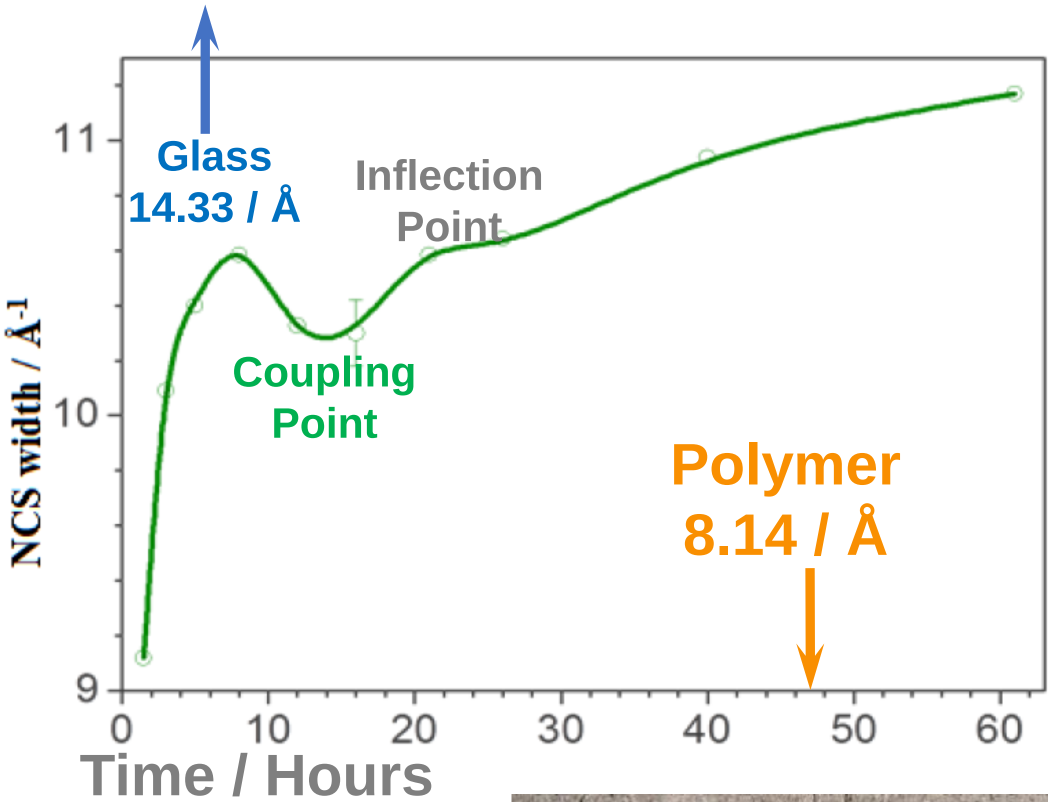
- NCS measures momentum distribution $n(p)$ of nuclei reflecting the effective potential experienced

Energy transfer 1 eV to 30 eV, Momentum transfer 30 to 200 Å^{-1}
Impact Approximation holds – single atom scattering

PRL **100,** 177801 (2008)



Watching ~~Paint~~ Cement Dry

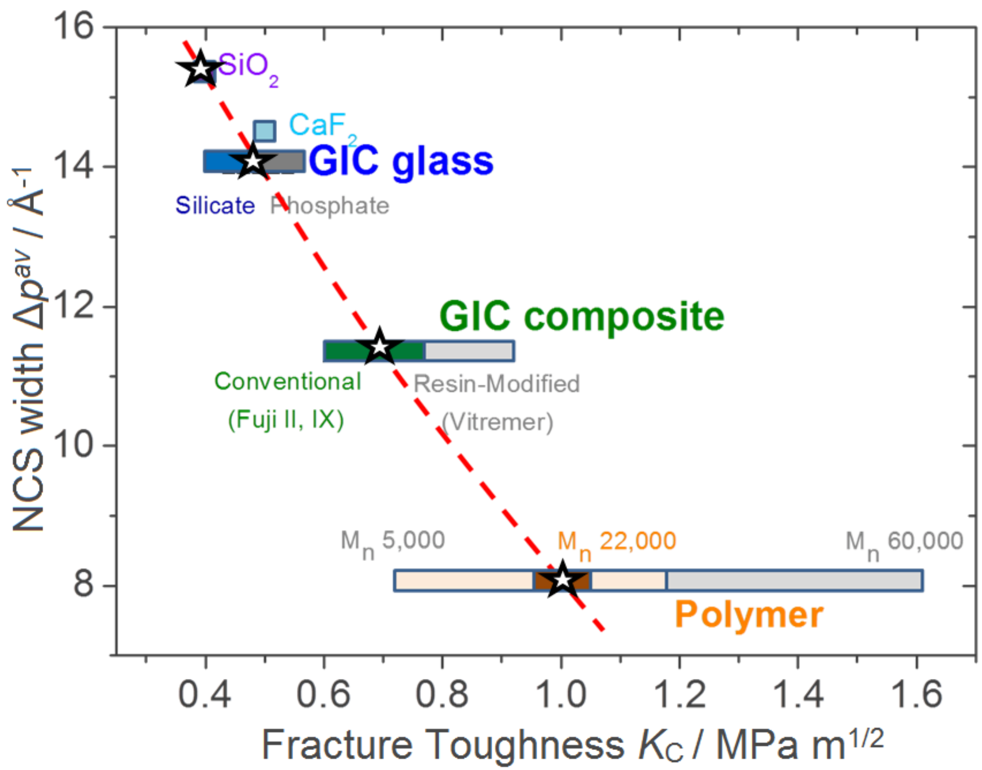


Though hesitant at first, Hank orders the 'Watching Paint Dry Network' offered exclusively through his satellite provider.

