Properties and redox of silicate melts at high temperature

Daniel R. Neuville

Special thanks to Allain Guillot, and students and professors Lycée Jean Monnet, Yzeure 63

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Ashutosh Goel, Rutger University
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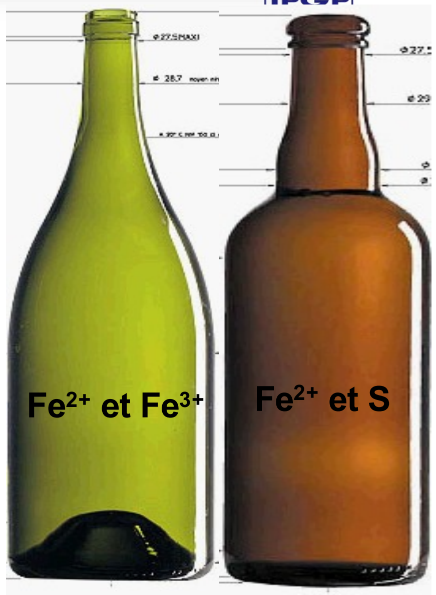
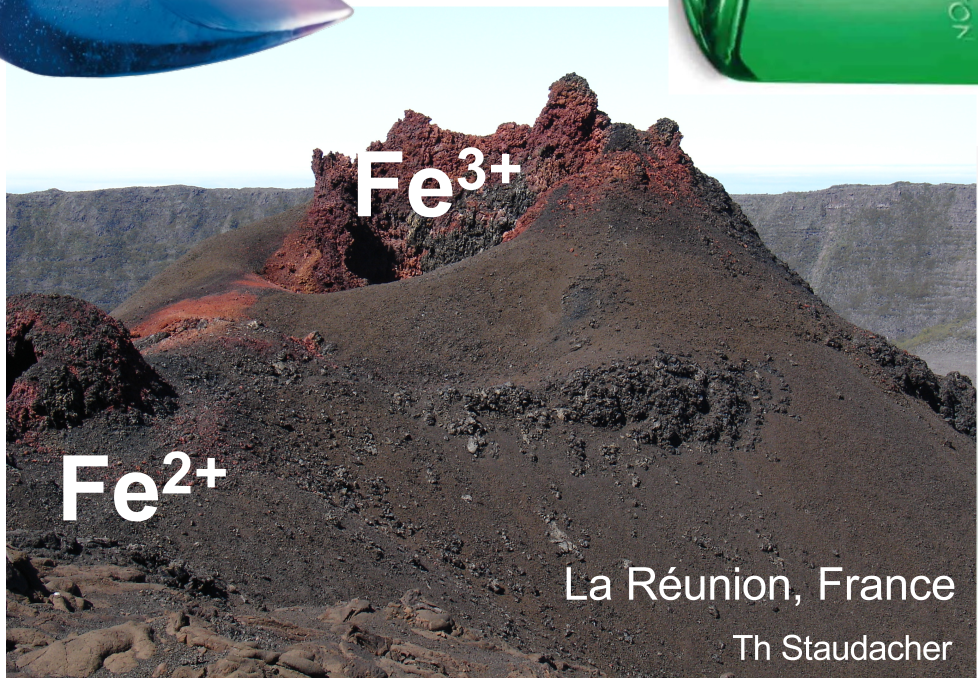
IPGP students and *postdoc* **:** *Rita Cicconi,* **Rawan El Hayek, Véronique Magnien, Isabelle Tannou, Benjamin Cochain, Adrien Donatini,**

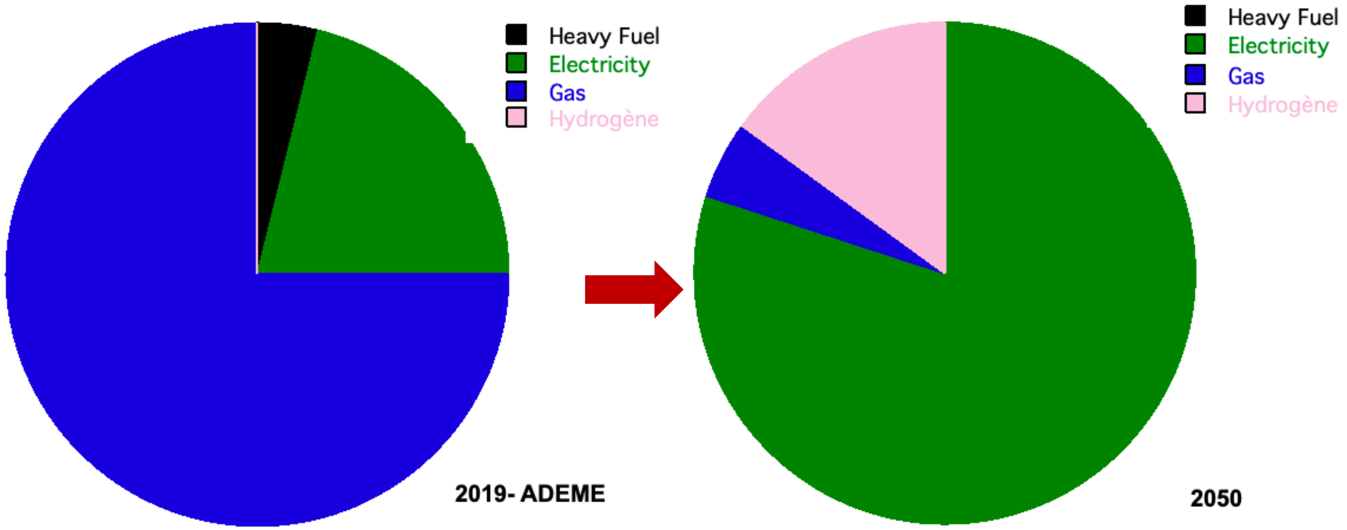
Why determine redox of glasses and melts ?





Two main sources of CO_2 emissions in the glass industry:

✓ Fossil fuels : 80% of emissions

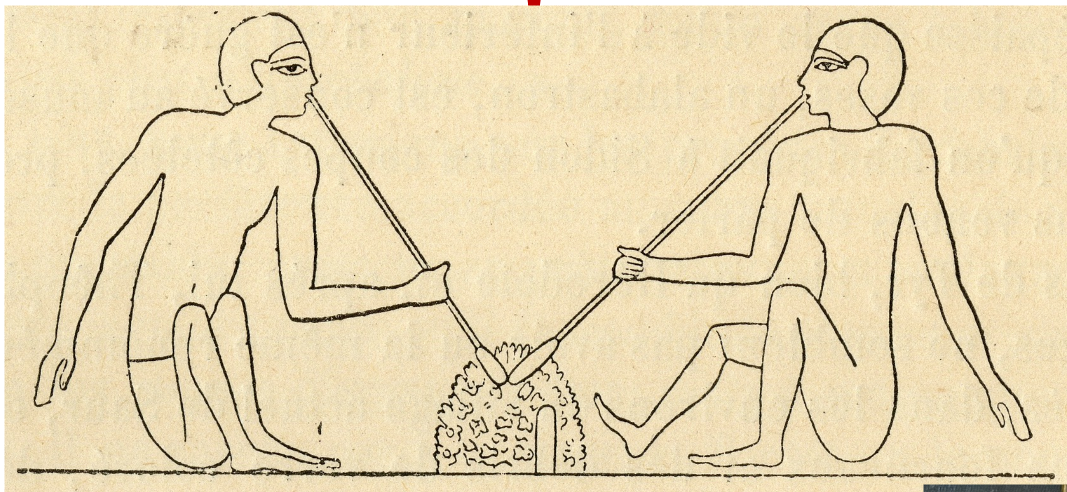


✓ Decarbonation of raw materials : 20% of emissions

Sand
+ Plant ashes

Sand
+ Natron

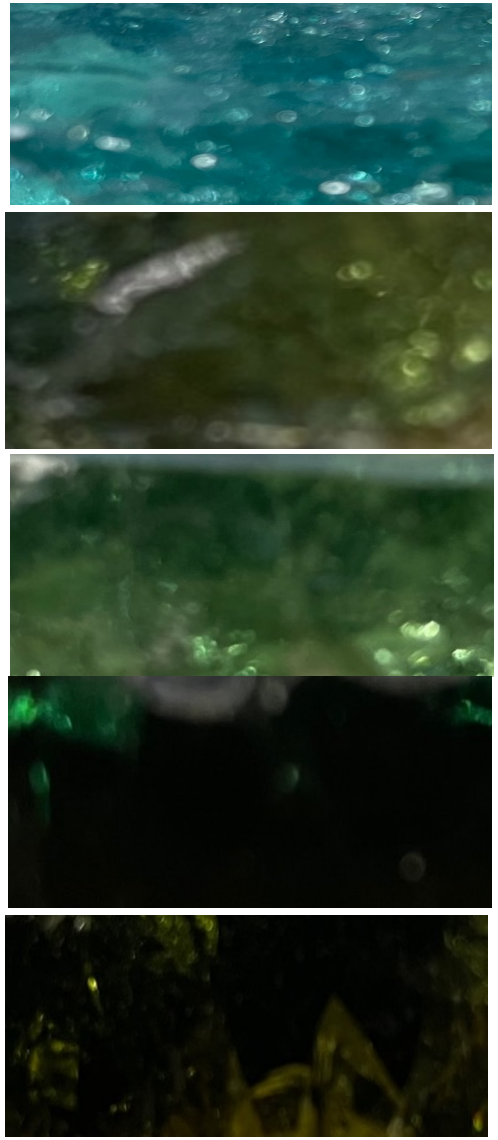
Charred remains of the glass partition in the eastern portico of the uiridarium of the Casa dell'Atrio a Mosaico (IV, 1-2) at Herculaneum



Raw materials

+

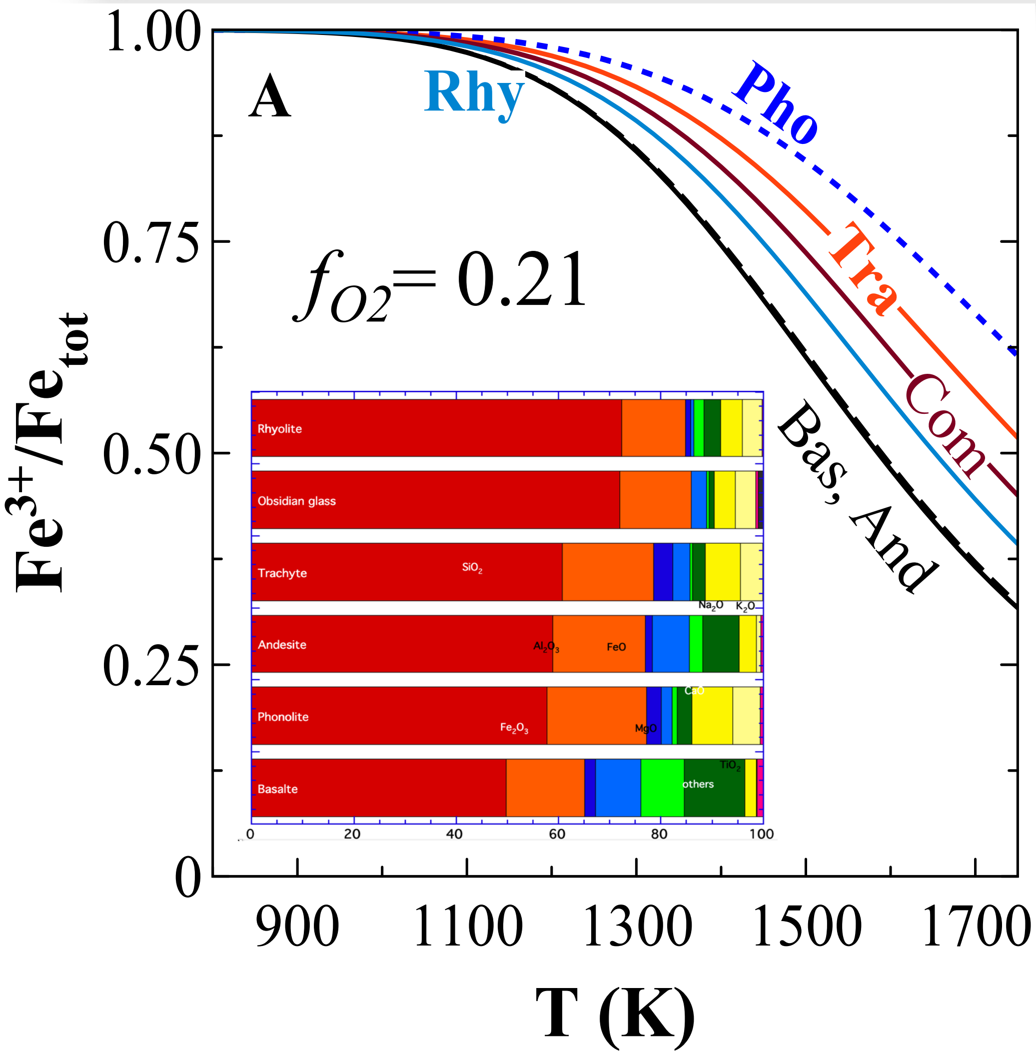
=



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

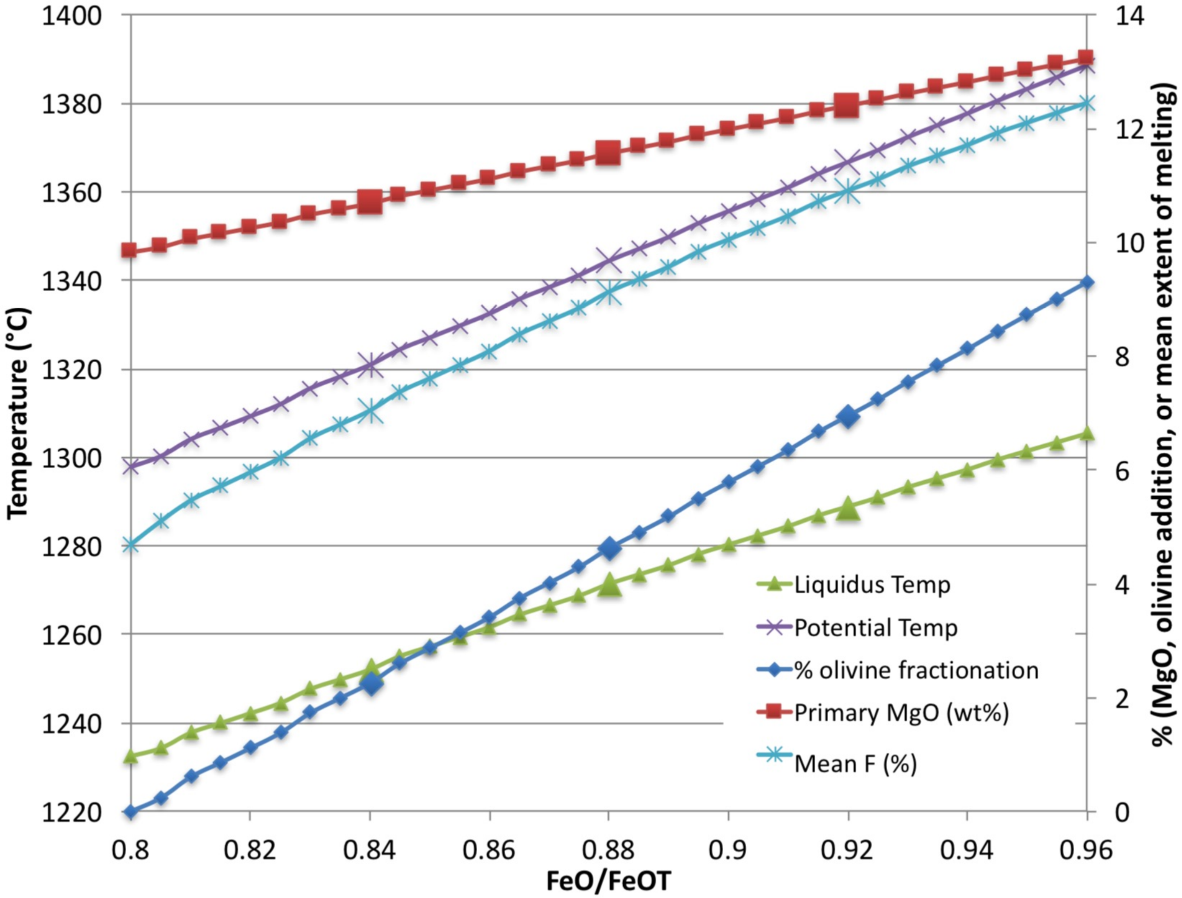
To limit CO_2 emissions, it will probably be necessary to change the chemical compositions and operating modes of furnaces, and therefore to know the oxidation-reduction of the final product and the oxidation-reduction at high temperature.

- *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*

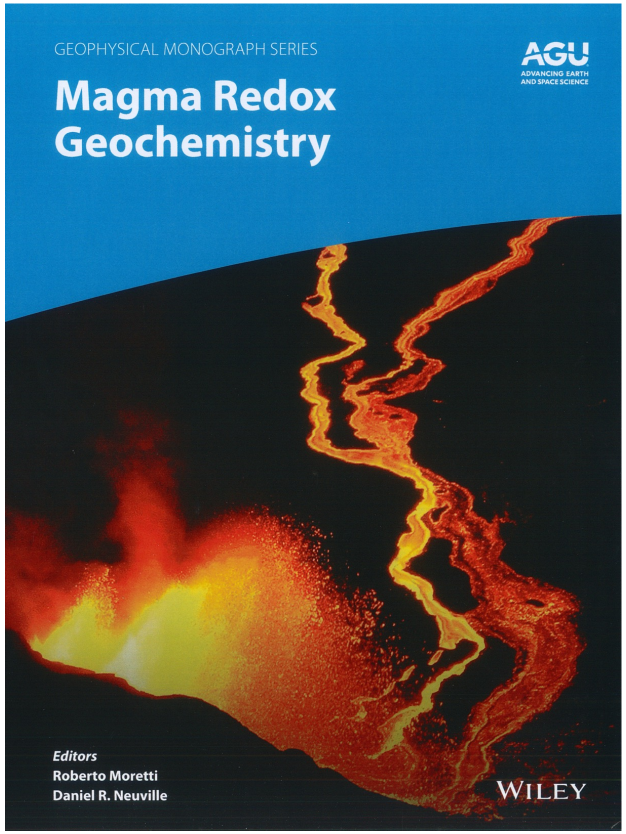


Kress VC, Carmichael ISE (1991) The compressibility of silicate liquids containing Fe2O3 and the effect of composition, temperature, oxygen fugacity and pressure on their redox states. Contributions to Mineralogy and Petrology 108:82–92

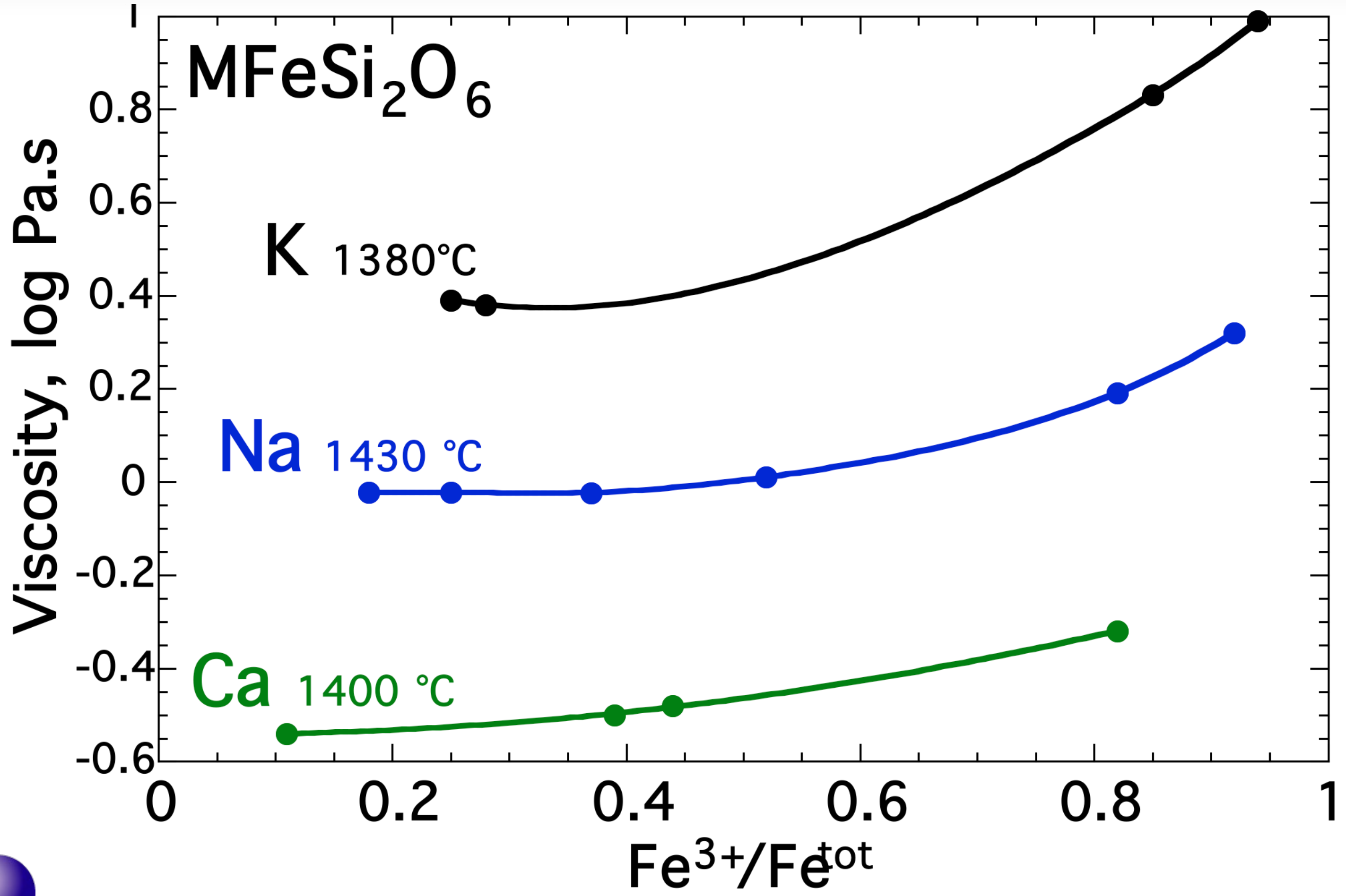
Cicconi M.R., Moretti R., Neuville D.R. (2020) Earth Electrodes, Elements, edt. Moretti R., Cicconi M.R., Neuville "The redox engine of the Earth". DOI: 10.2138/gselements.16.3.157



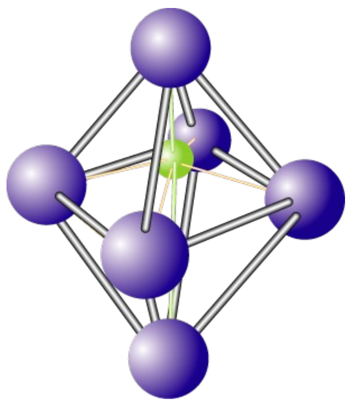
Redox can plays a very important role on ***liquidus temperature,***
crystallization….
Glass transition….



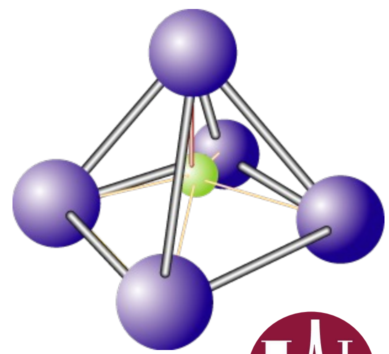
Asimow P. (2020) The petrological consequences of the estimated oxidation state of primitive MORB glass. AGU Monograph on Magma Redox Geochemistry edt by Moretti and Neuville.



