How the redox play for structure and properties: implication for glass industry

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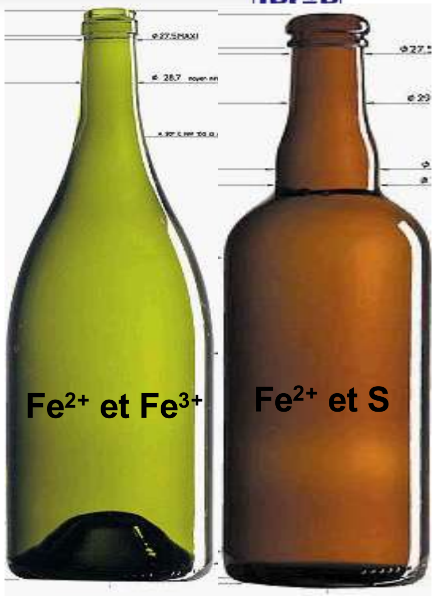
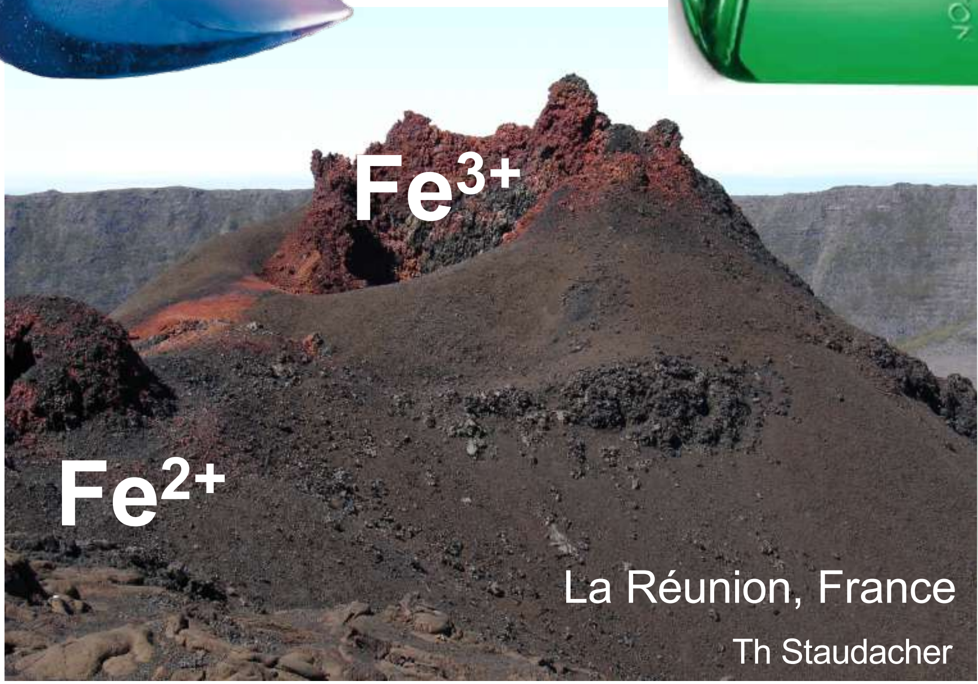
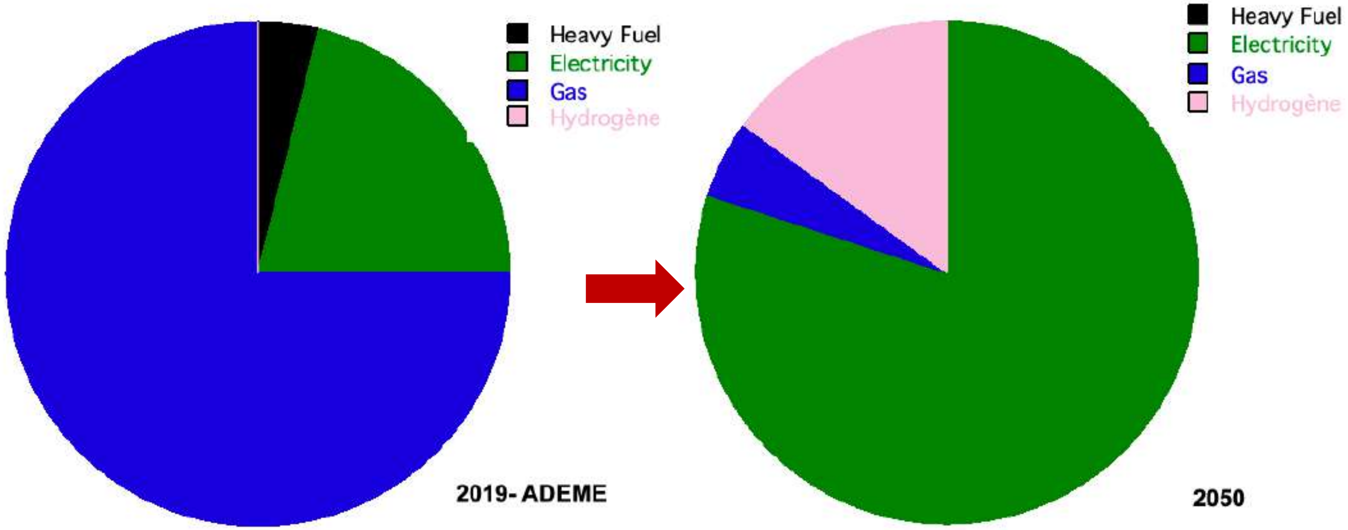
Why determine redox of glasses and melts ?





Two main sources of CO_2 emissions in the glass industry:

✓ Fossil fuels : 80% of emissions

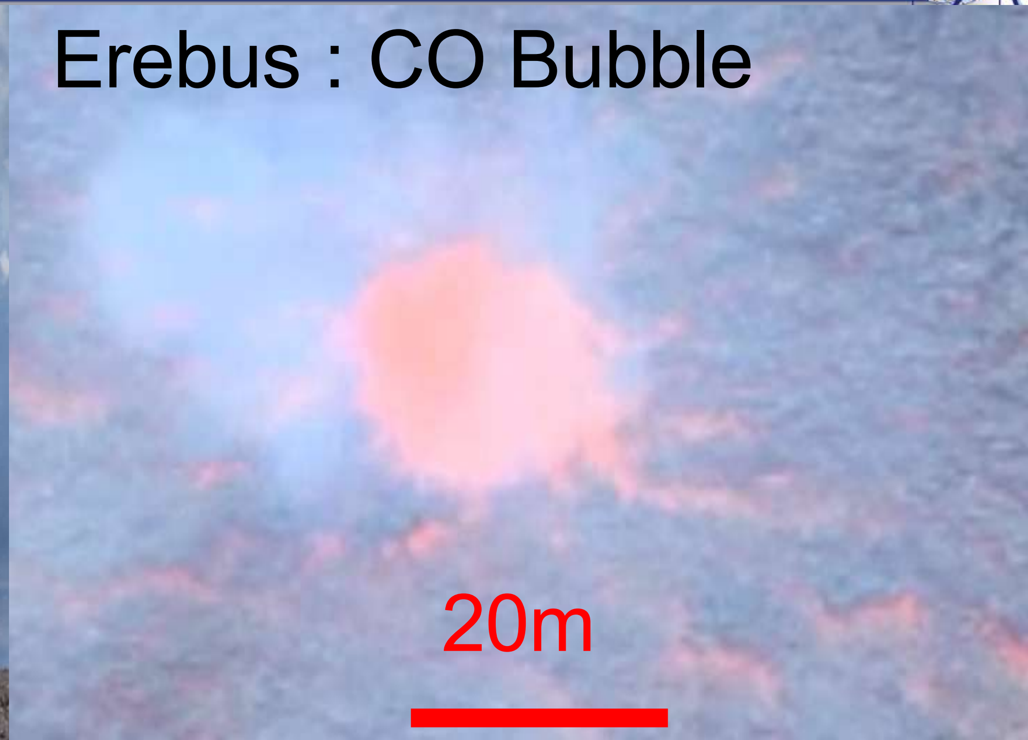


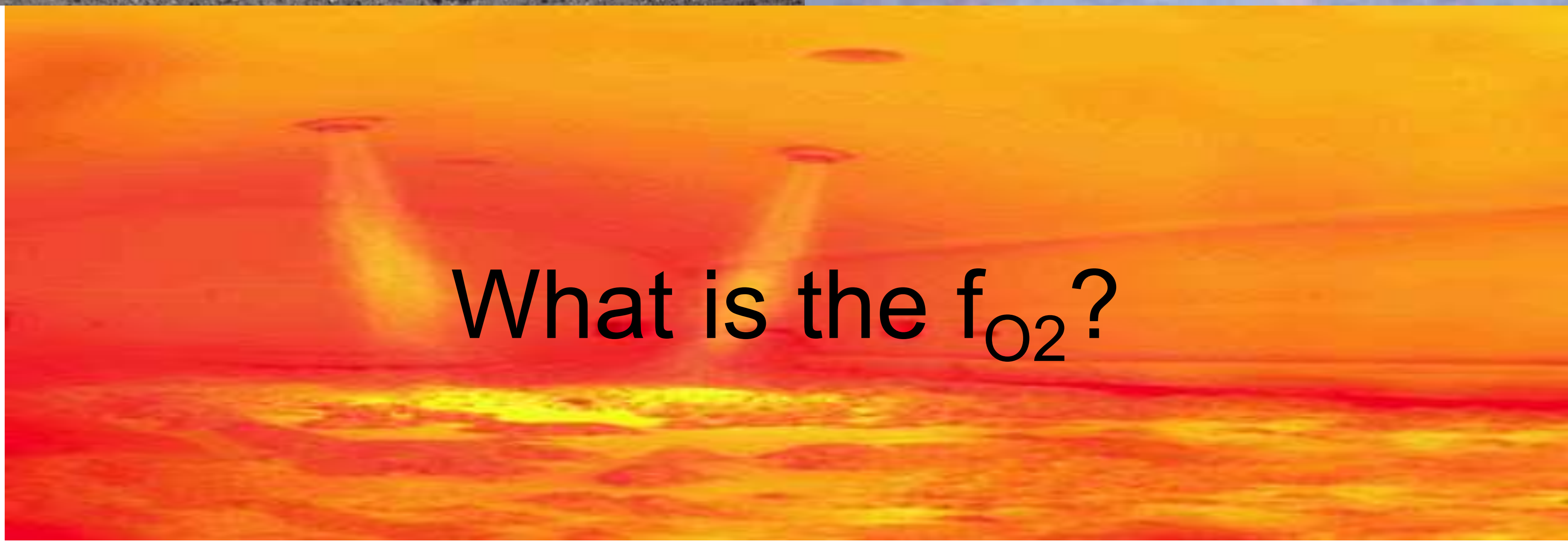
✓ Decarbonation of raw materials : 20% of emissions

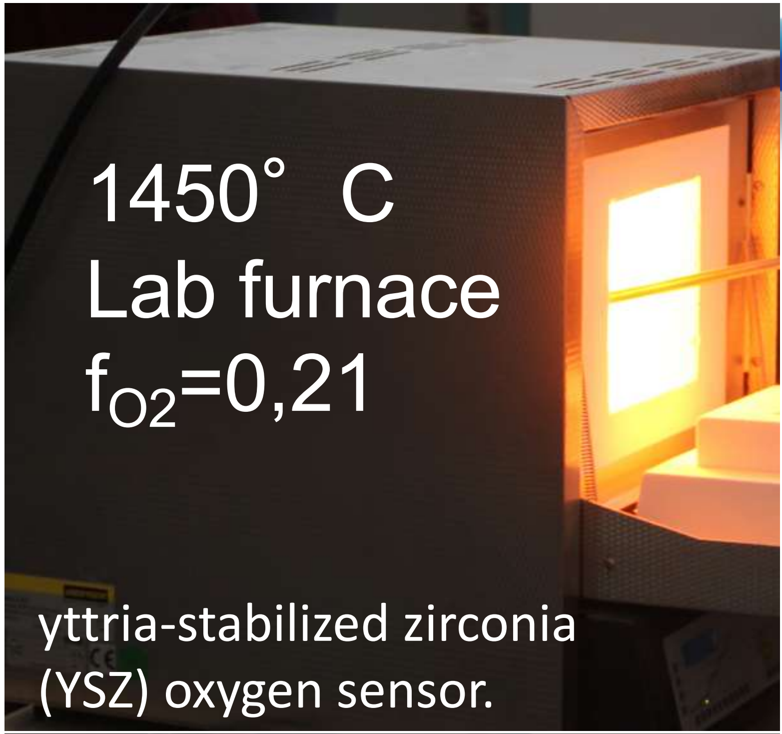
To limit CO_2 emissions, it will probably be necessary to change the chemical compositions and operating modes of furnaces, and therefore to know the oxidation-reduction of the final product and the oxidation-reduction at high temperature.

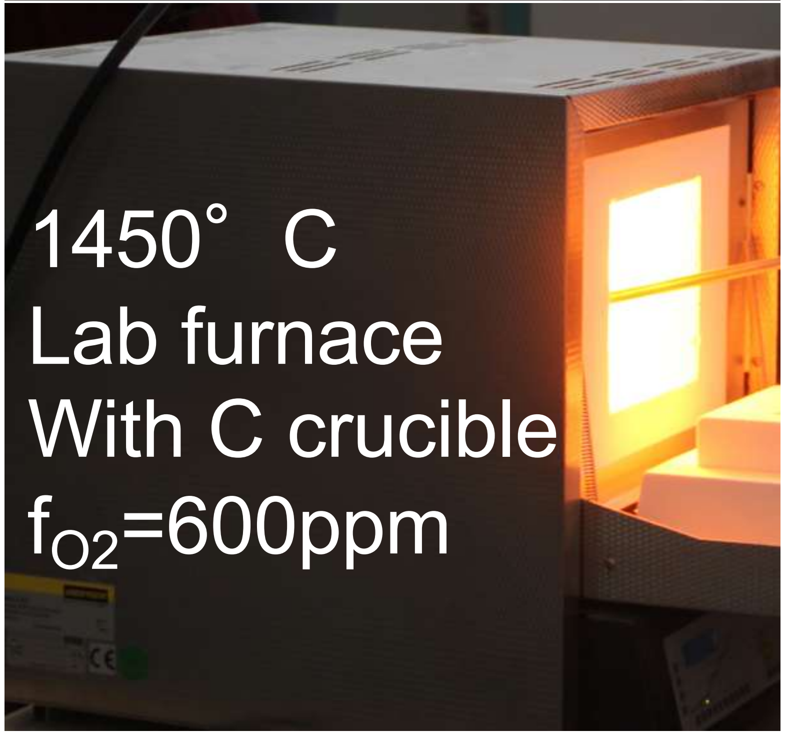
- *How redox modify the properties at HT?*
- *Is the redox of a glass the same as that of a liquid?*
- *How analyze redox state?*
- *Redox at HT in silicate glasses and melts*
- *Mixing multivalent elements*
- *Redox and nucleation*

Different furnace – different crucible = same f_{O2}?









1000° C

Celtic furnace
f_{O2}=0,21

Celtic furnace
Totally close
f_{O2}~0

1150° C 1180° C

fO_2=7% fO_2=4,4%

950° C

fO_2=3%

1150° C

fO_2=10%

1150° C

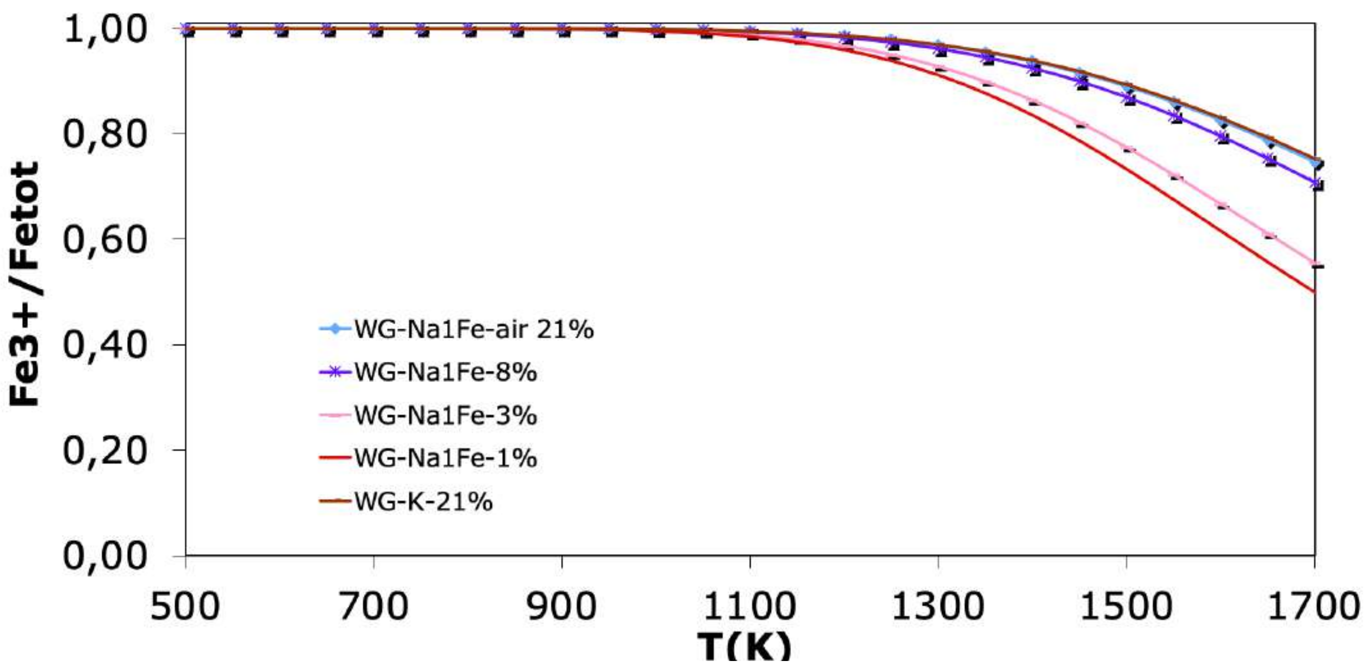
fO_2=10%

fO_2=2%

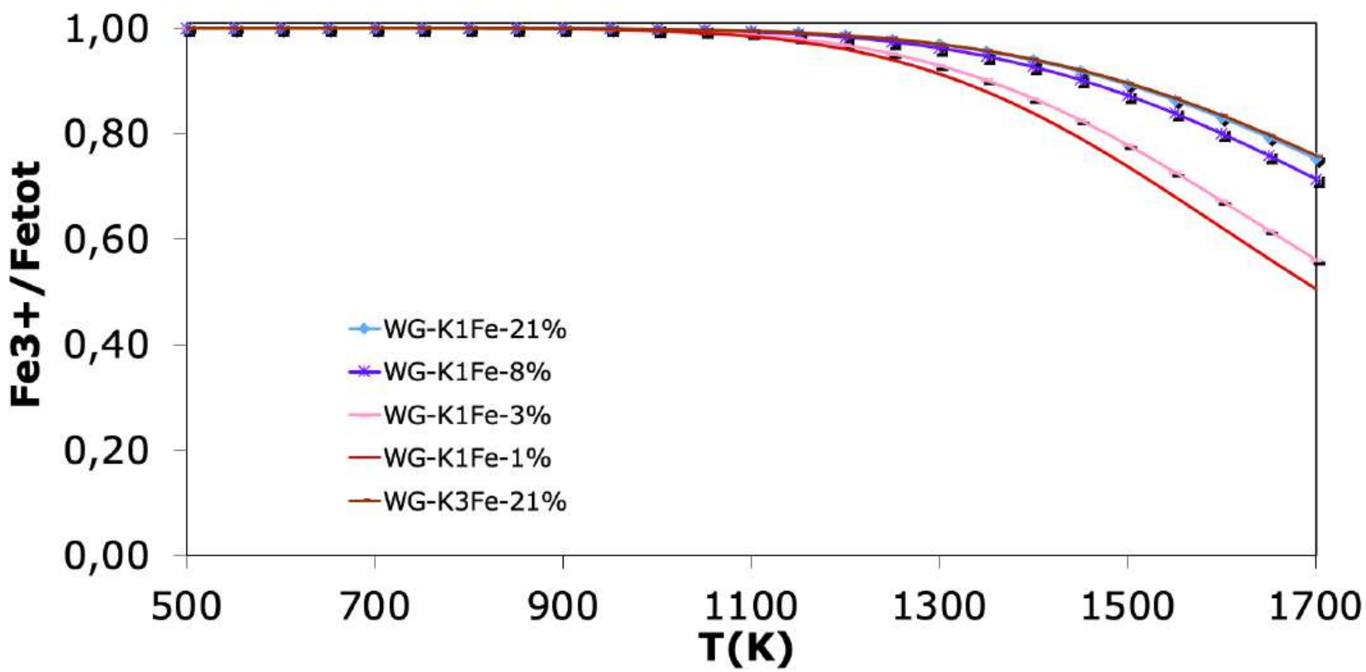
Roman glasses

SiO2	70,01
Na2O	16,50
MgO	1,00
CaO	8,50
K20	1,00
Li2O	0,00
Al2O3	2,00
FeO	1,00
total	100,00

Wt%



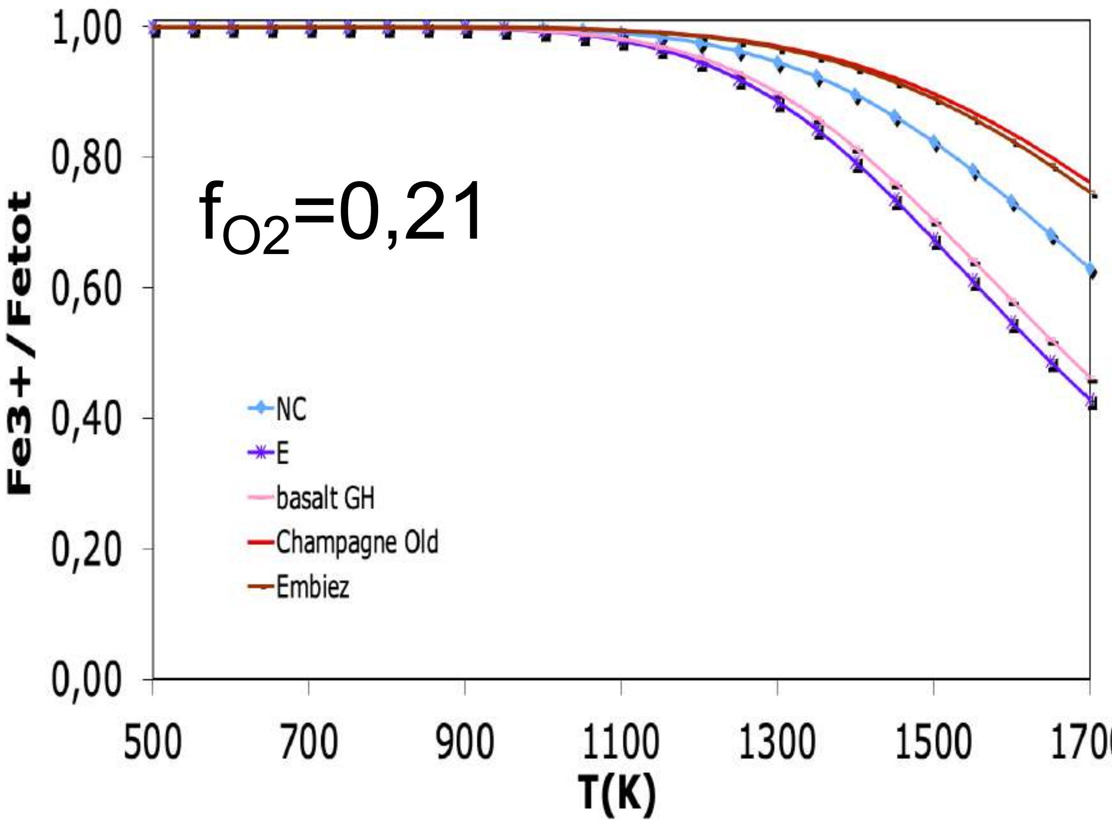
SiO2	56,99
Na2O	0,98
MgO	3,50
CaO	14,19
K20	20,11
Li2O	0,00
Al2O3	3,22
FeO	1,00
total	100,00

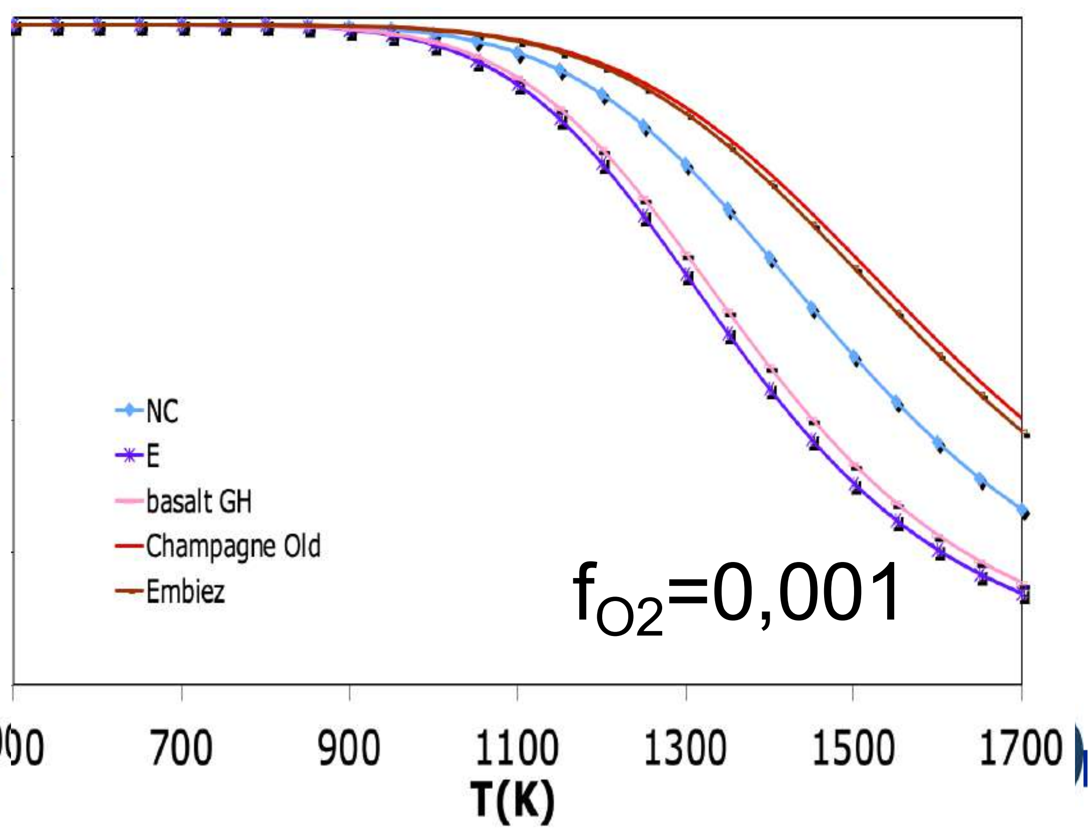


How redox vary as a function of chemical composition, T and f_{O2}?

	NC	E	basalt GH	champagne old	Embiez
SiO2	72,61	56,51	48,37	58,50	72,75
Na2O	14,32	0,45	3,11	9,90	19,00
MgO	3,64	2,65	8,59	0,00	0,40
CaO	8,67	18,36	10,28	18,60	5,23
K20	0,21	0,35	1,36	1,80	0,39
Li2O	0,00	0,00	0,00	0,00	
Al2O3	0,61	6,40	14,56	2,10	1,78
FeO	0,78	0,55	13,00	8,90	0,33

Wt%



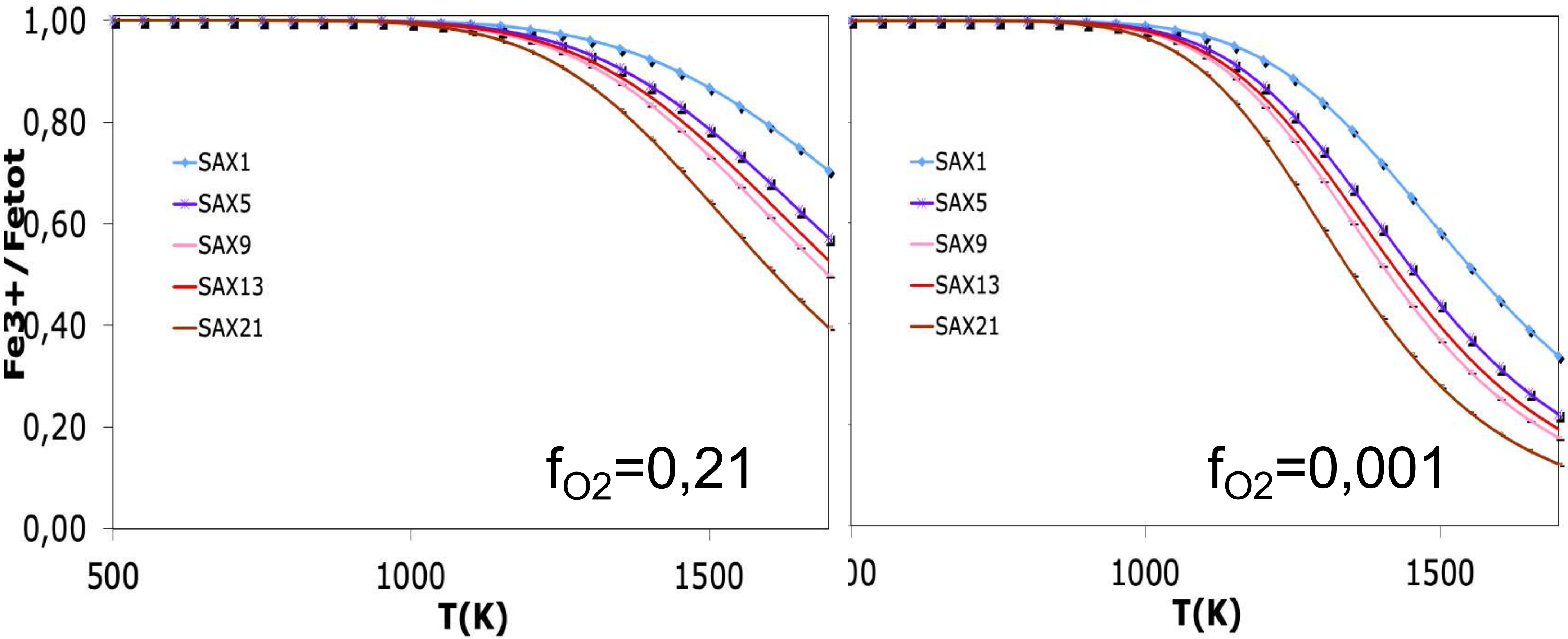


How redox vary as a function of chemical composition, T and f_{O2}?

Wt%	SAX1	SAX5	SAX9	SAX13	SAX21
SiO2	70,00	70,00	72,00	68,23	73,97
Na2O	20,00	15,00	10,61	0,00	5,45
MgO	5,00	7,50	6,90	6,54	7,09
CaO	5,00	7,50	9,60	9,10	9,86
K2O				15,28	
Li2O					2,63
Al2O3	0,50	7,00	0,87	0,83	0,90
FeO	0,02	0,02	0,02	0,02	0,02

Wt%

Ultra clear glass

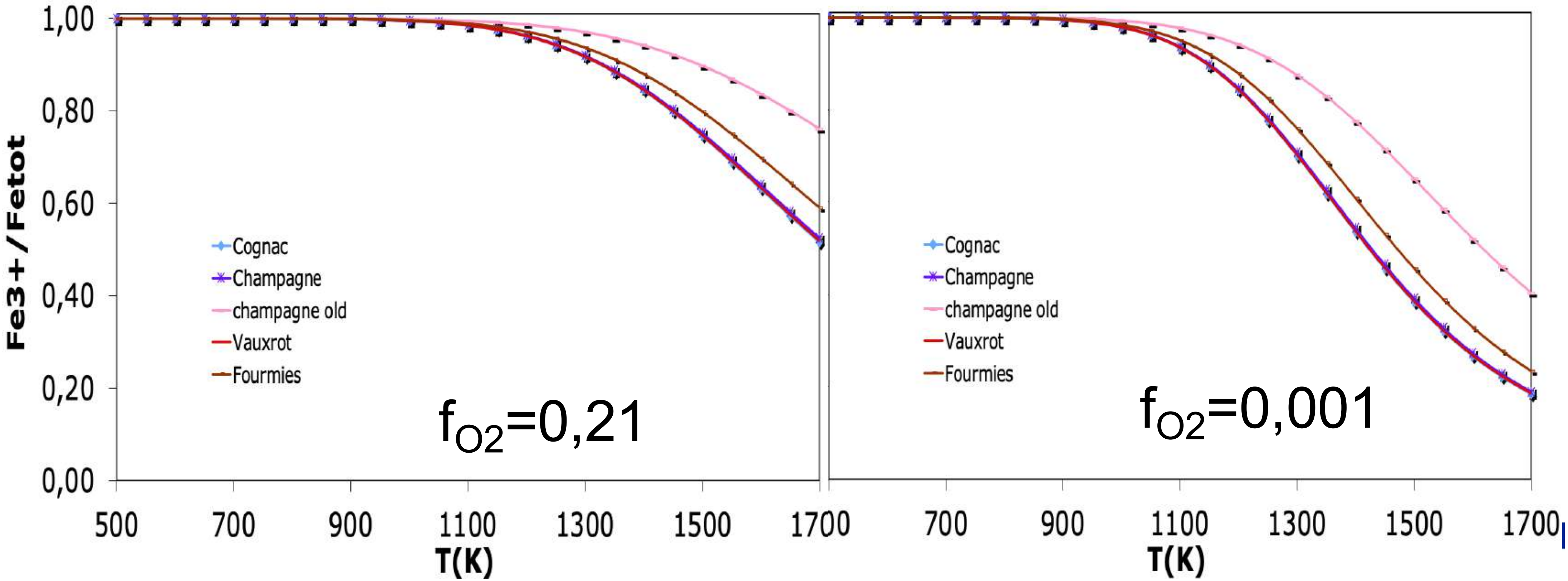


How redox vary as a function of chemical composition, T and f_{O2}?

