



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

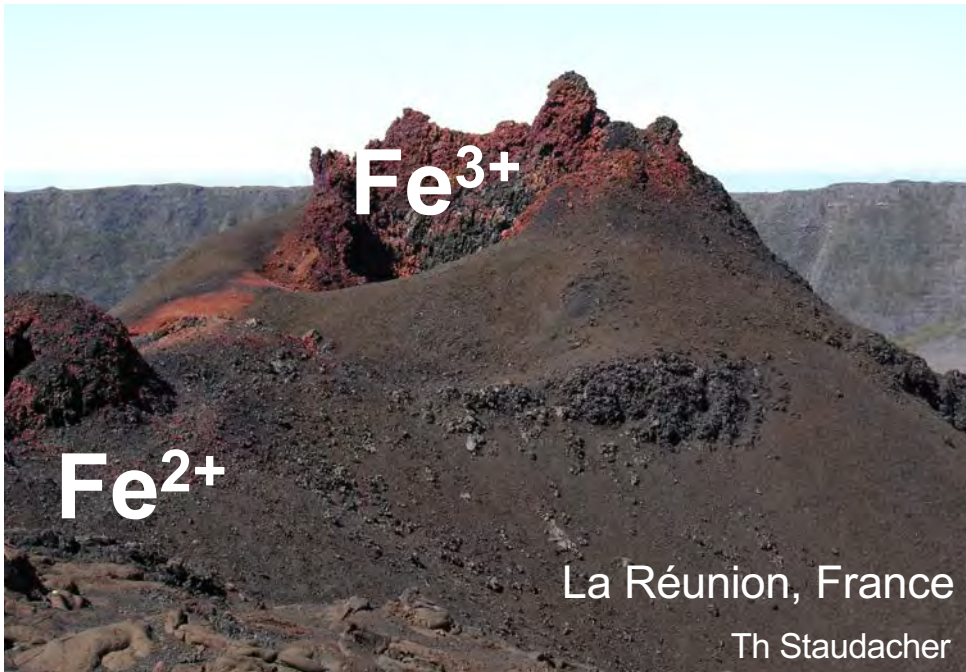
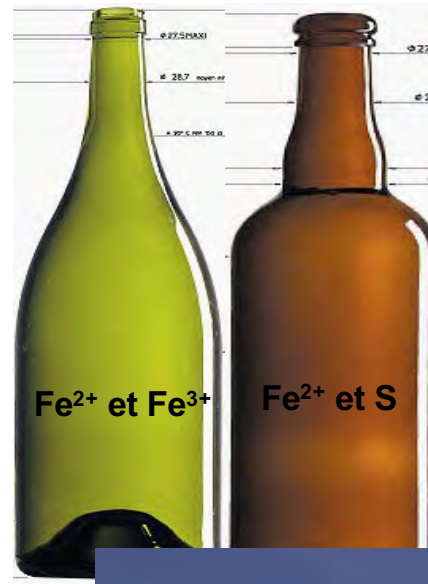
Daniel R. Neuville - Laurent Cormier

Géomatériaux,
CNRS – IPGP
Université de Paris

IMPMC,
CNRS
Sorbonne University



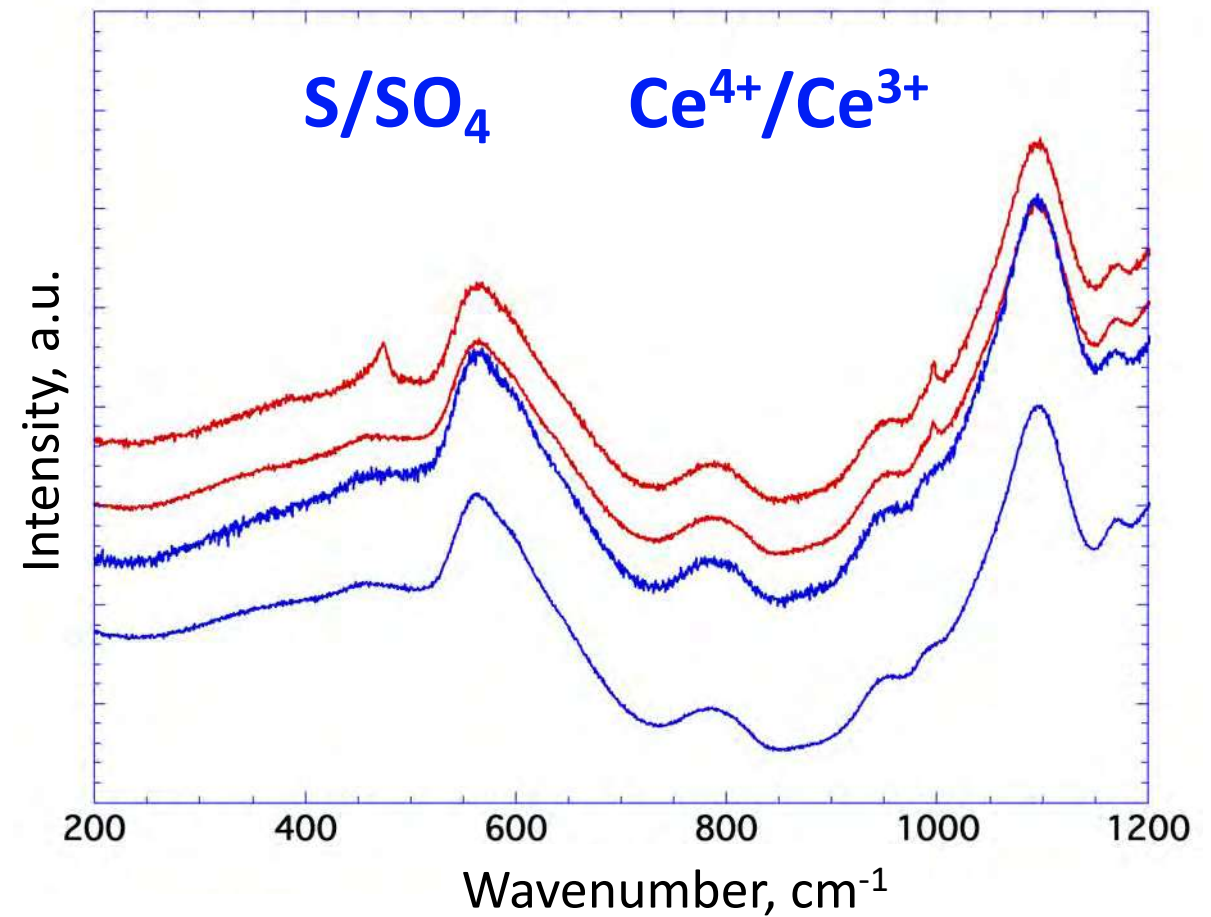
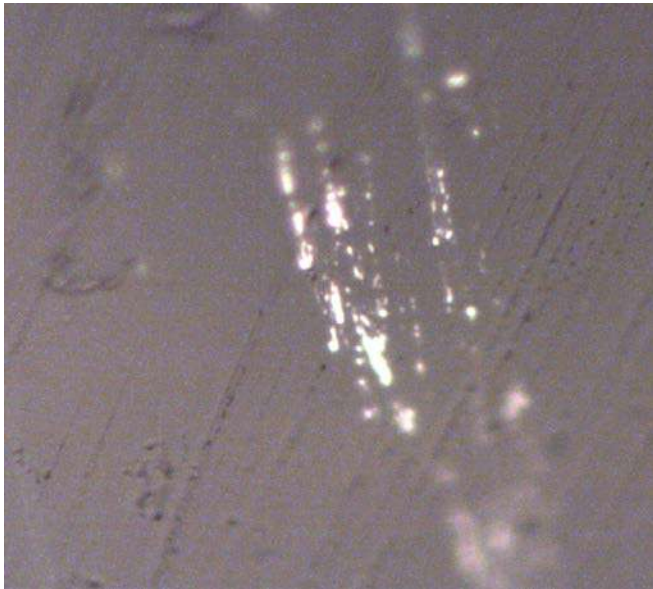
Why determine redox of glasses and melts ?



La Réunion, France
Th Staudacher

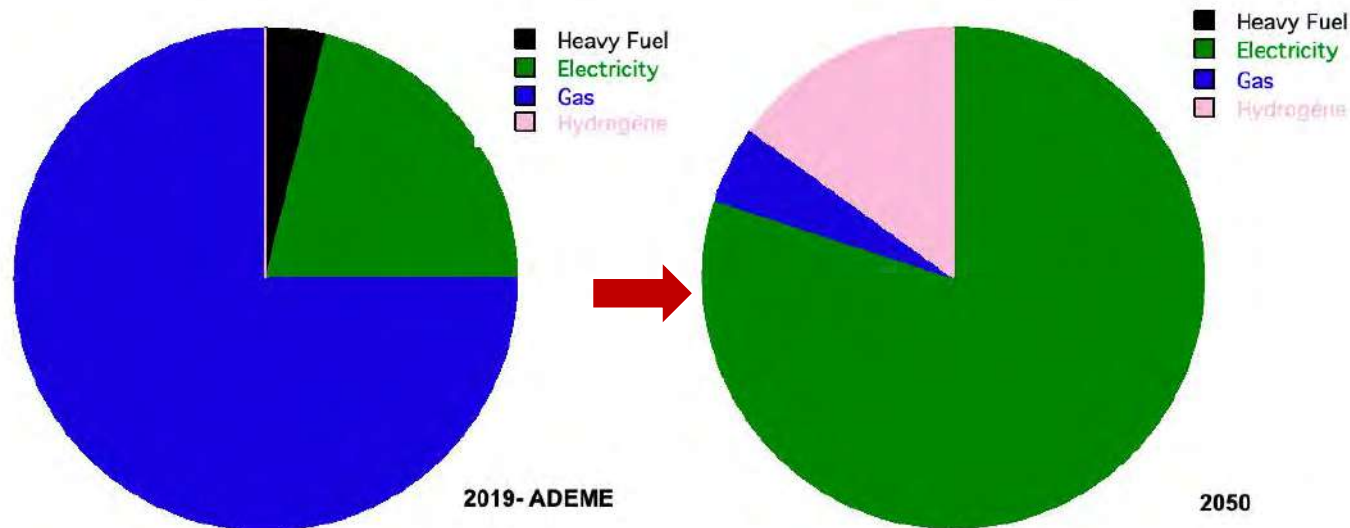


Mix of different cullets ?



Two main sources of CO₂ emissions in the glass industry:

- ✓ Fossil fuels : 80% of emissions



- ✓ Decarbonation of raw materials : 20% of emissions
- Thursday morning...



To limit CO₂ 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_{O_2} ?

Erebus : CO Bubble

20m

What is the f_{O_2} ?

1450° C
Lab furnace
 $f_{O_2}=0,21$

yttria-stabilized zirconia
(YSZ) oxygen sensor.

