

Quantification of iron redox ratios in silicate glasses and melts by Raman spectroscopy

B. Cochain^{1,2}, D. R. Neuville¹, V. Magnien^{1,2},
G. S. Henderson⁴, and P. Richet¹

¹Physique des Minéraux et des Magmas, CNRS-IPGP, 4 place Jussieu, 75252 Paris Cedex 05, France

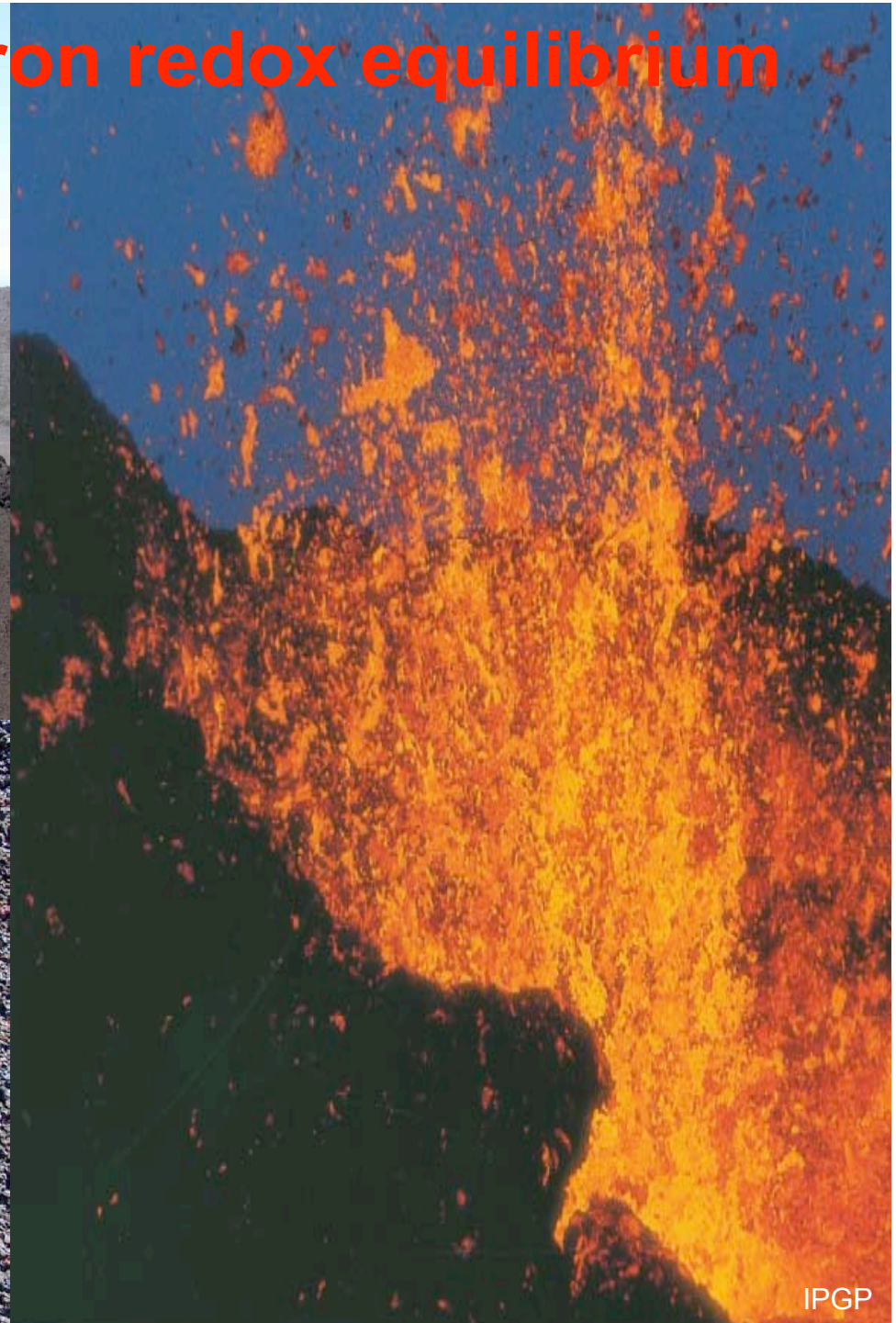
E-mail : cochain@ipgp.jussieu.fr

²SCDV-LEBV, CEA Valrhô, Centre de Marcoule, 30207 Bagnols-sur-cèze, France

³Laboratoire Structure et Propriété de l'Etat Solide, Université de Lille 1, 59655 Villeneuve d'Ascq, France

⁴ Dept of Geology, University of Toronto, Toronto, Canada

Determination of iron redox equilibrium



Determination of iron redox equilibrium

Industrial interest :

- glass production
- nuclear waste storage glass



Determination of iron redox



- **Lack of *in situ* data**
 - Knowledge on iron redox kinetics
 - => XANES spectroscopy (limited access)
- **Raman spectroscopy**
 - Calibration to quantify iron redox ratios
 - In situ experiments possible
 - Ready access

