Sulphate quantification using Raman spectroscopy in borosilicate glass matrix

Agnès GRANDJEAN[1], Marion LENOIR[1,2], Sylvie POISSONNET[3], Daniel R. NEUVILLE[2]

[1] CEA Nuclear Energy Division/ Waste Treatment and Conditioning Department, Marcoule (France)

[2] Physique des Minéraux et des Magmas, UMR 7047 – CNRS, Institut de Physique du Globe de Paris

[3] CEA Nuclear Energy Division / DMN/SRMP, Saclay

Sulphur in oxide glasses

Commercially produced soda-lime-silica glasses

Sulphur deliberately added (low level) :
- as sulphate : refining agent
- as sulphide : amber colour

Silicate melts of geological :

may contain substantial quantities of sulphur.

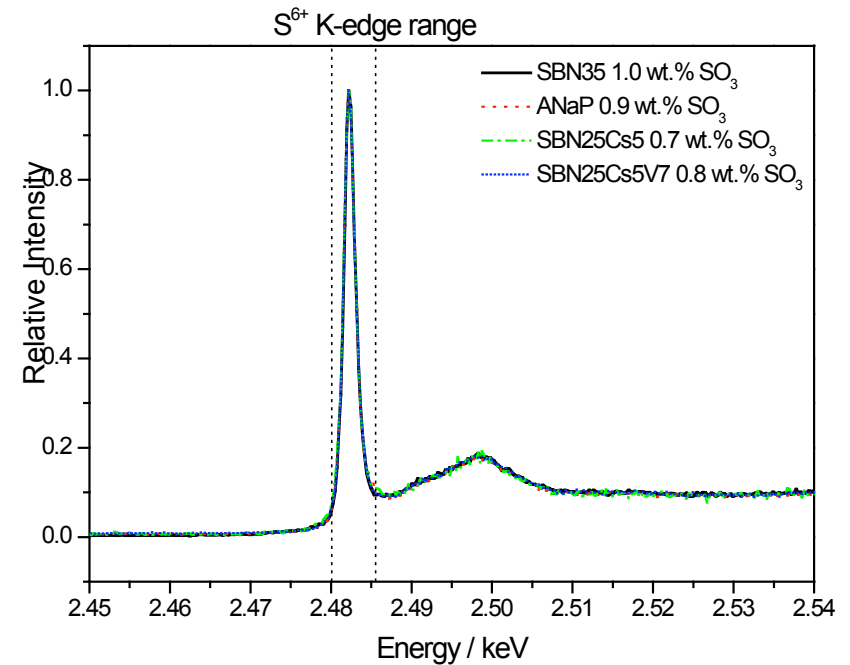*Sulphur species : present in radioactive and toxic wastes.*

-> immobilization through vitrification

In case of radiaoactive wastes : Sulphur solubility can be the
« *limiting factor* » for the glass waste loading.

•Compound	SiO$_2$		B$_2$O$_3$		Na$_2$O	
Glass sample	Nominal (mol %)	EDS-XRF * (mol %)	Nominal (mol %)	EDS-XRF * (mol %)	Nominal (mol %)	EDS-XRF * (mol %)
SBN 54.26.20	54.36	56 ± 0.5	25.64	25 ± 0.3	20	19 ± 1
SBN 48.22.30	47.56	48 ± 0.5	22.44	21 ± 0.5	30	28.5 ± 1

Added around 6% mol Na$_2$SO$_4$

Analysed glasses

sulphur speciation
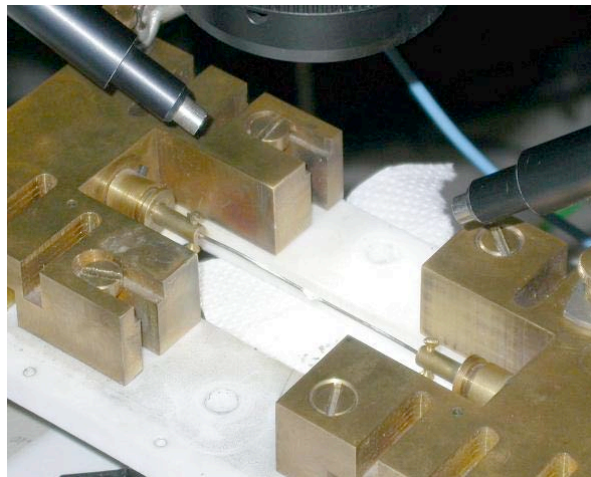
S (+VI) sulphate $SO_3(gas)$, SO_4^{2-}, $S_2O_7^{2-}$

