UCCS
UNITÉ DE CATALYSE
ET CHIMIE DU SOLIDE

ATELIER CEA-USTV: Physical properties of glasses from low to high temperatures
12-14/04/2023 – Avignon

Hot-Stage Microscopy: a thermo-optical tool for many fields of application

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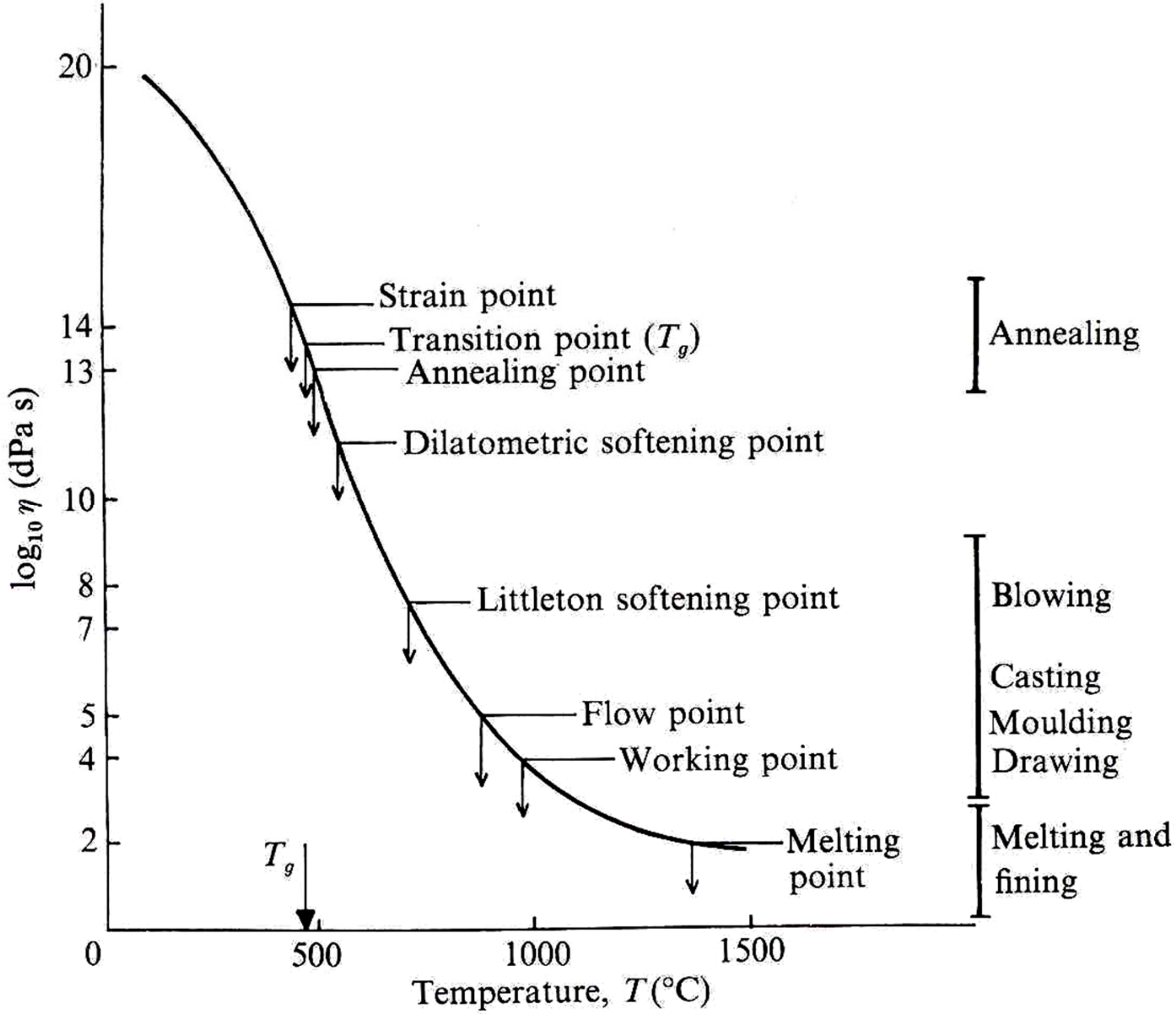
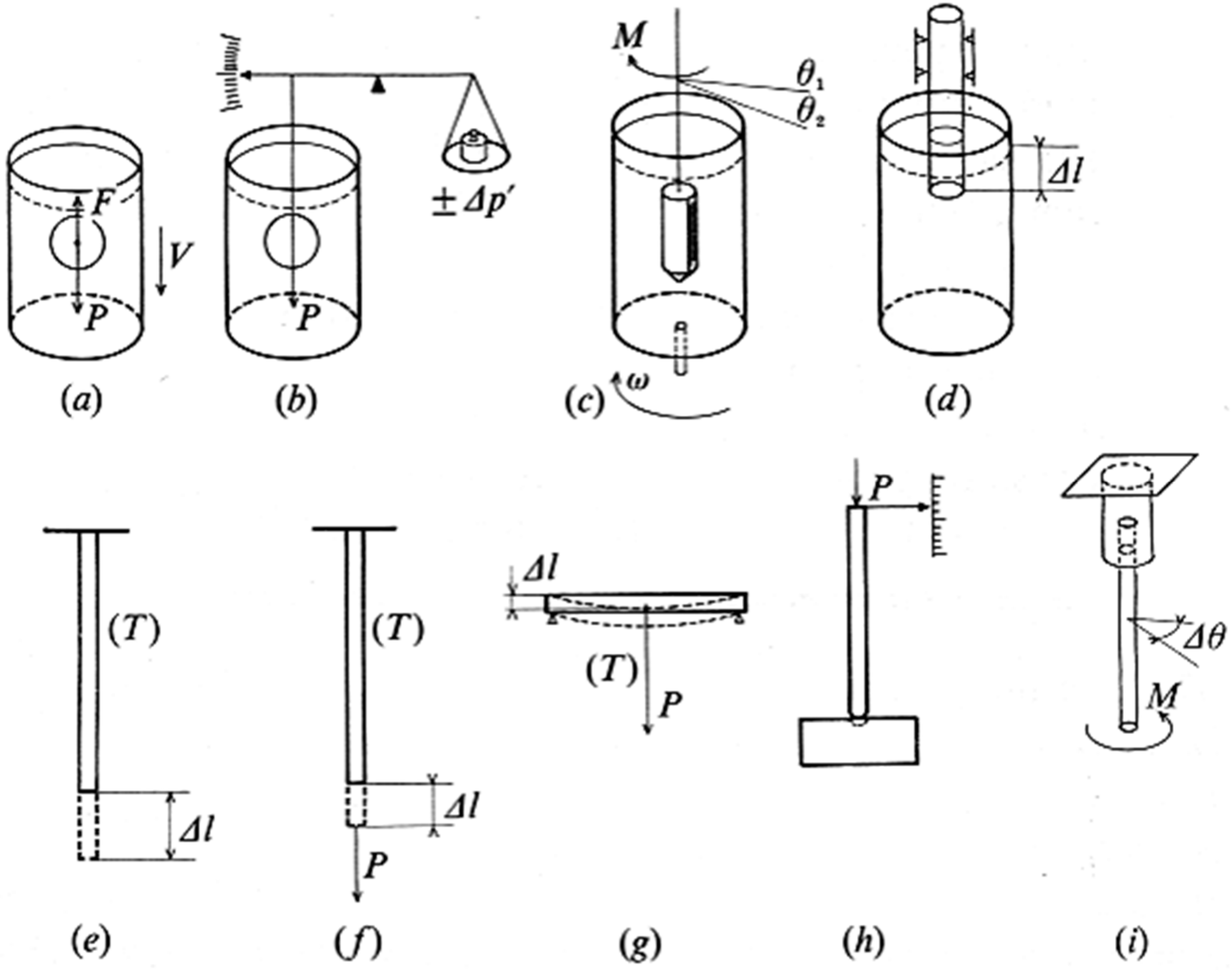
Common viscosities



Methods of viscosities measurements



a) Falling Ball

b) Counterweight ball

c) Rotation

d) Sink-point

e) Free fiber elongation

f) Load fiber elongation

g) Creep deformation

h) Penetrometer

i) Torsion of a tube

j) Parallel plates

Introduction

Viscosities commonly evaluated by viscometers

- depending on the temperature range (rotation for HT and fiber elongation for LT)
- depending on the composition of the glass (one curve / composition)
- require large amounts of sample

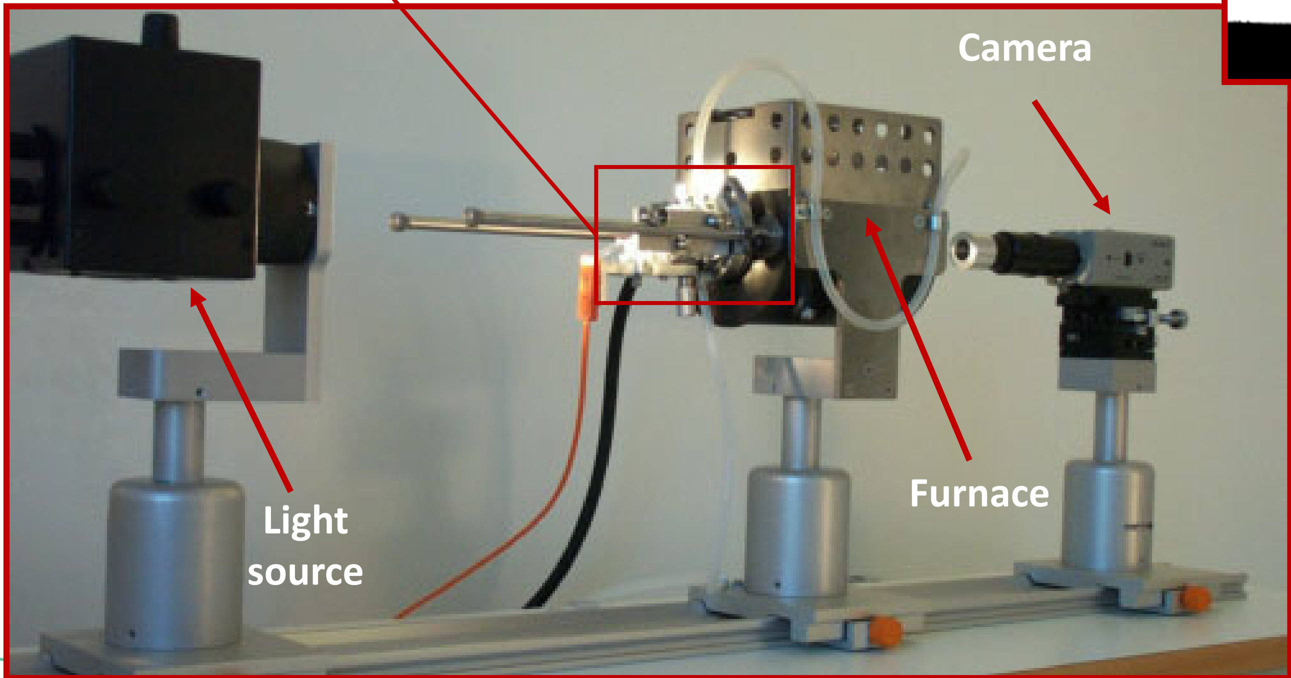
Indirectly method by heating microscopy firstly developed by Scholze in 1962

- viscosity-temperature curve established from three characteristics temperatures using the VFT relation : transition point, Littleton point and working point
- relationship between viscosity and temperature in float and borosilicate glasses as a function of specific shape during heating

Nieto et al. (1997) & Pascual et al. (2001) established the relation between the characteristic points of viscosity obtained by HSM and the corresponding values measured on the viscosity curve for different glass compositions

Hot-stage microscope (HSM): *apparatus*

Support sample / thermocouple

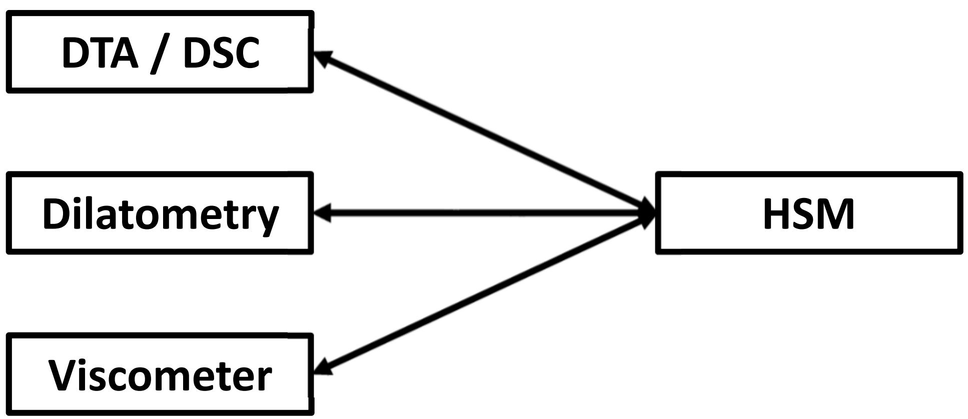


Characterization of sample evolution:

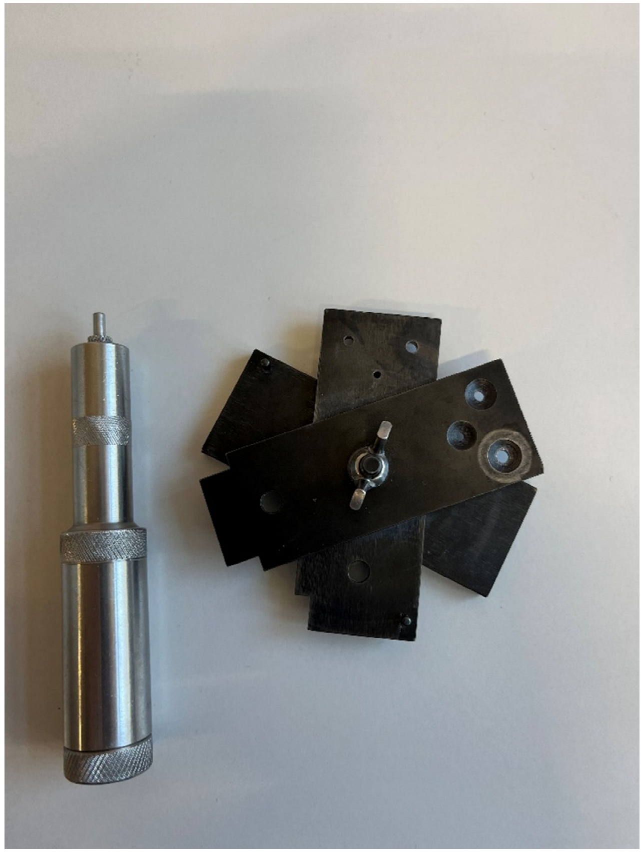
→ area (S/S_0)
→ shape factor
→ wetting

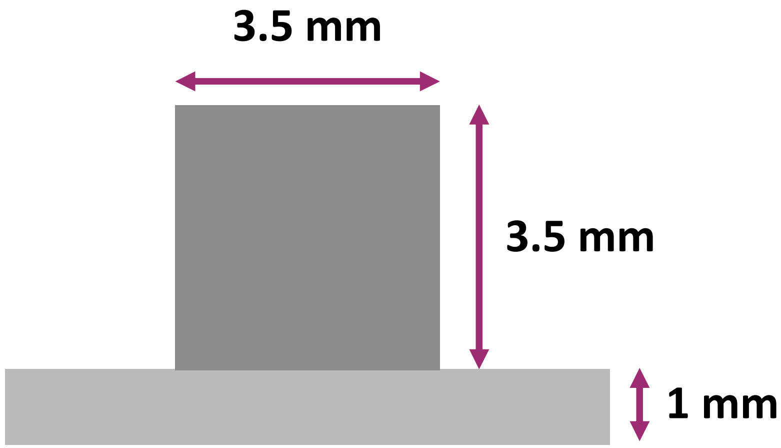
Measurements parameters

- $\Delta L/L$: thermal expansion
- $\Delta S/S \rightarrow \Delta V/V$: sintering / deformation
- Shape factor: viscosity
- Wettability
- Surface tension / density

