Synthesis and properties of new geopolymeric foams

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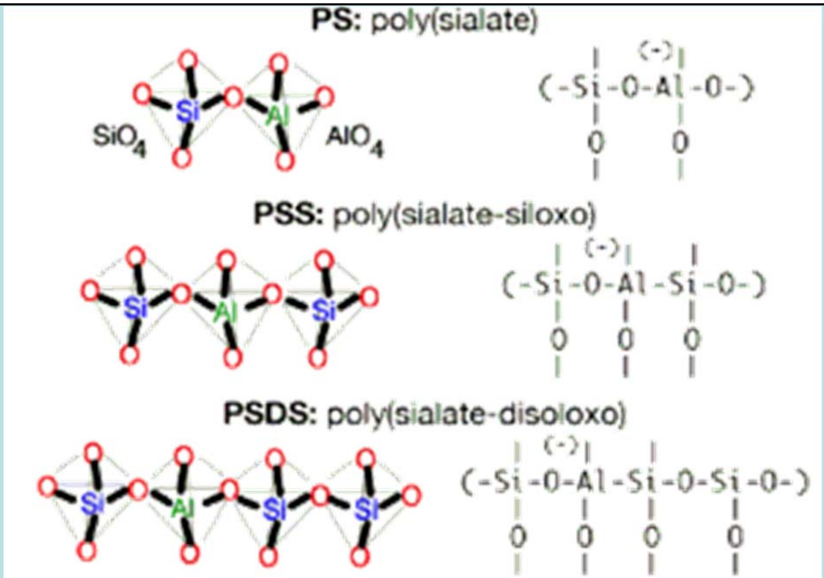
What are Geopolymers?
Alkali-bonded inorganic polymers

The reaction of a solid aluminosilicate with a highly concentrated aqueous alkali hydroxide or silicate solution produces a synthetic amorphous to semi-crystalline alkali aluminosilicate material called "GEOPOLYMER"

The word "Geo" implies that these materials mimic natural minerals (ex. clay)

These synthetic materials can be considered INORGANIC POLYMERS because they are made of long chain molecules of alumino-silicates



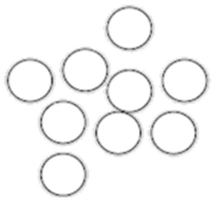
The geopolymers are designated as poly(sialate), an abbreviation for poly(silico-oxo-aluminate) or (- Si-O-Al-O -)n (with n degree of polymerization).

The sialate network consists of SiO_4 and AlO_4^- tetrahedra linked in an alternating sequence by sharing all of the interstitial oxygens.

Positive ions (Na^+, K^+, Li^+, Ca^{++}, Ba^{++}, NH_4^+ and H_3O^+) must be present in the framework cavities to balance the negative charge of Al^{3+} in IV-fold co-ordination.

Aim of the work

Consolidation of ceramic-like materials, geopolymeric resins and foams, with tailored porosity in the nano-ultramacro range, in the view of potential applications (catalysis, thermal insulation, filtration..).



Metakaolin

Highly reactive raw material

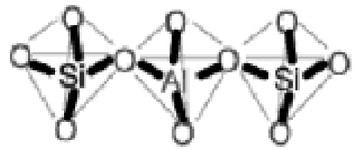
+

KOH/K_2SiO_3

$SiO_2:K_2O= 2$

→

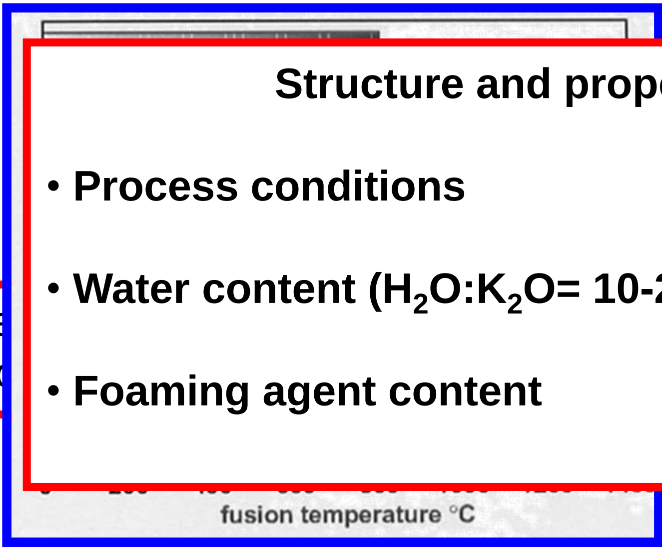
PSS: poly(sialate-siloxo)