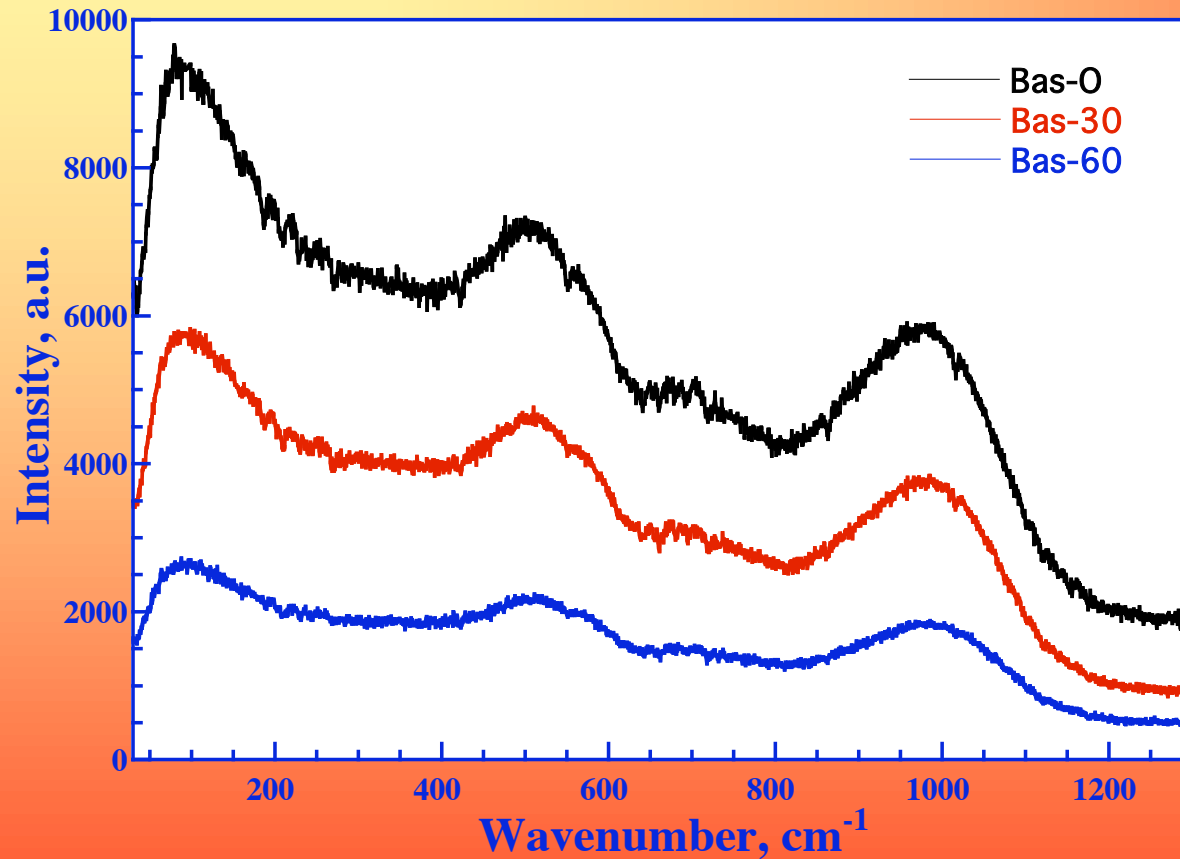
Compositions investigated

	SiO ₂	Al ₂ O ₃	B ₂ O ₃	Fe ₂ O ₃	FeO	CaO	MgO	Na ₂ O	Li ₂ O
Pyroxenes based									
Pyrox	53.17				12.71	19.85	14.27		
PyrNa	52.53				12.56	17.16	12.33	5.42	
PyrLi	54.04				12.92	17.65	12.69		2.69
Borosilicates									
NB67.18Fe1	64.78		20.44		1.16			13.63	
NB67.18Fe5	61.78		19.49		5.74			12.99	
NB67.18Fe10	58.07		18.32		11.39			12.22	
Alumino-borosilicate									
FAMA	46.5	10,00	18.5	5,00				20,00	

- **Synthesis under different oxygen fugacities
≠ redox ratios**
- **Iron redox ratios :**
 - **Wet chemical analysis**
 - **Mössbauer spectroscopy**
 - **Electron Microprobe analysis**

Experimental conditions

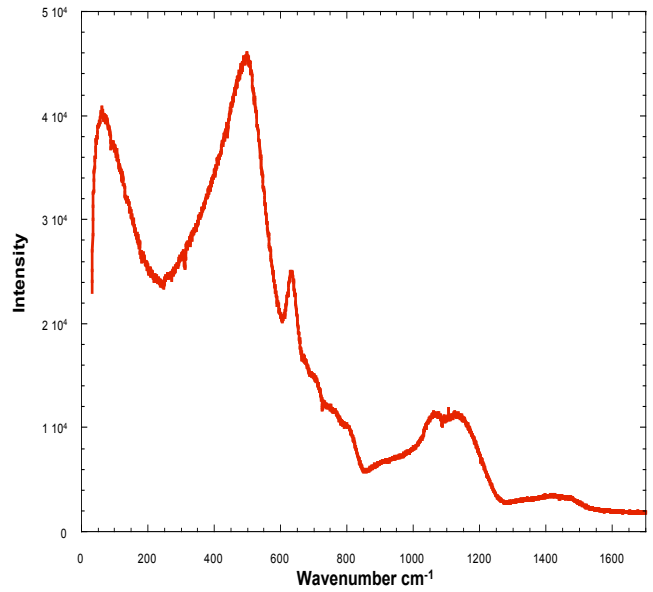
Effect of focus on Raman spectra



With iron-bearing glasses :
Strong decrease in intensity
with the focus depth due to
absorption

Need to focus on the surface of the glass

Raman spectra analysis



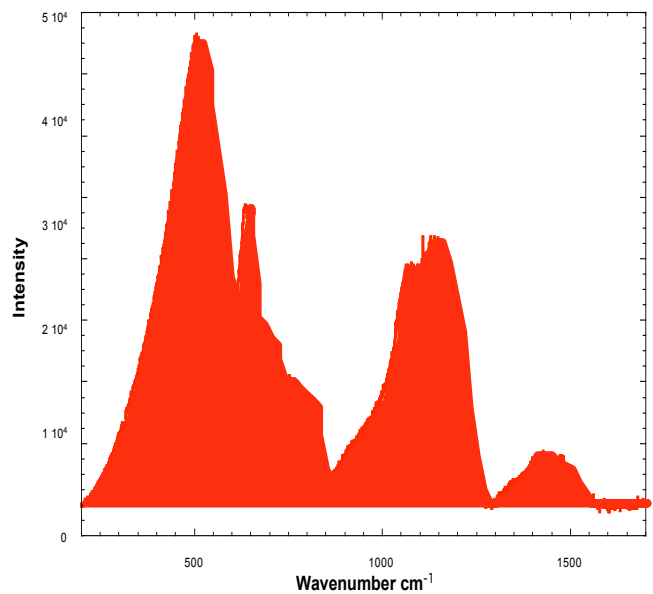
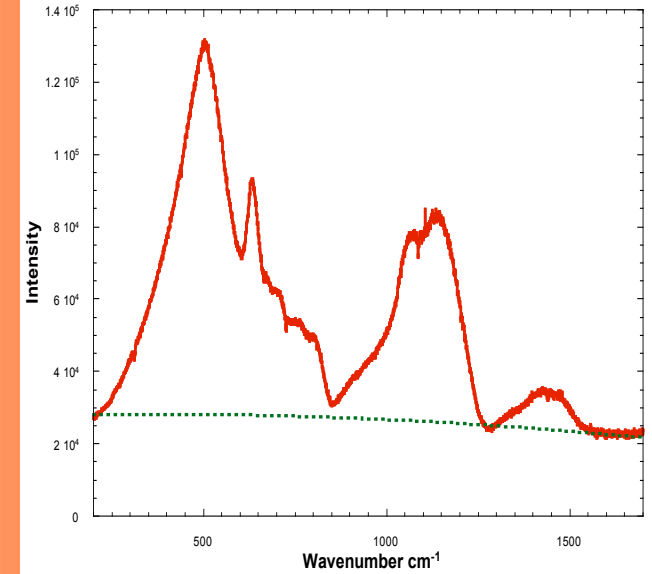
**Raman spectra
correction and
normalization**

Raman spectra

Long correction (1977)