S(+IV) sulphite $SO_2(gas)$, SO_3^{2-}

S(0)

S(-II) sulphide
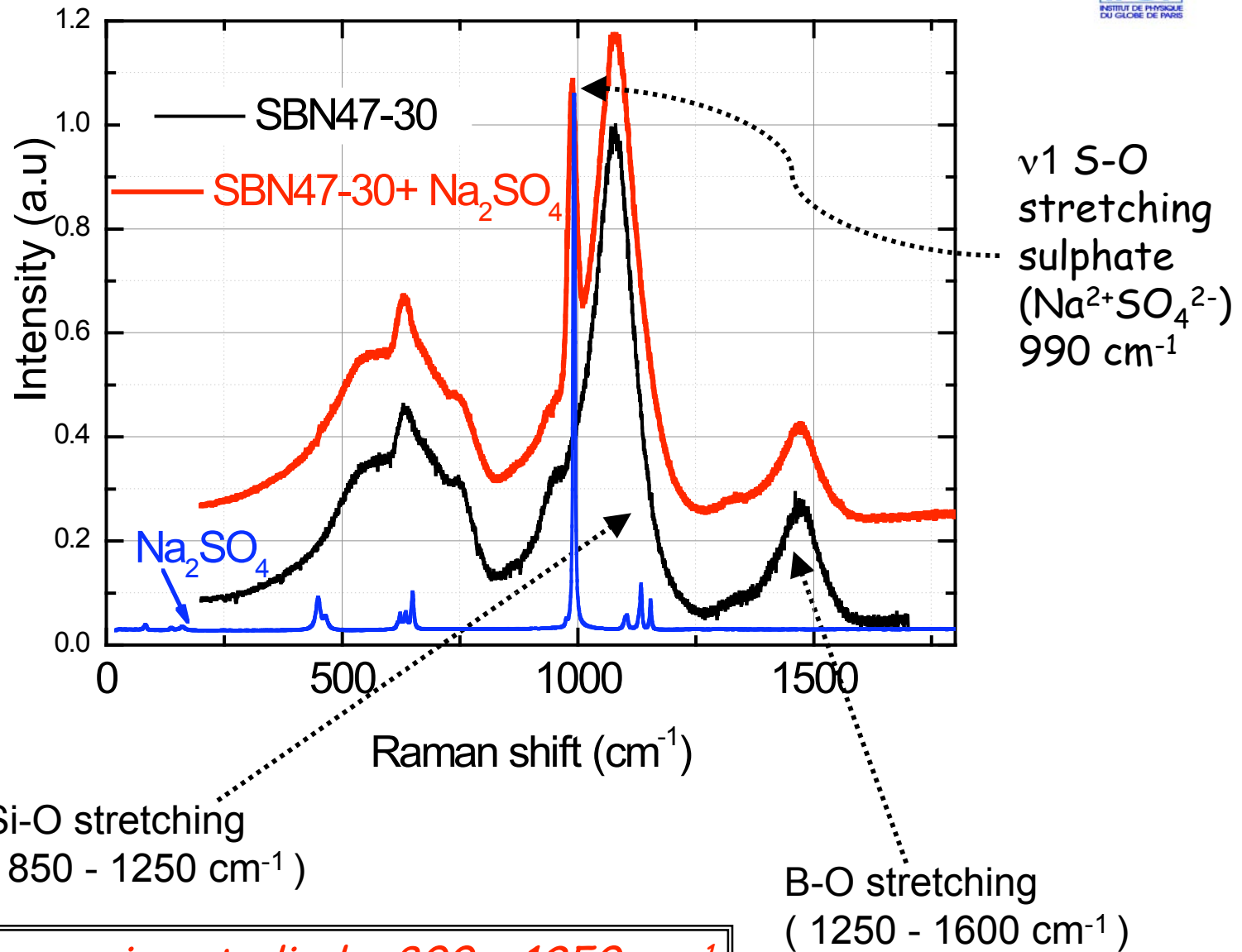
Raman spectroscopy

Non destructive and very flexible technique.
In situ measurement

Source = 514.532 nm line of a coherent

70 Ar+ laser,

Power = 1 W at the sample surface.