1450° C
Lab furnace
With C crucible
 $f_{O_2}=600\text{ppm}$

1000° C



Celtic furnace
 $f_{O_2}=0,21$



Celtic furnace
Totally close
 $f_{O_2}\sim 0$



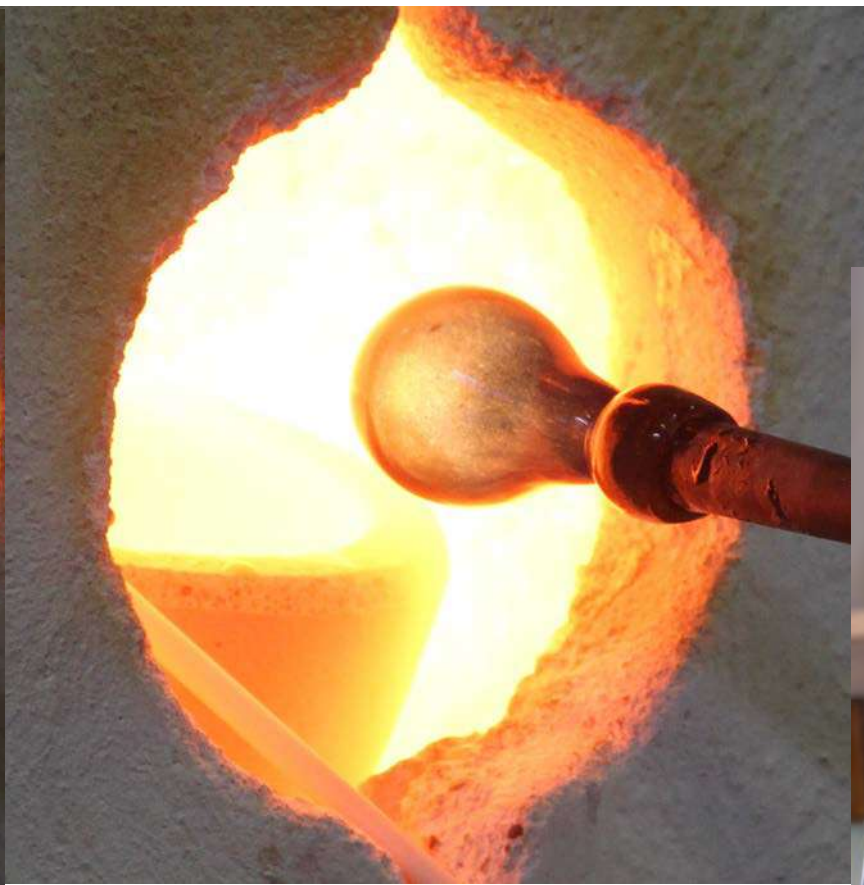
1150° C 1180° C
fO₂=7% fO₂=4,4%



950° C
fO₂=3%



1150° C
fO₂=10%



1150° C

fO₂=10%

fO₂=2%

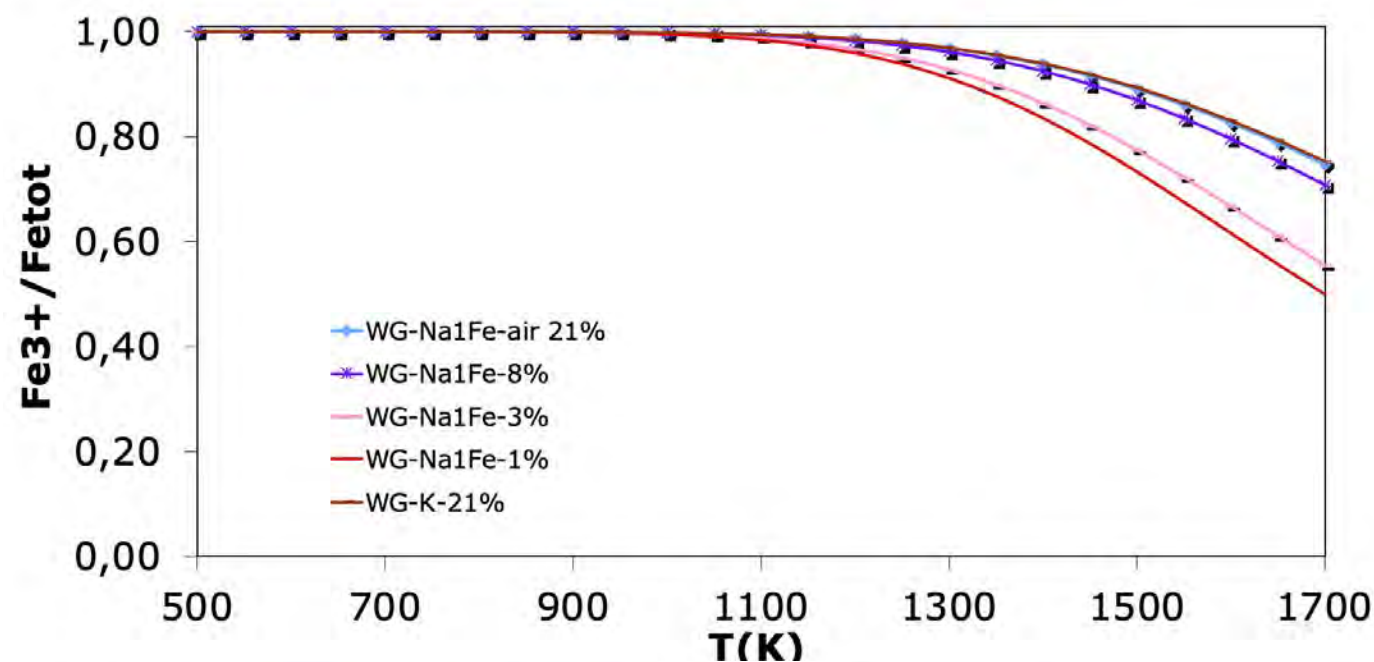


How redox vary as a function of chemical composition, T and f_{O_2} ?

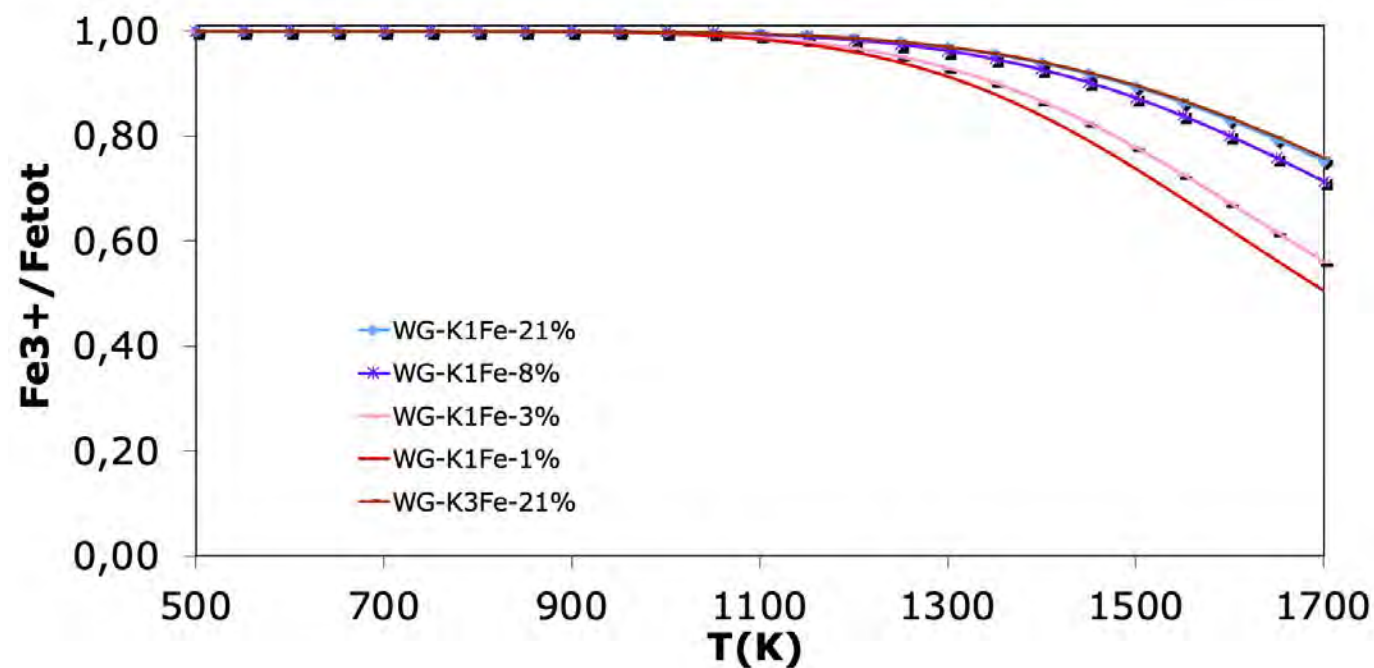
Roman glasses

SiO ₂	70,01
Na ₂ O	16,50
MgO	1,00
CaO	8,50
K ₂ O	1,00
Li ₂ O	0,00
Al ₂ O ₃	2,00
FeO	1,00
total	100,00

Wt%



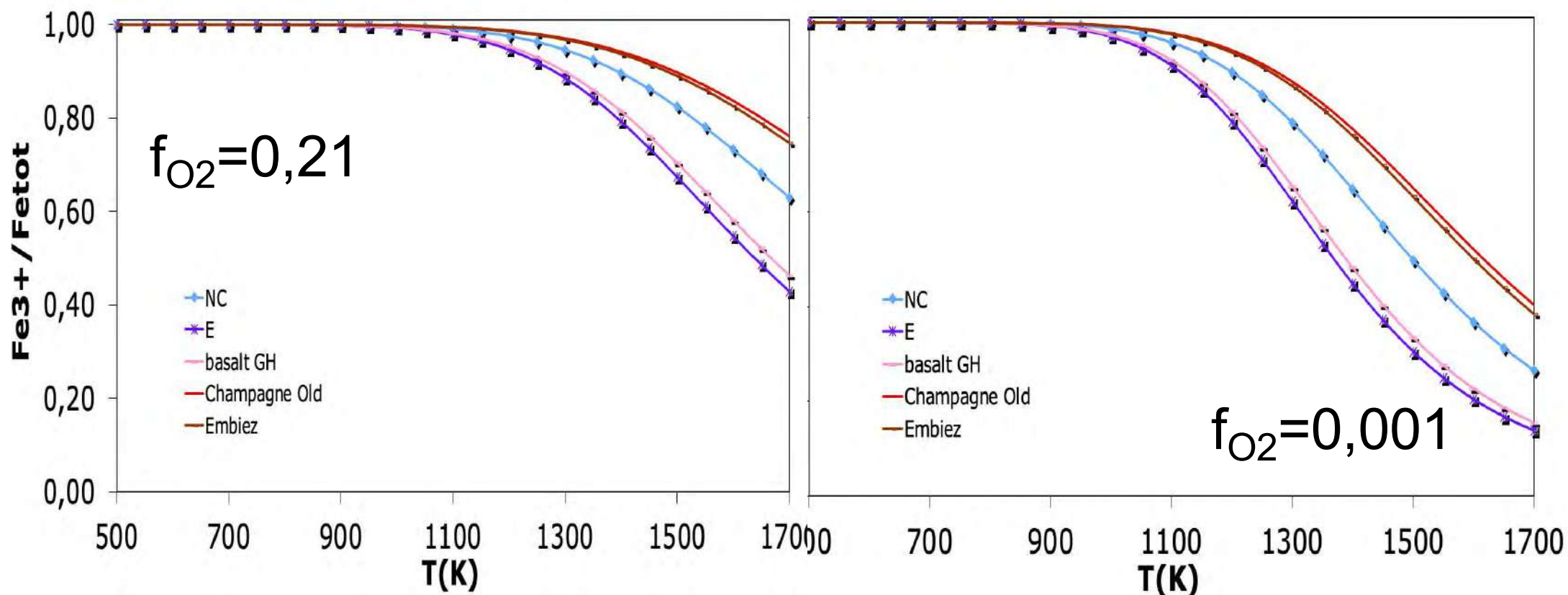
SiO ₂	56,99
Na ₂ O	0,98
MgO	3,50
CaO	14,19
K ₂ O	20,11
Li ₂ O	0,00
Al ₂ O ₃	3,22
FeO	1,00
total	100,00



How redox vary as a function of chemical composition, T and f_{O_2} ?

	NC	E	basalt GH	champagne old	Embiez
SiO ₂	72,61	56,51	48,37	58,50	72,75
Na ₂ O	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
K ₂ O	0,21	0,35	1,36	1,80	0,39
Li ₂ O	0,00	0,00	0,00	0,00	
Al ₂ O ₃	0,61	6,40	14,56	2,10	1,78
FeO	0,78	0,55	13,00	8,90	0,33