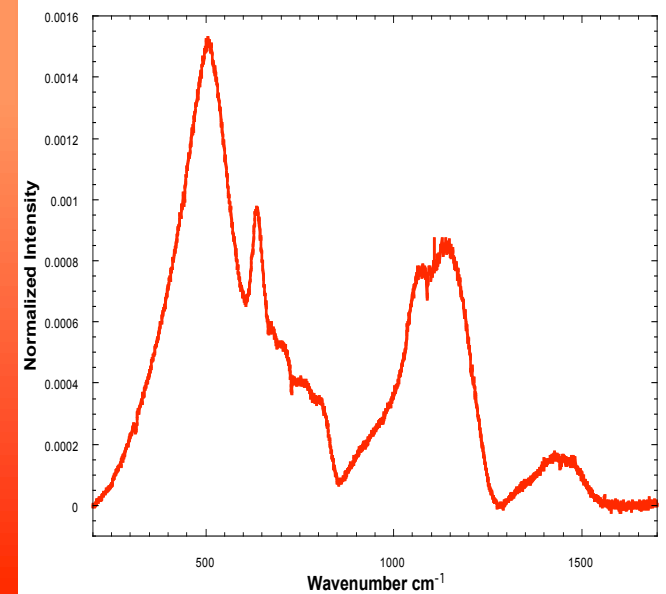
$$I = I_{obs} \times R$$

Avec $R = f(\nu_0, \nu, \text{et } T)$



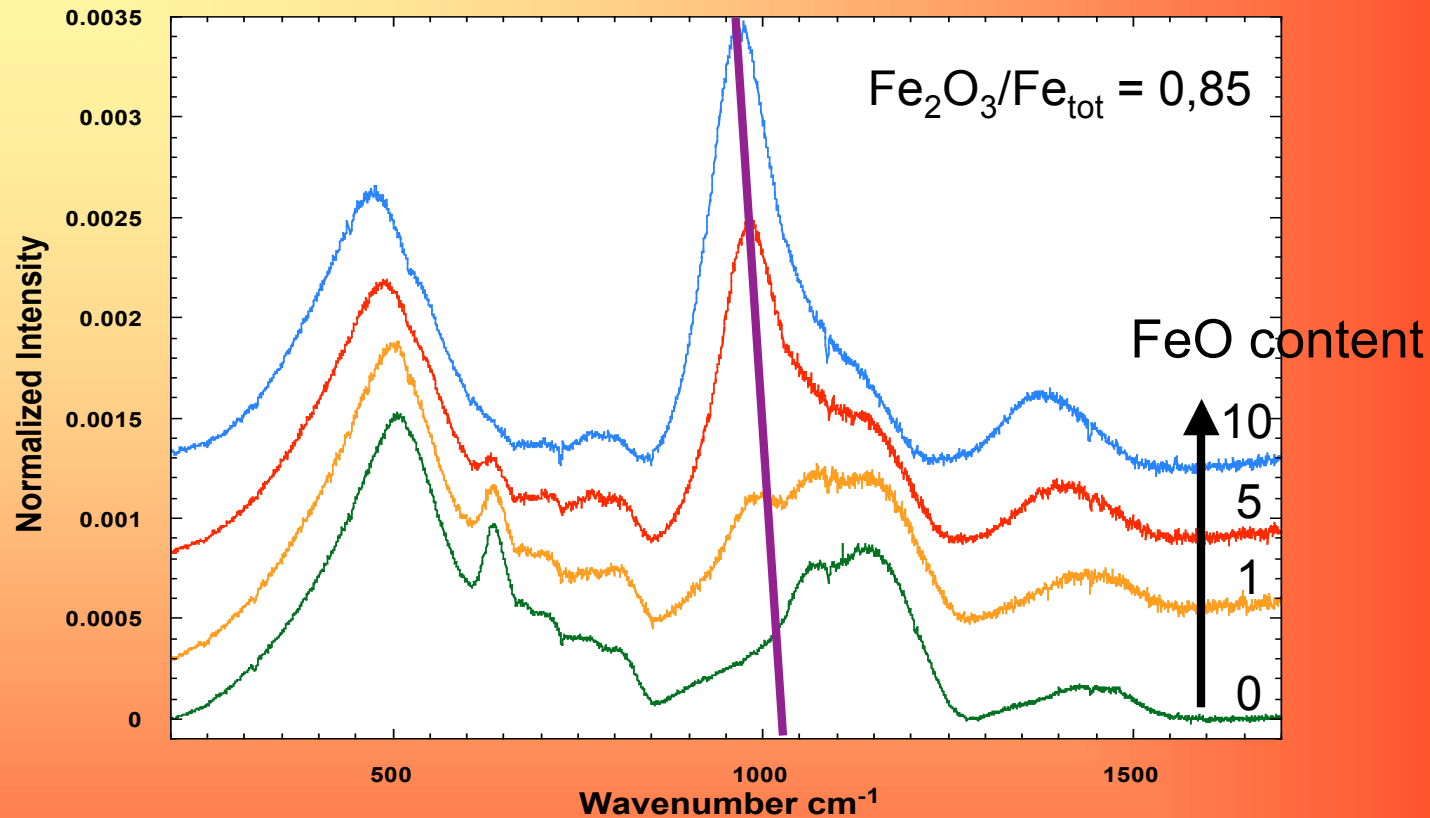
**Baseline
subtraction**

Normalization



Evolution of Raman spectra with mol% Feo

Case of borosilicates

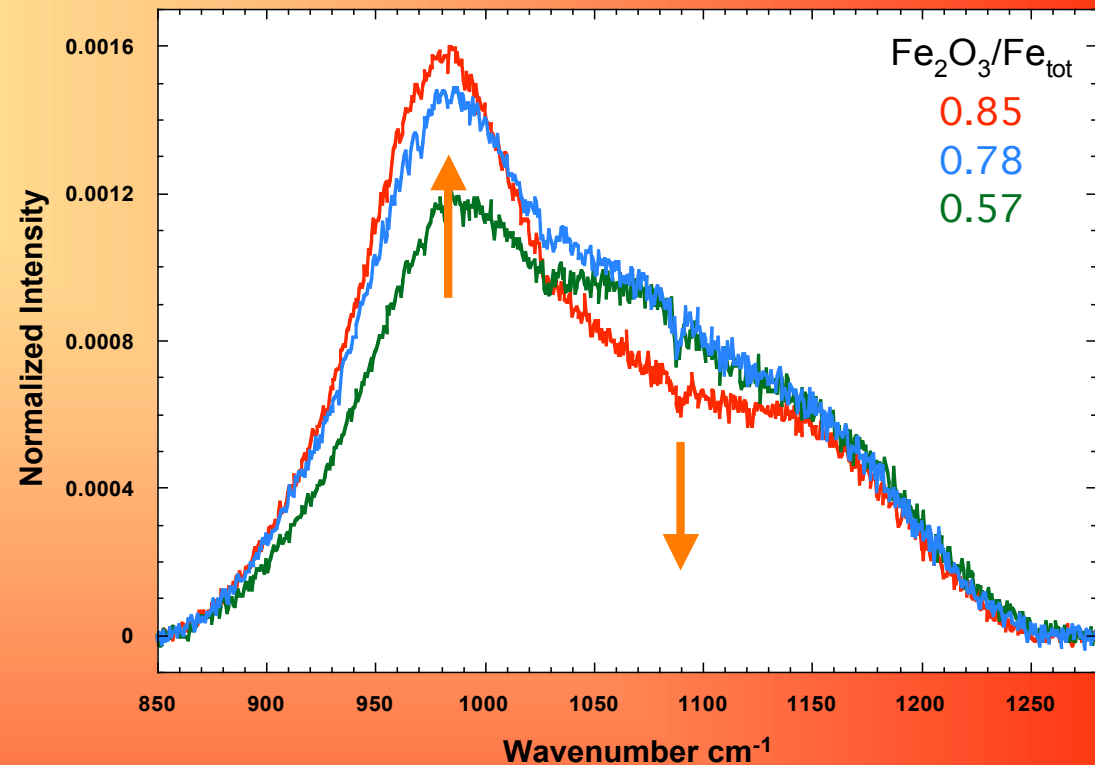
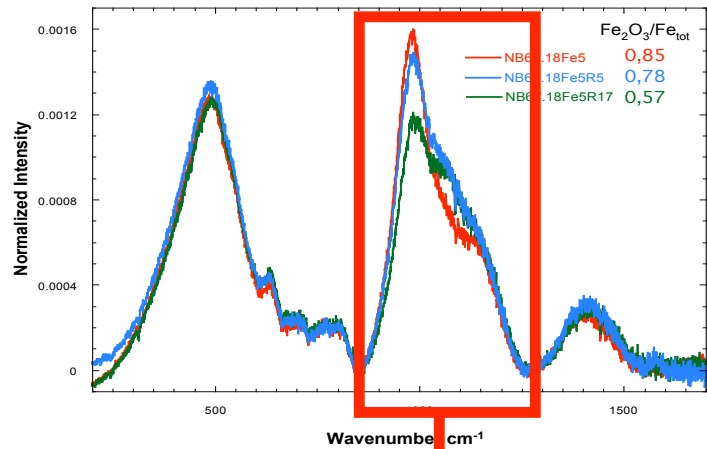