[6]Fe^{2+}

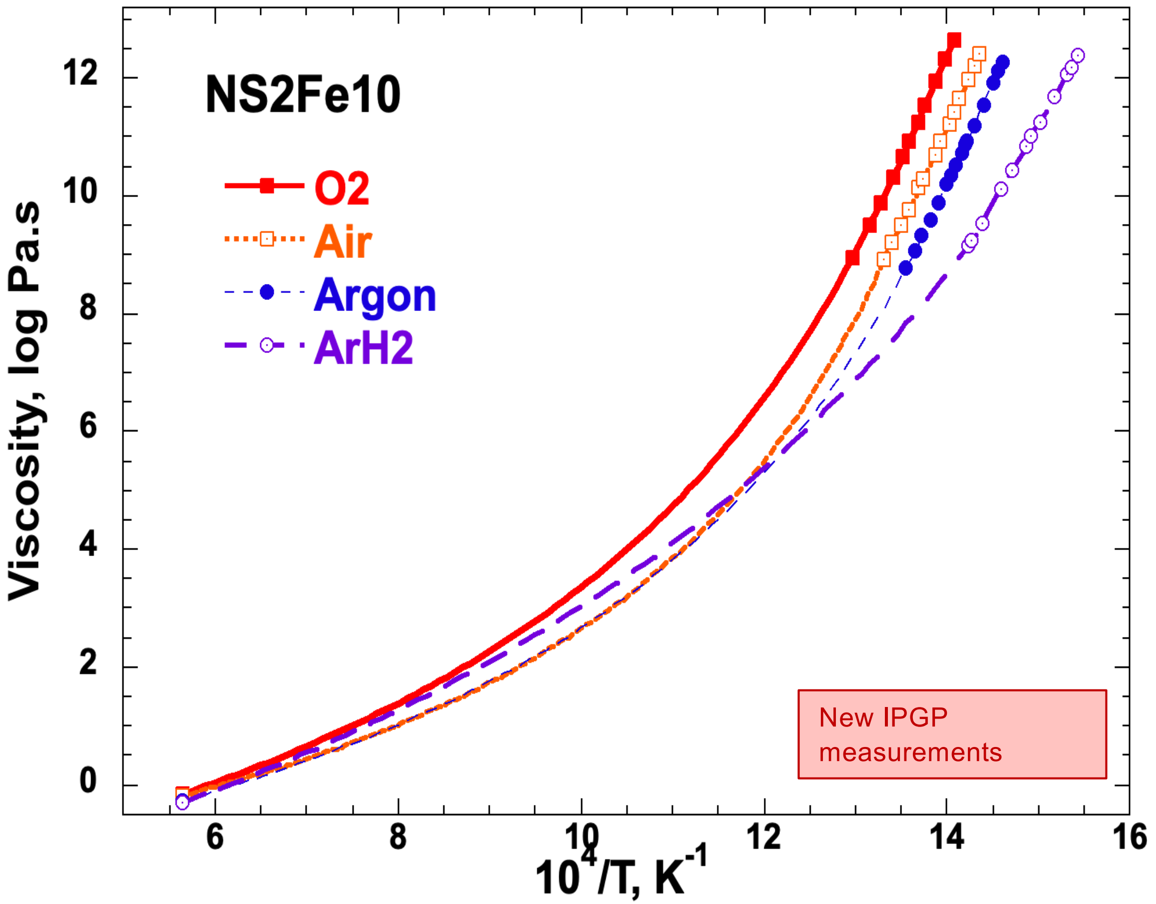


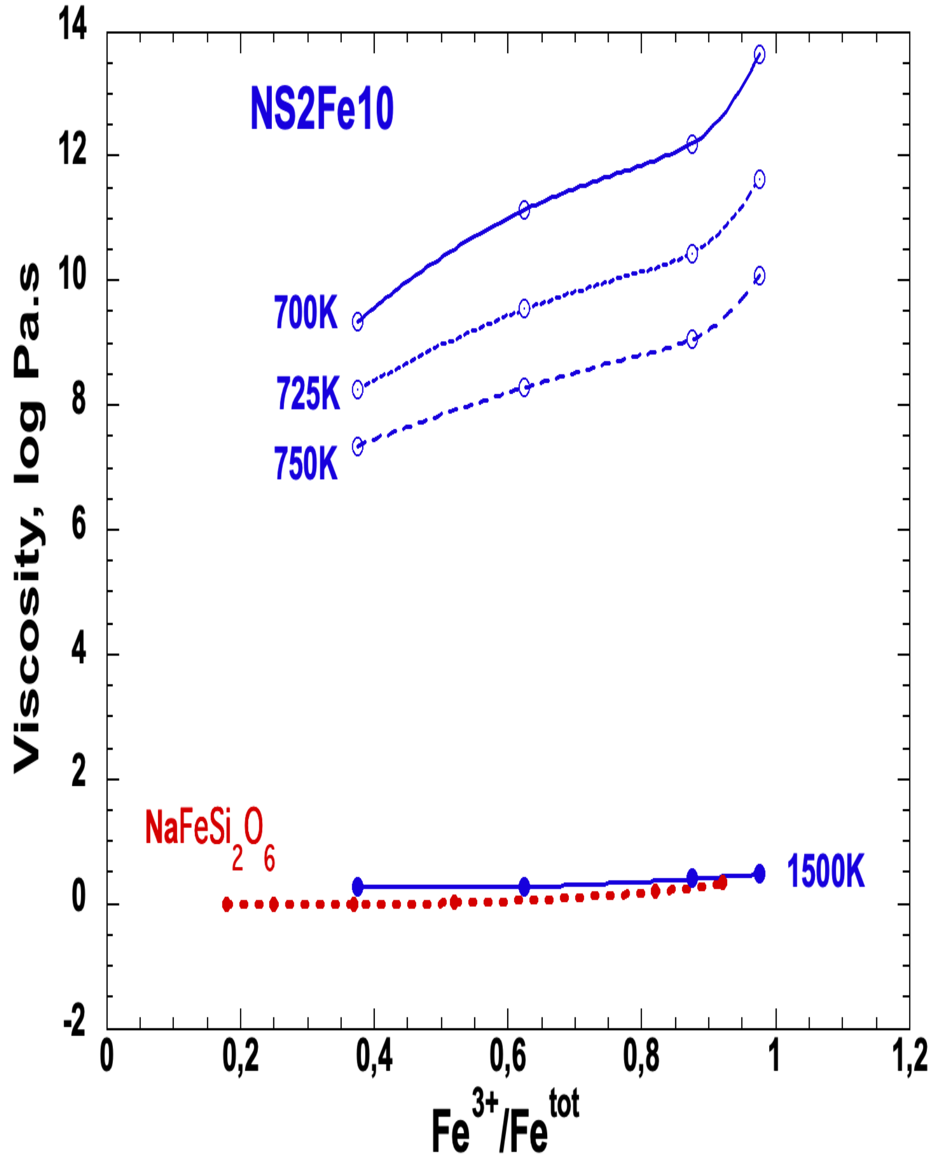
[4]Fe^{3+}



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

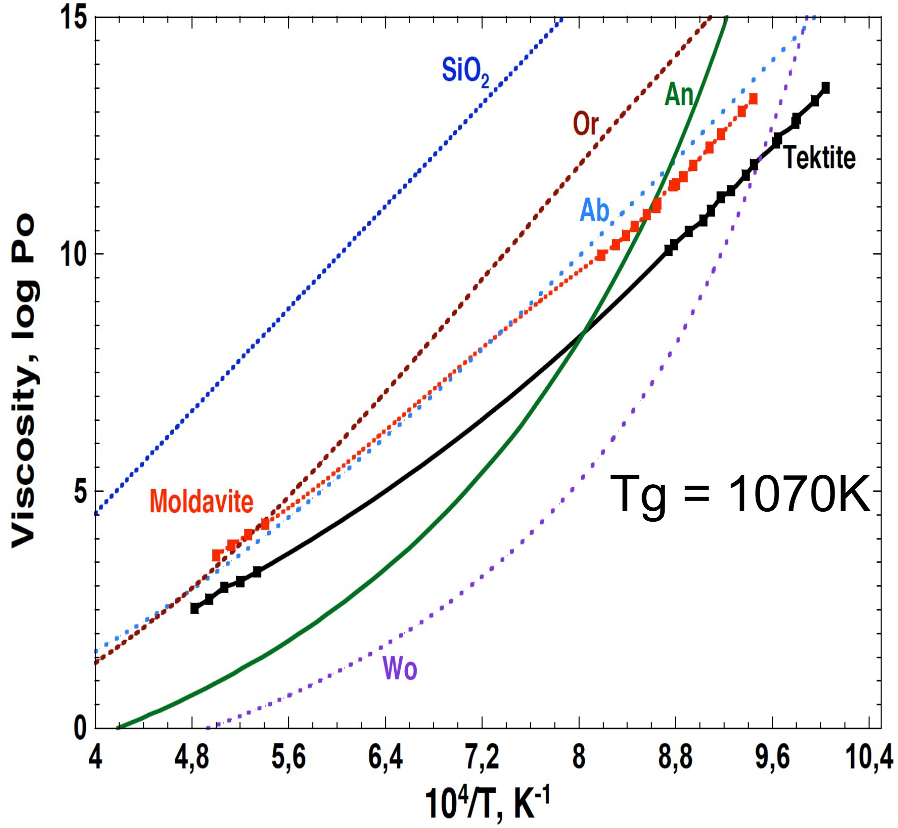
Dingwell DB, Virgo D (1987) The effect of oxidation state on the viscosity of melts in the system Na2O-FeO-Fe2O3-SiO2. Geochimica et Cosmochimica Acta 51:195–205

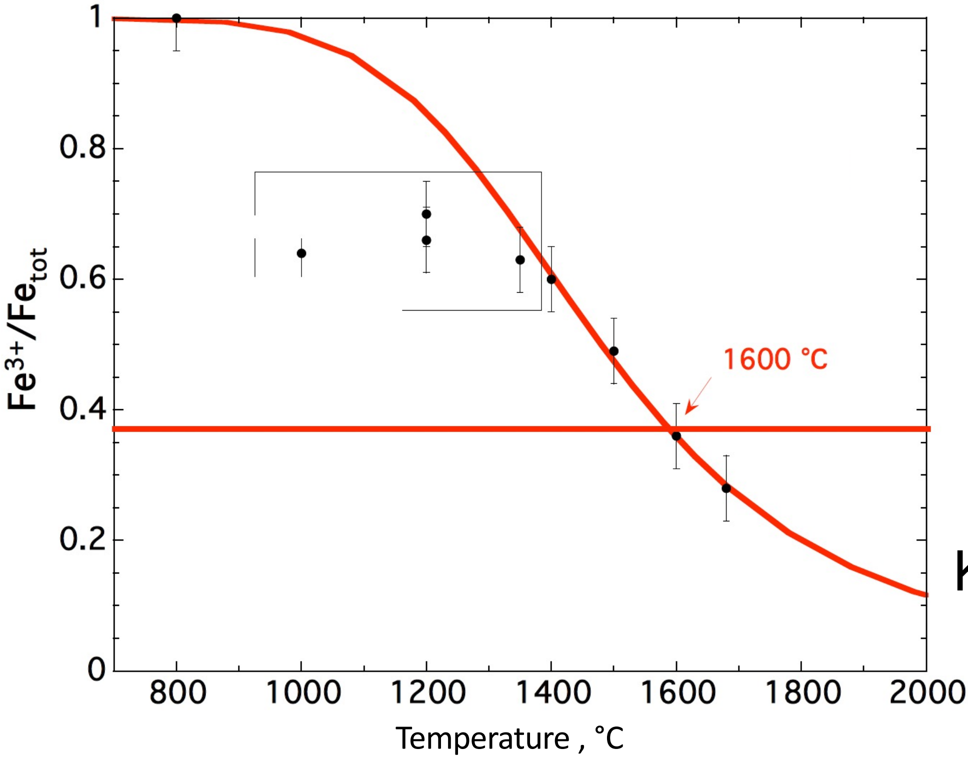

NS2Fe10
O2
Air
Argon
ArH2
New IPGP measurements
Viscosity, log Pa.s
10^4/T, K^-1


NS2Fe10
700K
725K
750K
NaFeSi2O6
1500K
Viscosity, log Pa.s
Fe3+/Fetot

- 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

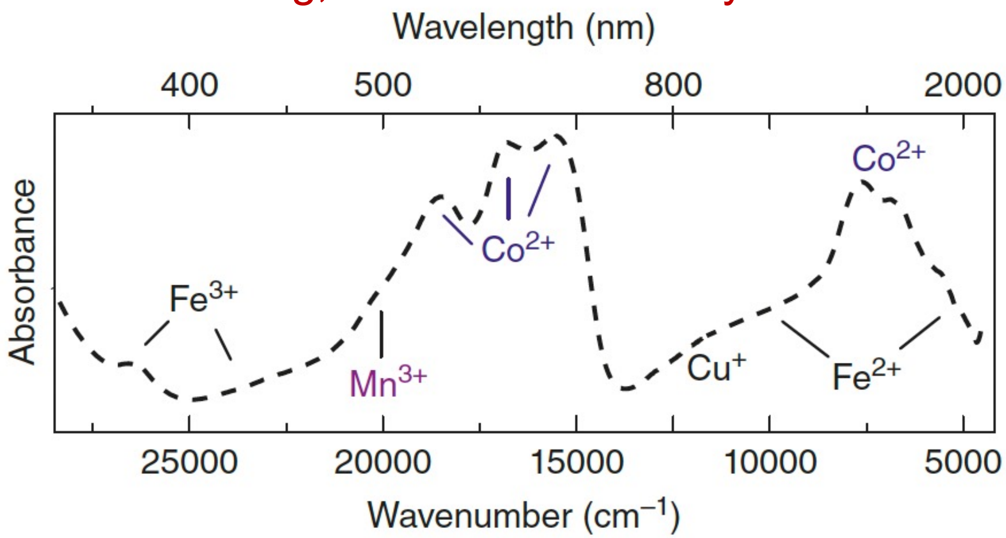
Cicconi M.R., Neuville D.R. (2019) Natural glasses. Springer Hanbook of Glass.771-804 – DOI 10.1007/978-3-319-93728-1

Wet chemistry analyzed

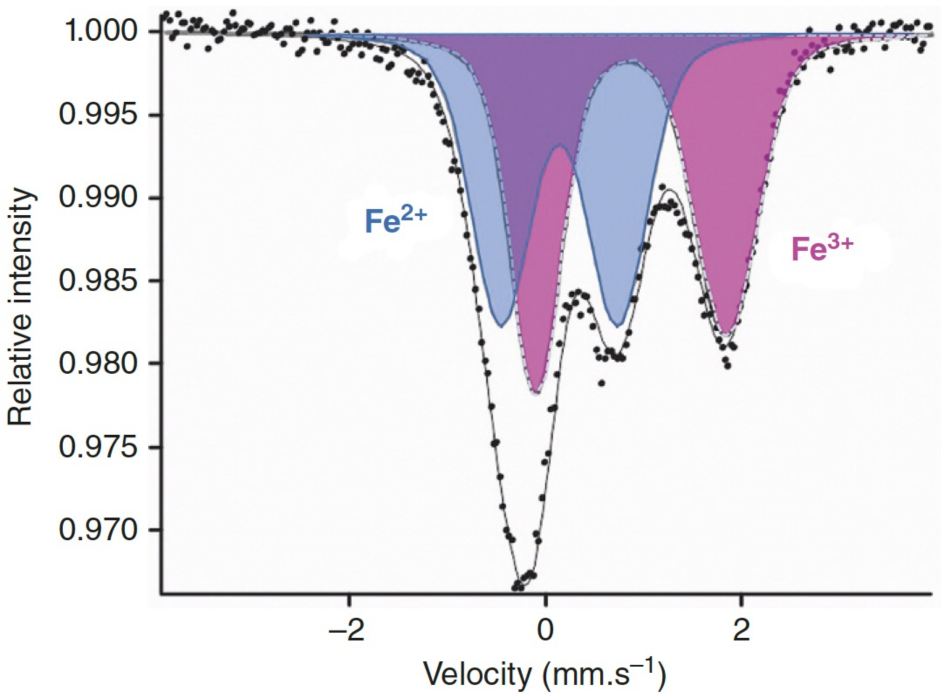
Wet chemistry FeO content, sensibility limit ≈10 ppm
Precision Δ=+/ - 5 ppm

Optical spectroscopy

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

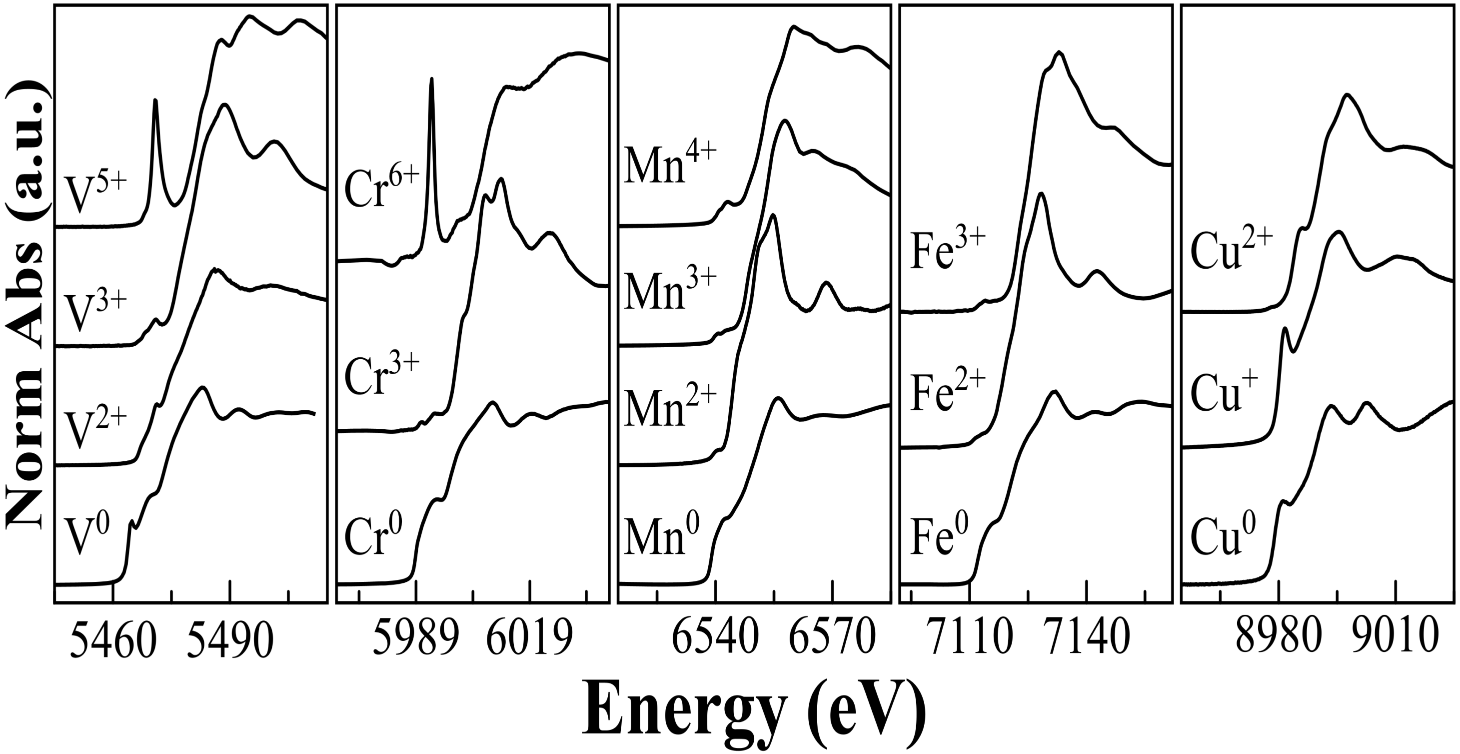


Mossbauer spectroscopy



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



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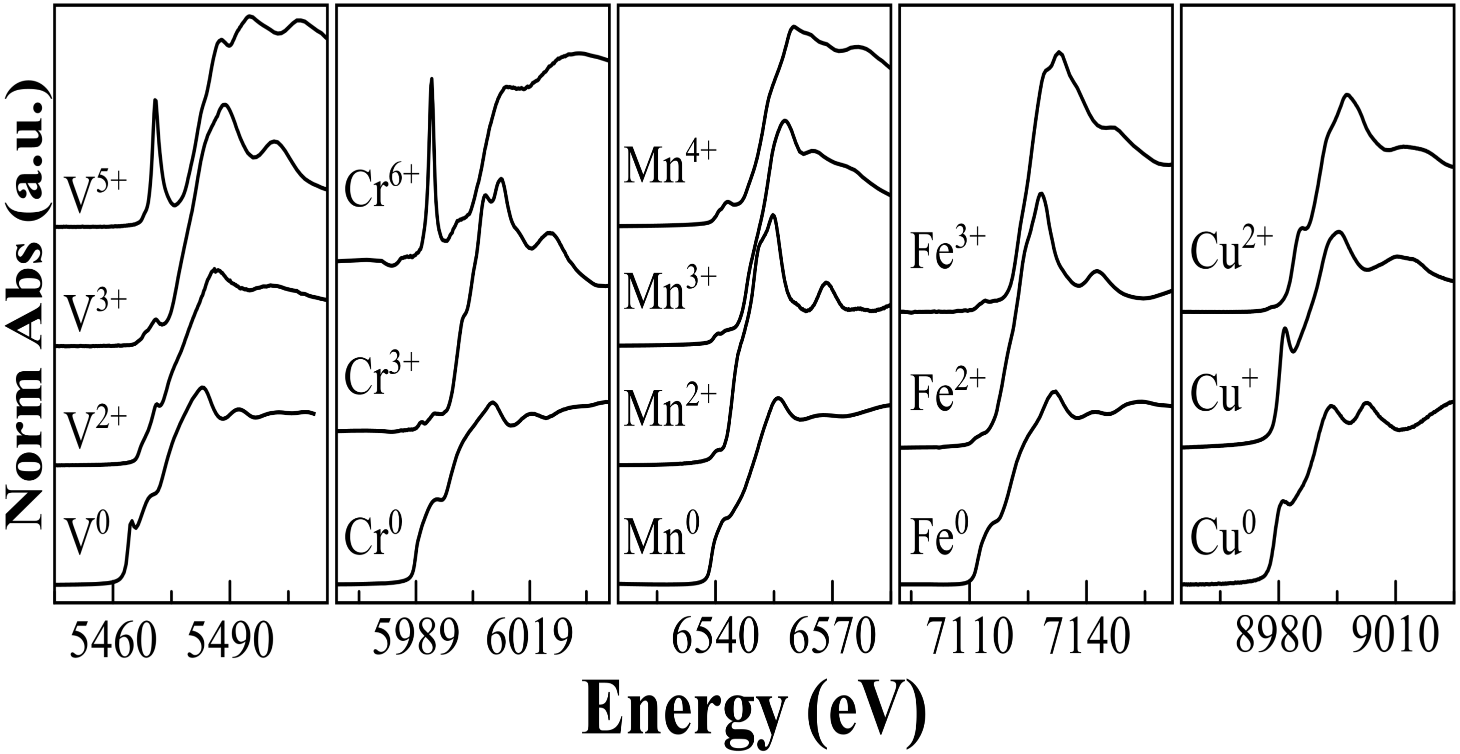
XANES possible for almost all elements
depend on light source
Possible measurement at HT, HP, mapping…..