Spectral resolution = $\pm$ 1 cm^{-1}

Spatial resolution = around 1μm^3

T64000
Jobin-Yvon

IPGP

High temperature cell = using a micro heater. A single PtRh alloy wire, heated by Joule effect. Small hole.

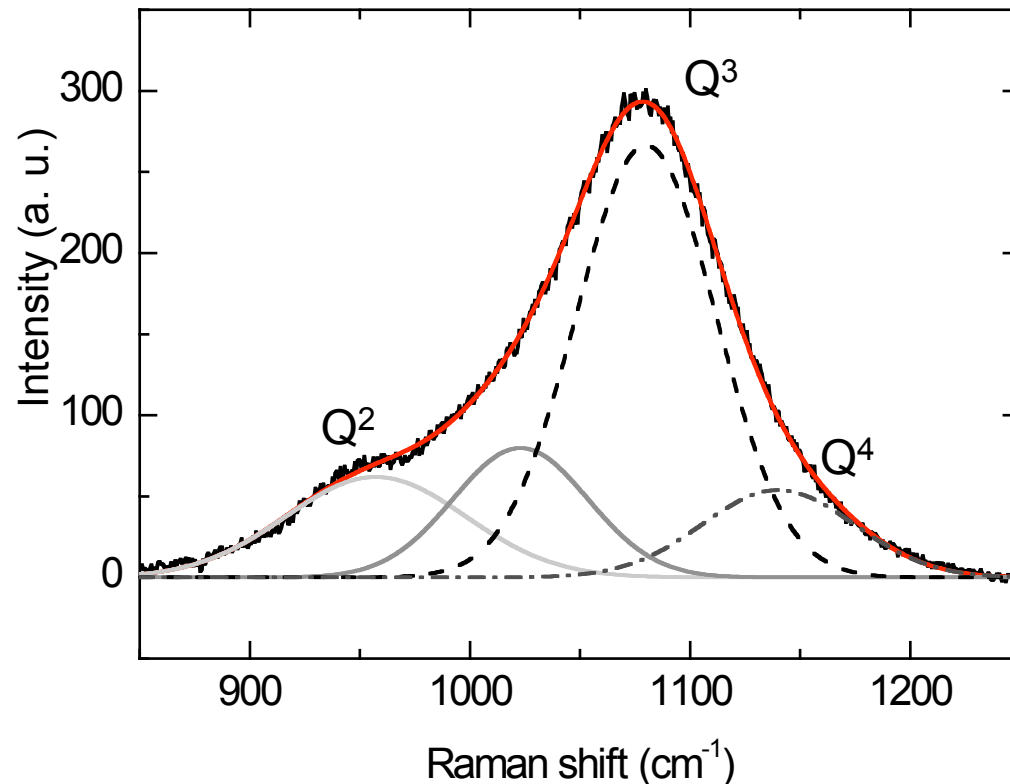B.O. Mysen and J.D. Frantz, Chem. Geol. 96 (1992) 321.

Raman spectra : effect of sulphate

$\nu 1$ S-O stretching sulphate ($Na^{2+}SO_4^{2-}$) 990 cm^{-1}

Si-O stretching (850 - 1250 cm^{-1})

B-O stretching (1250 - 1600 cm^{-1})

Interesting region studied = 800 – 1250 cm^{-1}

Correction for temperature and frequency dependent scattering intensity

$$I = \left[\nu_0^3 \left(1 - e^{\frac{-hc\nu}{kT}} \right) \frac{\nu}{(\nu_0 - \nu)^4} \right] I_{obs.}$$

ν_0 = 514.32 nm.

Linear baseline.