With increasing FeO content :

- Apparition and increase of a band at 980cm^{-1} in borosilicates
- Shift to lower frequency of the 980 cm^{-1} band \Rightarrow $[\text{Fe}^{3+}]_4\text{-O}$ bonds shared with Si

Evolution of Raman spectra with iron redox ratio

borosilicates : NB67.18Fe5

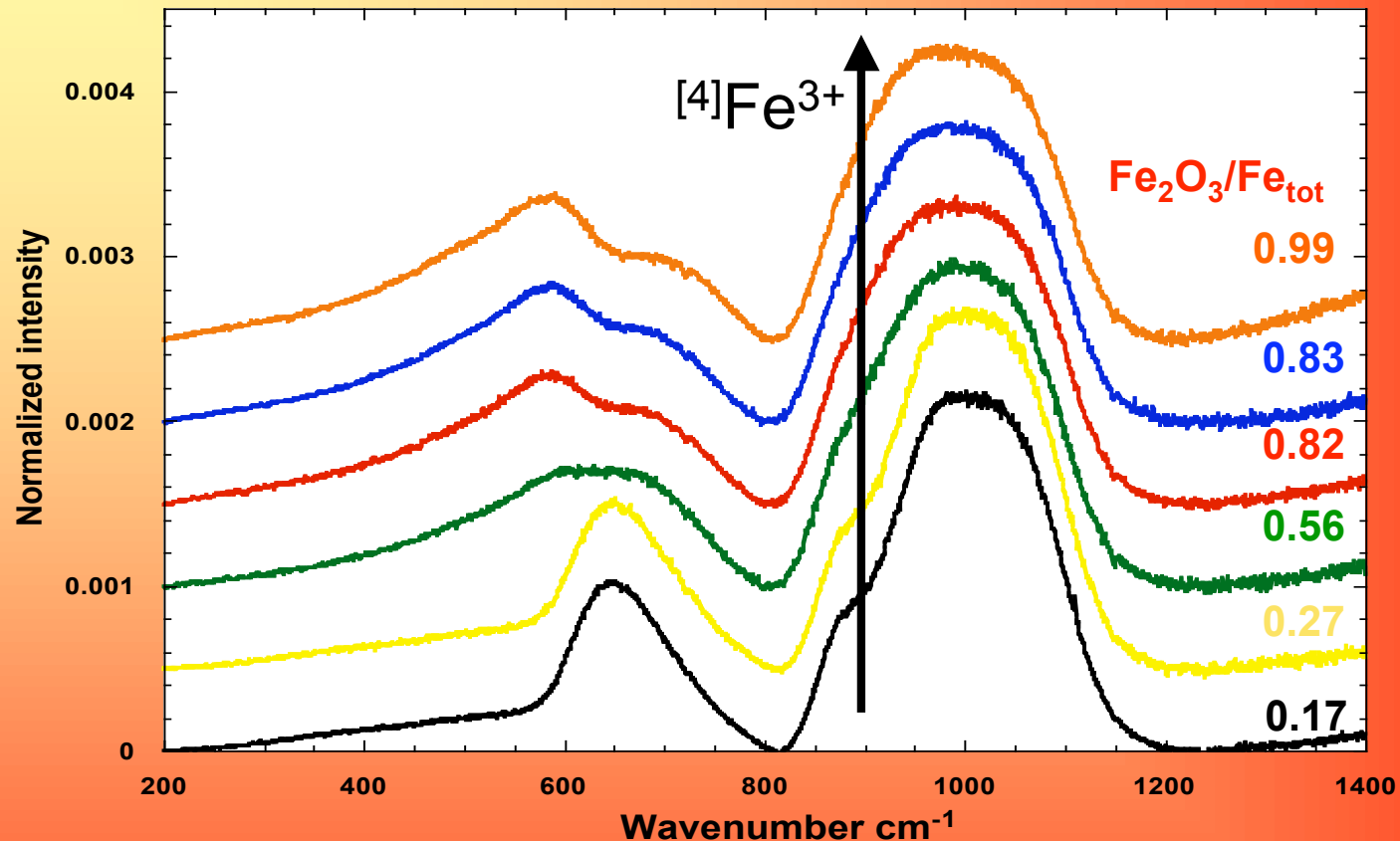


With increasing Fe^{3+} content:

- Evolution of the 980 cm^{-1} band
- Clear changes in Raman spectra for a given composition

Evolution of Raman spectra with iron redox ratio

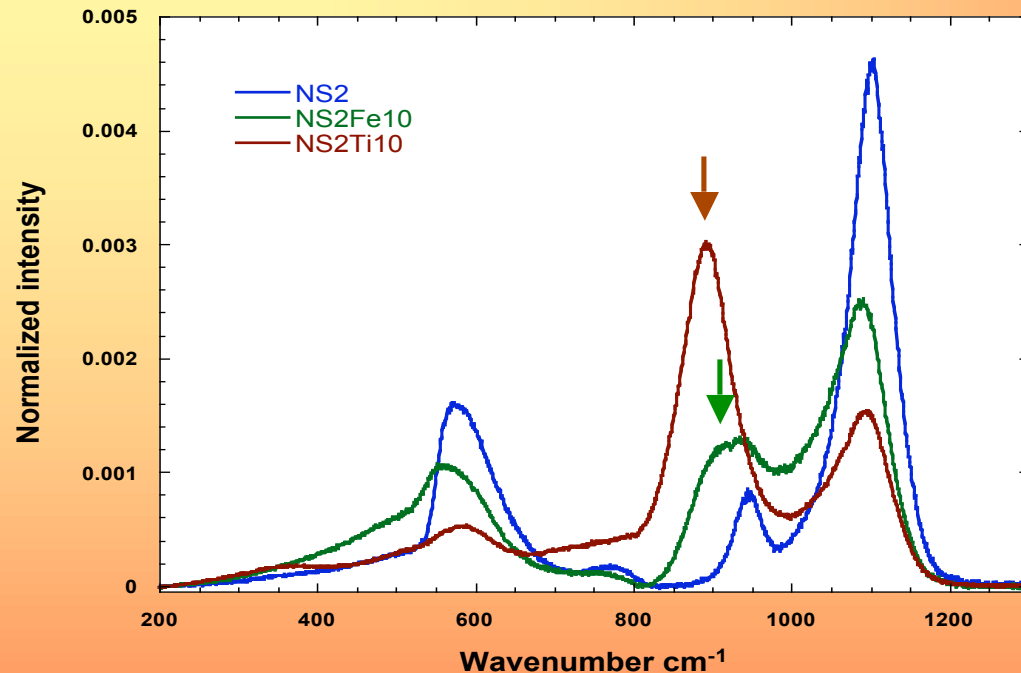
PyrNa



With increasing Fe^{3+} content:

- Evolution of the 915 cm⁻¹ band in based pyroxenes
- Clear changes in Raman spectra for a given composition

Validity of the method : band assignement

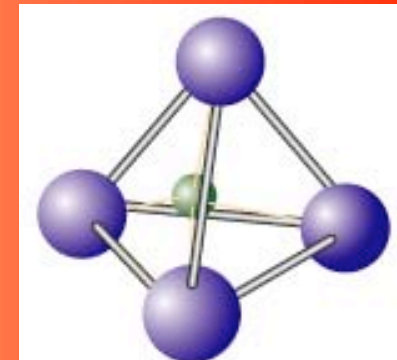


NS_2 , NS_2Ti_{10} , NS_2Fe_{10}



$[5]Ti$

$[4]Fe^{3+}$



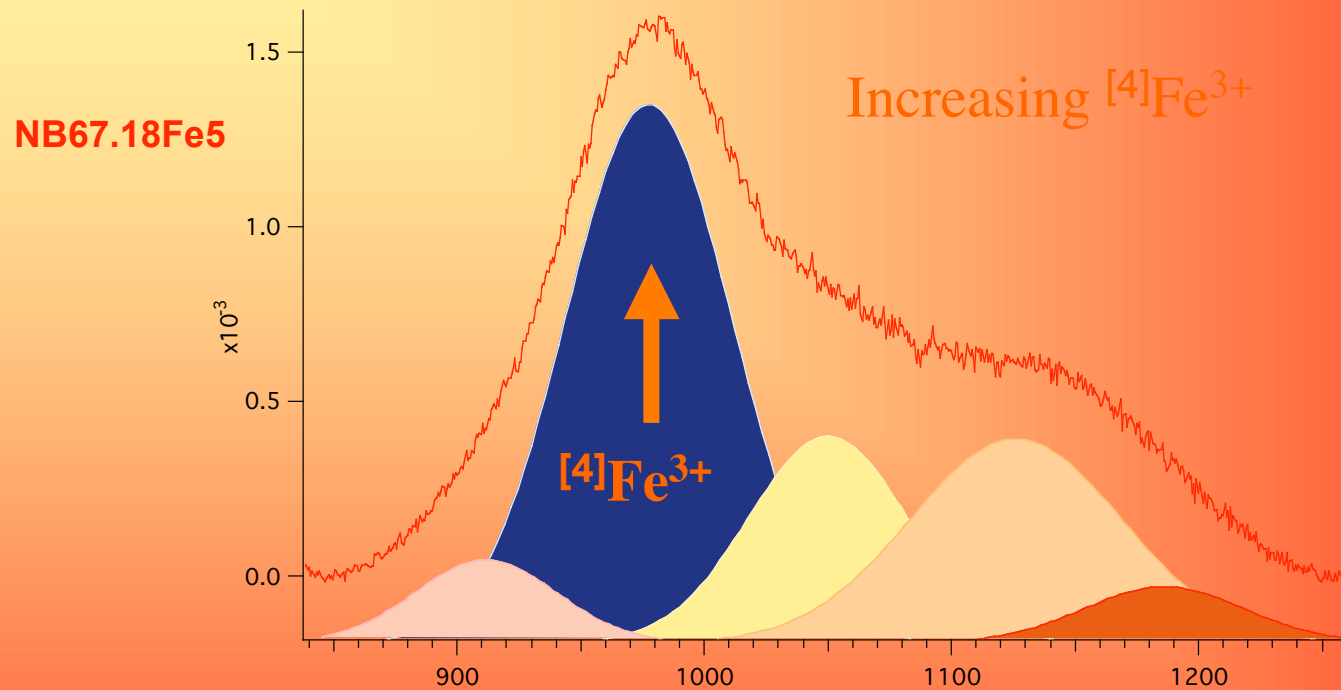
Distinct bands appear for Ti and Fe :

- around 885 cm^{-1} for NS_2Ti_{10} => attributed to Ti (Mysen & Neuvill, 1995, Reynard & Webb, 1998)
=> **Ti in five fold coordination according with XANES and Raman** (Henderson & Fleet, 1995, Farges et al 1996, Reynard & Webb, 1998)
- around 920 cm^{-1} for $NS_2 [4]Fe^{3+}_{10}$ (Mysen et al., 1985; Magnien et al., 2006)

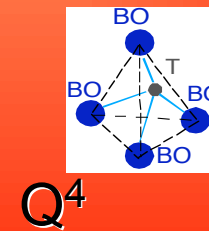
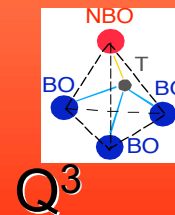
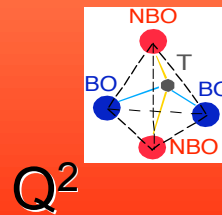
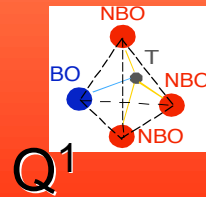
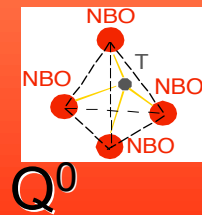
Evolution of Raman spectra with iron redox ratio

Deconvolution of Raman spectra Mysen et al. (1982) :

Intensity, position, width : unconstrained and independent parameters



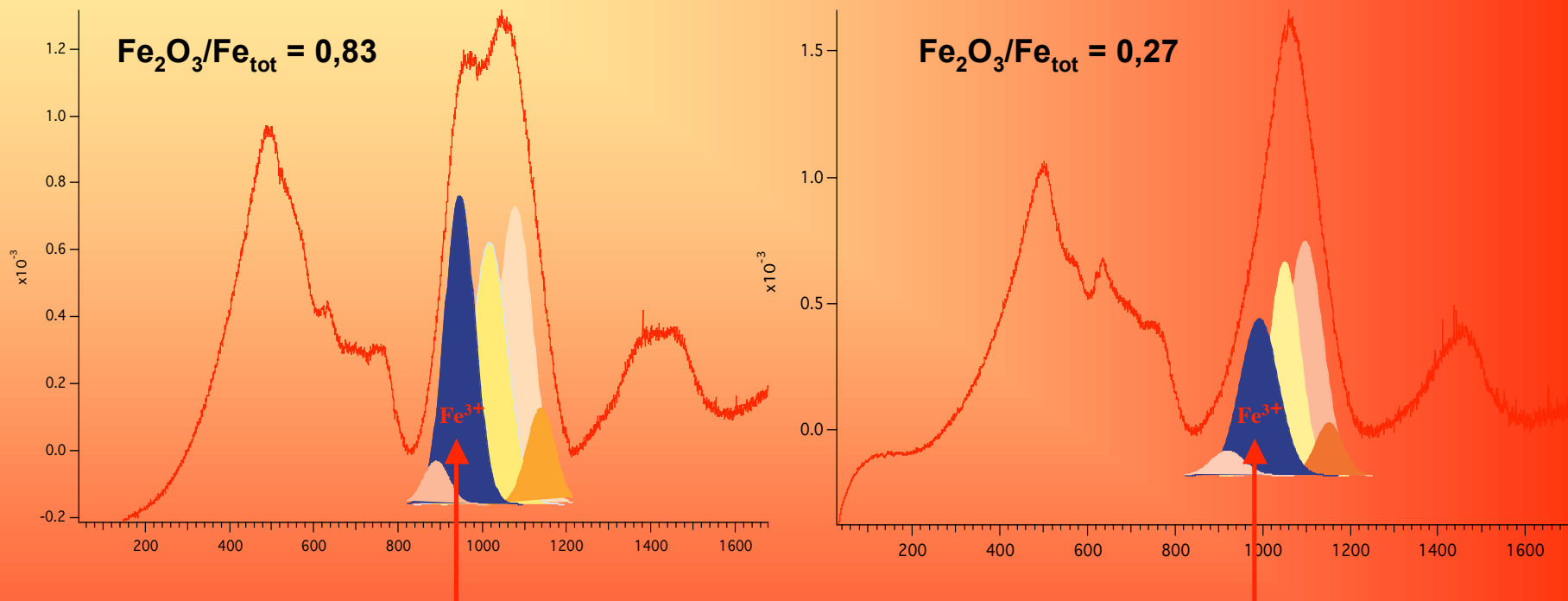
Bands of Q^n species (T = Si, Al)