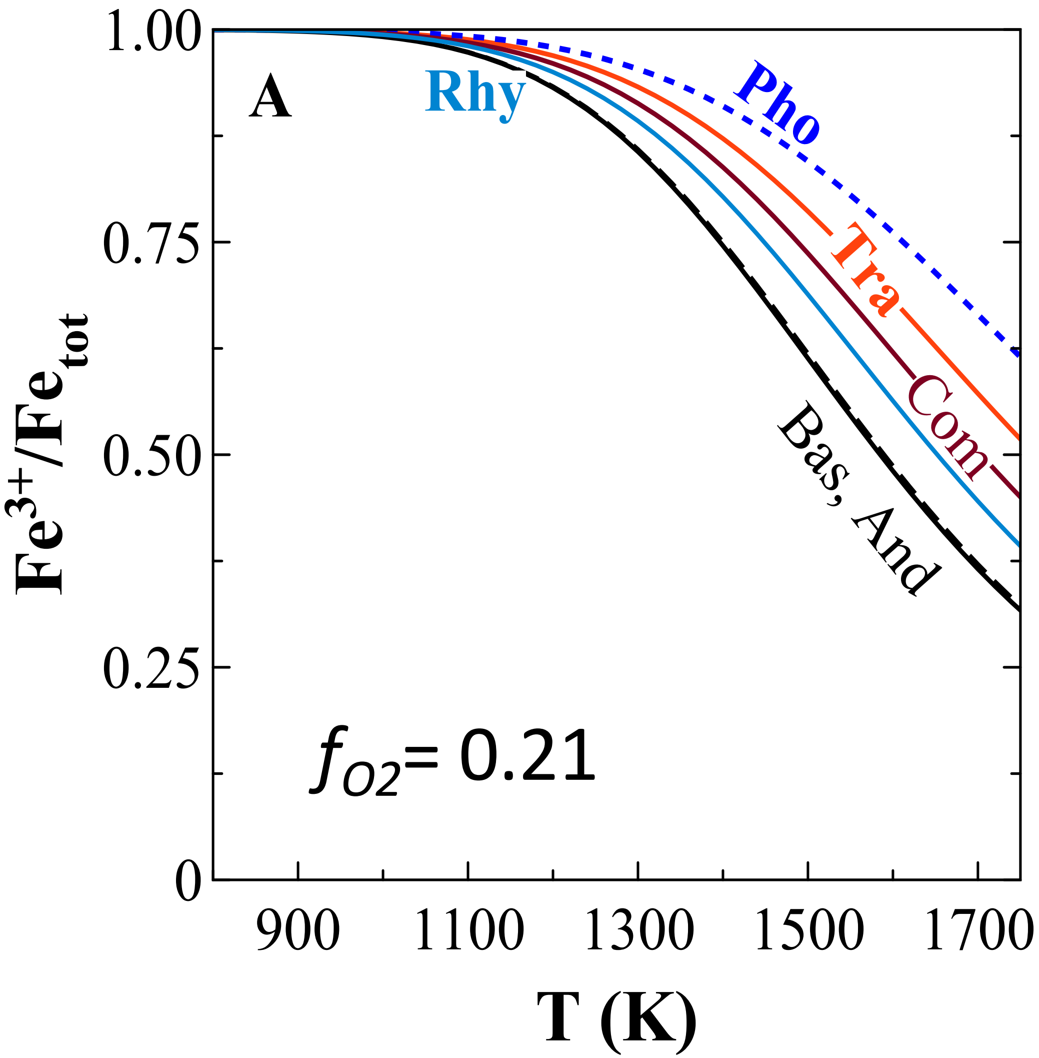
	Cognac	Champagne	champagne old	Vauxrot	Fourmies
SiO2	62,54	61,90	58,50	59,70	62,50
Na2O	4,73	6,16	9,90	6,10	6,80
MgO	5,41	6,38	0,00	8,00	4,00
CaO	20,47	17,95	18,60	21,40	21,30
K20	0,94	1,13	1,80	0,00	0,50
Li2O	0,00	0,00	0,00	0,00	
Al2O3	4,42	4,44	2,10	2,39	2,93
FeO	1,34	1,85	8,90	2,21	2,17

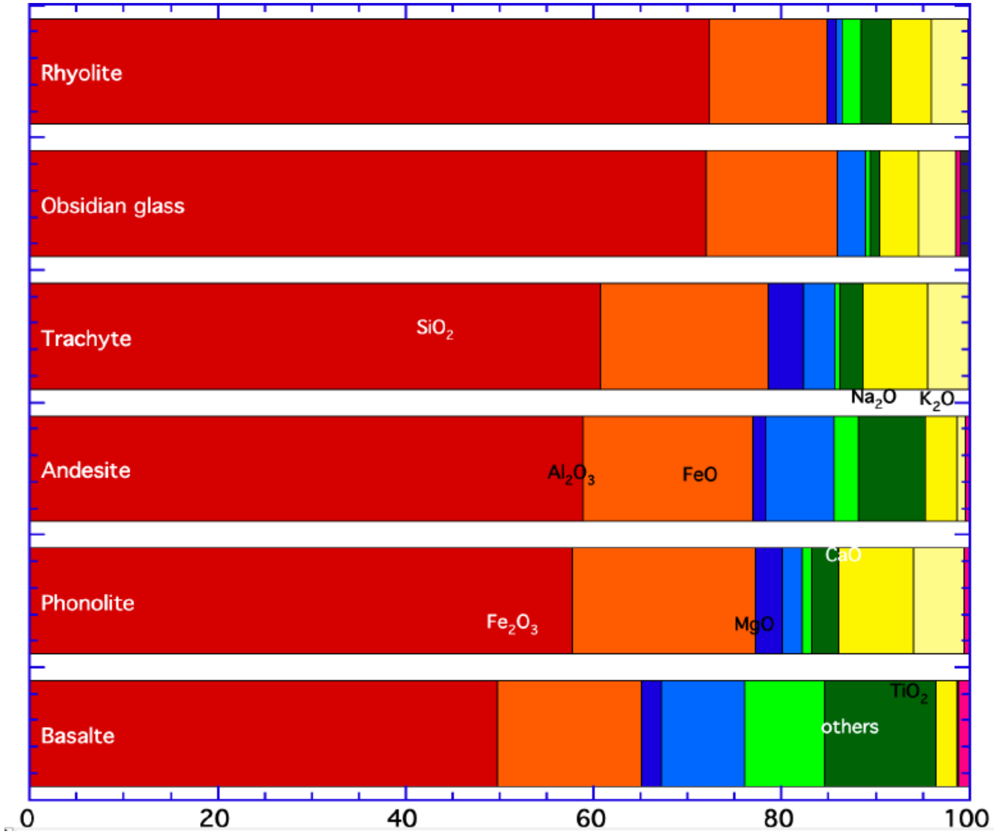
Bottles

Wt%



- How redox vary as a function of chemical composition, T and f_{O2}?





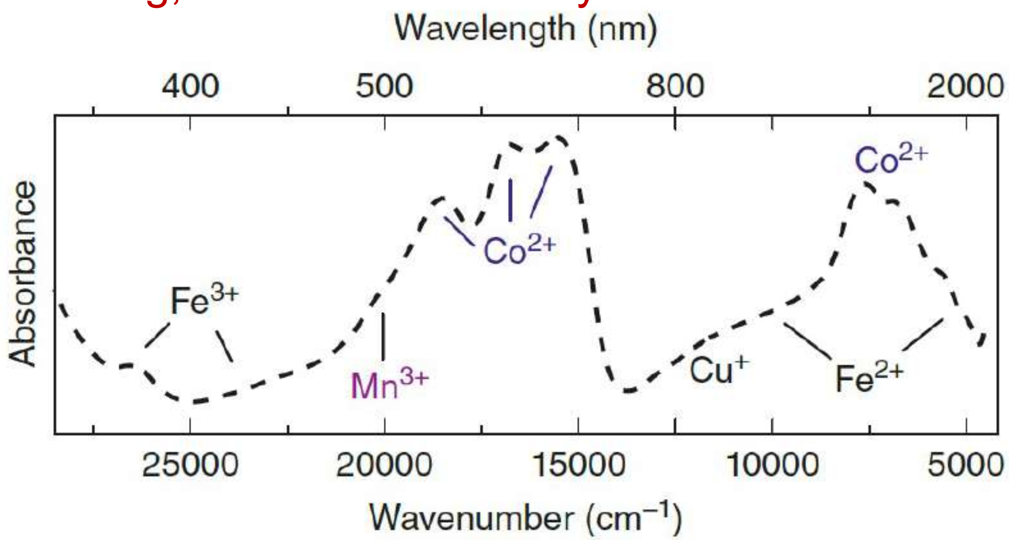
Cicconi M.R., Moretti R., Neuville D.R. (2020) Earth Electrodes, Elements, edt. Moretti R., Cicconi M.R., Neuville "The redox engine of the Earth". DOI: 10.2138/gselements.16.3.157

Wet chemistry analyzed

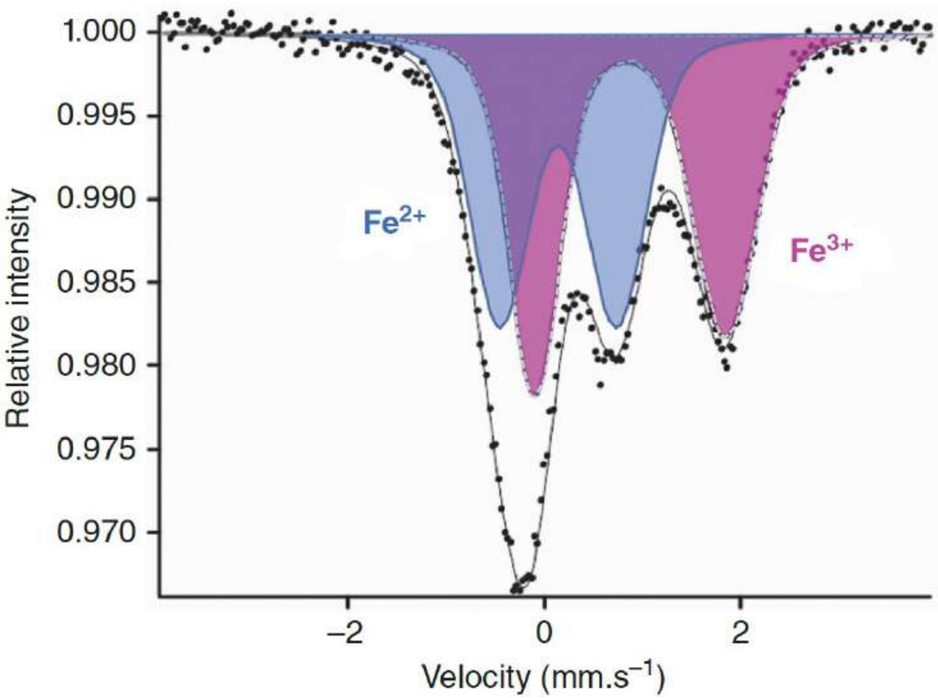
Wet chemistry FeO content, sensibility limit ≈10 ppm
Precision Δ=+/ - 5 ppm

Optical spectroscopy

=> possible at HT, Laurent Cormier or Gérald Lelong, Sorbonne University

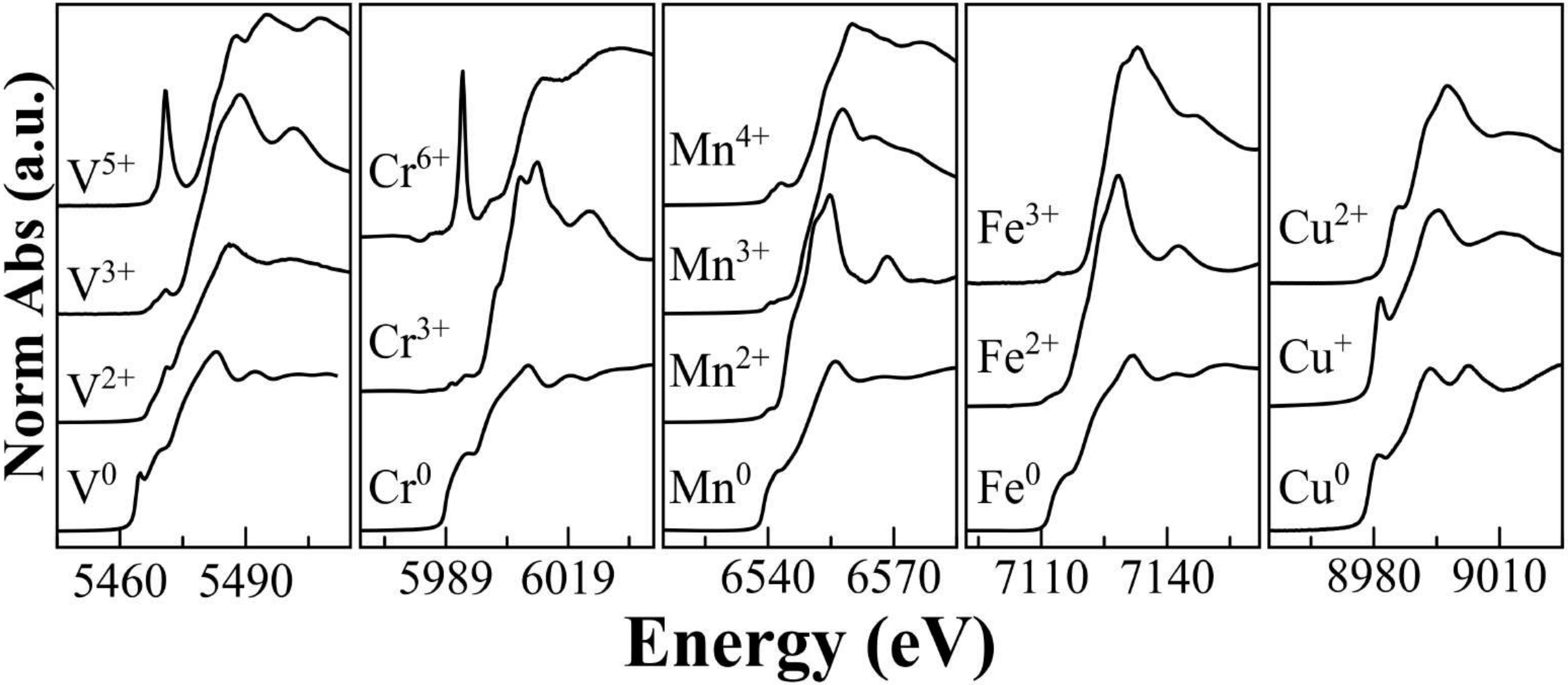


Mossbauer spectroscopy



Limitations:
- **at room temperature**
- **big samples**
- **no spatial resolution**
- **difficult to prepare**

Neuville D.R., Cicconi M.R. (2021) How measure a redox state? Magma Redox Geochemistry. AGU Geophysical Monography Series eds Moretti and Neuville. – DOI : 10.1002/9781119473206.ch13

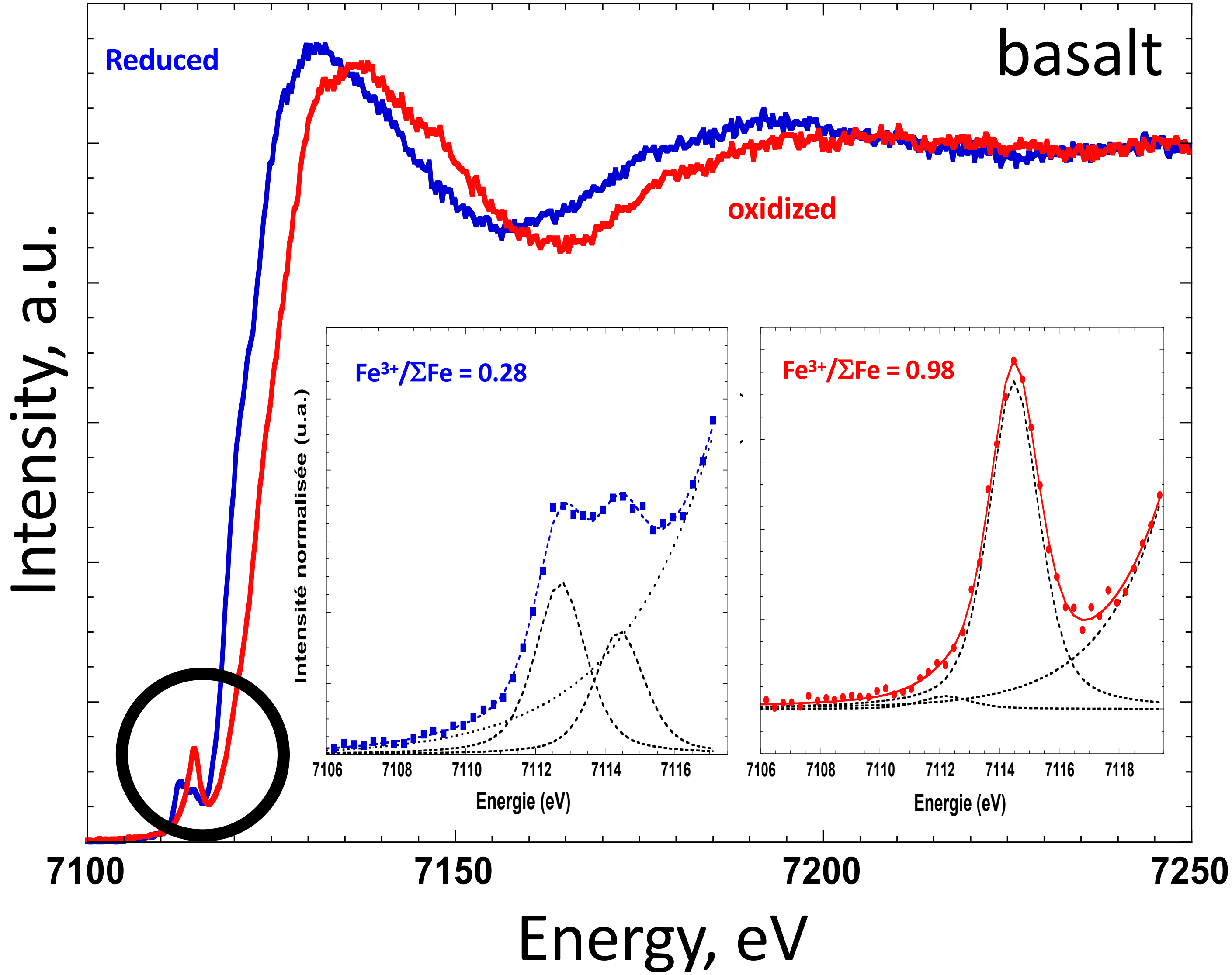


XANES possible for almost all elements depend on light source

Possible measurement at HT, HP, mapping…..

Neuville D.R., Cicconi M.R. (2021) How measure a redox state? Magma Redox Geochemistry. AGU Geophysical Monography Series eds Moretti and Neuville. – DOI : 10.1002/9781119473206.ch13

Determination of iron redox by Fe-K edge XANES



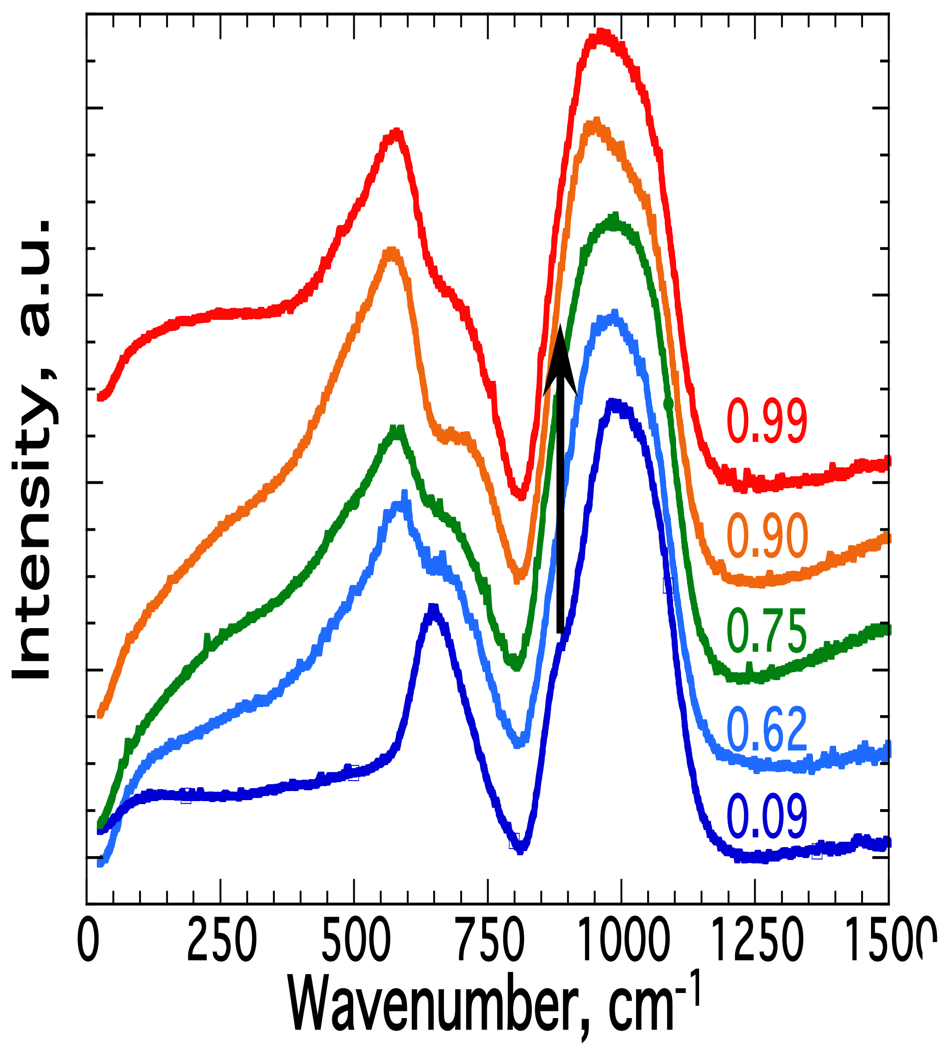
Iron K-edge: redox state and local structure

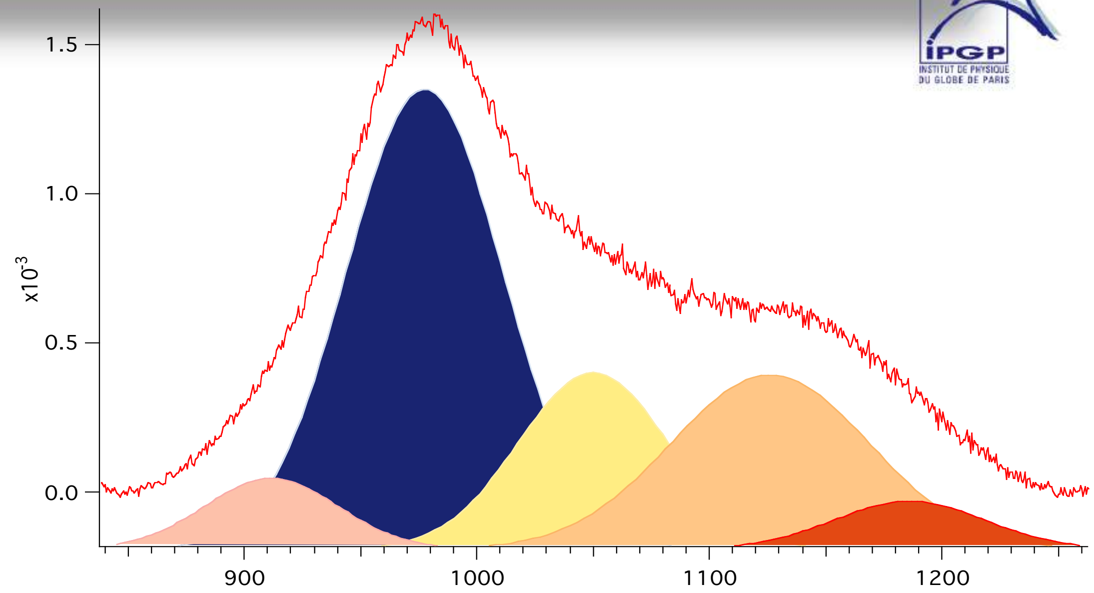
Magnien V., Neuville D.R., Cormier L., Mysen B.O. and Richet P. (2004) Kinetics of iron oxidation in silicate melts: A preliminary XANES study. Chem. Geol., 213, 253-263

*Experiments made on the **ODE** beamline at SOLEIL, France with **F. Baudelet**, on the **FAME** beamline at ESRF with **Denis Testemale** , on the **ID24** beamline at ESRF with **A. Trapananti** and on the **XAFS** beamline at ELETTRA, ITALY with **L. Olivi***

Raman spectroscopy

50%SiO2-20%MgO-20%CaO-5%Na2O-5%FeO



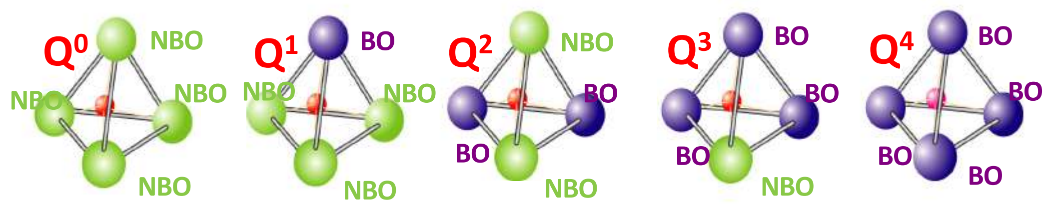


Magnien V., Neuville D.R., Cormier L., Roux J., Pinet O. and Richet P. (2006) Kinetics of iron redox reactions: A high-temperature XANES and Raman spectroscopy study. Journal of Nuclear Materials, 352, 190-195.

Evidence of Fe^{3+} in tetrahedral coordination in Q^4:

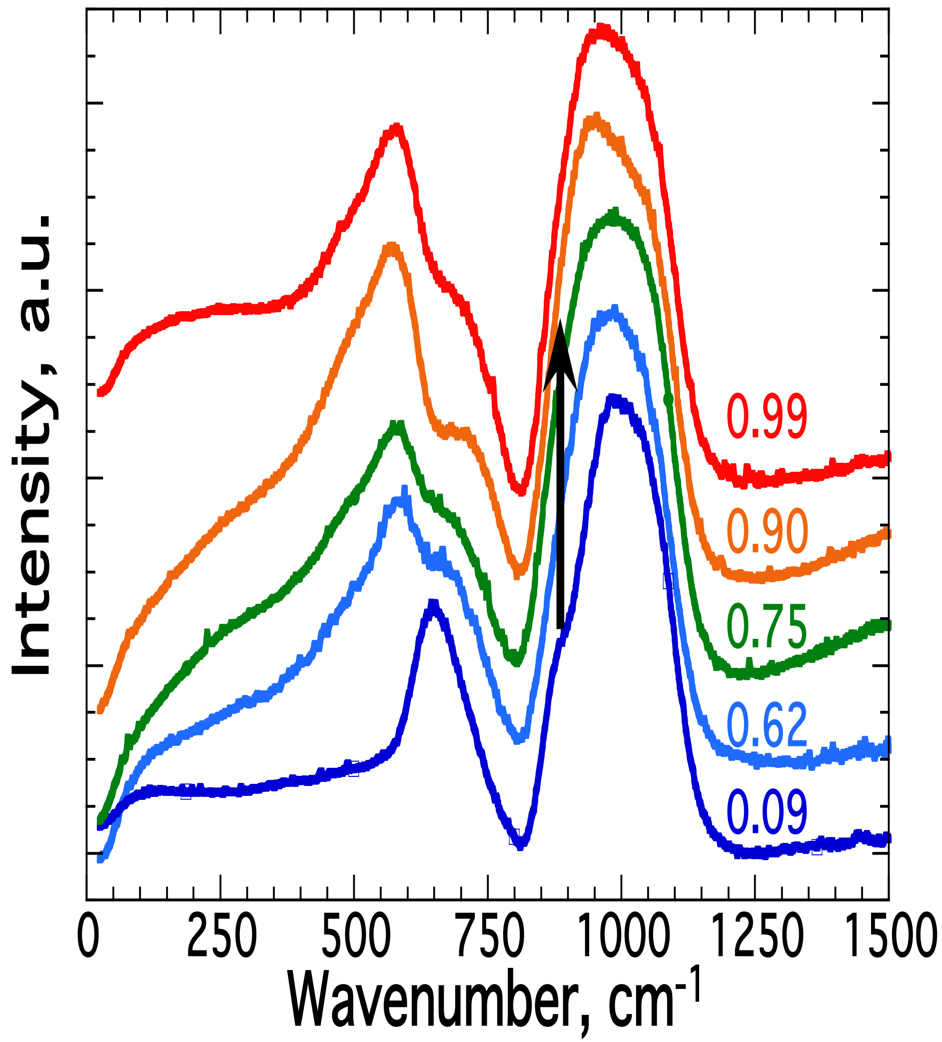
- Mössbauer => center shift < 0.30mm/s (Mysen, 1983; Alberto et al. 1996)
- Iron K -edge XANES => integrated pre-edge area characteristic for $^{[4]}Fe^{3+}$

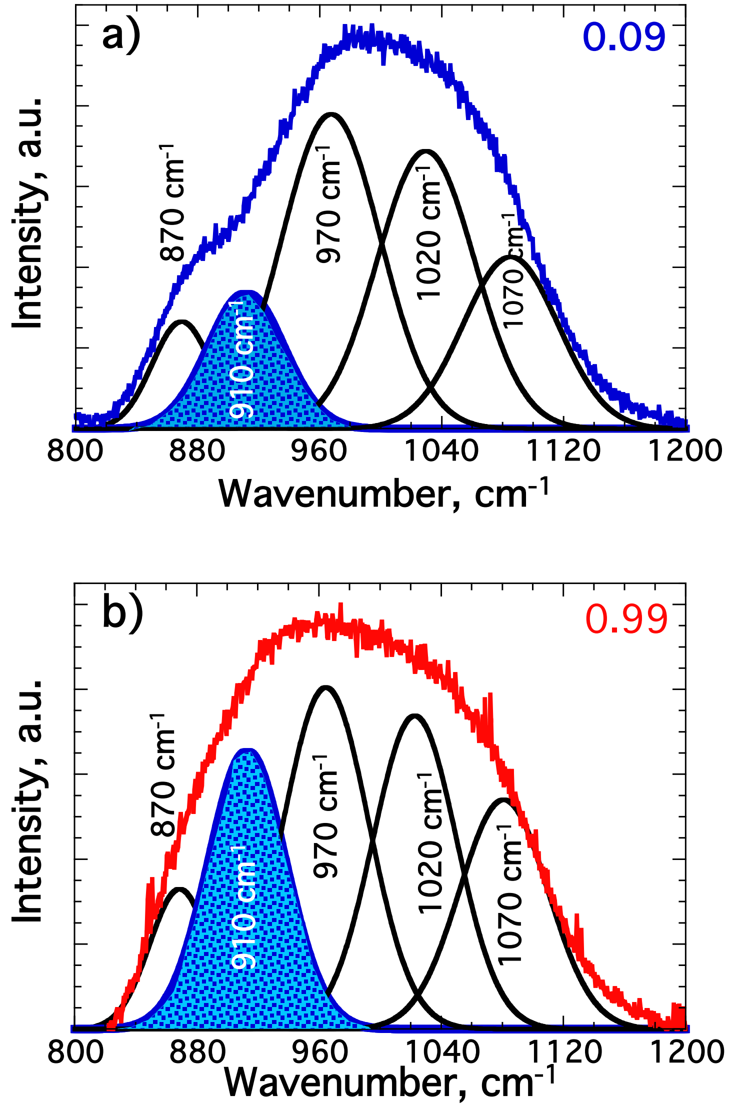
Bands of Qn species (Q = Si, Al)