XANES



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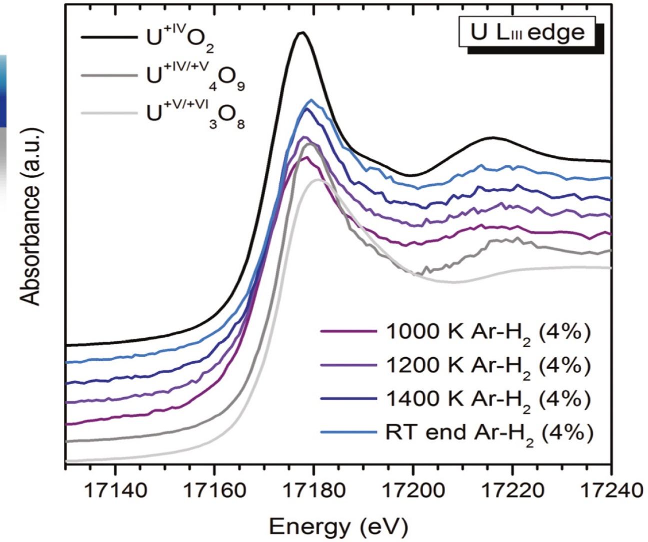
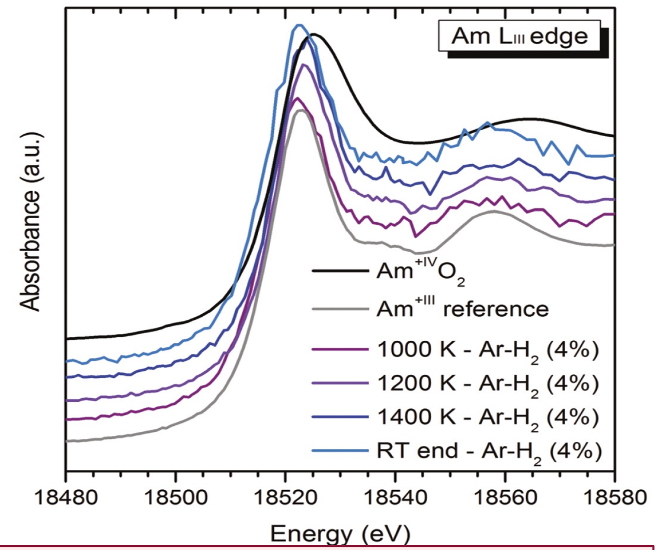
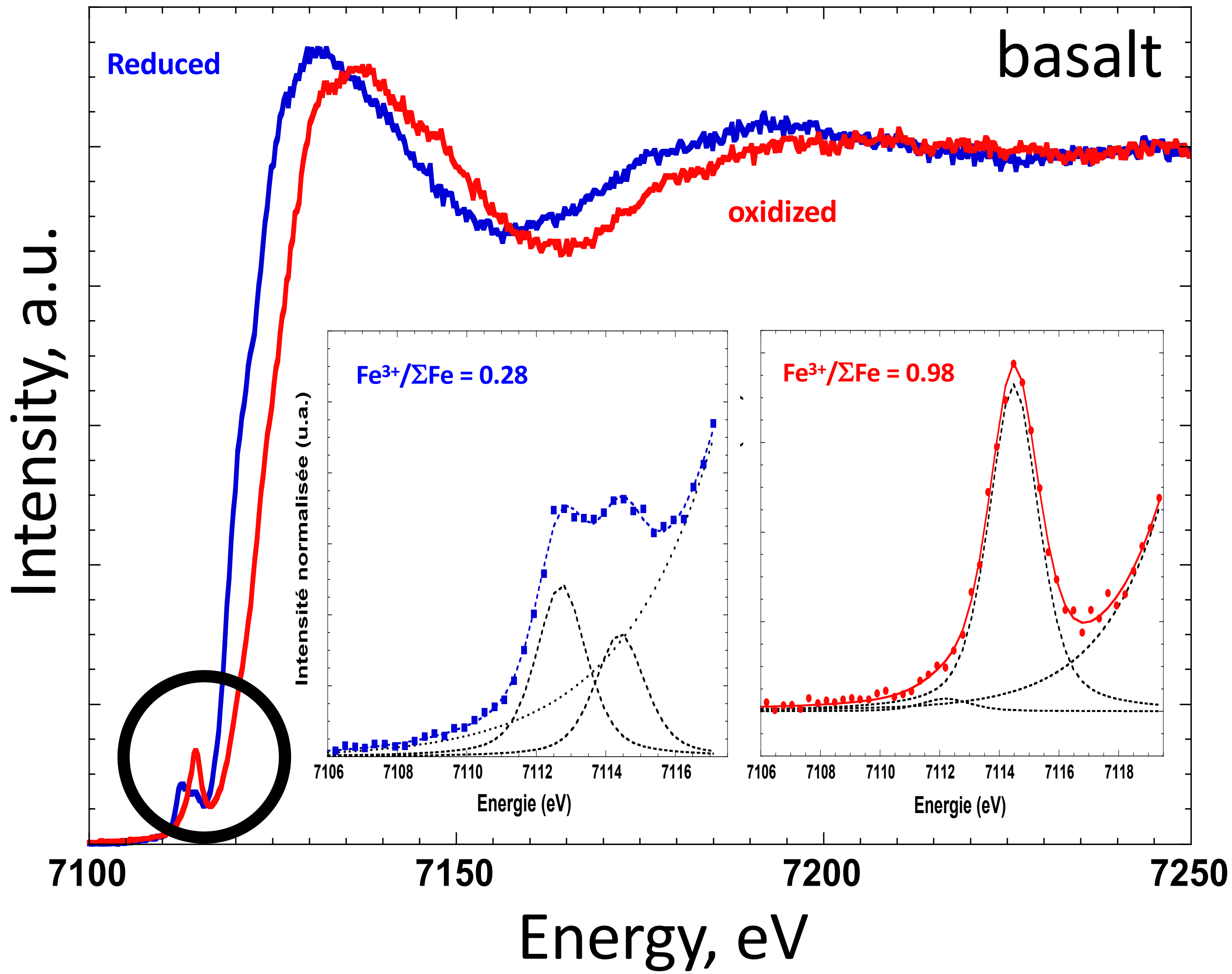




Caisso, M. Picart S., Belin R., Lebreton F., Martin P. Dardenne K. Rothe J., Neuville, D.R., Delahaye T., Ayral A. (2015) In-situ characterization of uranium and americium solid solution formation for CRMP process: first combination of in-situ XRD and XANES measurements. Dalton Transactions, 44, 6391-6399.

Prieur D., Epifano E., Dardenne K., Rothe J., Hennig C., Scheinost A. C., Neuville D.R., Somers J., Martin P. M. (2018) Negative thermal expansion of the UO2 fluorite local structure. Inorganic Chemistry. DOI: 10.1021/acs.inorgchem.8b02657

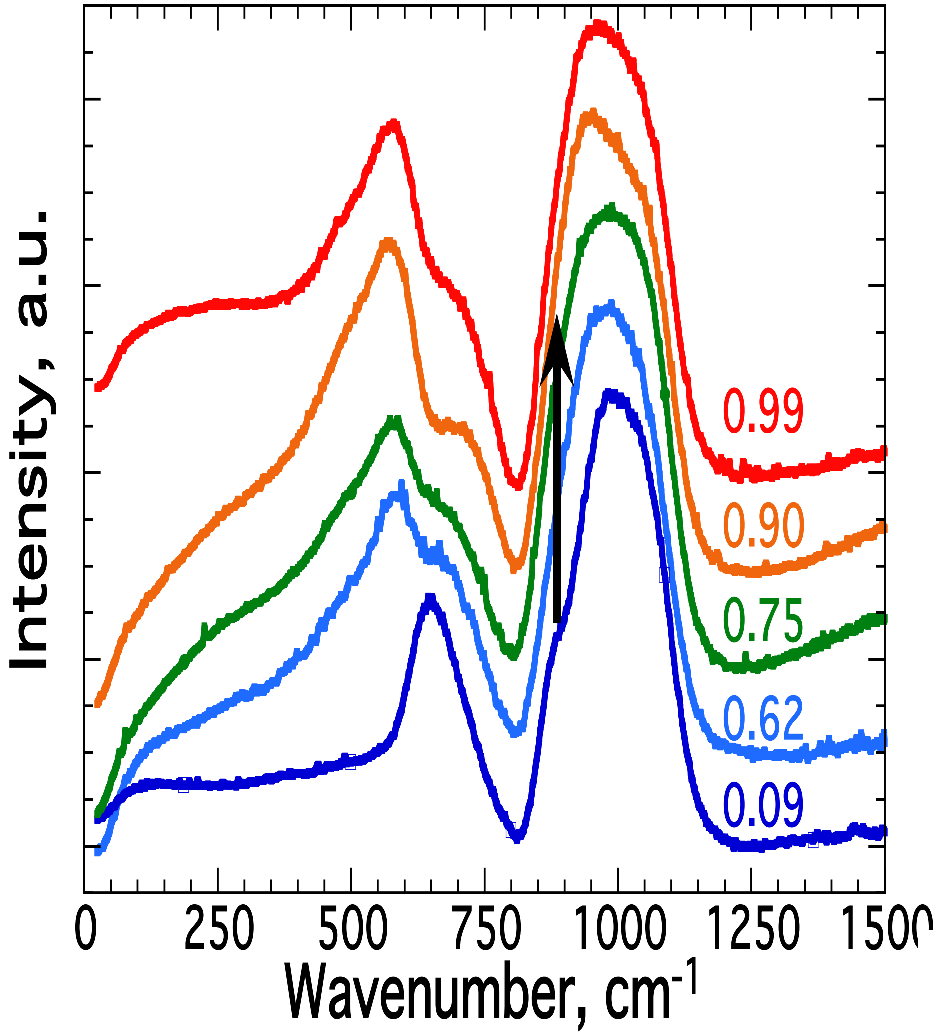


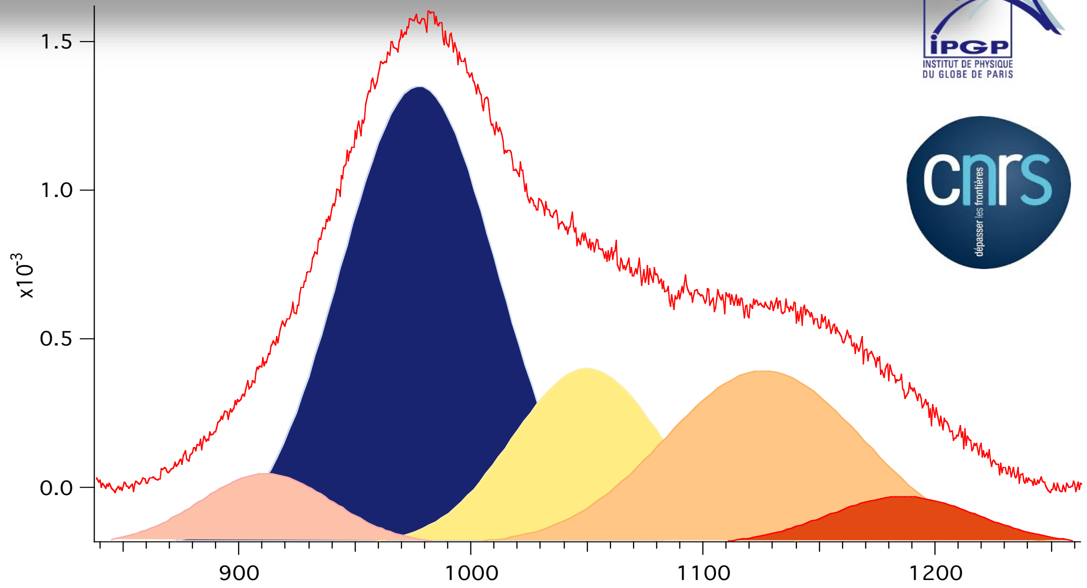
Iron K-edge: redox state and local structure

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***

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

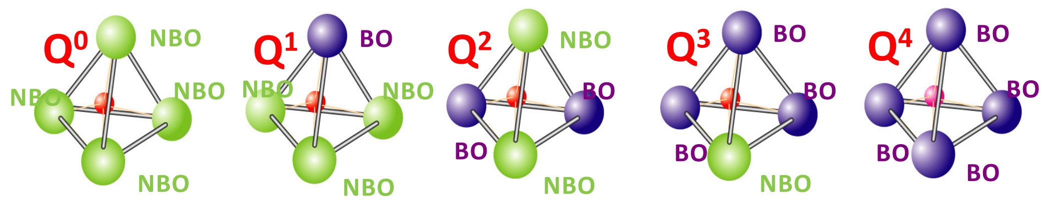




Evidence of Fe^{3+} in tetrahedral coordination in Q^4:

- 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+}**

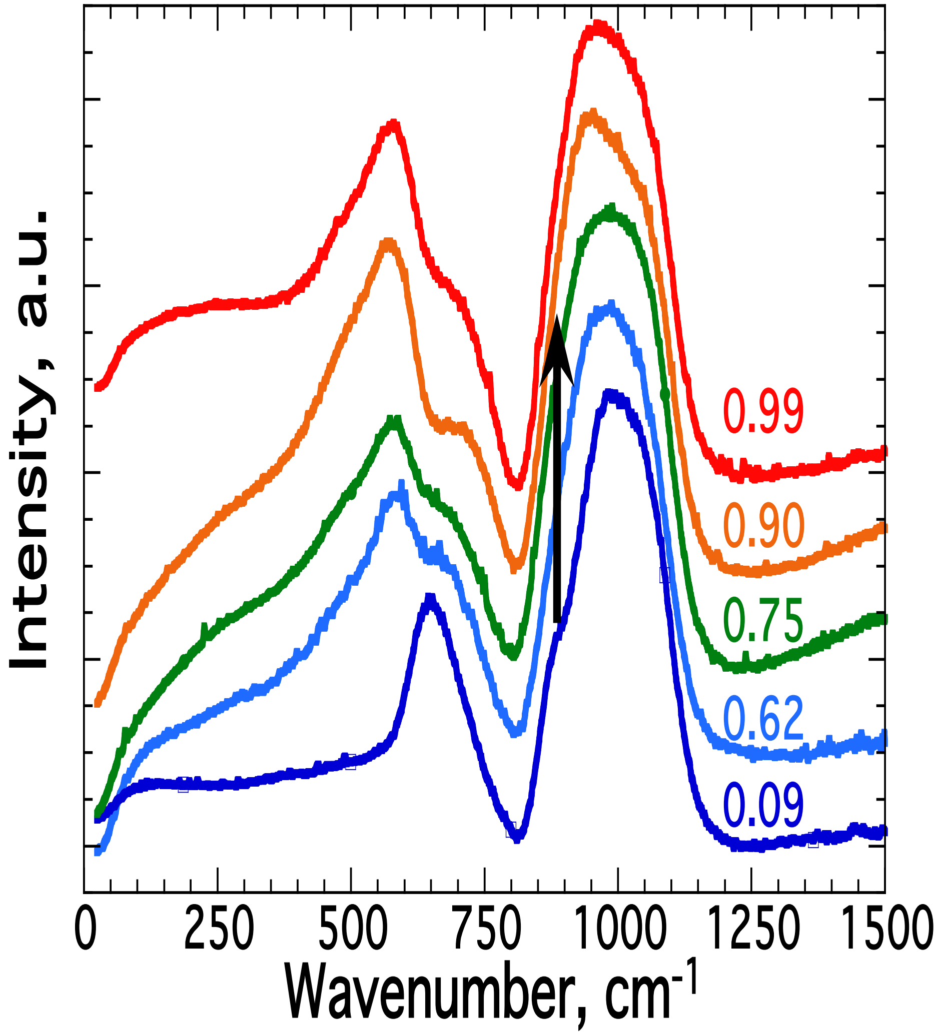
Bands of Qn species (Q = Si, Al)

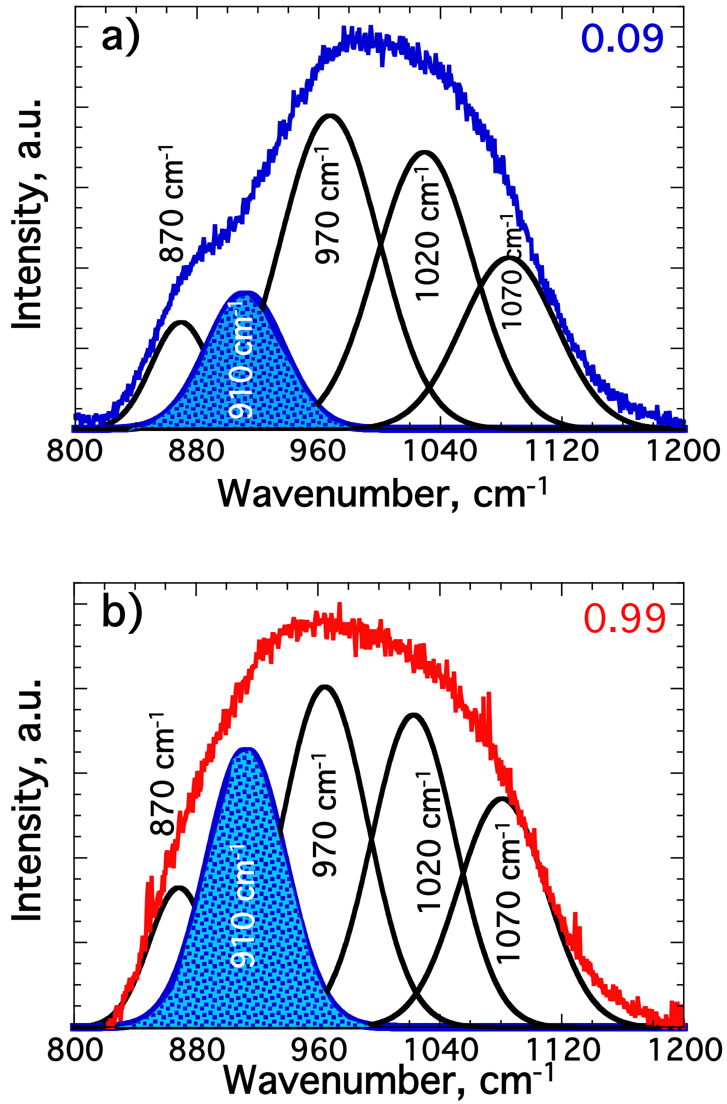


Magnien V., Neuville D.R., Cormier L., Roux J., Pinet O. and Richet P. (2006) Kinetics of iron redox reactions: A high-temperature XANES and Raman spectroscopy study. Journal of Nuclear Materials, 352, 190-195.

Raman spectroscopy

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





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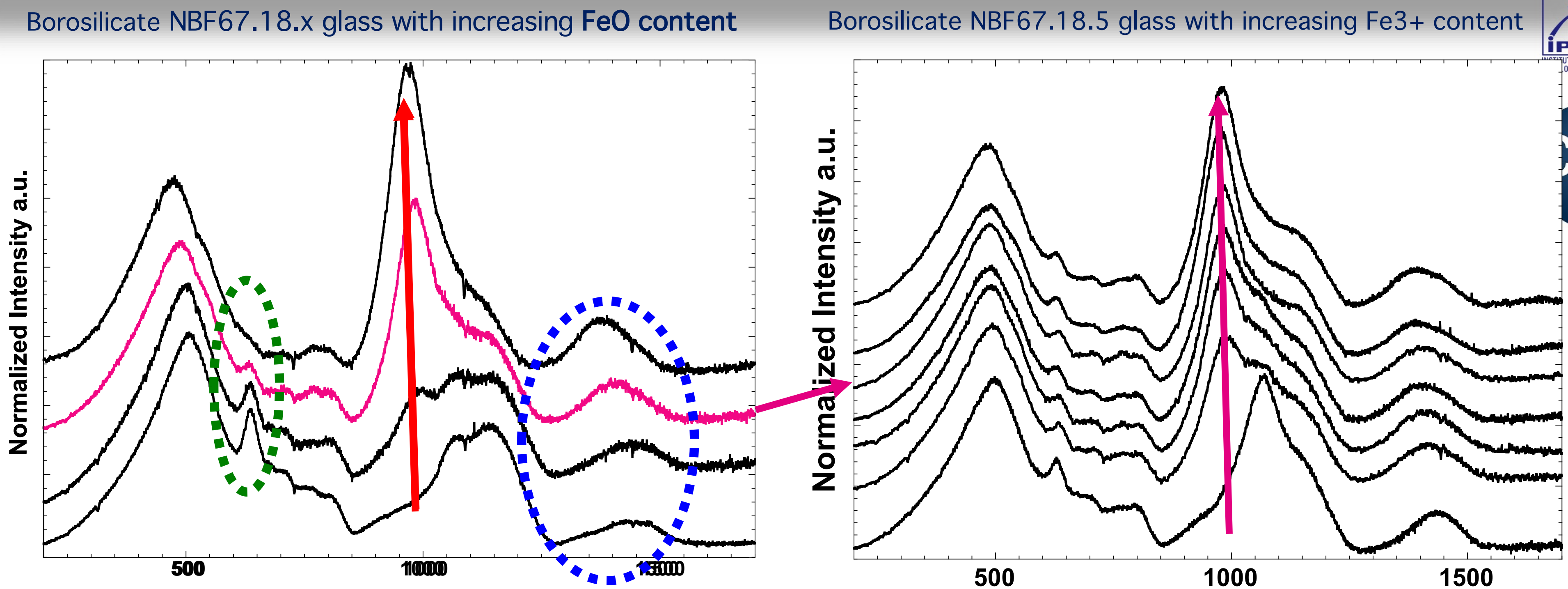
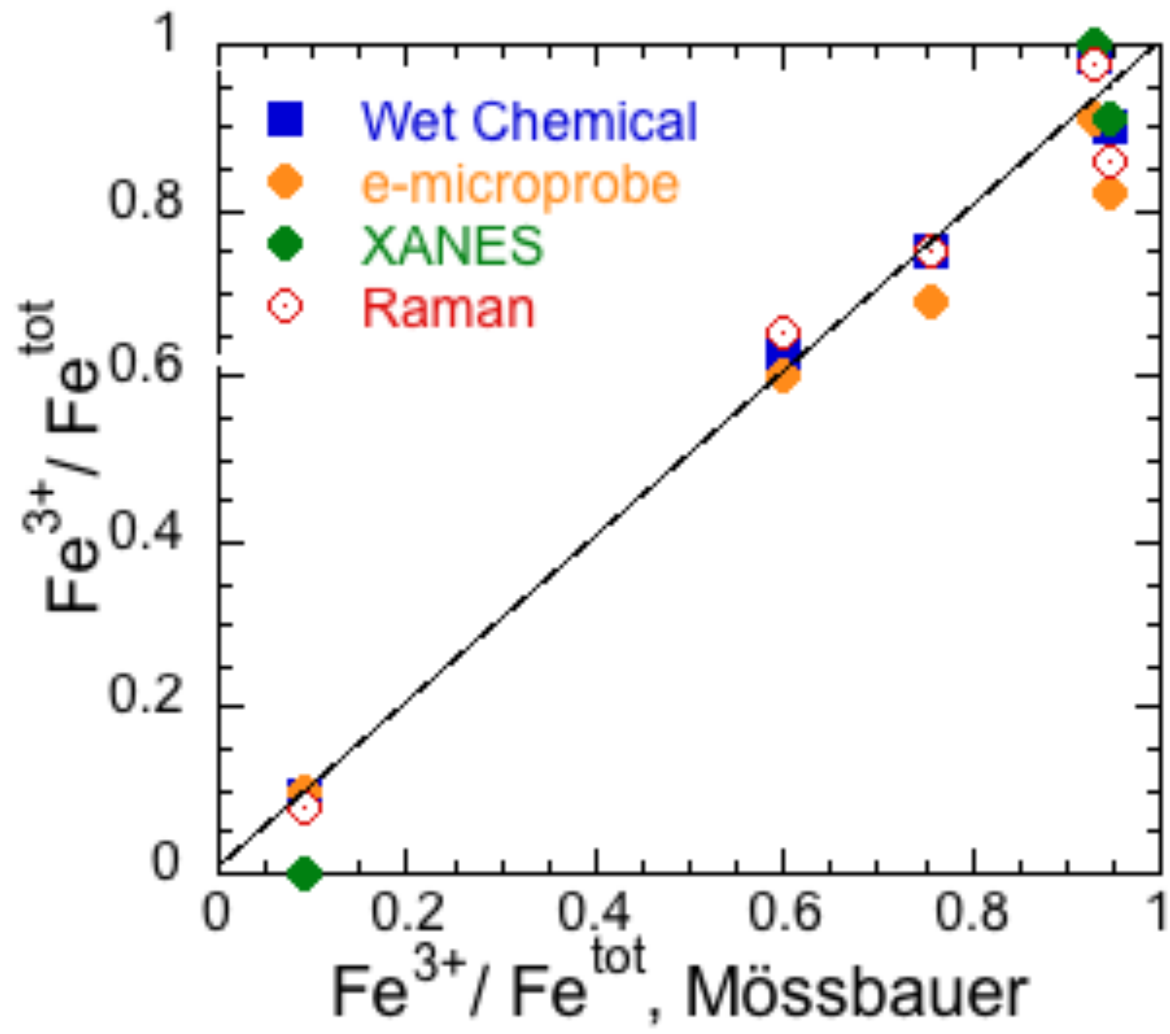


Increasing FeO content at constant redox ratio + **inscreasing** Fe^{3+} content:

- **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



=> 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

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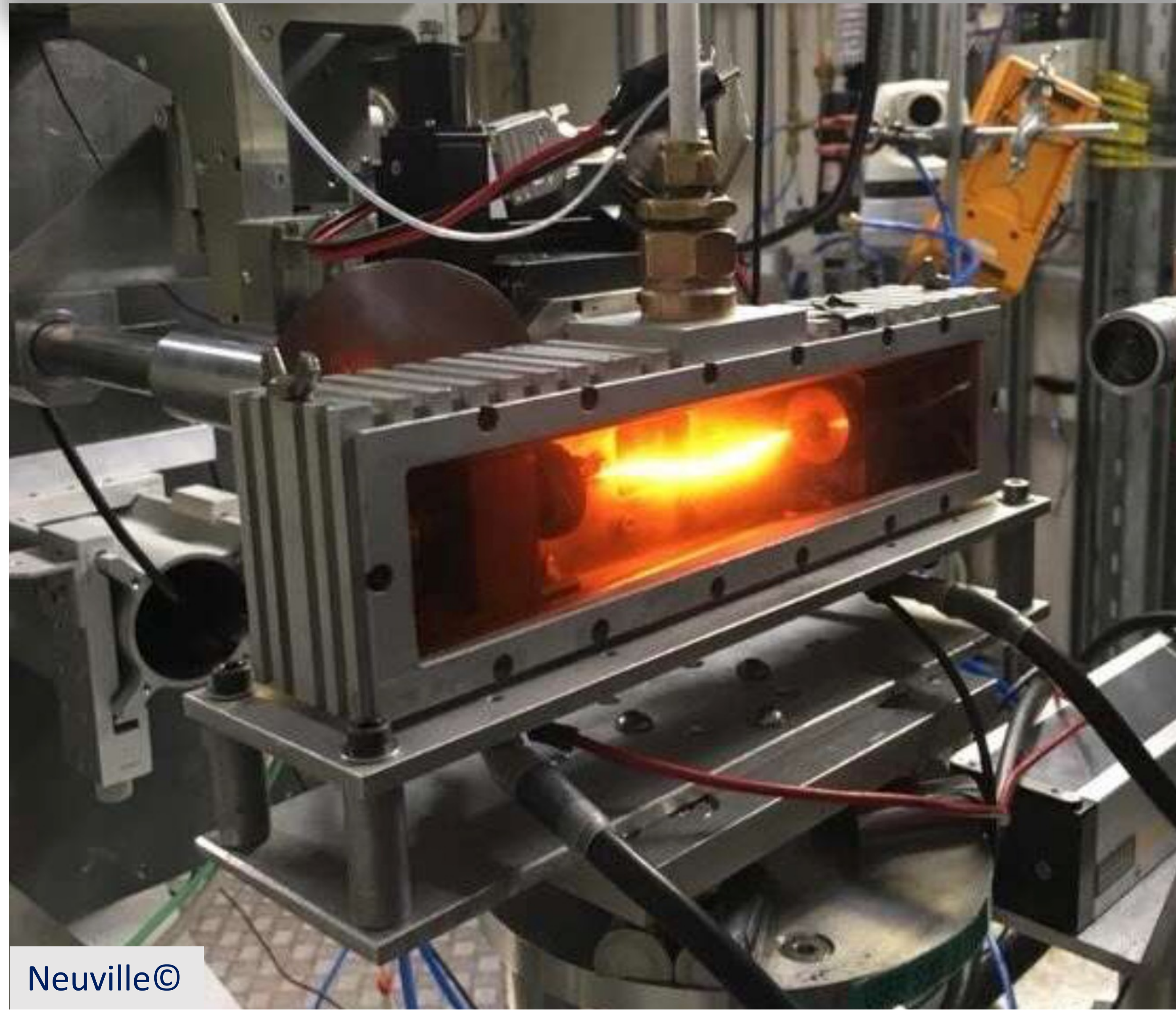


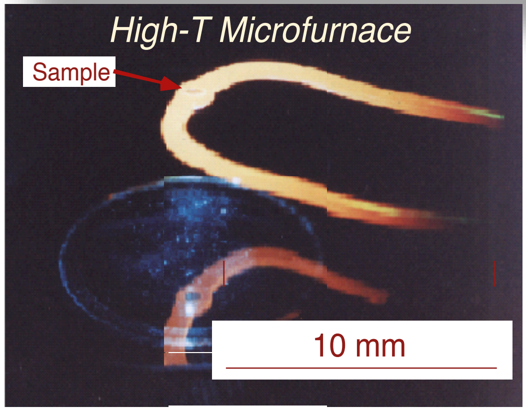
Neuville©

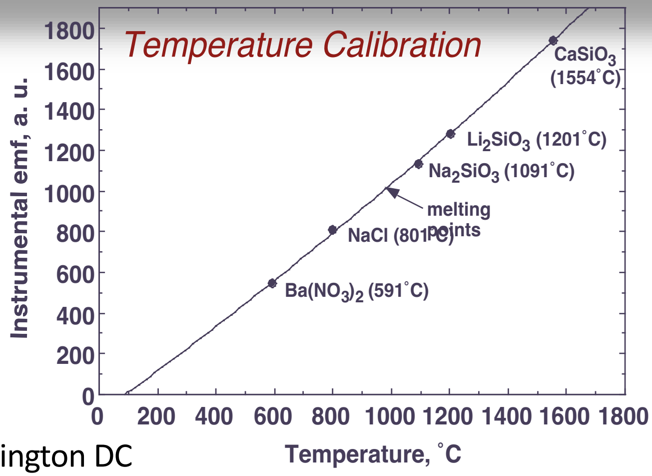
- Raman spectroscopy

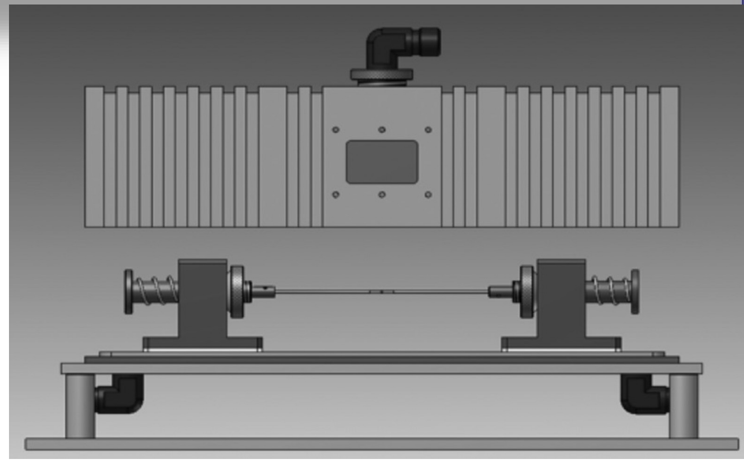
- In situ redox measurements,
XANES at K, L or M edge

- in situ nucleation and growth
WAXS and SAXS

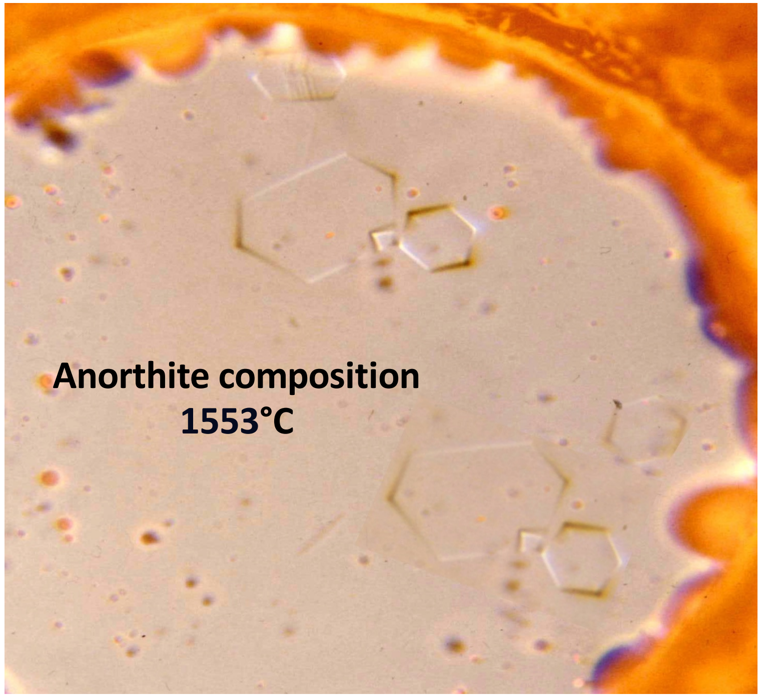
Neuville D.R., Hennet L., Florian P., de Ligny D. (2014) In situ high temperature experiment. In Henderson G.S, Neuville D.R., Down B. (2014) "Spectroscopic methods in Mineralogy and Material Sciences" Review in Mineralogy and Geochemistry, Vol 78, 779-800.

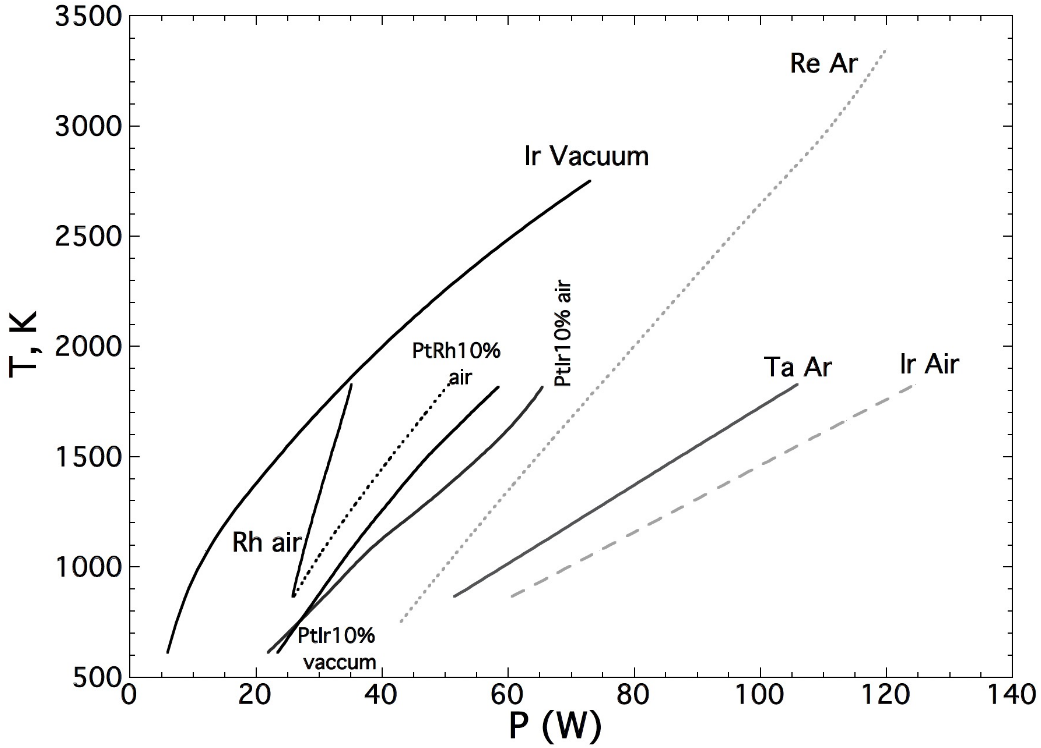






Original idea: B. Mysen, Carnegie, Washington DC





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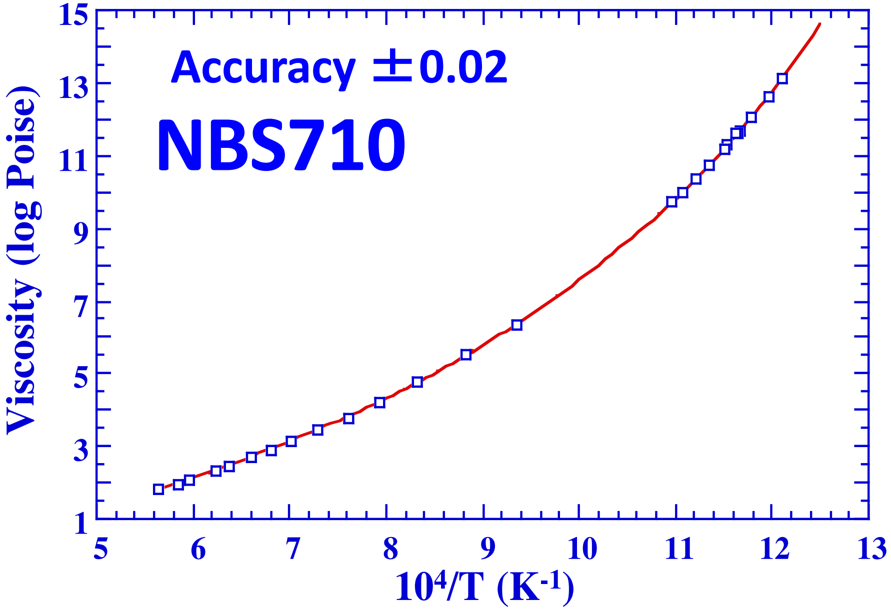
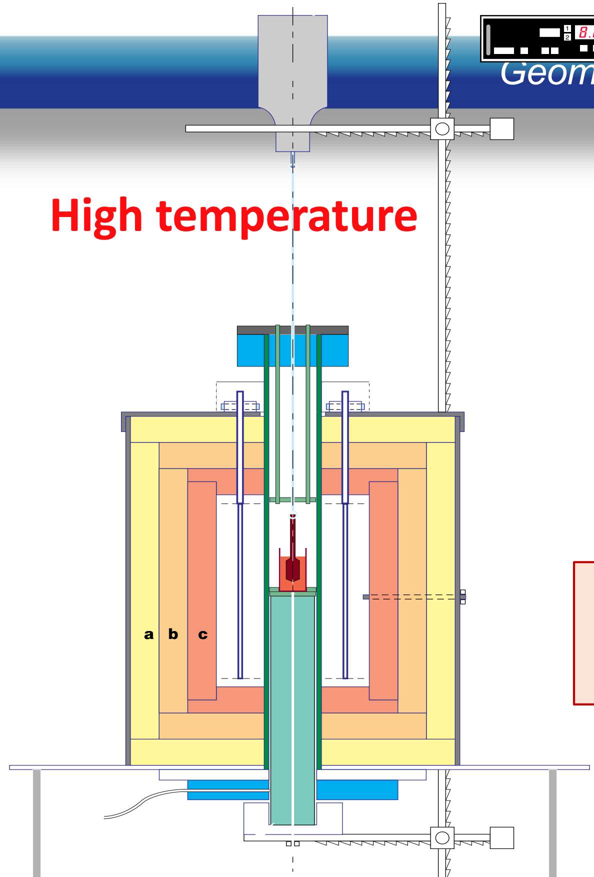


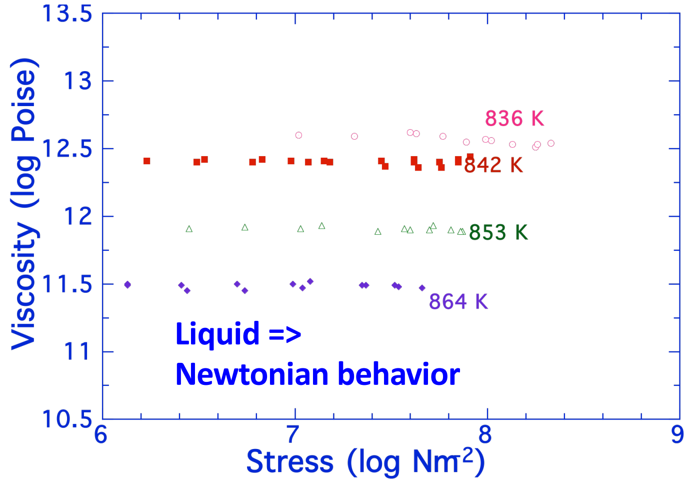
High temperature



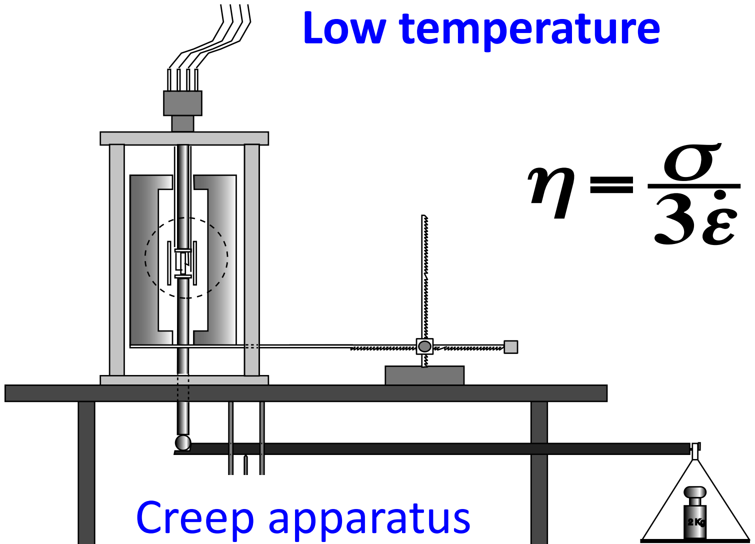
Couette apparatus

Neuville, 2006

Neuville D.R. (2006) Viscosity, structure and mixing in (Ca, Na) silicate melts. Chem. Geol., 229, 28-42.



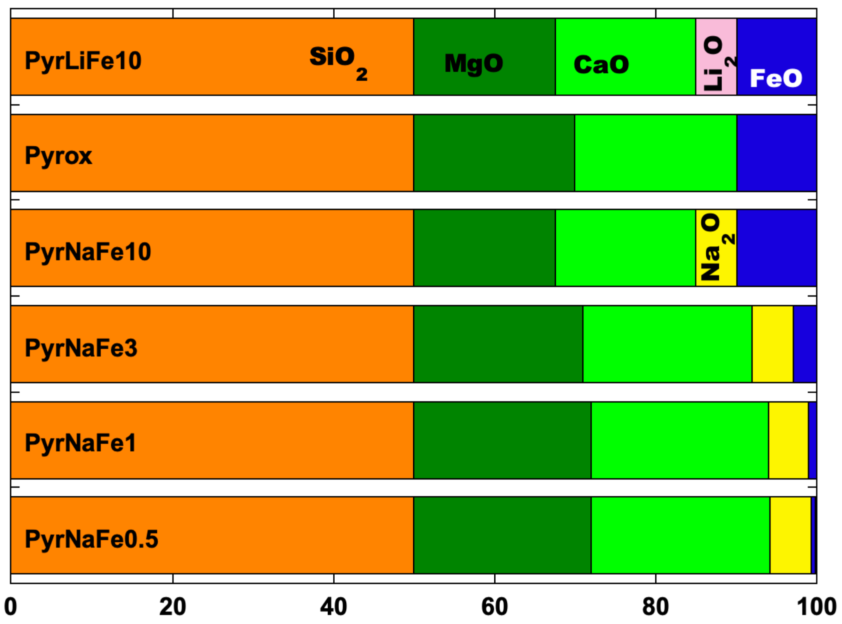
Low temperature

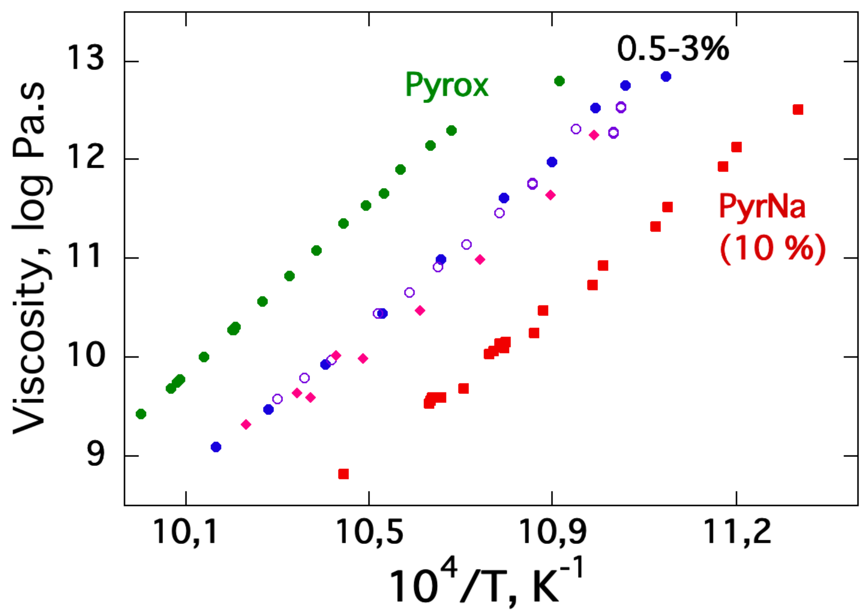


$$\eta = \frac{\sigma}{3\dot{\varepsilon}}$$

Creep apparatus

Neuville and Richet, 1991





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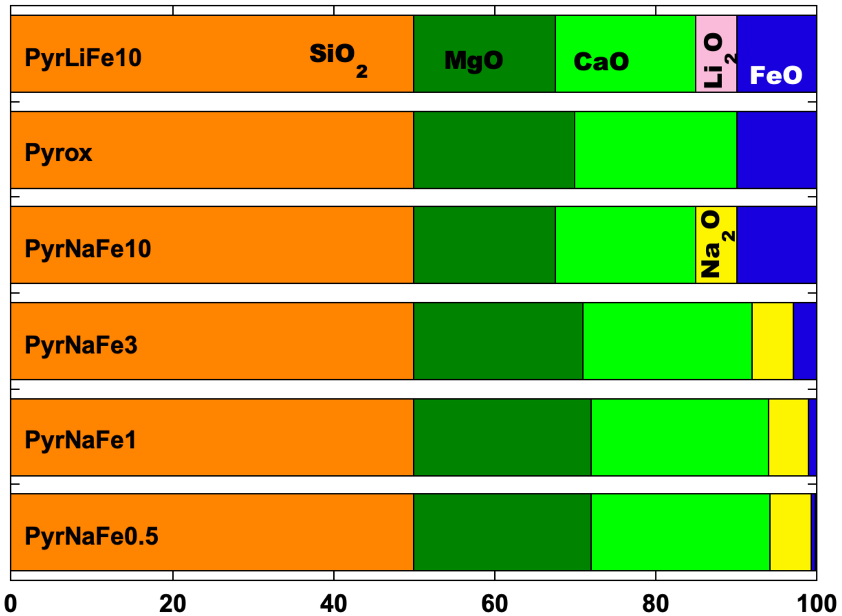