Gelation and plasticity

Calibrating NCS with Engineering

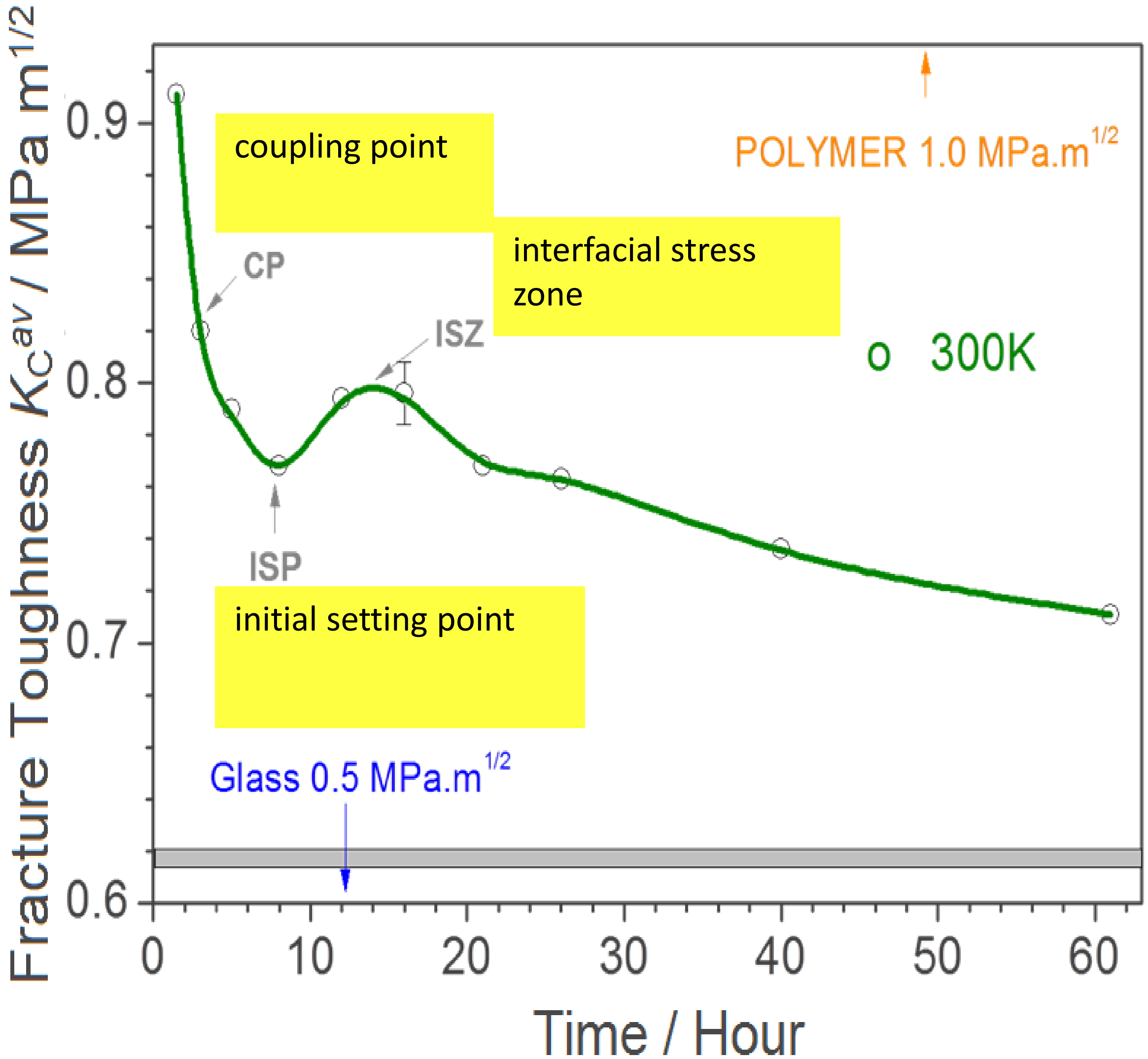
- NCS width Δp versus Fracture Toughness



Look-up table for converting measured Δp^{av} into K_C

K. Tian, G. Chass, et al., Nature Communications **6** 8631 pp 1-10 (2015) **|** DOI: 10.1038/ncomms9631

Cementation Profile
Engineering Units

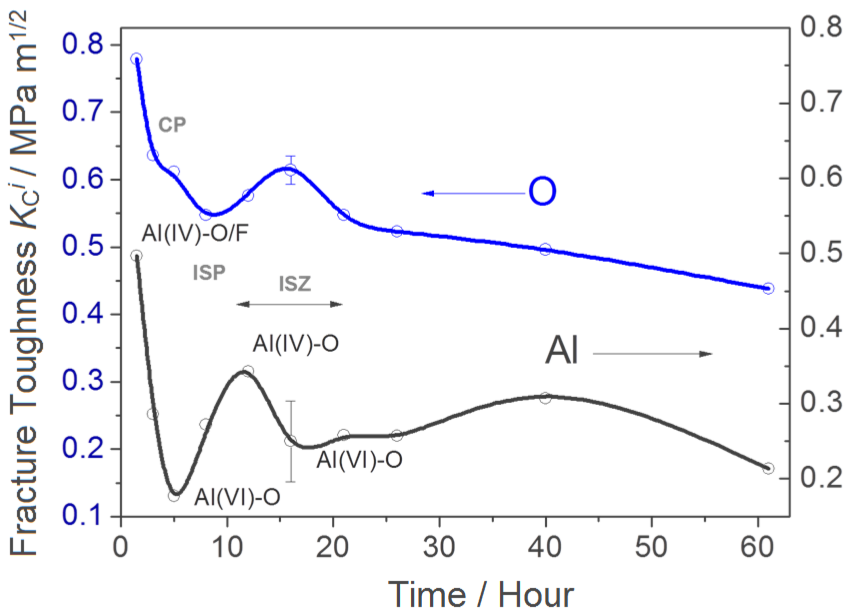


- Effects of individual elements O and Al

decreasing

atomic cohesion

increasing



CP: Bridging Oxygens ruptured (GP1) + Al^{3+} released

ISP: polyacrylic acid carboxylation at interface

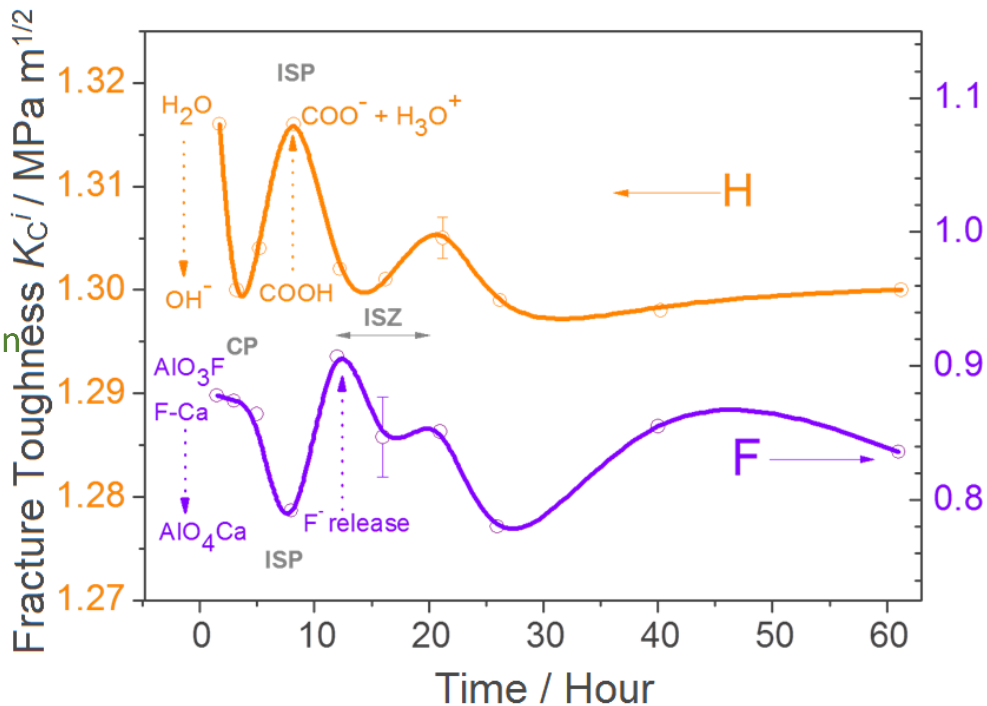
ISP: F release from fluortite (GP2) phosphate phases (GP3) at ISP

- Effects of individual elements: H and F

decreasing

atomic cohesion

increasing



CP: H_2O corrodes glass surface (GP1)