Frequency region = 850 – 1250 cm^{-1}

Si-O$^-$ stretching
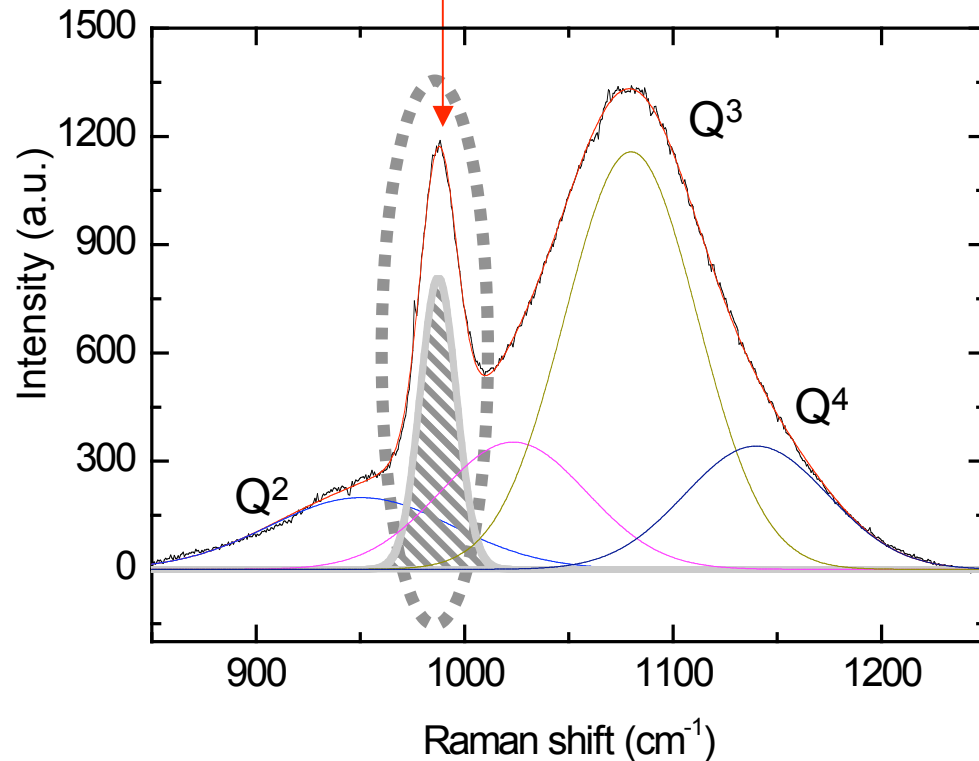
950 to 980 cm^{-1} : Q^2

1050 to 1100 cm^{-1} : Q^3

1060 to 1190 cm^{-1} : Q^4

1000 to 1050 cm^{-1} : Si-O^0 bridging

oxygen stretching mode
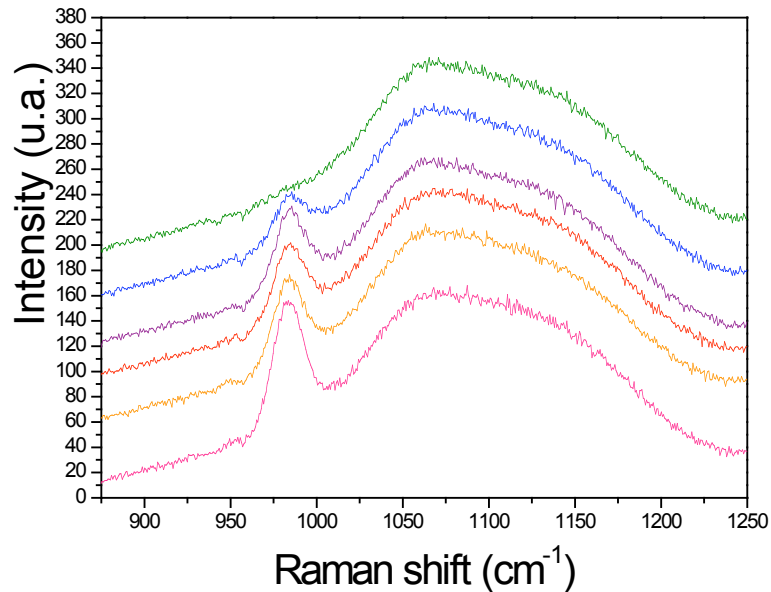
Reconvolution of Raman spectra