Evolution of Raman spectra with iron redox ratio

Alumino-boro-silicate : **FAMA**

Proportions of diverse structural entities:
Area ratio of individual bands (Mysen et al.,1892; Mysen et al.,1984)



$$\text{Fe}_2\text{O}_3/\text{Fe}_{\text{tot}} = A([\text{Fe}^{3+}]) / A_{\text{tot}}$$

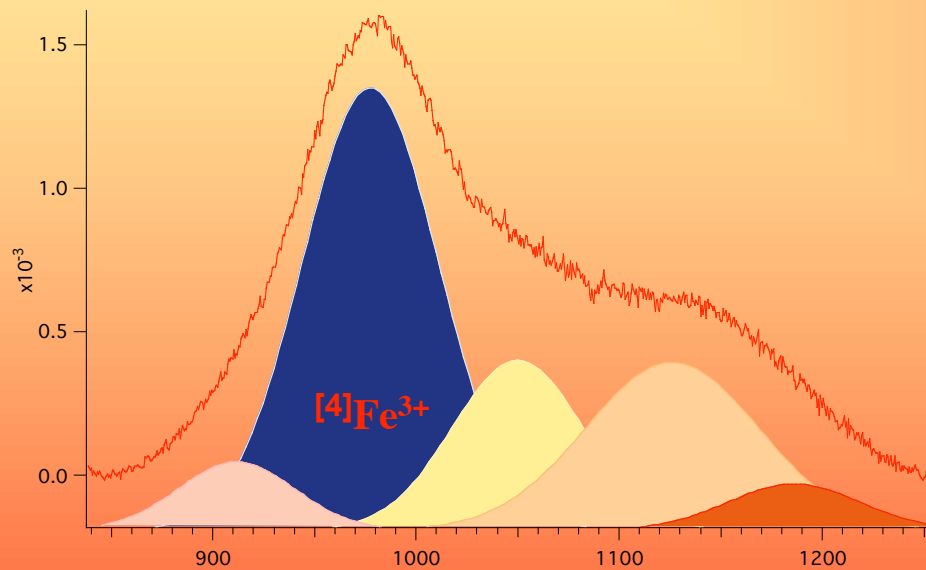
$$\text{Calibration equation } \text{Fe}_2\text{O}_3/\text{Fe}_{\text{tot}} = 6 * A([\text{Fe}^{3+}]) / A_{\text{tot}} - 0,34$$

Evolution of Raman spectra with iron redox ratio

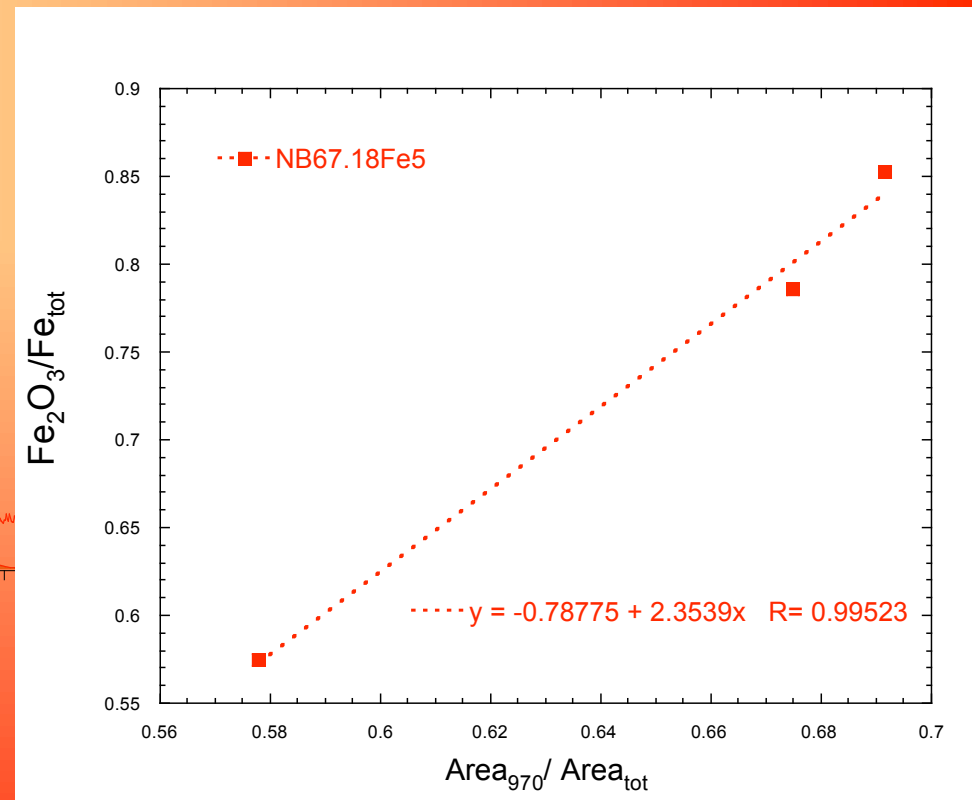
borosilicates : NB67.18Fe5

Proportions of diverse structural entities :