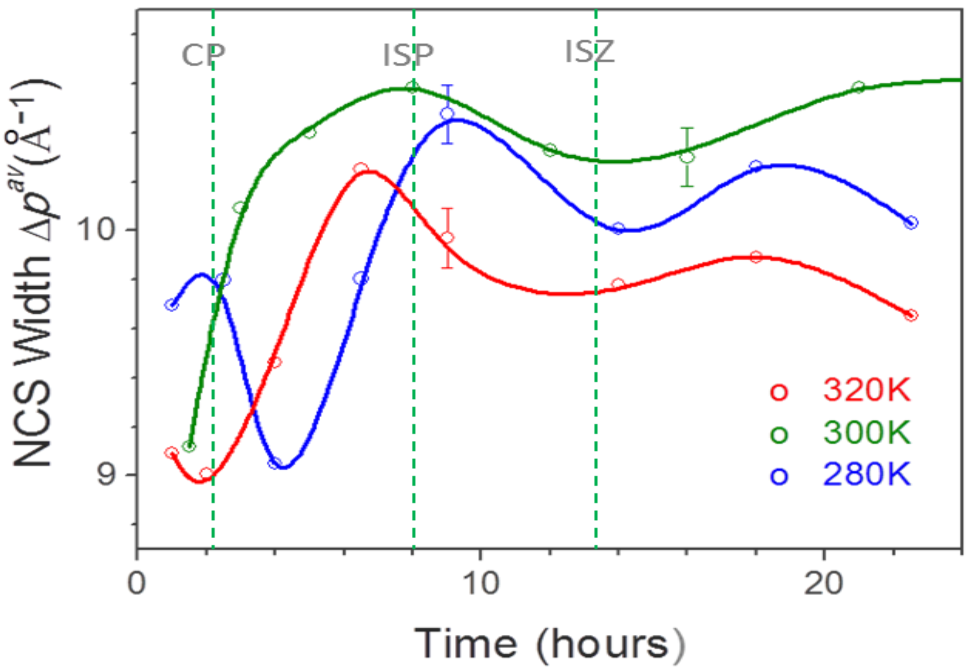
ISP: polyacrylic acid carboxylation at interface

ISP: F release from fluortite (GP2) phosphate phases (GP3) at ISP

- Effects of setting temperature

Average NCS width

$$\Delta p = \sum_i c_i \Delta p_i$$



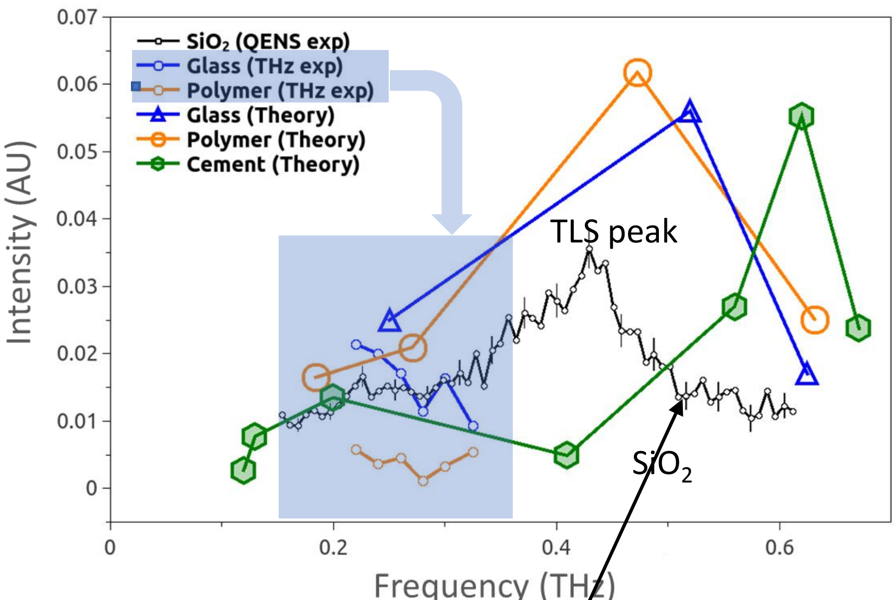
Cementation Profiles

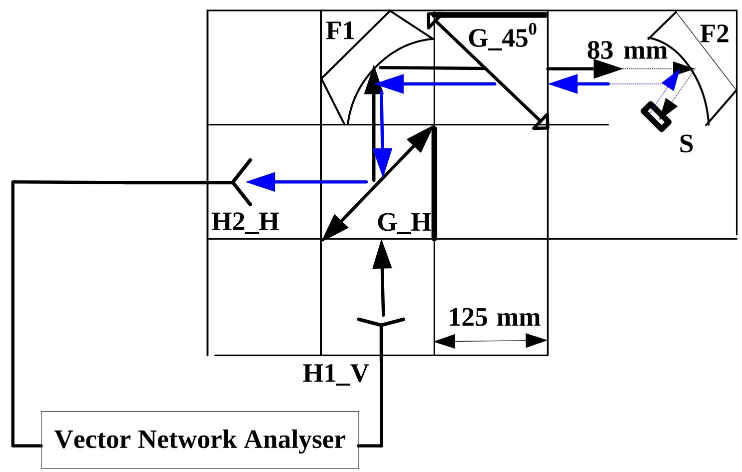
THz-Spectroscopy

• Coherent Terahertz Spectroscopy

QMUL

McIntosh, A. I., Yang, B., Goldup, S. M., Watkinson, M. & Donnan, R. S.
Terahertz spectroscopy: a powerful new tool for the chemical sciences?
Chem. Soc. Rev. 41, 2072–2082 (2012).

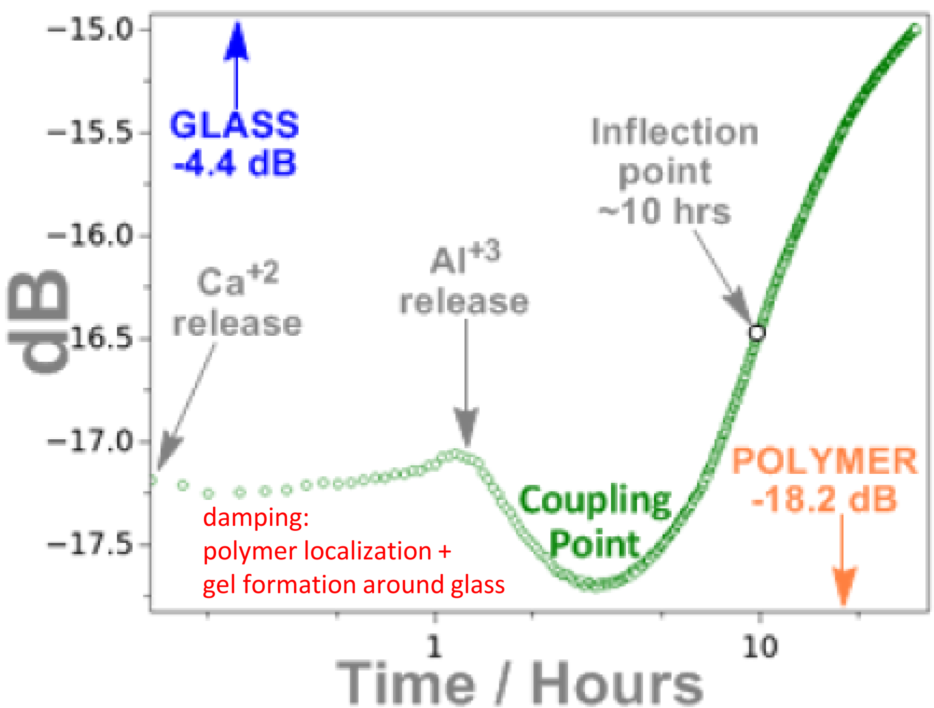




Greaves, G. N., Meneau, F., Maje´rus, O., Jones, D. G. & Taylor, J.
Identifying the vibrations that destabilize crystals and characterize the glassy state.
Science 308, 1299–1302 (2005).