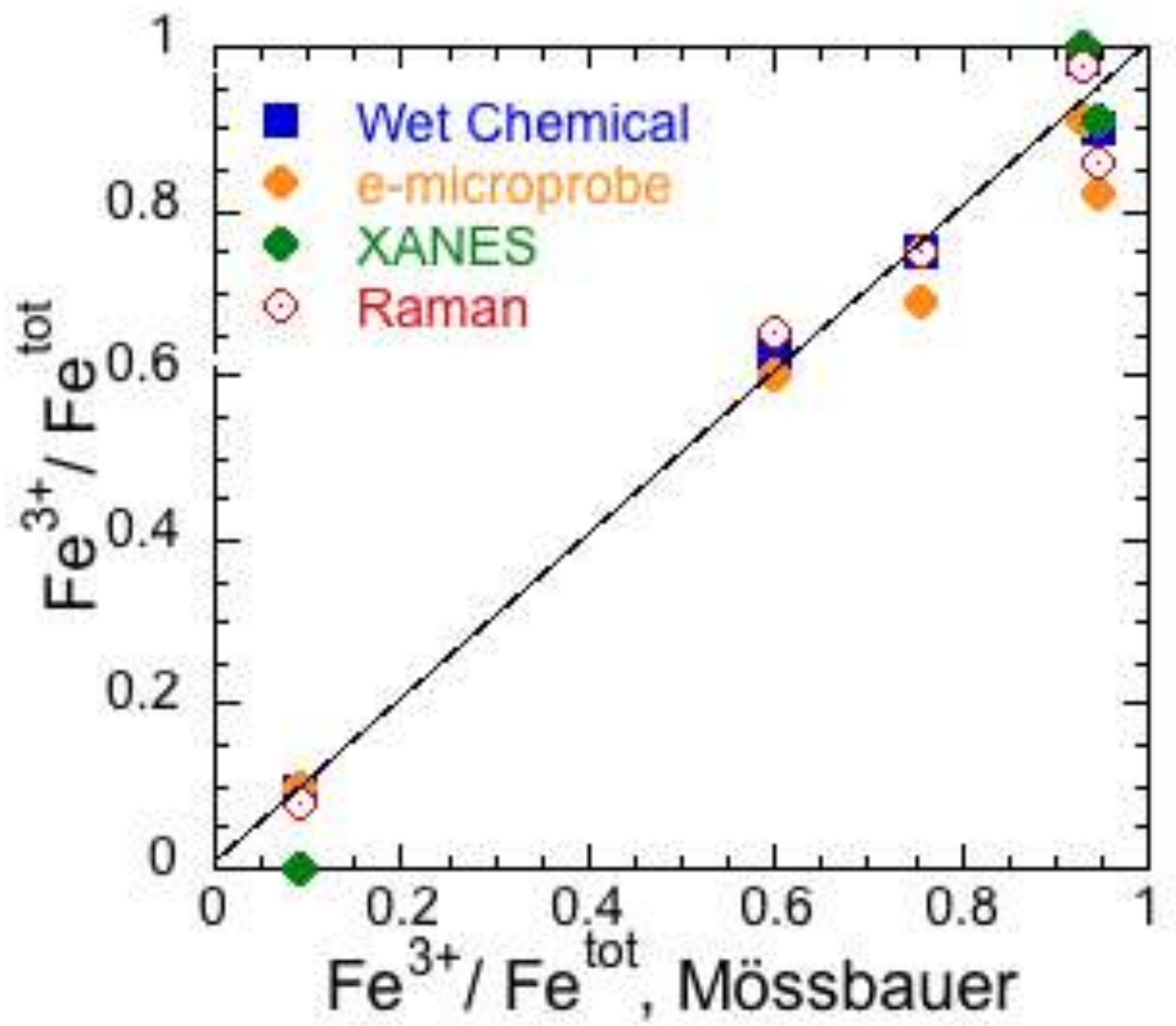
Raman spectroscopy

50%SiO2-20%MgO-20%CaO-5%Na2O-5%FeO





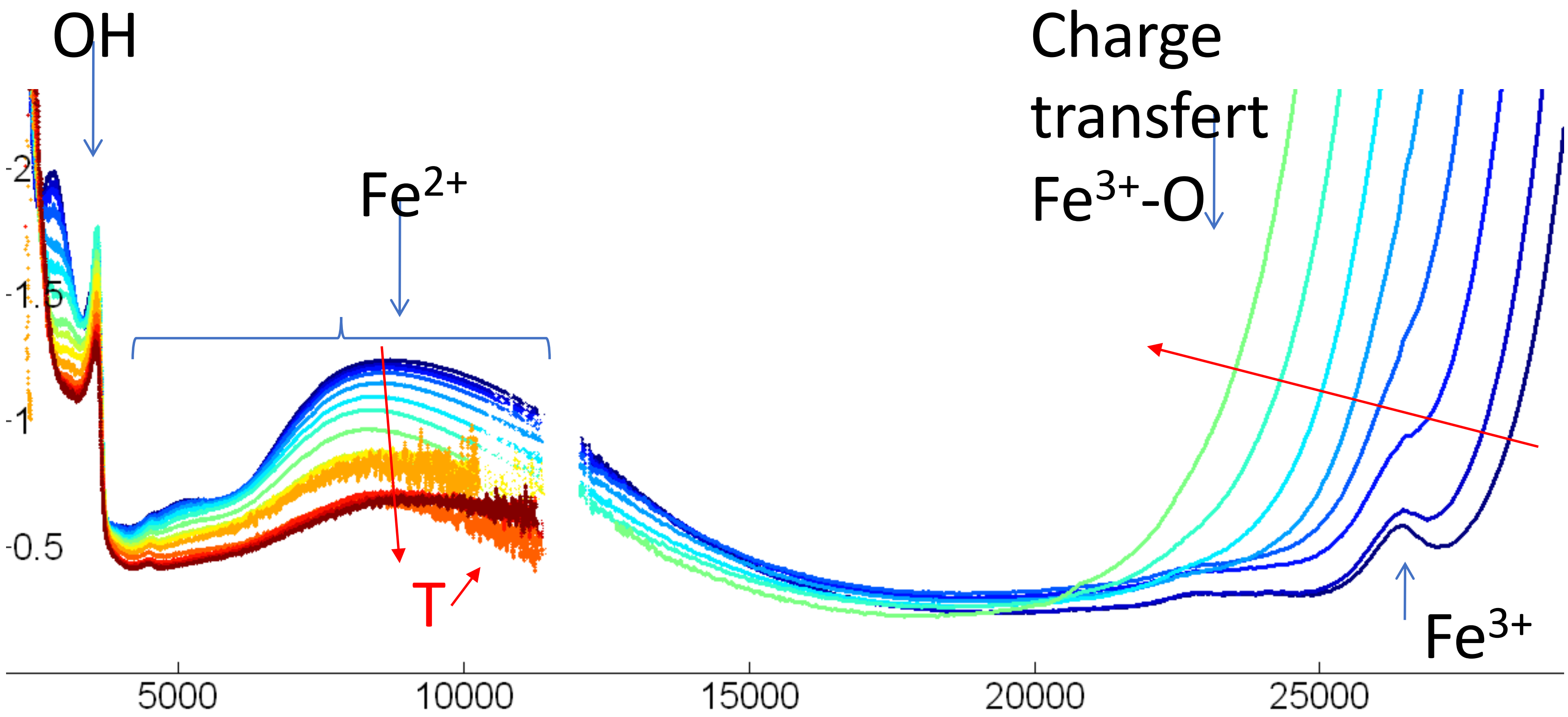
Magnien V., Neuville D.R., Cormier L., Roux J., Pinet O. and Richet P. (2006) Kinetics of iron redox reactions: A high-temperature XANES and Raman spectroscopy study. Journal of Nuclear Materials, 352, 190-195.



=> Good compatibility between different techniques

Neuville D.R., Cicconi M.R. (2021) How measure a redox state? Magma Redox Geochemistry. AGU Geophysical Monograph Series eds Moretti and Neuville. – DOI : 10.1002/9781119473206.ch13

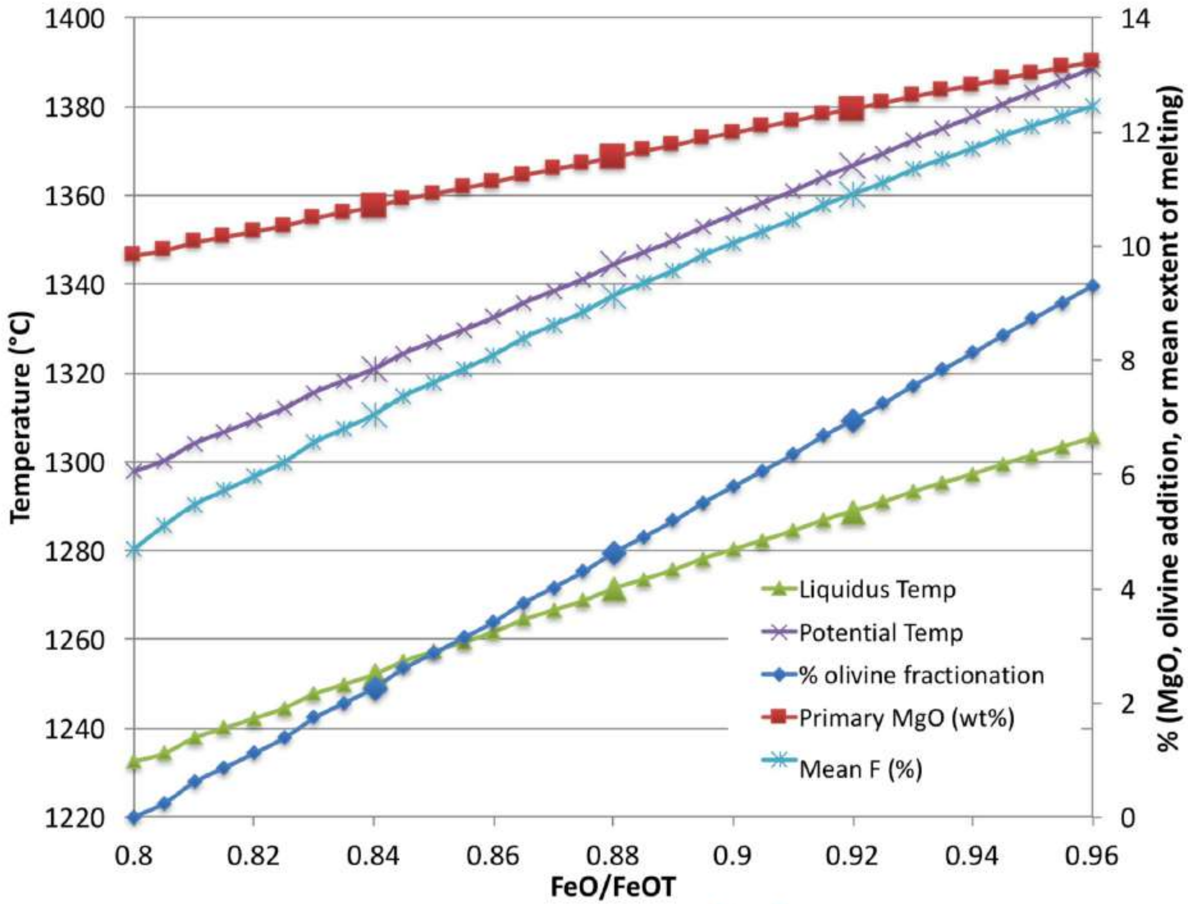
Fe redox state can be follow with Fe^{2+} band



Evolution of optical properties from the glass to the liquid
Importance for radiative transfer in glass furnace

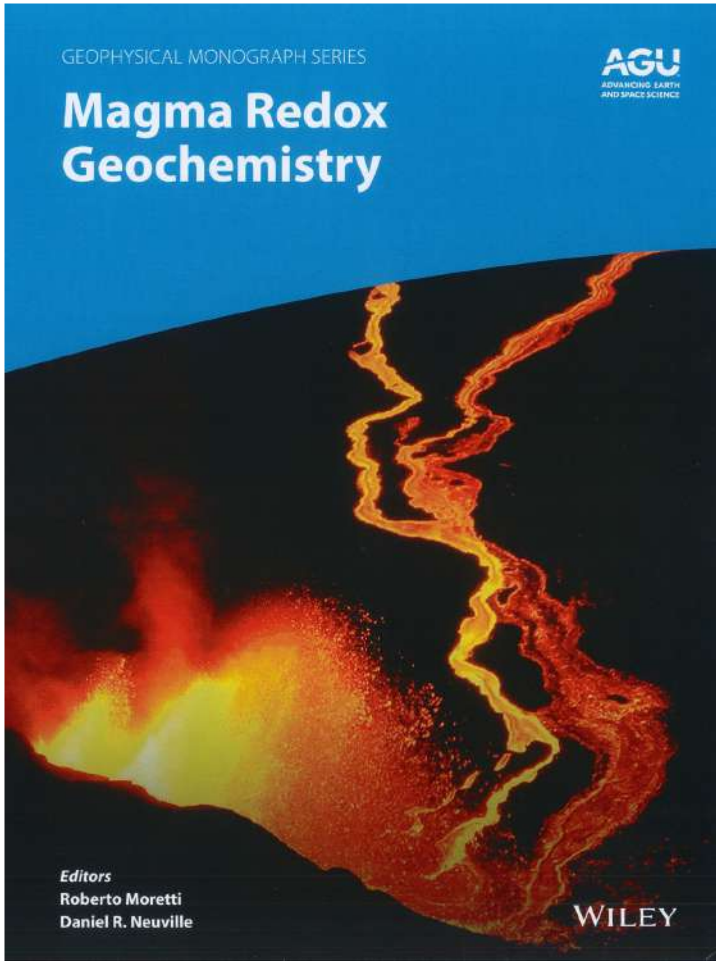
Michel, PhD Thesis (2013)

- How liquidus temperature varies with redox ?

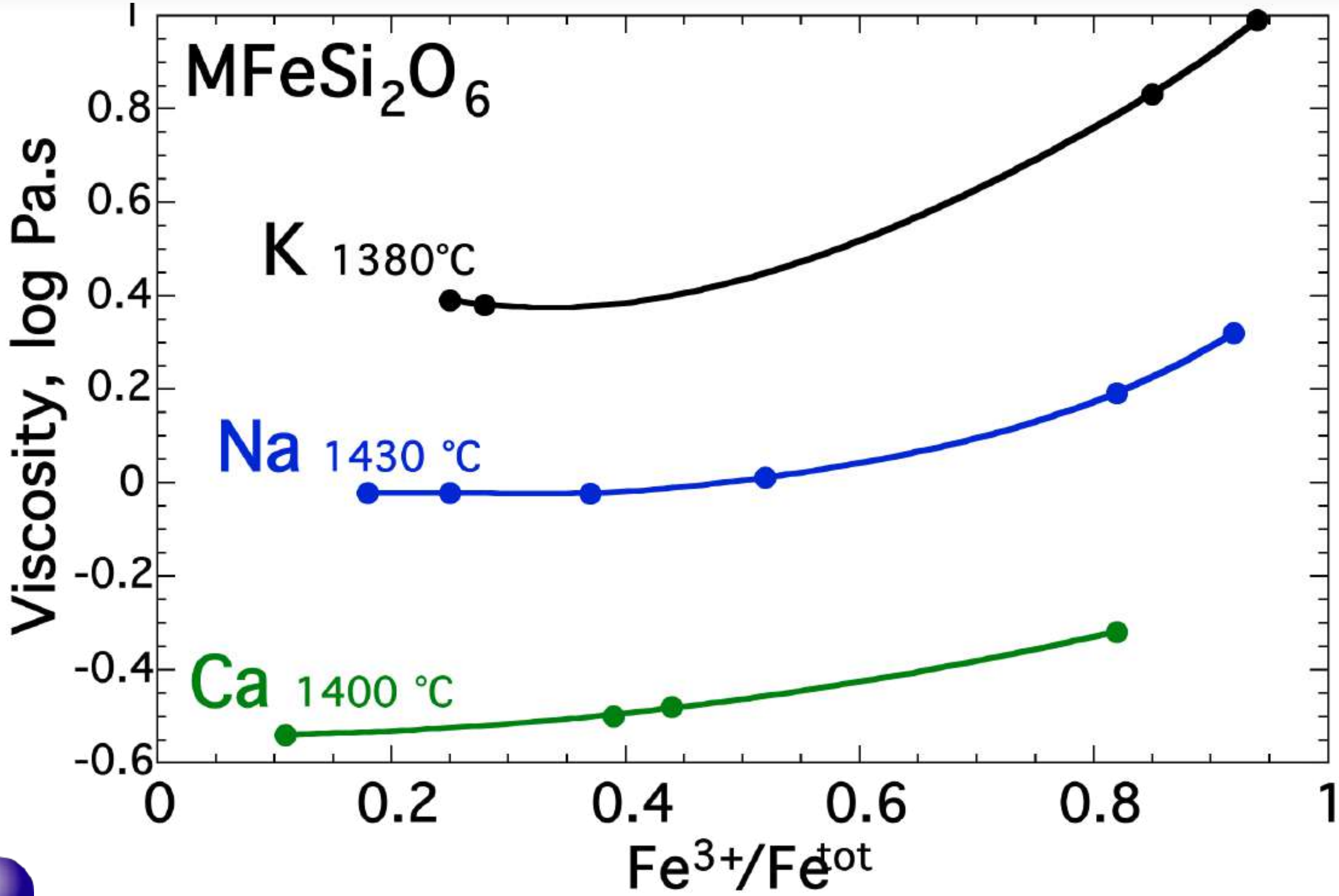


Asimow P. (2020) The petrological consequences of the estimated oxidation state of primitive MORB glass. AGU Monograph on Magma Redox Geochemistry edt by Moretti and Neuville.

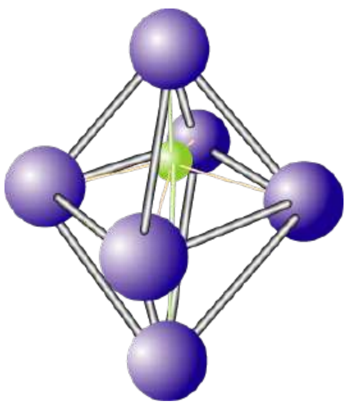
*Redox can plays a very important role on **liquidus temperature, crystallization…. Glass transition….***



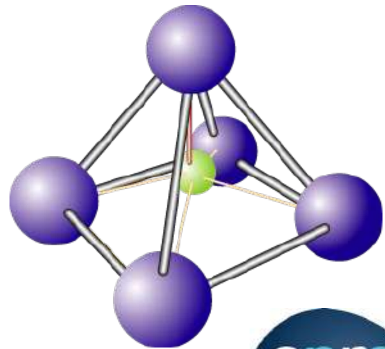
- What is the role of redox on viscosities ?



$^{[6]}Fe^{2+}$



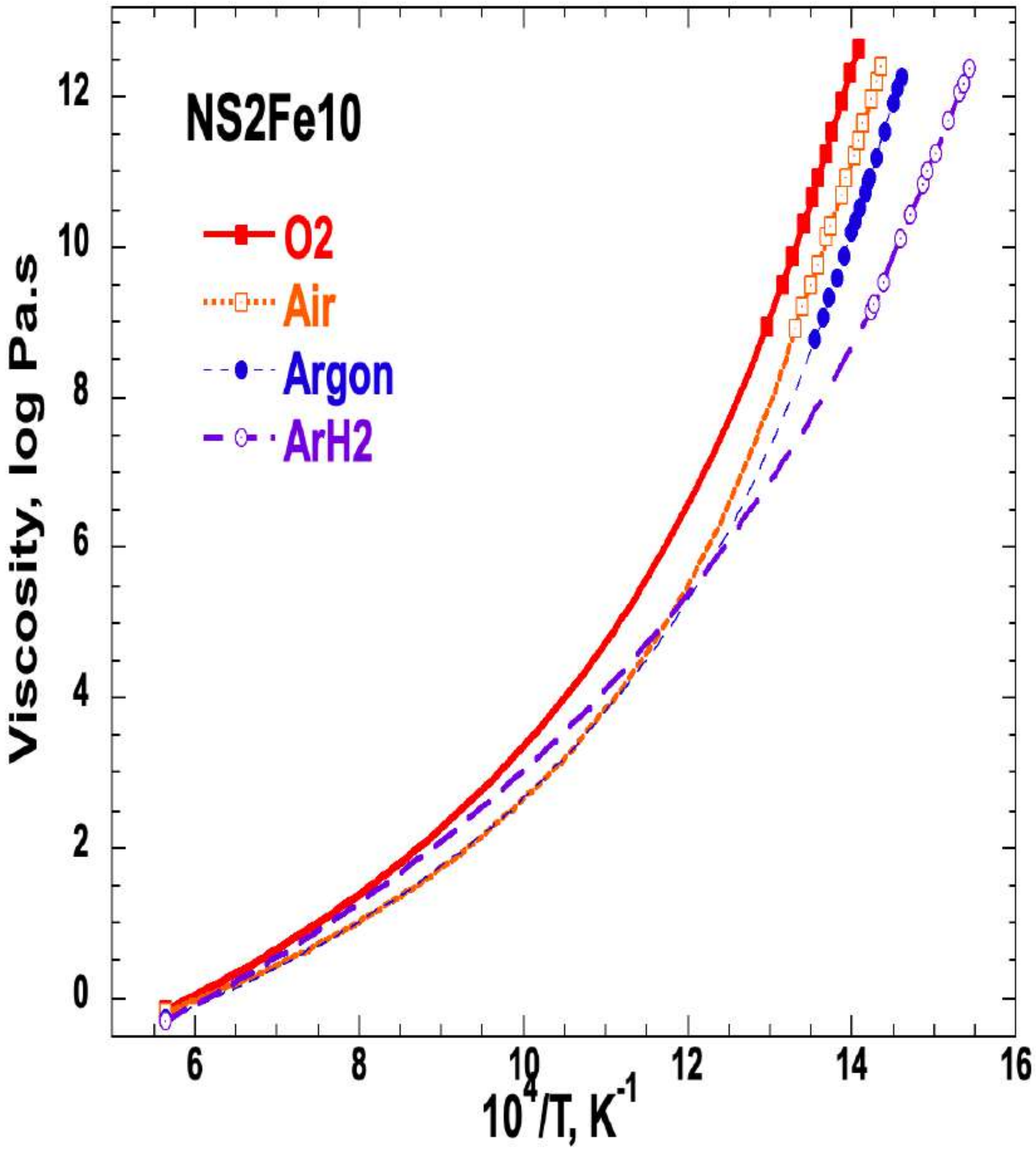
$^{[4]}Fe^{3+}$

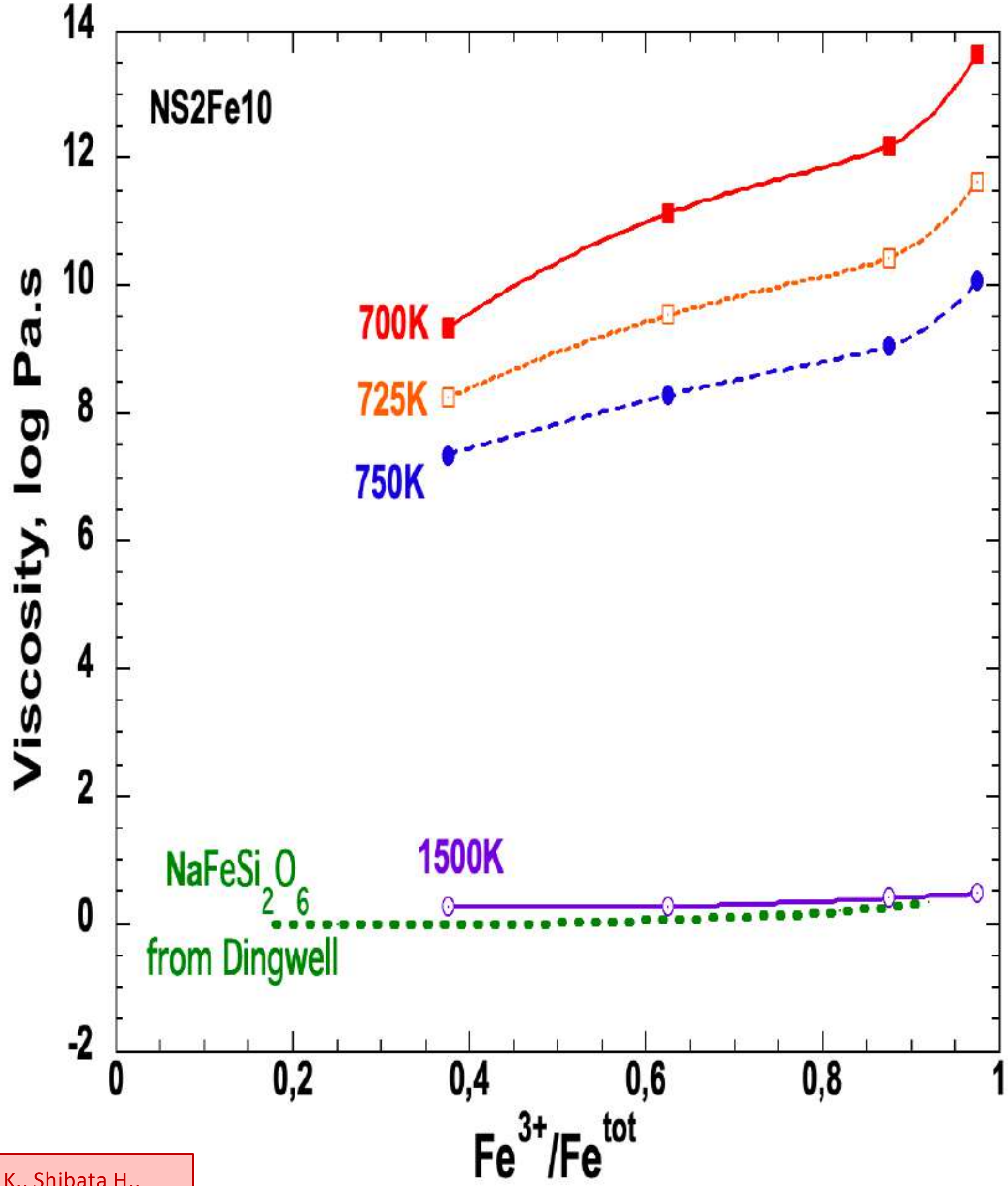


Dingwell (1991) Redox viscometry of some Fe-bearing silicate melts American Mineralogist, Volume 76, pages 1560-1562.

Dingwell DB, Virgo D (1987) The effect of oxidation state on the viscosity of melts in the system Na2O-FeO-Fe2O3-SiO2. Geochimica et Cosmochimica Acta 51:195–205

- What is the role of redox on viscosities ?

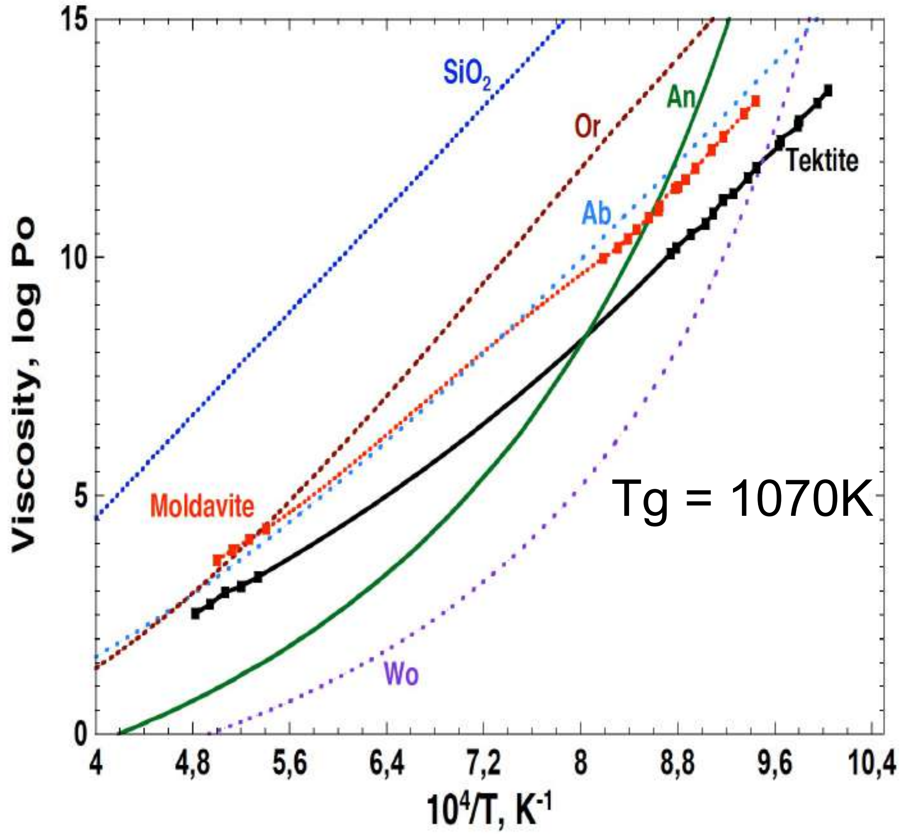


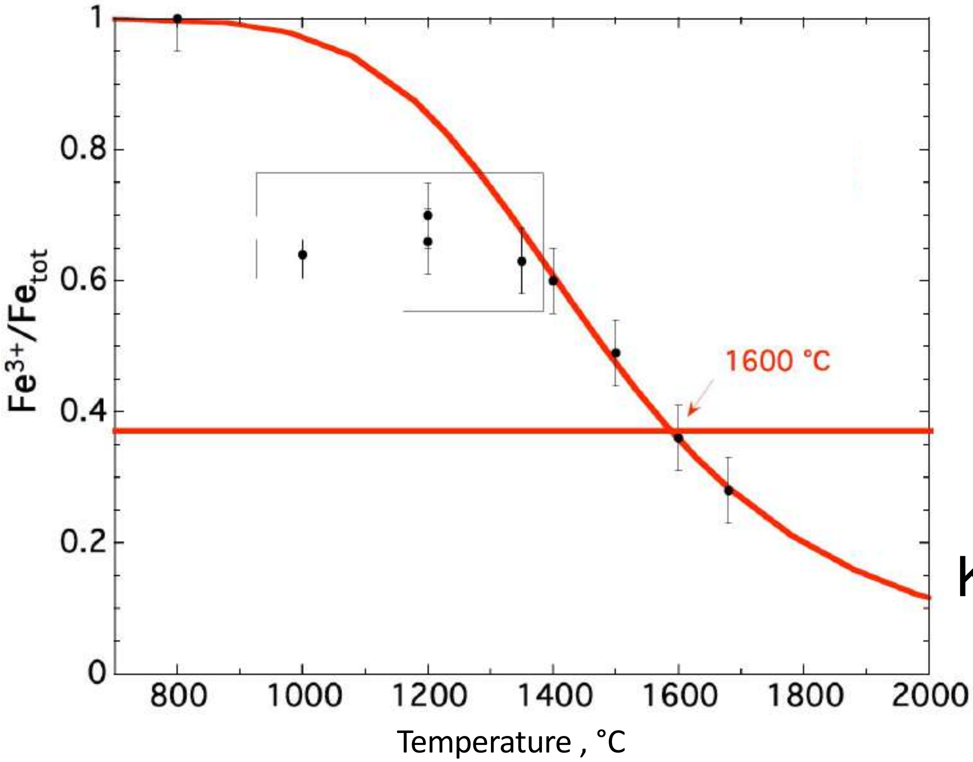


Sukenaga S., Yamada H., Wakihara T., *Cicconi M.R.*, Ohara K., Shibata H., and Neuville D.R. (2020) Redox effect on the viscosity of silicate glasses and melts. Earth and Planetary Sciences Letters (soumis).

- is the redox of a glass the same as that of a liquid?