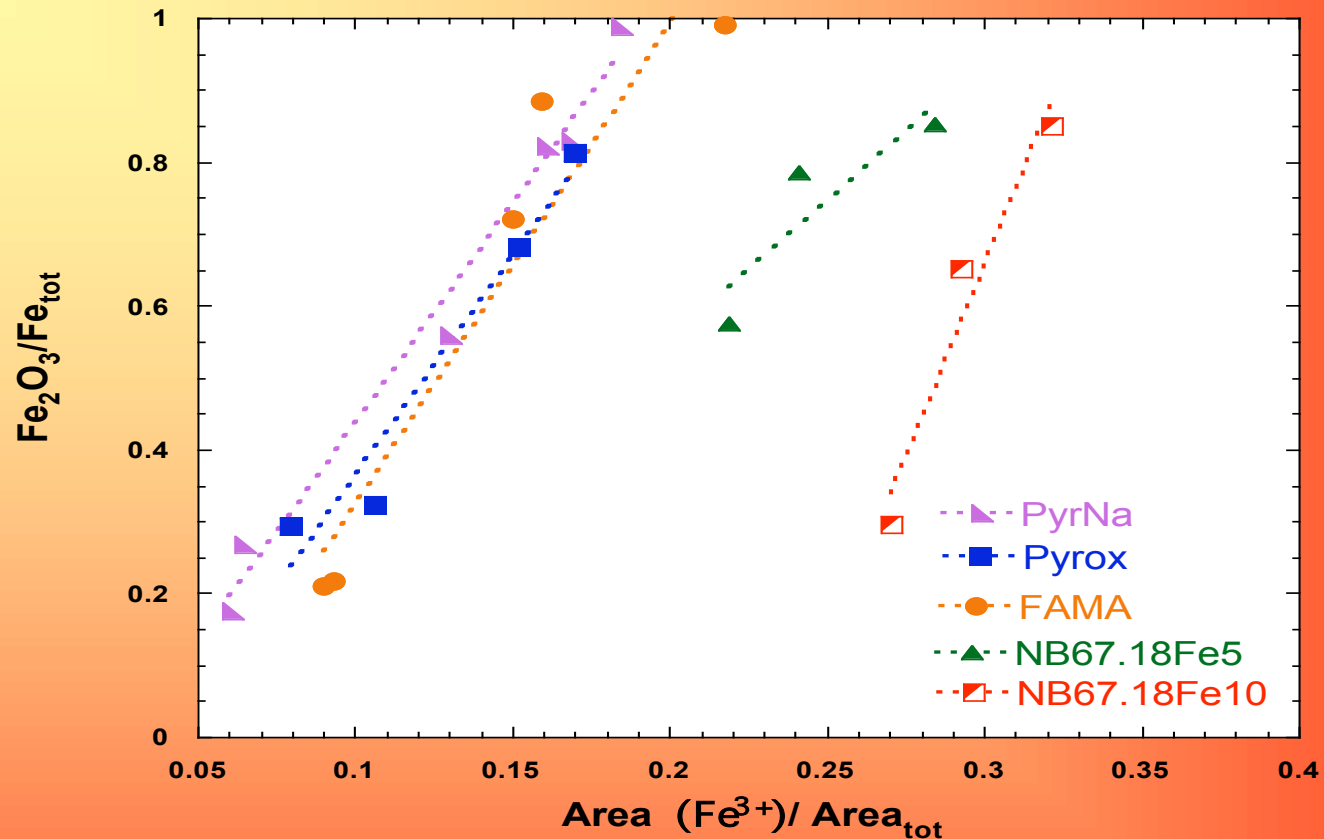
Area ratio of individual bands (Mysen et al.,1892; Mysen et al.,1984)