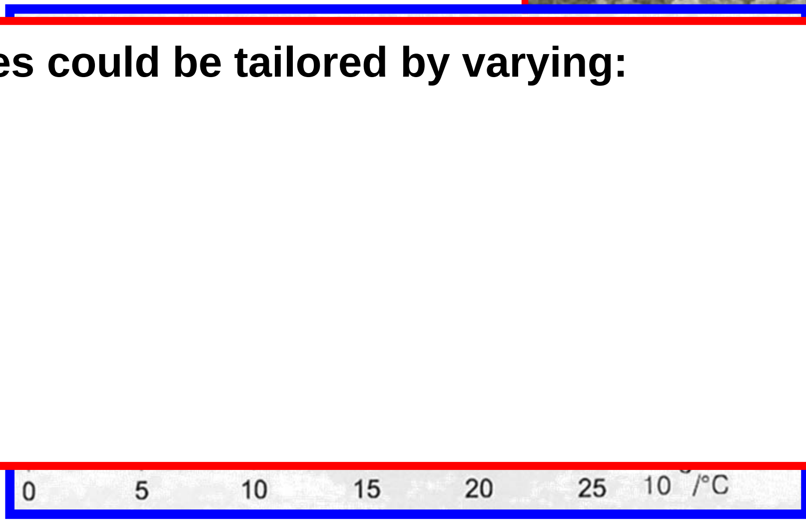


K-PSS

Si/Al=2

Thermal expansion coefficient





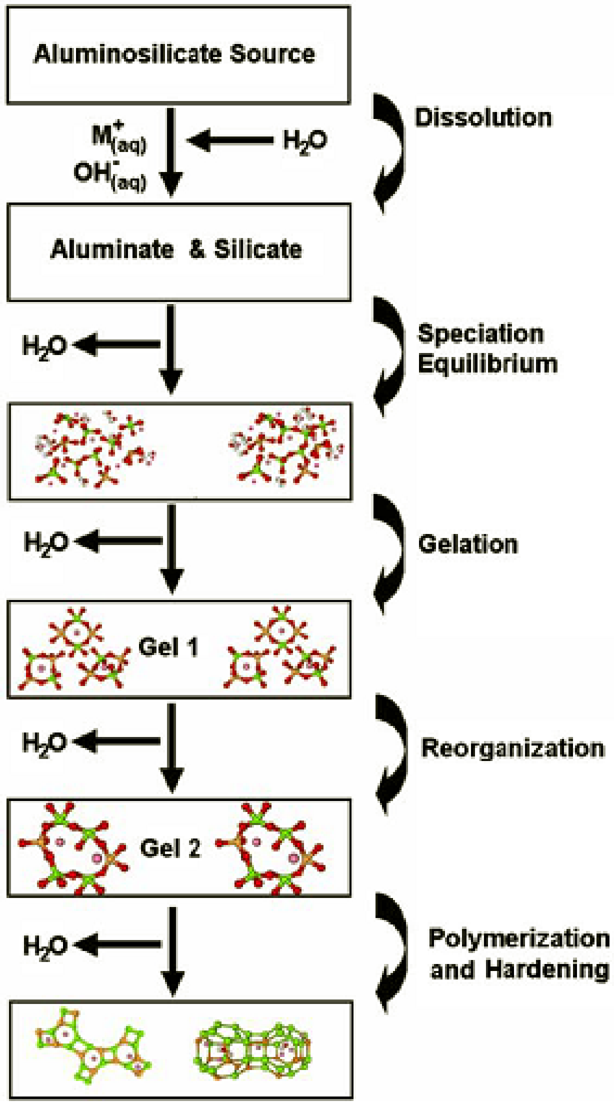
Structure and properties could be tailored by varying:

- **Process conditions**
- **Water content ($H_2O:K_2O= 10-23$)**
- **Foaming agent content**

The

sinc

Variation of K-PSS intrinsic porosity by water dilution



Geopolymerization steps:

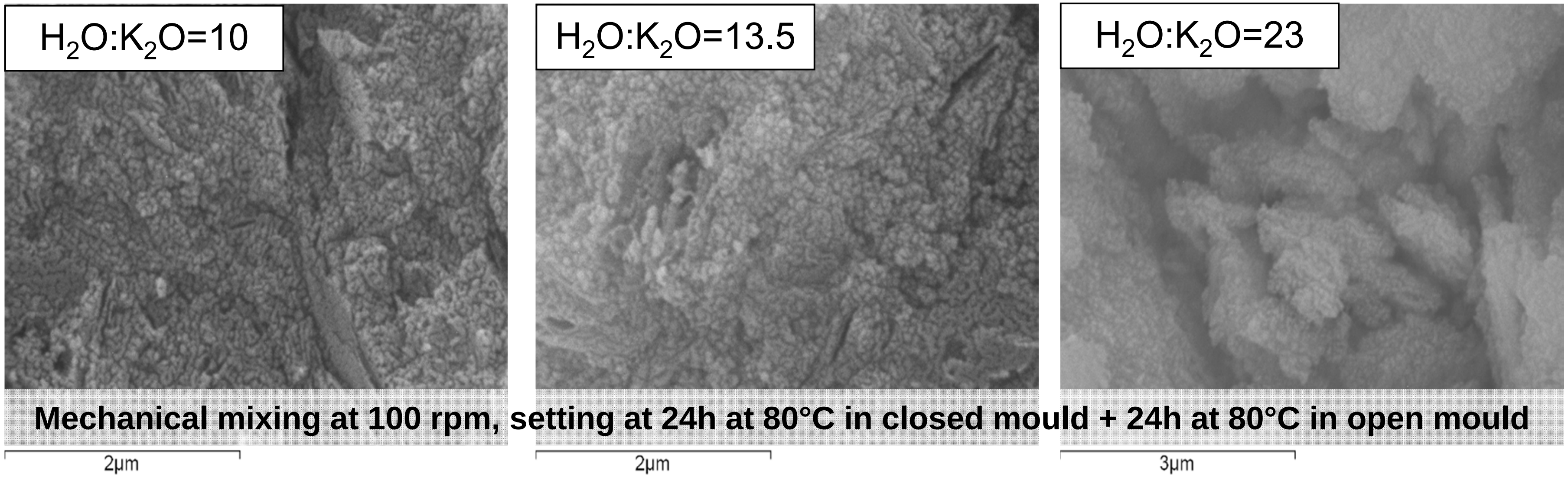
1) Dissolution - hydrolysis

2) Hydrolysis - polycondensation

Water = necessary to dissolve the solid particles and hydrolyze the Al $^{3+}$ e Si $^{4+}$ ions.

Water does not enter into the geopolymeric framework, it gives rise to a steric hindrance and acts as a pore forming agent upon its removal during setting

Variation of K-PSS intrinsic porosity by water dilution



Mechanical mixing at 100 rpm, setting at 24h at 80°C in closed mould + 24h at 80°C in open mould

$H_2O:K_2O$	Porosity* %	Mean pore diameter* μm	S_{BET} m^2/g	Vp cm^3/g
10	29.2	0.01	40	0.168
13.5	35.6	0.03	40	0.245
23	56.2	0.54	16	0.078

*by Hg intrusion porosimetry

Design of intrinsic nano-micro porosity:

Filtering

Heat exchanger and passive cooling

Catalysis (ionic exchange of M^{n+})

Inorganic *in situ* foam formation

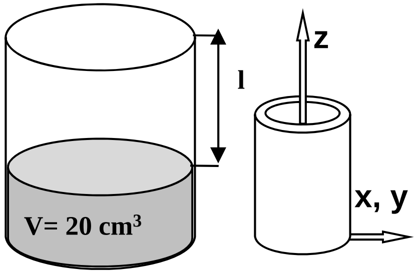
Gas evolution leads to foamed architectures when the viscosity of the slurry contemporary increases and the material consequently consolidates.