Fig. 22.8 Tektite specimens with typical aerodynamic shapes and characteristic surface features (square dimension = 5 mm)

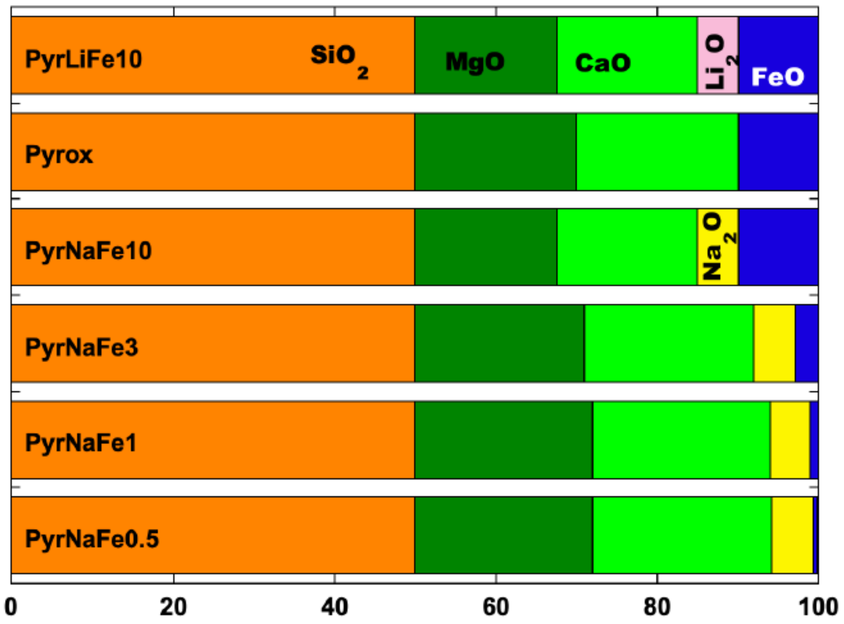


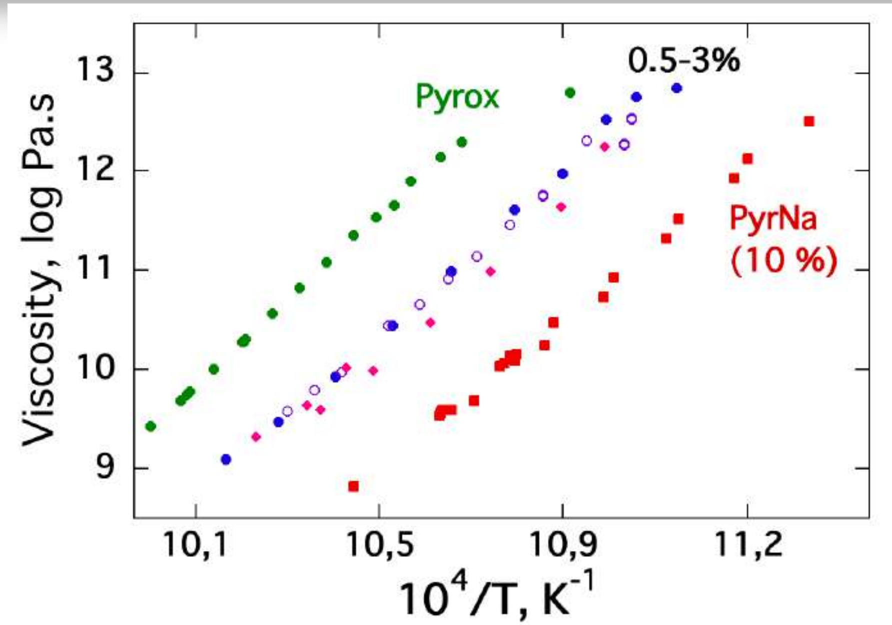


Redox of the tektite

Kress&Carmichael redox curve

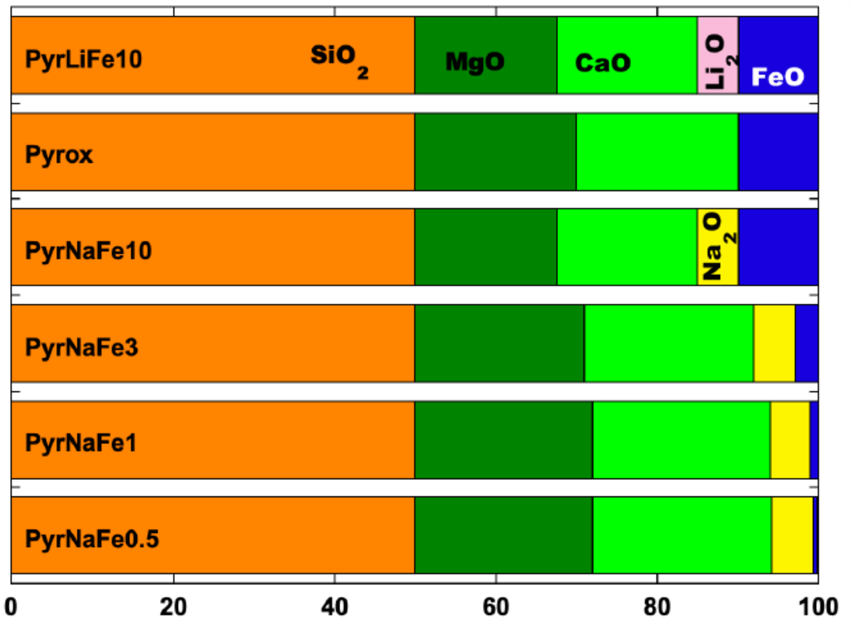
Cicconi M.R., Neuville D.R. (2019) Natural glasses. Springer Hanbook of Glass.771-804 – DOI 10.1007/978-3-319-93728-1

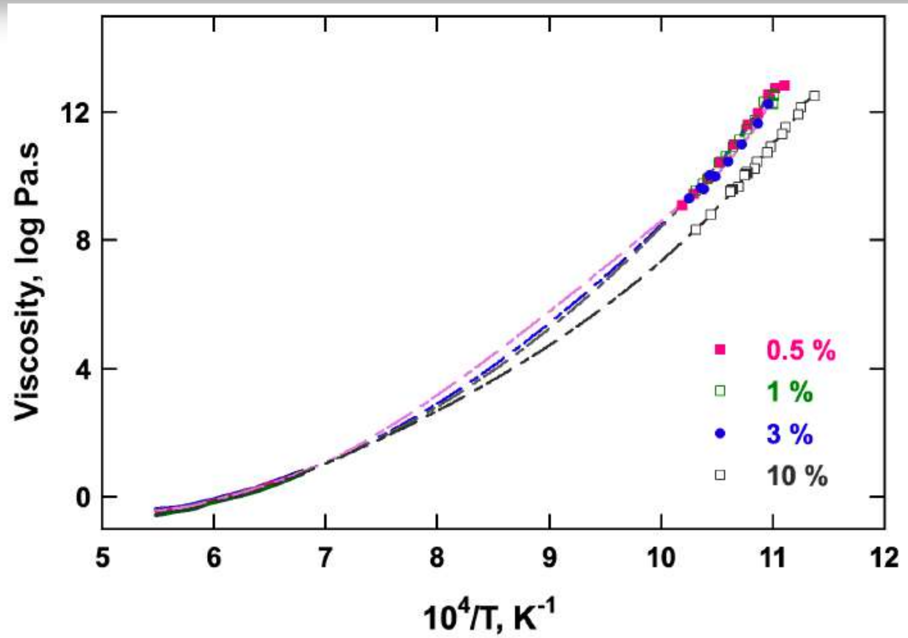




Magnien V., Neuville D.R., Cormier L., Mysen B.O. and Richet P. (2004) Kinetics of iron oxidation in silicate melts: A preliminary XANES study. Chem. Geol., 213, 253-263

Iron effect on viscosity





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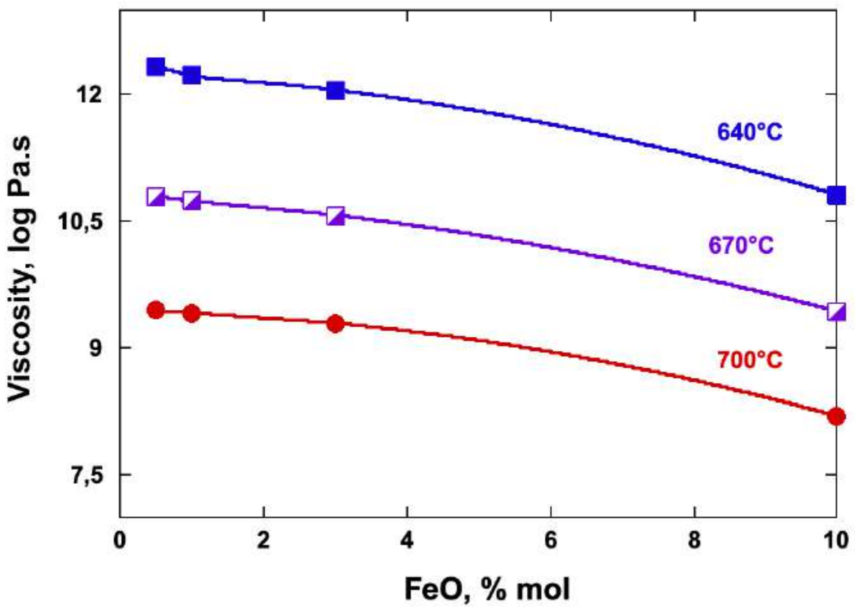
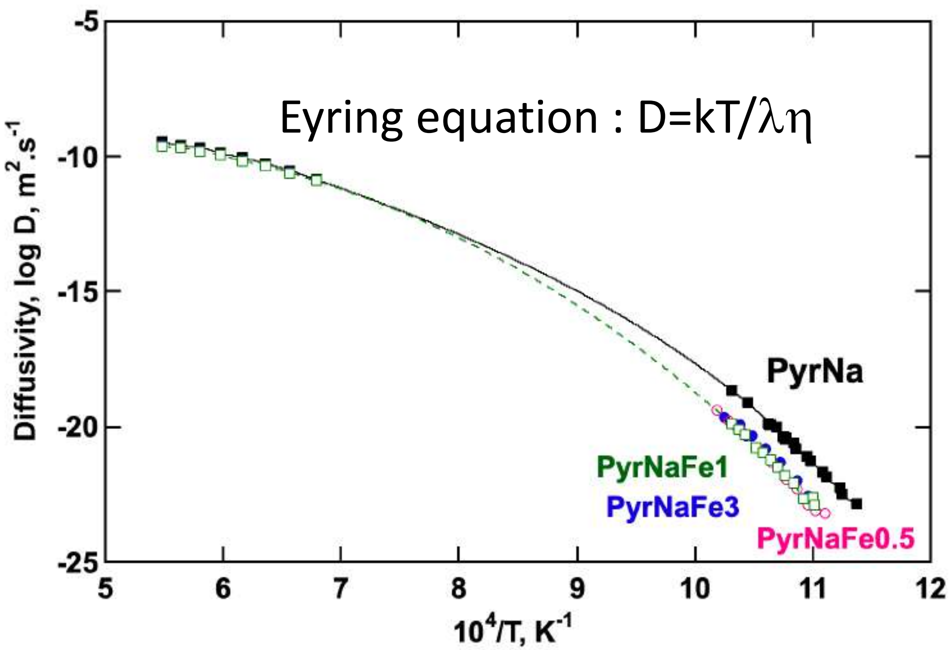
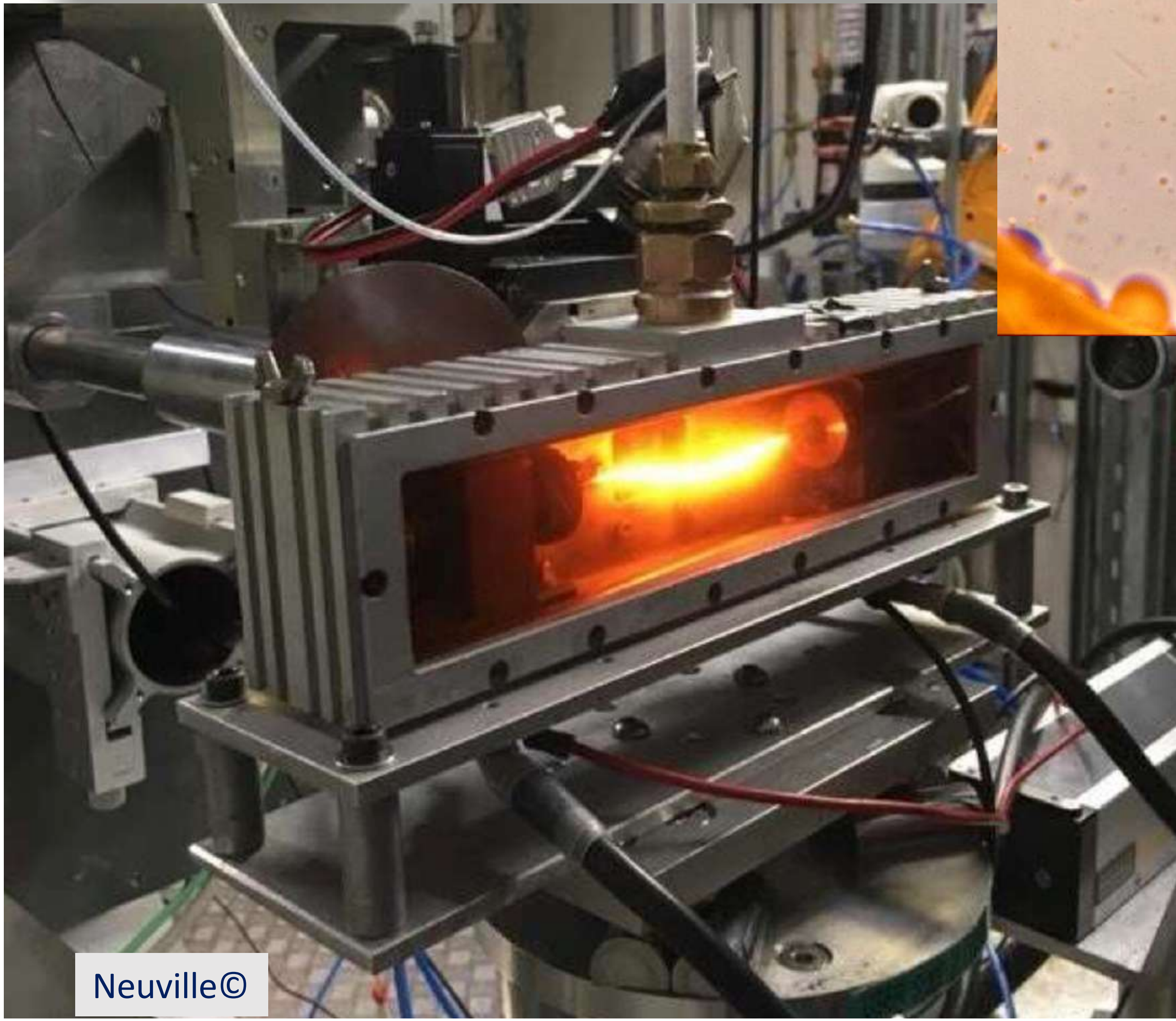
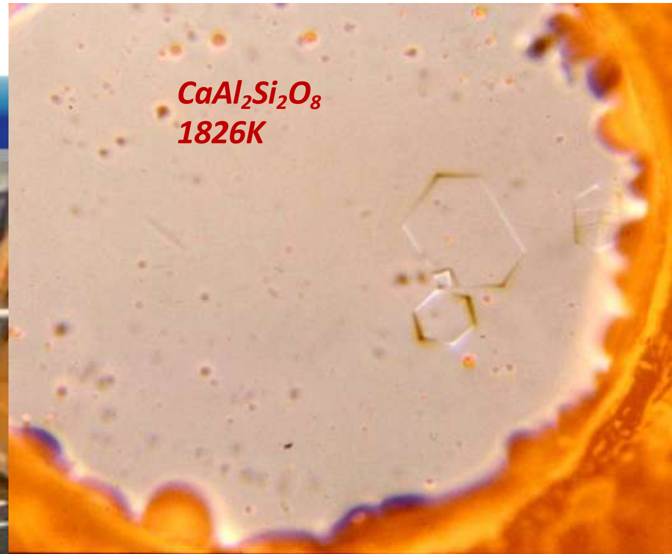




In situ experiment

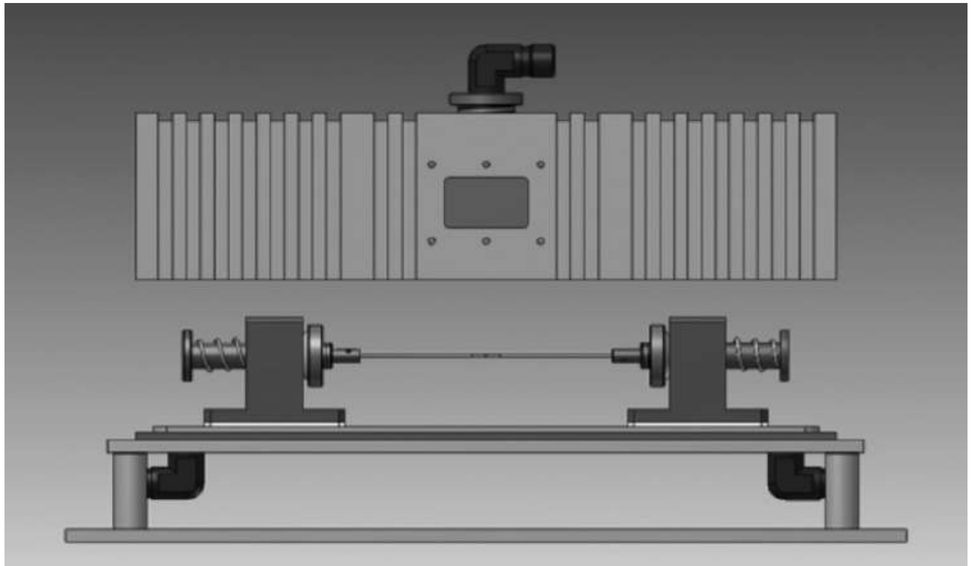


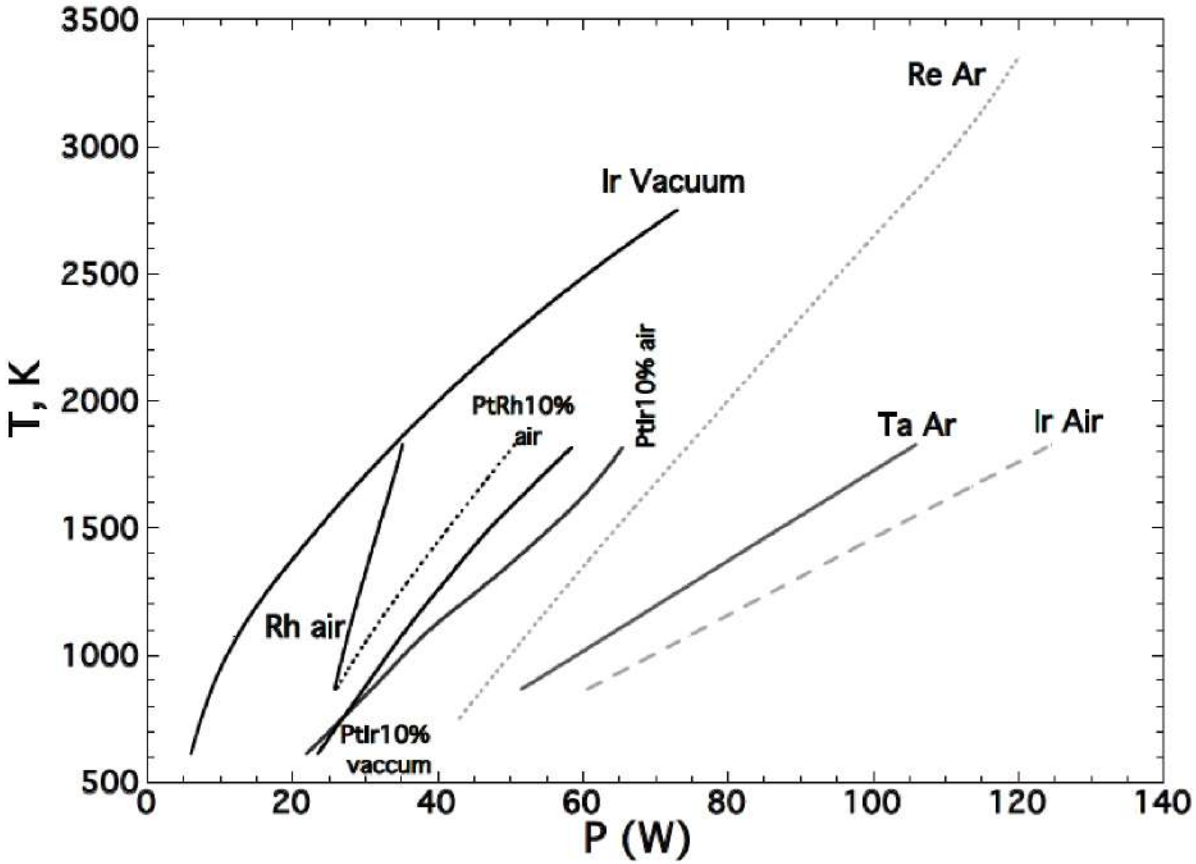


- In situ redox measurements,
XANES at the Fe K-edge

- in situ nucleation and growth
WAXS and SAXS

Neuville D.R., Hennet L., Florian P., de Ligny D. (2014) In situ high temperature experiment. In Henderson G.S, Neuville D.R., Down B. (2014) "Spectroscopic methods in Mineralogy and Material Sciences" Review in Mineralogy and Geochemistry, Vol 78, 779-800.





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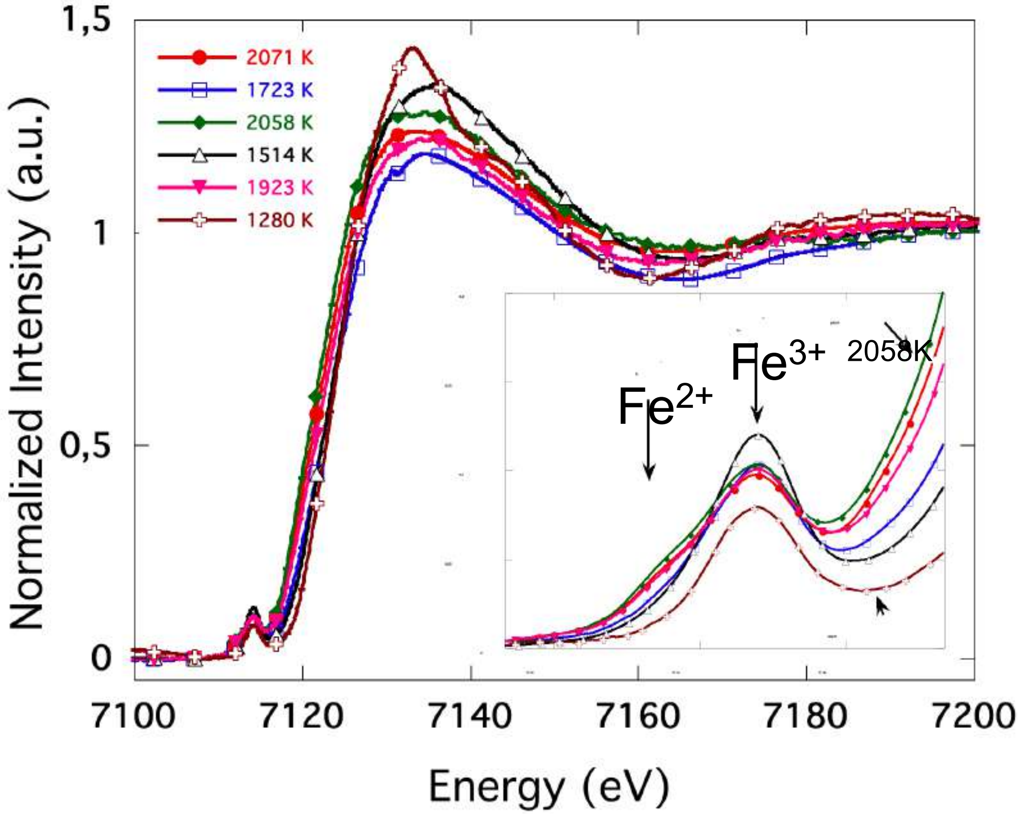
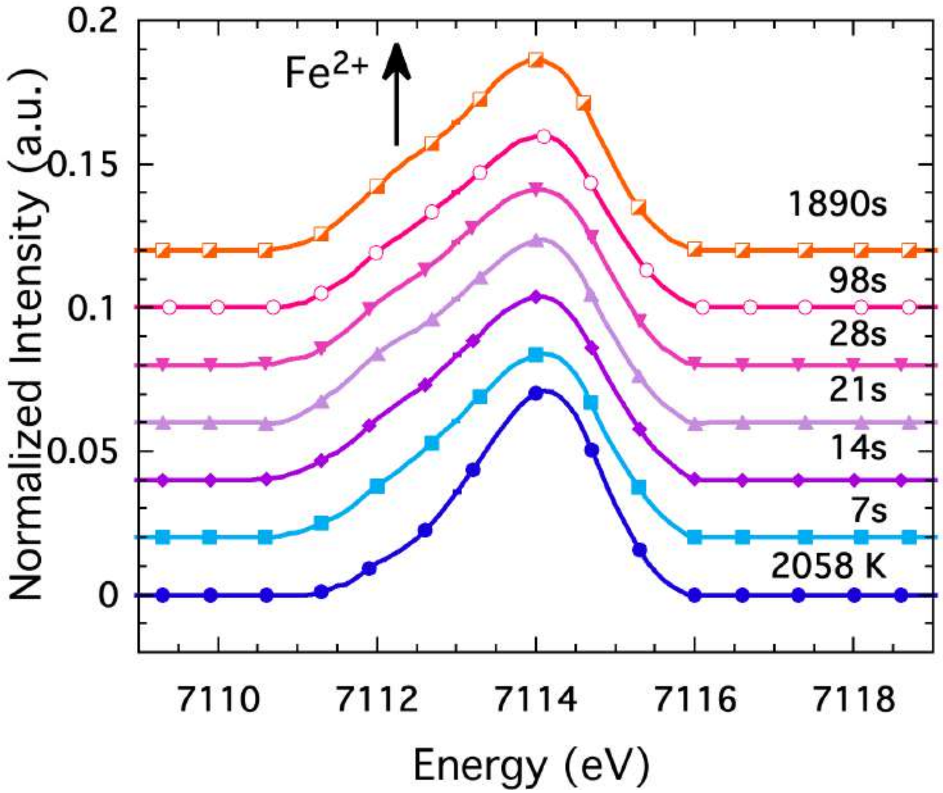
XANES spectra of Pyrox after reduction or oxidation induced in air by temperature changes from 2071 to 1723 K, 1723 to 2058 K, 2058 to 1514 K, 1723 to 1923 K and 1923 to 1280 K



Time dependence during reduction in air at 2058 K of a Pyrox sample previously equilibrated at 1723 K



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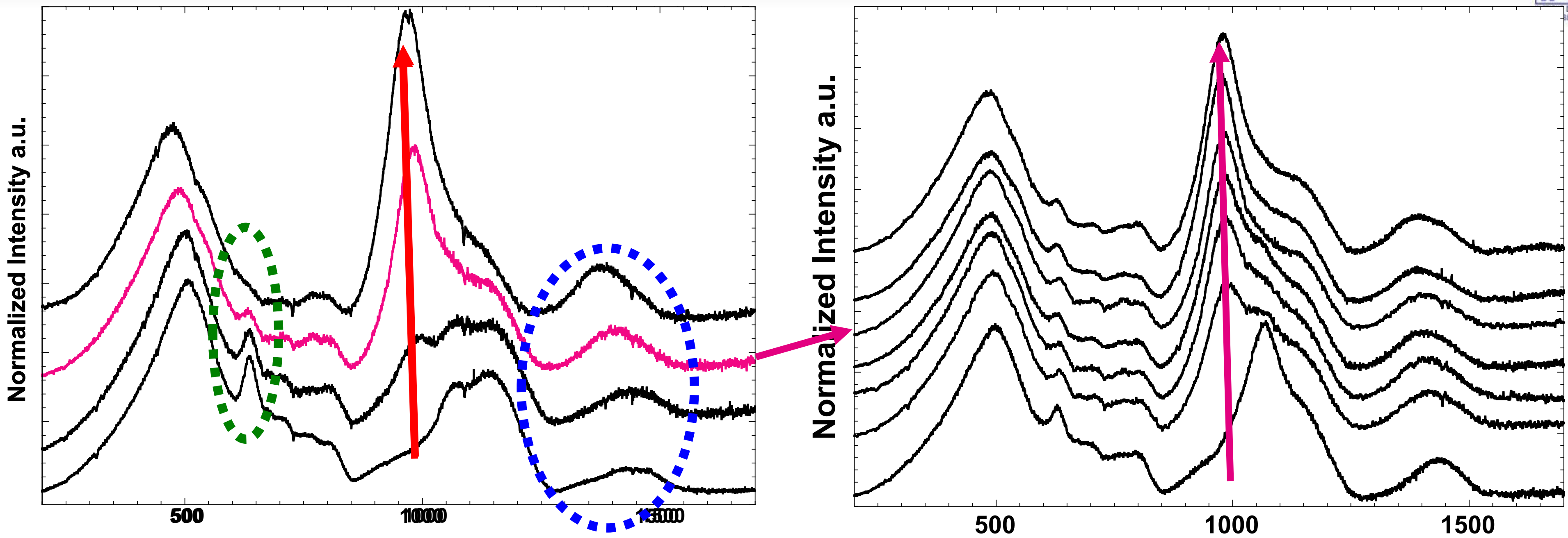
Raman spectroscopy

Borosilicate NBF67.18.x glass with increasing **FeO content** Borosilicate NBF67.18.5 glass with increasing Fe3+ content