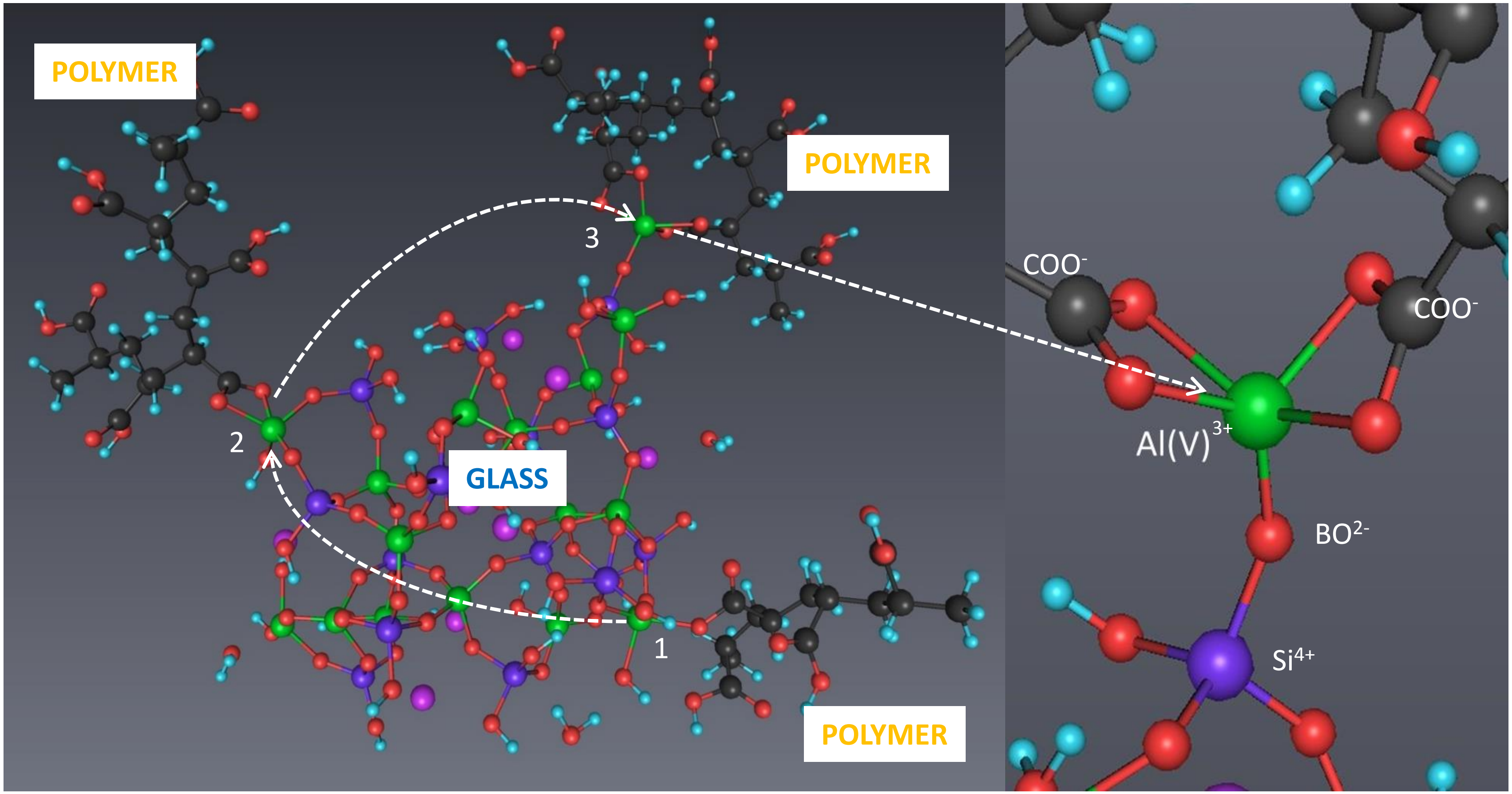
Cementation Dynamics
Coherent-THz vs. Inelastic Neutrons

Coherent THz
(0.10-0.65 THz @ 300K)