Stretching sulphate band
(around 990 cm^{-1})

$$[SO_3]_{glass} \, \alpha \, \frac{area(990cm^{-1})}{area(entire-region)}$$

Relative SO$_3$ content obtained from Raman spectra

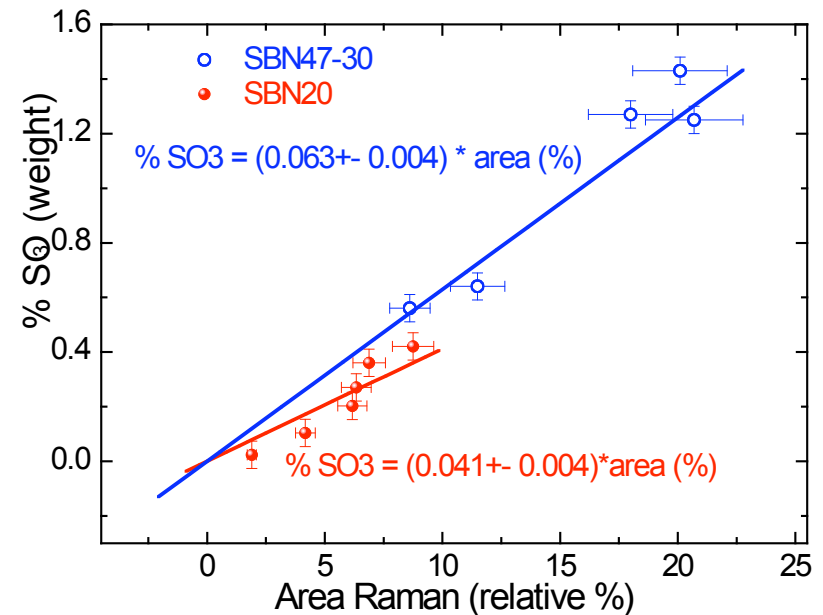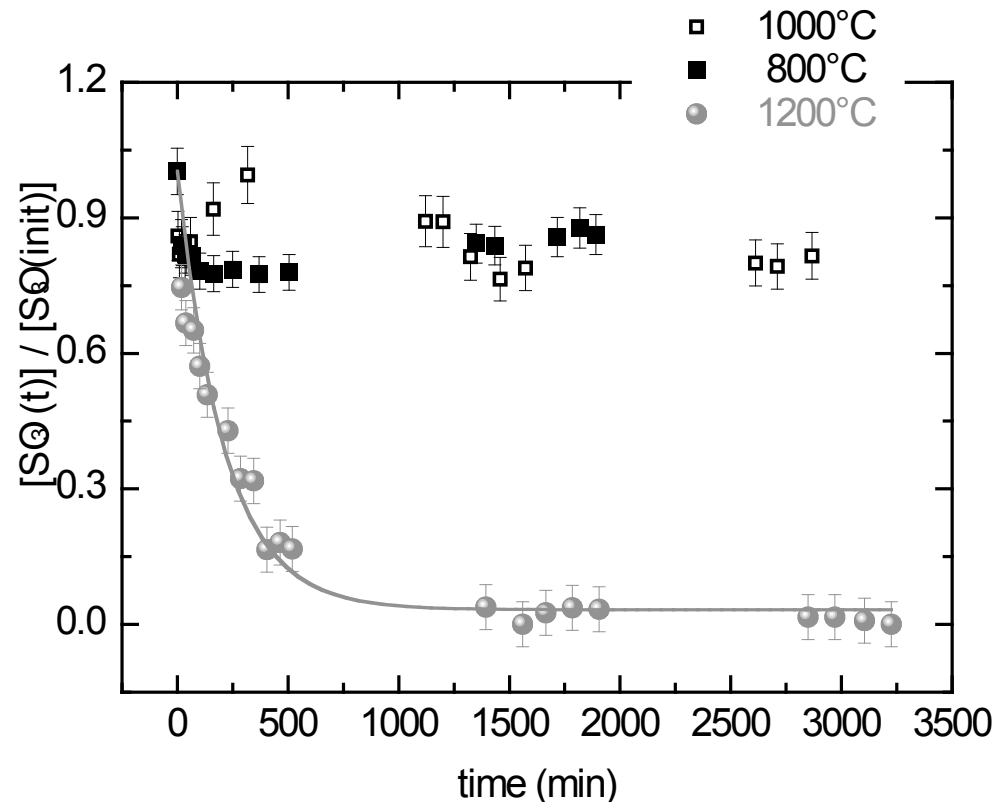# Reconvolution of Raman spectra