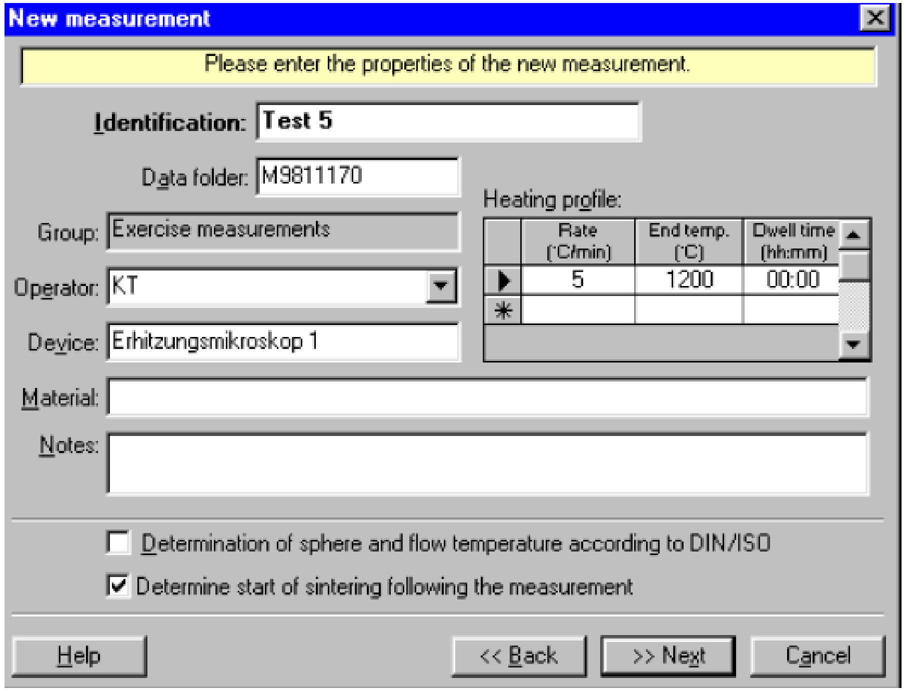


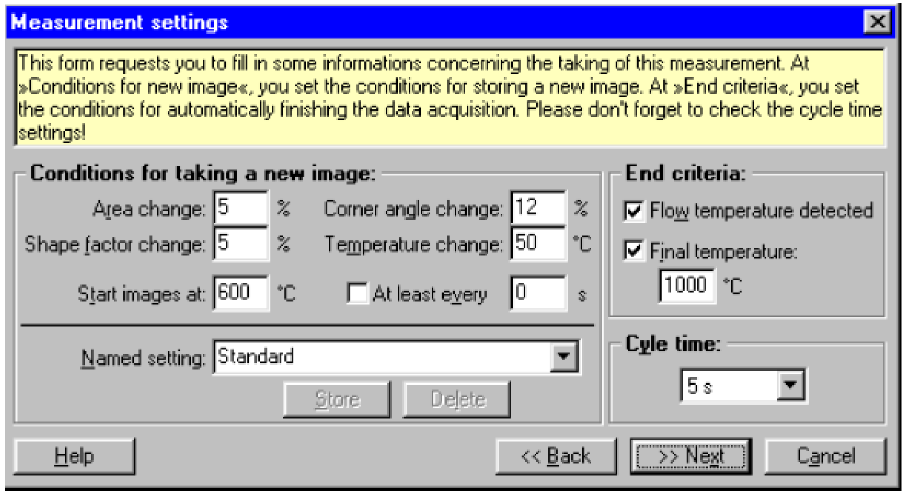
Hot-stage microscope (HSM): *sample*



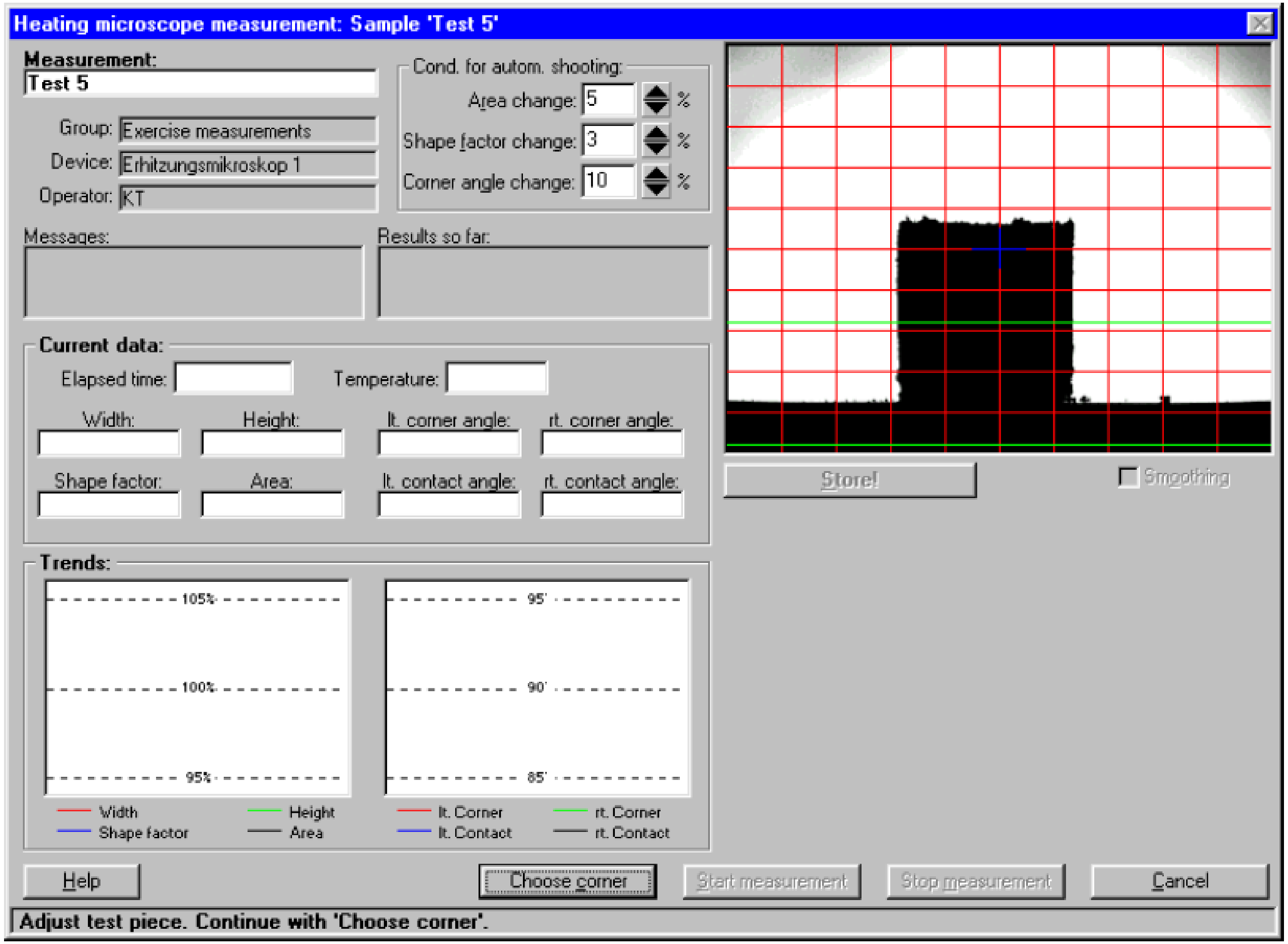


Hot-stage microscope (HSM): *software*

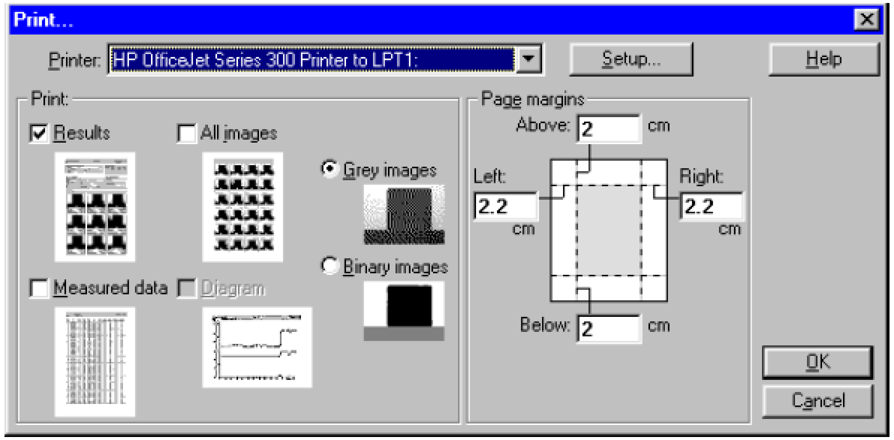


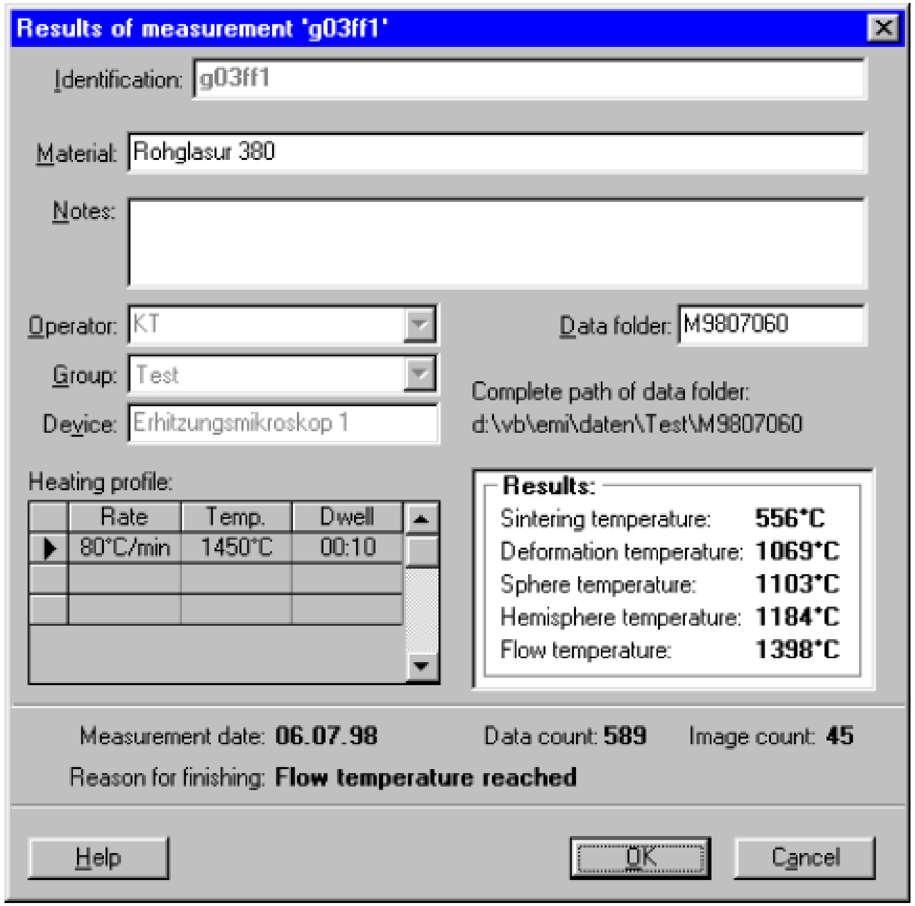


Hot-stage microscope (HSM): *software*

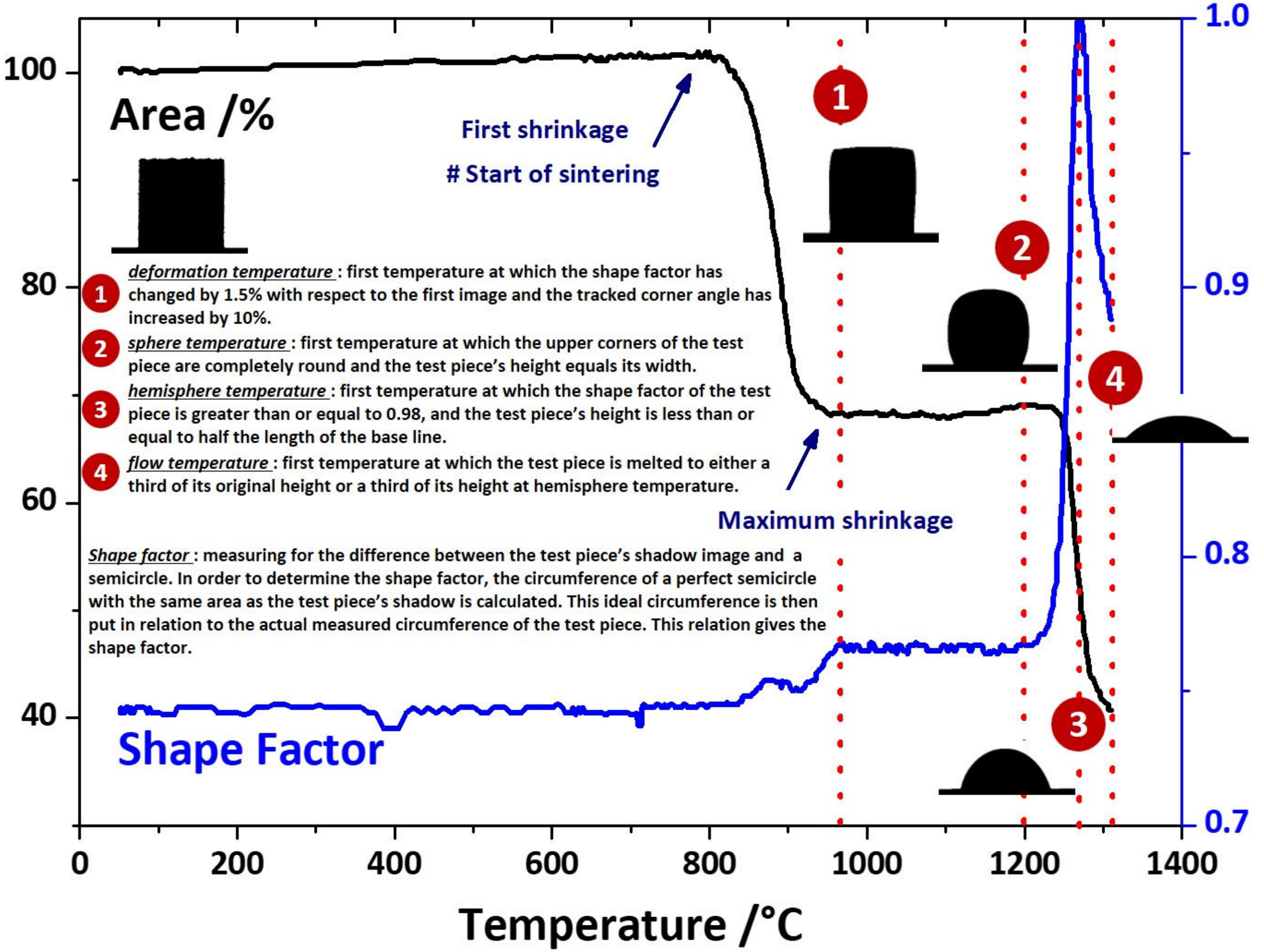


Hot-stage microscope (HSM): *results*





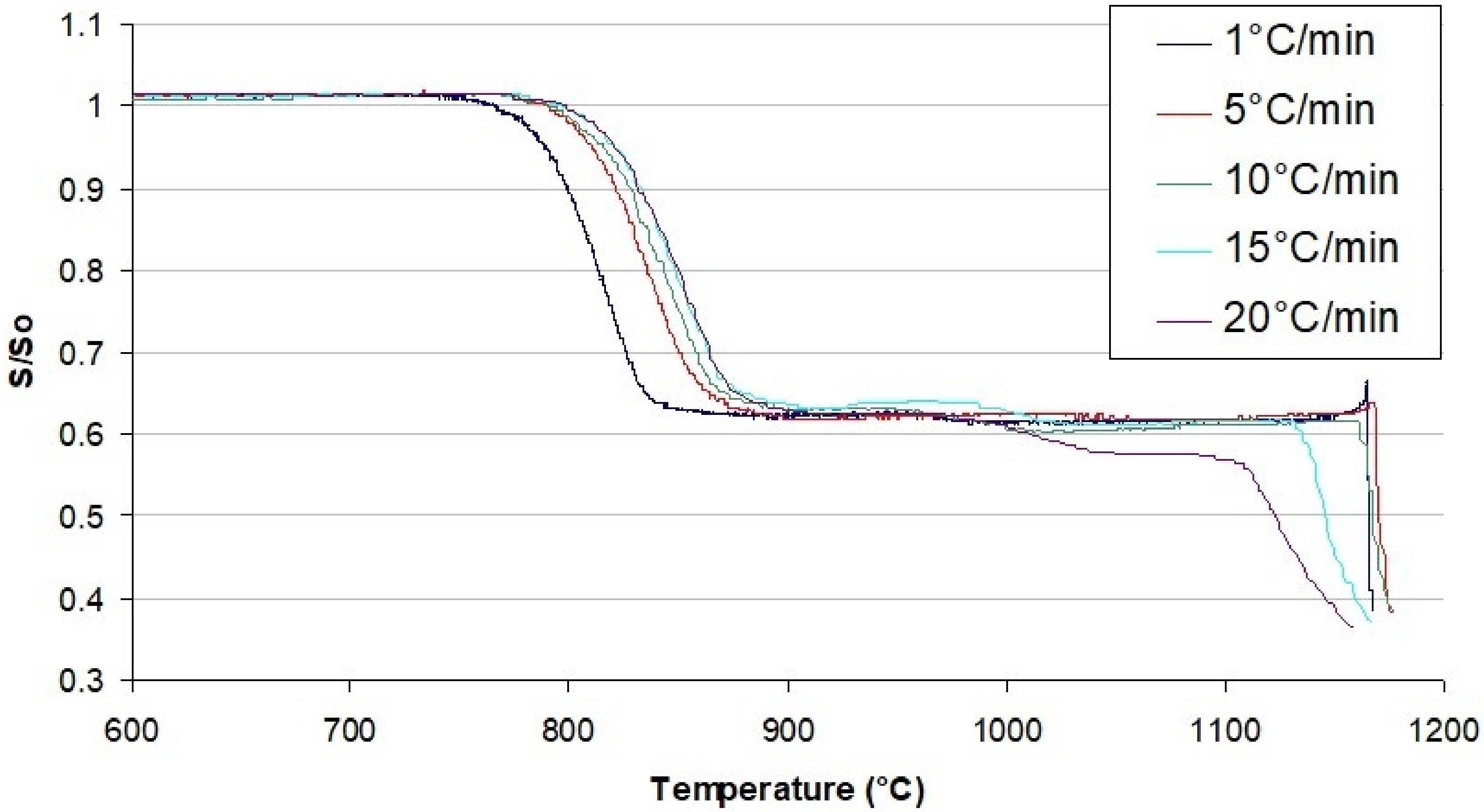
Hot-stage microscopy curves



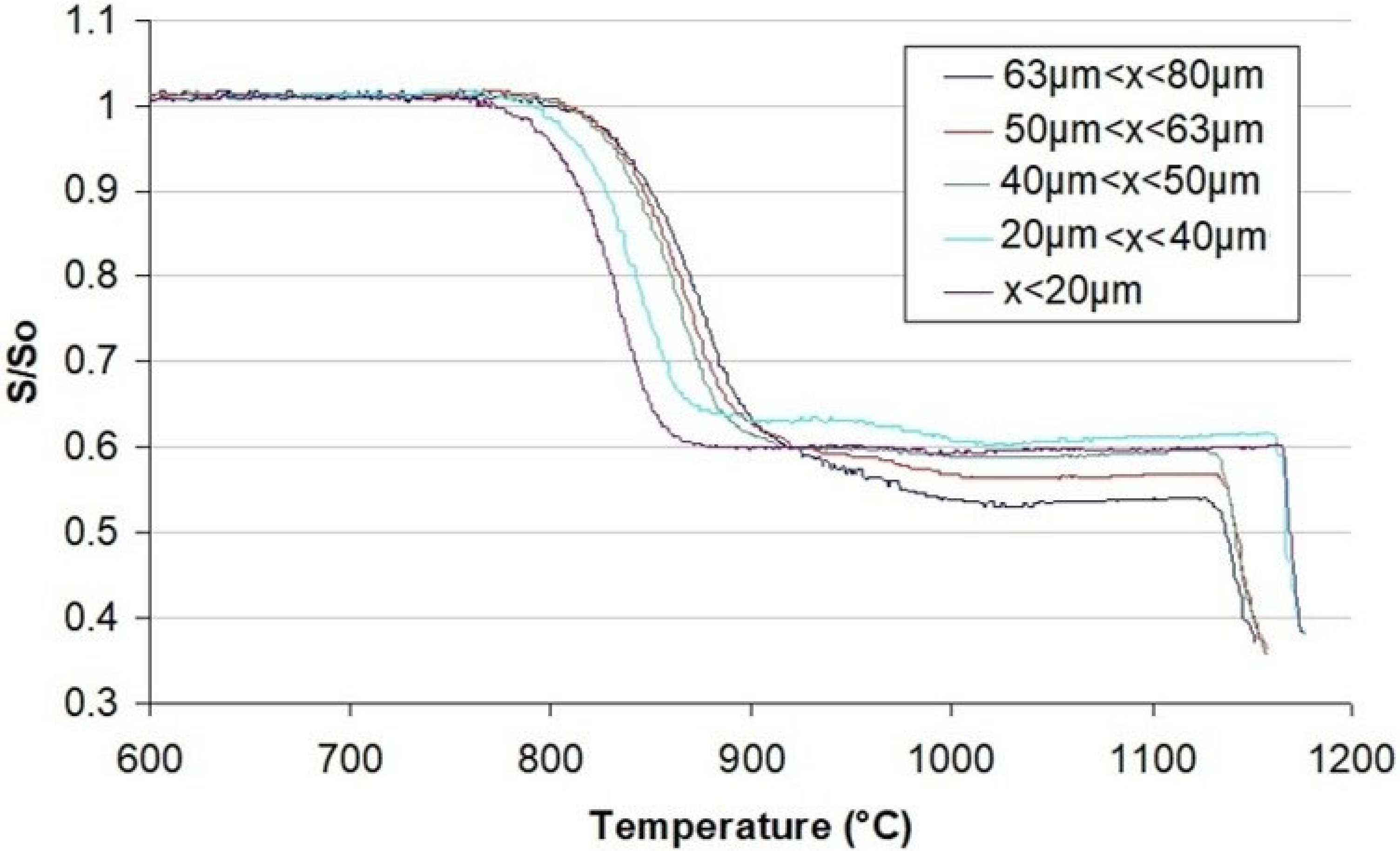
Influencing measurements parameters

- Heating rate
- Granulometry
- Atmosphere (Air; Ar; N_2; H_2/H_2O)
- Substrate
- Composition