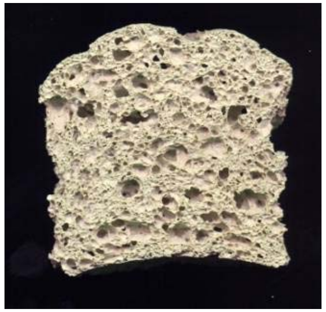
Redox reaction with H_2 evolution

$Si^0 \rightarrow Si^{4+} + 4e^-$ (1)

$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$ (2)

$4H_2O + Si_0 \rightarrow 2H_2\uparrow + Si(OH)_4$ (3)





Water consuming and exothermic reaction

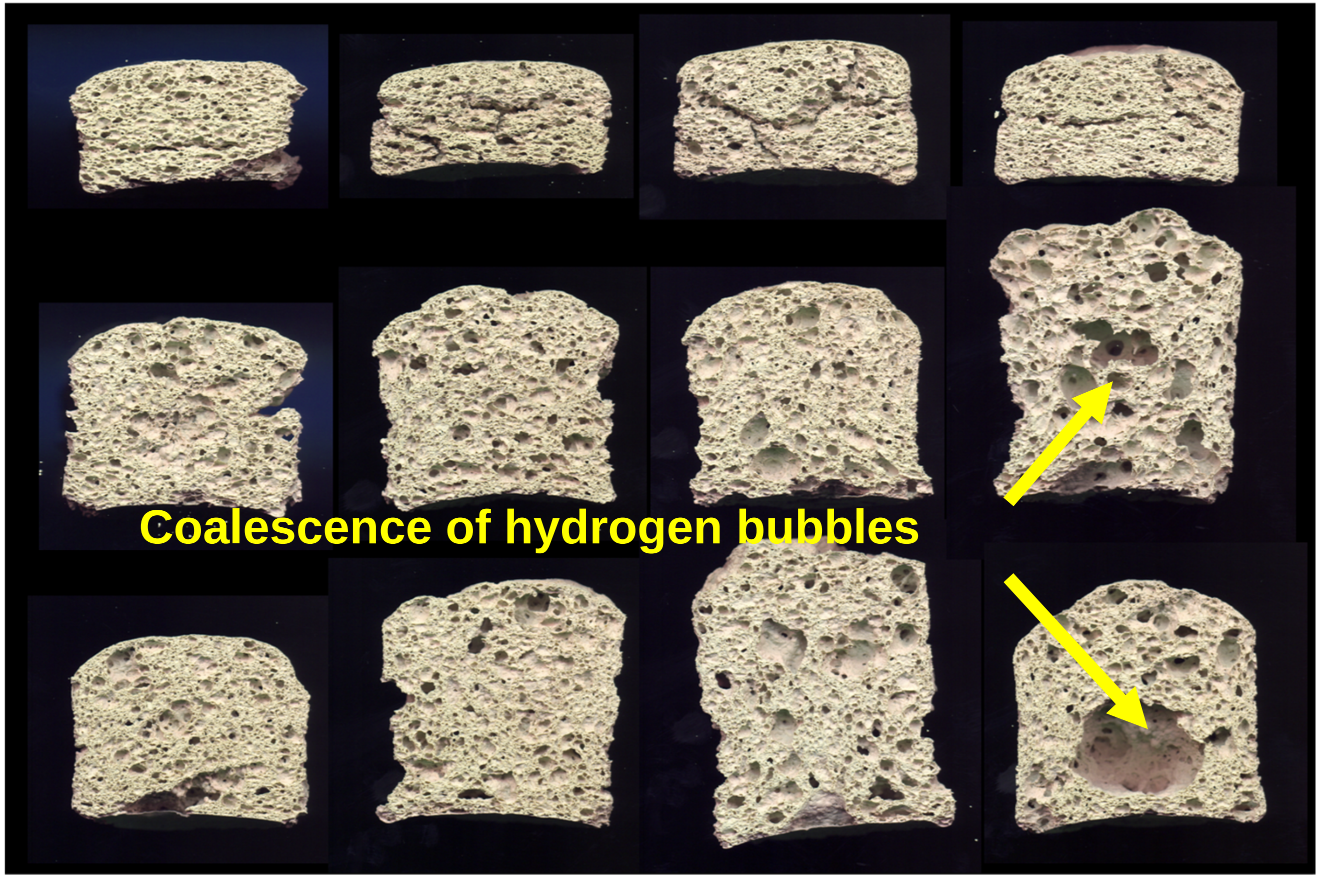
$\Delta H = -314$ kJ/mol at 25°C

Study of the foaming in situ conditions to obtain fully reacted structures with tailored ultra-macro porosity.

Si^0 addition effects

Sample F13 (H_2O:K_2O=13.5) added with increasing amounts of metallic Si and treated with different curing temperatures

	RT	40°C	60°C	80°C



0.38% Si

1.15% Si

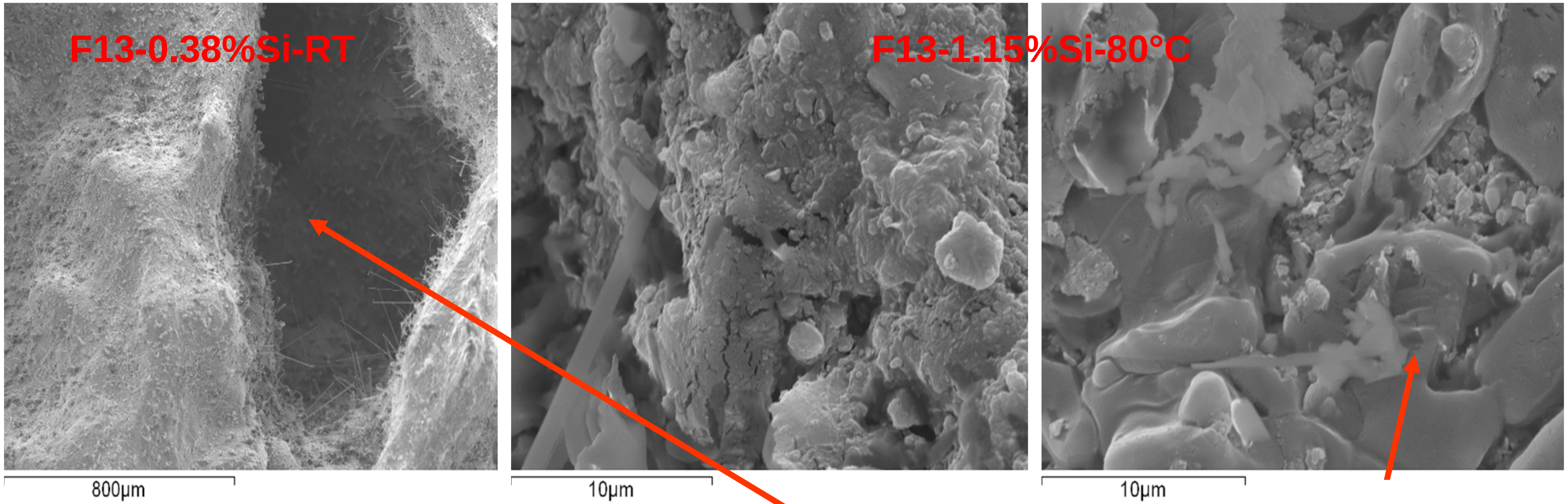
1.90% Si

Si^0 addition effects

Sample F23 (H_2O:K_2O=23): high dilution and high content of Si^0 make the structure collapse.