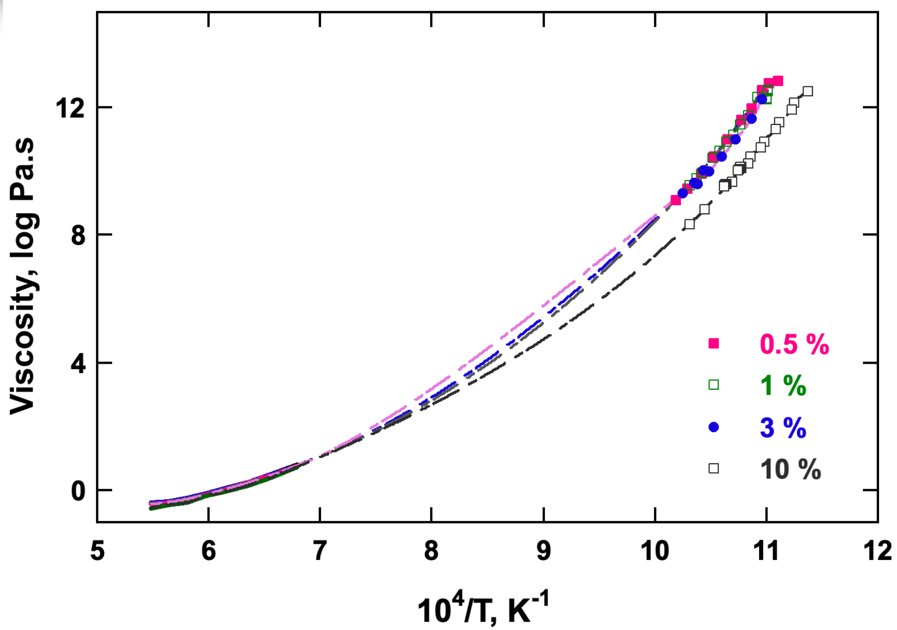

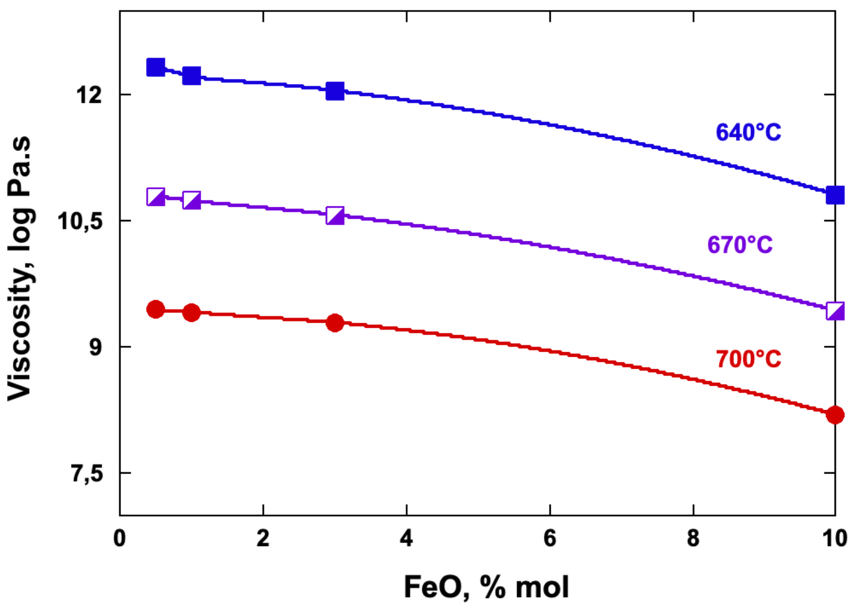

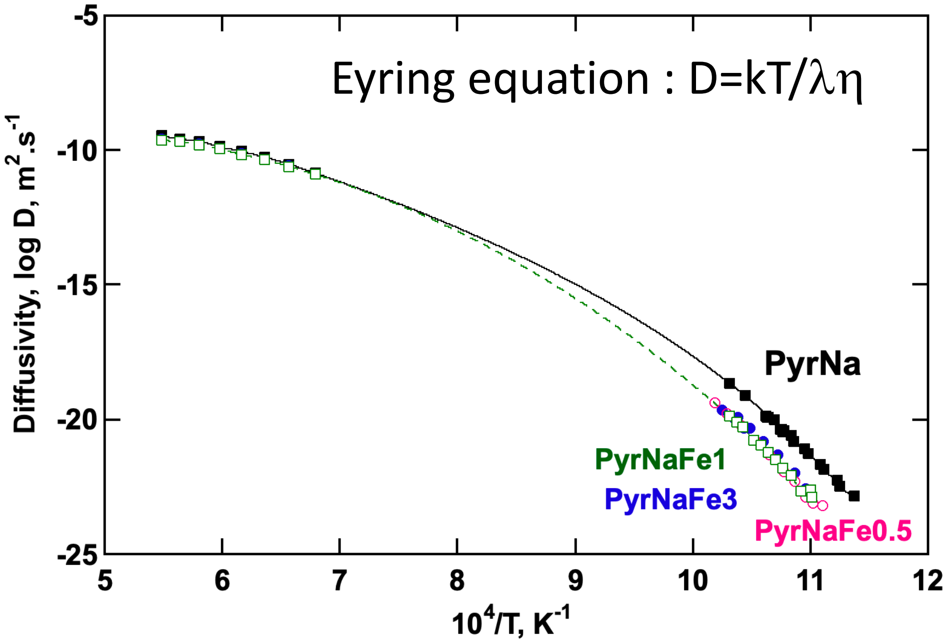

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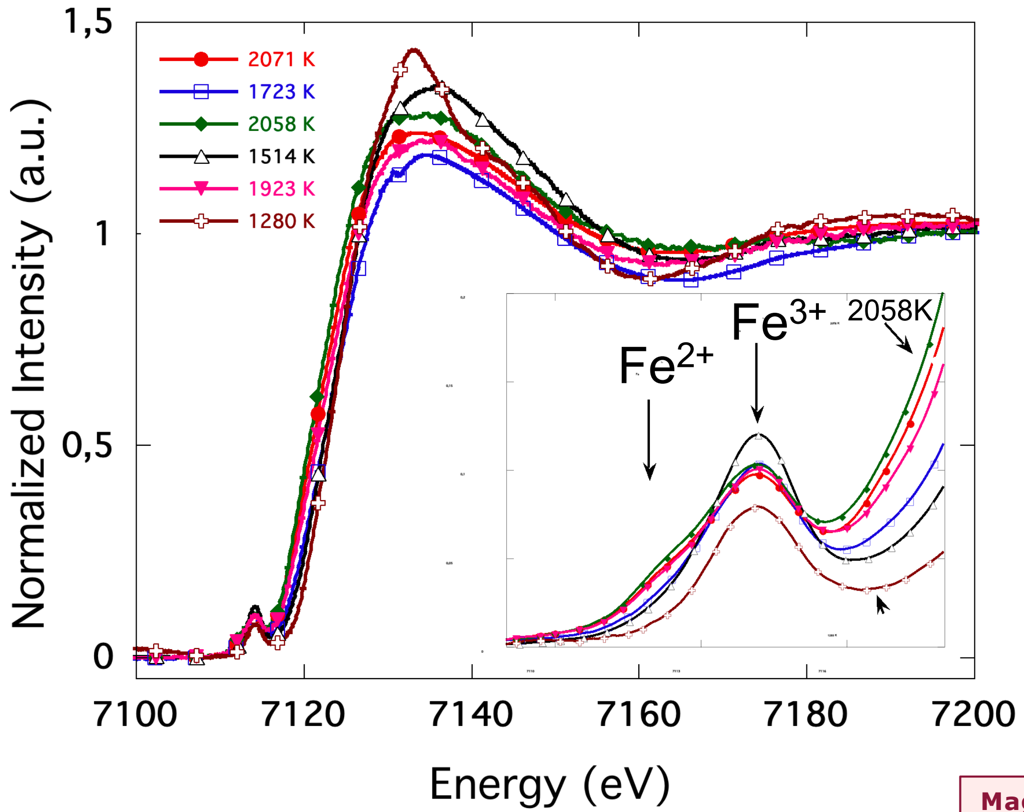
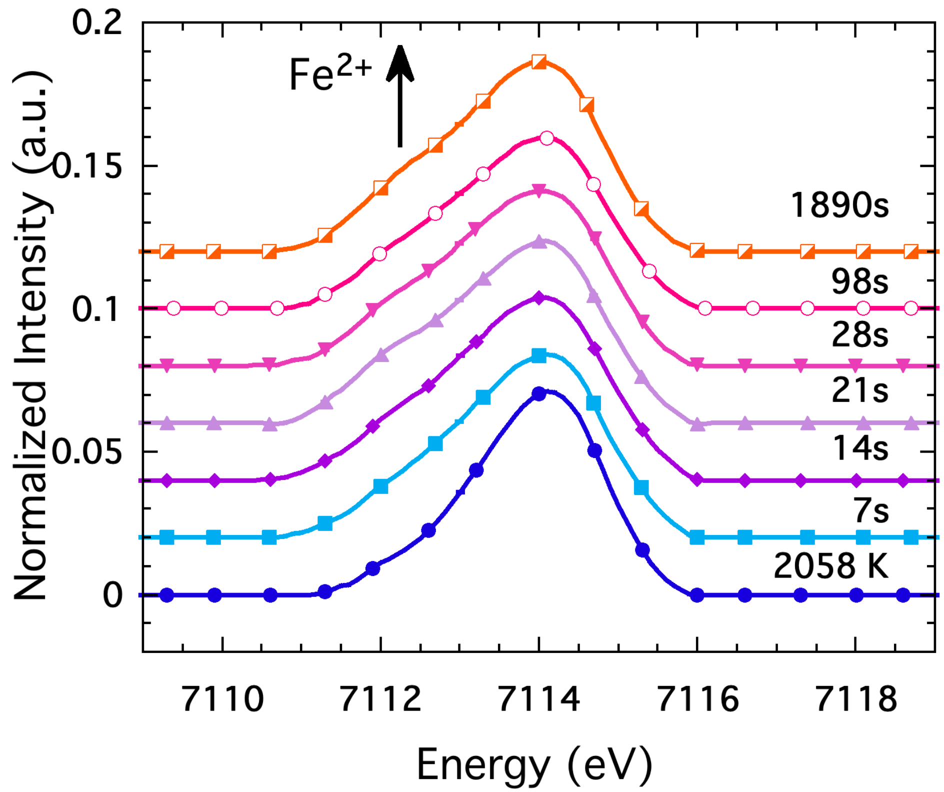
XANES spectra of Pyrox after reduction or oxidation induced in air by temperature changes from 2071 to 1723 K, 1723 to 2058 K, 2058 to 1514 K, 1723 to 1923 K and 1923 to 1280 K

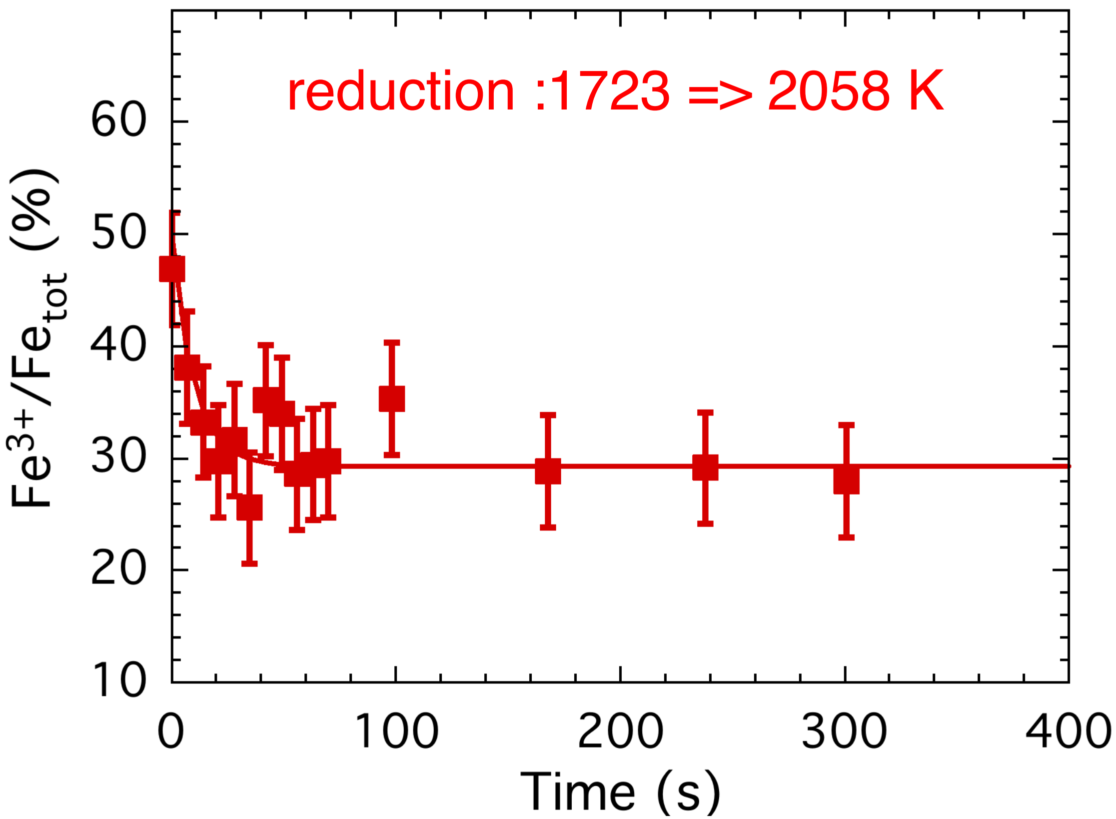


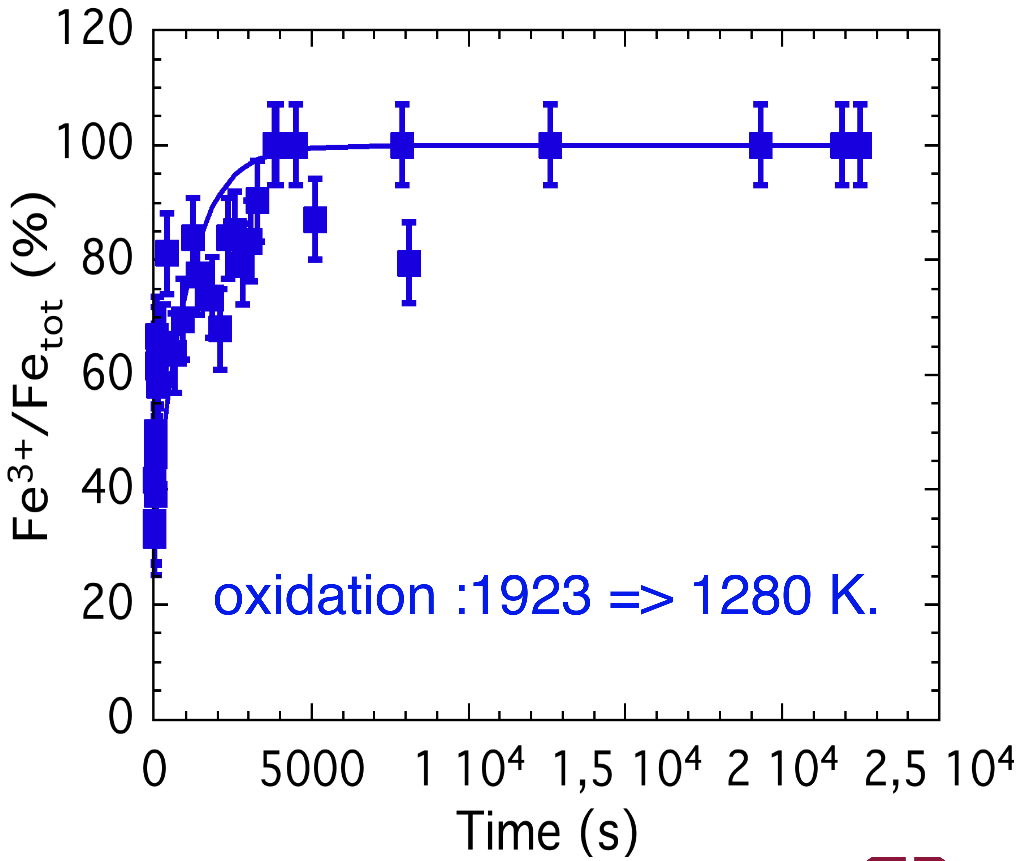
Time dependence during reduction in air at 2058 K of a Pyrox sample previously equilibrated at 1723 K

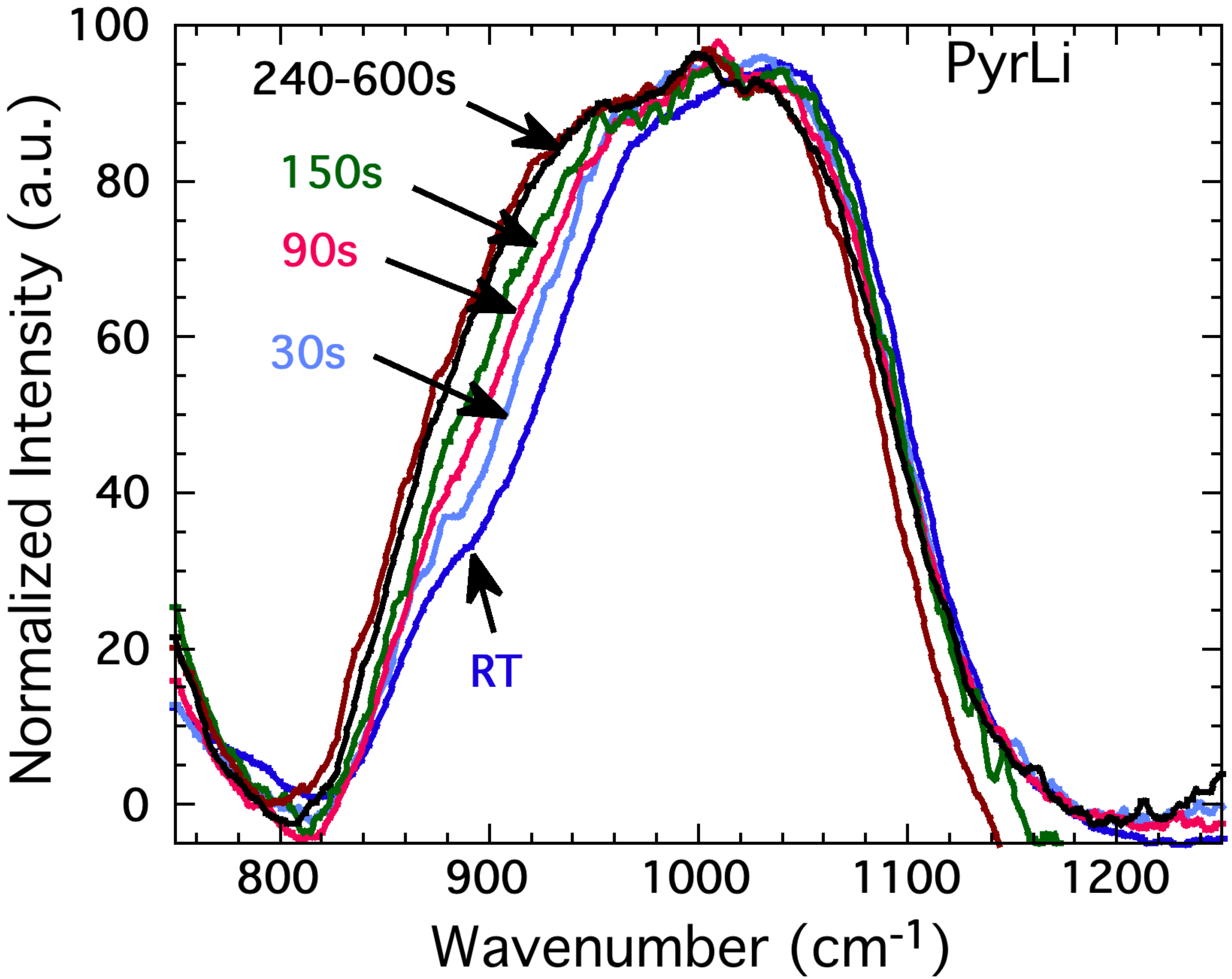


Magnien V., Neuville D.R., Cormier L., Mysen B.O..... (2004) Kinetics of iron oxidation in silicate melts: A preliminary XANES study. Chem. Geol., 213, 253-263

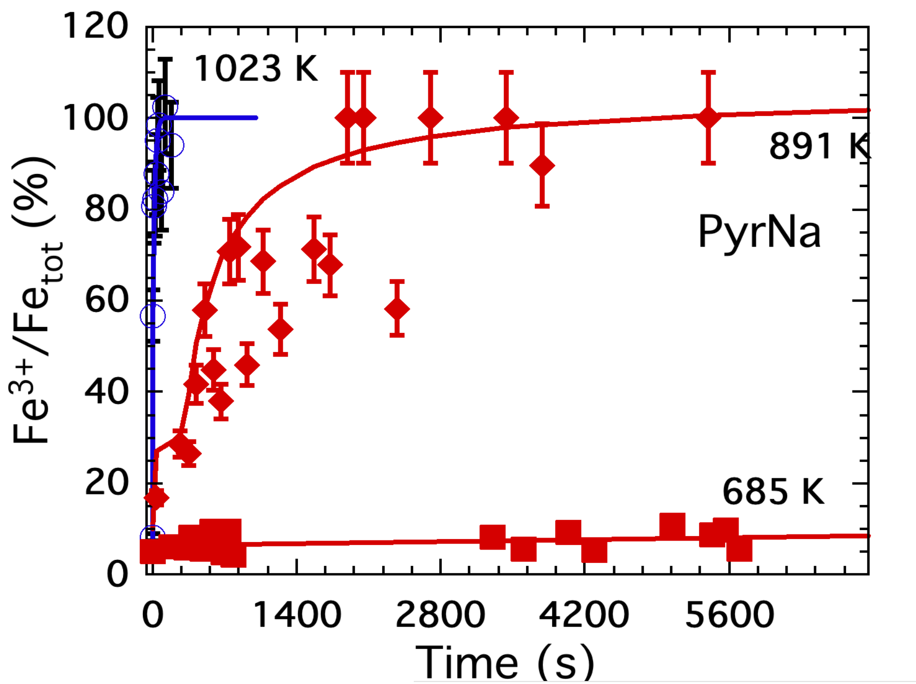
Time dependence of the iron redox ratio of Pyrox