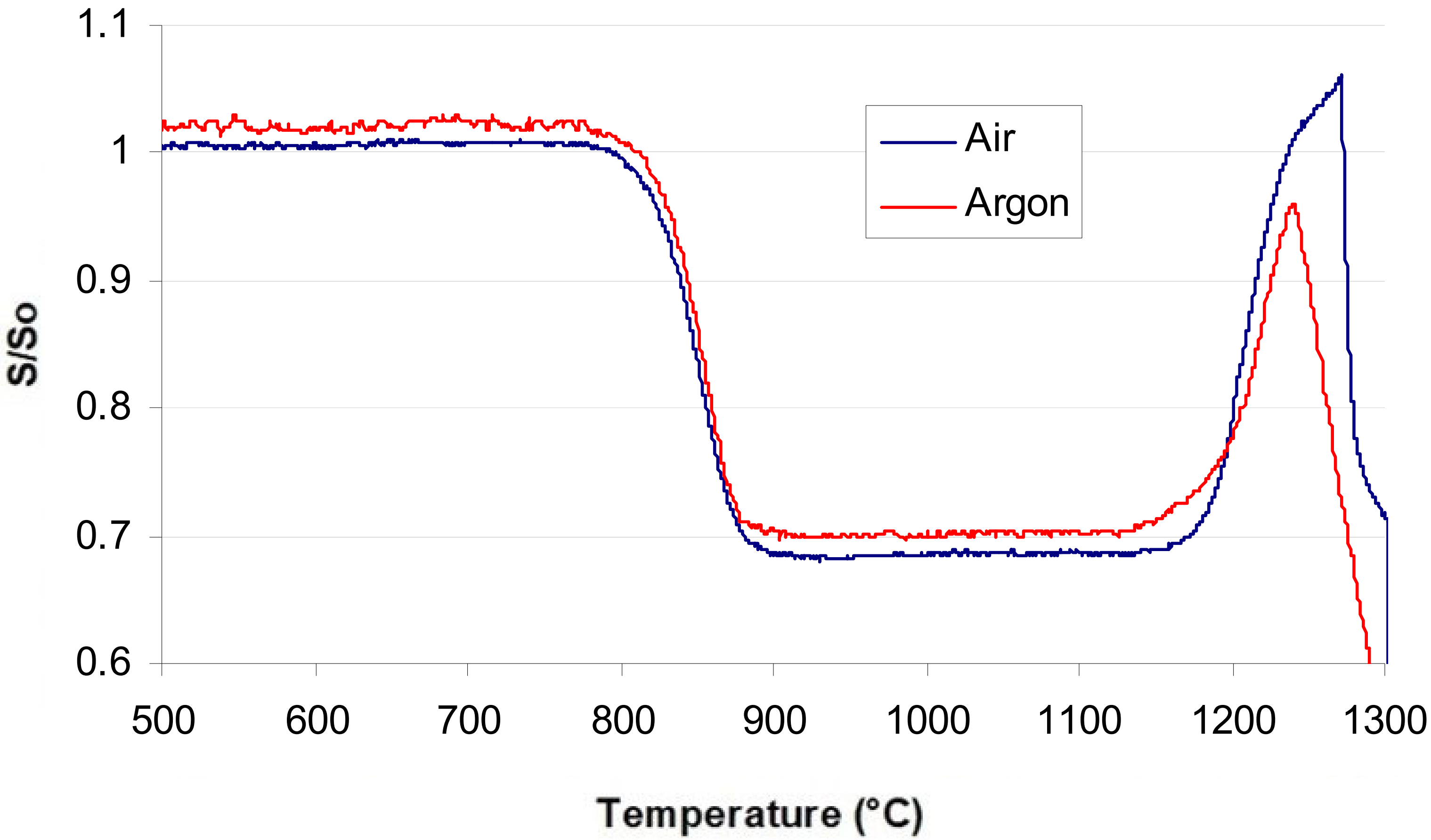
Influence of the heating rate



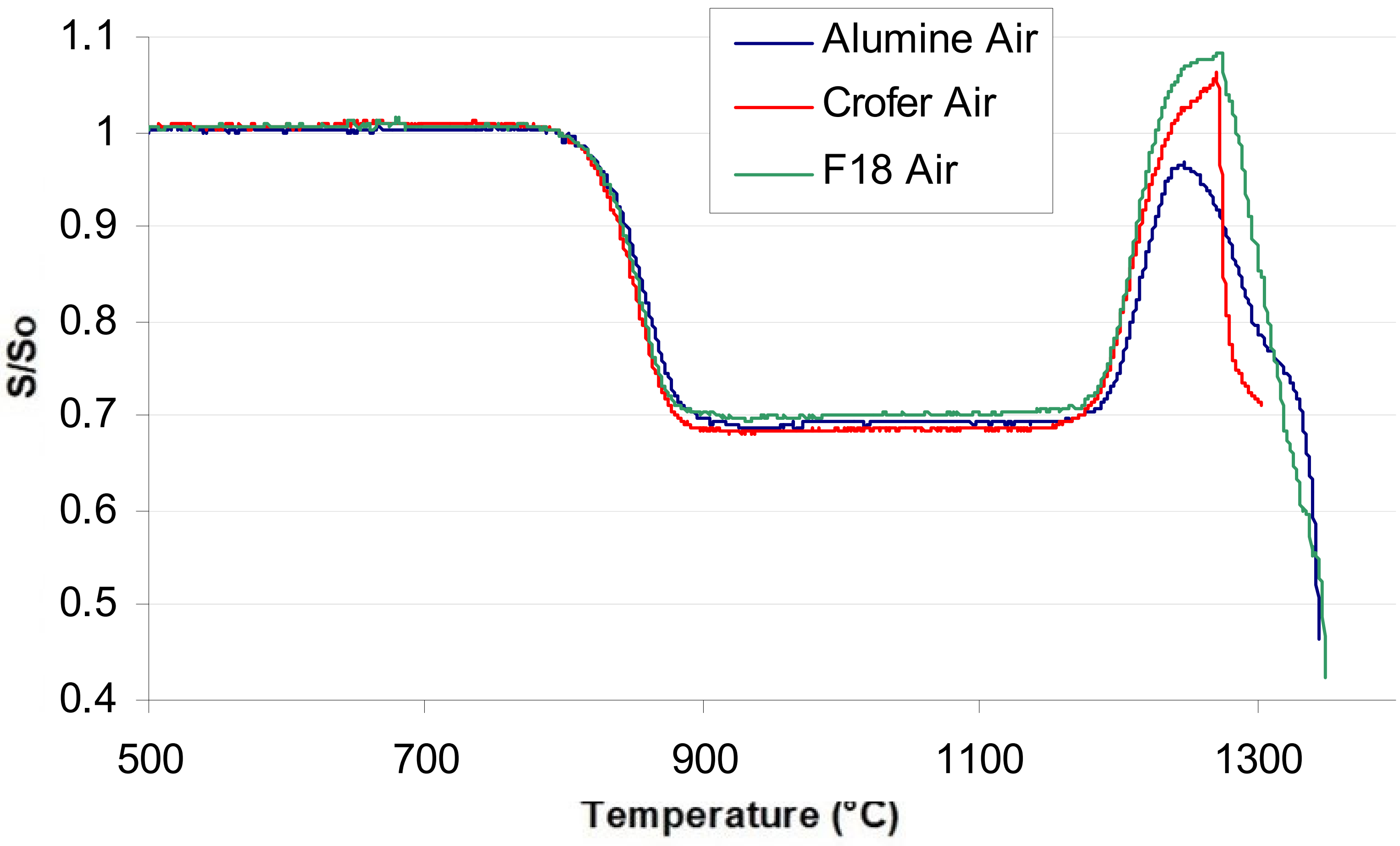
Influence of the granulometry



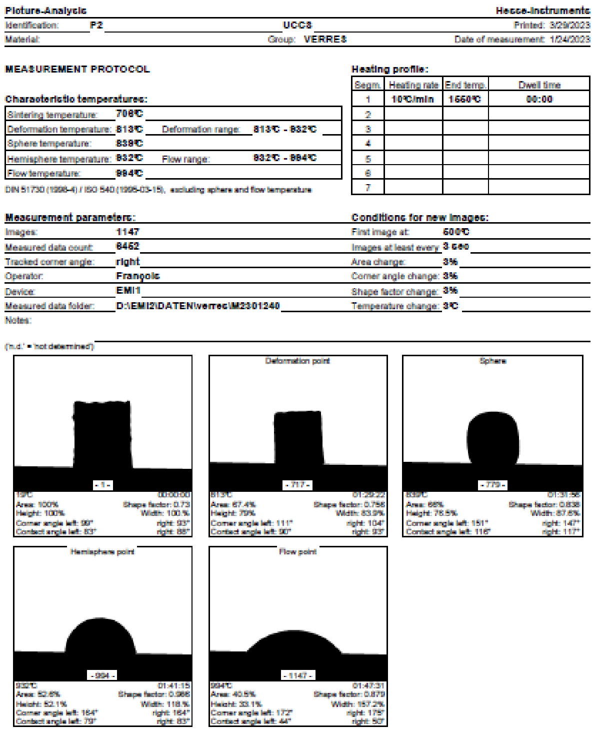
Influence of the atmosphere



Influence of the substrate



Influence of the composition


Picture-Analysis			**Hesse-Instruments**
Identification: P2	UCCS		Printed: 3/29/2023
Material:	Group: VERRES		Date of measurement: 1/24/2023

MEASUREMENT PROTOCOL

Characteristic temperatures:

Sintering temperature:	706°C		
Deformation temperature:	813°C	Deformation range:	813°C - 932°C
Sphere temperature:	839°C		
Hemisphere temperature:	932°C	Flow range:	932°C - 994°C
Flow temperature:	994°C		

DIN 51730 (1998-4) / ISO 540 (1995-03-15), excluding sphere and flow temperature

Heating profile:

Segm.	Heating rate	End temp.	Dwell time
1	10°C/min	1650°C	00:00
2			
3			
4			
5			
6			
7			

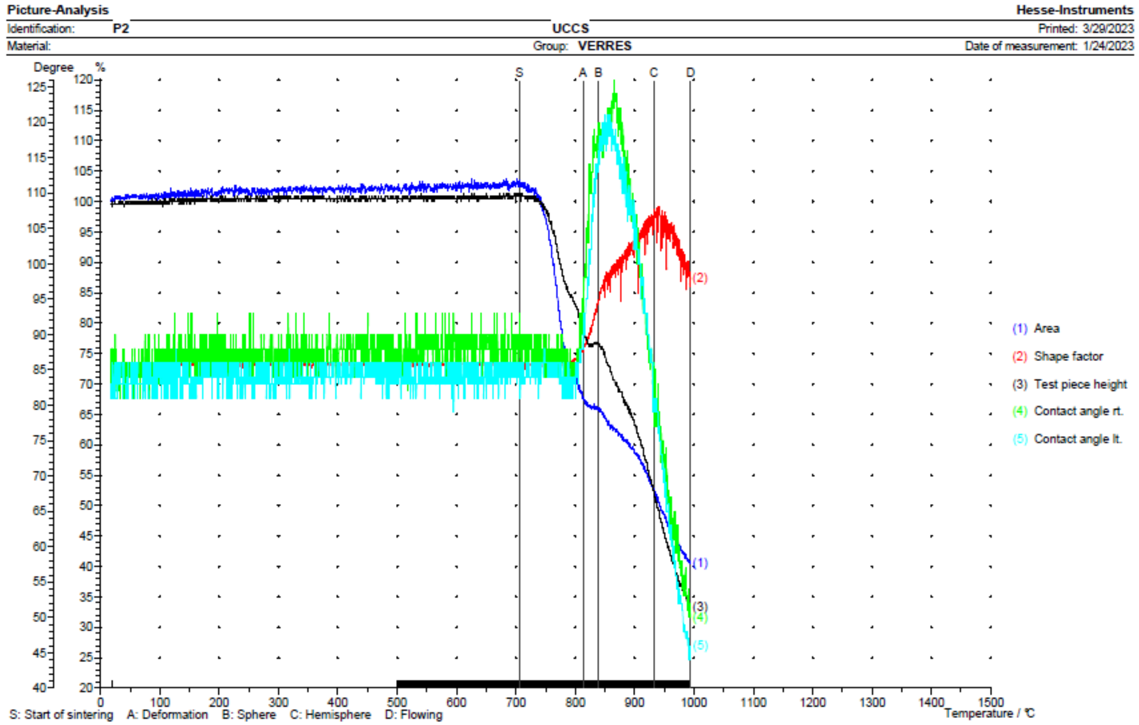
Measurement parameters:

Images:	1147
Measured data count:	8452
Tracked corner angle:	right
Operator:	François
Device:	EMI1
Measured data folder:	D:\EMI2\DATEN\verres\M2301240
Notes:	

Conditions for new images:

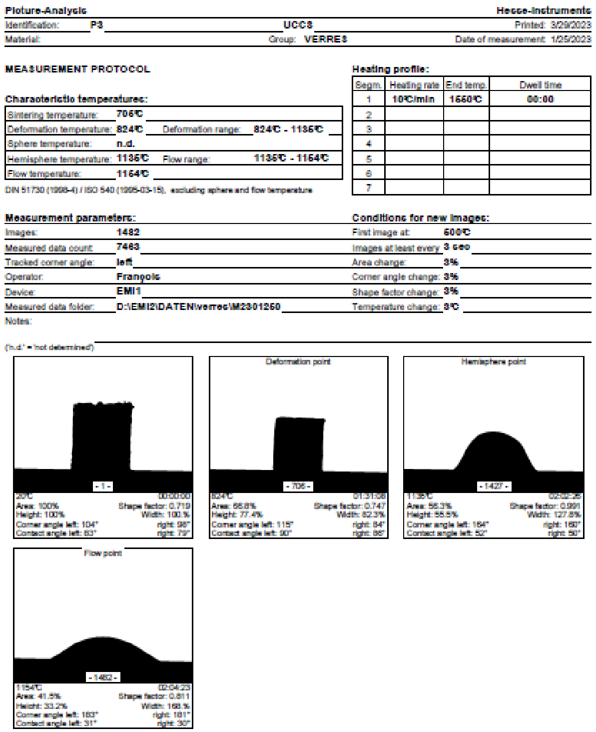
First image at:	500°C
Images at least every	3 sec
Area change:	3%
Corner angle change:	3%
Shape factor change:	3%
Temperature change:	3°C

('n.d.' = 'not determined')



$45SiO_2$ - $10B_2O_3$ - 27SrO - 18MgO (Tg = 653°C)

Influence of the composition



Picture-Analysis — **Hesse-Instruments**

Identification: P3 — UCCS — Printed: 3/29/2023

Material: — Group: VERRES — Date of measurement: 1/25/2023

MEASUREMENT PROTOCOL

Characteristic temperatures:

Sintering temperature:	706°C		
Deformation temperature:	824°C	Deformation range:	824°C - 1135°C
Sphere temperature:	n.d.		
Hemisphere temperature:	1135°C	Flow range:	1135°C - 1164°C
Flow temperature:	1164°C		

DIN 51730 (1998-4) / ISO 540 (1995-03-15), excluding sphere and flow temperature

Heating profile:

Segm.	Heating rate	End temp.	Dwell time
1	10°C/min	1550°C	00:00
2			
3			
4			
5			
6			
7			

Measurement parameters:

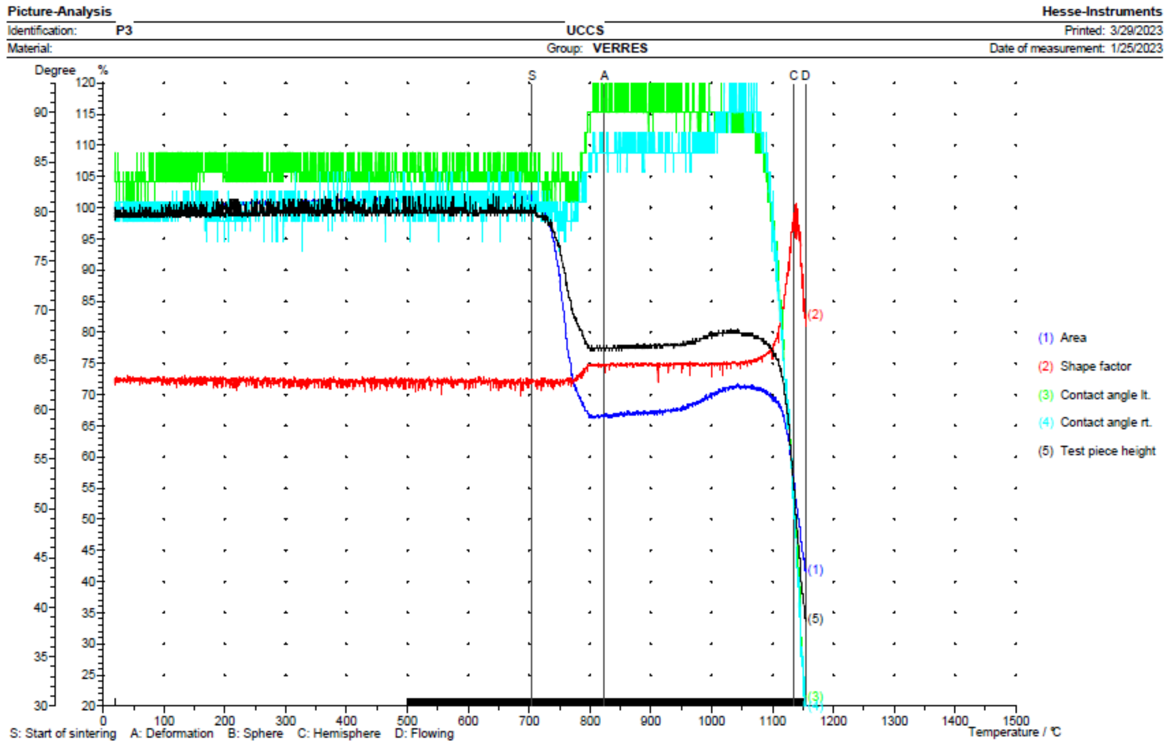
Images:	1482
Measured data count:	7463
Tracked corner angle:	left
Operator:	François
Device:	EMI1
Measured data folder:	D:\EMI2\DATEN\verres\M2301250