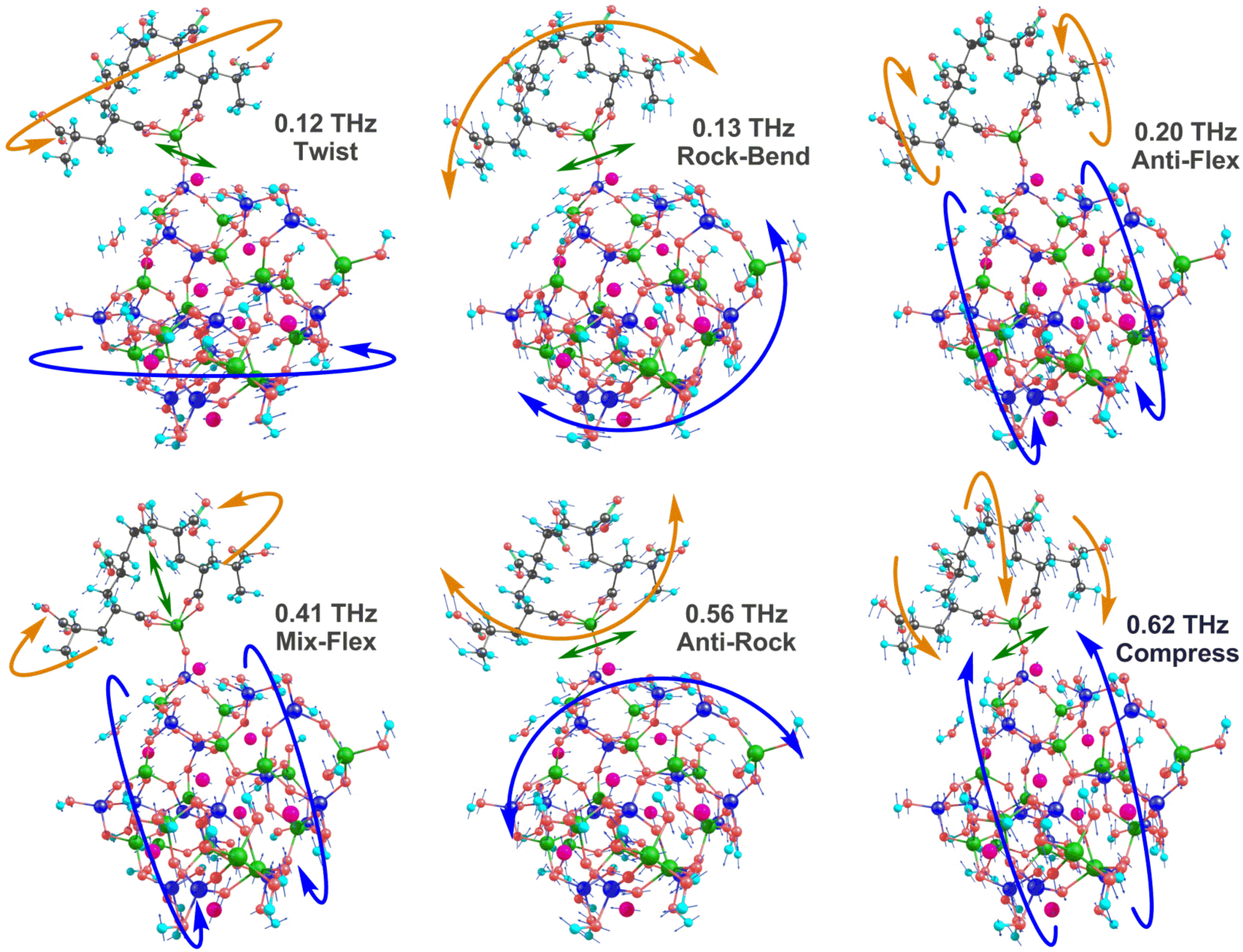


increasing interfacial
collective modes

‘Bare’ Cluster Model of ‘hybrid’ GIC

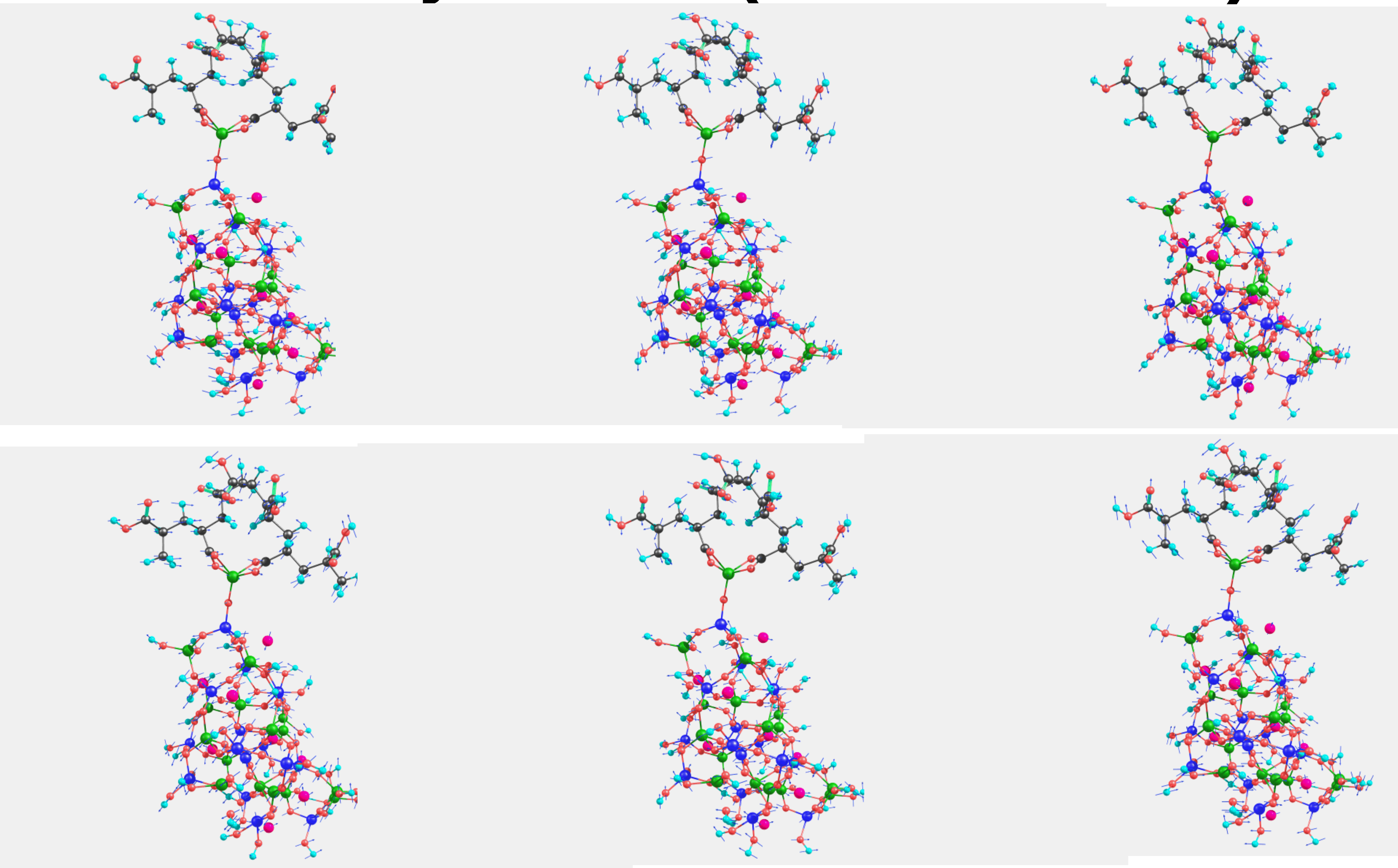


Interfacial Dynamics (0.10-0.65 THz)



KV Tian, GA Chass, et al., Periodic vs. Molecular Cluster Approach to Modelling Glassy Systems, *J. Non. Cryst. Sol*, 451 (2016) 138-145

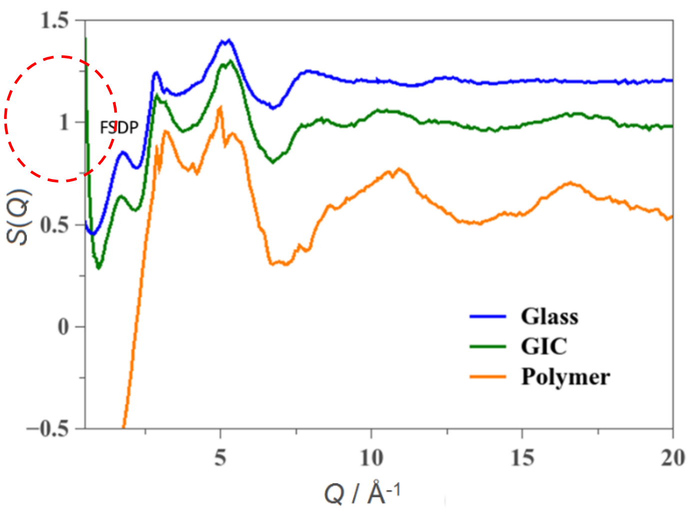
Interfacial Dynamics (0.10-0.65 THz)