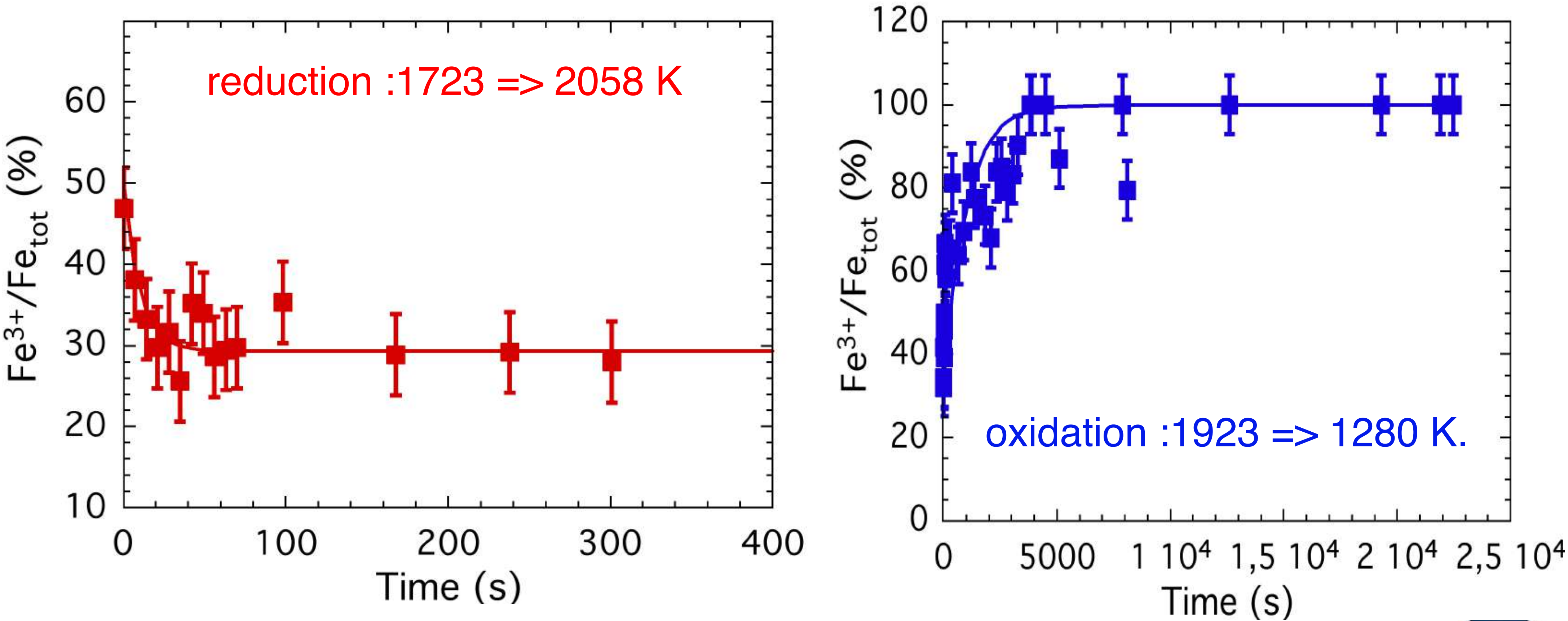


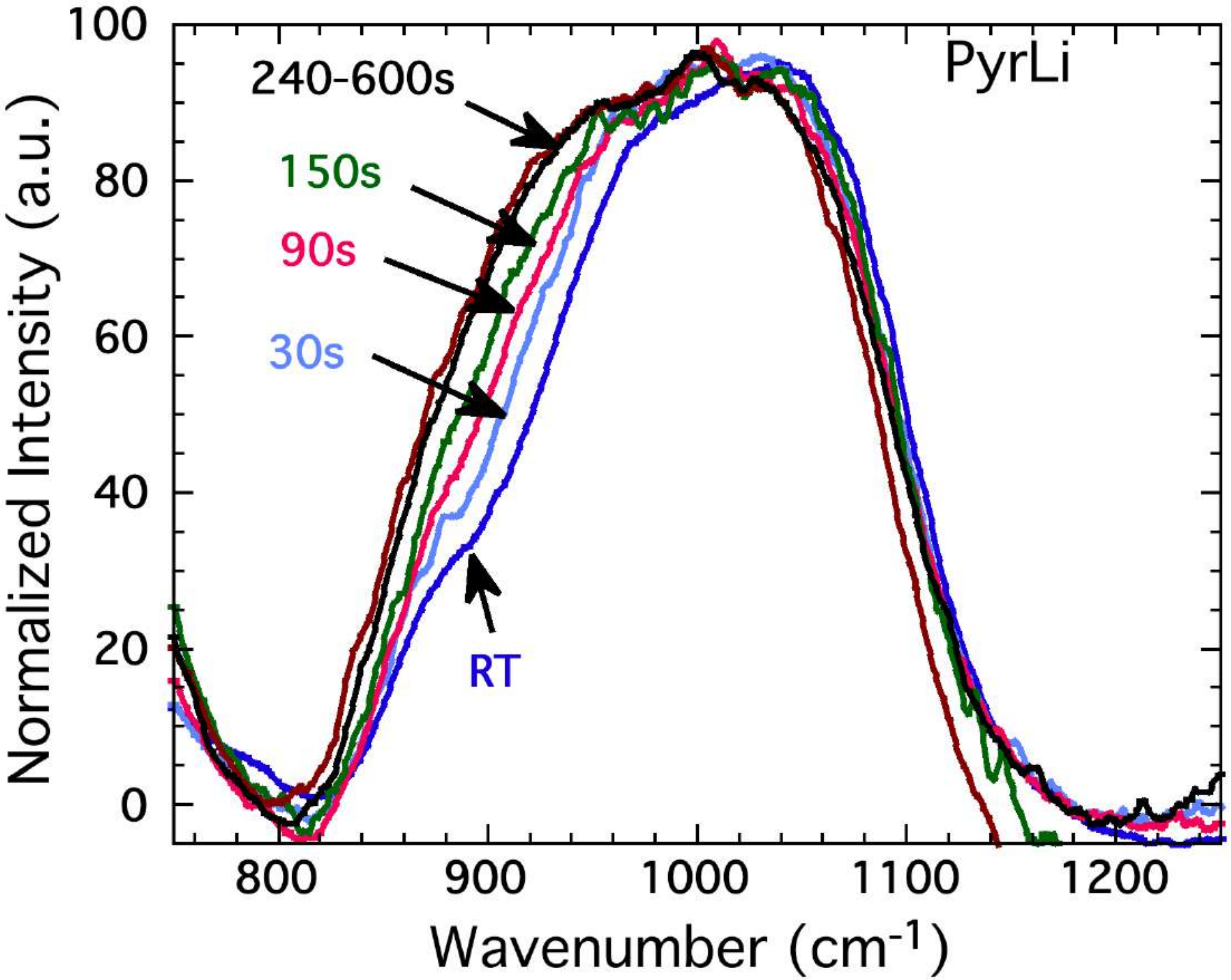
Increasing **FeO content** at constant redox ratio + **inscreasing** **Fe^{3+} content:**

- **Increasing band** at 980cm^{-1} in borosilicates
- Shift to lower frequency of the 980 cm $^{-1}$ band **=> $^{[4]}Fe^{3+}$-O bonds shared with Si**
- **BO_3/BO_4 modification**
- **Decreasing danburite like rings band** *($2SiO_2$-$2BO_4$-Na_2O)*

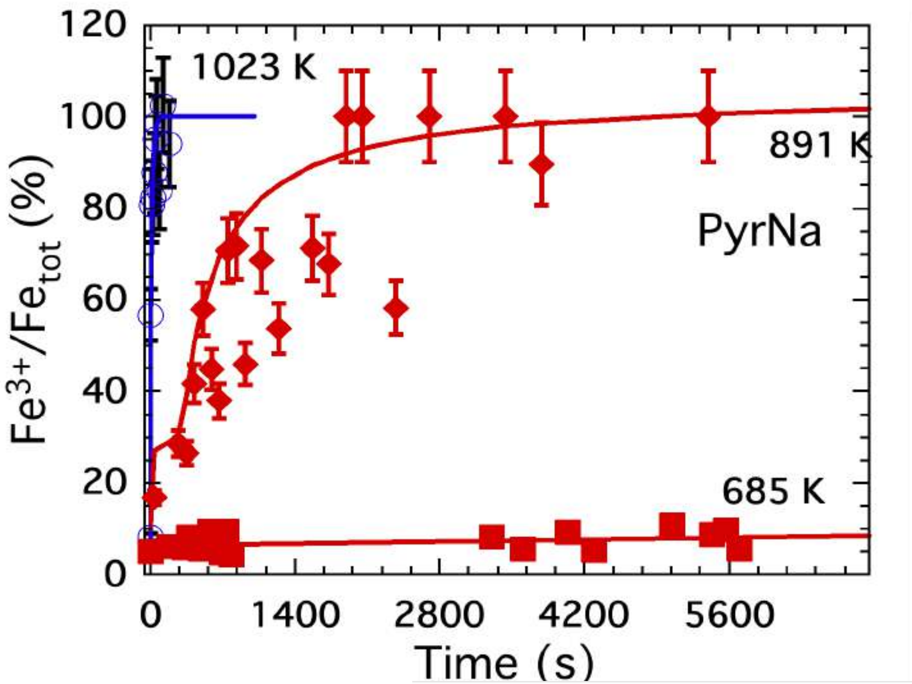
Cochain B., Neuville D. R., Henderson G. S., McCammon C., Pinet O. and P. Richet (2012) Iron content, redox state and structure of sodium borosilicate glasses: A Raman, Mössbauer and boron K-edge XANES spectroscopy study. Journal of the American Ceramics Society, 94, 1-12

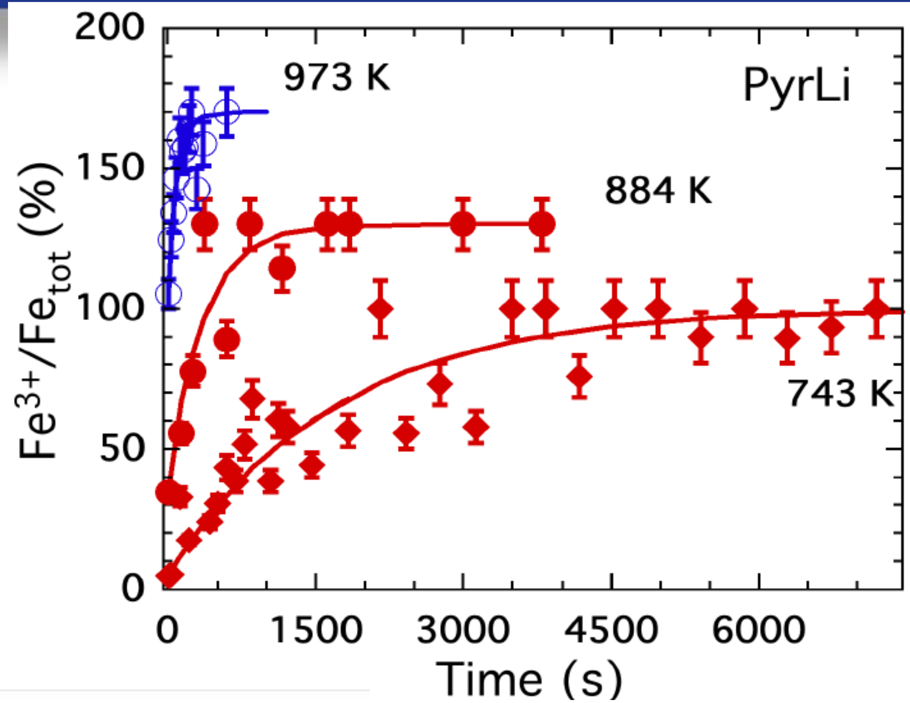
Time dependence of the iron redox ratio of Pyrox

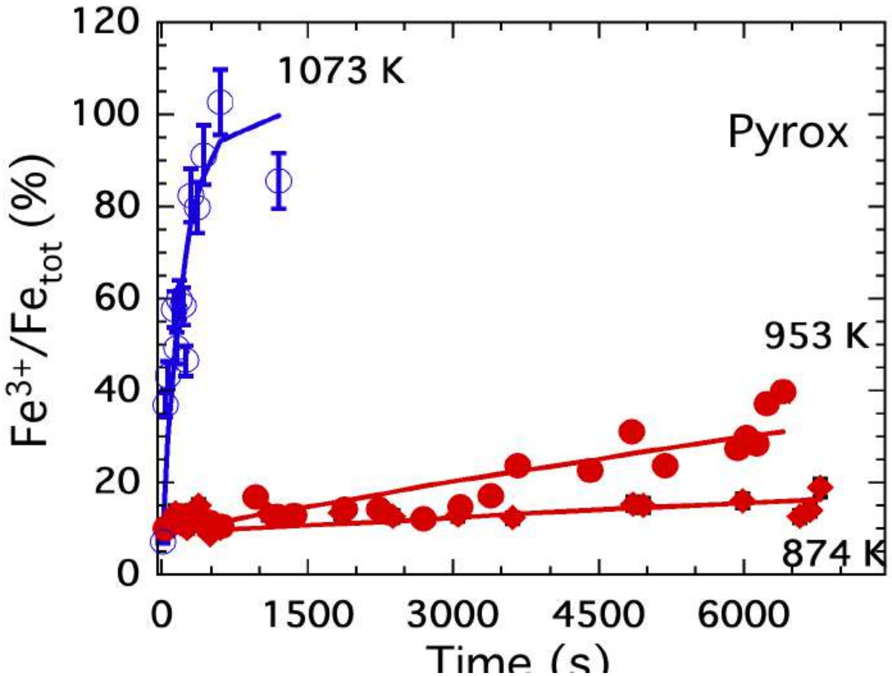




Time dependence of the Raman spectrum of PyrLiR at 973 K

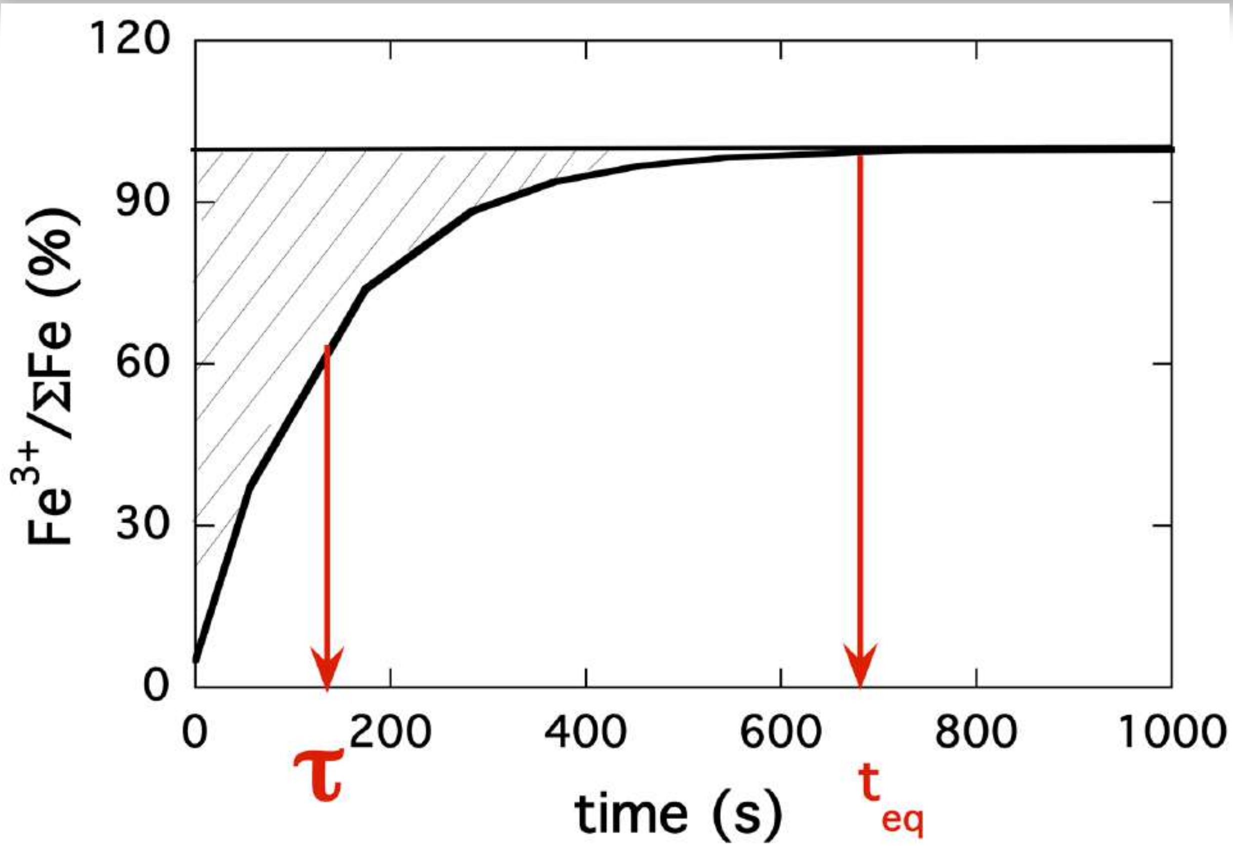

1023 K
891 K
PyrNa
685 K
Fe^{3+}/Fe_{tot} (%)
Time (s)
0
20
40
60
80
100
120
0
1400
2800
4200
5600


973 K
PyrLi
884 K
743 K
Fe^{3+}/Fe_{tot} (%)
Time (s)
0
50
100
150
200
0
1500
3000
4500
6000


1073 K
Pyrox
953 K
874 K
Fe^{3+}/Fe_{tot} (%)
Time (s)
0
20
40
60
80
100
120
0
1500
3000
4500
6000

Raman

XANES



Time dependence of redox ratio

$$R_t - R_{eq} = (R_0 - R_{eq}) \times \exp\left(\frac{-t}{\tau}\right)$$

- R_0 et $R_{eq,}$ initial redox and equilibrium redox
- $R_{t,}$ redox @ time t
- τ, characteristic time

$$t_{eq} = -\tau \ln(0{,}01)$$

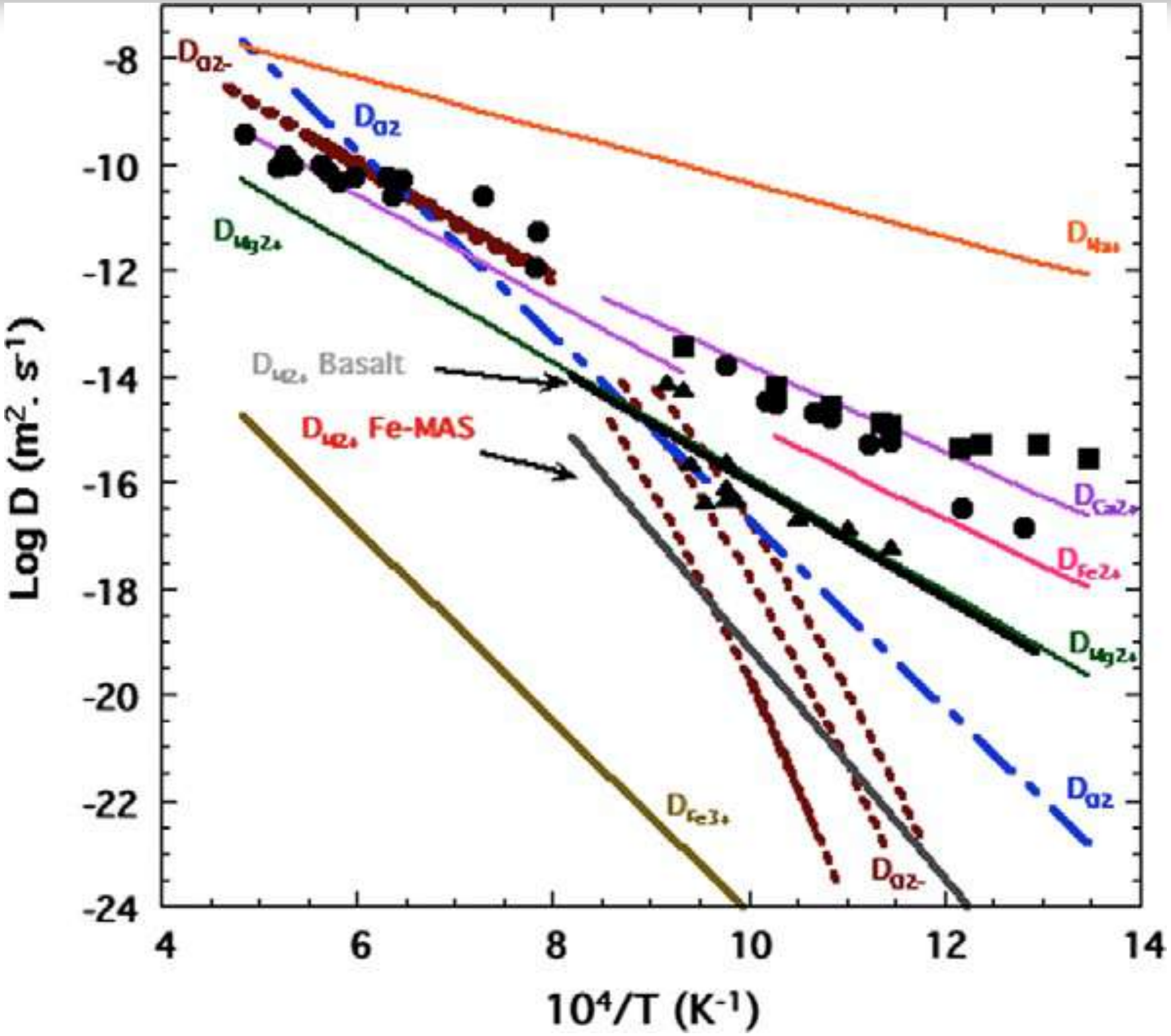
and

$$t_{eq} = r_0^2/(4*D)$$

=> D, "redox diffusivity"

r_0, sample size

« Redox diffusivity »



D_{O2} from Semkow and Haskin (1985) for diopside composition; D_{Ca} and D_{Mg} frome Jambon and Semet (1977), Roselieb and Jambon (2002) for albite, jadeite or orthoclase compositions; D_{Na} from Jambon and Carron (1976), Lowry et al. (1981) for albite, obsidienne and basaltic compositions ; D_{Fe} from Kohler and Frischat (1978) for Na_2O-FeO-Al_2O_3-SiO_2 compositions and from Henderson et al. (1985) for aluminosilicates; D_{M2+} Basalte et Fe-MAS (MAS= MgO-Al_2O_3-SiO_2 system) from Cooper et al. (1996) and Cook et al. (1990).

Magnien V, Neuville D.R., Cormier L., Roux J., Hazemann J-L., de Ligny D., Pascarelli S., Vickridge I., Pinet O. and Richet P. (2008) Kinetics and mechanisms of iron redox reactions in silicate melts: The effects of temperature and alkali cations. Geochim. Cosmochim. Acta., 72, 2157-2168.

What are the diffusing species ? Predominating mechanism => f(T, composition, f(O_2))

Atmosphere	Oxidized Silicate	Reduced Silicate

Molecular Oxygen (Schreiber et al, 1986)

O_2

$O_2 \longrightarrow 4\,Fe^{3+} + 2\,O^{2-}$ | $4\,Fe^{2+} + O_2$ | HT liquidus

Ionic Oxygen (Schreiber et al, 1986)

$O_2 + 4\,e^-$

$2\,O^{2-} \rightleftarrows 4\,Fe^{3+} + 8e^- + O_2$ (O^{2-} →, e^- ←) | $4\,Fe^{2+} + 2\,O^{2-}$ | HT liquidus

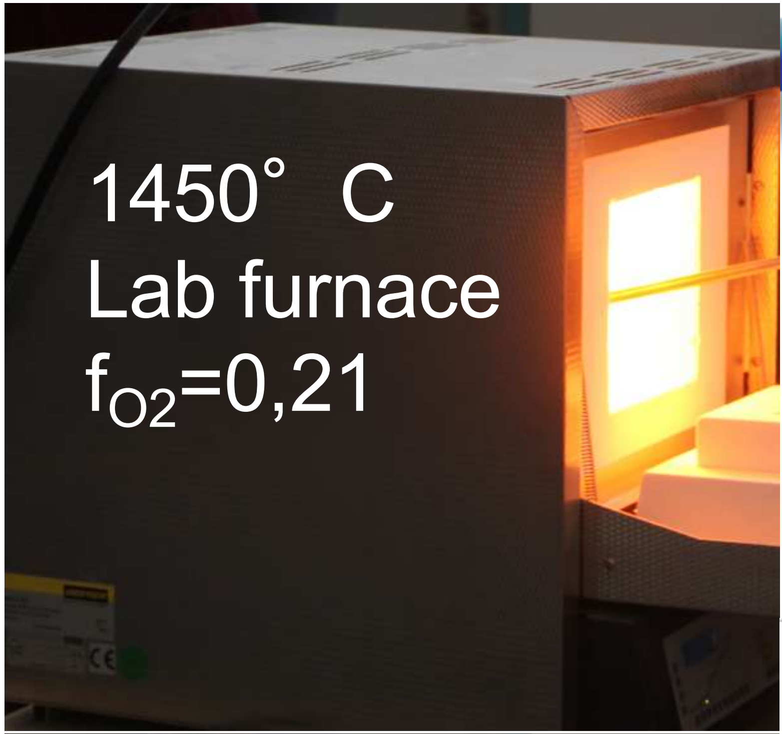
Divalent cations (Cooper et al, 1996)

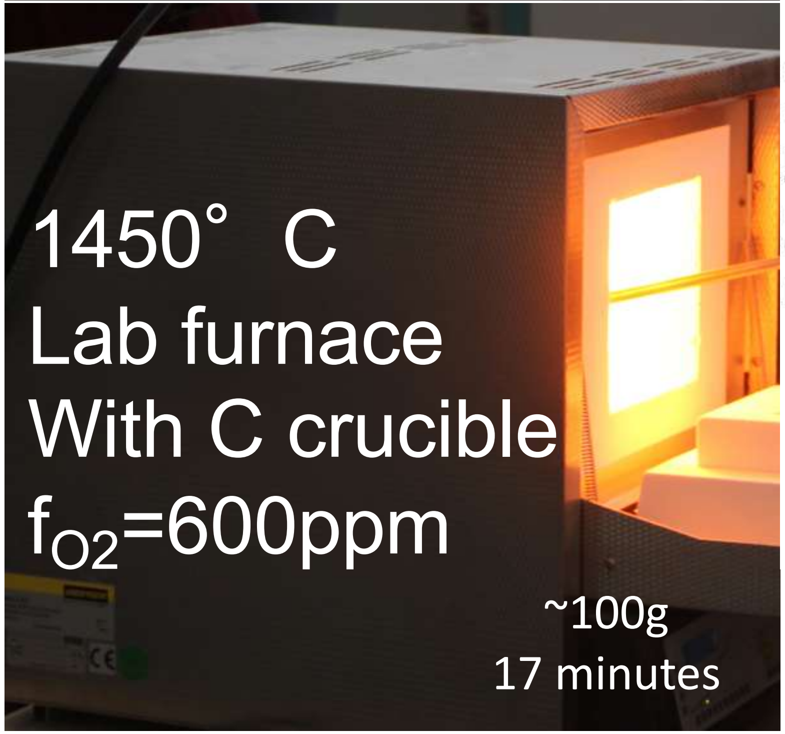
2 MO ↙

$2\,M^{2+} + O_2 + 4e^- \leftarrow 2\,M^{2+} + 4Fe^{3+} + 2O^{2-} + 4\,e^-$ ($2\,M^{2+}$ ←, e^- ←) | $2\,MO + 4\,Fe^{2}$ | BT ~Tg

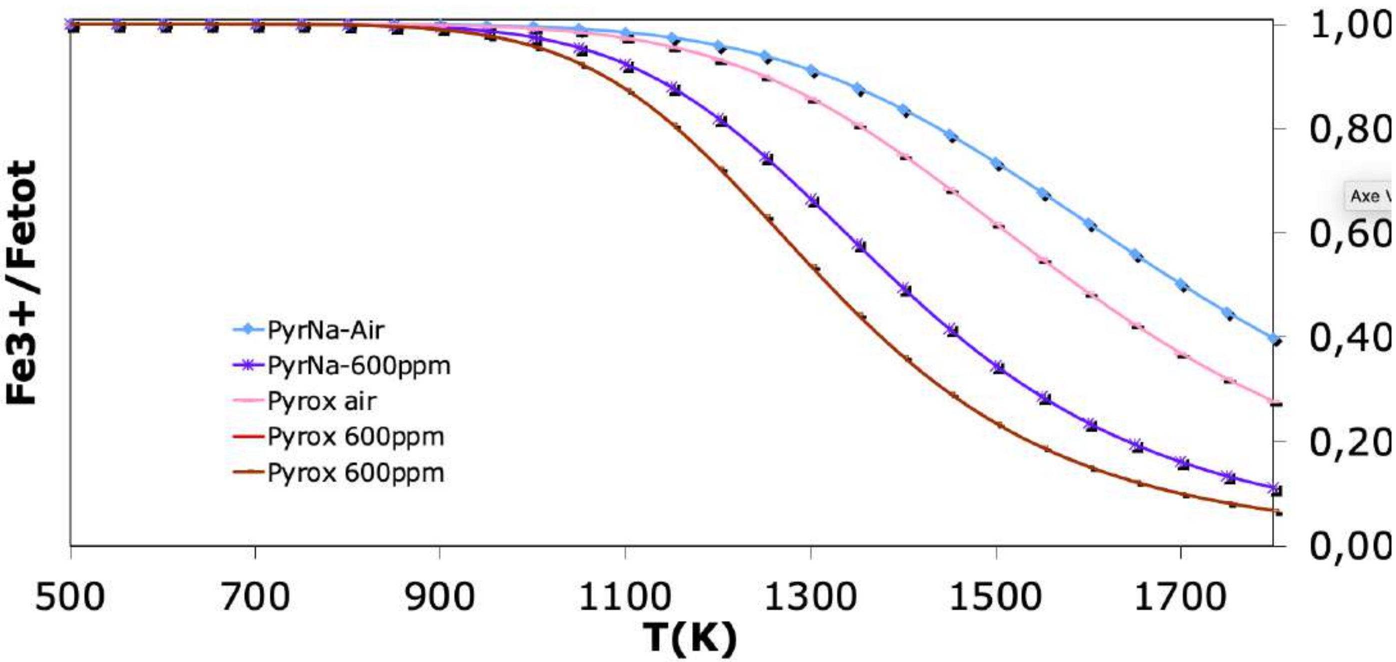
Magnien V, Neuville D.R., Cormier L., Roux J., Hazemann J-L., de Ligny D., Pascarelli S., Vickridge I., Pinet O. and Richet P. (2008) Kinetics and mechanisms of iron redox reactions in silicate melts: The effects of temperature and alkali cations. Geochim. Cosmochim. Acta., 72, 2157-2168.

cnrs





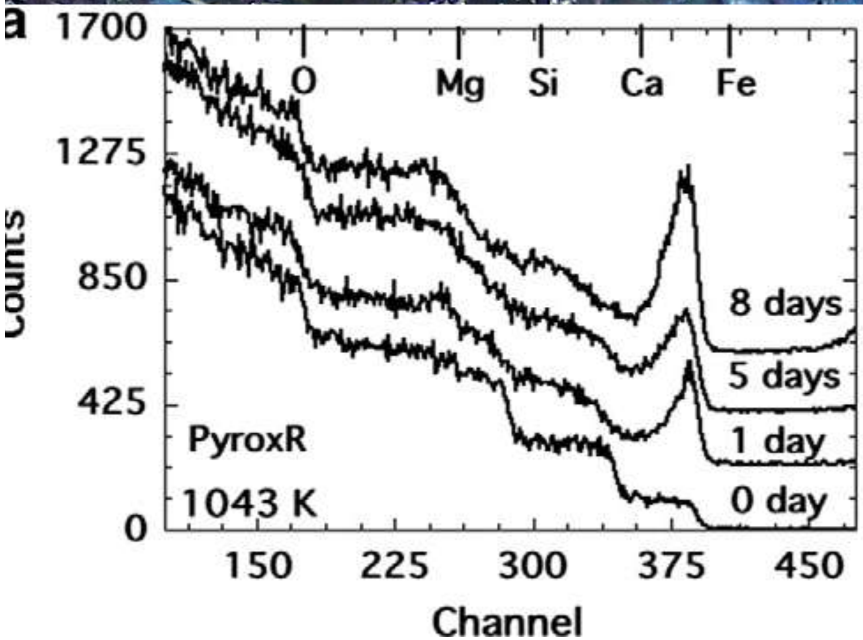
	PyrNa	Pyrox
SiO2	52,6	53,27
Na2O	5,46	0
MgO	11,98	14,08
CaO	17,01	19,54
FeO	12,83	13,03
Fe3+/Fetot air	0,75	0,65
Fe3+/Fetot 600ppm	0,09	0,07

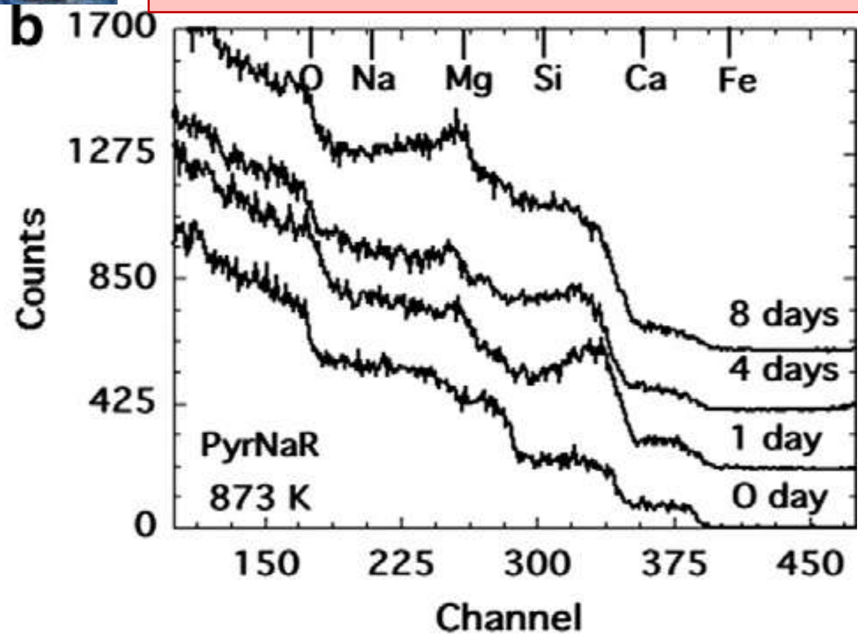


Magnien V, Neuville D.R., Cormier L., Roux J., Hazemann J-L., de Ligny D., Pascarelli S., Vickridge I., Pinet O. and Richet P. (2008) Kinetics and mechanisms of iron redox reactions in silicate melts: The effects of temperature and alkali cations. Geochim. Cosmochim. Acta., 72, 2157-2168.

Rutherford back-scattering spectra

Magnien V, Neuville D.R., Cormier L., Roux J., Hazemann J-L., de Ligny D., Pascarelli S., Vickridge I., Pinet O. and Richet P. (2008) Kinetics and mechanisms of iron redox reactions in silicate melts: The effects of temperature and alkali cations. Geochim. Cosmochim. Acta., 72, 2157-2168.