Collapsed structure

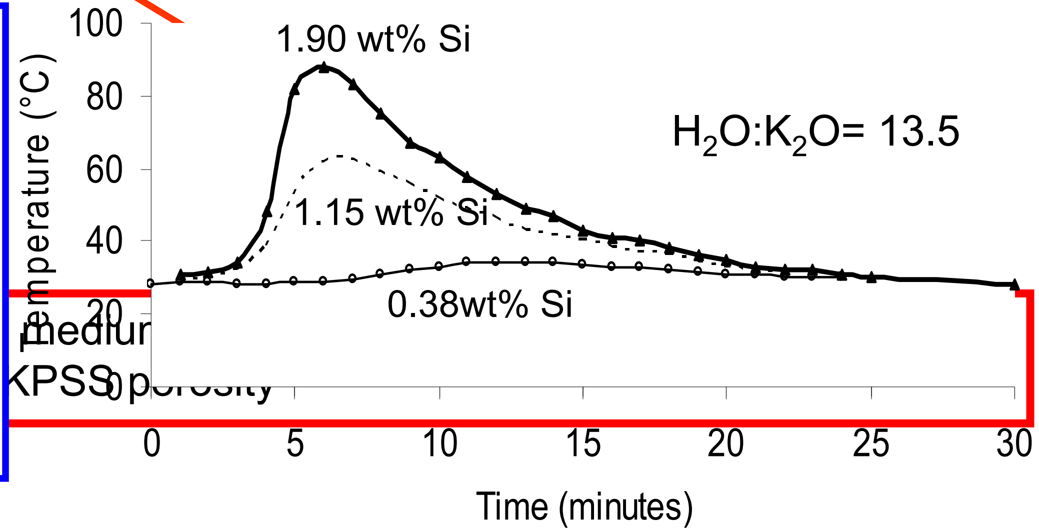
Microstructural characterization



Si^0 (s) + $4H_2O$ (l) → $2H_2$ (g) + H_4SiO_4 (aq)
ΔH= -314 kJ a 25 °C
ΔG = - 359.4 kJ a 25 °C e - 366.6 kJ a 80 °C

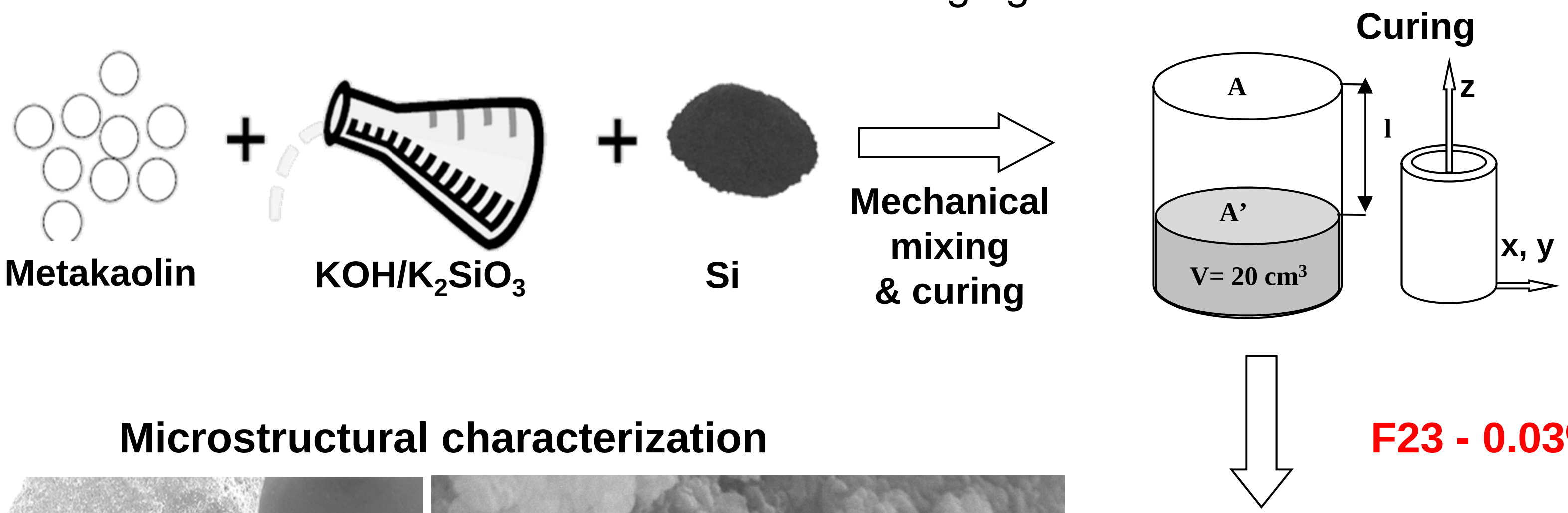
Elimination of the water (reaction medium) favored by:

- The redox reaction is water consuming
- Water evaporation

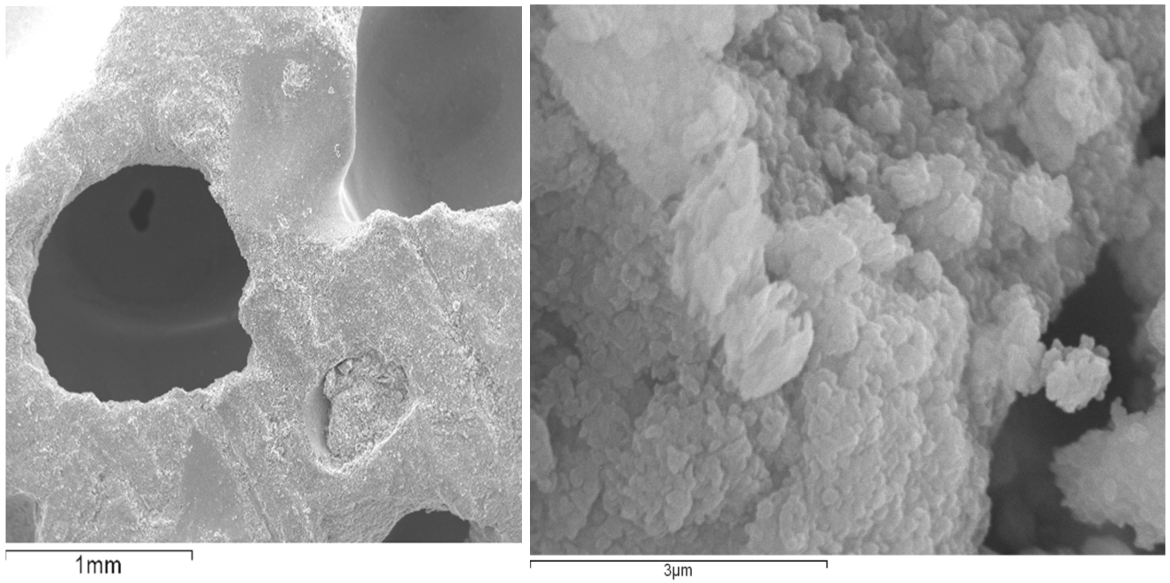


Best method to produce geopolymeric foams

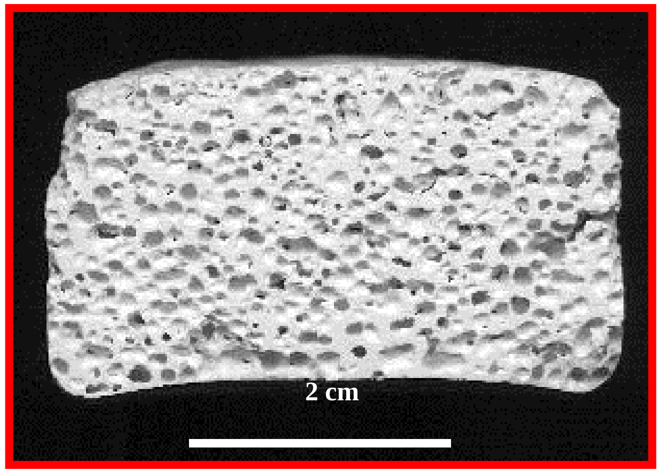
Lower content of foaming agent Si^0



Microstructural characterization



F23 - 0.03%Si

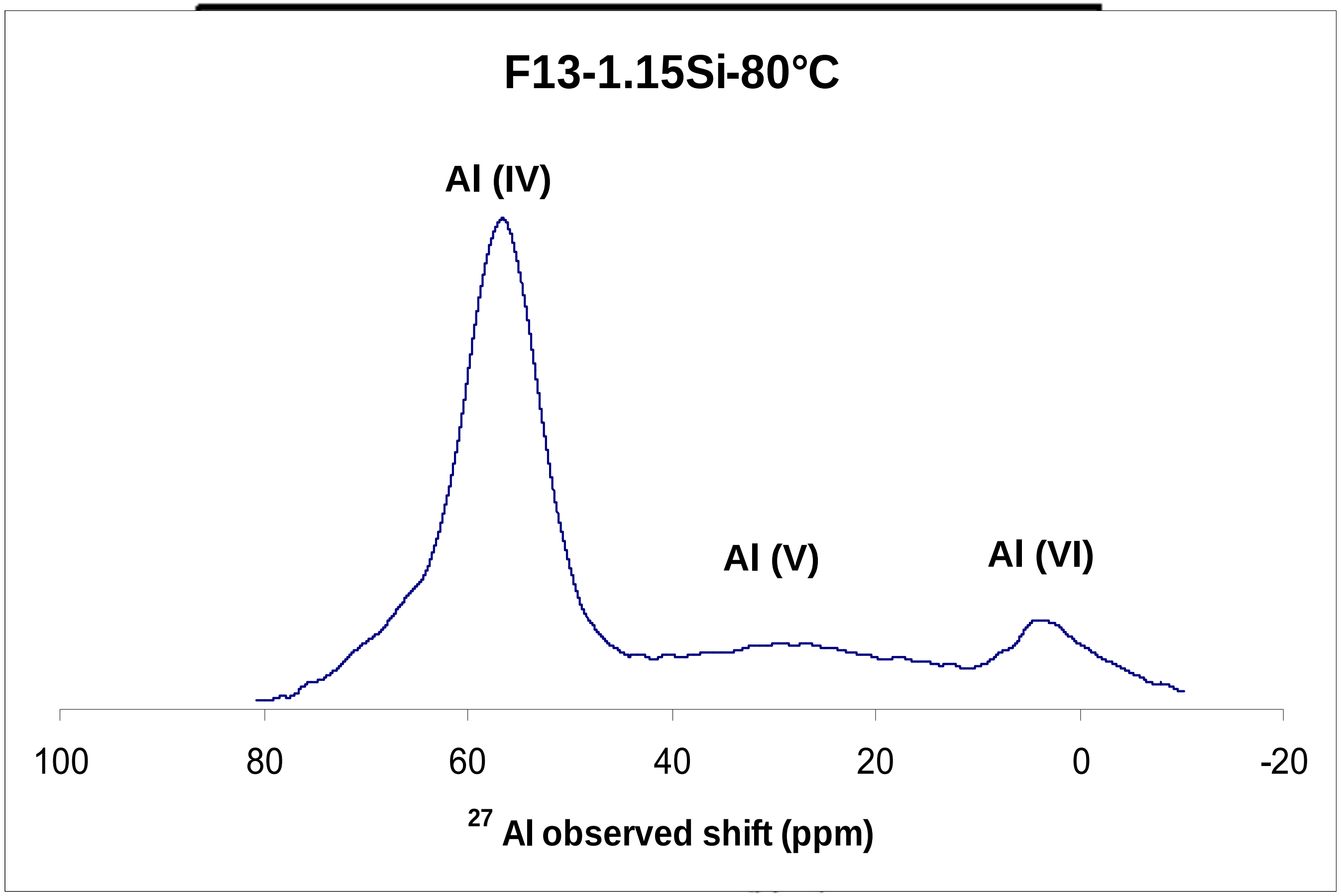


Geopolymerization degree and accessibility of the geopolymer inner volume

Samples	Geopolymerization degree (%)	$NH4^{+}$ exchange capacity (%)
G10	98	28
G13	98	26
G23	98	28
F13-0.04%Si	97	27
F23-0.03%Si	97	26
F13-1.15%Si-RT	64	9
F13-1.15%Si-80°C	63	7

Geopolymerization degree and accessibility of the geopolymer inner volume

Negligible presence of octahedral and penta-coordinated Al atoms, significant for metakaolin clearly evidence complete transformation of metakaolin to the geopolymer