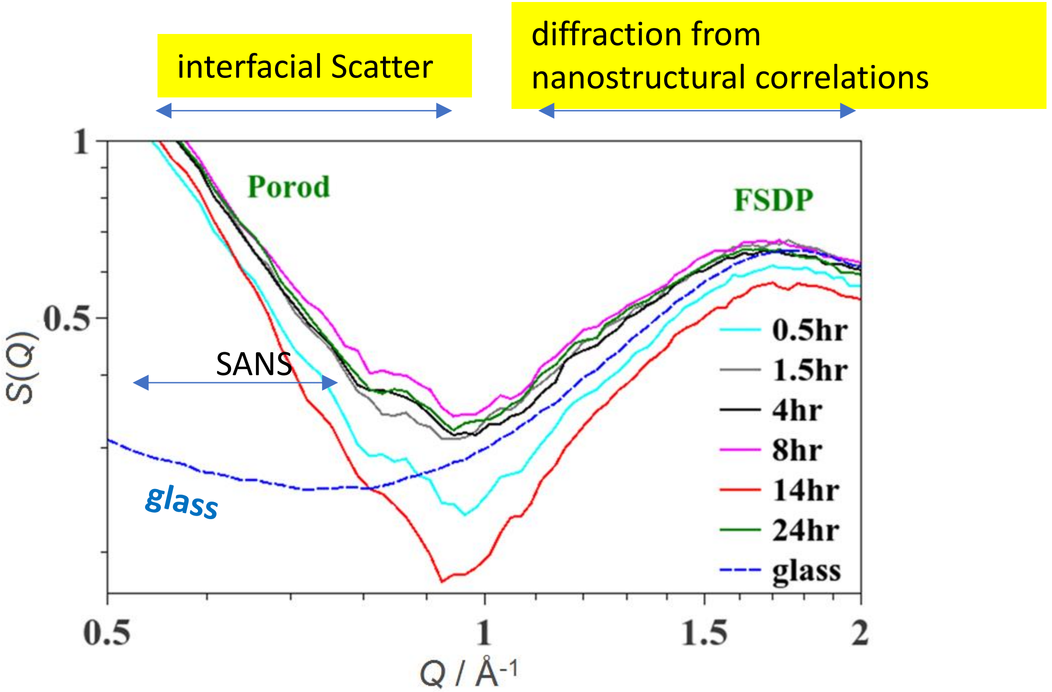


- *In situ* Elastic Neutron Scattering

S(Q) of Components & GIC Composite

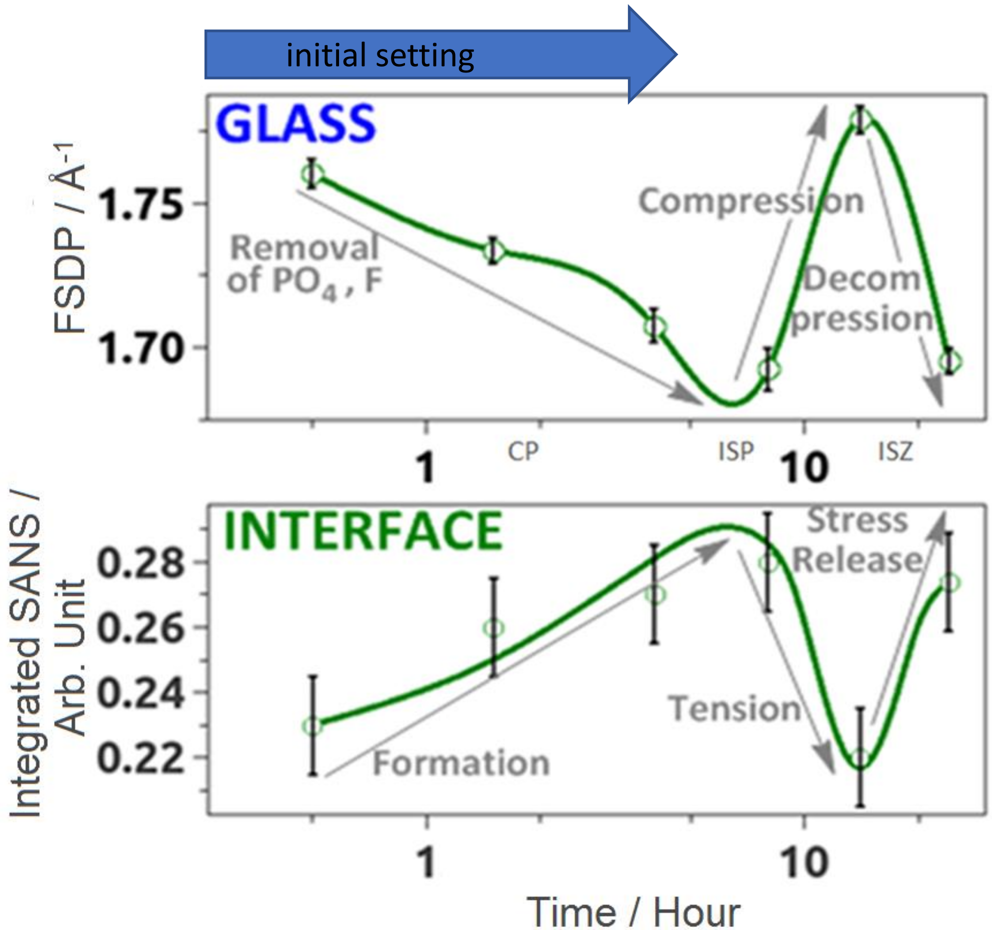
First Sharp Diffraction Peak (FSDP) and
Small Angle Neutron Scattering (SANS)





Fluctuations with setting in FSDP position and integrated SANS

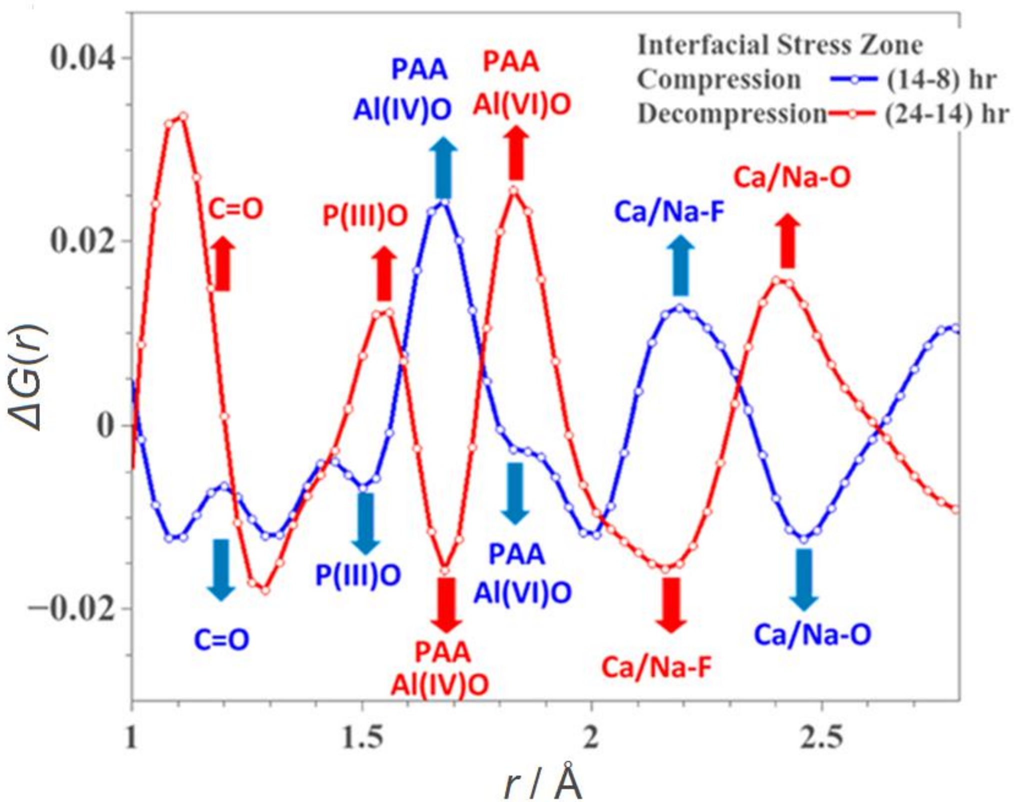
evidence for generation of internal pressure in glass, and interfacial tension and stress release in ISZ