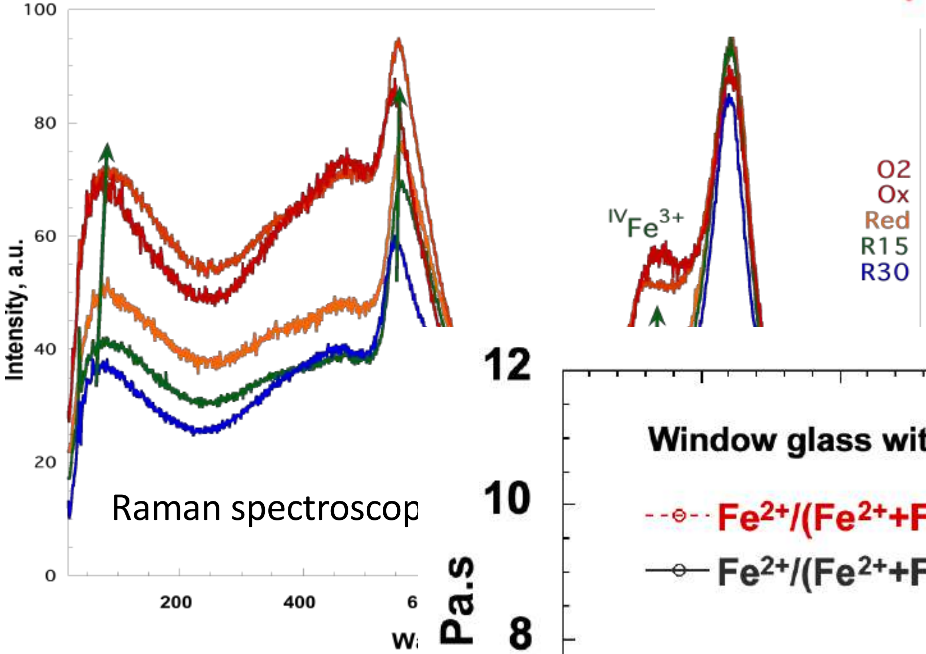


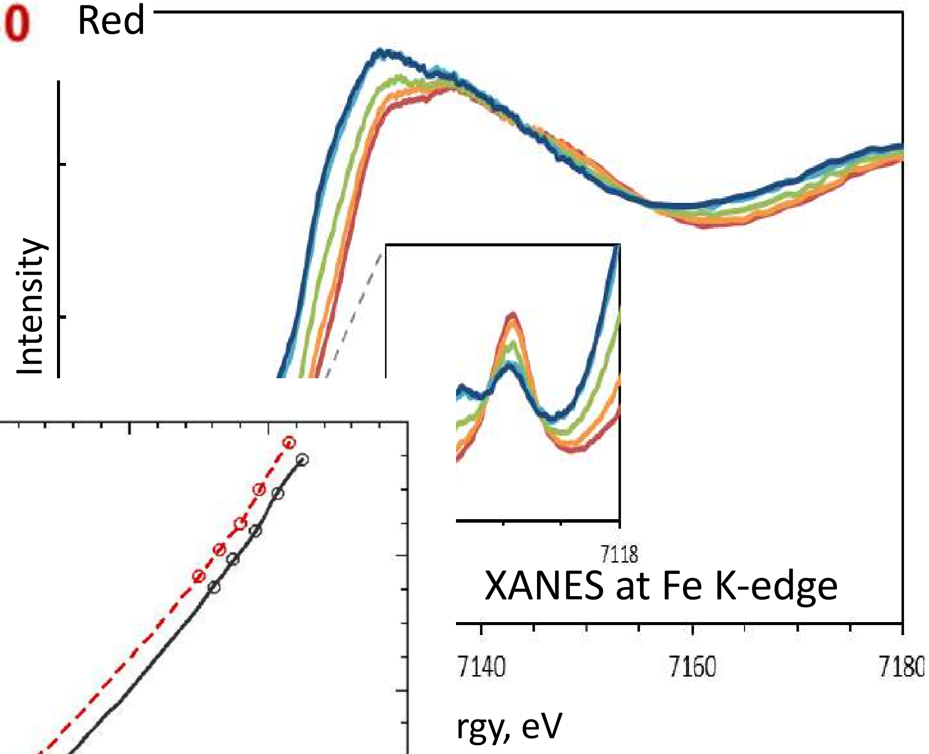
Rutherford backscattering (RBS)

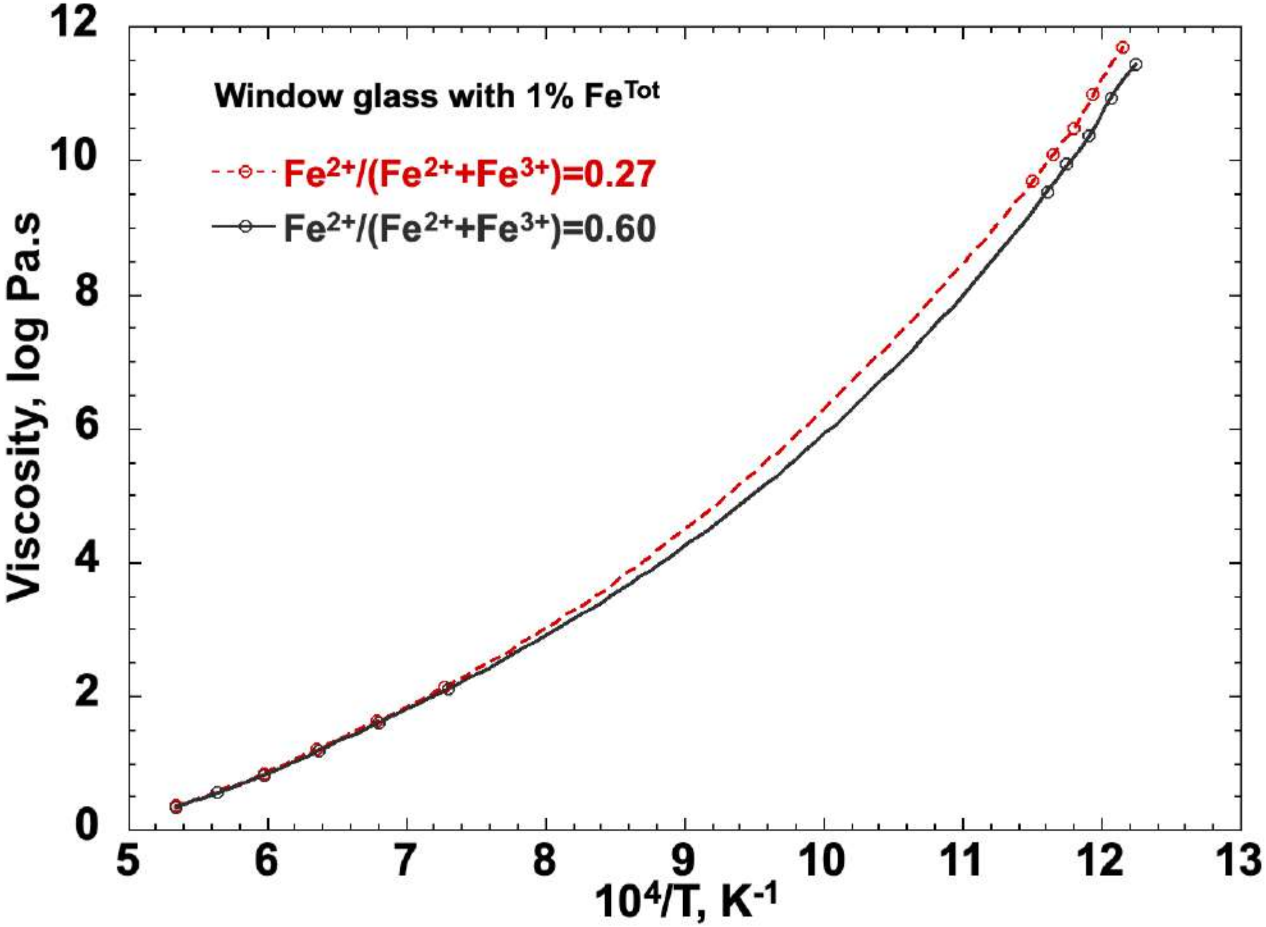
72%SiO2-15%Na2O-12CaO-1%FeO mole%

$Fe^{2+}/(Fe^{2+}+Fe^{3+})=0.27$ Ox

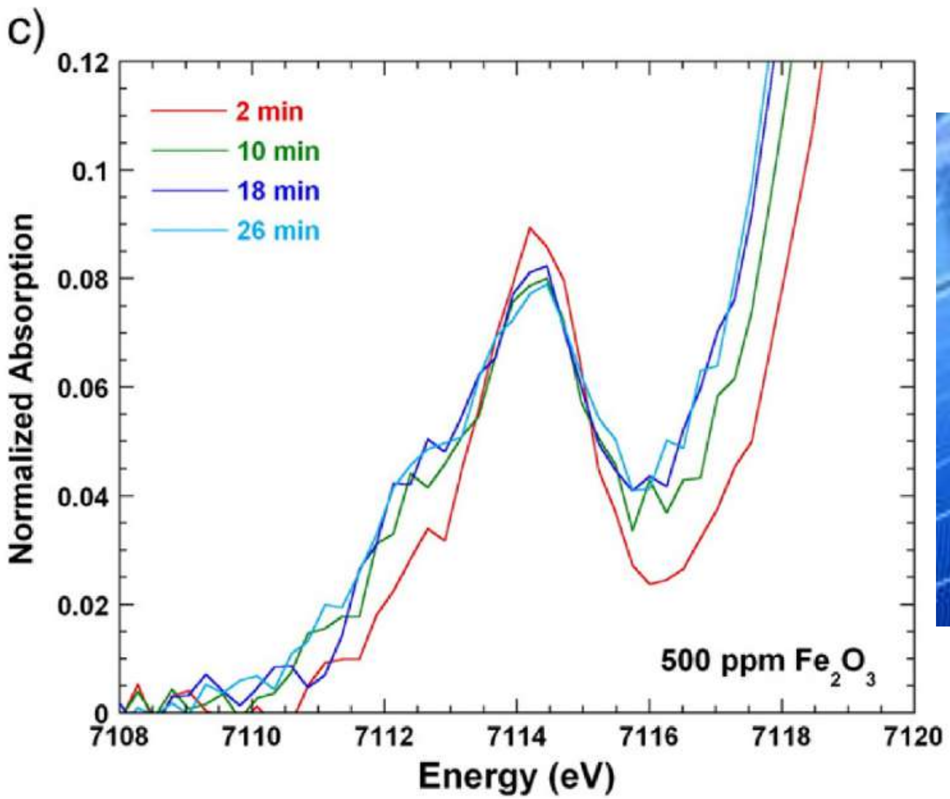
$Fe^{2+}/(Fe^{2+}+Fe^{3+})=0.60$ Red

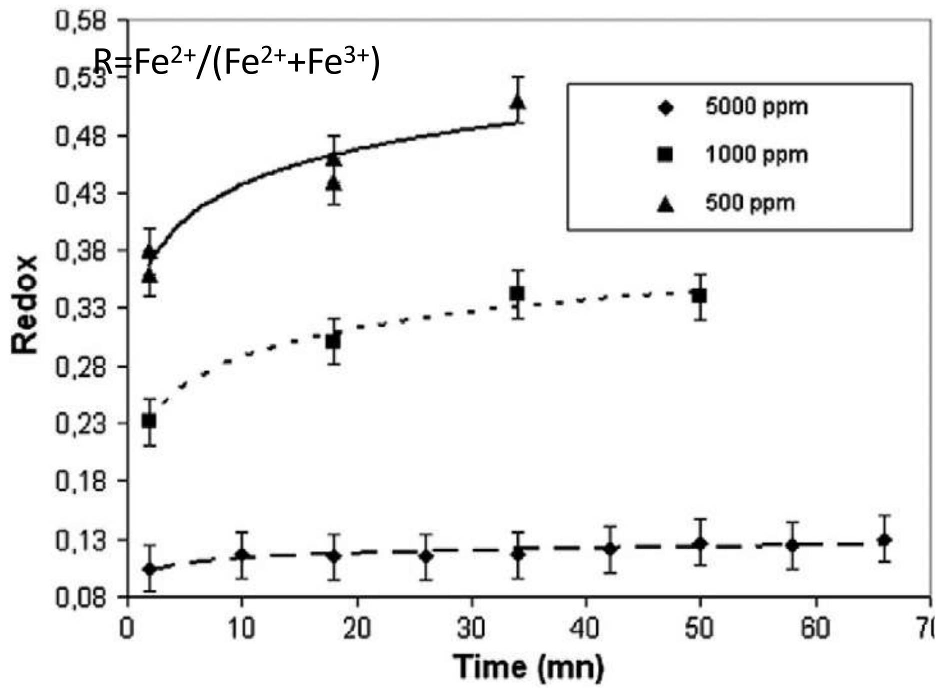


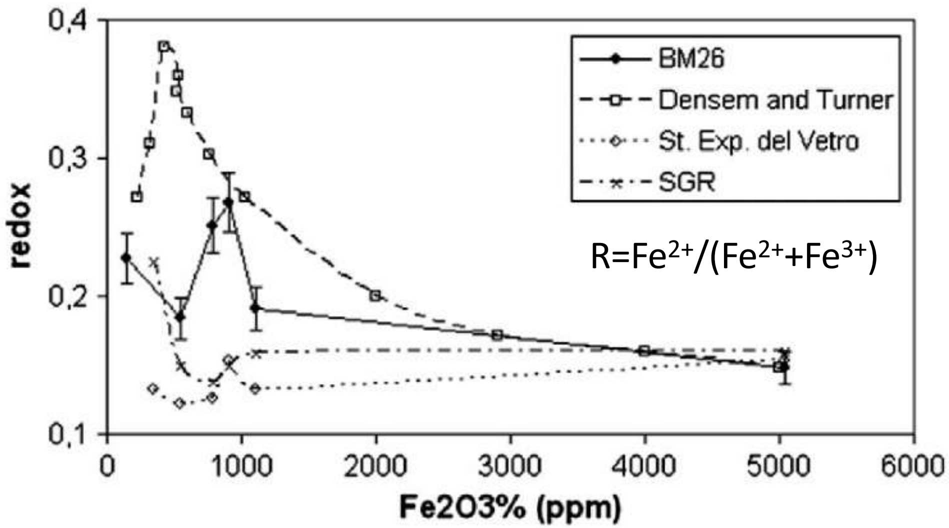




Ultra-clear glasses

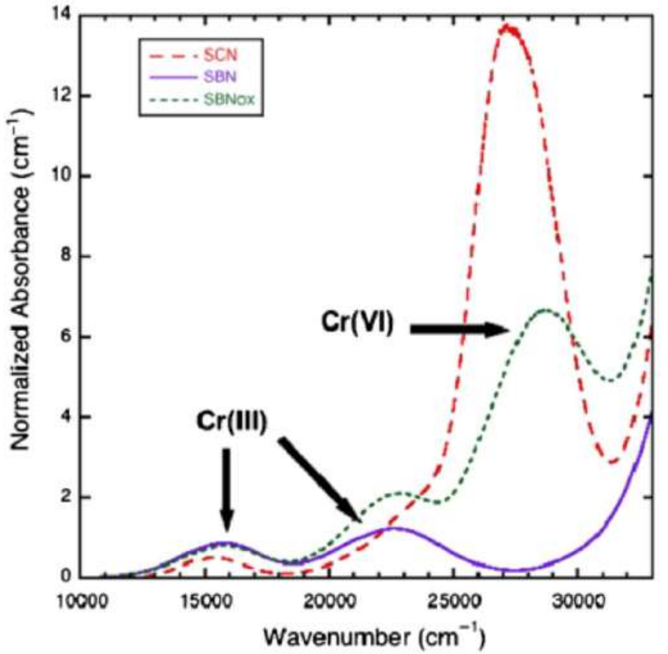


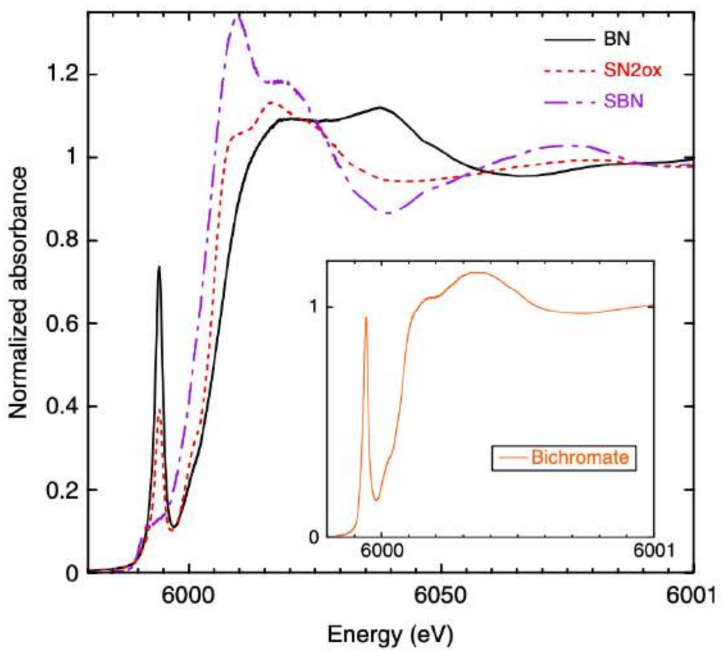


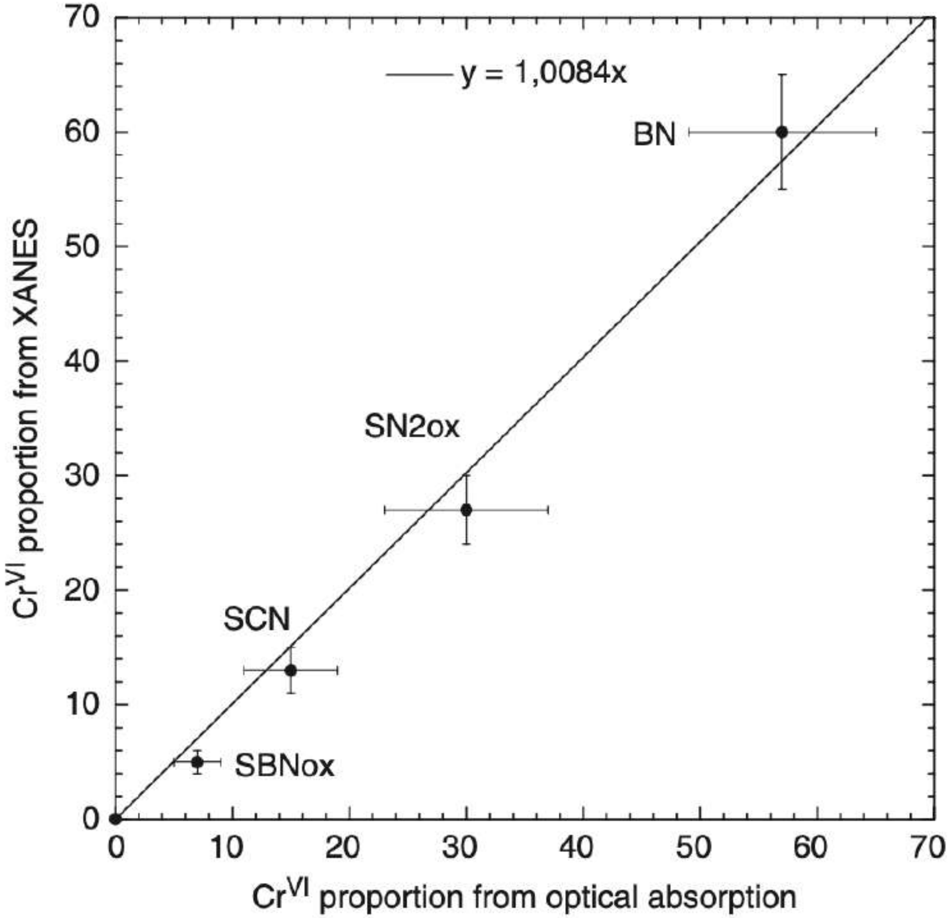


good agreement with Densen and Turner,
the redox of elements in diluted condition
does not follow the expected rules

Gonçalves Ferreira P., de Ligny D., Lazzari O., Jean A., Cintora Gonzalez O. and Neuville D. R. (2013) Photoreduction of iron by a synchrotron X-ray beam in low iron content soda-lime silicate glasses. Chemical Geology, 346, 106-112- DOI: 10.1016/j.chemgeo.2012.10.029



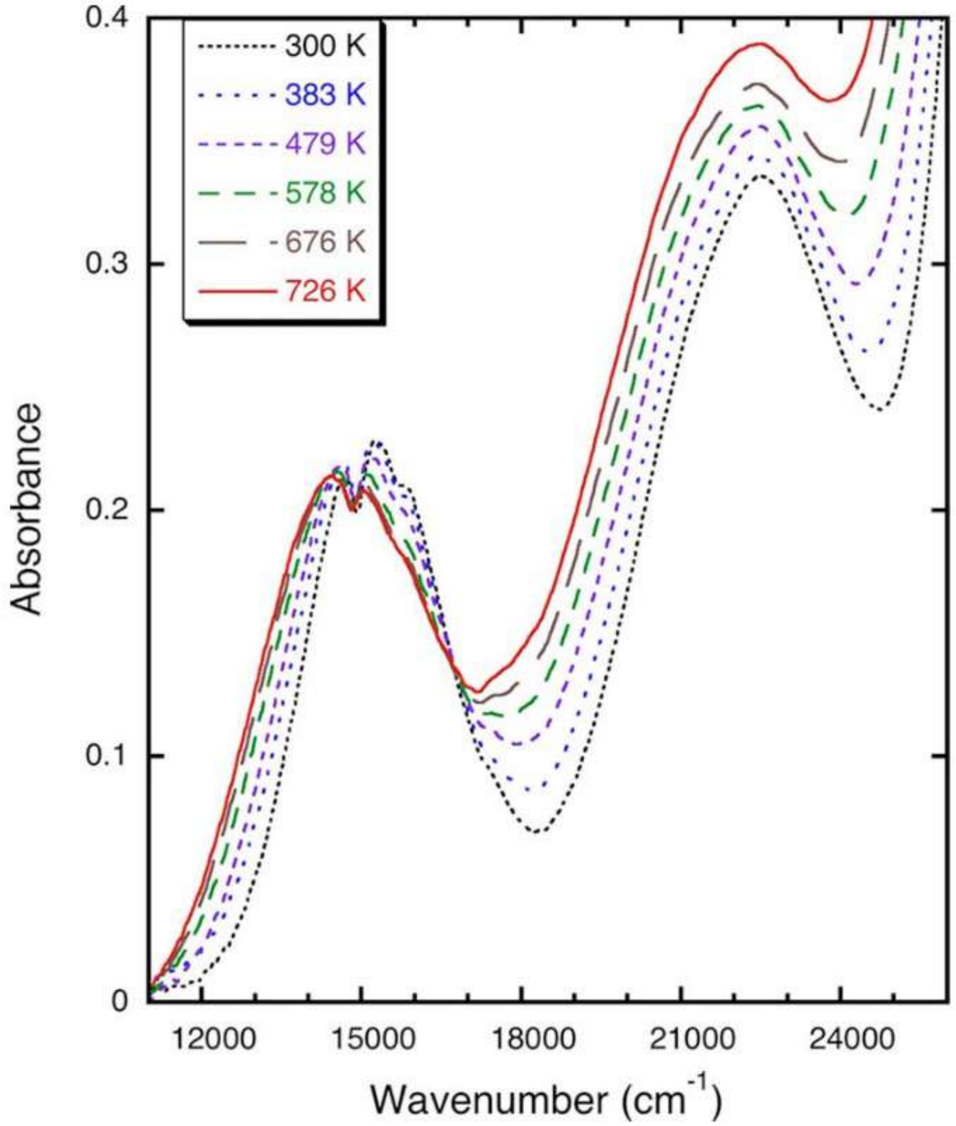




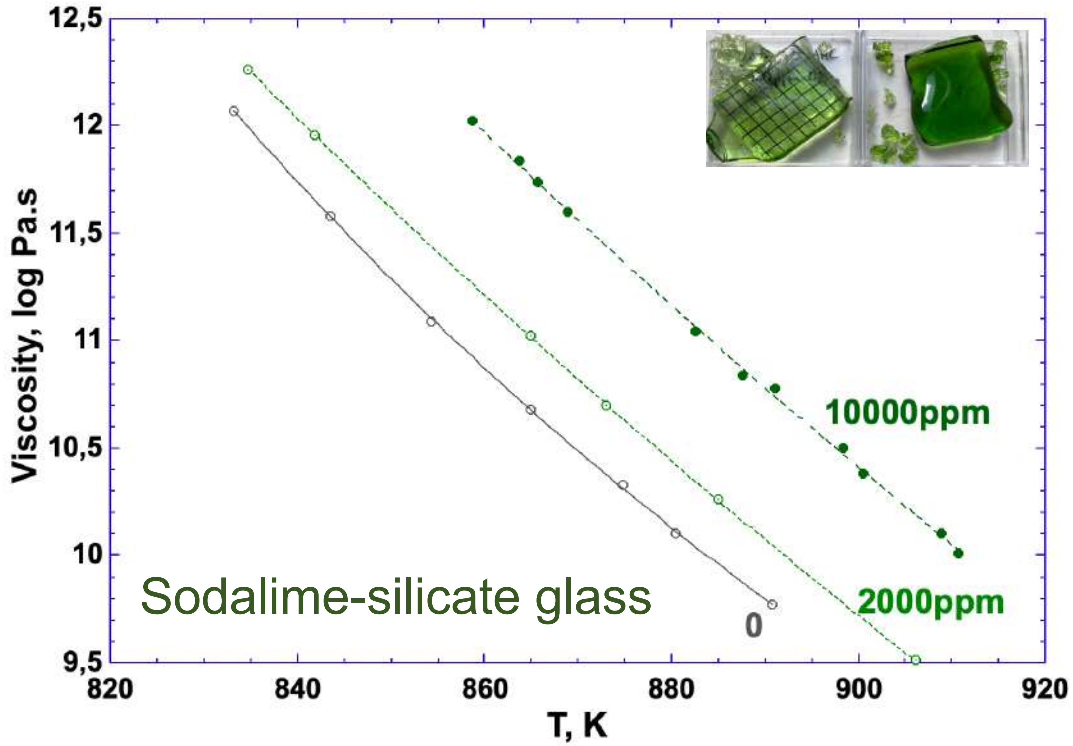
Good correlation between optic and XANES

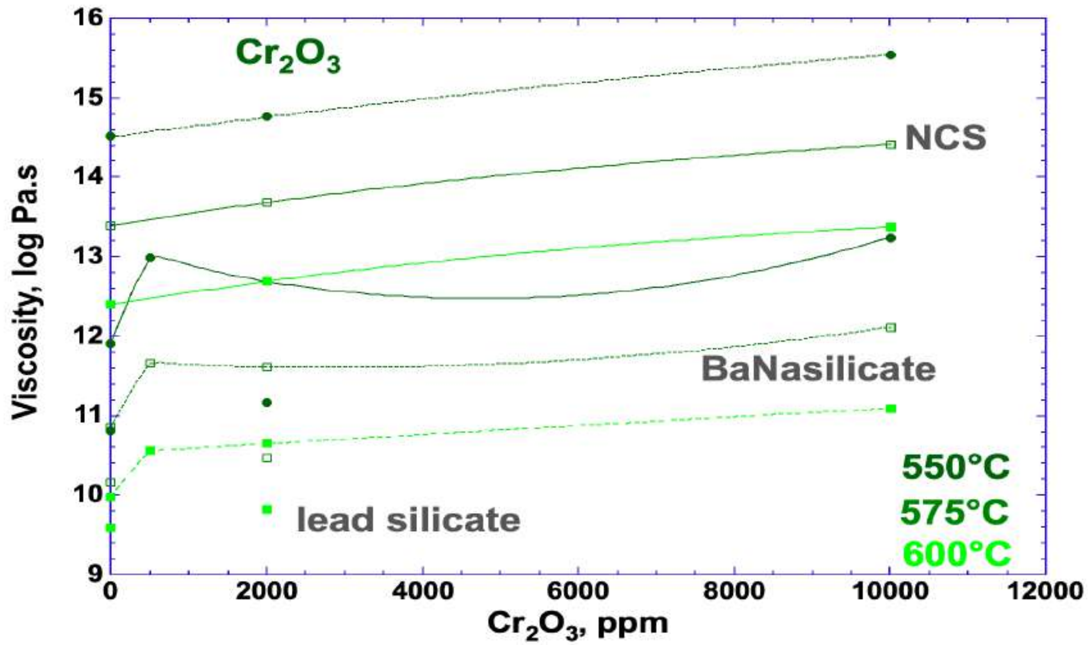
Villain, Calas, Galoisy, Cormier (2007) XANES Determination of Chromium Oxidation States in Glasses: Comparison With Optical Absorption Spectroscopy. J. Am. Ceram. Soc., 90 [11] 3578–3581

Redox Chrome

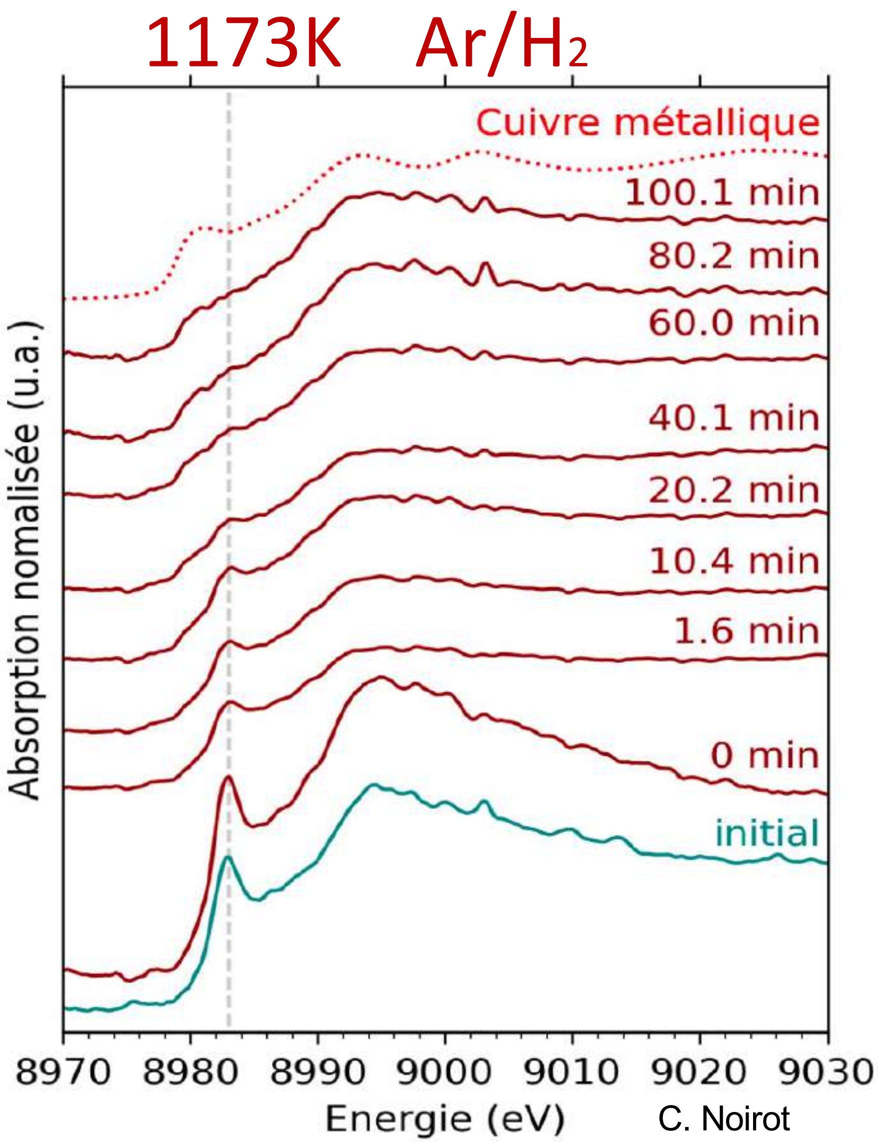


Calas, Majerus, Galoisy, Cormier (2006) Determination of the thermal expansion of Cr3+ sites in glasses. APPLIED PHYSICS LETTERS 88, 121918