Wt%

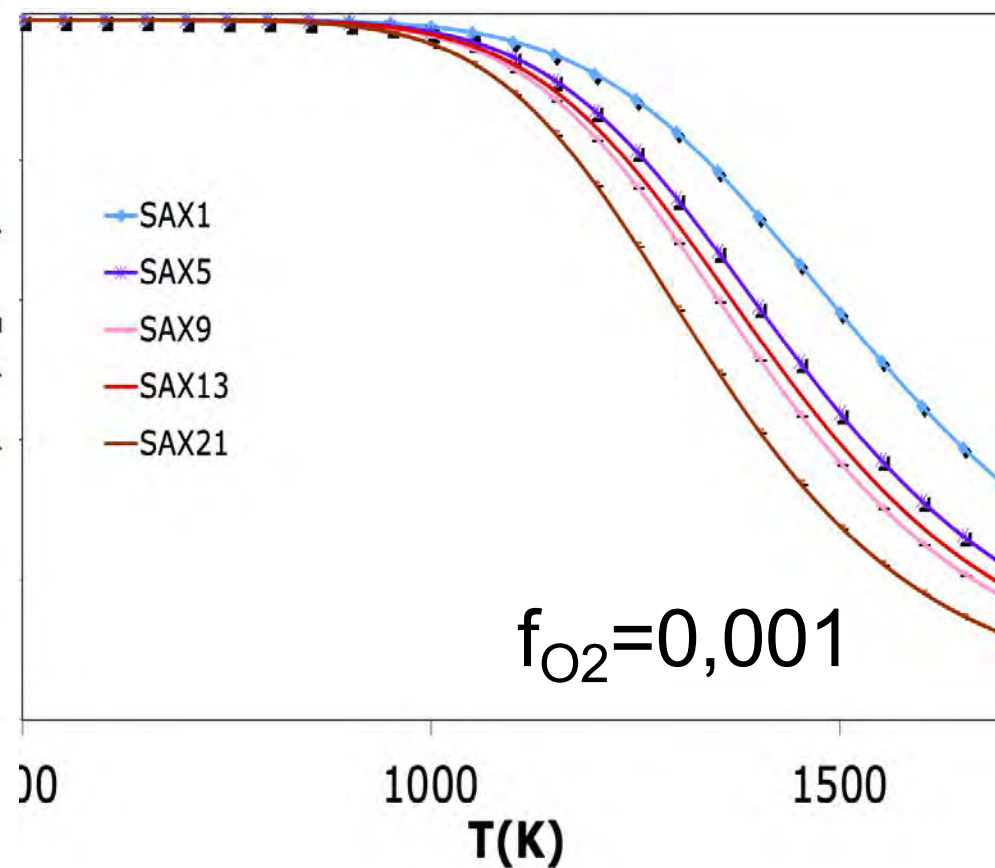
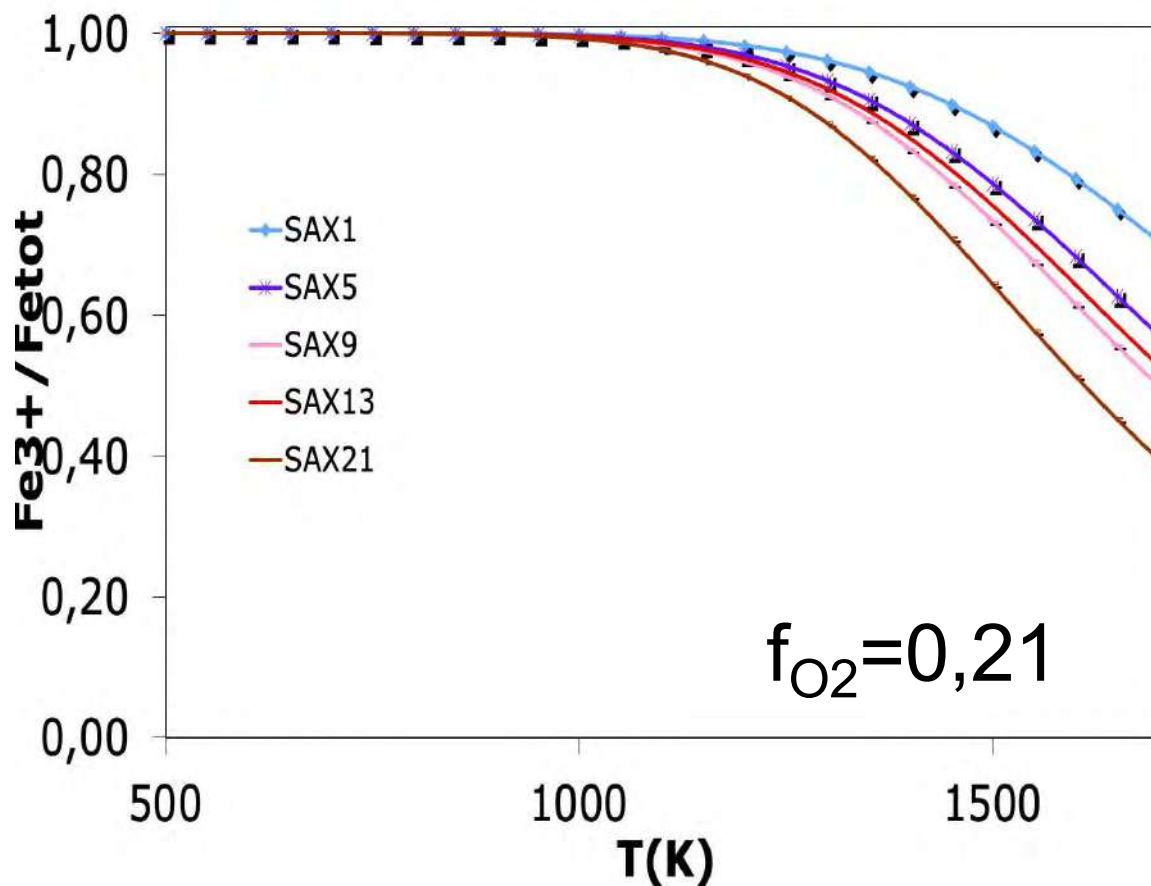


How redox vary as a function of chemical composition, T and f_{O_2} ?

Wt%	SAX1	SAX5	SAX9	SAX13	SAX21
SiO ₂	70,00	70,00	72,00	68,23	73,97
Na ₂ O	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
K ₂ O				15,28	
Li ₂ O					2,63
Al ₂ O ₃	0,50	7,00	0,87	0,83	0,90
FeO	0,02	0,02	0,02	0,02	0,02

Wt%

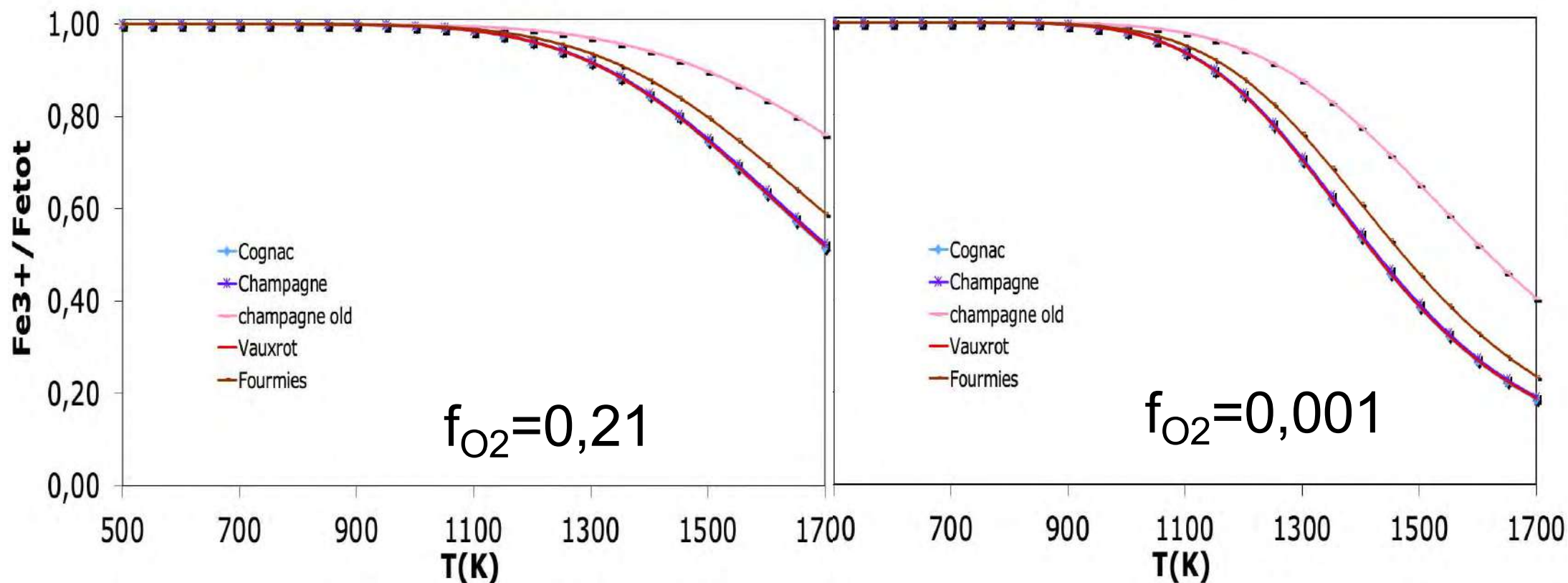
Ultra clear glass



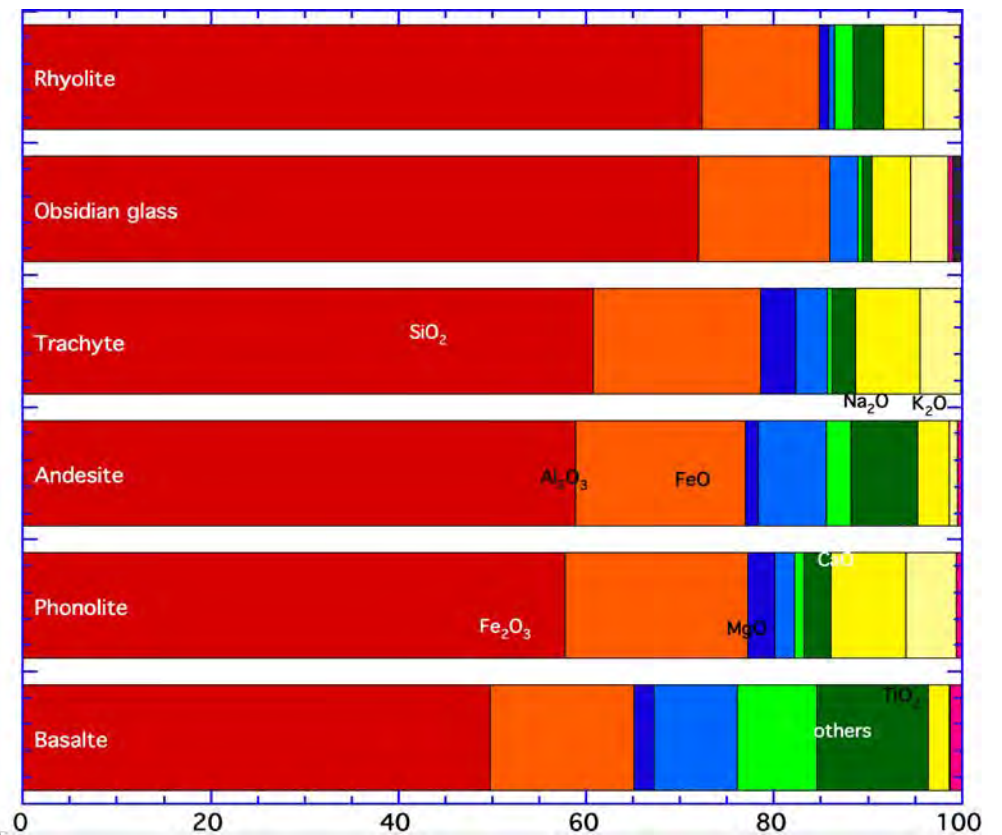
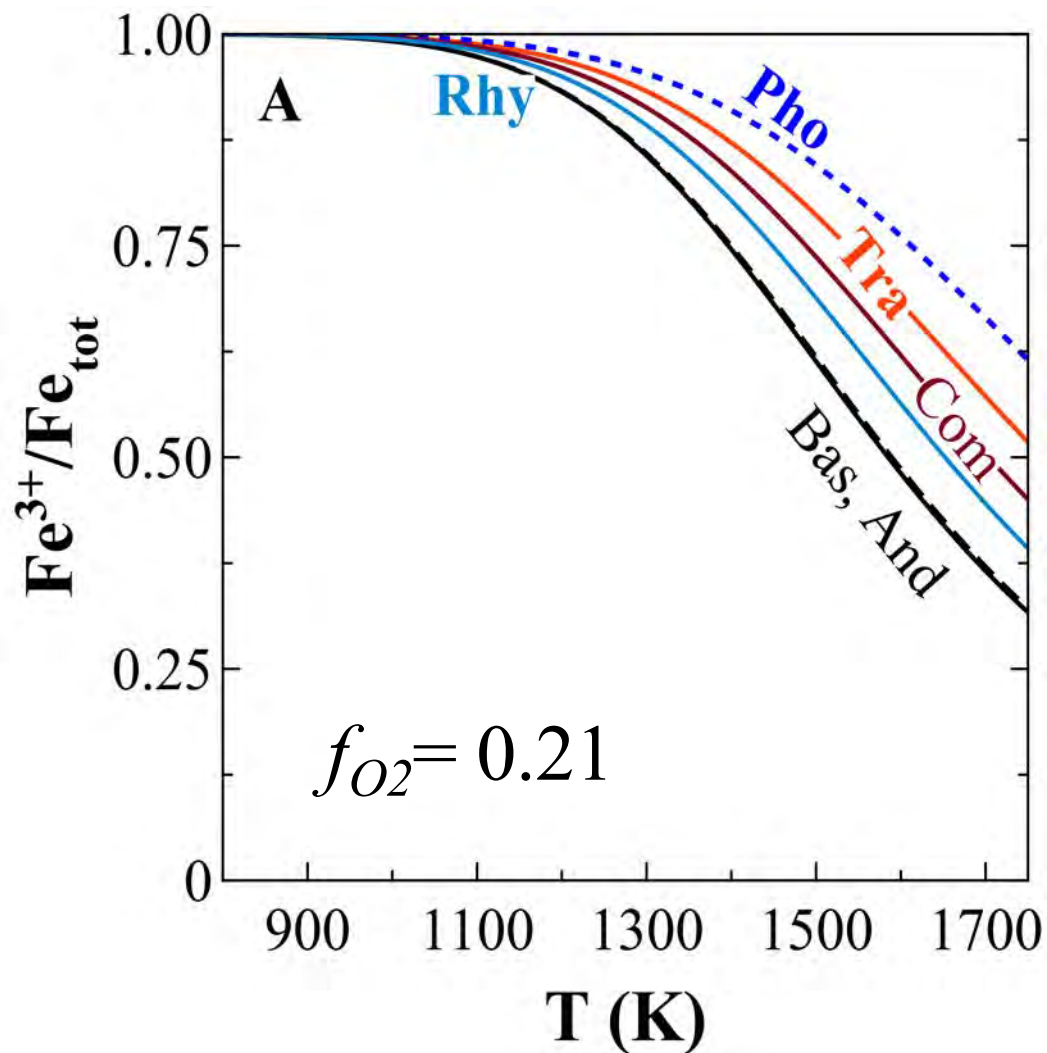
How redox vary as a function of chemical composition, T and f_{O_2} ?