Nature Communications **6** 8631 pp 1-10 (2015) **|** DOI: 10.1038/ncomms9631

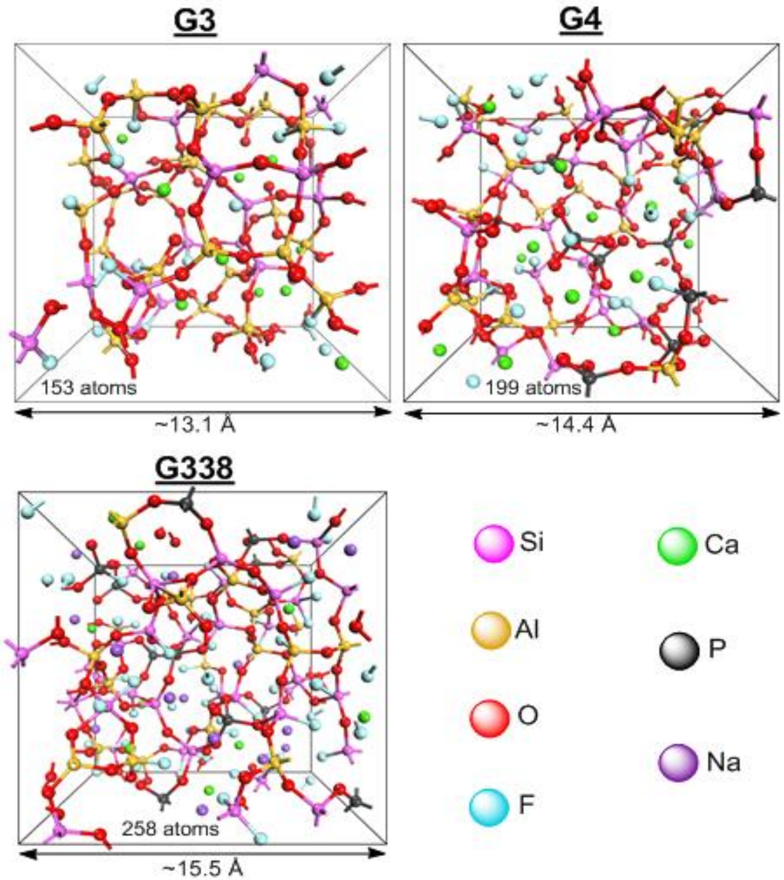
ΔG(r) changes occurring over ISZ

Switch between Al(IV) and Al(VI) co-ordinations; C=O, Ca/Na-O and Ca/Na-F configurations

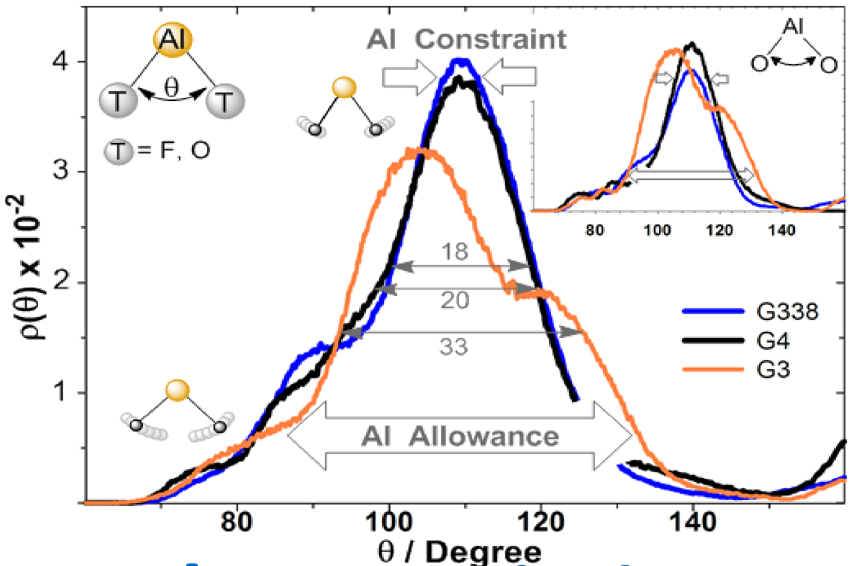


Nature Communications **6** 8631 pp 1-10 (2015) **|** DOI: 10.1038/ncomms9631

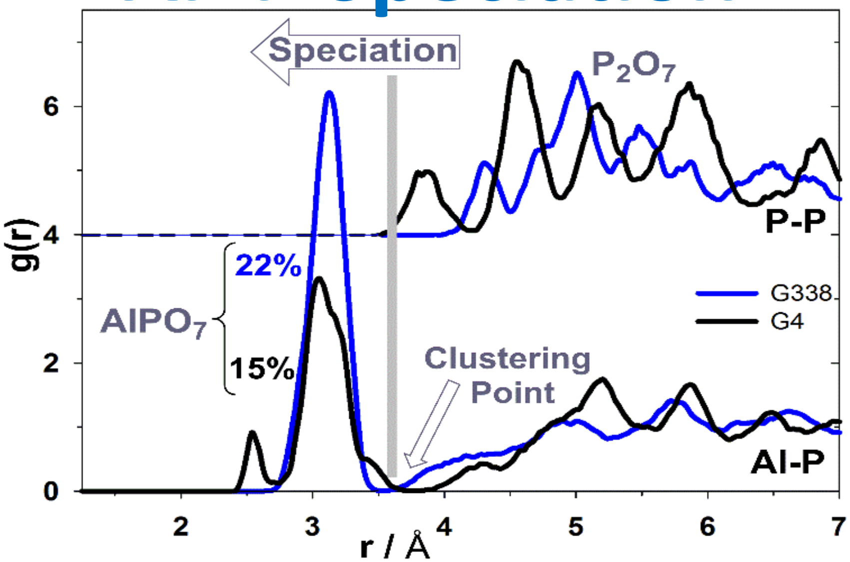
Modelling Influence of F Content



Al - Constraint



Al–P Speciation



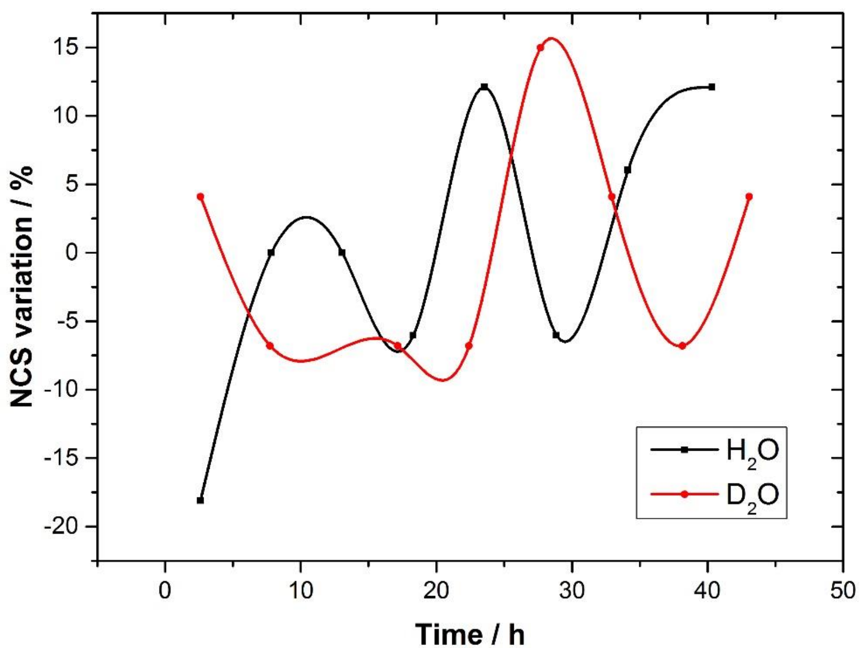
KV Tian, GA Chass, D. DiTommaso, *Phys.Chem.Chem.Phys*, 18, (2016), 837-845.