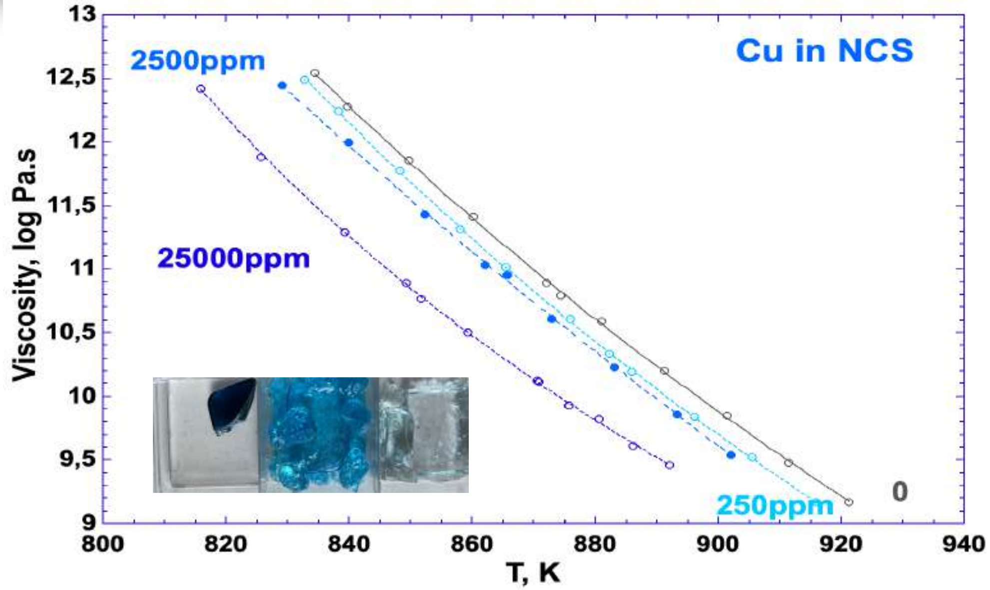


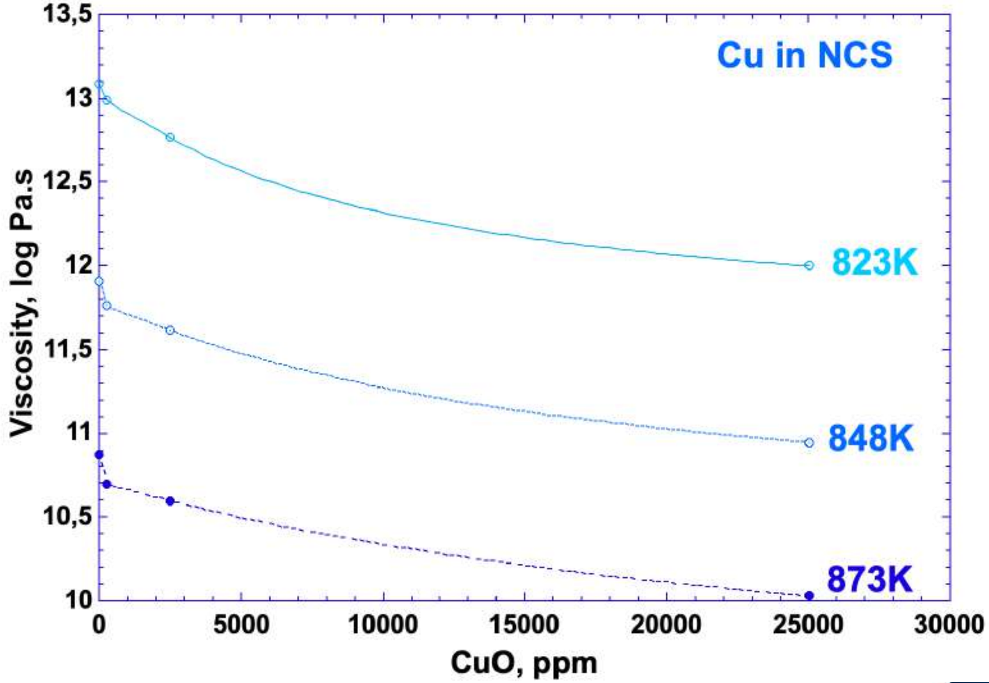


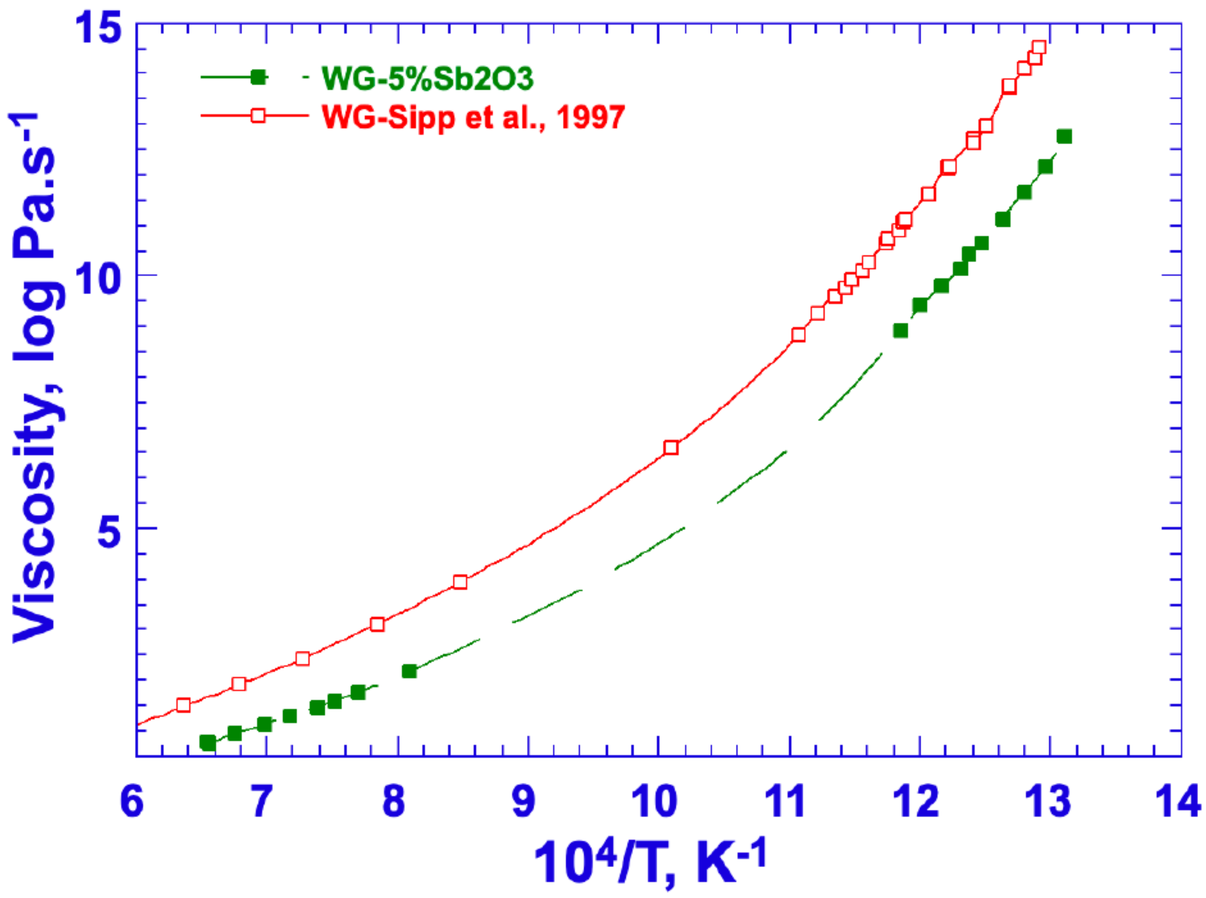
Copper

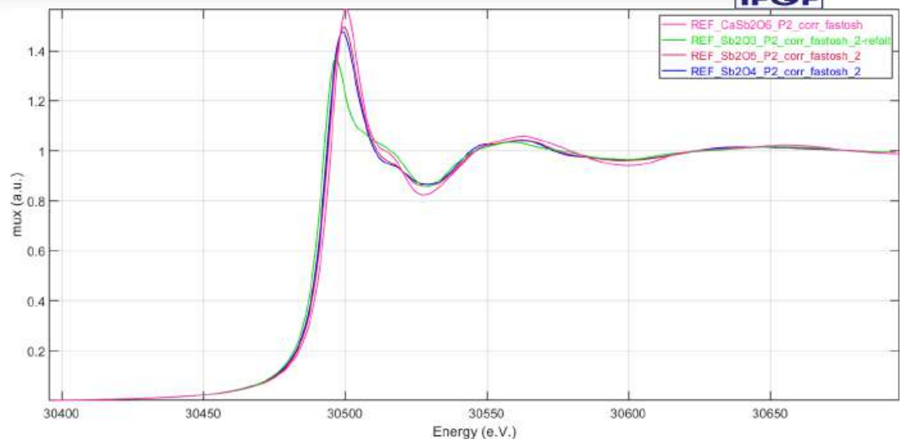


C. Noirot

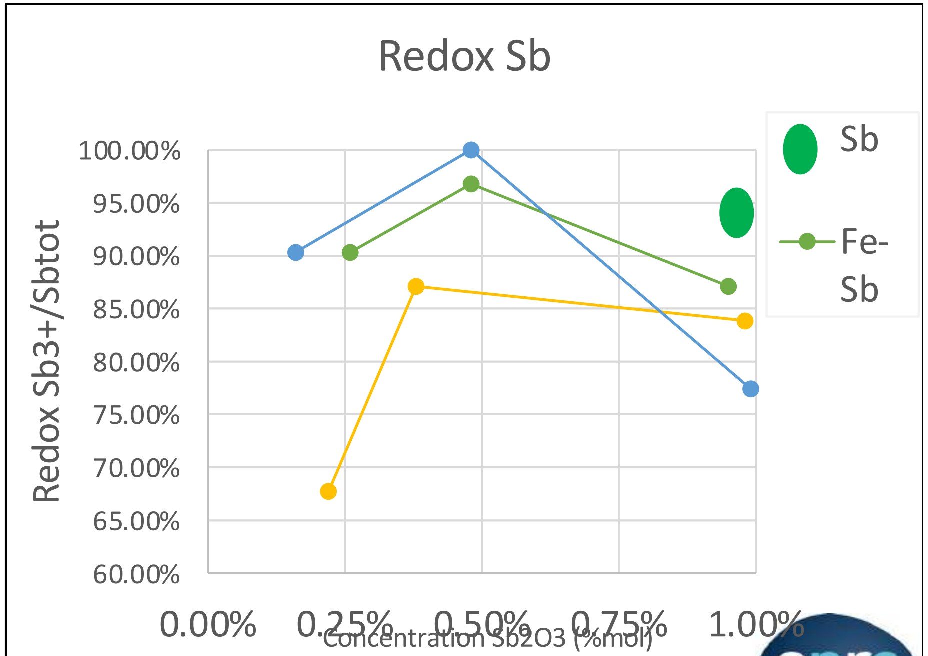






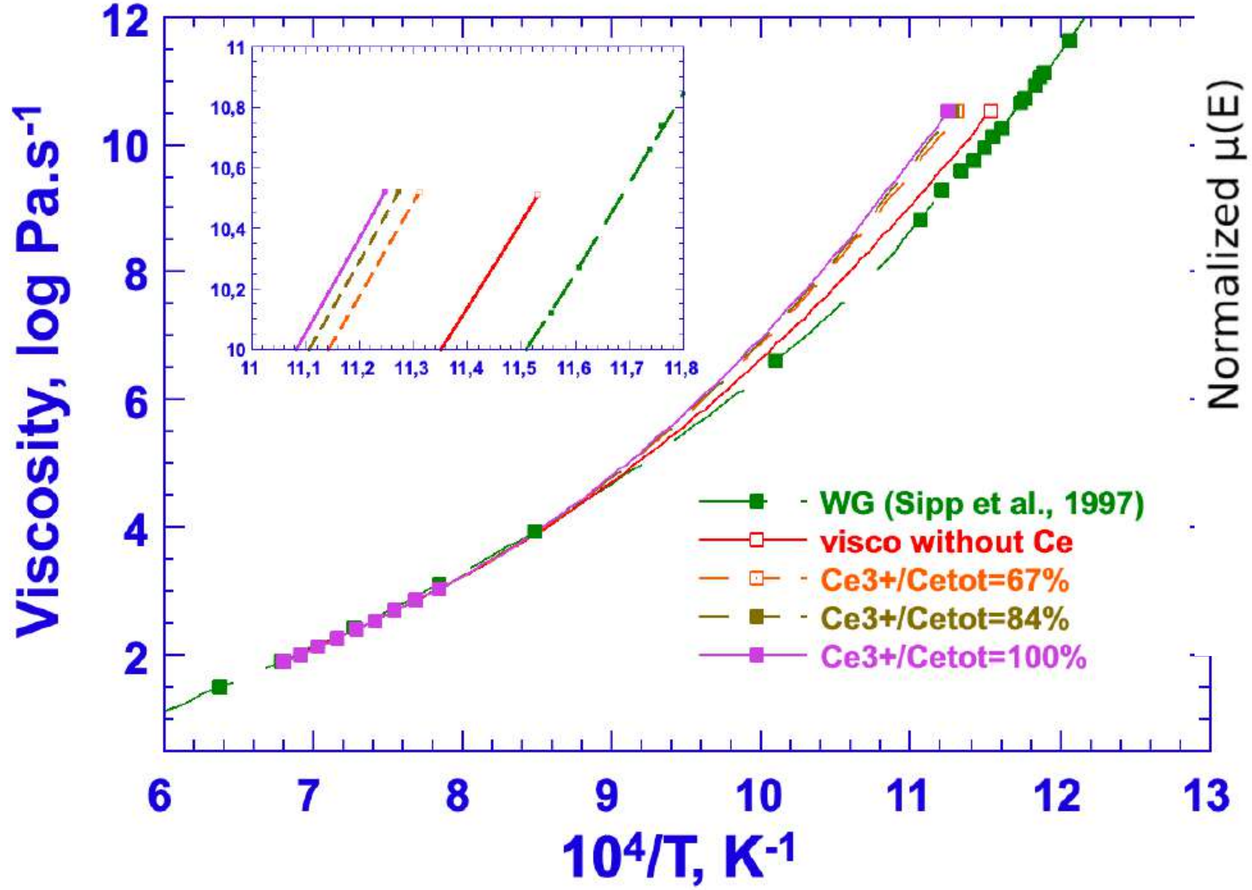


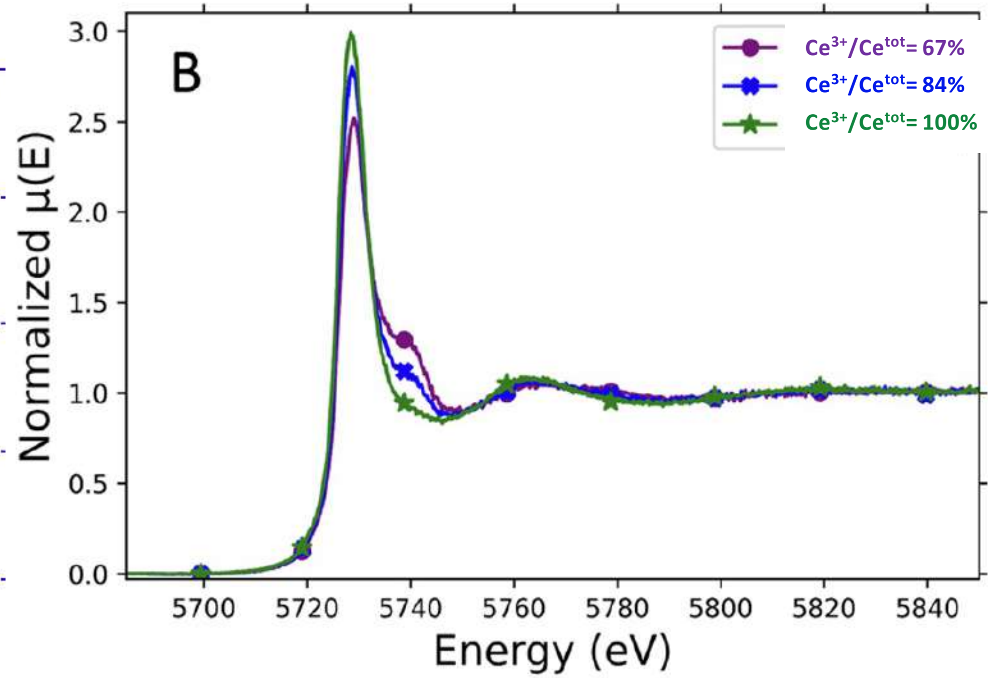
Sb K-edge XANES (Samba, SOLEIL)



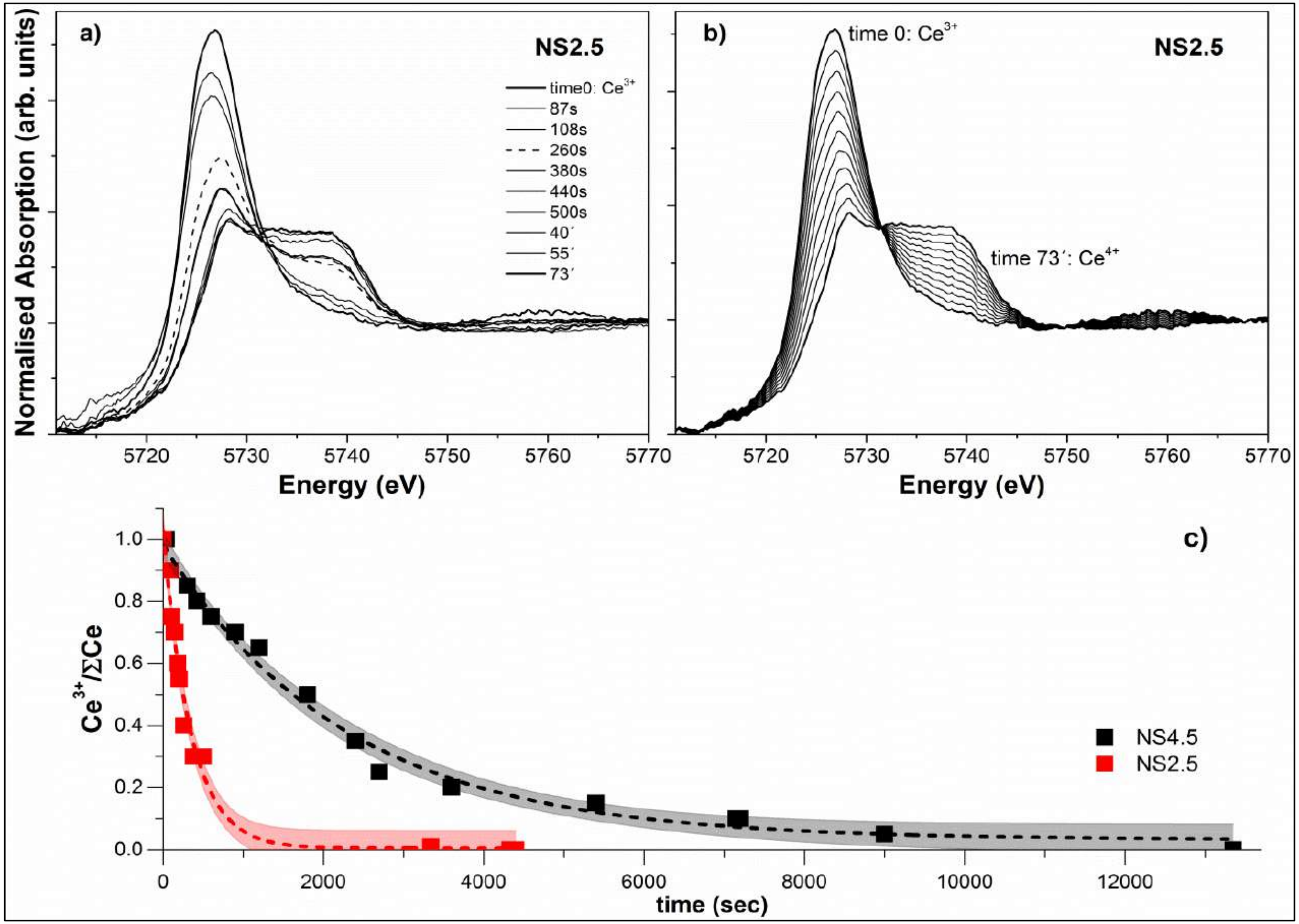
Sb^{3+} decreases viscosity

Cerium effect



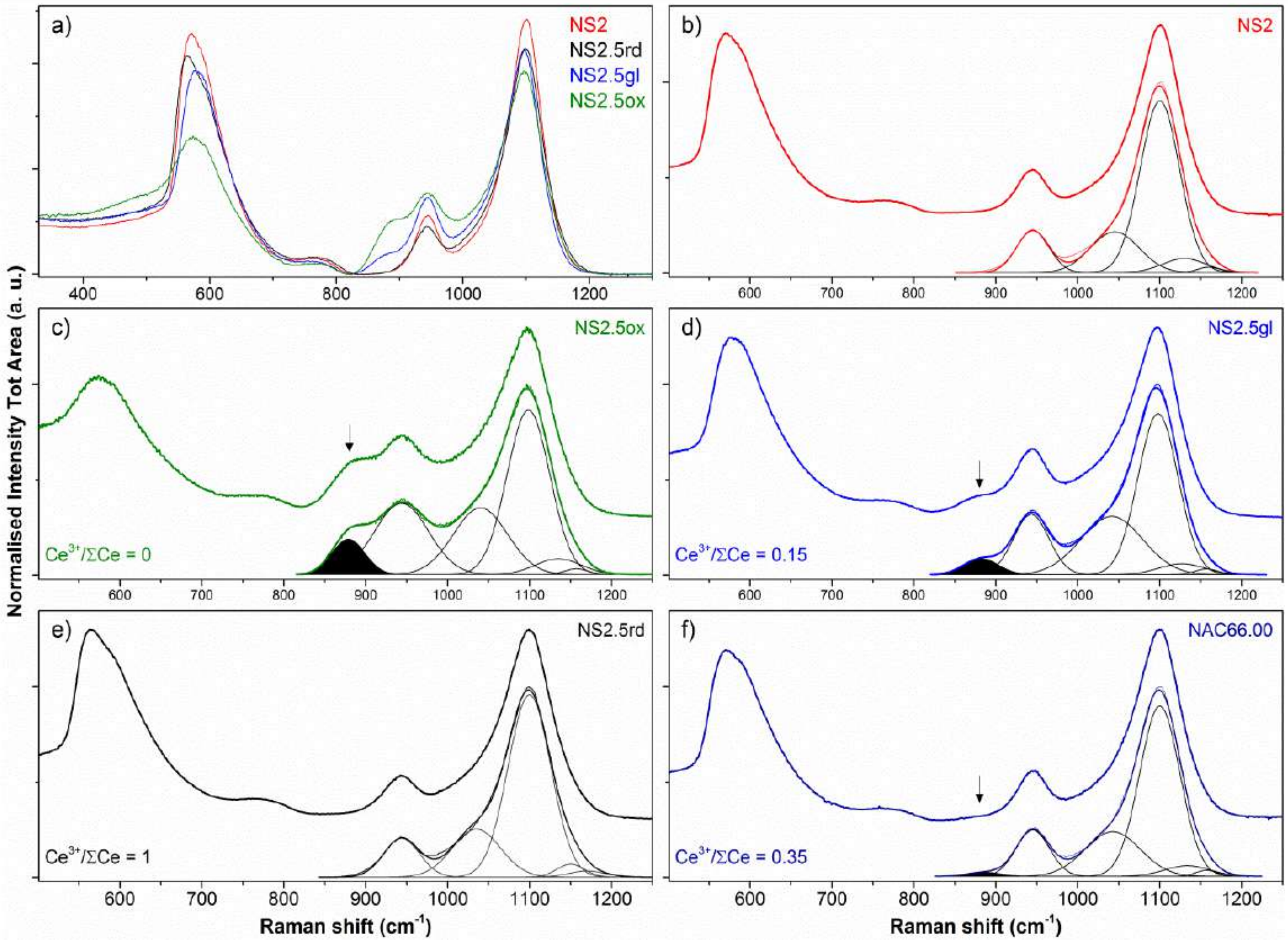


Donatini A., Pereira L., Dingwell D.B., Hess K-U, Müller D., Cormier L., Neuville D.R. (2024) The effect of cerium addition and redox state on silicate structure and viscosity. Journal of the American Ceramic Society. submitted

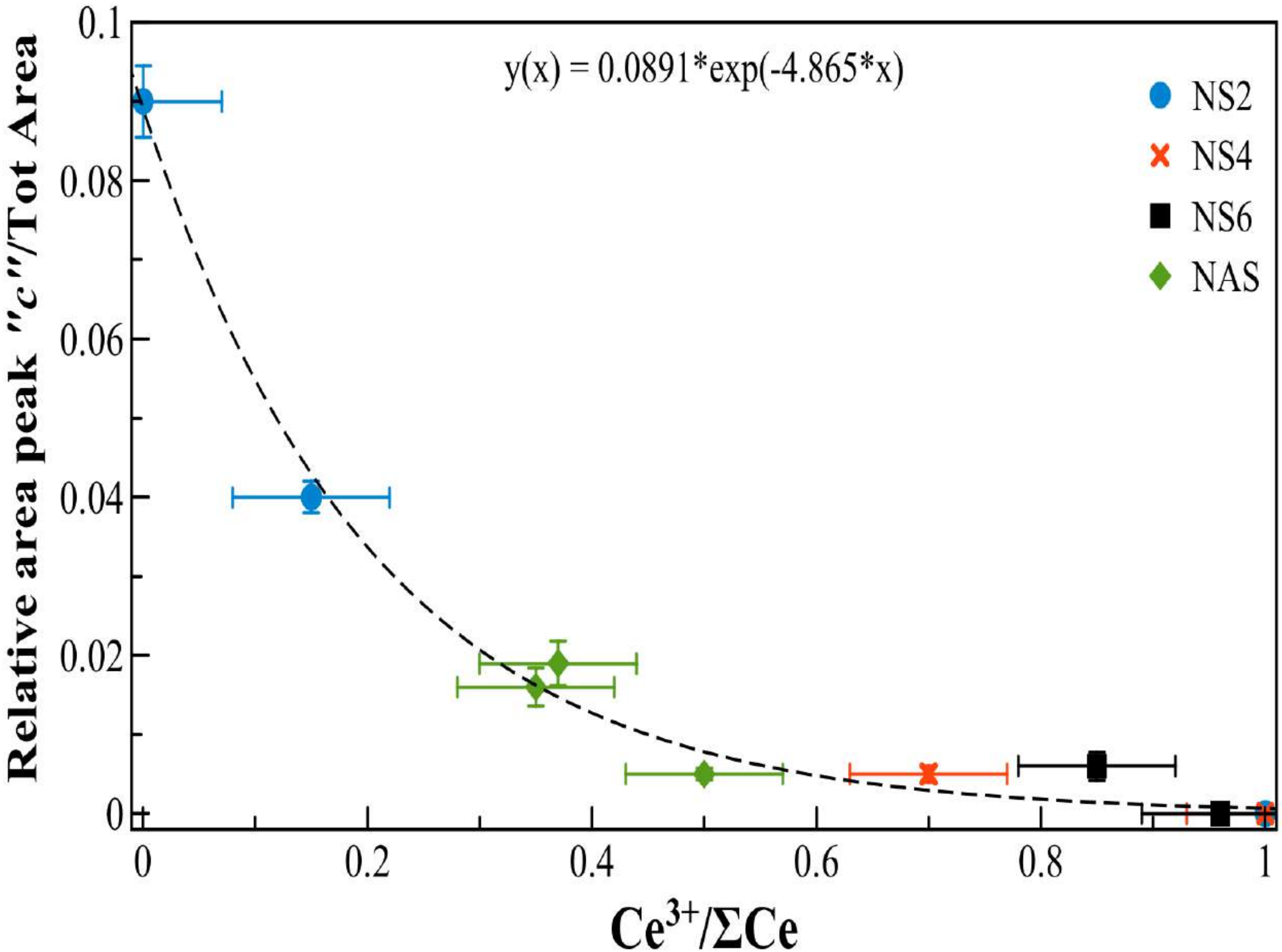


Cicconi M.R., Neuville D.R., Blanc W., Lupi J.F., Vermillac M., de Ligny D. (2017) Cerium structural role in silicate glasses and Ce-activated silica glasses. Journal of Non-Crystalline Solids. 475, 85–95.

Raman spectroscopy on Ce-NSx silicate glasses

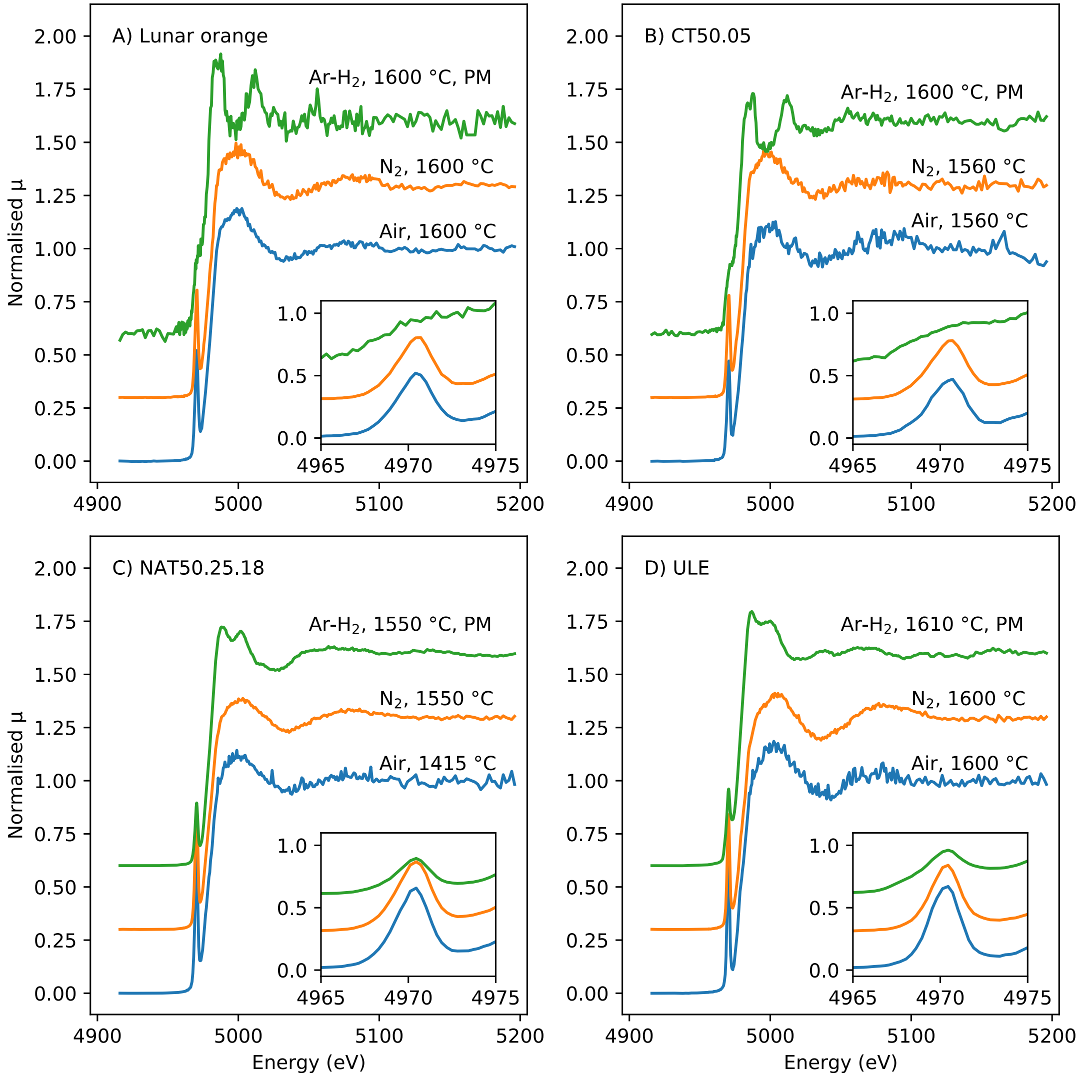


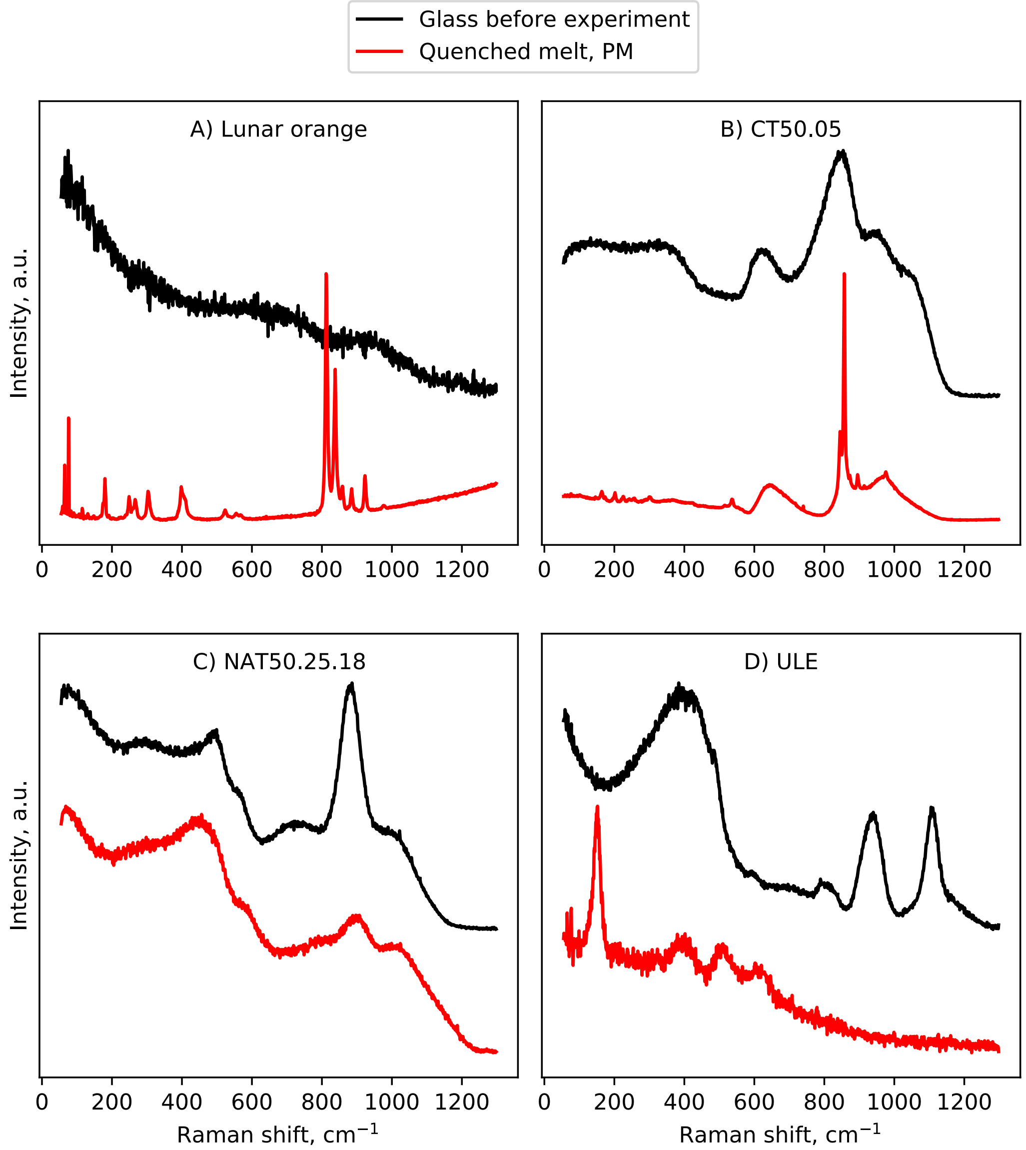
Cicconi M.R., Neuville D.R., Blanc W., Lupi J.F., Vermillac M., de Ligny D. (2017) Cerium structural role in silicate glasses and Ce-activated silica glasses. Journal of Non-Crystalline Solids. 475, 85–95.