	Cognac	Champagne	champagne old	Vauxrot	Fourmies
SiO ₂	62,54	61,90	58,50	59,70	62,50
Na ₂ O	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
K ₂ O	0,94	1,13	1,80	0,00	0,50
Li ₂ O	0,00	0,00	0,00	0,00	0,50
Al ₂ O ₃	4,42	4,44	2,10	2,39	2,93
FeO	1,34	1,85	8,90	2,21	2,17

Bottles
Wt%

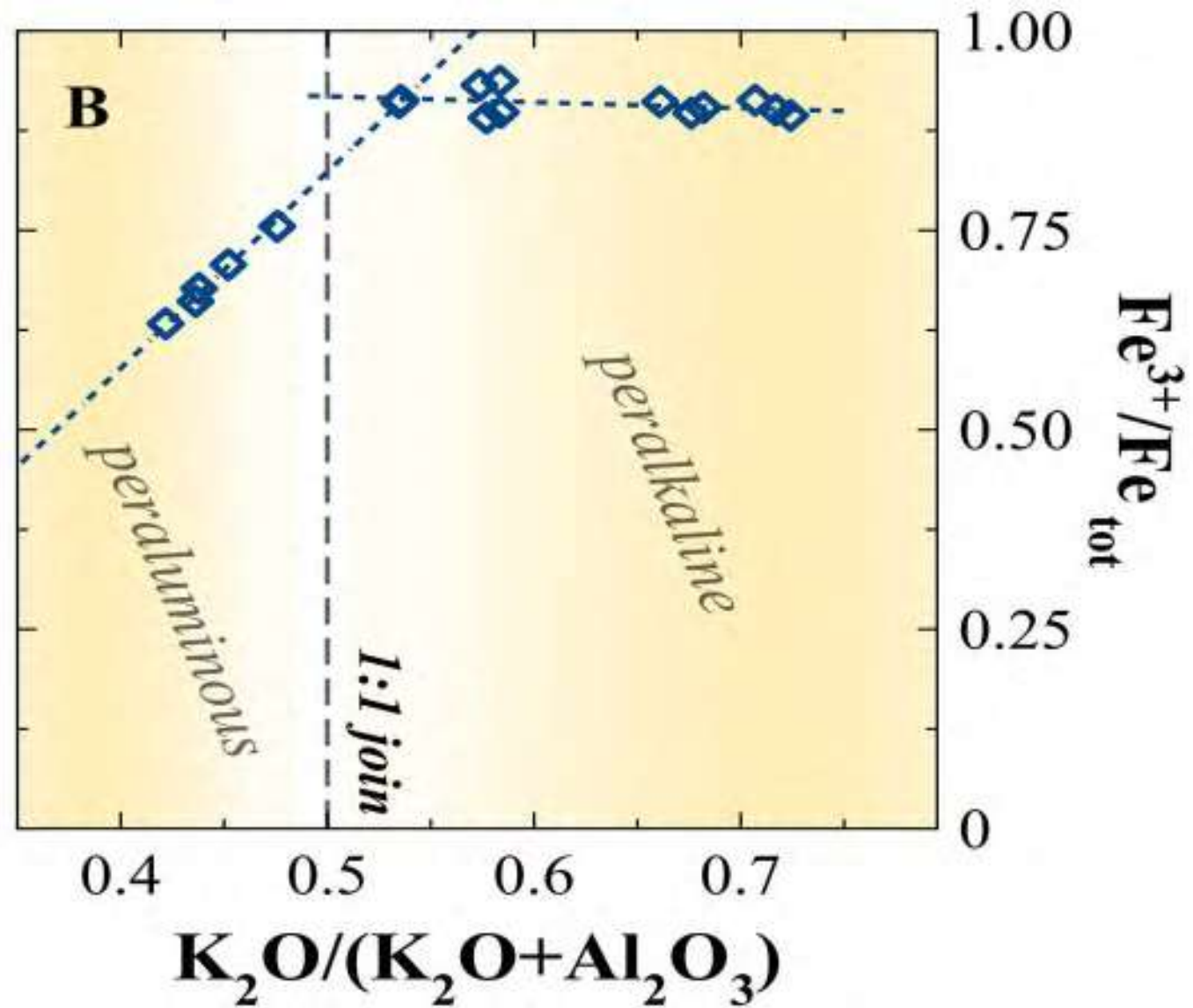


How redox vary as a function of chemical composition, T and f_{O_2} ?



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

How redox vary as a function of chemical composition?



Dickenson MP, Hess PC (1982) Redox equilibria and the structural role of iron in aluminosilicate melts. *Contributions to Mineralogy and Petrology* 78:352–357

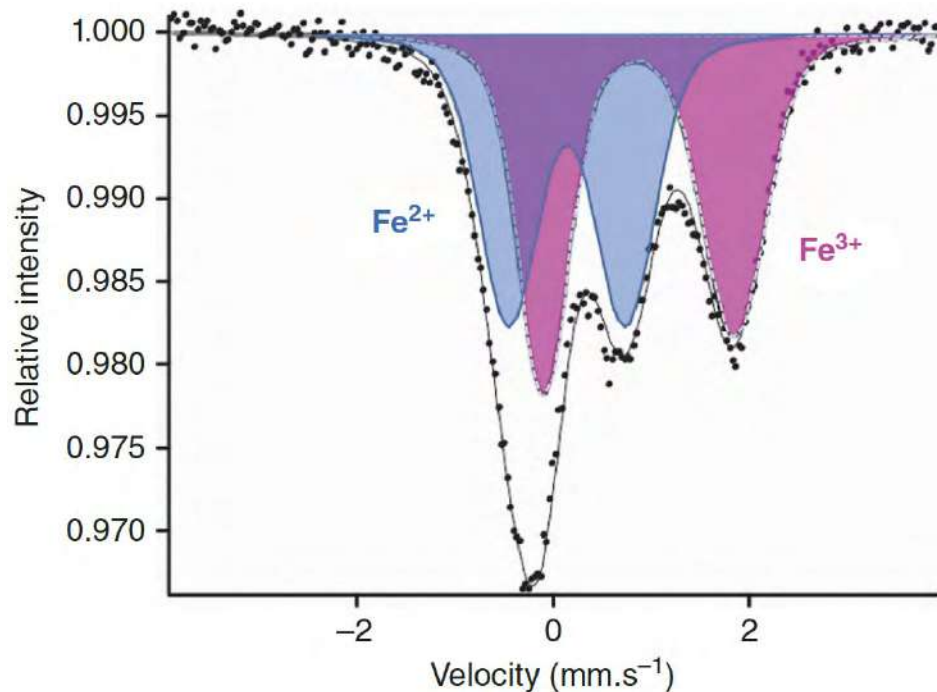
How to measure a redox state?



Wet chemistry analyzed

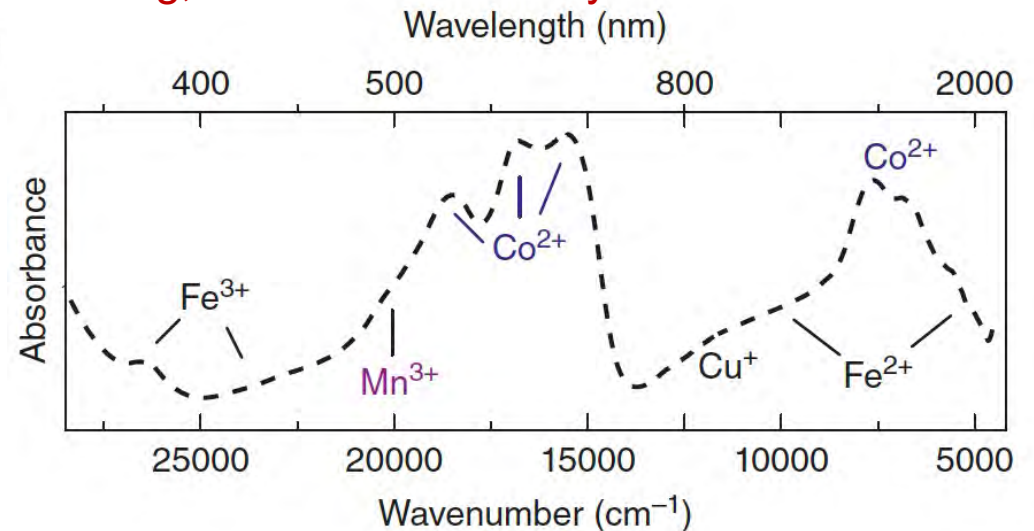
Wet chemistry FeO content,
sensitivity limit ≈ 10 ppm
Precision $\Delta = \pm 5$ ppm

Mossbauer spectroscopy



Optical spectroscopy

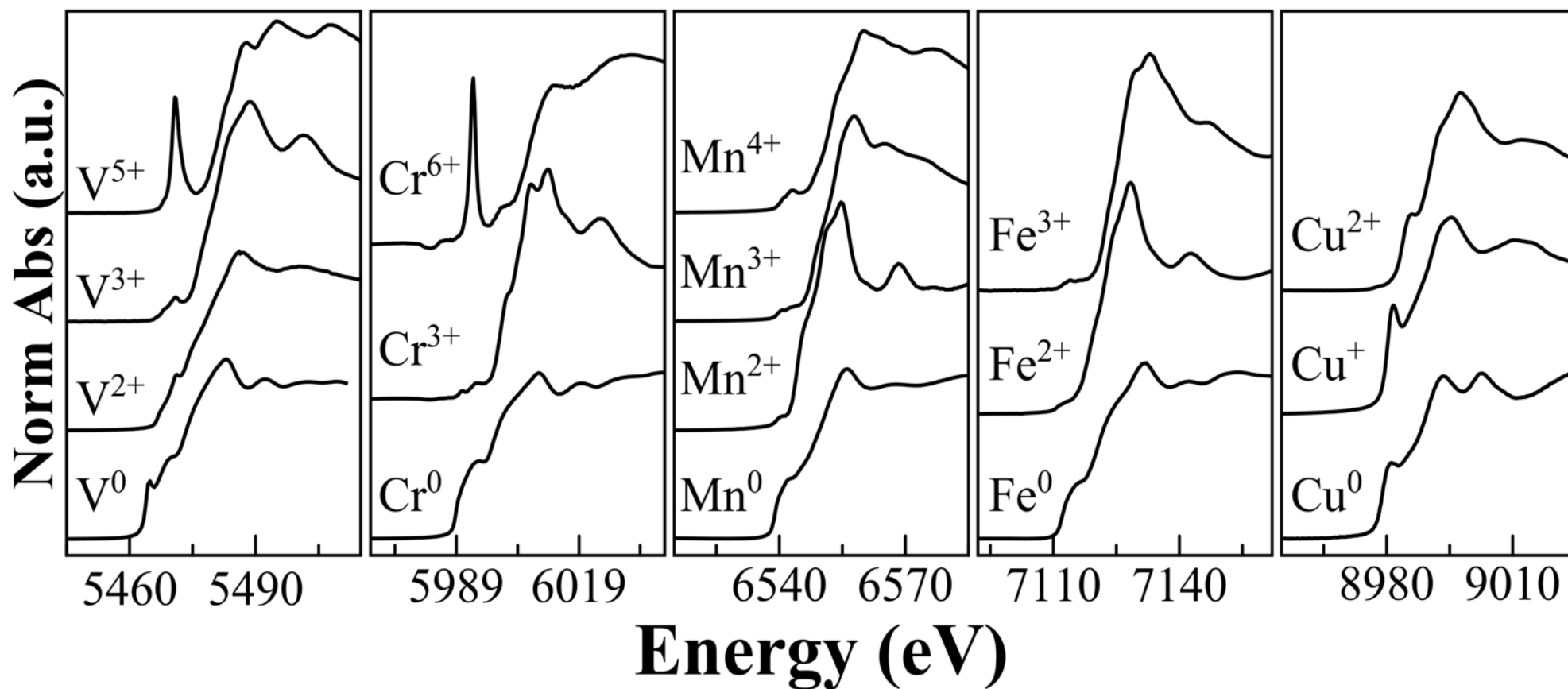
=> possible at HT, Laurent Cormier or Gérald Lelong, Sorbonne University