$$Fe_2O_3/Fe_{tot} = A([4]Fe^{3+})/A_{tot}$$

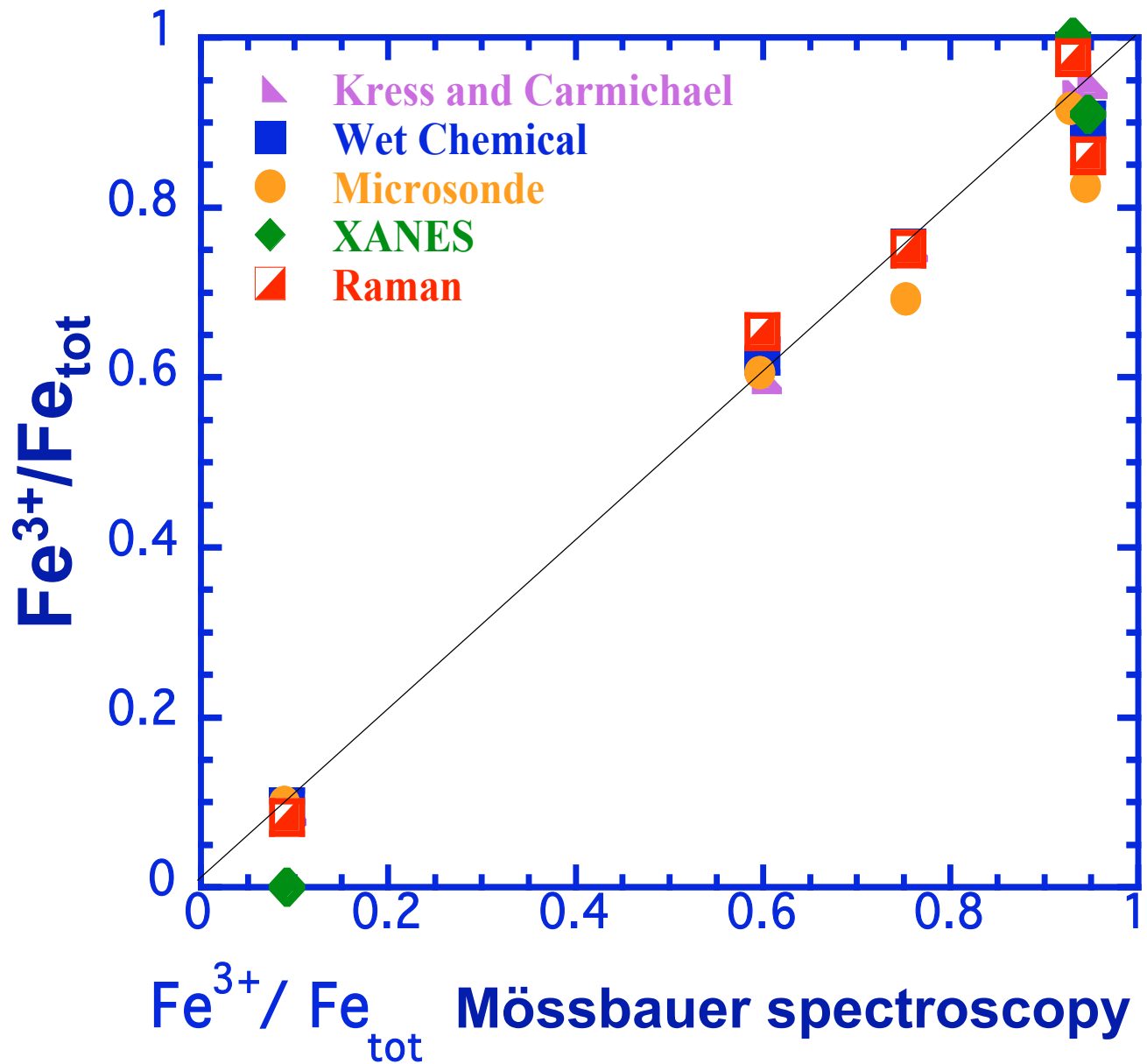


Evolution of Raman spectra with iron redox ratio

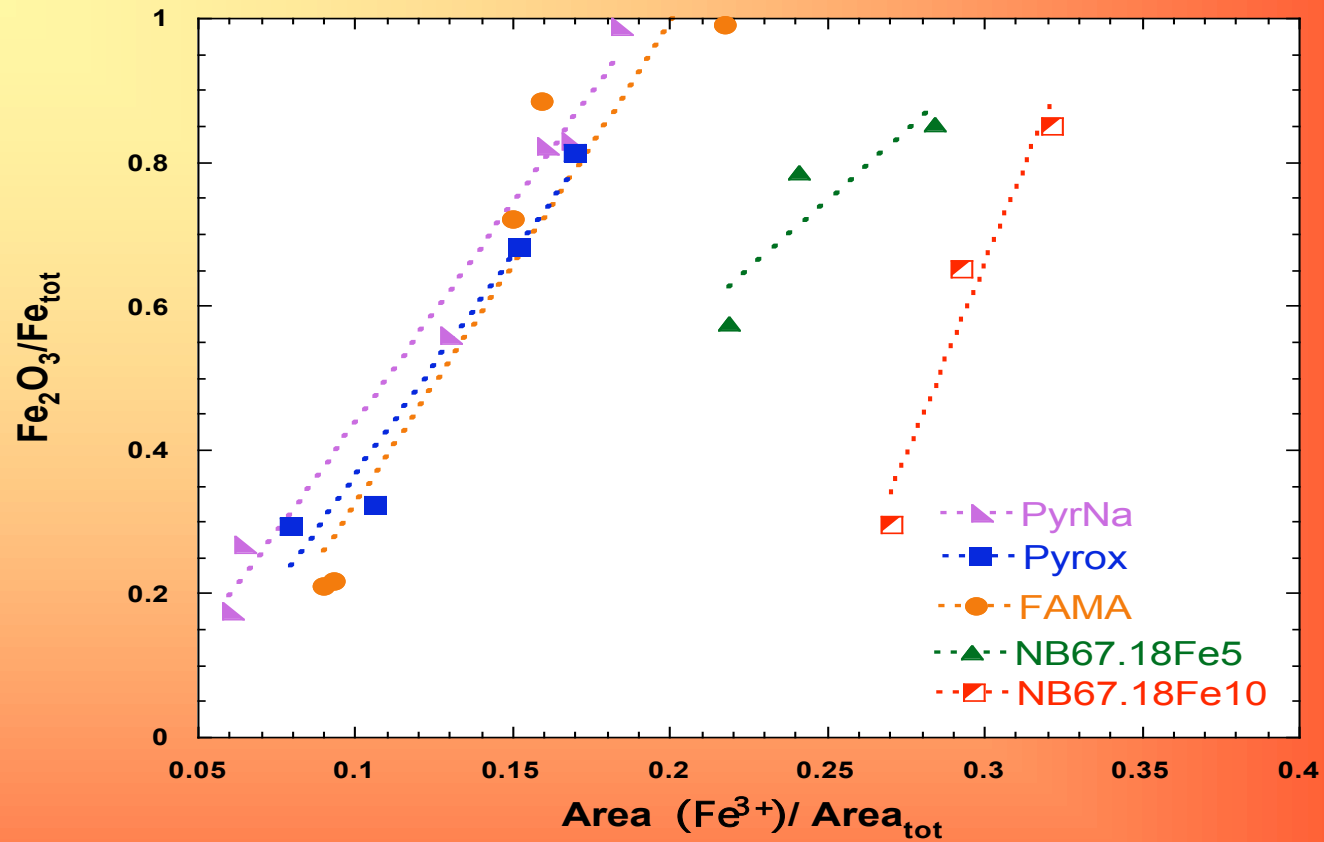


Calibration :

for each composition => need to know two redox ratios
(ideally the most reduced and most oxidized) and after we can
determine intermediate redox states

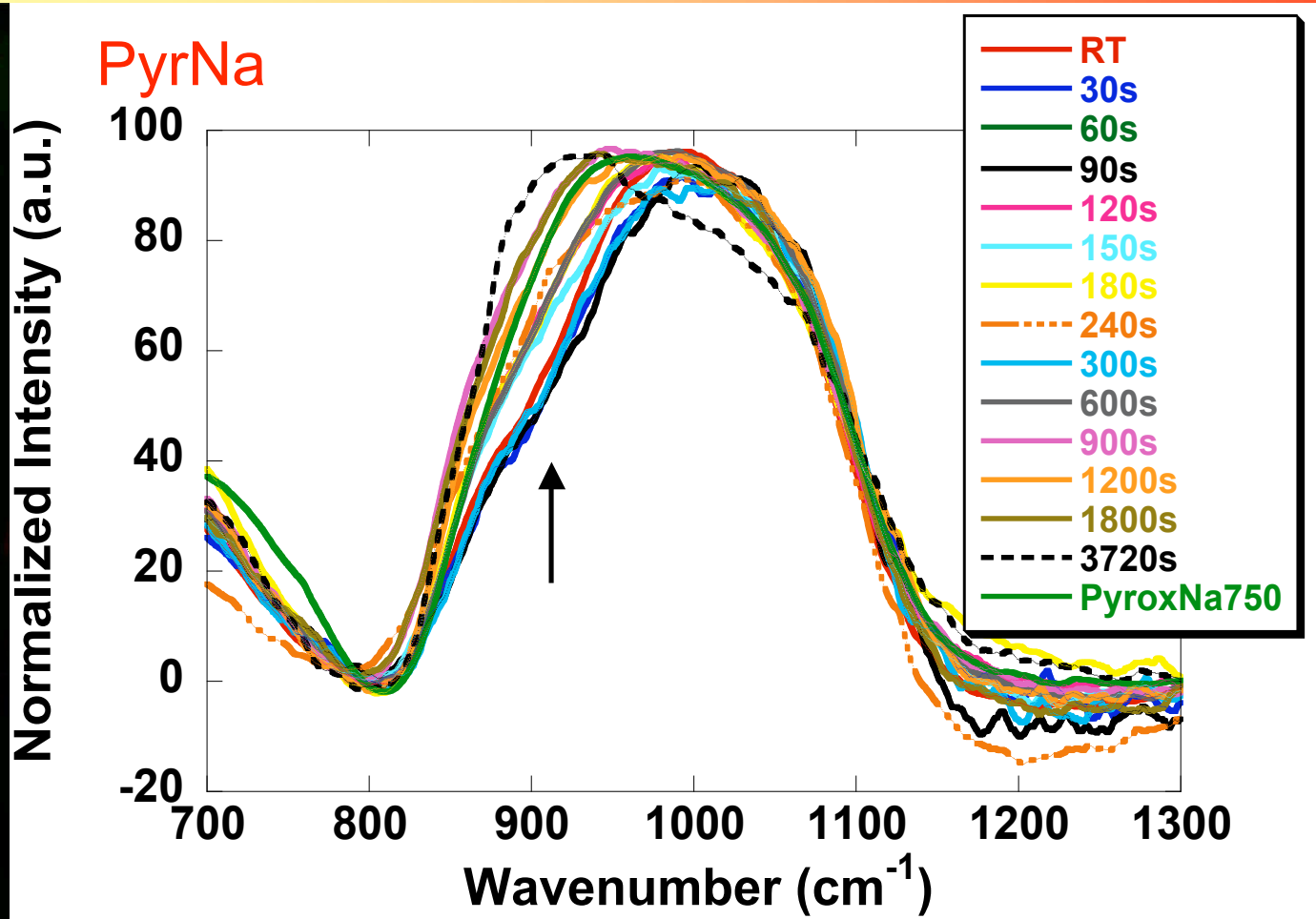


Evolution of Raman spectra with iron redox ratio



=> follow all other redox, and especially redox variation in T

Application : In situ determination of Iron redox ratio



A resolution of the 915 cm^{-1} band => progressive oxydation

Conclusion

- **Clear changes** in Raman spectra visible with the **evolution of iron redox ratio** for a given composition
- Gaussian band around 950 cm^{-1} assigned to the vibration of $[\text{Fe}^{3+}]_4\text{-O}$ bonds, and not to T-O bonds (T = $[\text{Ti}]_4$, $[\text{Ti}]_5$ or all other network formers)
- **Empirical calibration** between the area ratio of the bands in the Raman spectra and wet chemical analysis
- *In situ* determination of iron redox ratio

Thank you for your attention