Conditions for new images:

First image at:	600°C
Images at least every:	3 sec
Area change:	3%
Corner angle change:	3%
Shape factor change:	3%
Temperature change:	3°C

Notes:

('n.d.' = 'not determined')



45SiO$_2$ - 10B$_2$O$_3$ - 27SrO - 18CaO (Tg = 608°C)

Determination of the viscosity-temperature

Phys. Chem. Glasses., 2005, **46** (5), 512–520

A new method for determining fixed viscosity points of glasses

M. J. Pascual, A. Durán*
Instituto de Cerámica y Vidrio (CSIC), Campus de Cantoblanco, 28049 Madrid, Spain
M. O. Prado
Centro Atómico Bariloche-Comisión Nacional de Energía Atómica, 8400 S.C. de Bariloche, Río Negro, Argentina

Influence of:

- Glass composition ⇔ surface tension (calculated by Dietzel coefficient)
- Heating rate: 5 – 10°C.min^{-1}
- Particle size / relative density: ϕ < 20 µm; 20-40 µm; 40-60 µm

➢ Viscosity values at the first shrinkage temperature TFS
Frenkel model (based on the particle size)

➢ Viscosity values at the maximum shrinkage temperature TMS
Mackenzie–Shuttleworth model (based on the softening of the glass)

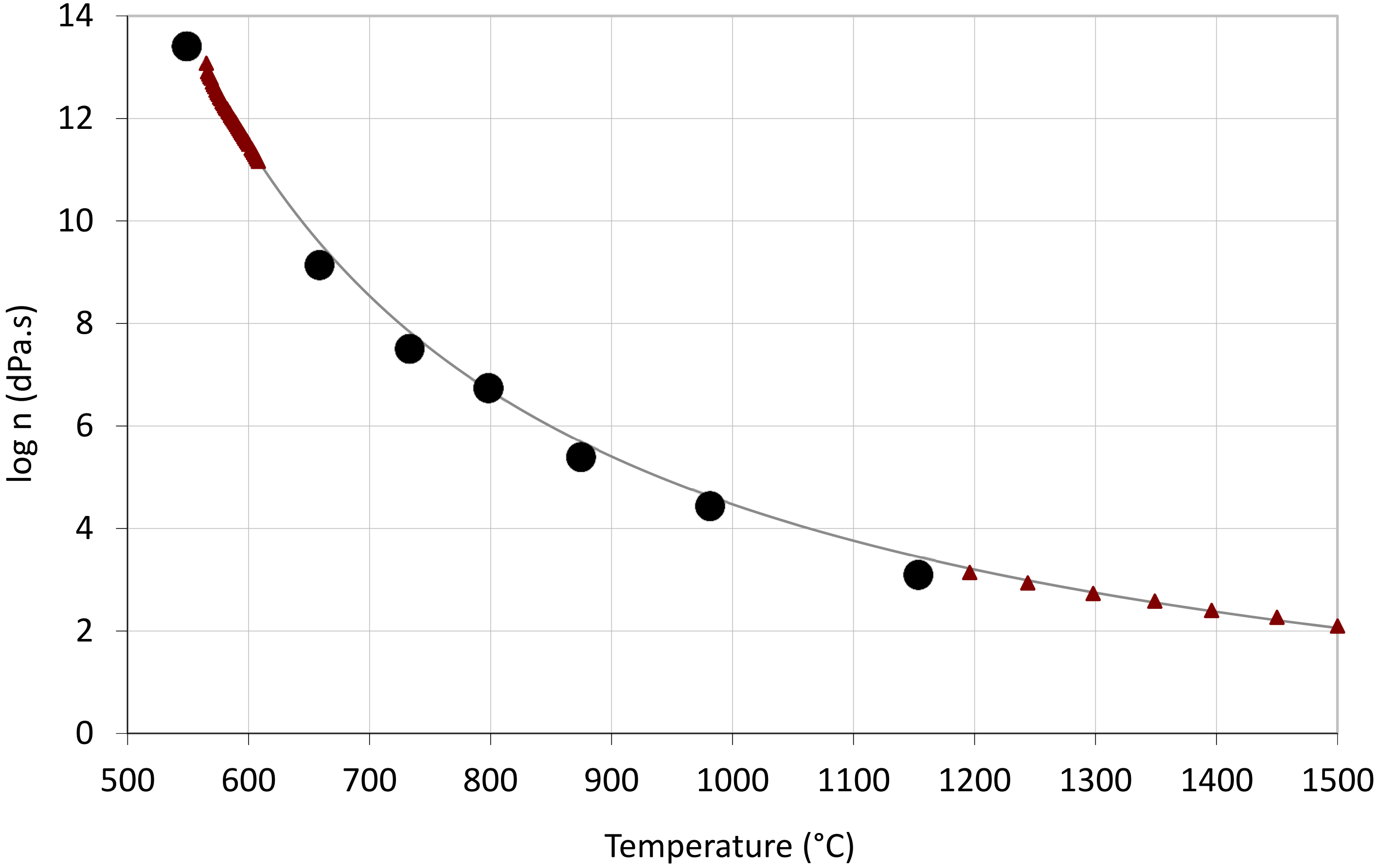
Fixed viscosity points vs. models

Viscosity points	*Scholze* [5] $\log\eta \pm \sigma$ (P)	*Pascual* et al [4] $\log\eta \pm \sigma$ (P)	*This work* $\log\eta \pm \sigma$ (P)
First shrinkage	10·0±0·3	8·9±0·25	9·1±0·1
Maximum shrinkage	8·2±0·5	7·9±0·2	7·8±0·1
Deformation	6·1±0·2	6·6±0·1	6·3±0·1
Sphere	-	-	5·4±0·1
Half ball	4·6±0·1	4·5±0·1	4·1±0·1
Flow	4·1±0·1	3·1±0·15	3·4±0·1

qualitative **quantitative**

Example: Schott 8422

$$\log \eta = A + \frac{B}{T - T_0}$$



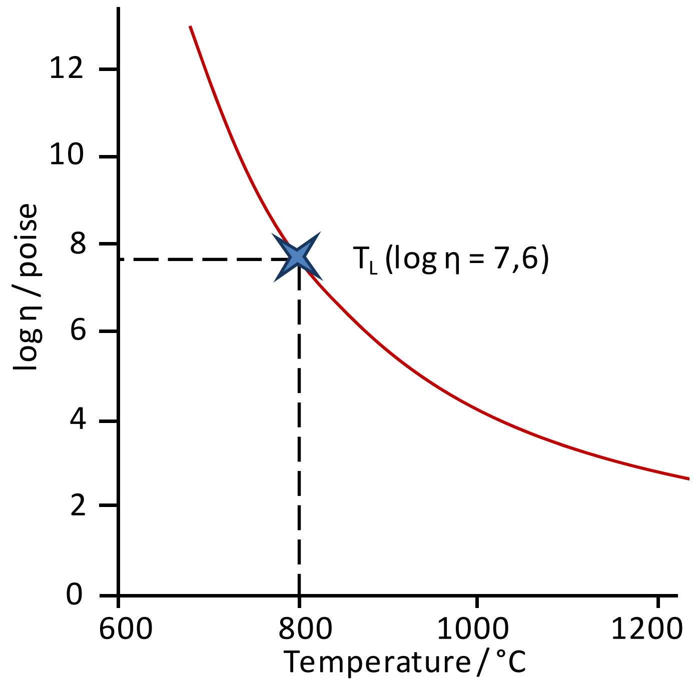
Viscous seal for SOEC

Requirements

→ $T_{Littleton}$ ($\eta = 10^{7.6}$ Poise) = 800˚C
→ Low viscosity at 900˚C
→ No crystallization at 800˚C
→ Limited interactions with other components of electrochemical systems

Selection criteria (Sciglass software)

→ $T_g > 600$˚C
→ 750˚C < $T_{Littleton}$ < 900˚C
→ TEC > 5×10^{-6} K^{-1}
→ Limited amount of P_2O_5



Coillot et al, International Journal of Hydrogen Energy, 2012

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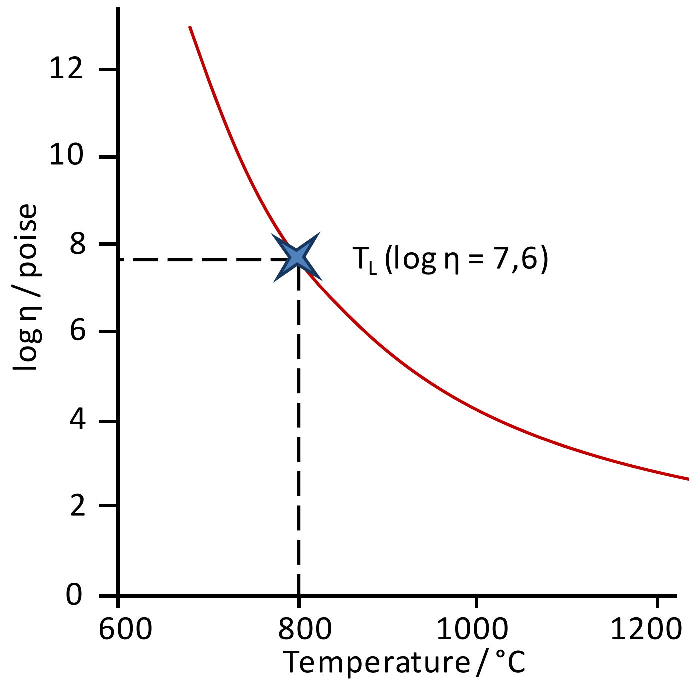

Molar %	SiO_2	ZrO_2	B_2O_3	Al_2O_3	Ga_2O_3	La_2O_3	Y_2O_3	Na_2O	K_2O	CaO	BaO	ZnO	MgO	SrO	Crystallisation	T_g / °C
Vsc1	70.24	-	1.92	5.26	-	-	-	3.60	1.19	0.60	3.32	9.05	4.82	-	Yes	650
Vsc2	63.30	-	-	-	-	-	4.99	20.72	6.81	4.45	-	-	-	-	Yes	566
Vsc3	67.46	13.34	-	-	-	1.03	-	13.67	4.50	-	-	-	-	-	No	765
Vsc4	61.39	-	6.14	-	14.34	-	-	13.67	4.46	-	-	-	-	-	No	580
Vsc5	66.01	3.43	5.57	4.21	-	-	-	2.16	0.71	12.21	-	-	-	5.70	Yes	686

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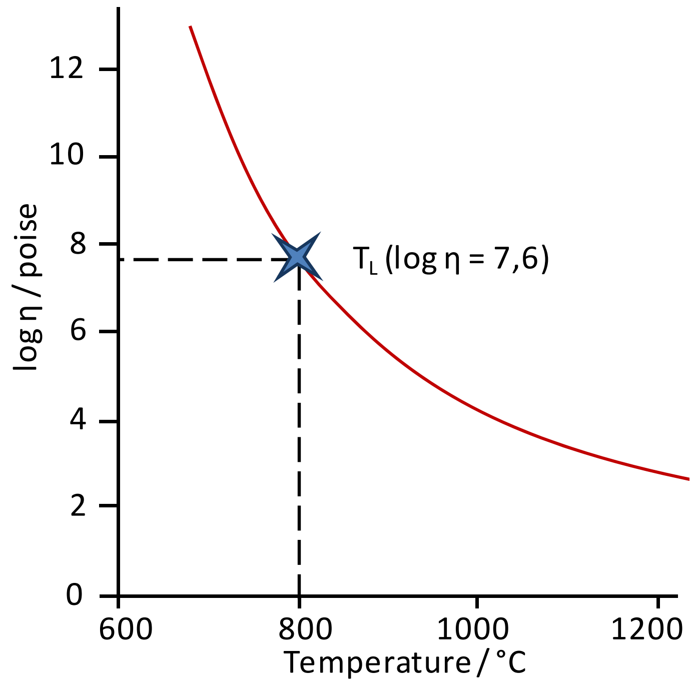

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Molar %	SiO_2	ZrO_2	B_2O_3	Al_2O_3	Ga_2O_3	La_2O_3	Y_2O_3	Na_2O	K_2O	CaO	BaO	ZnO	MgO	SrO	Crystallisation	T_g / °C
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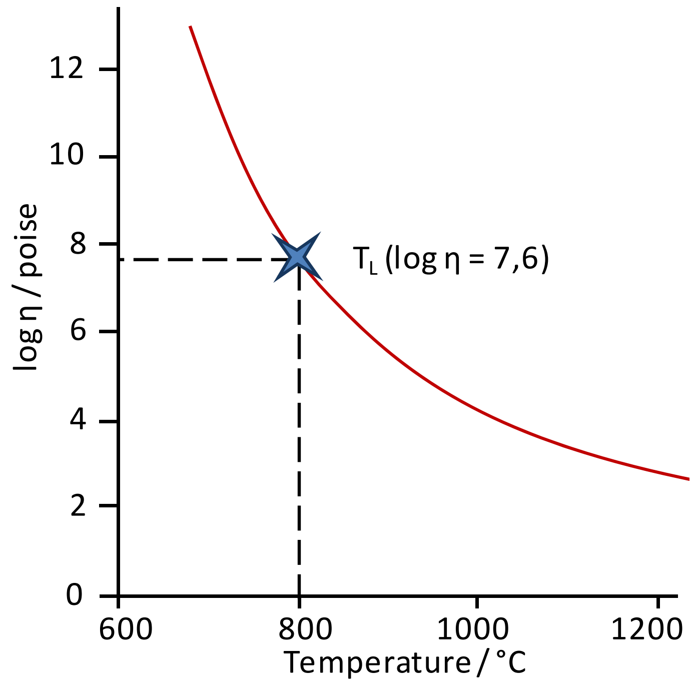