Limitations:

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

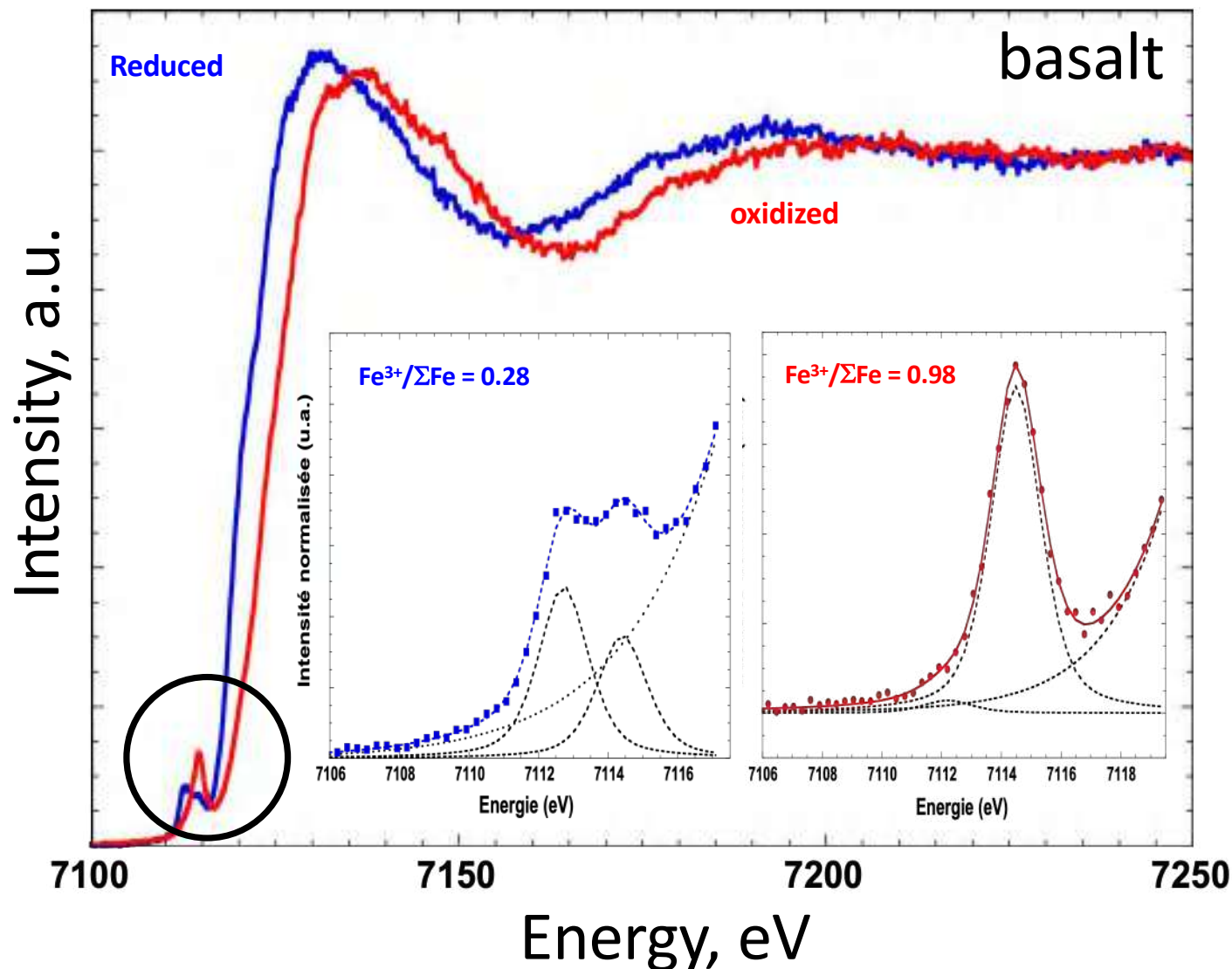
Neuvill D.R., Cicconi M.R. (2021) How measure a redox state?
Magma Redox Geochemistry. AGU Geophysical Monography Series
eds Moretti and Neuvill. – DOI : 10.1002/9781119473206.ch13



XANES possible for almost all elements depend on light source

Possible measurement at HT, HP, mapping.....

Determination of iron redox by Fe-K edge XANES



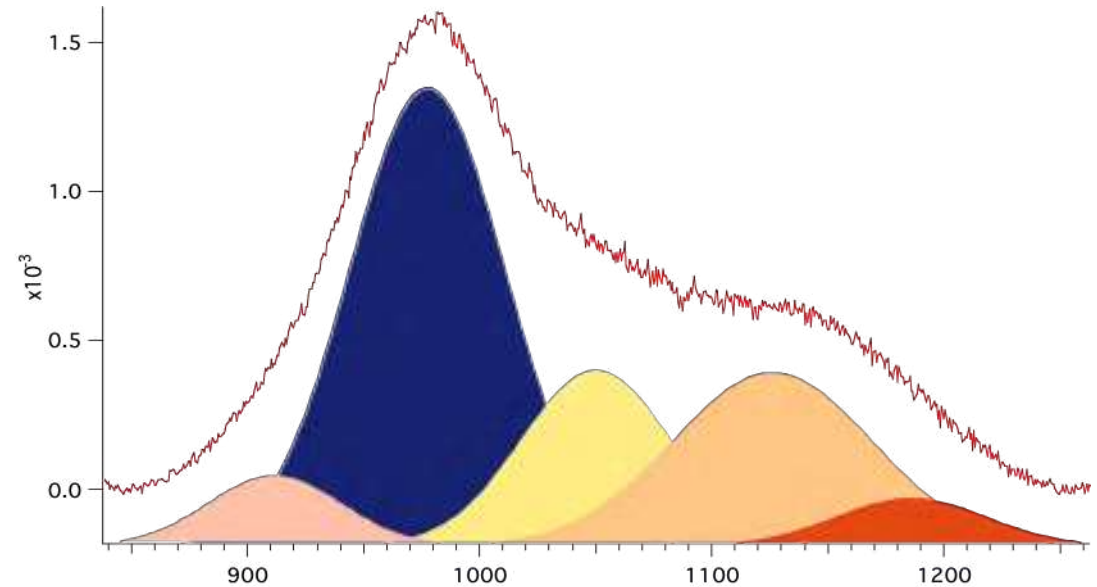
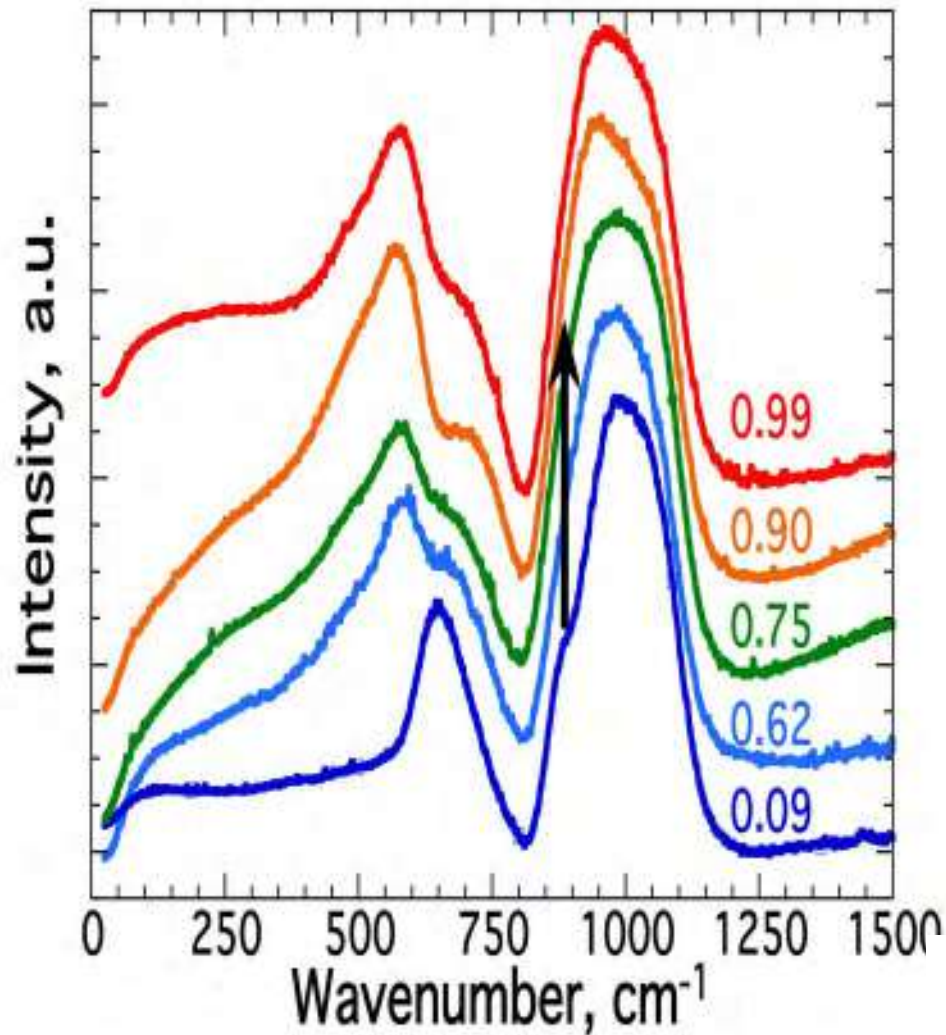
Iron K-edge: redox state and local structure

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. Baudalet**, 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



Evidence of Fe³⁺ in tetrahedral coordination in Q⁴:

- Mössbauer => center shift < 0.30mm/s (Mysen, 1983; Alberto et al. 1996)
- Iron K-edge XANES => integrated pre-edge area characteristic for [4]Fe³⁺

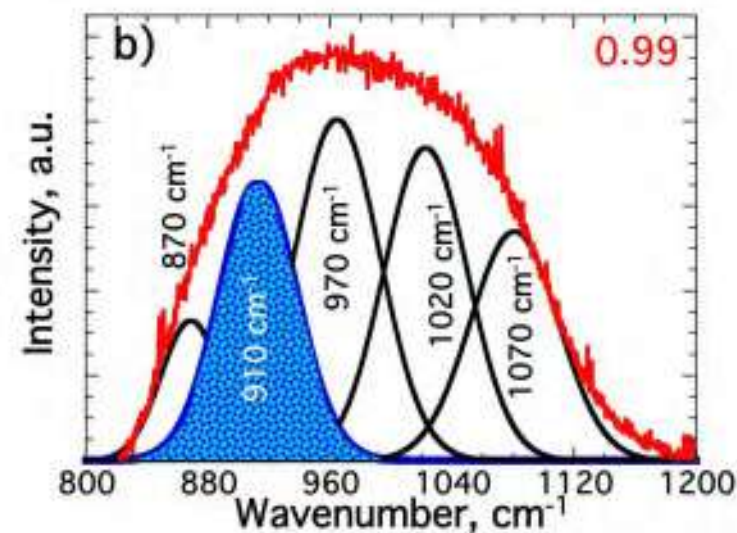
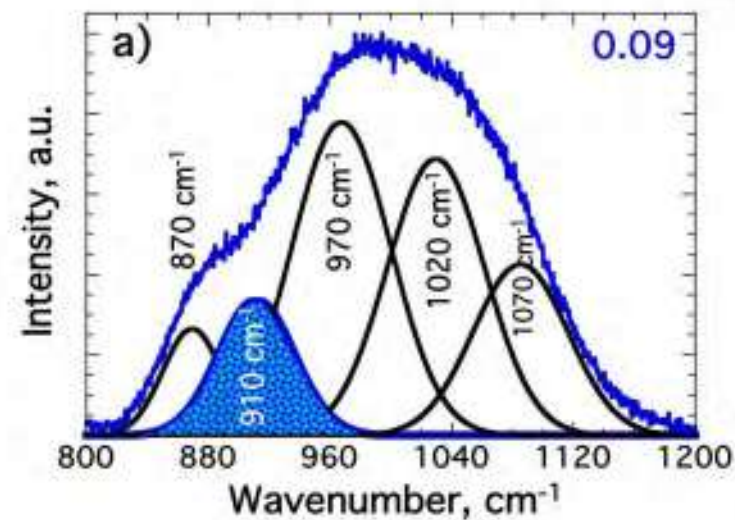
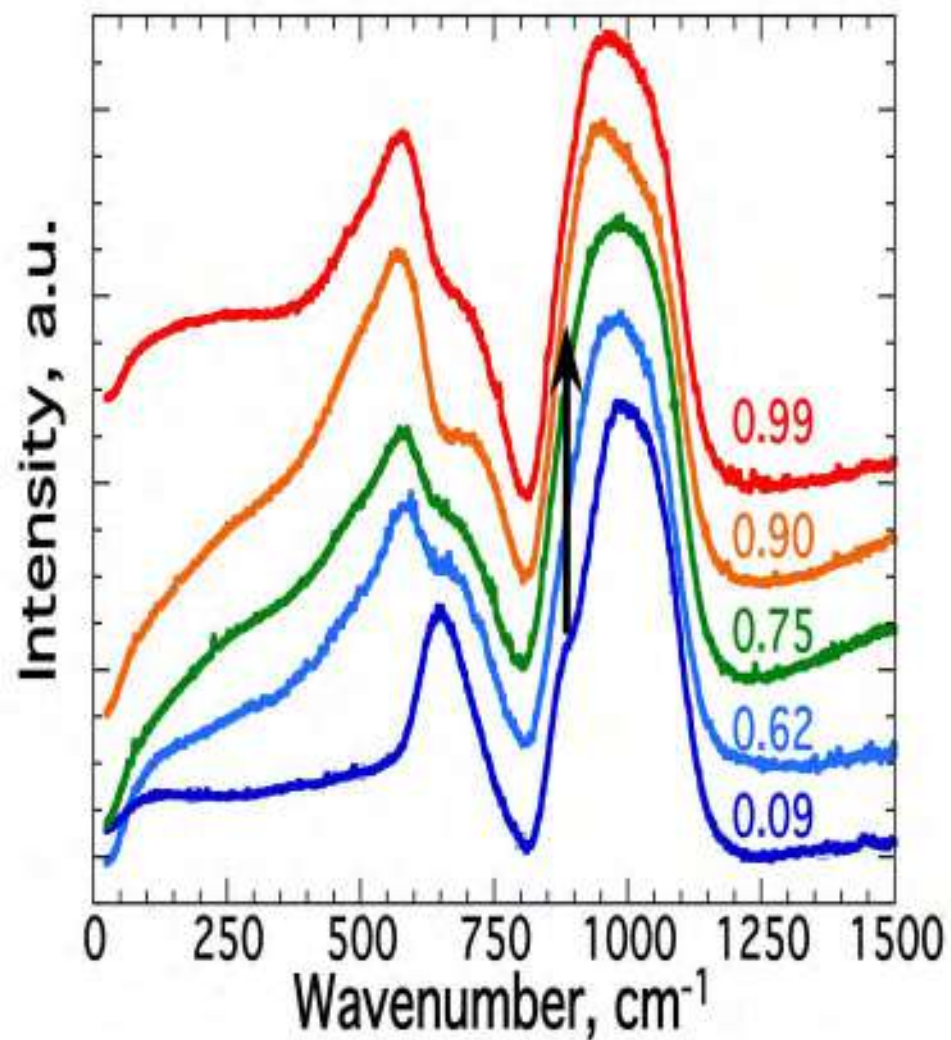
Bands of Q_n species (Q = Si, Al)