various content of sulphate

Comparison with microprobe analysis
(calibration curve)

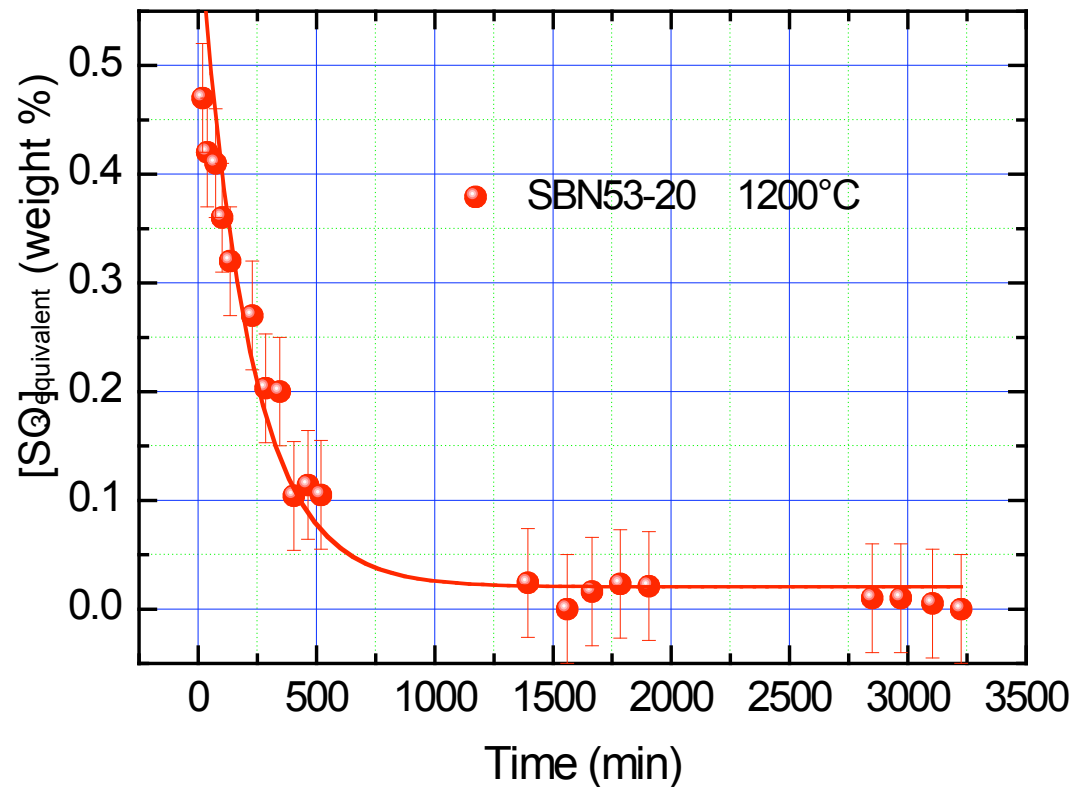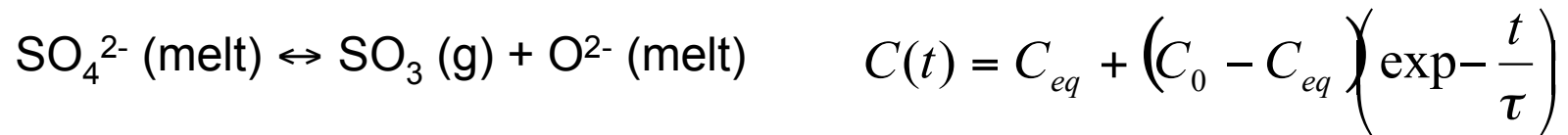*Thanks to S. Poissonnet (CEA – Saclay, SRMP) for microprobe analysis.*