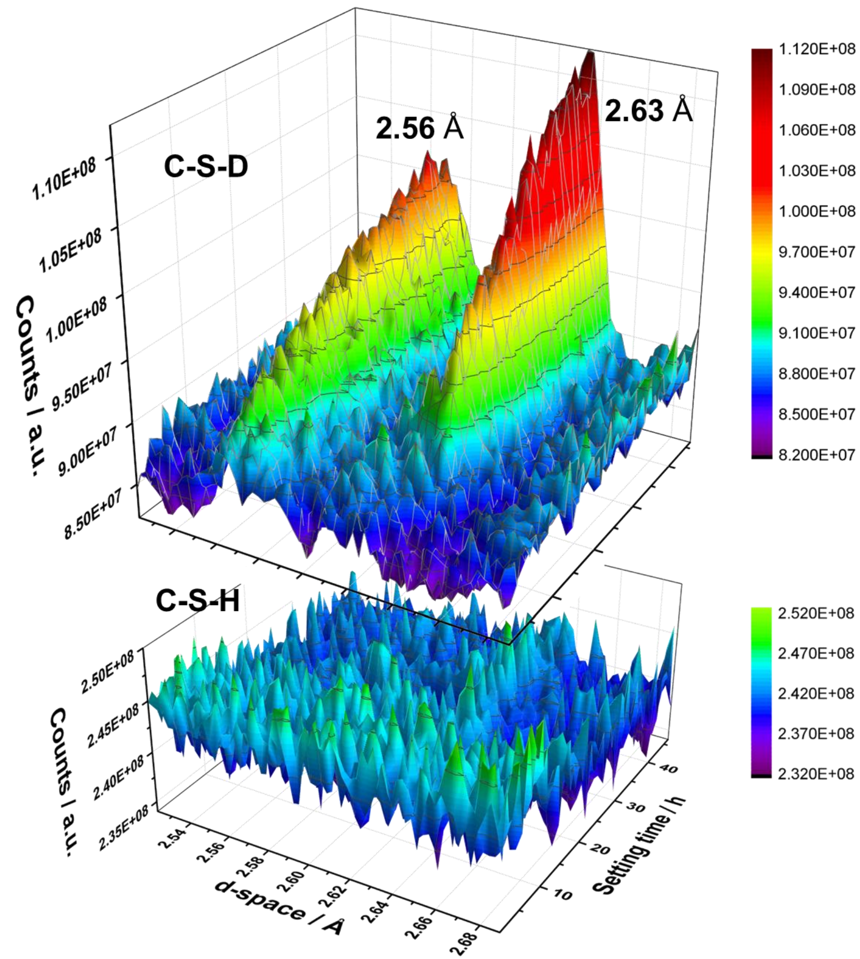
Findings & Conclusions

- Impact: need for replacing Hg amalgam with non-toxic restoratives of similar toughness
- Non-monotonic decrease in fracture toughness of GIC with setting (*in situ* Neutron Compton Scattering) – scenarios for arresting cementation
- Collective interfacial vibrations influence GIC setting (Coherent THz Spectroscopy)
- Evidence for development of interfacial stress in Al coordination (*in situ* Elastic Neutron Scattering)

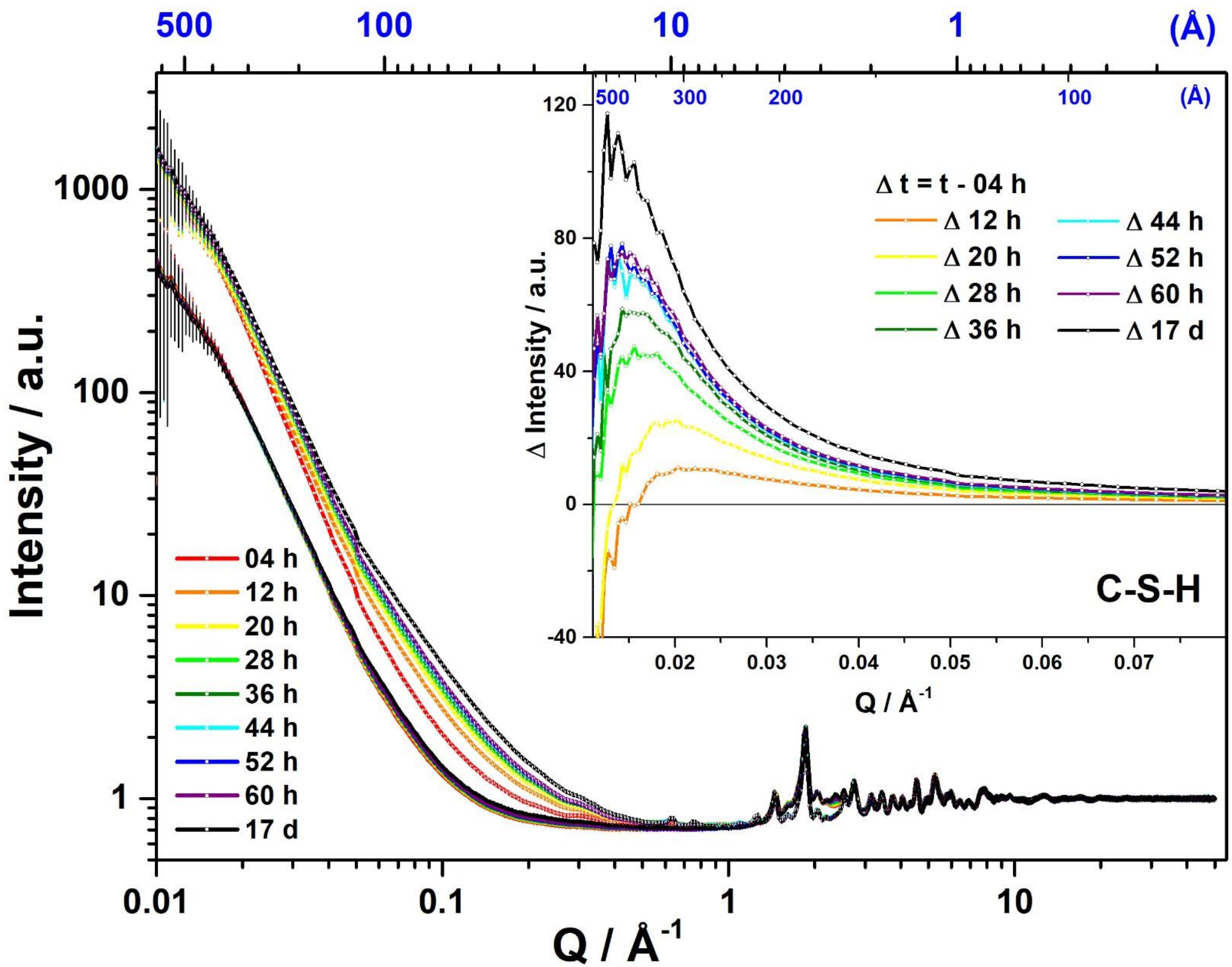
Impact & Transferability

Construction Cements (chicken soup) on VESUVIO





Construction Cements on NIMROD



Proof of Concept & Refinement

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