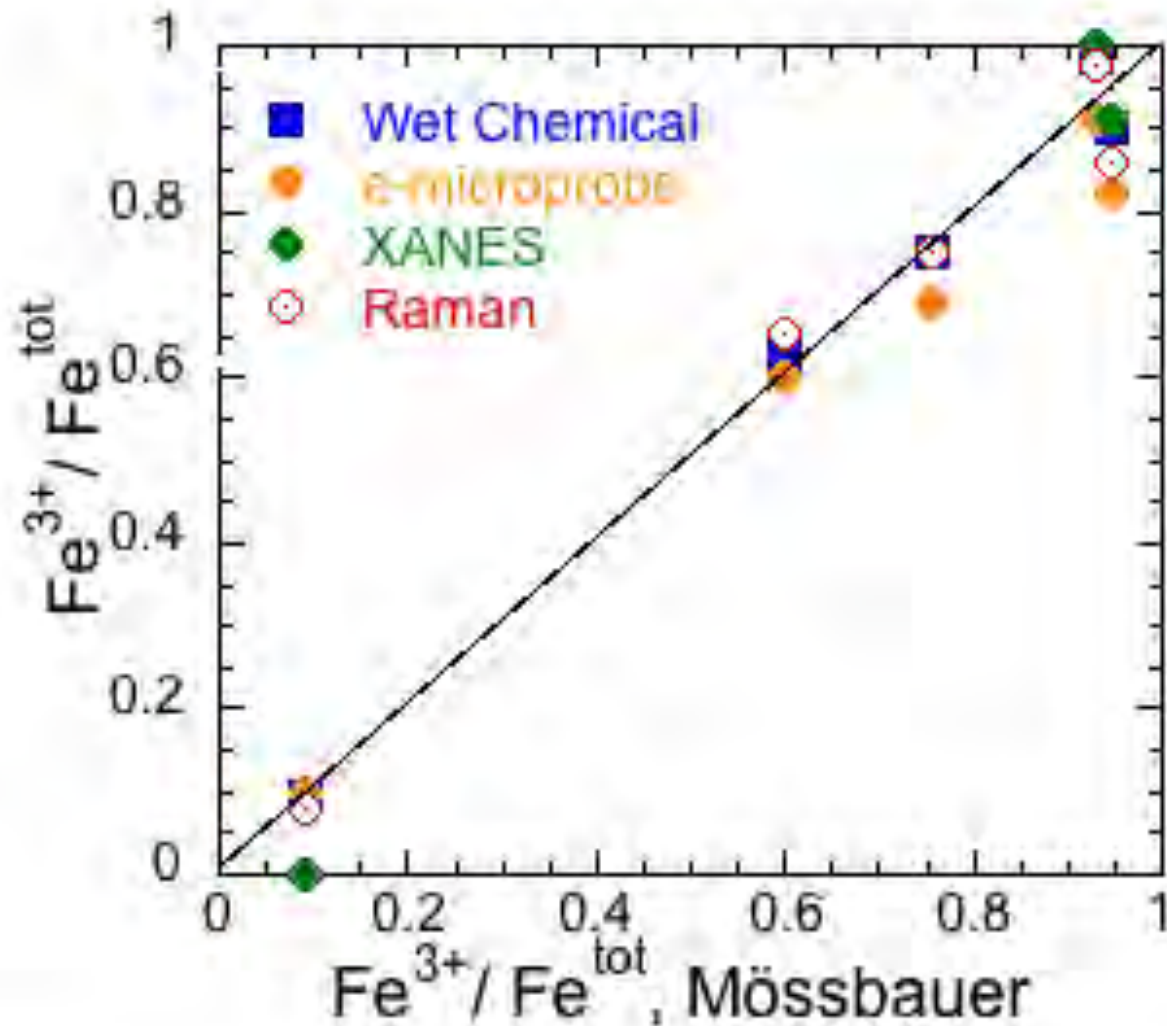
Magnien V., Neuville D.R., Cormier L., Roux J., Pinet O. and Richet P. (2006) Kinetics of iron redox reactions: A high-temperature XANES and Raman spectroscopy study. *Journal of Nuclear Materials*, 352, 190-195.

Raman spectroscopy

50%SiO₂-20%MgO-20%CaO-5%Na₂O-5%FeO

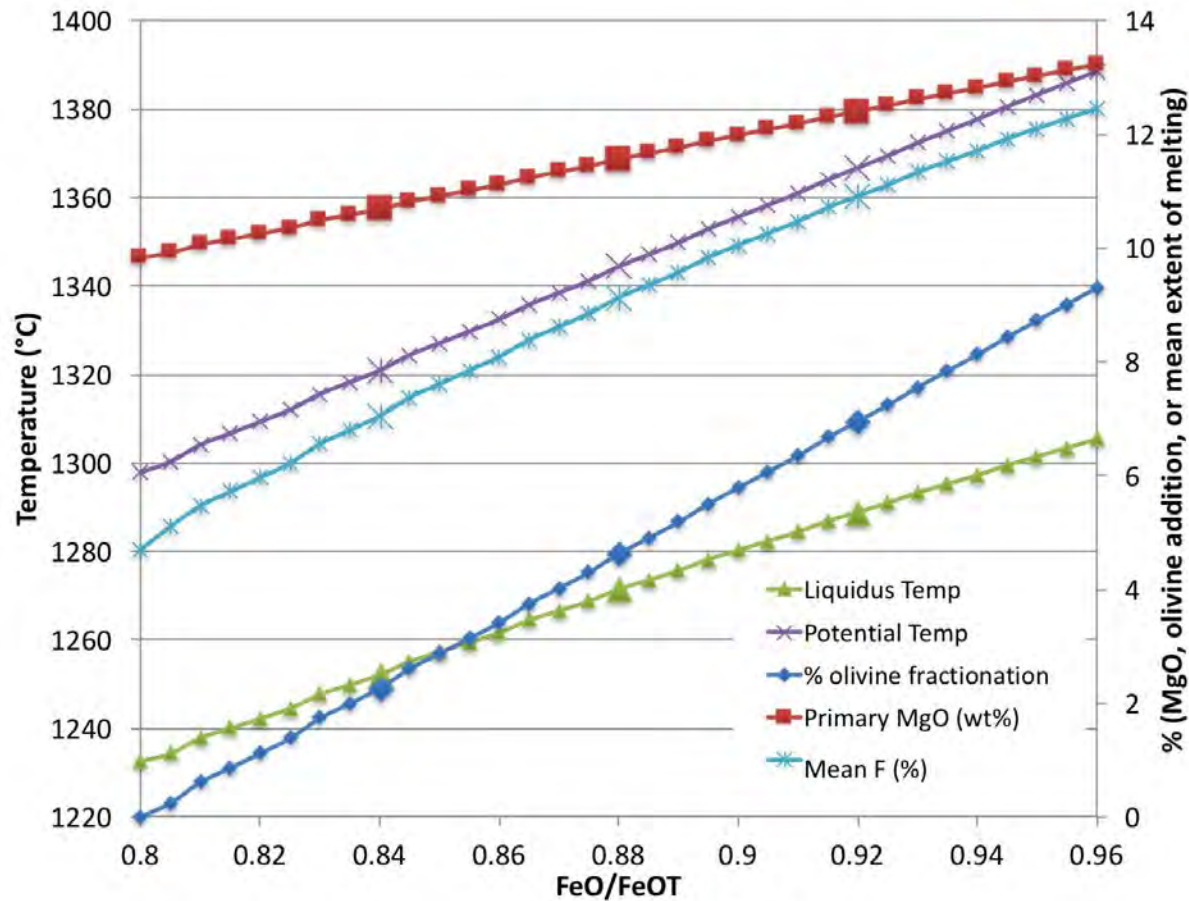


Magnien V., Neuville D.R., Cormier L., Roux J., Pinet O. and Richet P. (2006) Kinetics of iron redox reactions: A high-temperature XANES and Raman spectroscopy study. *Journal of Nuclear Materials*, 352, 190-195.



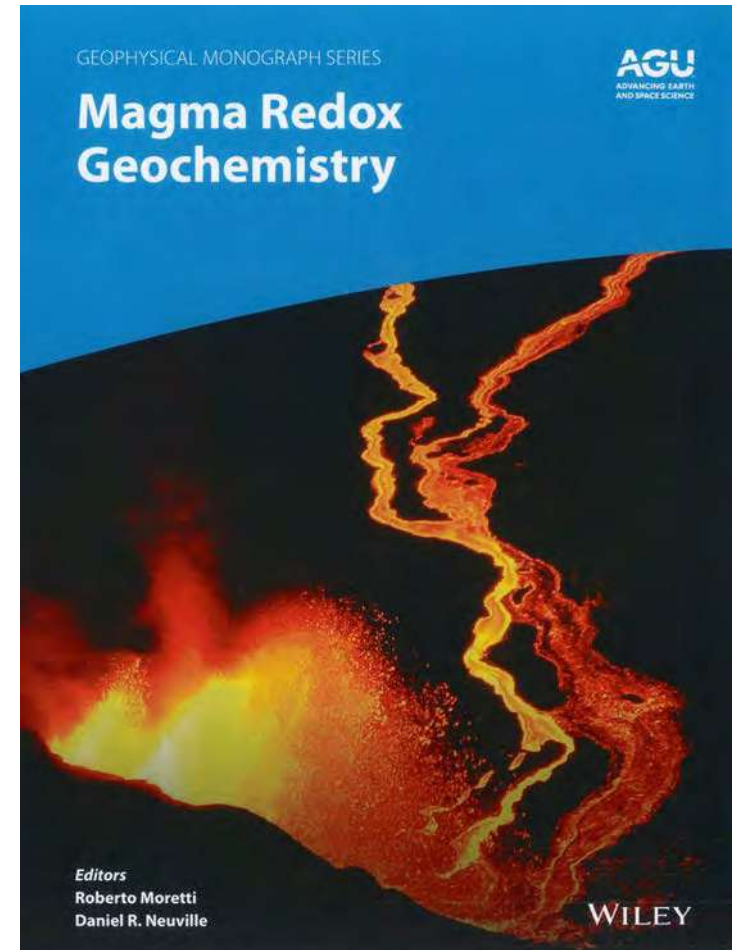
=> Good compatibility between different techniques

How liquidus temperature varies with redox ?