Raman spectroscopy in the frequency region 850-1250 cm^{-1} allows the quantification of relative sulphate content in a simple borosilicate glass using 5 to 6 gaussian bands for the reconvolution
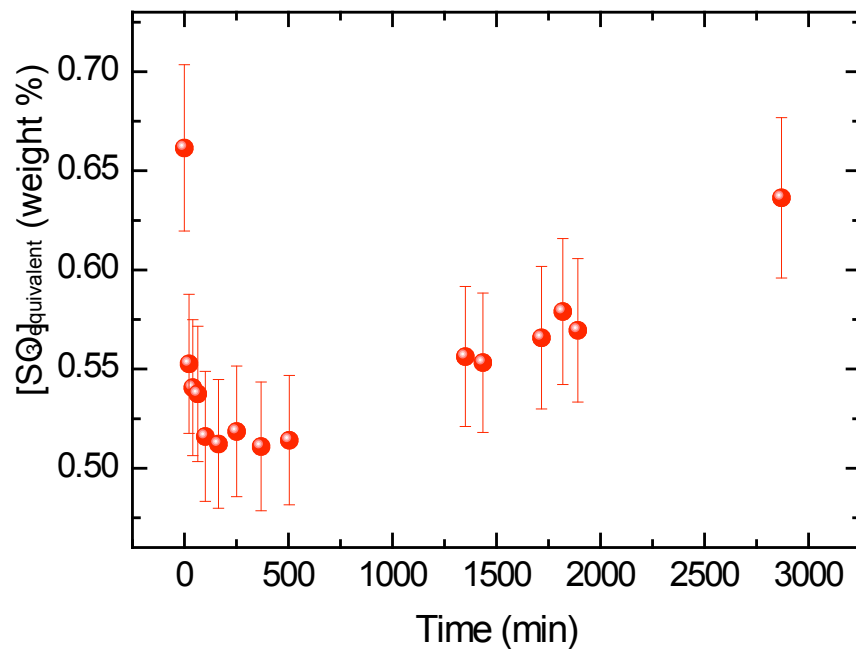-> *in situ* measurement in high temperature easy

Example : decomposition of sulphate from a borosilicate melt at high temperature
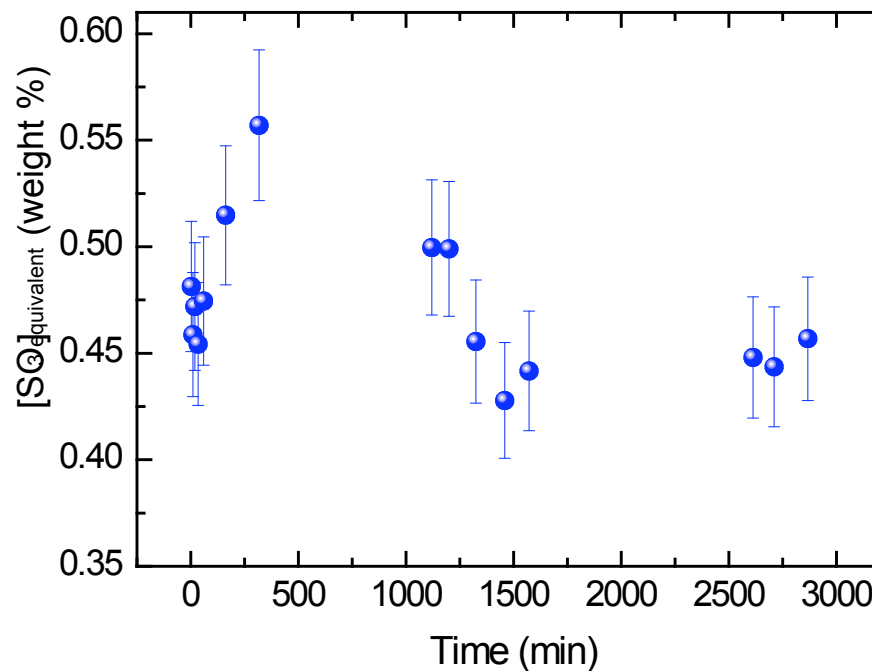
At high temperature :
diffusion of gaseous SO_3 species : fast reaction