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Molar %	SiO_2	ZrO_2	B_2O_3	Al_2O_3	Ga_2O_3	La_2O_3	Y_2O_3	Na_2O	K_2O	CaO	BaO	ZnO	MgO	SrO	Crystallisation	T_g / °C
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→ $T_{Littleton}$ (η = $10^{7.6}$ Poise) = 800˚C
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Objective → **decrease of thermal characteristics**

→ ZrO_2 substituted by SiO_2 and/or B_2O_3

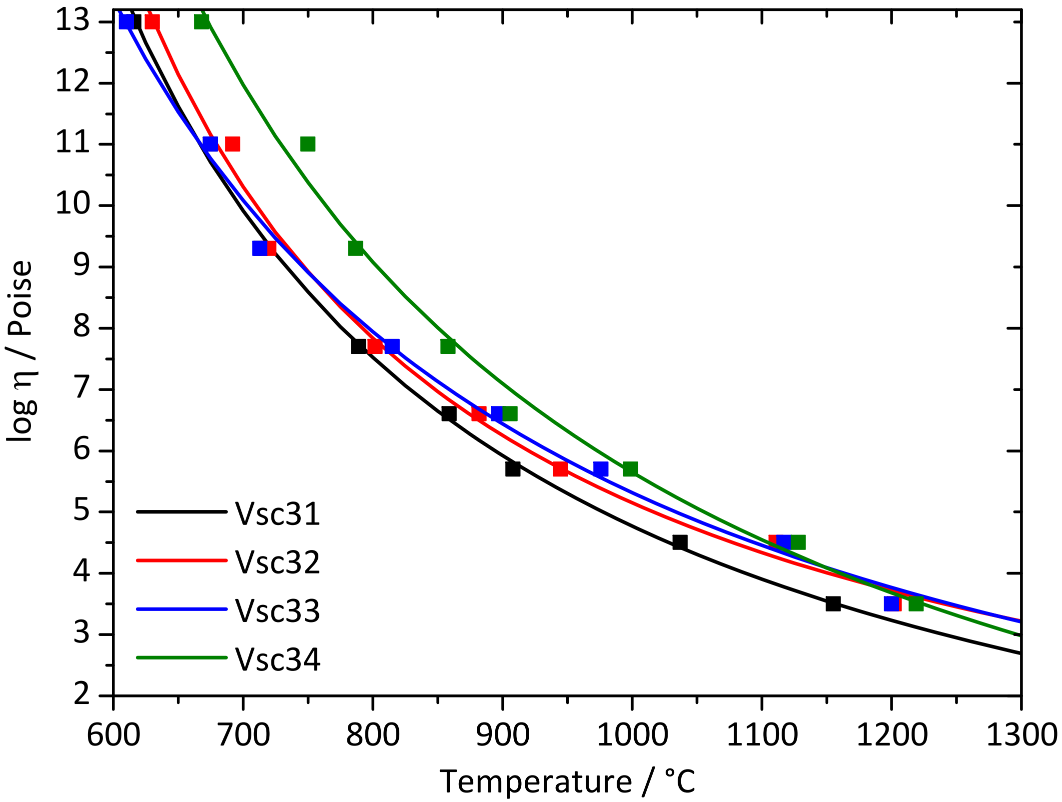
Molar %	SiO_2	ZrO_2	B_2O_3	La_2O_3	Na_2O	K_2O	Crystallisation	T_g / °C	T_s / °C
Vsc3	67.46	13.34	-	1.03	13.67	4.50	No	765	854
Vsc31	64.52	7.09	10.03	0.99	13.07	4.30	No	616	675
Vsc32	69.78	7.03	4.98	0.98	12.97	4.27	No	630	692
Vsc33	74.95	6.97	-	0.97	12.87	4.23	No	610	675
Vsc34	65.96	10.14	5.13	1.01	13.36	4.40	No	668	750

Viscous seal for SOEC

HSM Measurements

→ Applying the method to Vsc glasses

→ Least-square refinement by Vogel-Fulcher-Tammann equation: $\log \eta = A + \frac{B}{T - T_0}$



Viscous seal for SOEC

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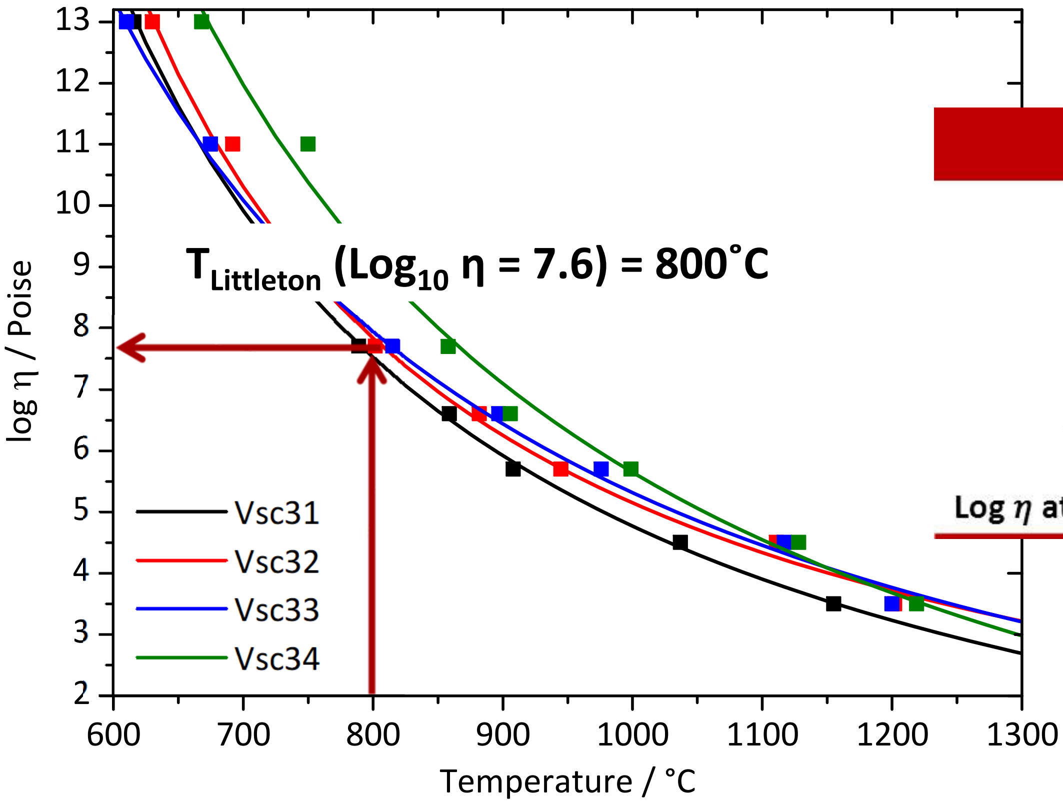
$$\log \eta = A + \frac{B}{T - T_0}$$



	Vsc31	Vsc32	Vsc33	Vsc34
a	-2.19	-1.00	-2.24	-3.58
b	4917.52	4053.35	5863.19	6809.79
t	293.96	341.80	224.28	262.17
T_L / °C	796	813	820	871
Log *η* at 900°C / Poise	5.9	6.3	6.4	7.1

Viscous seal for SOEC

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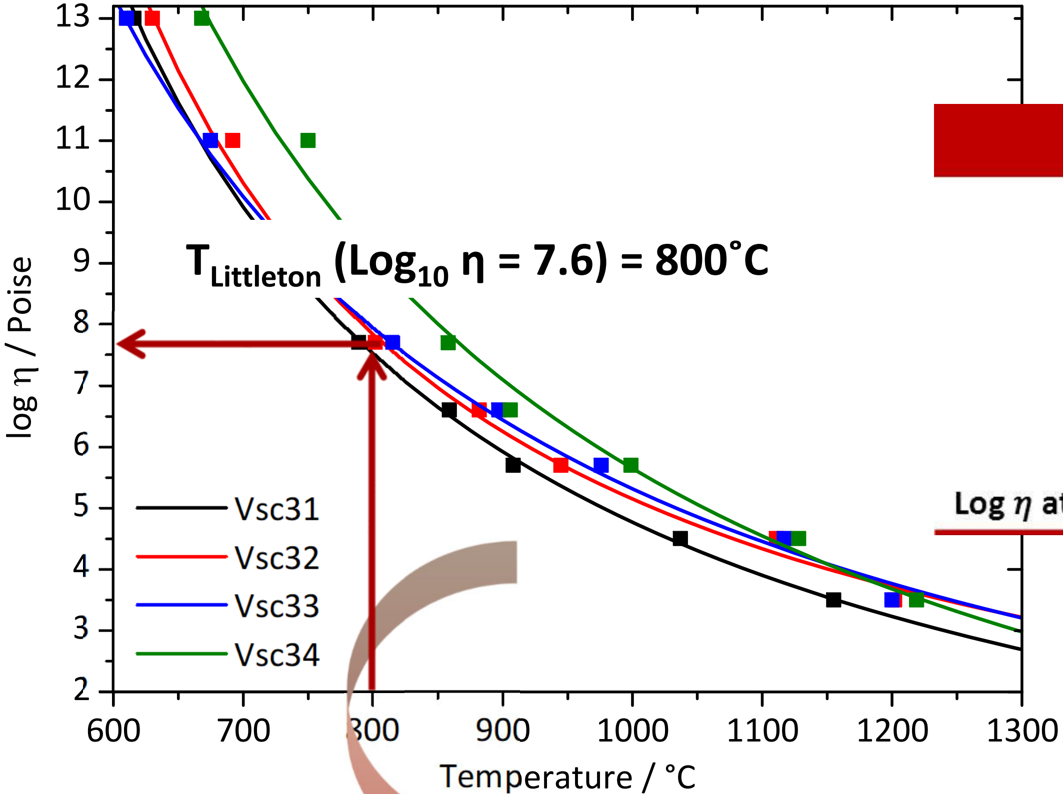
$$\log \eta = A + \frac{B}{T - T_0}$$



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t	293.96	341.80	224.28	262.17
T_L / °C	796	813	820	871
Log η at 900°C / Poise	5.9	6.3	6.4	7.1

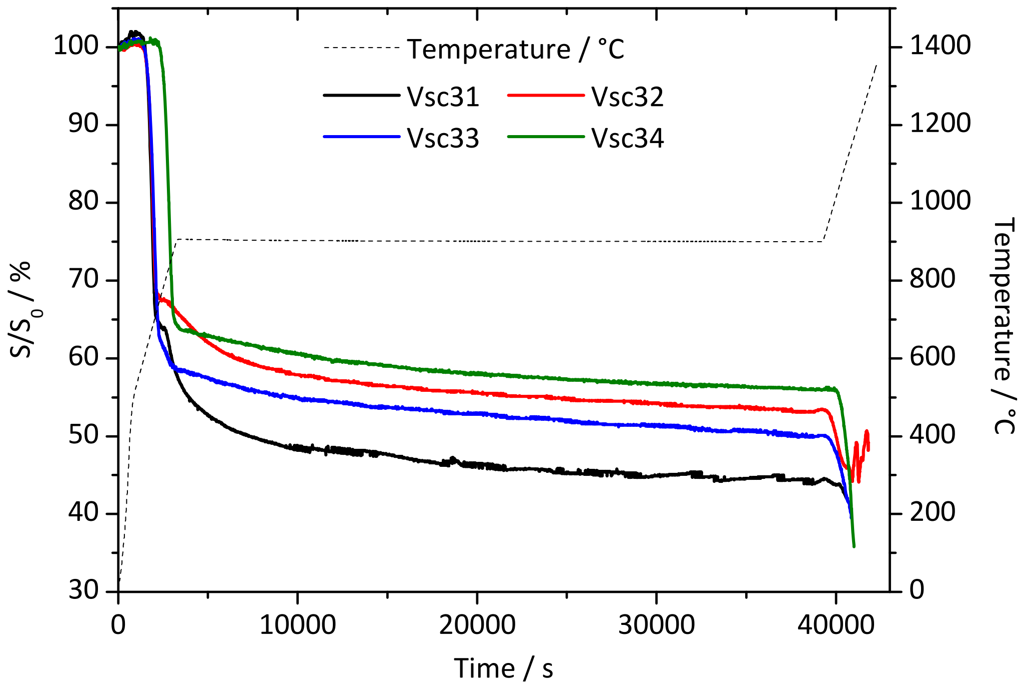
Only Vsc31, Vsc32 and Vsc33 appear suitable

Viscous seal for SOEC

HSM Measurements

→ Is the viscosity low enough to allow the seal forming at 900˚C ?