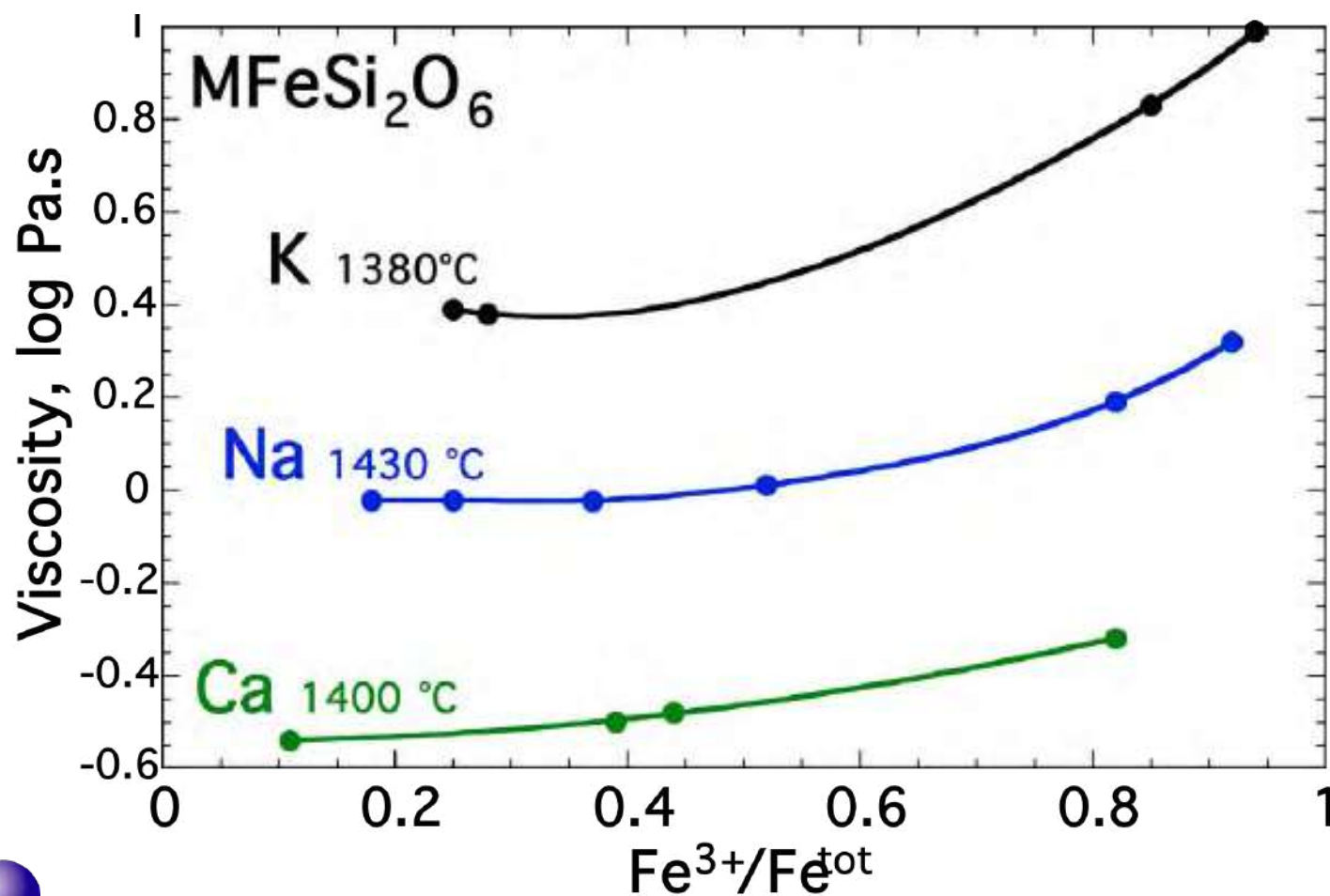


Redox can play a very important role on liquidus temperature, crystallization.... Glass transition....

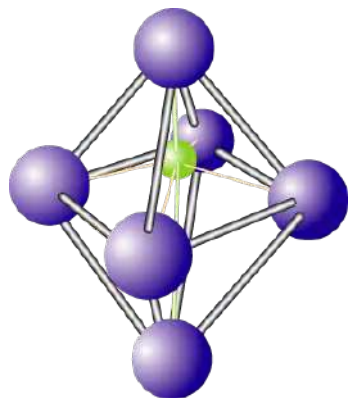
Asimow P. (2020) The petrological consequences of the estimated oxidation state of primitive MORB glass. AGU Monograph on Magma Redox Geochemistry ed by Moretti and Neuville.



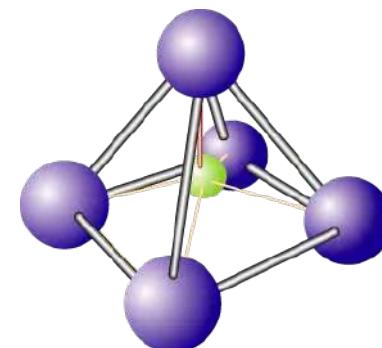
What is the role of redox on viscosities ?



[6]Fe²⁺



[4]Fe³⁺

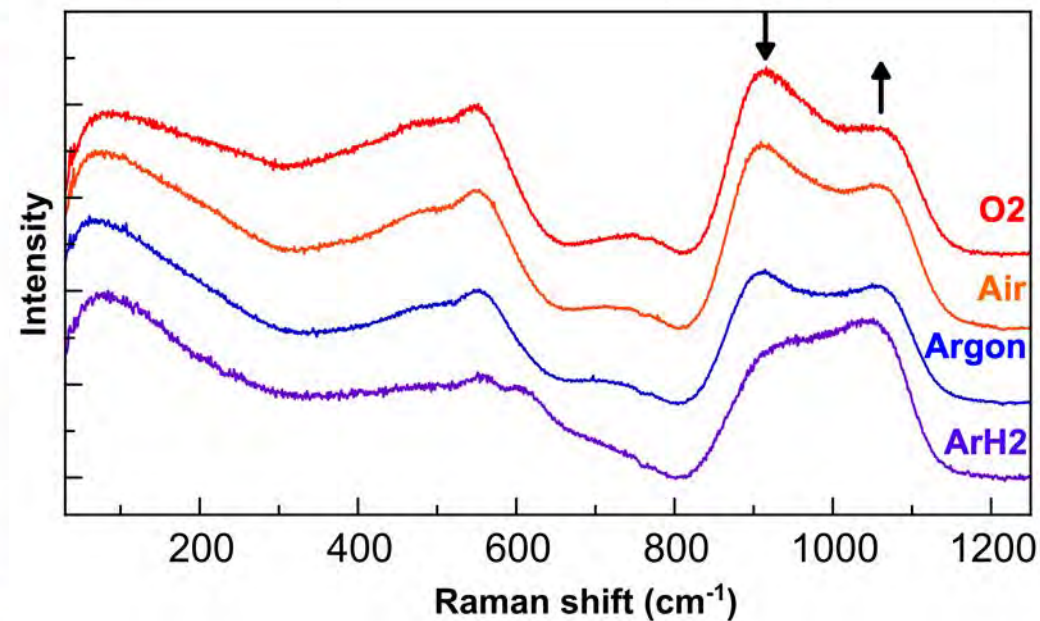
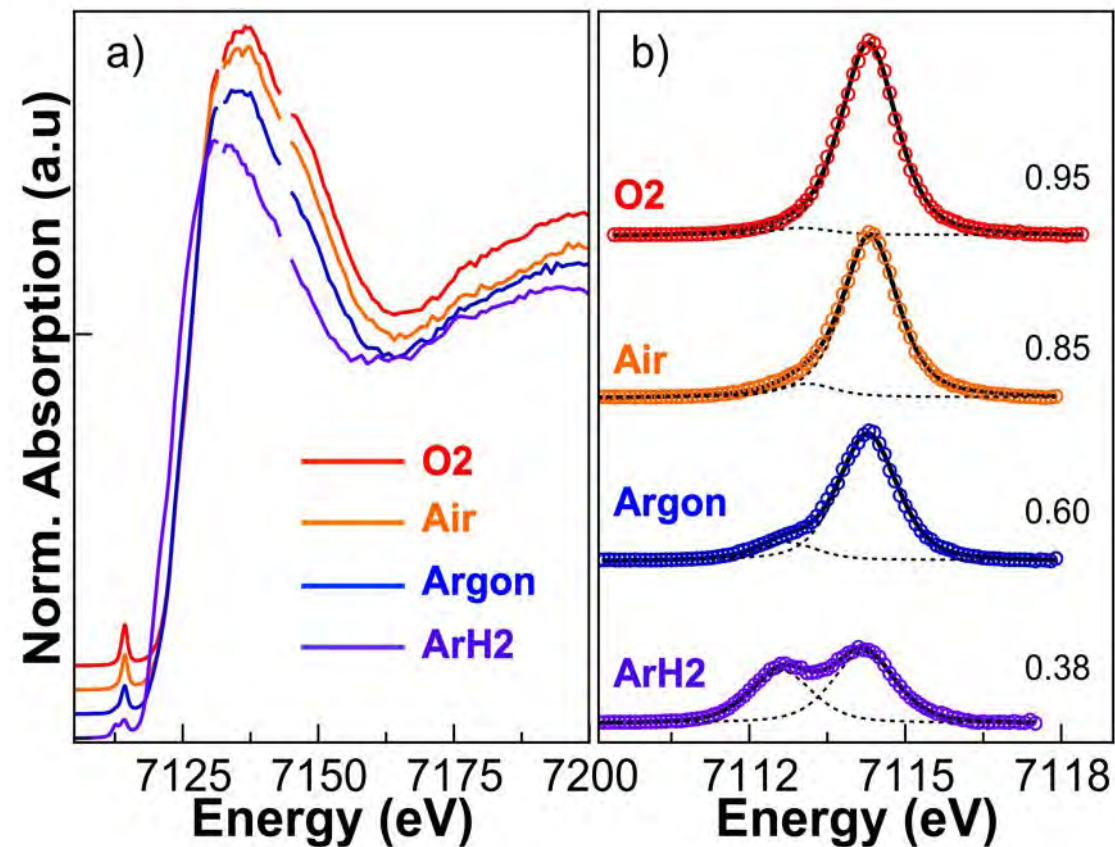


Dingwell (1991) Redox viscometry of some Fe-bearing silicate melts
American Mineralogist, Volume 76, pages 1560-1562.