$$SO_4^{2-} \text{ (melt)} \leftrightarrow SO_3 \text{ (g)} + O^{2-} \text{ (melt)}$$

$$C(t) = C_{eq} + \left(C_0 - C_{eq}\right)\exp{-\frac{t}{\tau}}$$

SBN53-20   1200°C

At low temperature :

SBN47-30 - 800 °C

SBN47-30 - 1000 °C

Kinetics of sulphate decomposition

At lower temperature : viscous flow
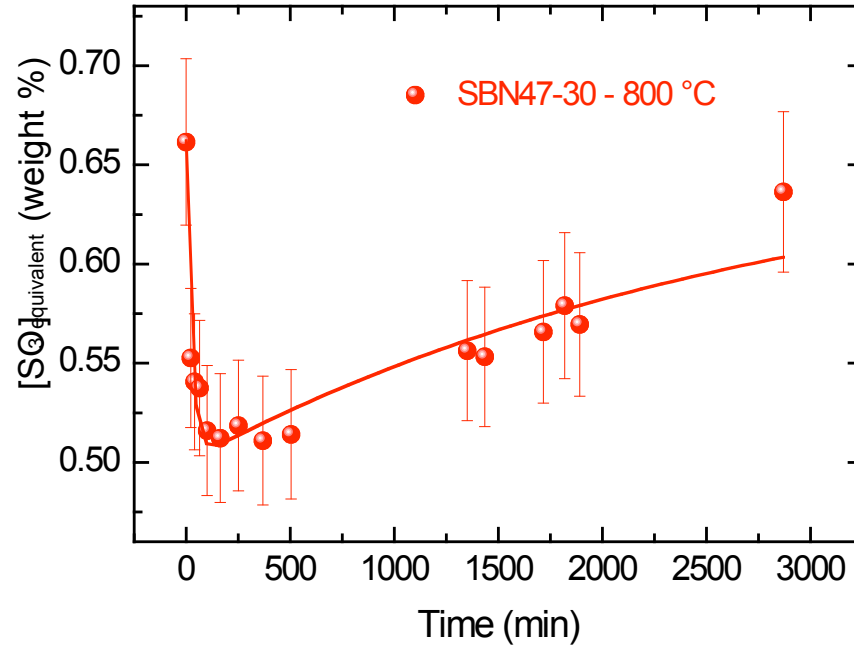diffusion of gaseous SO_3 species limiting reaction.
« Re »formation of $[SO_4^{2-}]$ from gaseous SO_3 species already present
in the glass sample.
Competition between formation and decomposition of ionic sulphate
species.

$$C(t) = C_0 + \left(C_0 - C_{eq}\right)\left[\exp\left(-\frac{t}{\tau_1}\right) - \exp\left(-\frac{t}{\tau_2}\right)\right]$$

Decomposition time characteristic

Formation time characteristic

1000°C

$C_0 = 0.45$

$C_{eq} = 0.18$

$\tau(\text{decomposition}) = 546$ min

$\tau(\text{formation}) = 208$ min

800°C

$C_0 = 0.66$

$C_{eq} = 0.82$

$\tau(\text{decomposition}) = 2825$ min

$\tau(\text{formation}) = 26$ min

Conclusion

1. Raman spectroscopy in the frequency region 850-1250 cm^{-1} allows the quantification of relative sulphate content in a simple borosilicate glass using 5 to 6 gaussian bands for the reconvolution

2. *in situ* measurement of time dependence of sulphate content at high temperature (in the molten state).

3. At 800°C and 1000°C : decomposition of sulphate present into the melt : very low compared to kinetics at 1000°C.

4. Fit of the kinetics data : sulphate variation at least at 800°C implies a competition between departure and formation of ionic sulphate content inside the melt.