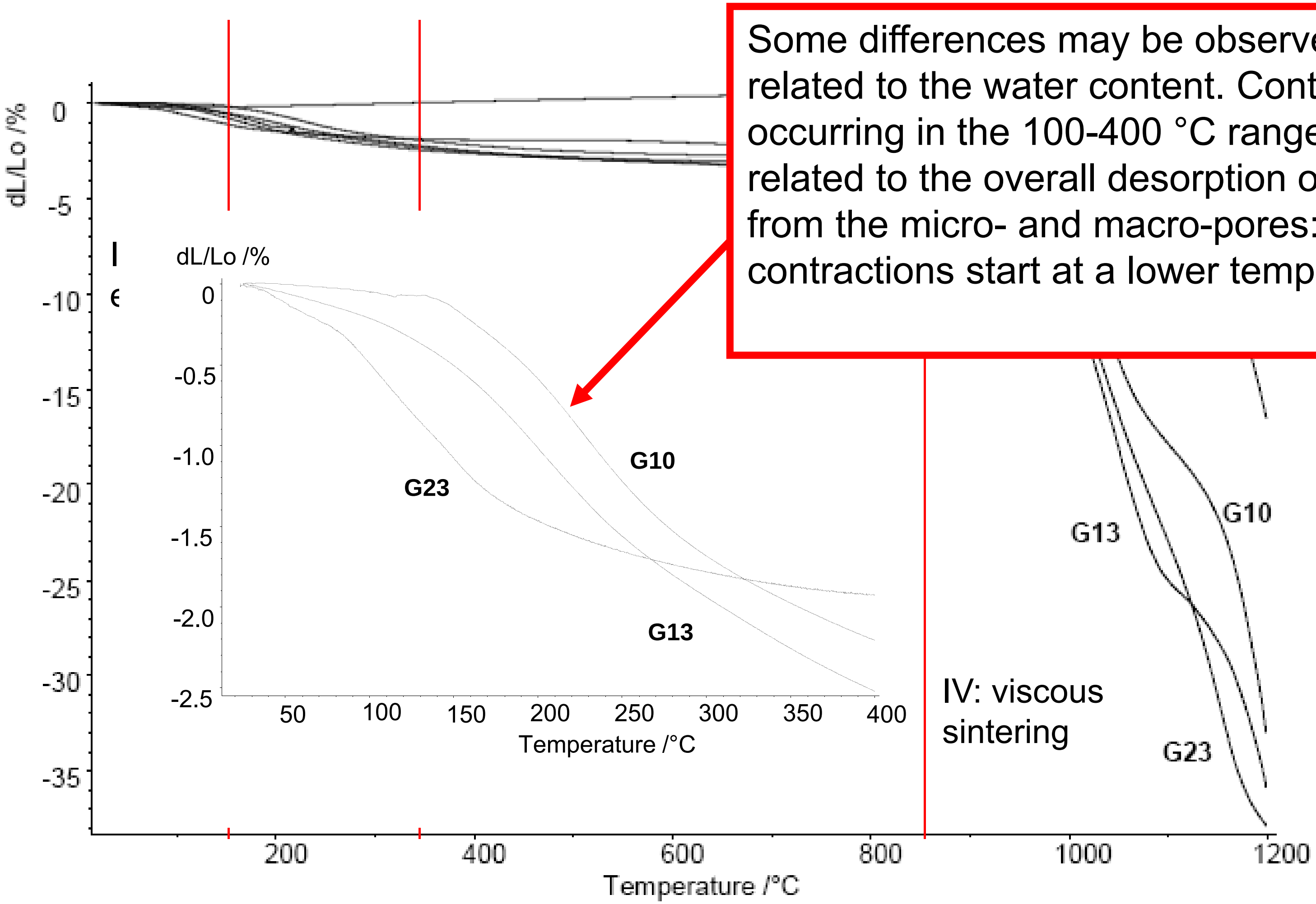


Textural analysis

Porosimetric and surface analyses

Samples	Porosity (%)	Average pore diameter (μm)	S_{BET} (m^2/g)	V_p (cm^3/g)
G10	29.2	0.01	40	0.168
G13	35.6	0.03	40	0.245
G23	56.2	0.54	16	0.078
F13-0.04%Si	37.1	0.03	50	0.243
F23-0.03%Si	33.7	0.03	98	0.480
F13-1.15%Si-RT	33.8	98.06	1	0.005
F13-1.15%Si-80°C	32.4	95.96	1	0.005