→ Heat treatment: 10h at 900˚C



Glass name and viscosity at 900°C	Initial pellet	Pellet before the plateau at 900°C	Pellet after the plateau
Vsc31 $10^{5.9}$ Poise			
Vsc32 $10^{6.3}$ Poise			
Vsc33 $10^{6.4}$ Poise			
Vsc34 $10^{7.1}$ Poise			

Viscous seal for SOEC

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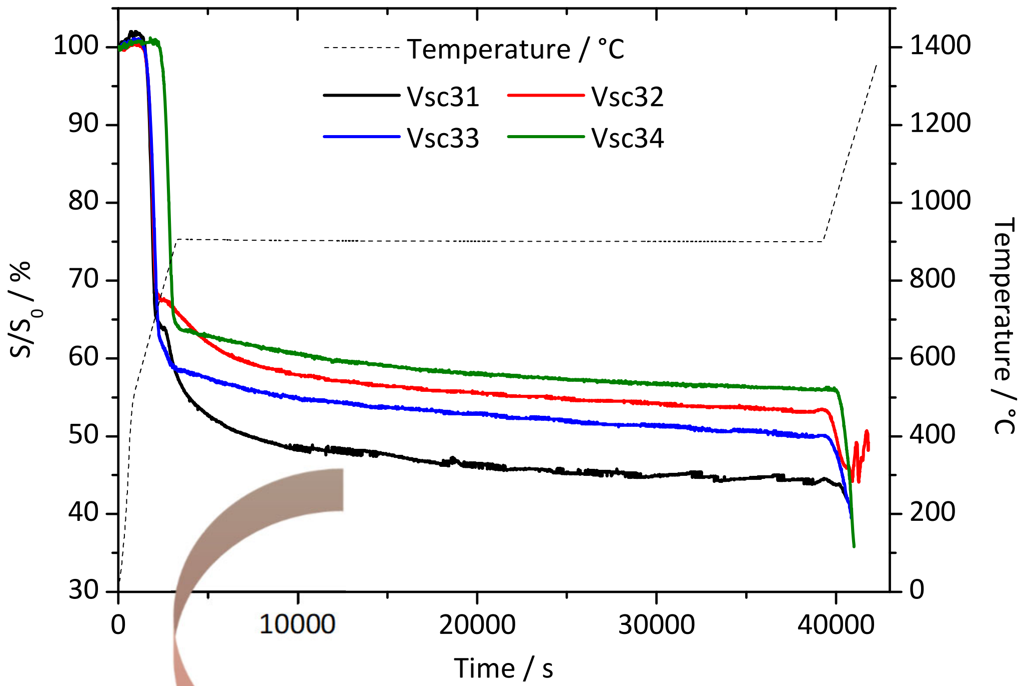
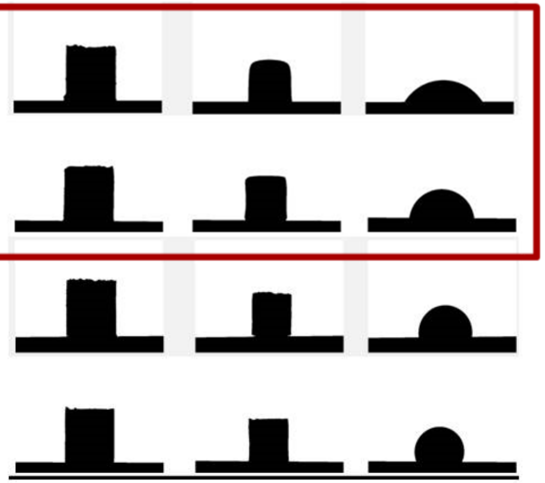


Glass name and viscosity at 900°C	Initial pellet	Pellet before the plateau at 900°C	Pellet after the plateau
Vsc31 $10^{5.9}$ Poise			
Vsc32 $10^{6.3}$ Poise			
Vsc33 $10^{6.4}$ Poise			
Vsc34 $10^{7.1}$ Poise			



⇒ Seal elaboration: easy at lower viscosity

⇒ Good wettability for Vsc31 and Vsc32 (θ < 90˚)

How to prepare a foam glass ?

➢ **Elaboration**

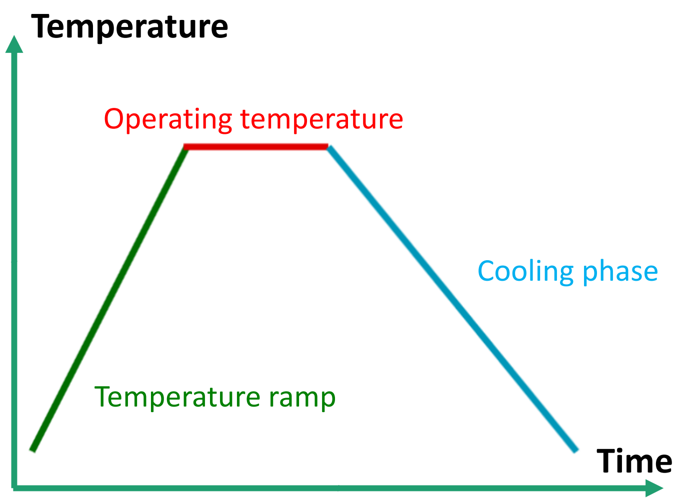
Glass waste + **Foaming agent** → (**Heat treatment**) → **Formation of gas bubbles (CO_2 or N_2)** → (**Expansion**) → **Glass foam**

➢ **Glass waste**

- **CRT**: Cathode Ray Tube glass
- **SLS**: Soda-Lime Silicate glass

➢ **Foaming agent**

e.g. AlN, **$CaCO_3$**, **SiC** or **C**

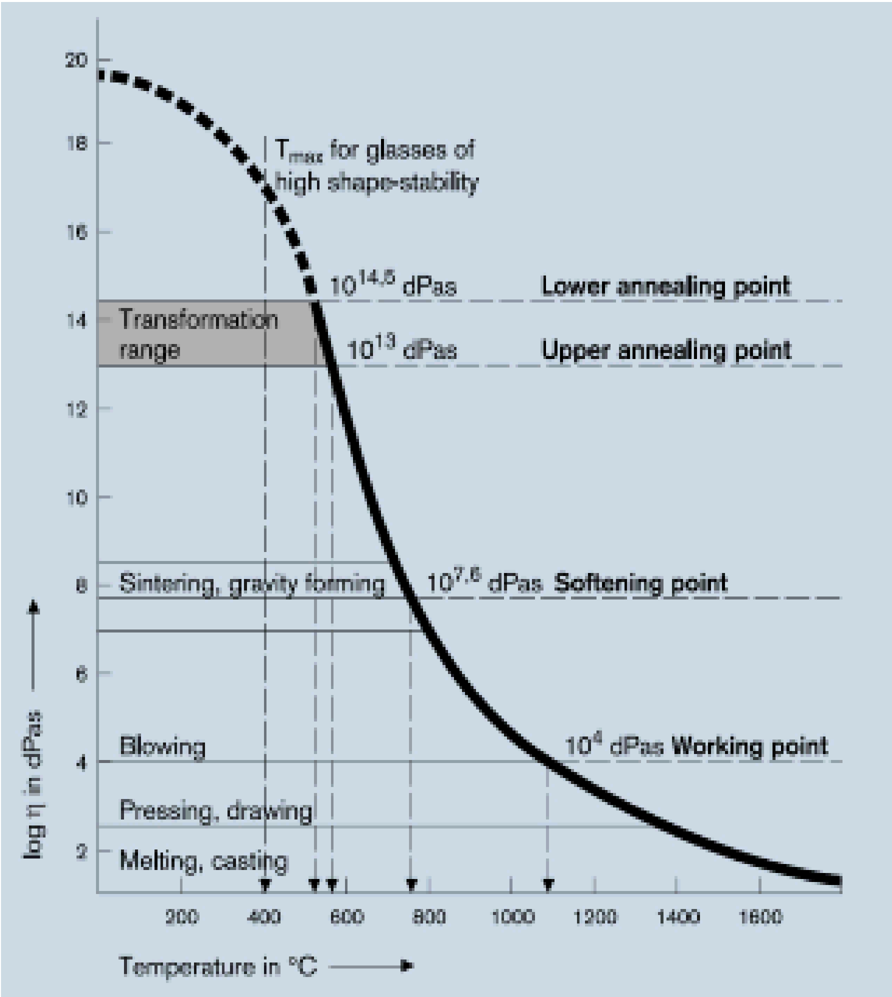


Furnace temperature vs. time

How to prepare a foam glass ?

Category	Foaming agent	Mechanism
Carbonates / sulfates	Na_2CO_3 **$CaCO_3$** $MgCa(CO_3)_2$ (Dolomite) Na_2SO_4 $CaSO_4$	Reactive- / Thermal decomposition
Metal oxides	**Mn_xO_y** Fe_xO_y Cr_xO_y PbO	Redox reaction in melt
Nitrides	**AlN** **TiN** Si_3N_4	Redox reaction
Carbonaceous	**SiC** **Carbon**	Surface reaction Solid-Gas reaction
	Water glass	
	Virgin glass	Redox