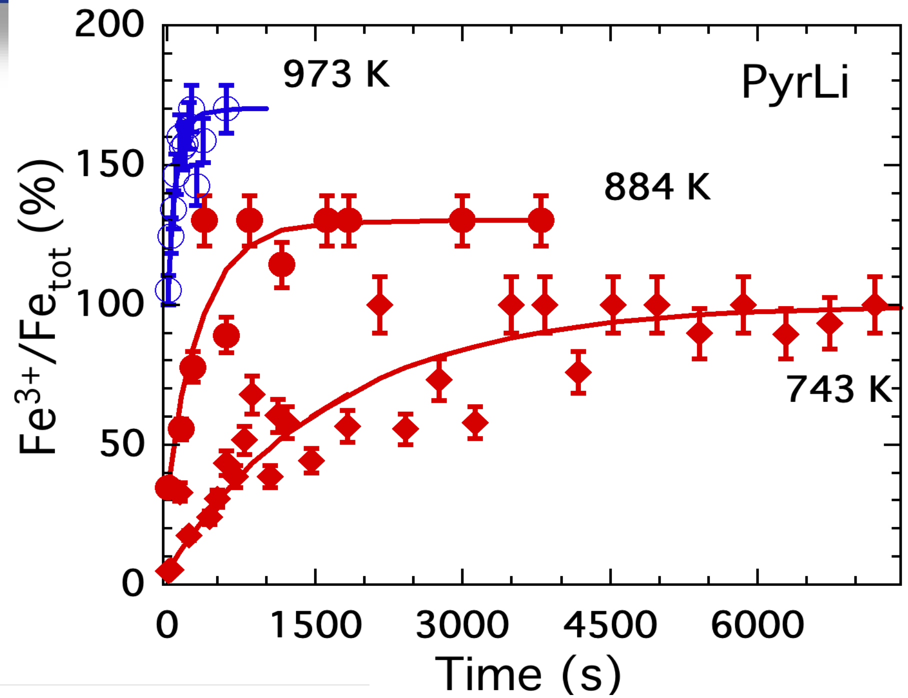


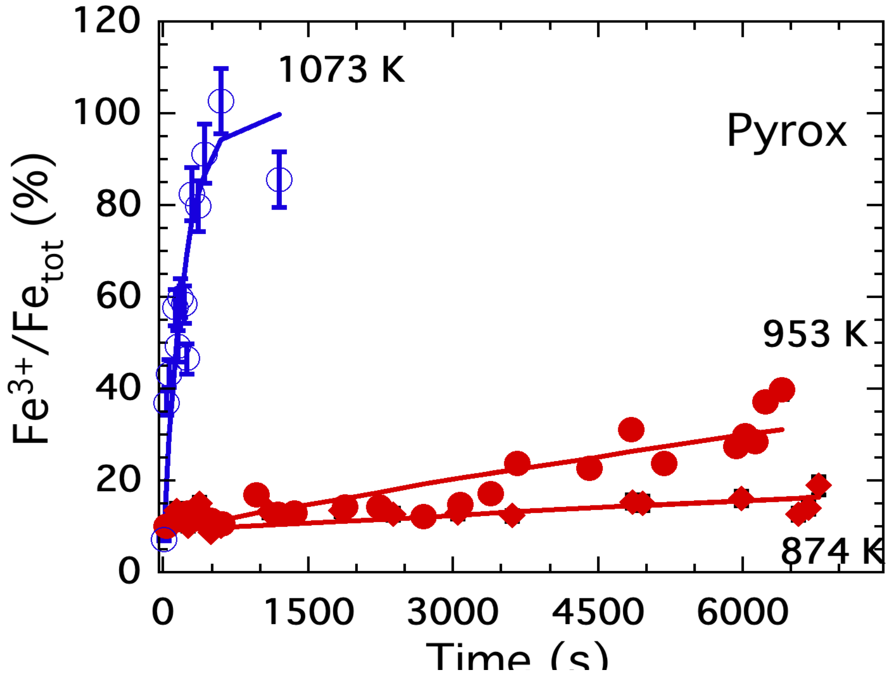




Time dependence of the Raman spectrum of PyrLiR at 973 K

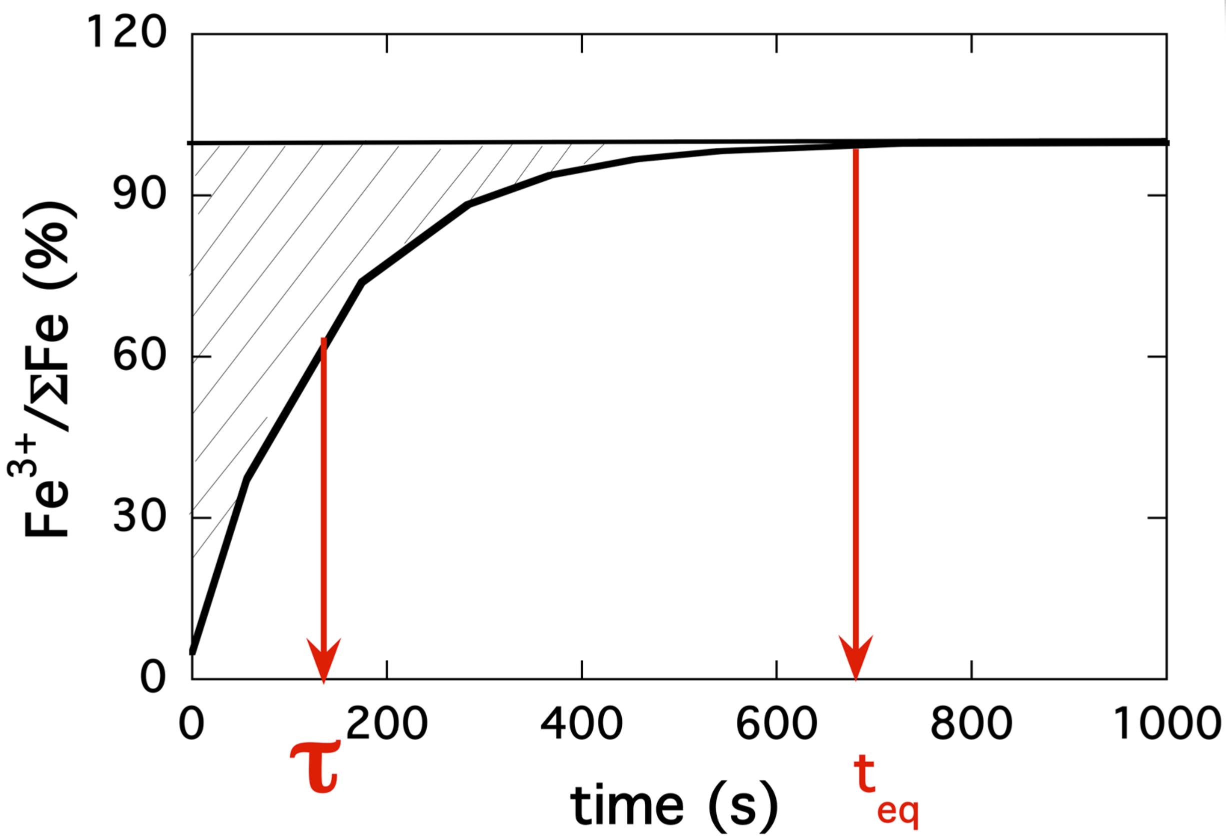

1023 K
891 K
PyrNa
685 K
Fe^{3+}/Fe_{tot} (%)
Time (s)
0
20
40
60
80
100
120
1400
2800
4200
5600


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


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

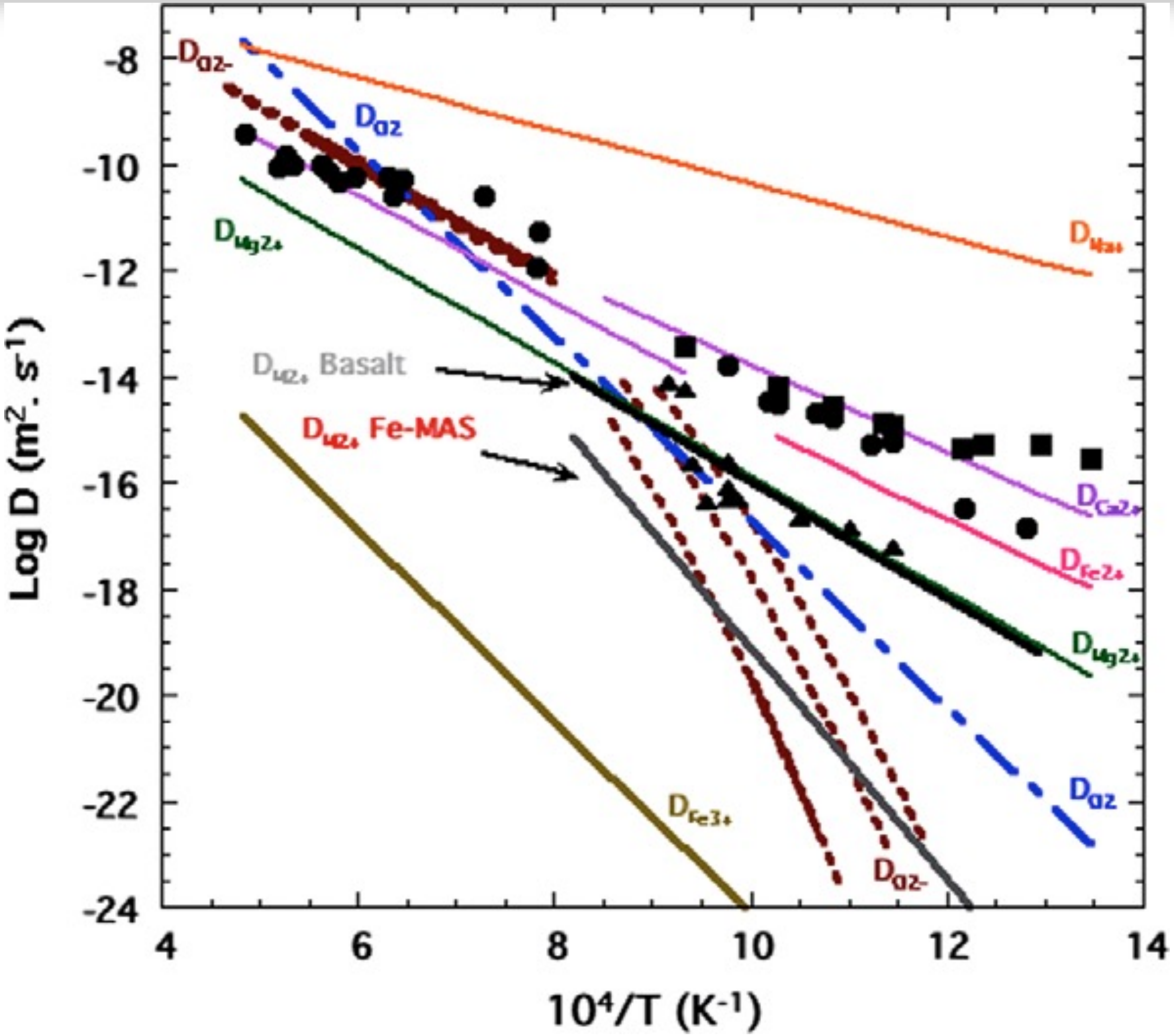
$$t_{eq} = -\tau \ln(0{,}01)$$

and

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

=> D, "redox diffusivity"

r_0, sample size



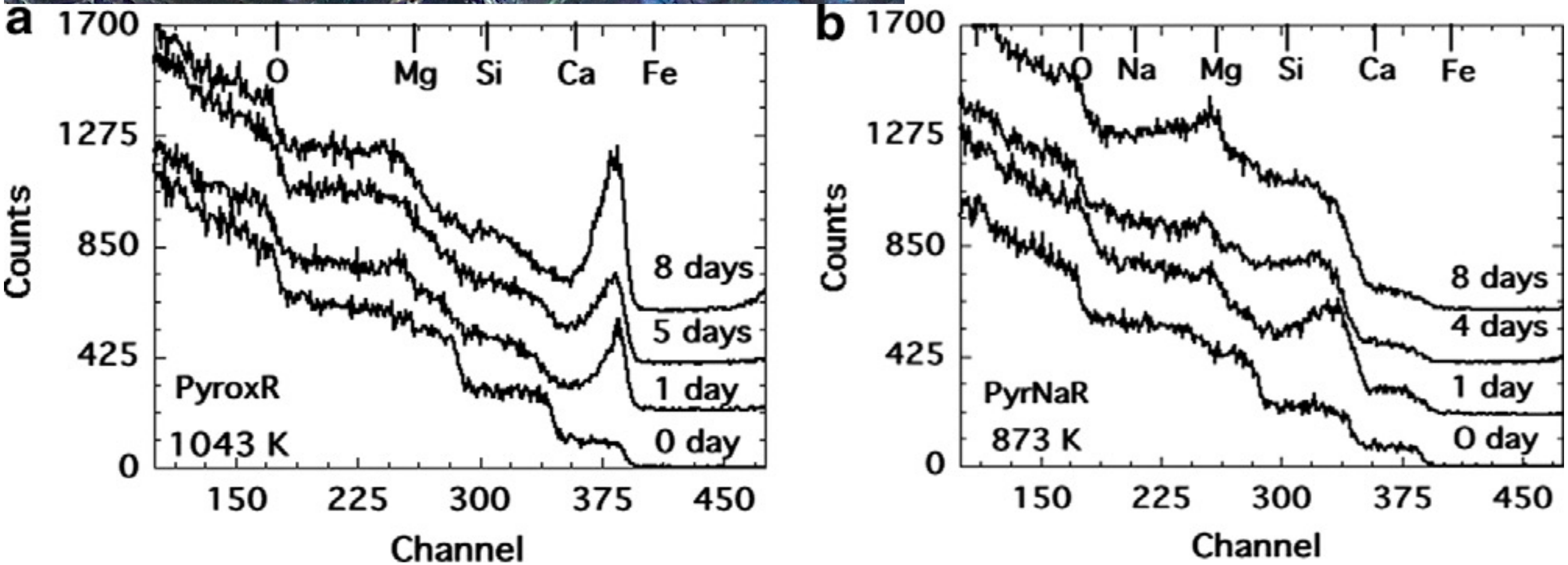
D_{O2} from Semkow and Haskin (1985) for diopside composition; D_{Ca} and D_{Mg} frome Jambon and Semet (1977), Roselieb and Jambon (2002) for albite, jadeite or orthoclase compositions; D_{Na} from Jambon and Carron (1976), Lowry et al. (1981) for albite, obsidienne and basaltic compositions ; D_{Fe} 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).

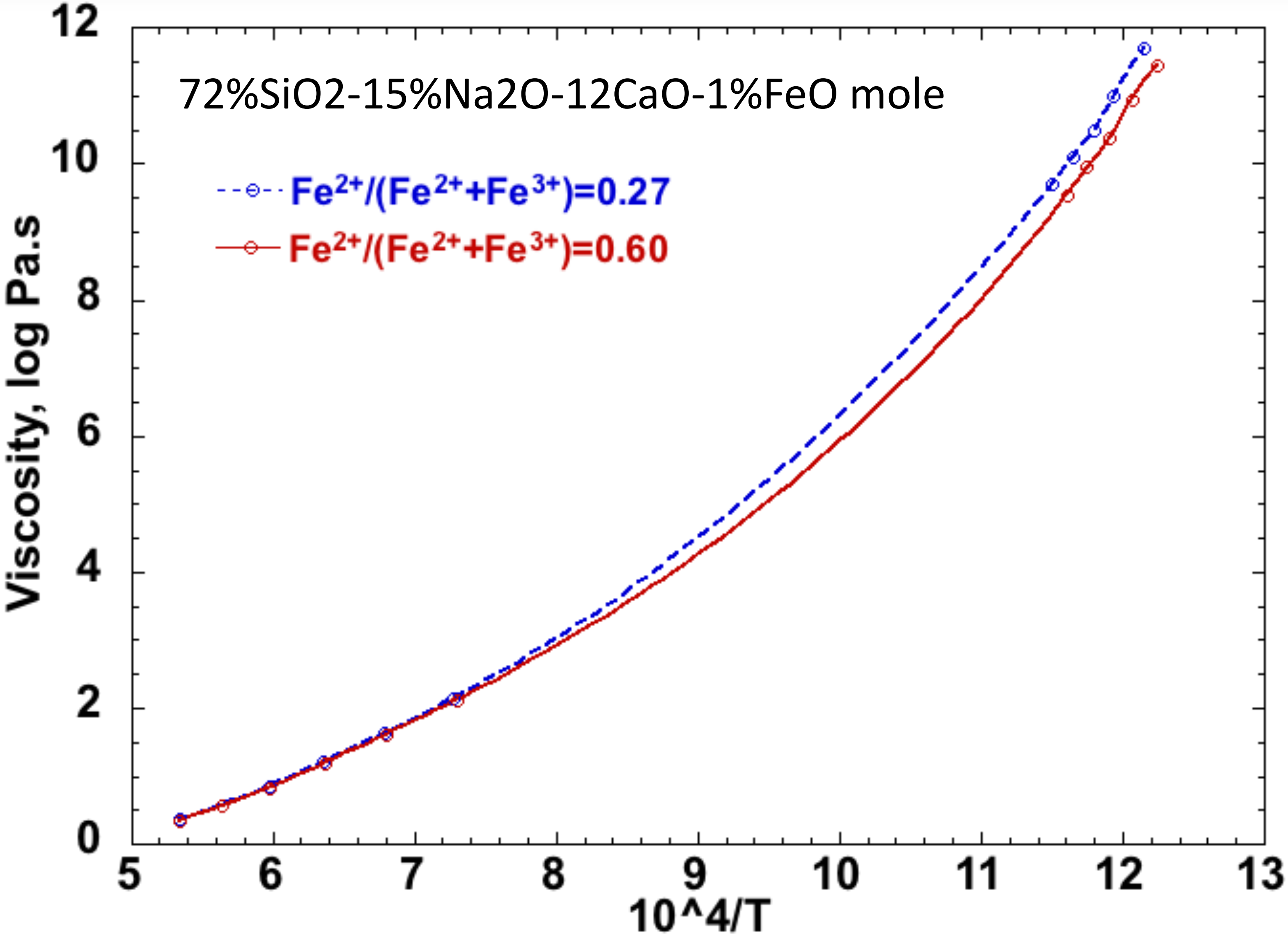
Magnien V, Neuville D.R., Cormier L., Roux J., Hazemann J-L., de Ligny D., Pascarelli S., Vickridge I., Pinet O. and Richet P. (2008) Kinetics and mechanisms of iron redox reactions in silicate melts: The effects of temperature and alkali cations. Geochim. Cosmochim. Acta., 72, 2157-2168.

Atmosphere	Oxidized Silicate			Reduced Silicate	
	Molecular Oxygen (Schreiber et al, 1986)				
O_2	O_2	→	$4\ Fe^{3+} + 2\ O^{2-}$	$4\ Fe^{2+} + O_2$	HT liquidus
	Ionic Oxygen (Schreiber et al, 1986)				
$O_2 + 4\ e^-$	$2\ O^{2-}$	O^{2-} → ← e^-	$4\ Fe^{3+} + 8e^- + O_2$	$4\ Fe^{2+} + 2\ O^{2-}$	HT liquidus
	Divalent cations (Cooper et al, 1996)				
2 MO ↙	$2\ M^{2+} + O_2 + 4e^-$	$2\ M^{2+}$ ← ← e^-	$2\ M^{2+} + 4Fe^{3+} + 2O^{2-} + 4\ e^-$	$2\ MO + 4\ Fe^2$	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.

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.



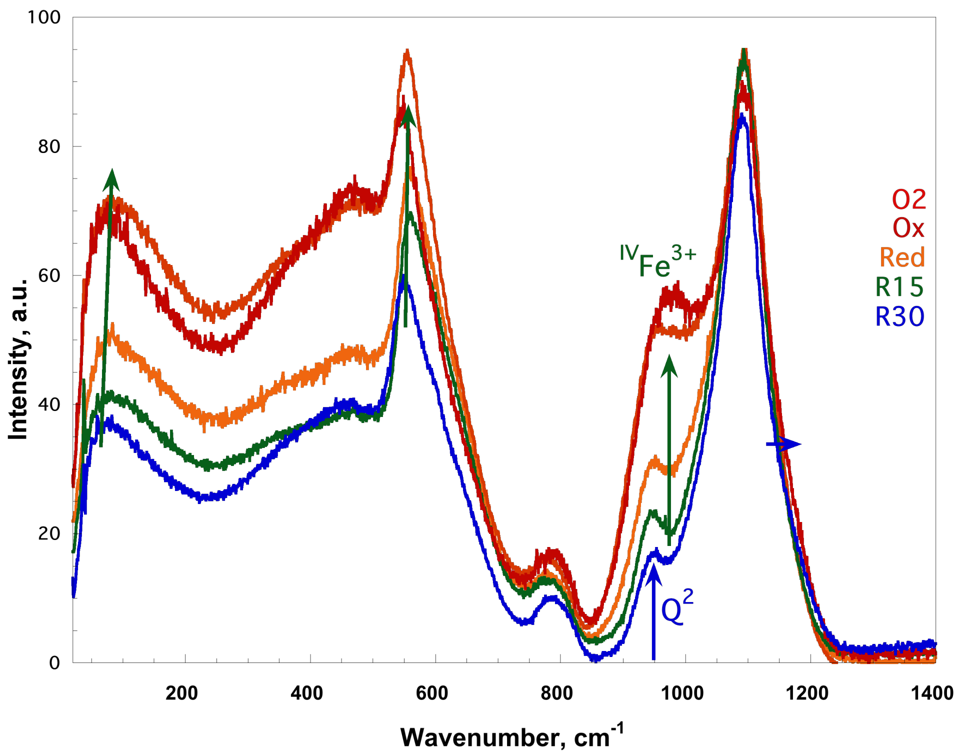

72%SiO2-15%Na2O-12CaO-1%FeO mole
Fe2+/(Fe2++Fe3+)=0.27
Fe2+/(Fe2++Fe3+)=0.60
Viscosity, log Pa.s
10^4/T
0
2
4
6
8
10
12
5
6
7
8
9
10
11
12
13