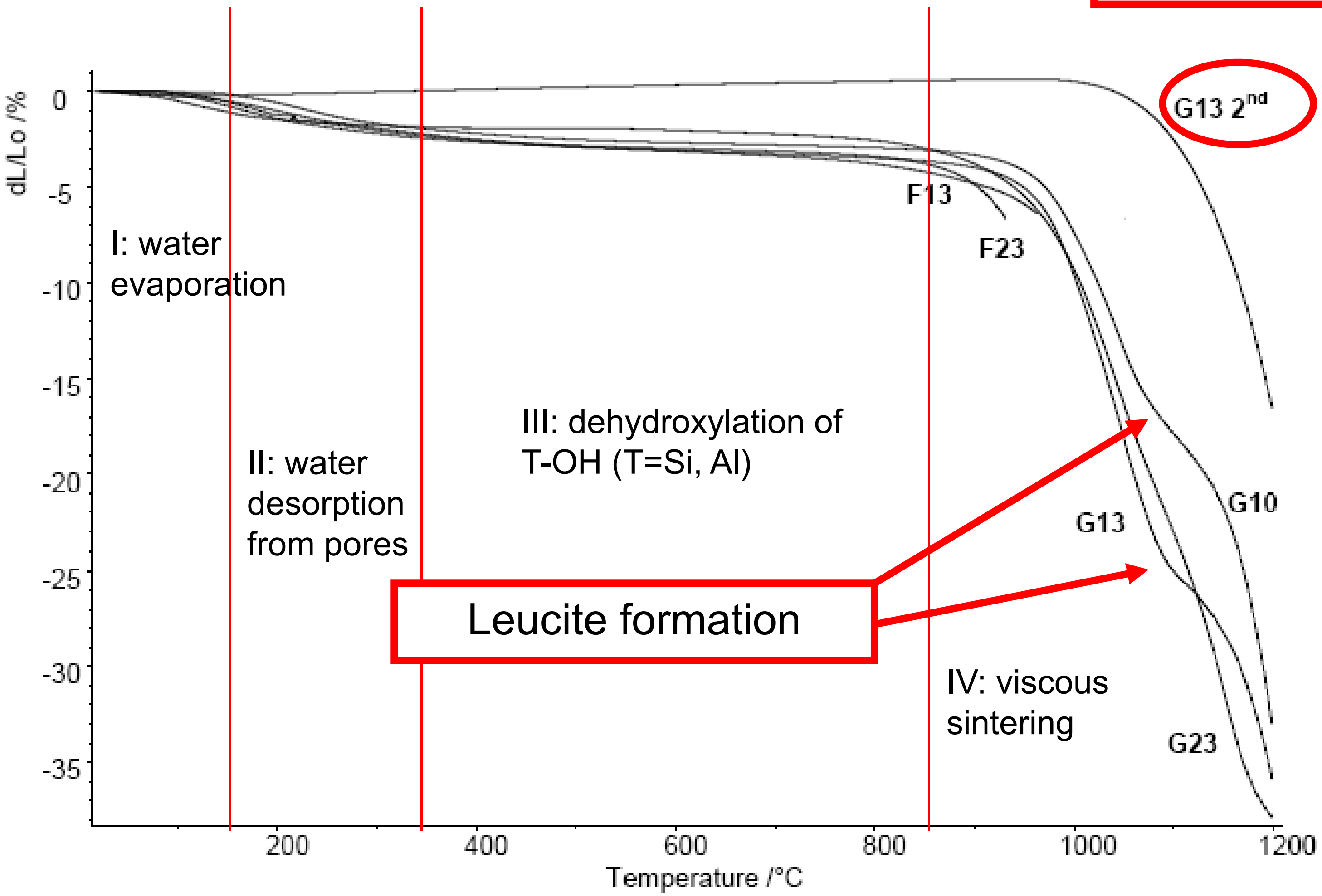
Thermal properties



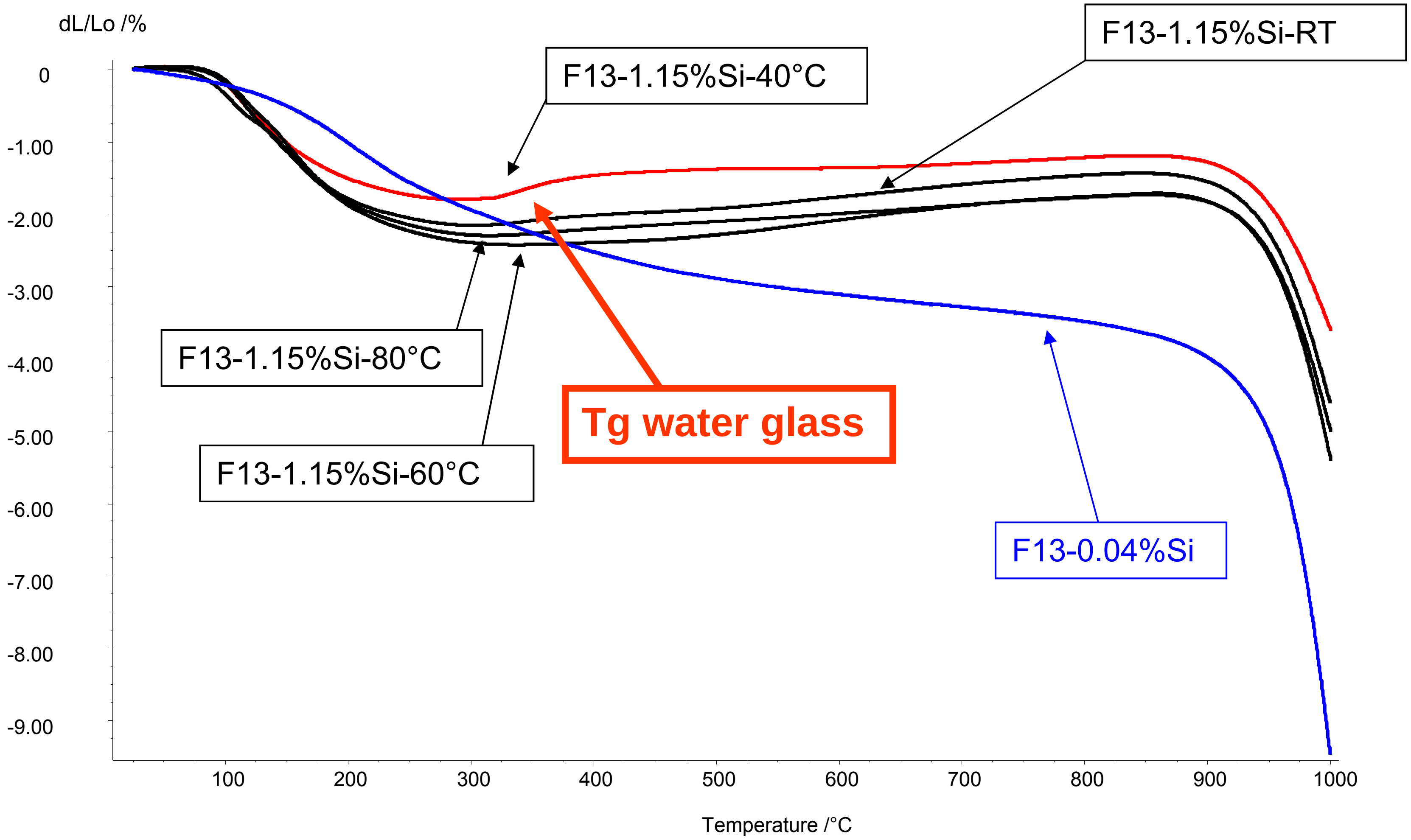
Some differences may be observed related to the water content. Contractions occurring in the 100-400 °C range were related to the overall desorption of water from the micro- and macro-pores: G23 contractions start at a lower temperature.