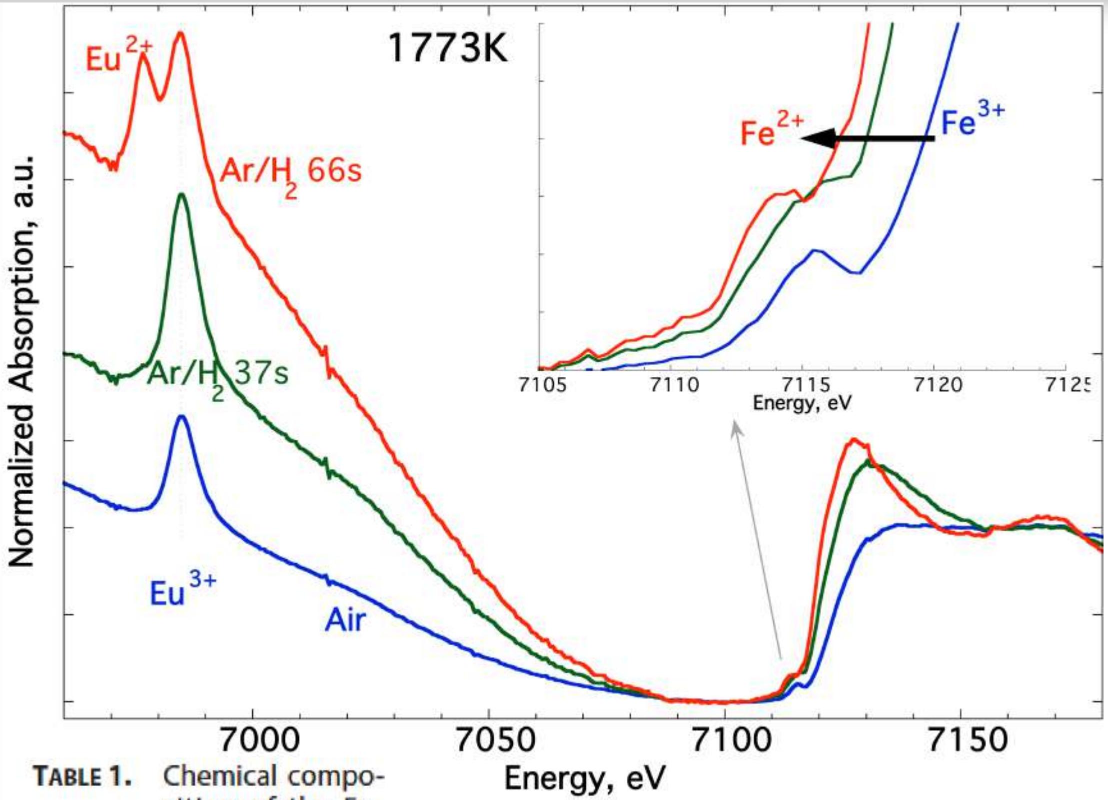
Cicconi M.R., Neuville D.R., Blanc W., Lupi J.F., Vermillac M., de Ligny D. (2017) Cerium structural role in silicate glasses and Ce-activated silica glasses. Journal of Non-Crystalline Solids. 475, 85–95.

Ti in glasses and melts





Tarrago, Losq, Robine T., Reguer S., Thiaudière D., Neuville D.R. (2022) Redox-induced crystallisation in Ti-bearing glass-forming melts: a Ti K-edge XANES study. Materials Letters DOI :10.1016/j.matlet.2022.132296



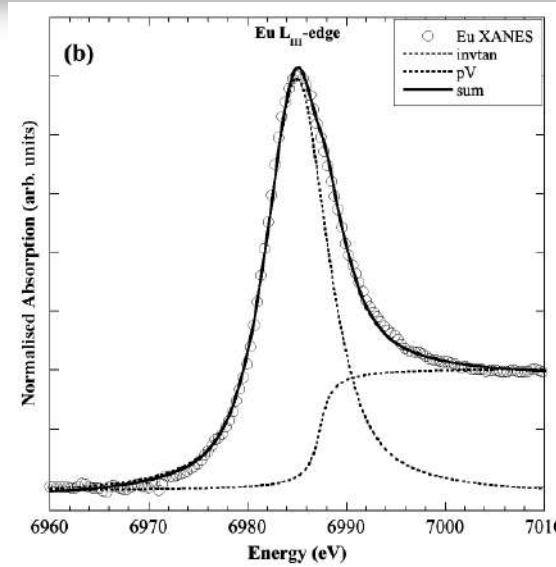
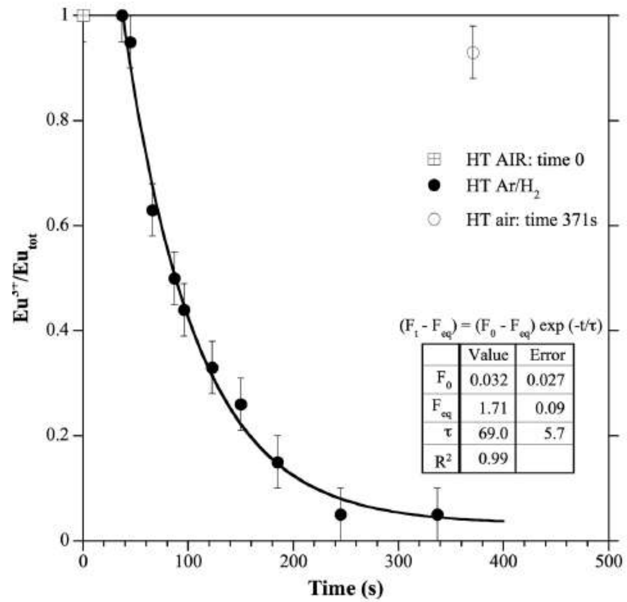
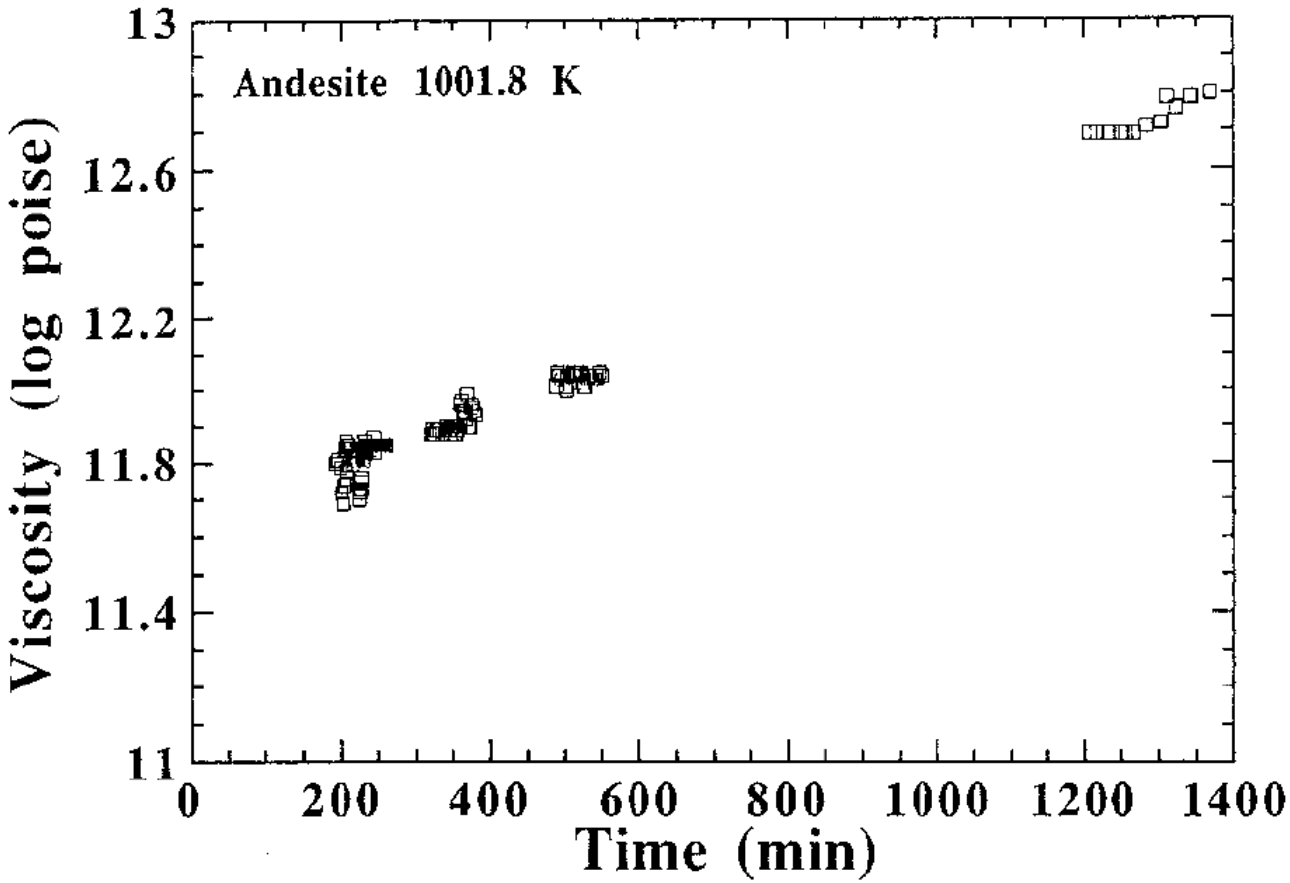


TABLE 1. Chemical composition of the Fe-basalt glass (wt%)

	wt%
SiO_2	44.12
Al_2O_3	9.90
FeO	15.10
CaO	5.28
MgO	5.39
K_2O	4.54
Na_2O	3.06
TiO_2	7.72
Eu_2O_3	4.89
Total	100.01



Cicconi M.R., Neuville D.R., Tannou I., Baudelet F., Floury P., Paris E., and Giuli G. (2015) Competition between two redox states in silicate melts: an in-situ simultaneous experiment at the Fe K-edge and Eu L3-edge. American Mineralogist. 100, 1013-1016.



Neuville D.R., Courtial P., Dingwell D.B. and Richet P. (1993) Thermodynamic and rheological properties of rhyolite and andesite melts. Contrib. Mineral. Petrol., 113, 571-581.

Questions : why η increases with time ?

Redox change? Nucleation and growth?

Basalt glass composition

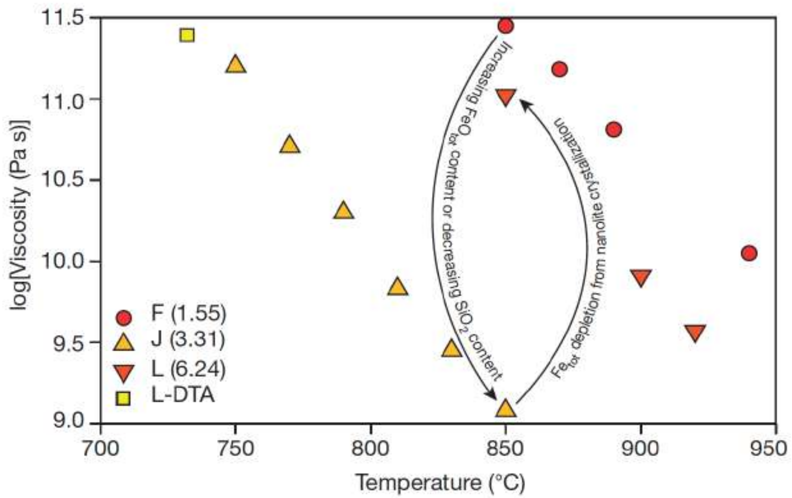
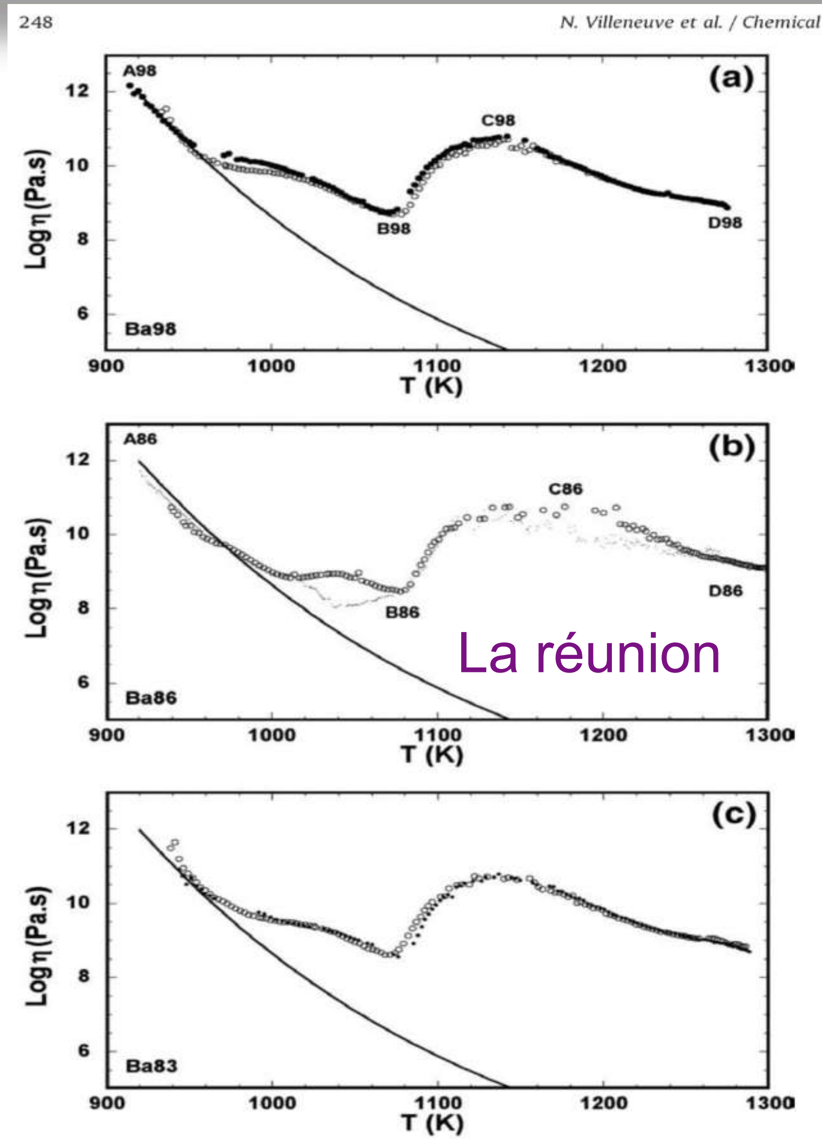


Figure 2 | Measured viscosity at 850 °C for samples F, J and L characterized by increasing FeO content. FeO content (in wt%) is given in parentheses; see

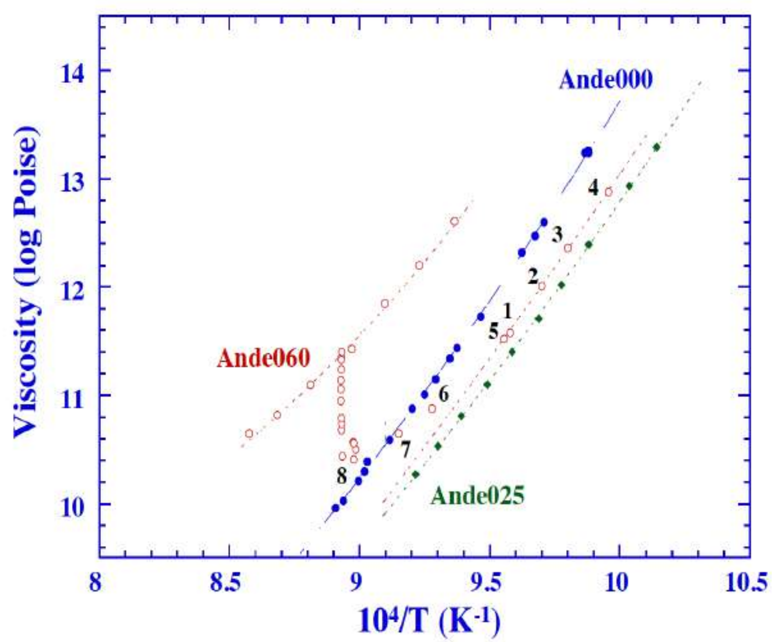
Di Genova D., Kolzenburg S., Wiesmaier S., Dallanave E., Neuville D.R., Hess K.U., Dingwell D.B. (2017) A subtle chemical tipping point governing mobilization and eruption style of rhyolitic magma. Nature. 552, 235-238

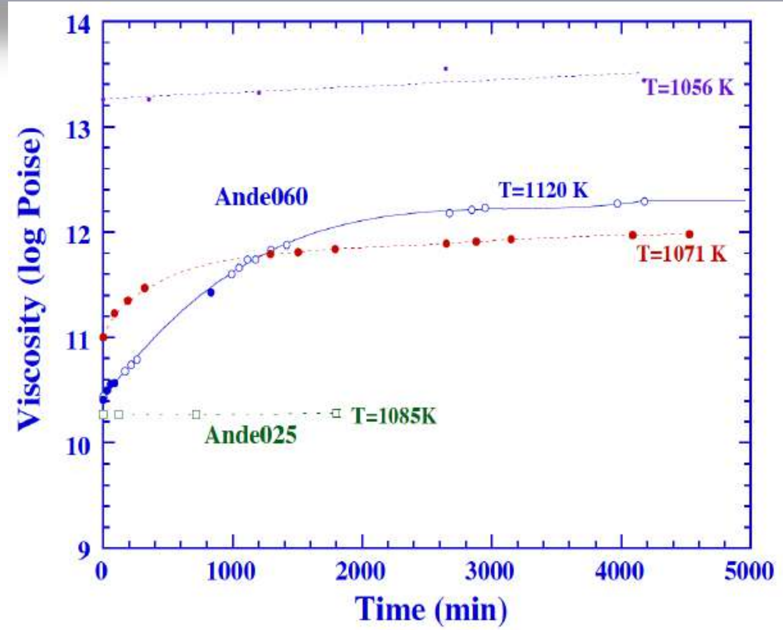


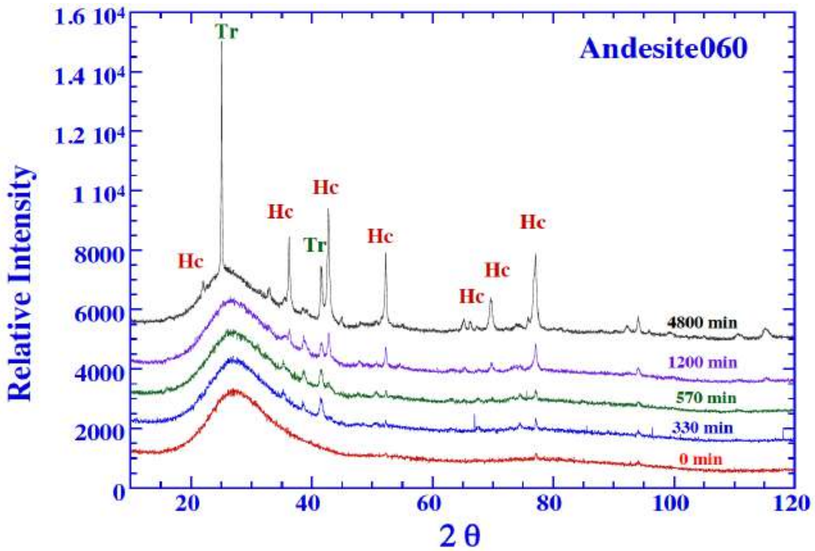
La réunion

Villeneuve N, Neuville D.R. Boivin P., Bachelery P. (2008) Magma crystallization and viscosity: A study of molten basalts from the Piton de la Fournaise volcano (La Réunion island) Chemical Geology, 256, 242-251

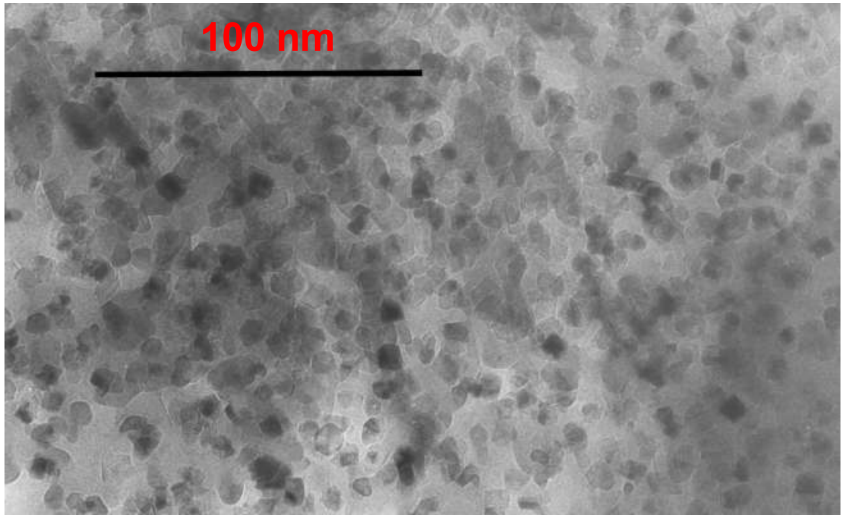
Nucleation, effect on viscosity?







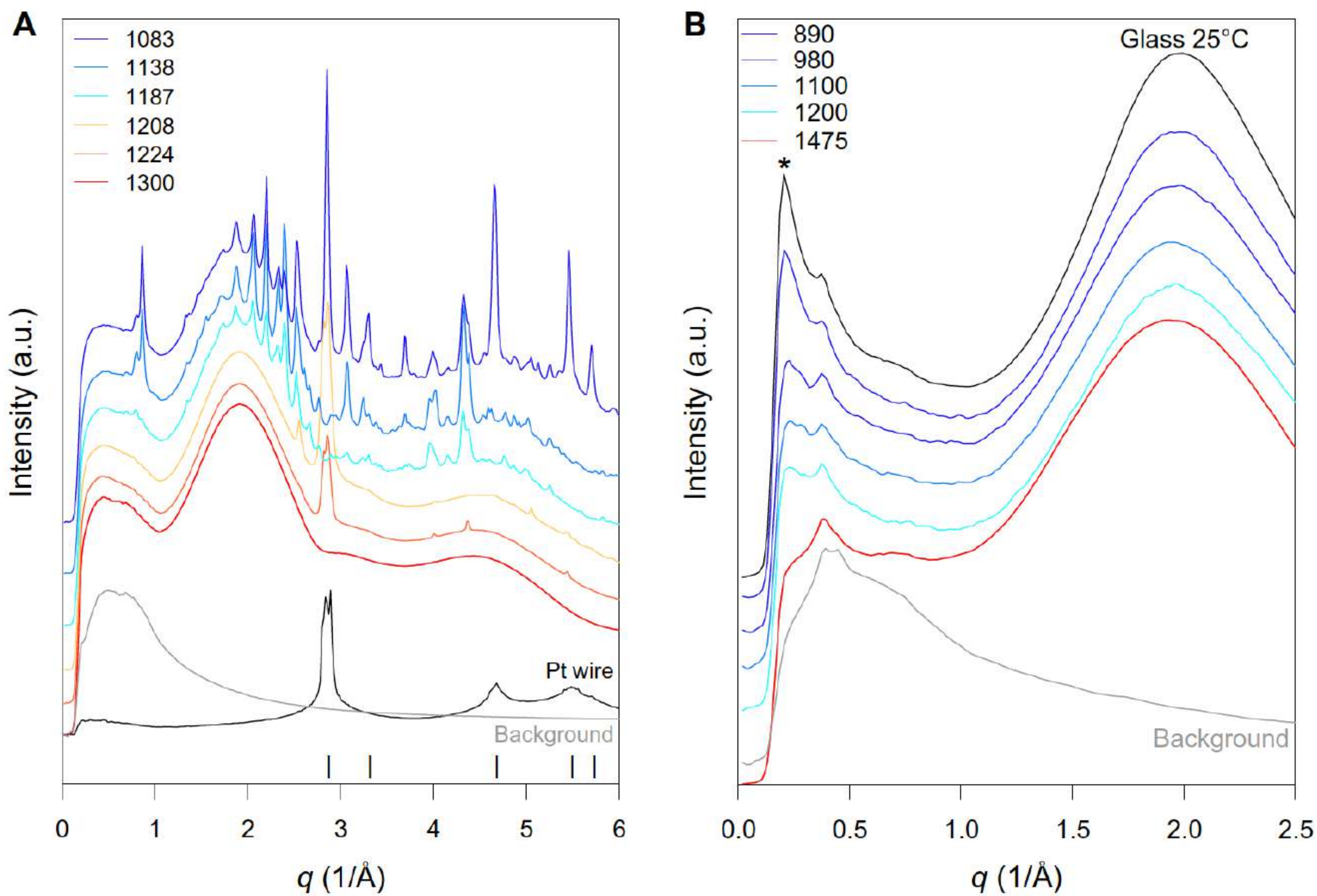
Andesitic glass composition



HR-TEM

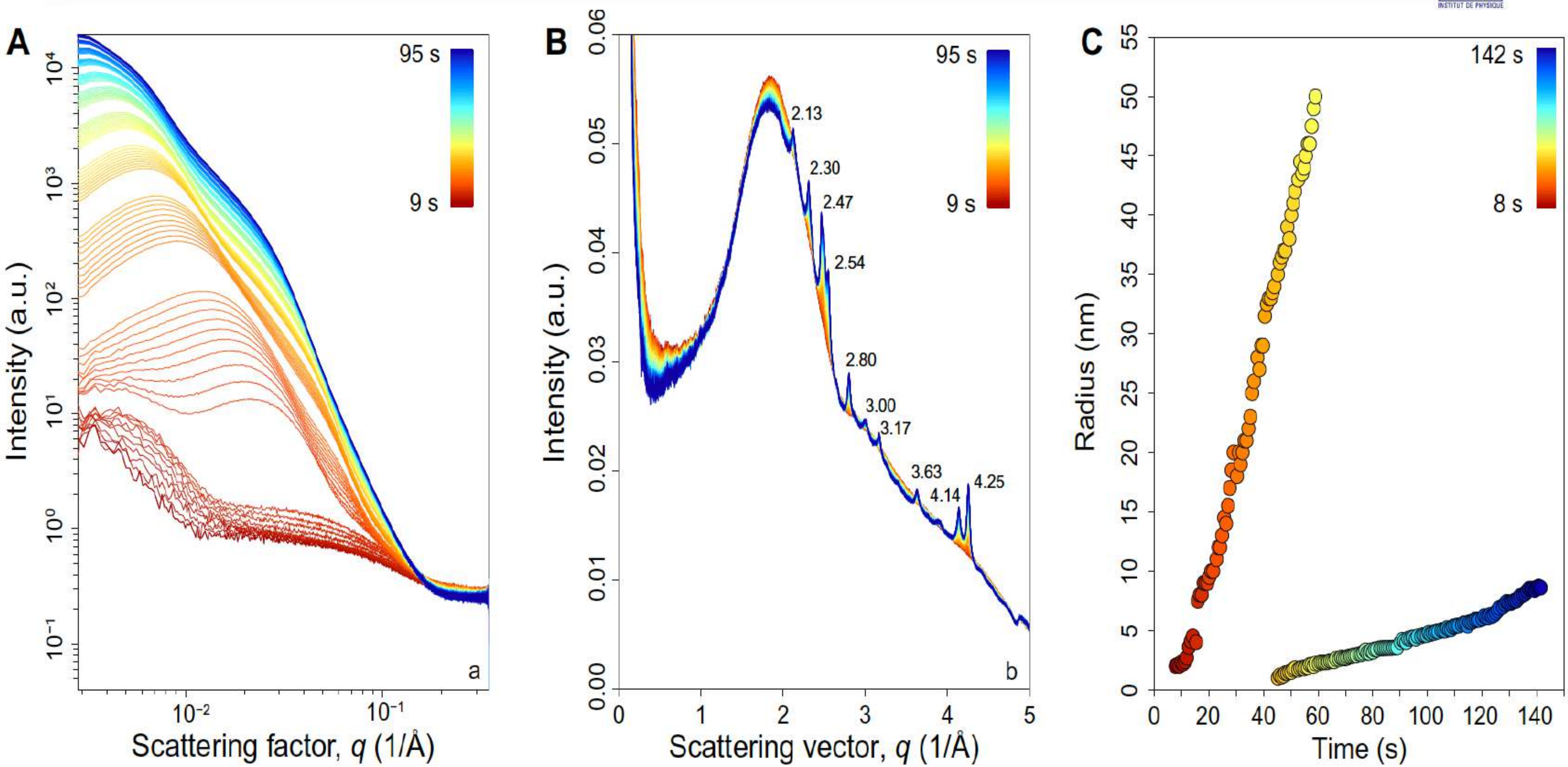
Pereira L., Linard Y., Wadsworth F.B., Vasseur J., Moretti R., Dingwell D.B., Neuville D.R. (2024) non stoichiometric nano-crystallization in magmas: the impact of composition change on viscosity. Journal of Volcanology and Geothermal Research.

Nucleation, effect on viscosity?



Di Genova D., Brooker R.A, Mader H.M., Drewitt J. W. E., Longo A., Deubener J., Neuville D.R., Fanara S., Shebanova O., Anzellini S., Arzilli F., Bamber E. C., Hennet L., La Spina G., Miyajima N. (2020) In situ observation of nanolite growth in volcanic melt: a driving force for explosive eruptions. Sciences Advances. – DOI : 10.1126/sciadv.abb0413

Nucleation, effect on viscosity?



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Conclusion

- ✓ Redox can greatly modify the properties and structure of silicate glasses and melts.
- ✓ There are many tools for studying the redox of glasses and XANES, Raman and optical spectroscopy can also investigated melts.
- ✓ Under dilute conditions, it seems that many elements do not follow thermodynamic models and behave in unexpected ways.
- ✓ These phenomena can give rise to numerous nucleation and crystallization processes, and it has recently been found that large quantities of nanolites are present in the majority of volcanic lavas.