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

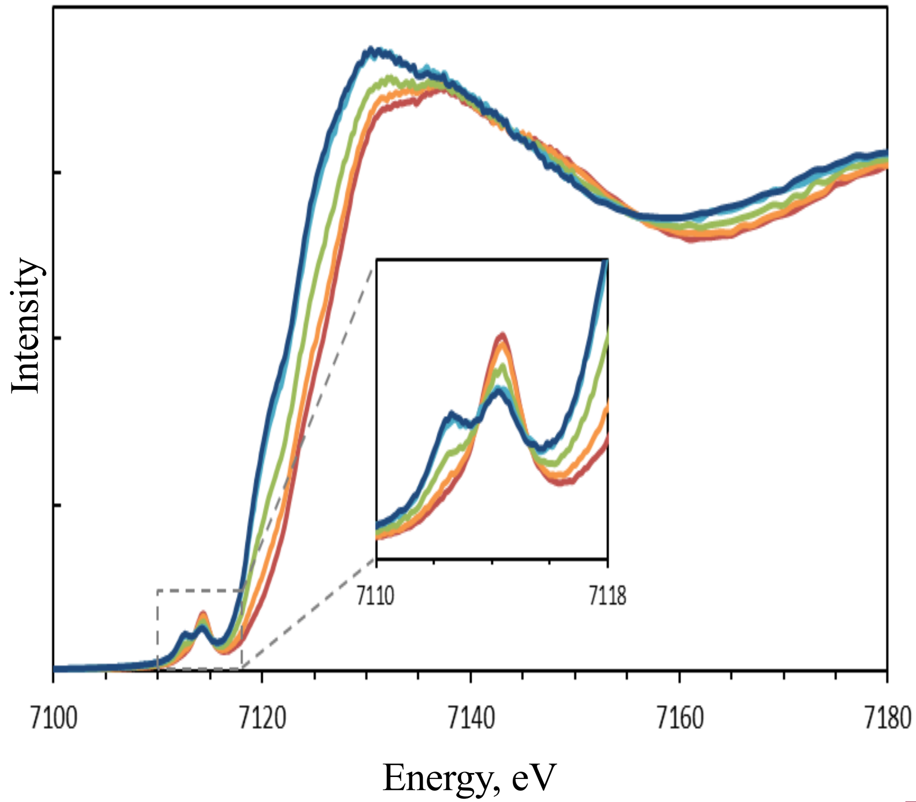
$Fe^{2+}/(Fe^{2+}+Fe^{3+})=0.27$ Ox

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

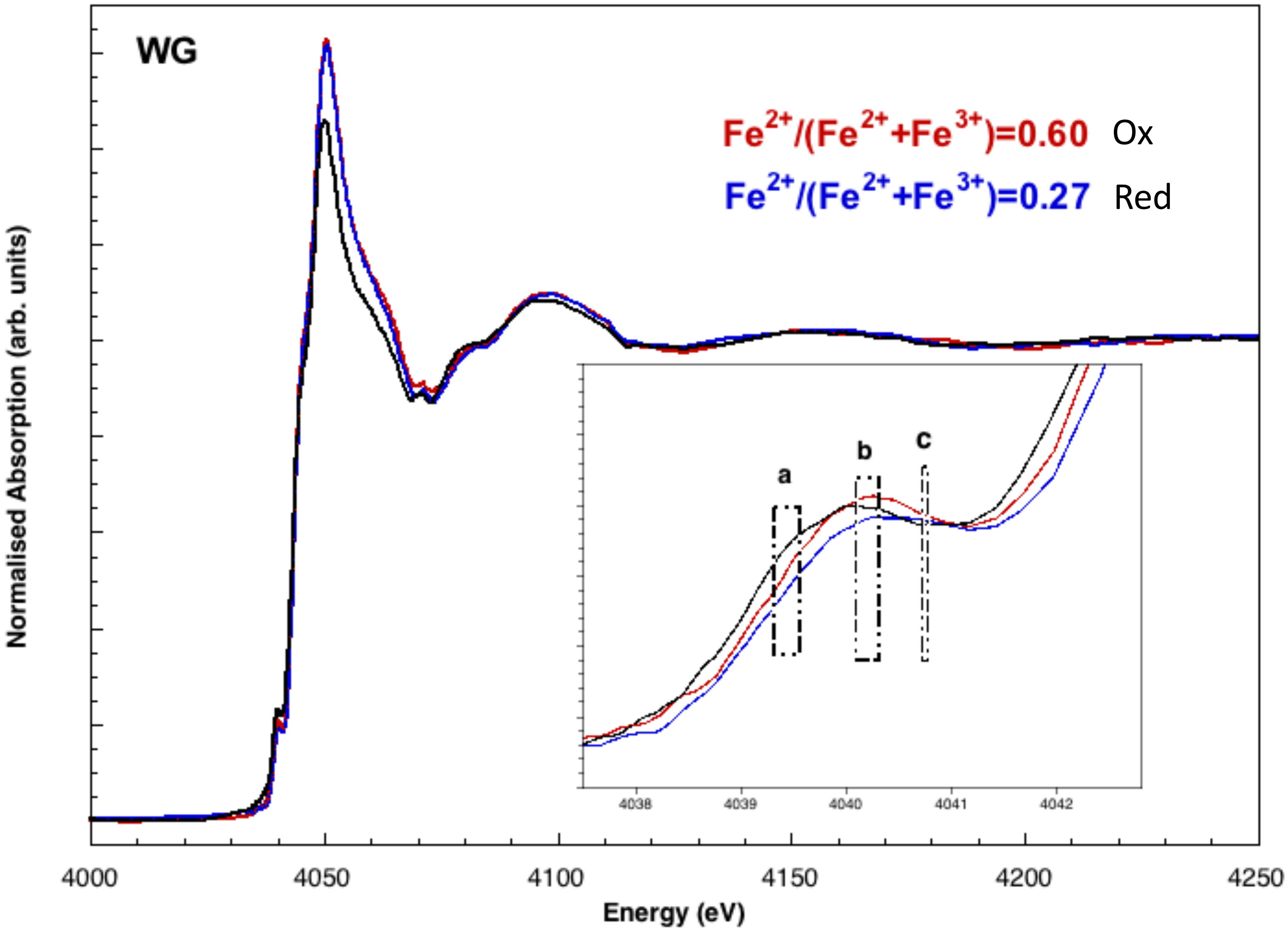
Raman spectroscopy



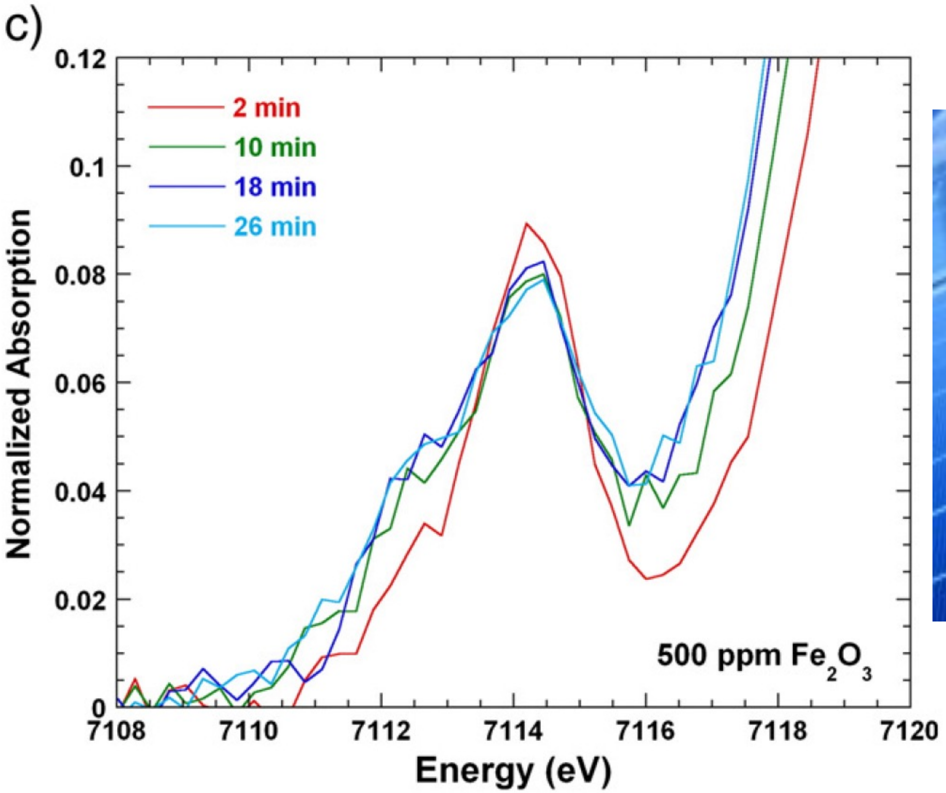
XANES at Fe K-edge

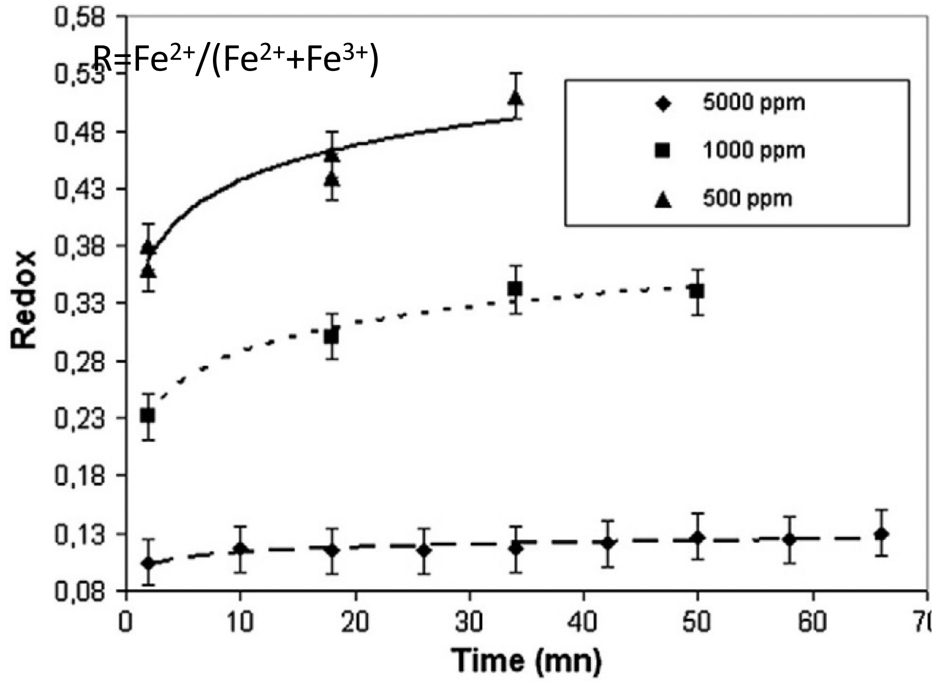


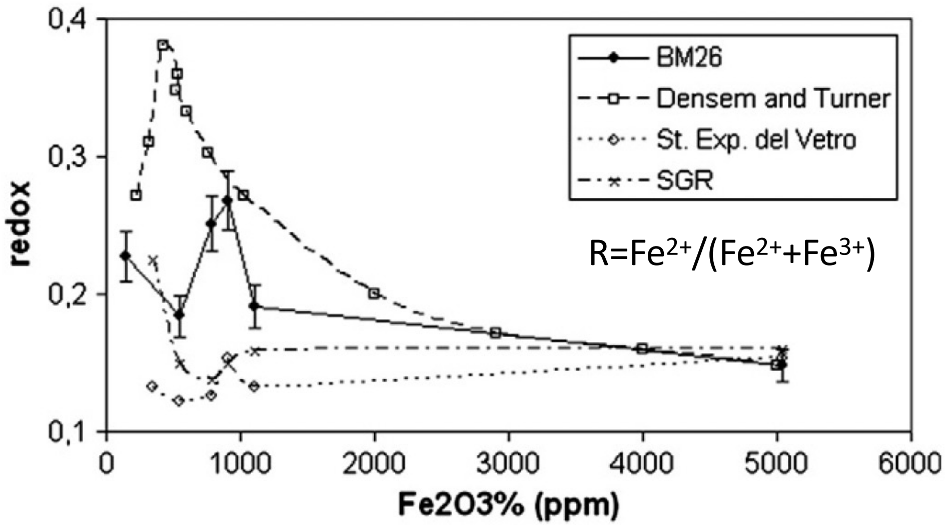
XANES at Ca K-edge



Cicconi M.R., de Ligny D., Gallo T. M., Neuville D.R. (2016) Ca Neighbors from XANES spectroscopy: a tool to investigate structure, redox and nucleation processes in silicate glasses, melts and crystals. American Mineralogist, 101, 1232-1236.

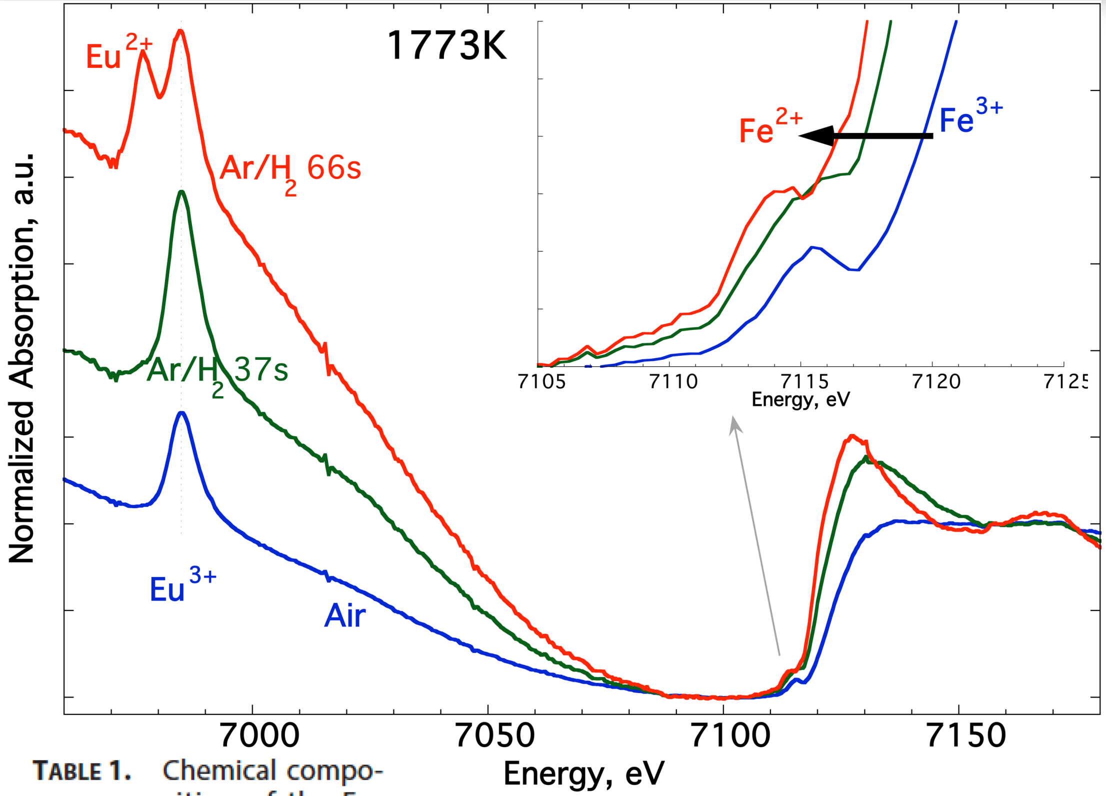


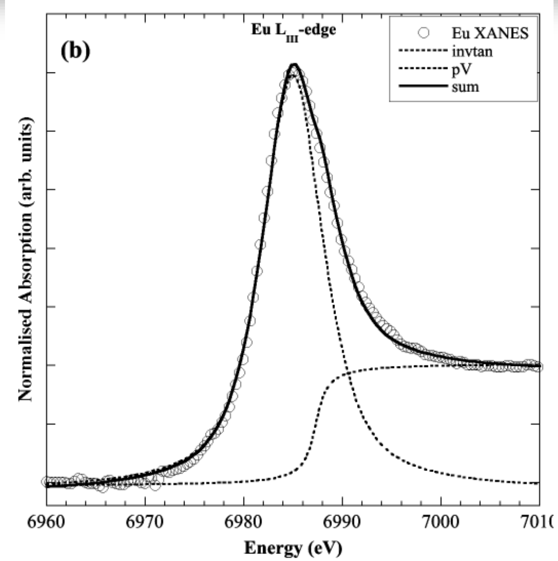




good agreement with Densen and Turner, the redox of elements in diluted condition does not follow the expected rules

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





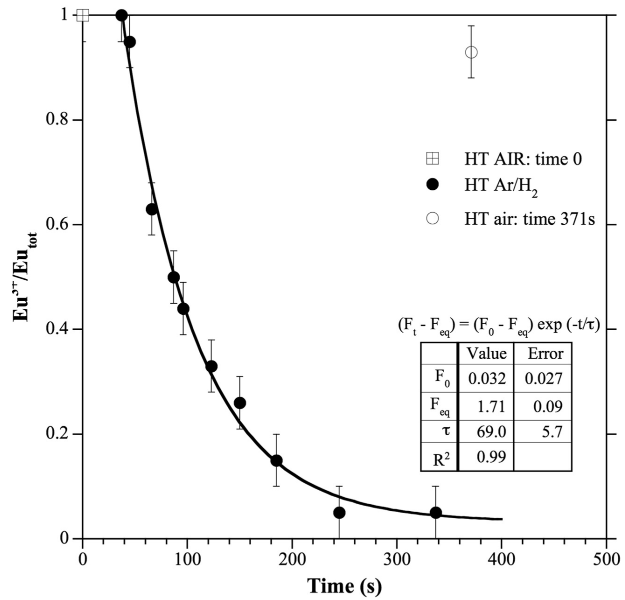
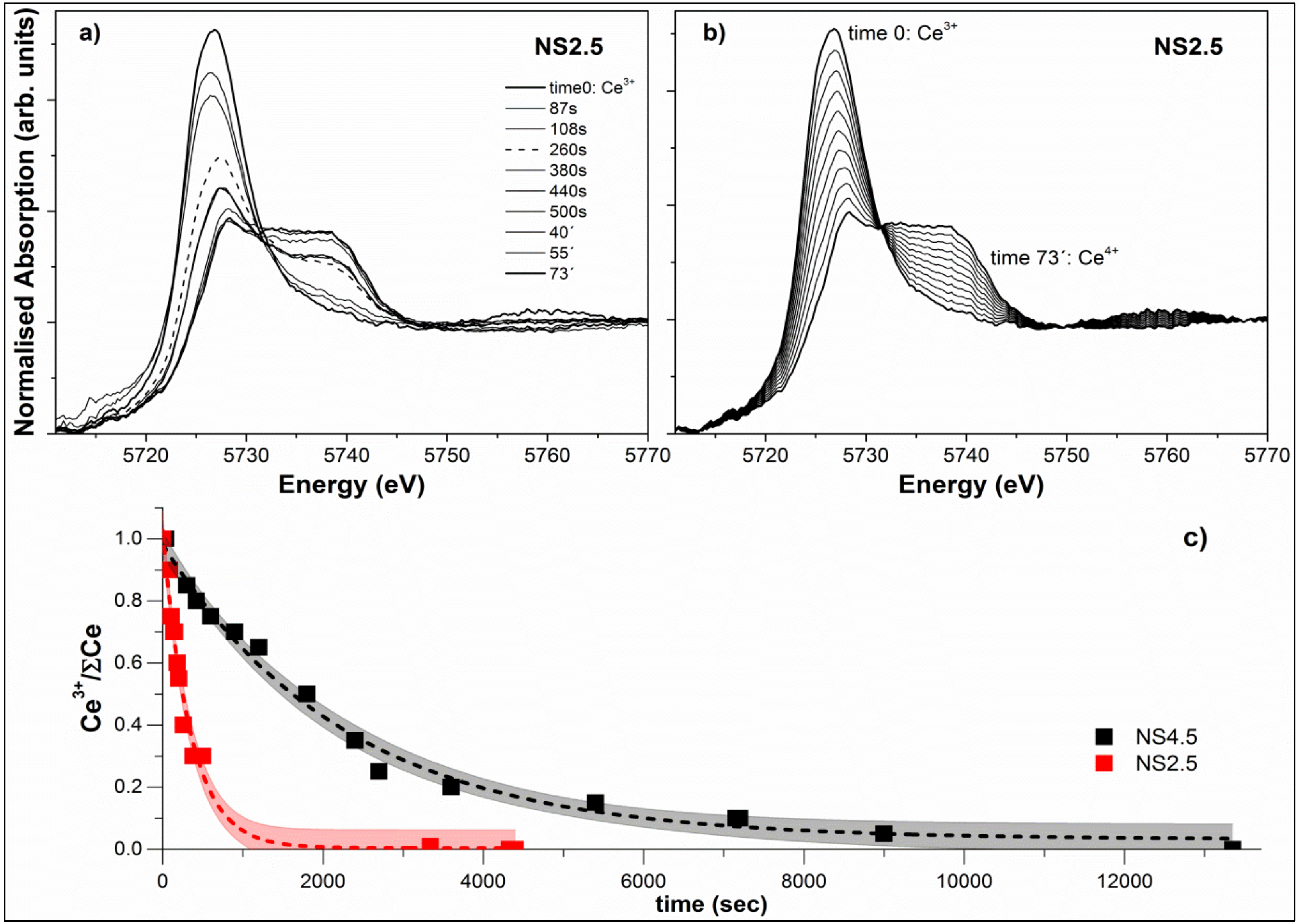


TABLE 1. Chemical composition of the Fe-basalt glass (wt%)

	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

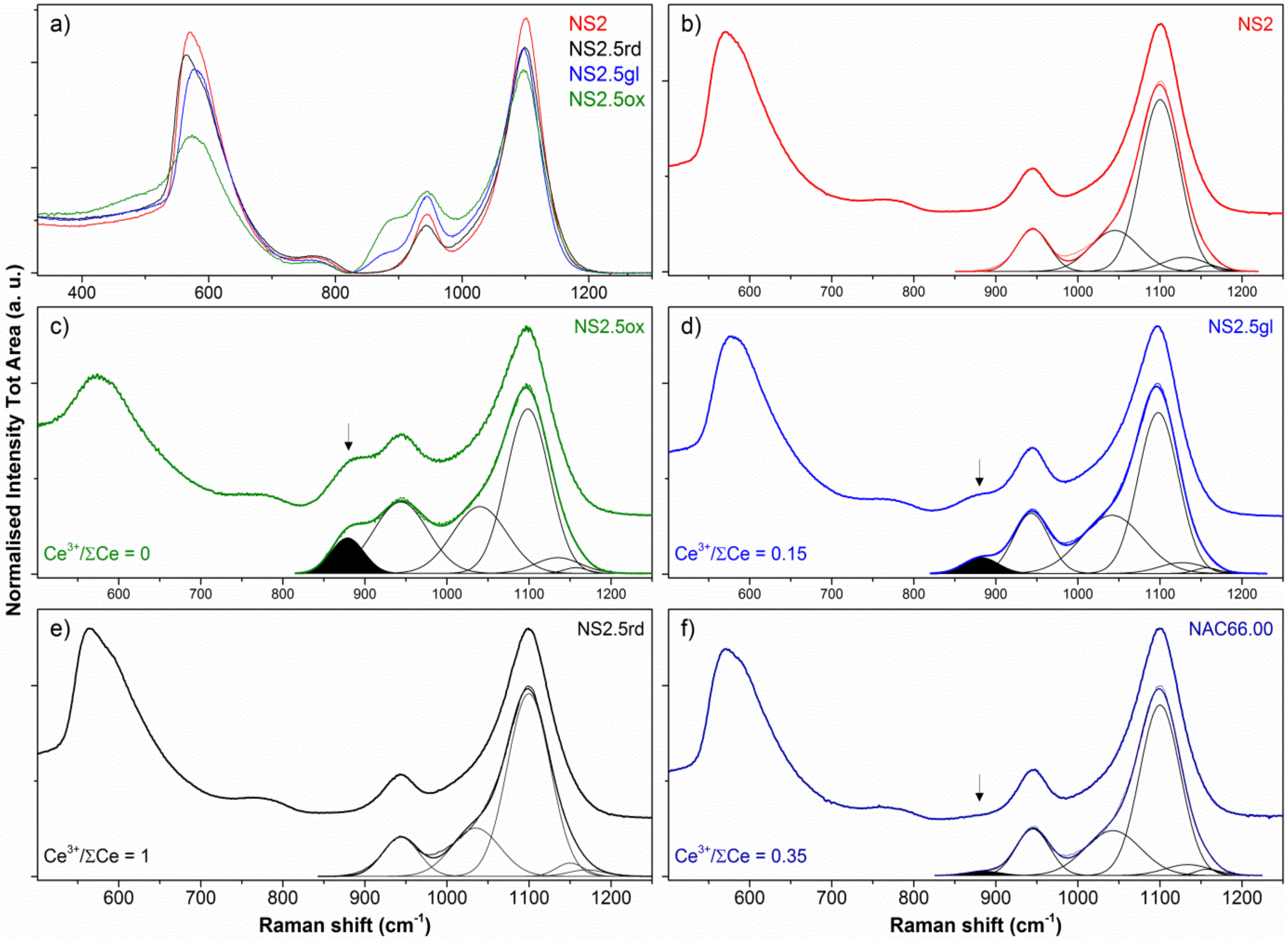
Cicconi M.R., Neuville D.R., Tannou I., Baudelet F., Floury P., Paris E., and Giuli G. (2015) Competition between two redox states in silicate melts: an in-situ simultaneous experiment at the Fe K-edge and Eu L3-edge. American Mineralogist. 100, 1013-1016.



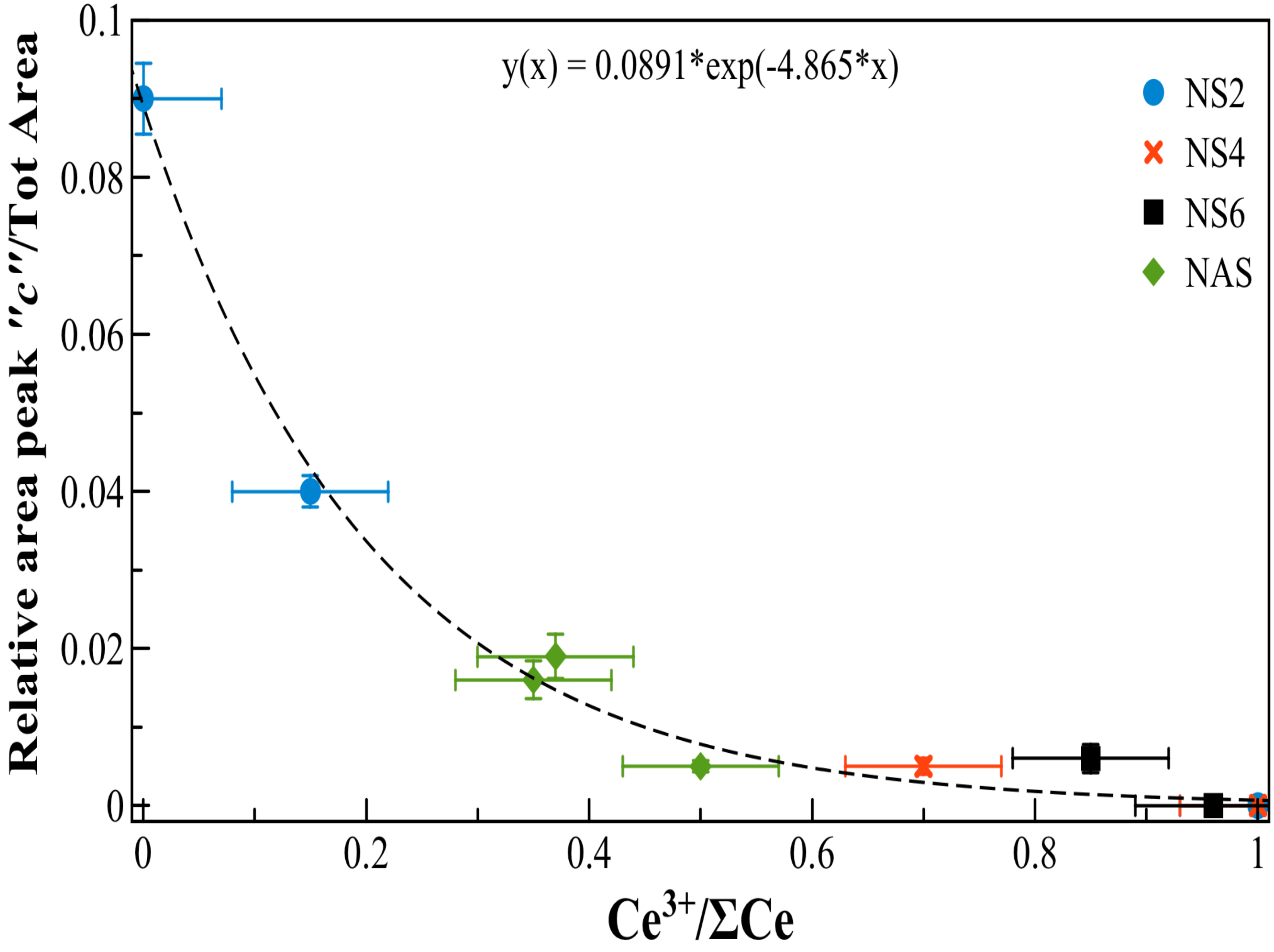
Cicconi M.R., Neuville D.R., Blanc W., Lupi J.F., Vermillac M., de Ligny D. (2017) Cerium structural role in silicate glasses and Ce-activated silica glasses. Journal of Non-Crystalline Solids. 475, 85–95.