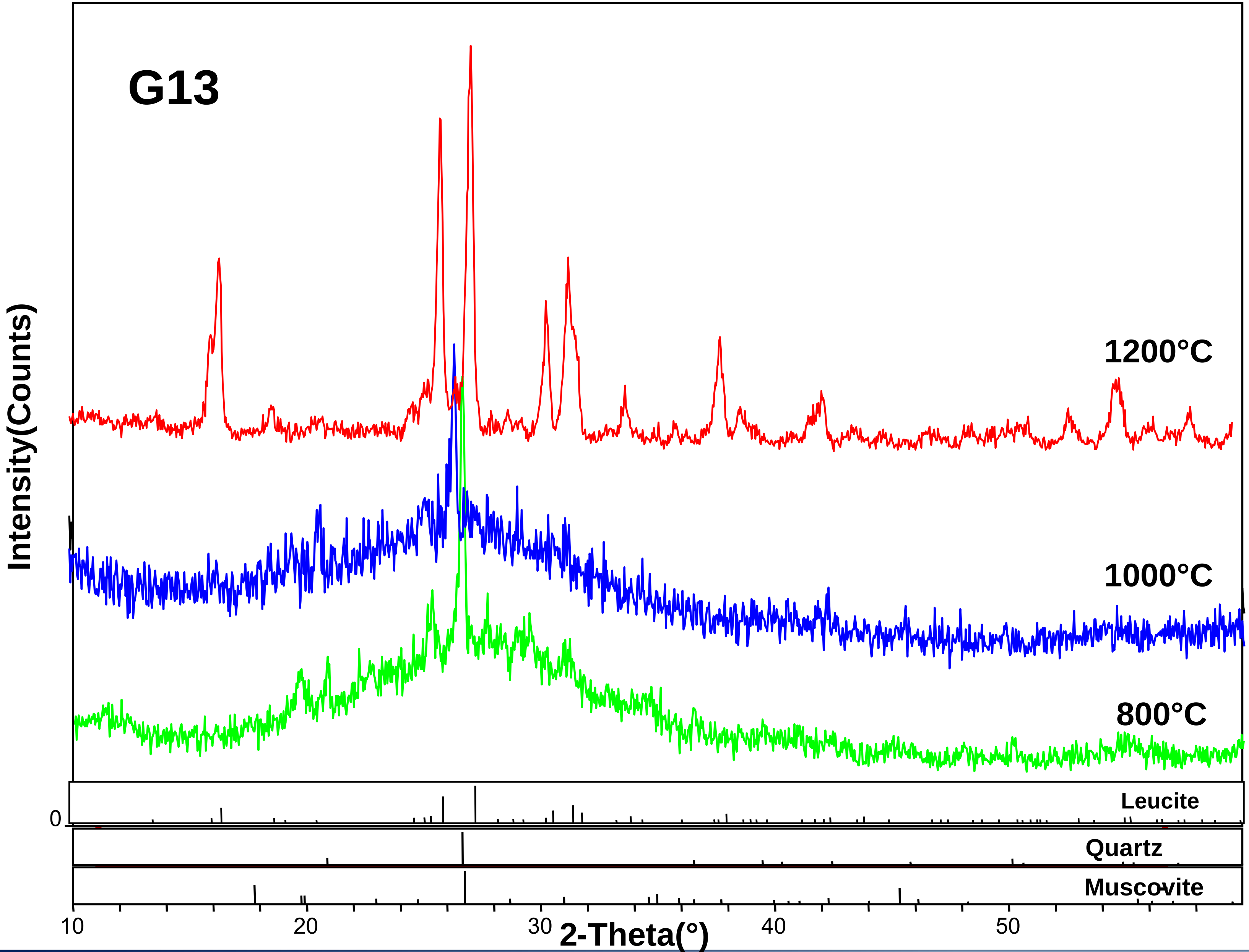
Thermal properties

CTE = 5.33 $\cdot 10^{-6}$ °C^{-1}



Thermal properties



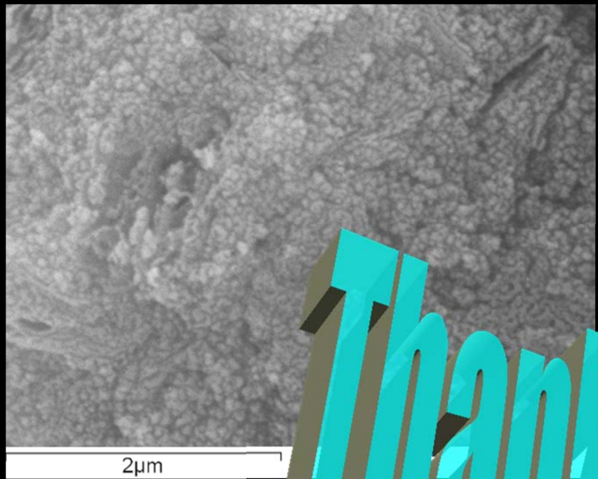

G13
Intensity(Counts)
1200°C
1000°C
800°C
0
Leucite
Quartz
Muscovite
10
20
30
40
50
2-Theta(°)

Conclusion

• Metallic silicon is used as inorganic foaming agent exploiting its ability in reacting in alkaline aqueous medium evolving H_2 gas.

• Both the intrinsic and induced porosity depend on the water availability in the geopolymer composition, because hydrolysis step during geopolymerization and silicon reaction are both water consuming processes.

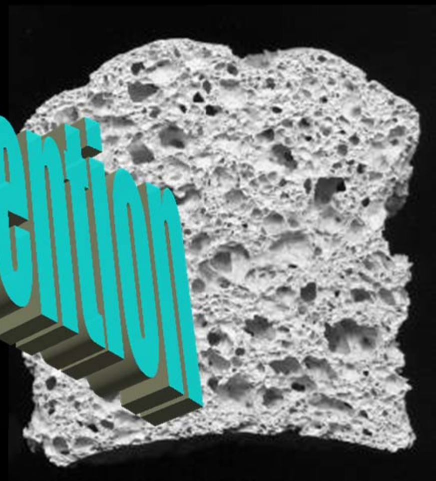
• The experimental findings highlighted the versatility of the foams that may be properly designed as a function of the possible application. The obtained porosity range are suitable for producing catalysis supports, filters and thermal insulators.

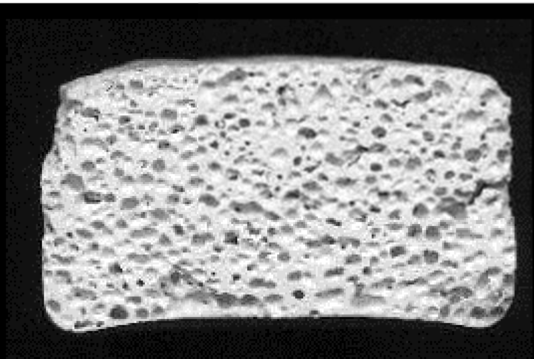


Porosity < 50%, nm-μ
- Catalysis [P.Sazar
- Evaporators and heat exchangers
- Ionic chromatography [MacKenzie et al. 2012]

Thanks for your attention

Work in progress





Porosity <70%, nm-mm, geop100%:
- Catalysis [P. Sazama et al., 2011]
- Biomedical: drug delivery and bone replacement

Porosity >70%, μm-mm, geop <70%:
- Thermal insulation