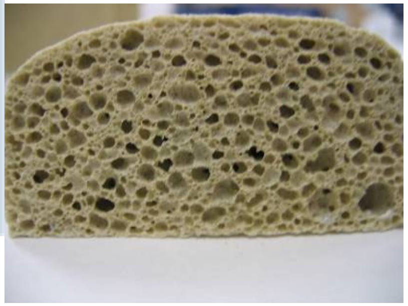
Viscous window



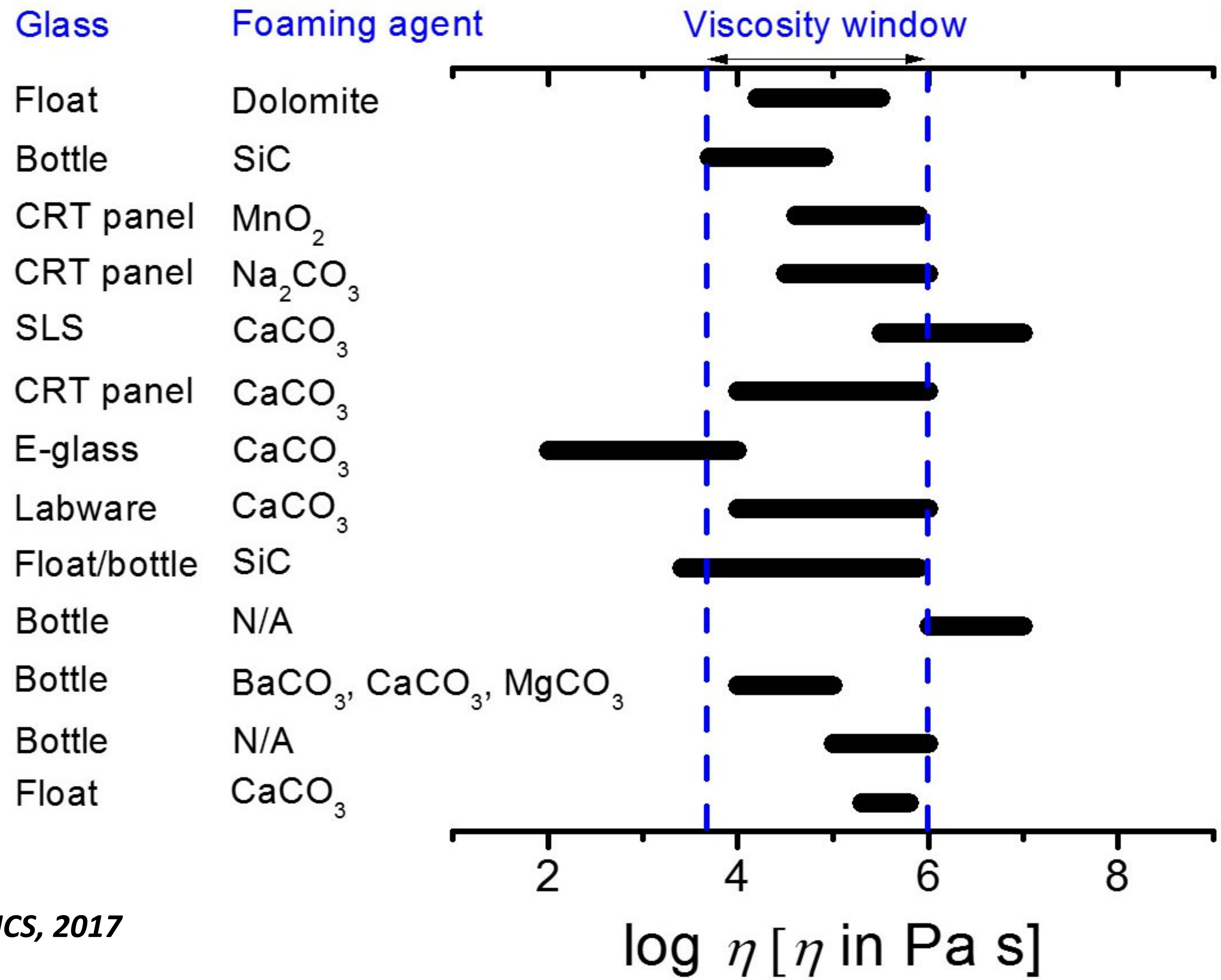
viscosity curve

Gas bubbles prisoners of the viscous melt

→ Expanded glass



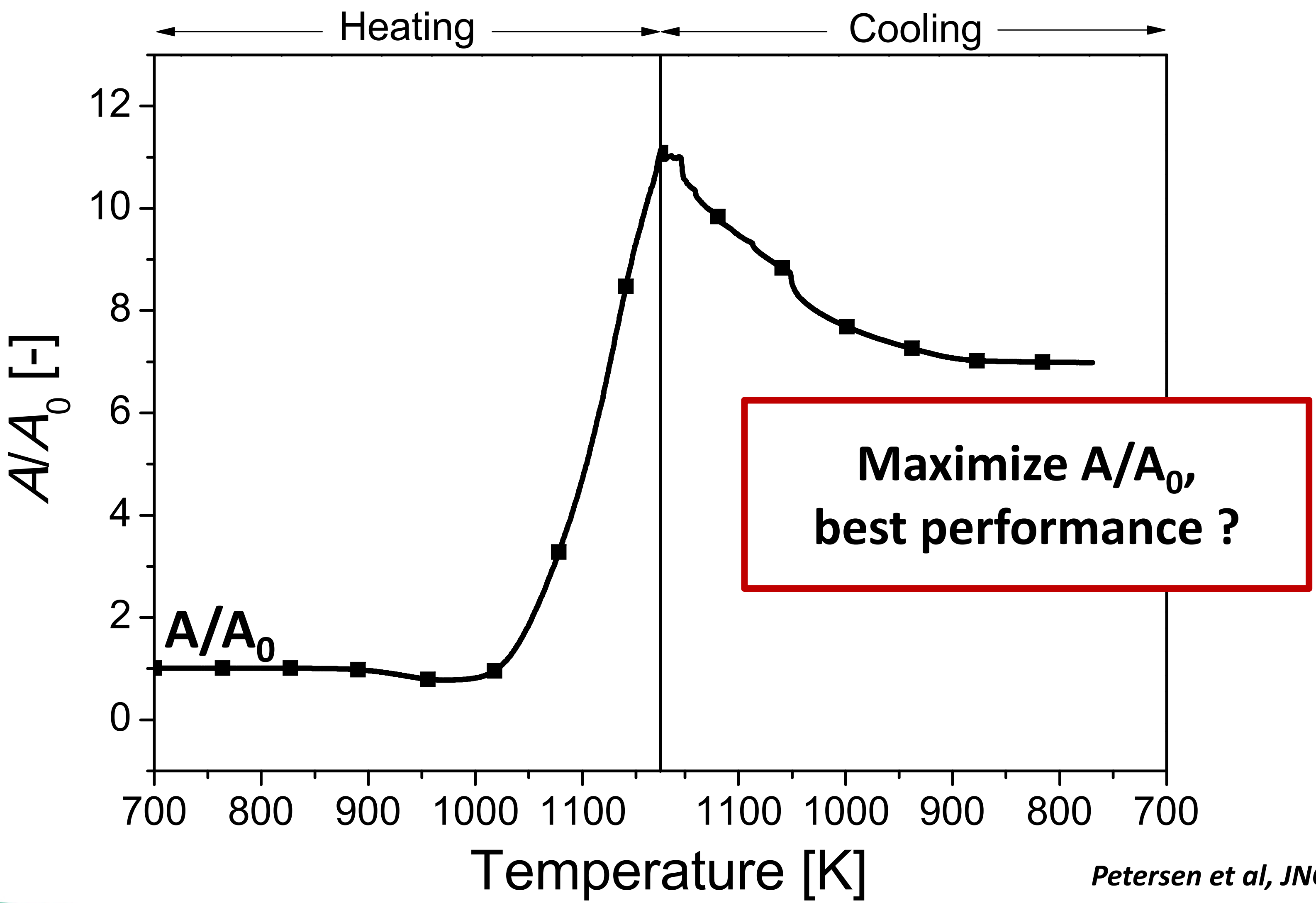
Viscous window



Petersen et al, JNCS, 2017

Foaming ability

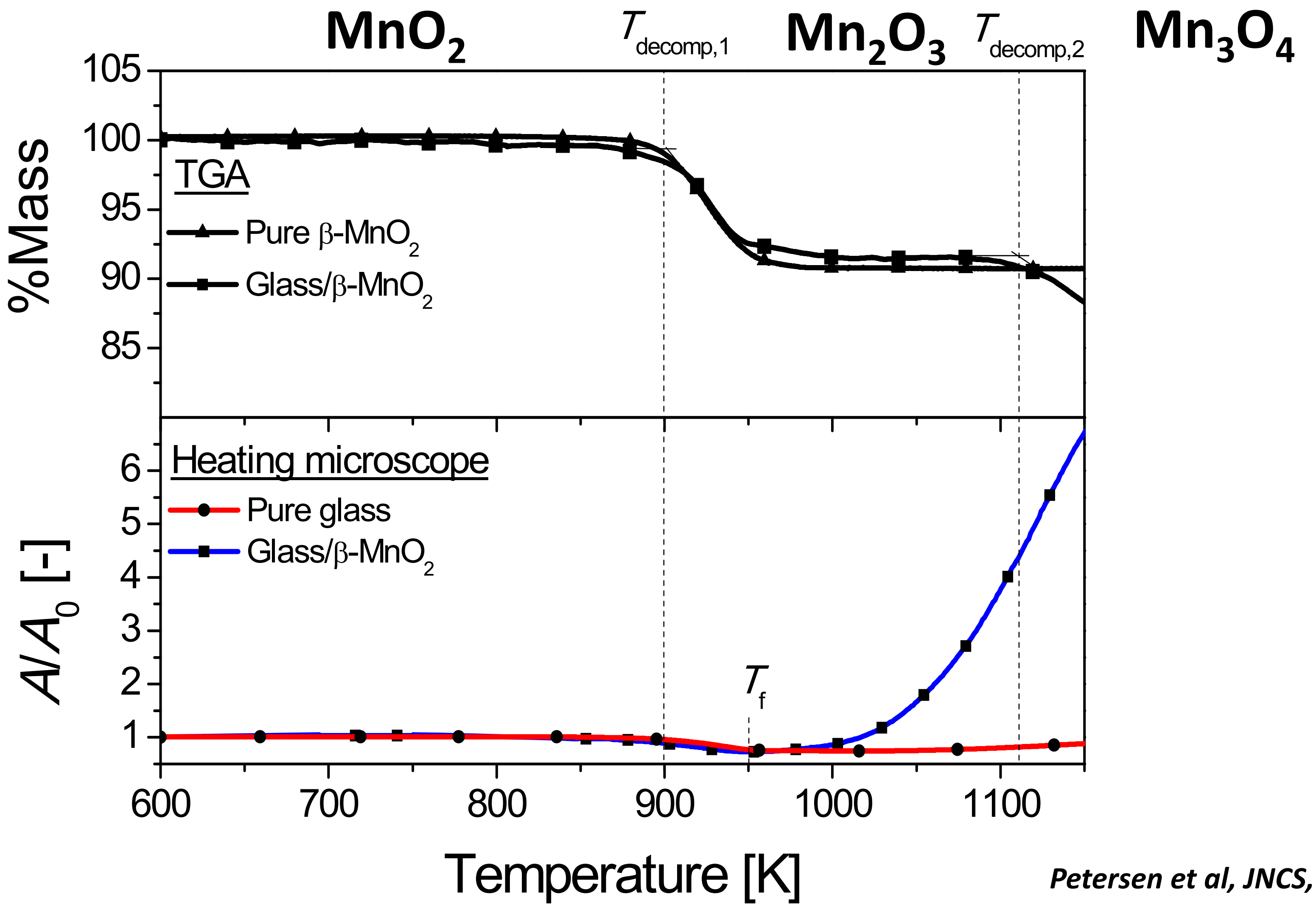
CRT panel + MnO_2



Petersen et al, JNCS, 2017

Foaming reaction

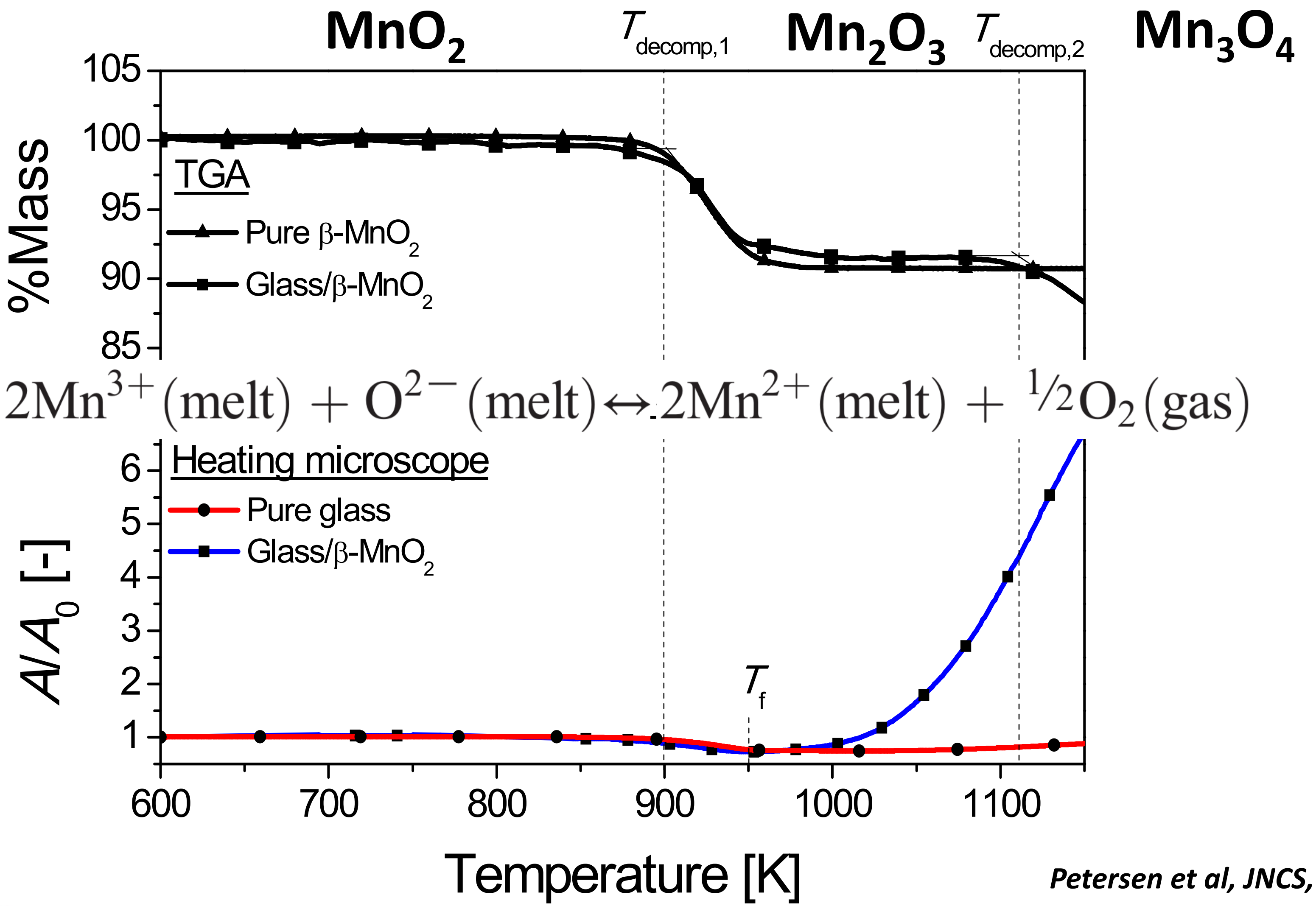
CRT panel + MnO_2



Petersen et al, JNCS, 2015

Foaming reaction

CRT panel + MnO_2

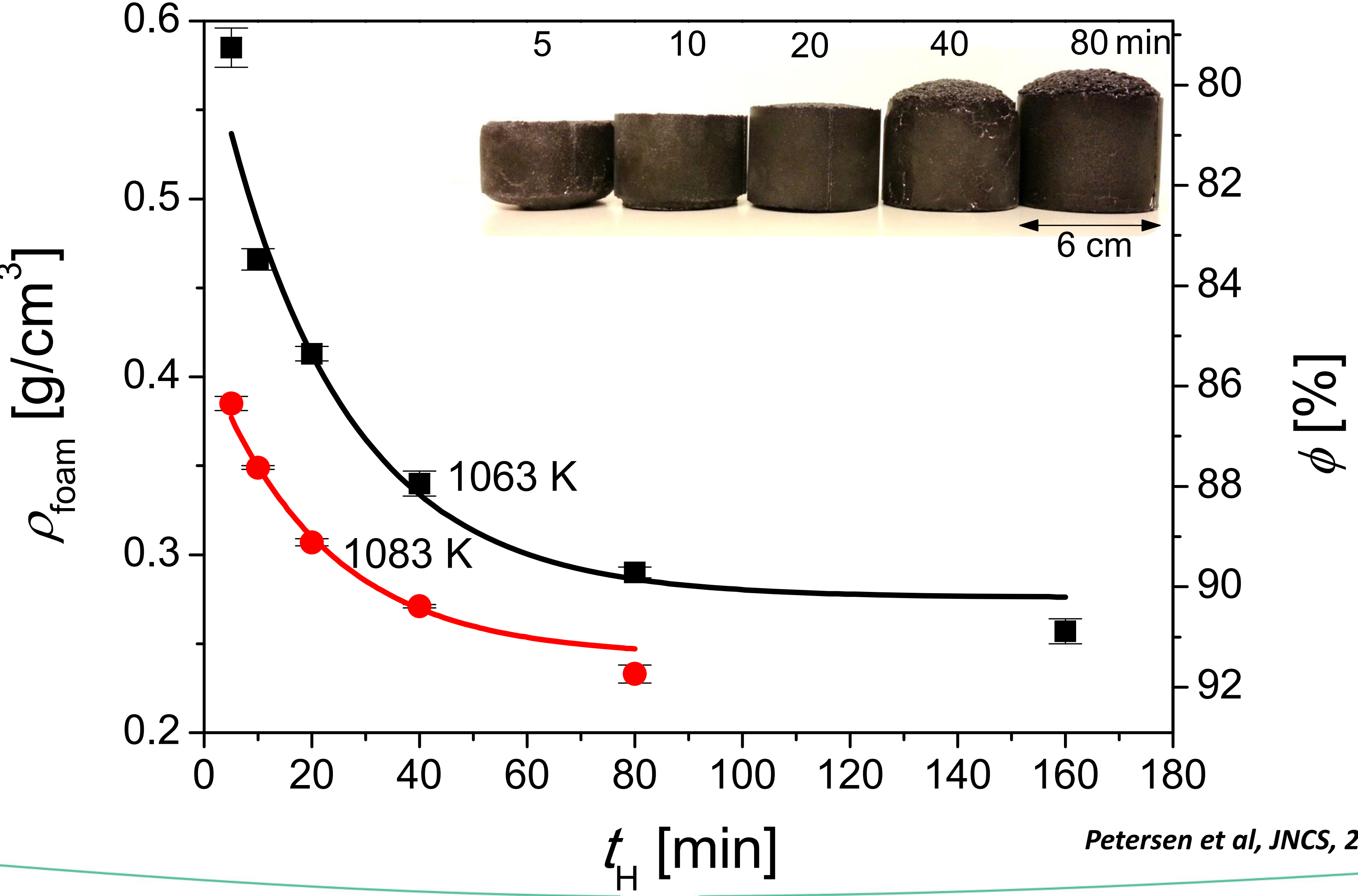


$$2Mn^{3+}(melt) + O^{2-}(melt) \leftrightarrow 2Mn^{2+}(melt) + \tfrac{1}{2}O_2(gas)$$

Petersen et al, JNCS, 2015

Volume expansion

CRT panel + MnO_2



Petersen et al, JNCS, 2015