Raman spectroscopy on Ce-NSx silicate glasses

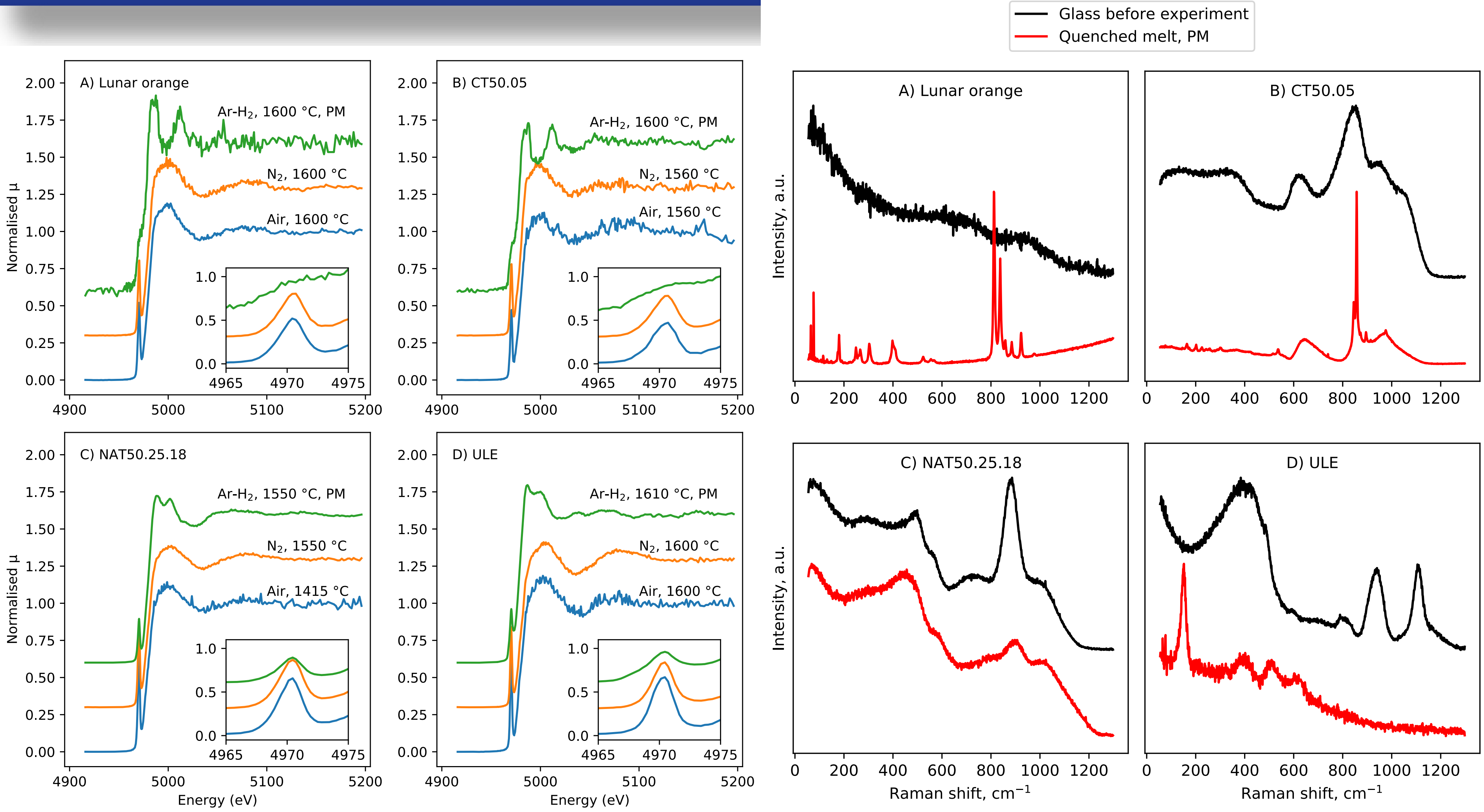
Géomatériaux



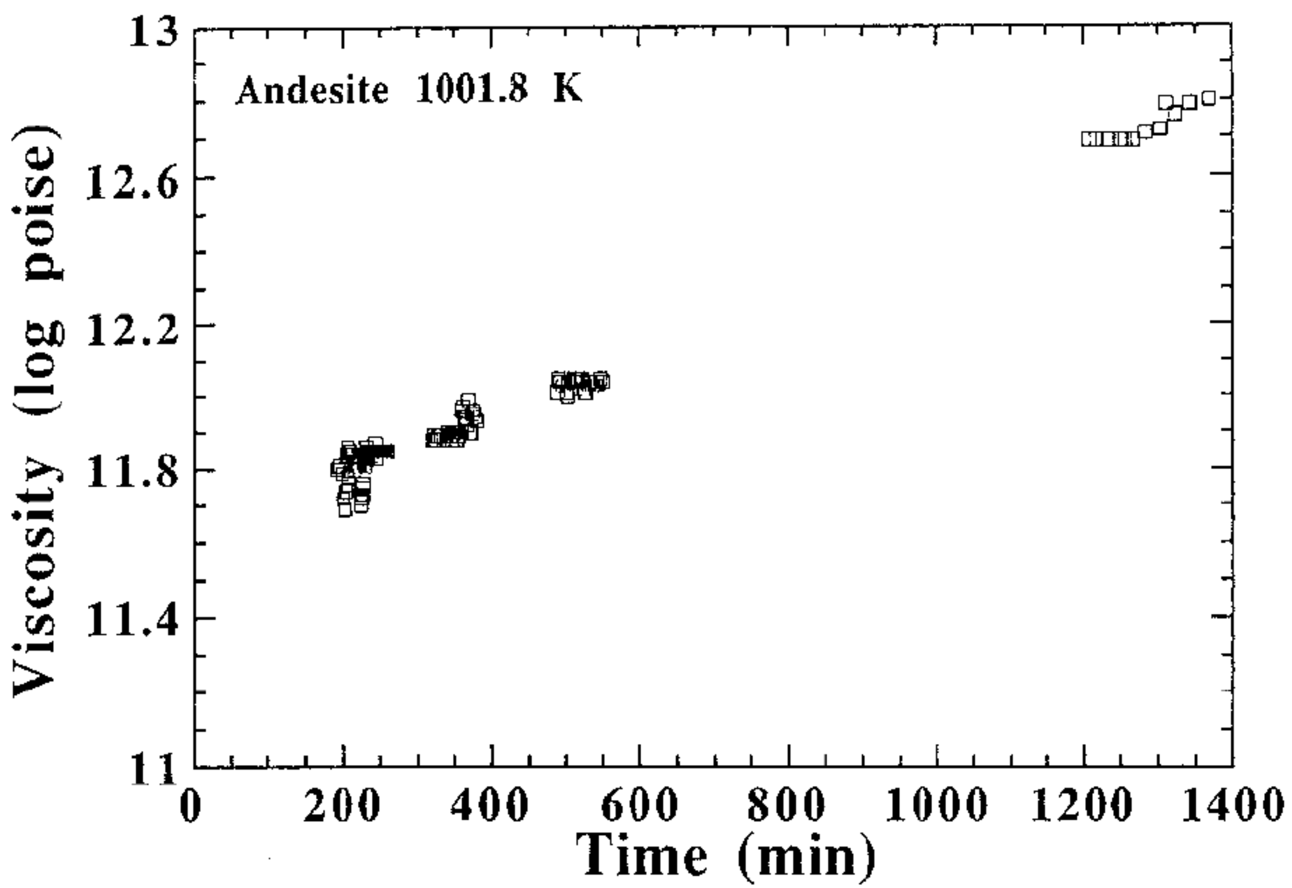
Cicconi M.R., Neuville D.R., Blanc W., Lupi J.F., Vermillac M., de Ligny D. (2017) Cerium structural role in silicate glasses and Ce-activated silica glasses. Journal of Non-Crystalline Solids. 475, 85–95.



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.



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



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 h increases with time ?

Redox change? Nucleation and growth?

Nucleation, effect on viscosity?

Géomatériaux

yellowstone

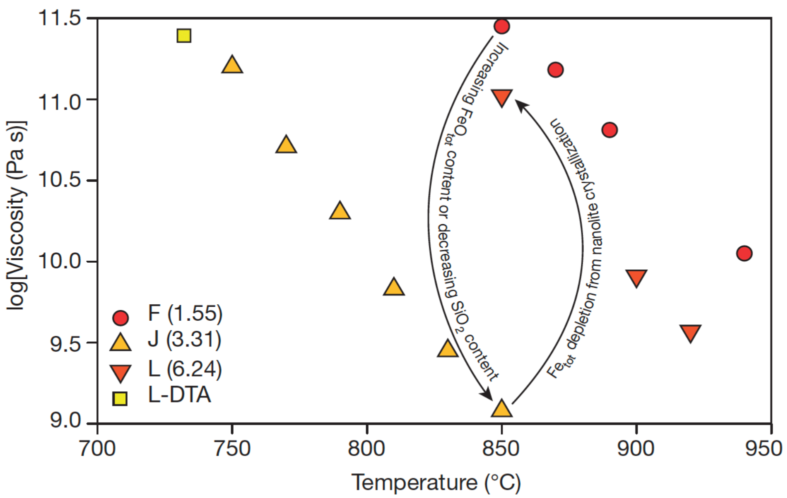
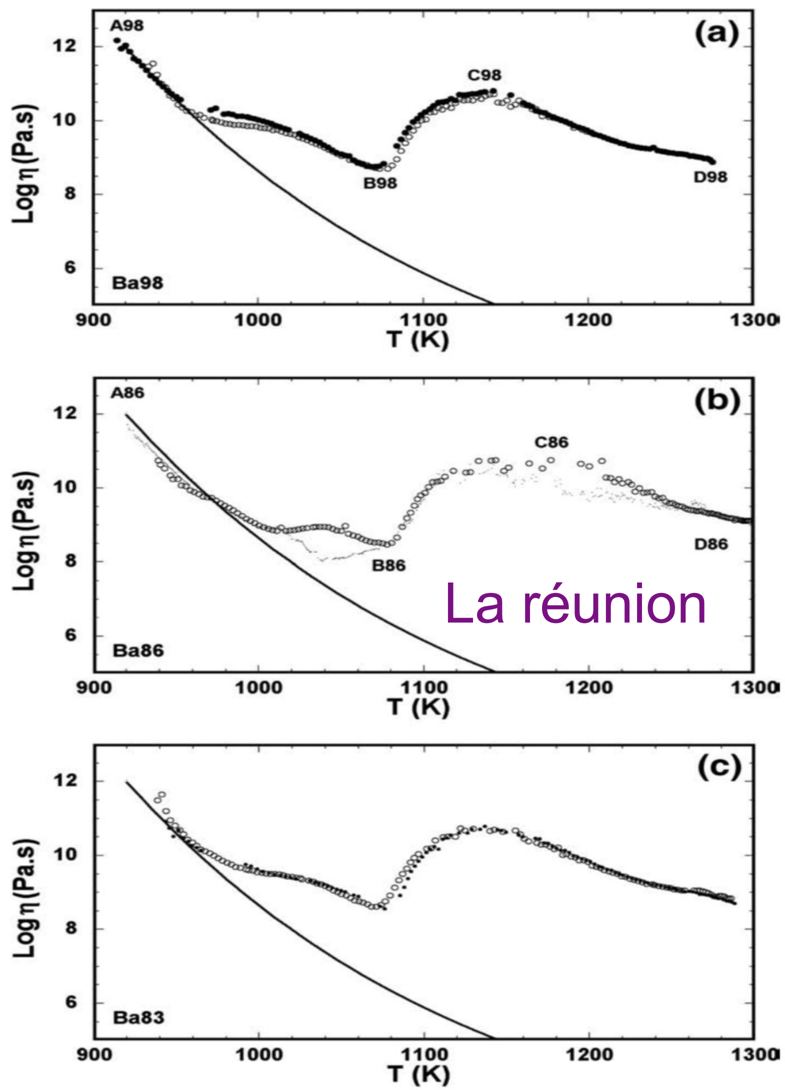


Figure 2 | Measured viscosity at 850 °C for samples F, J and L characterized by increasing FeO content. FeO content (in wt%) is given in parentheses; see

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

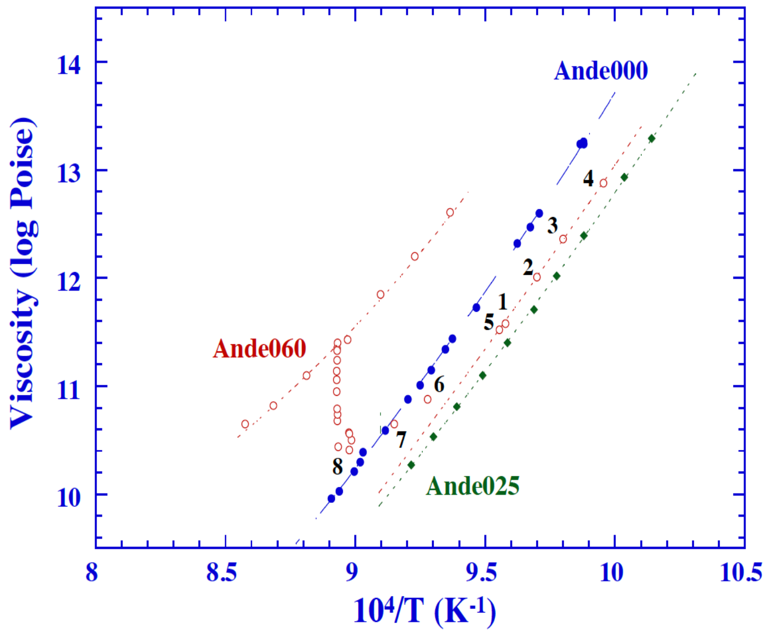
248 N. Villeneuve et al. / Chemical

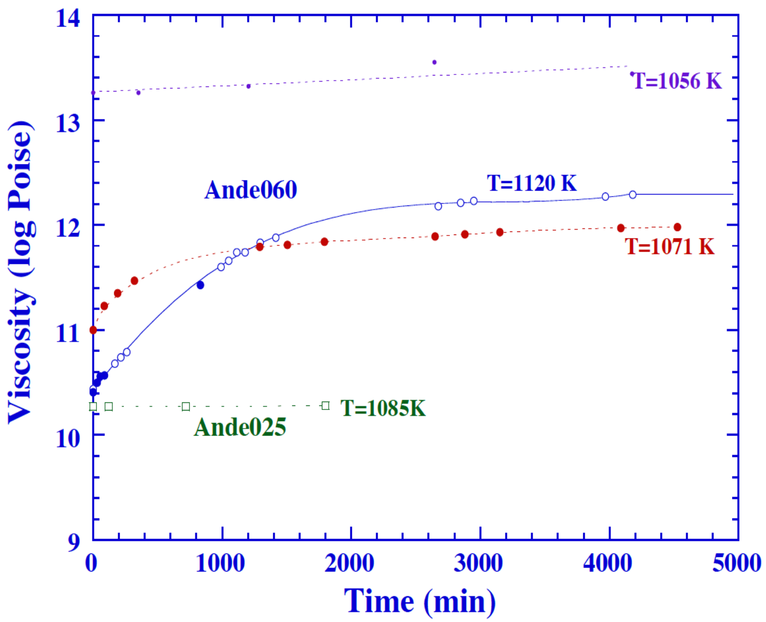


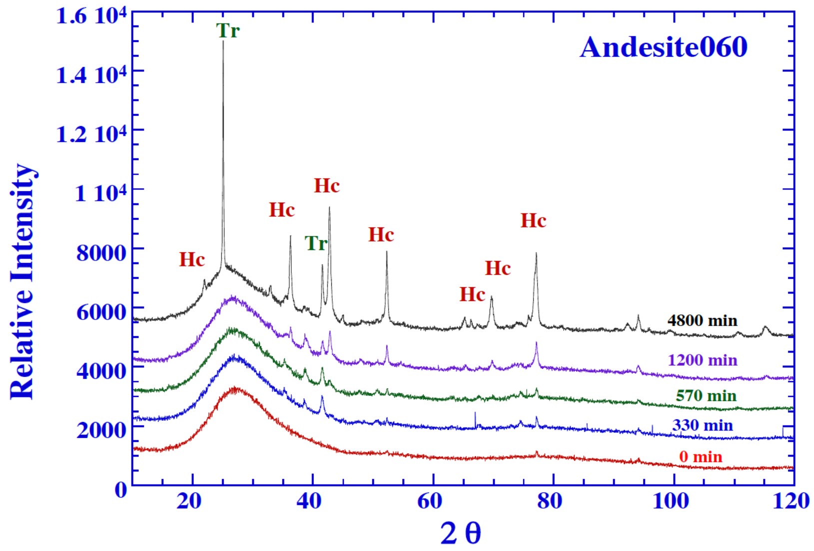
La réunion

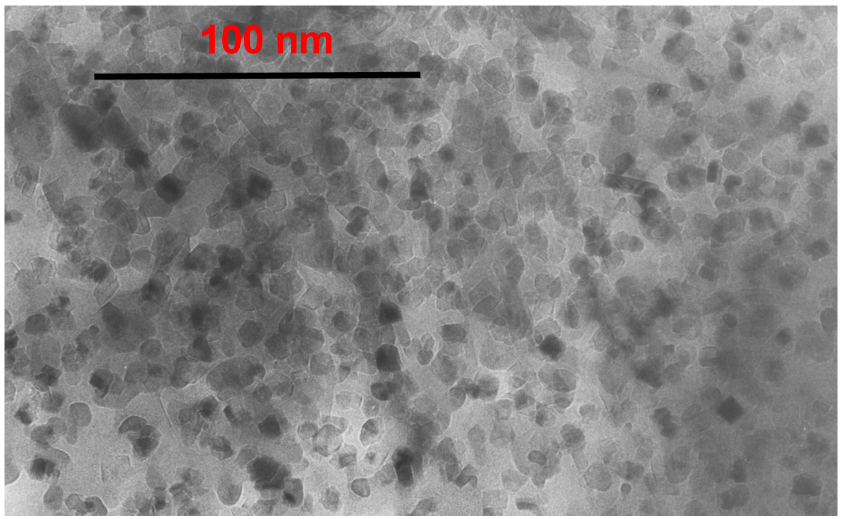
Villeneuve N, Neuville D.R. Boivin P., Bachelery P. (2008) Magma crystallization and viscosity: A study of molten basalts from the Piton de la Fournaise volcano (La Réunion island) Chemical Geology, 256, 242-251

Nucleation, effect on viscosity?



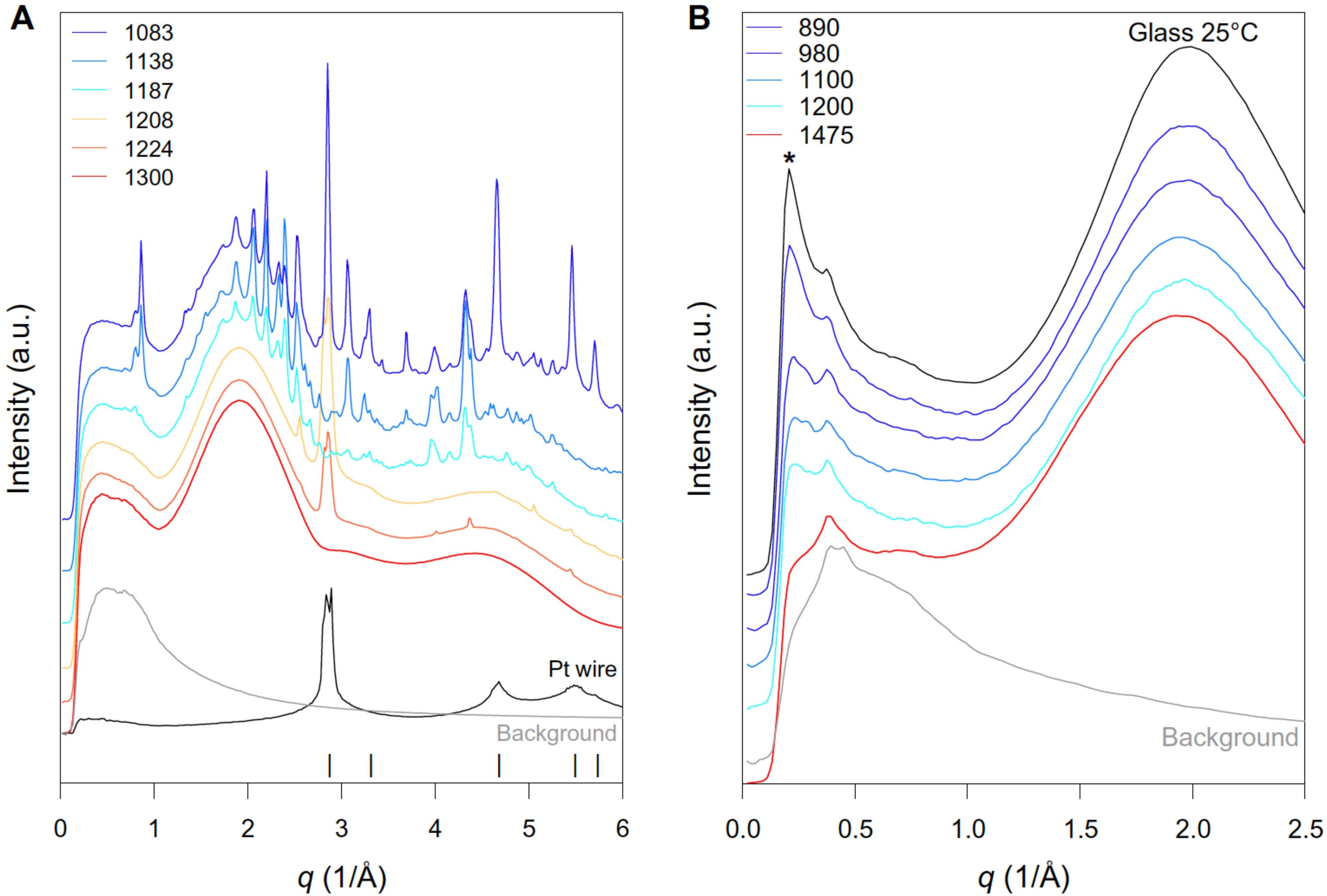




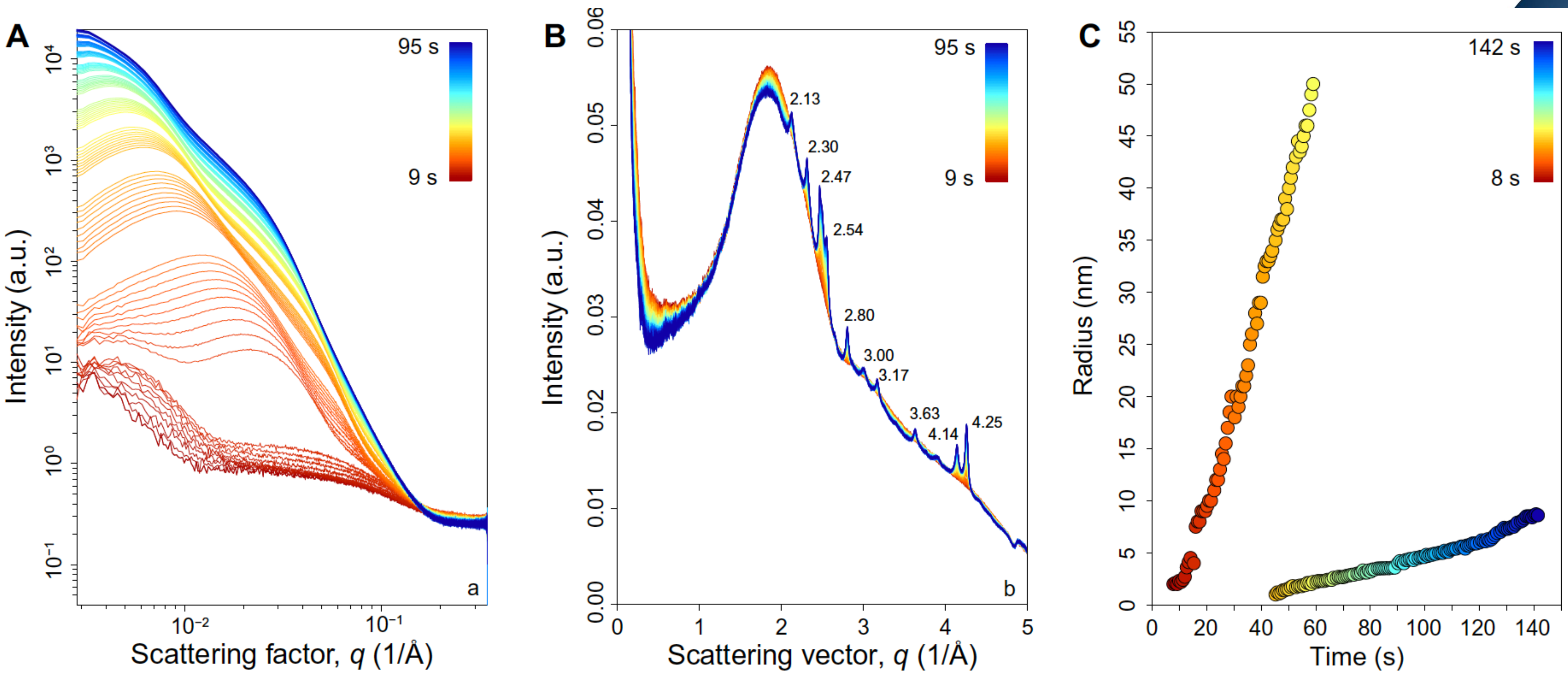


HR-TEM

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.



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



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

- ✓ 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.