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

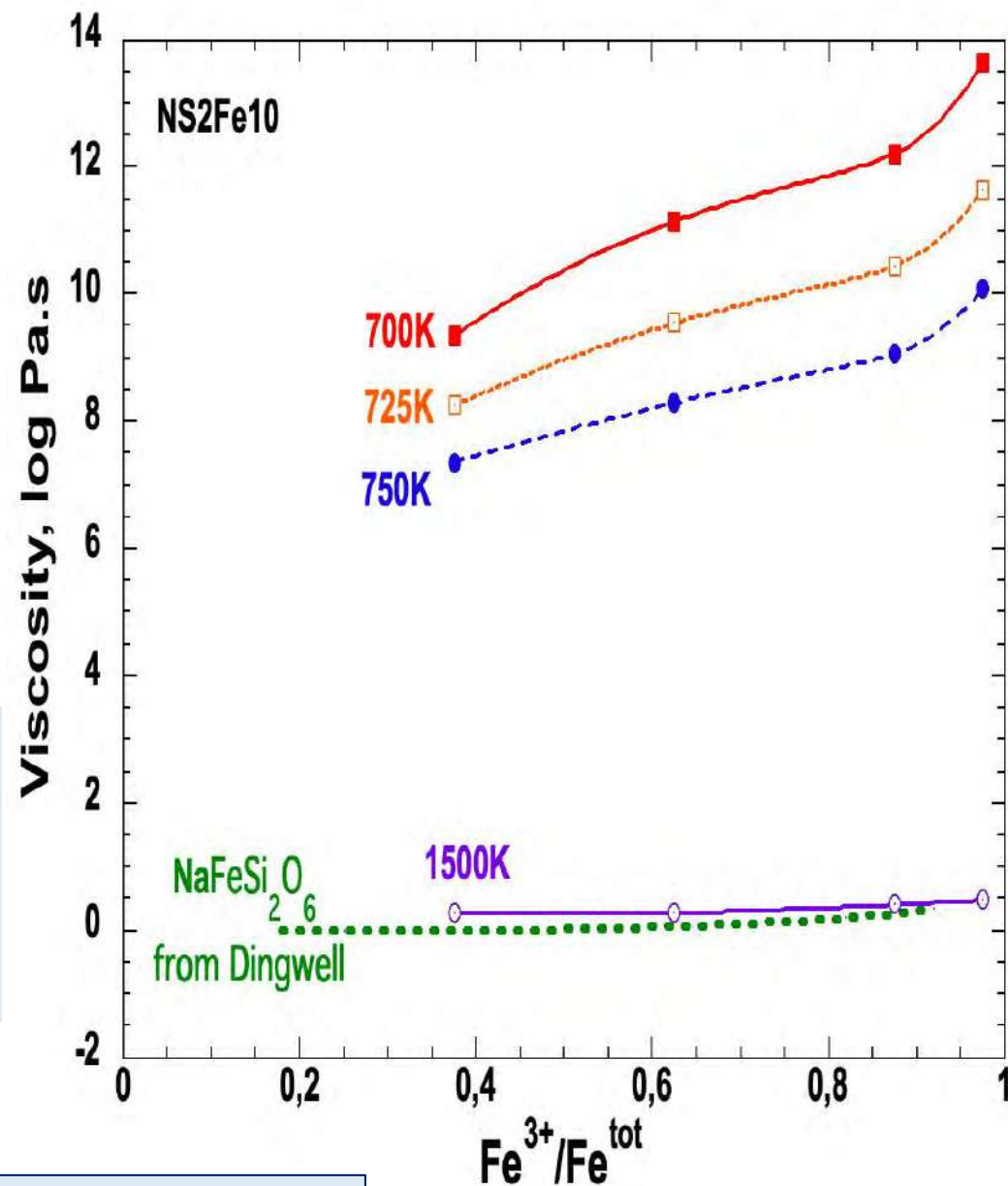
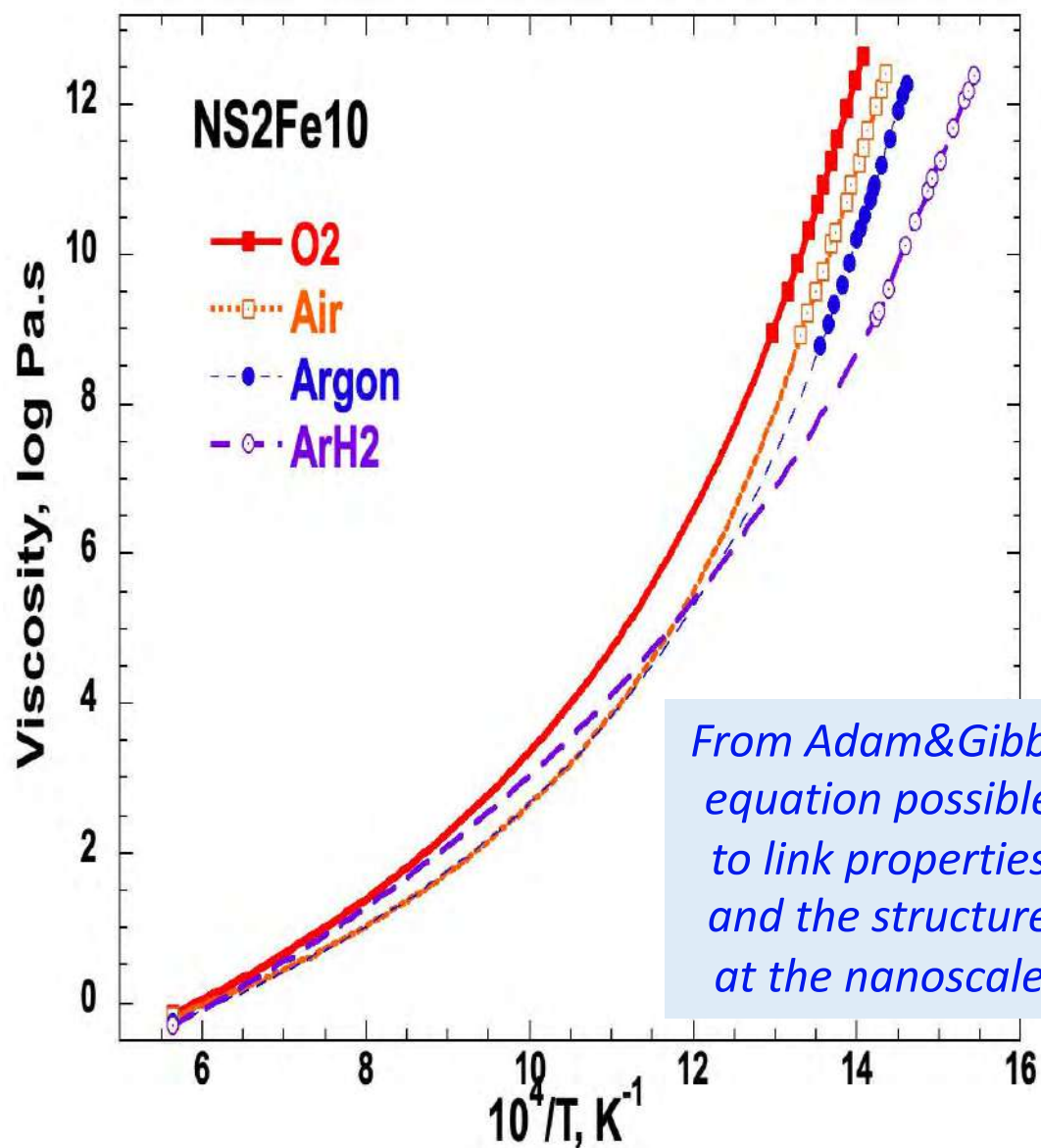
54.6SiO₂-27.2Na₂O-18.2FeO (mol%)

	O ₂	Air	Argon	ArH ₂
SiO ₂	54.8	55.5	54.8	56.7
Na ₂ O	27.1	26.4	26.9	26.6
FeO _{tot} ^a	18.1	18.1	18.3	16.7
Fe ³⁺ /Fe ^{tot} ^b	0.95	0.85	0.60	0.38
Si/Fe ^c	3.0	3.1	3.0	3.4
d, 10 ³ kg/m ³	2.755(2)	2.768(3)	2.782(2)	2.817(1)
V ^d , m ³ /mol	25.5	25.1	24.2	23.1
T _g ^e , K	720	702	688	654



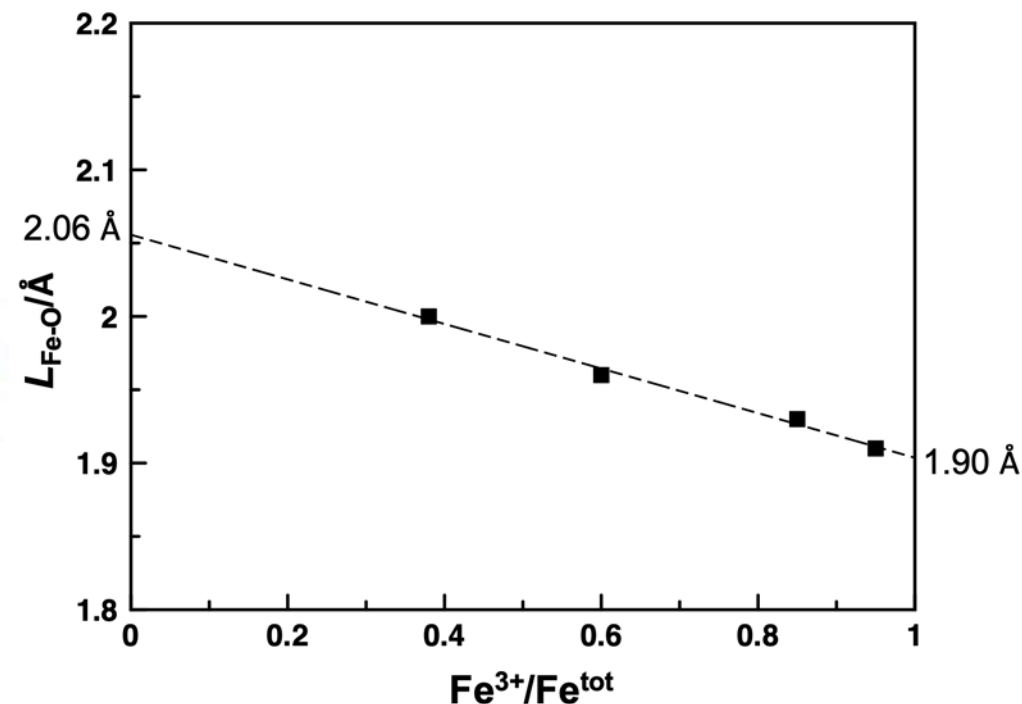
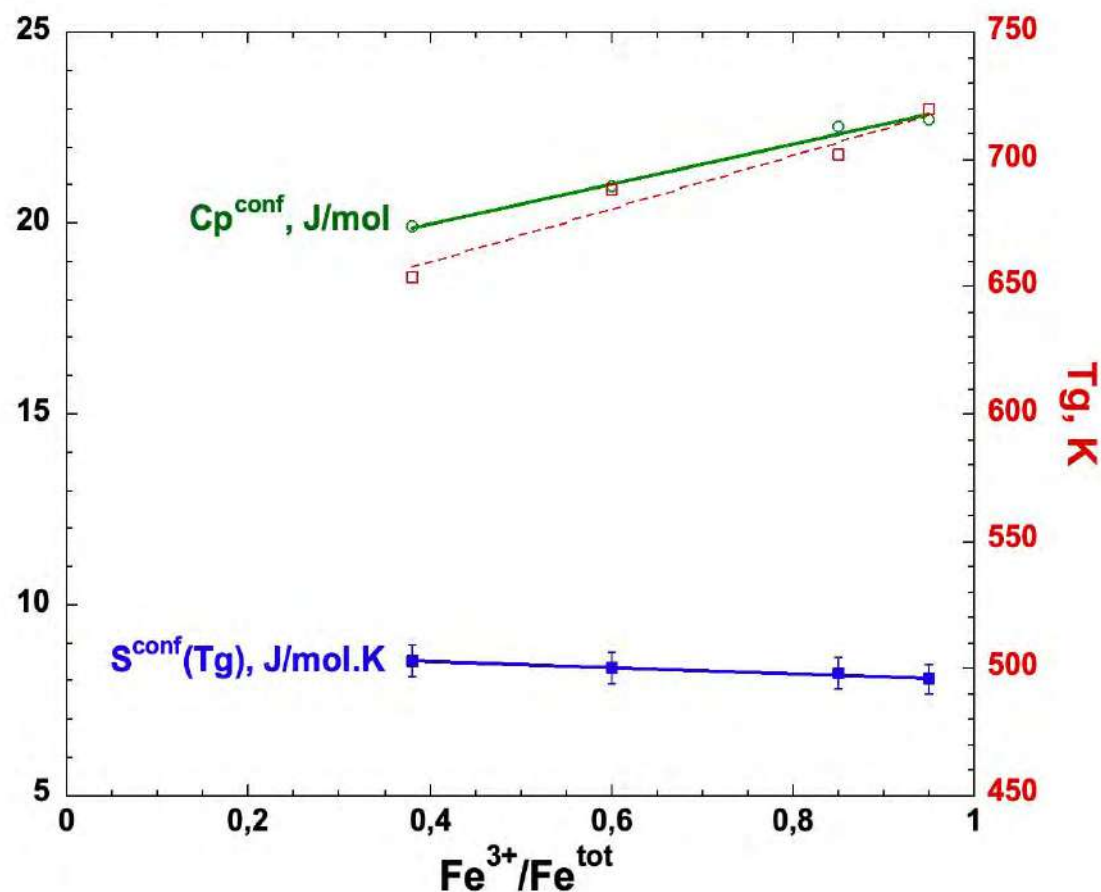
Sukenaga S., Yamada H., Wakiyara T., Cicconi M.R., Ohara K., Shibata H., and Neuville D.R. (2024) Redox effect on the viscosity of silicate glasses and melts. The Journal of Chemical Physics. DOI: 10.1063/5.0243427

- What is the role of redox on viscosities ?



Sukenaga S., Yamada H., Wakiyama T., Cicconi M.R., Ohara K., Shibata H., and Neuville D.R. (2024) Redox effect on the viscosity of silicate glasses and melts. The Journal of Chemical Physics. DOI: 10.1063/5.0243427

What is the role of redox on viscosities ?



$\text{IVFe}^{3+}\text{-O} \sim 1.86 \text{ \AA}$

$\text{VIFe}^{2+}\text{-O} \sim 2.06 \text{ \AA}$

In good agreement with neutron diffraction of Drewitt et al., (2023)

Tg increases with $\text{Fe}^{3+}/\text{Fe}^{\text{tot}}$ ratio
 $S^{\text{conf}}(\text{Tg})$ decreases with $\text{Fe}^{3+}/\text{Fe}^{\text{tot}}$ ratio
 IVFe^{3+} can play as a network former

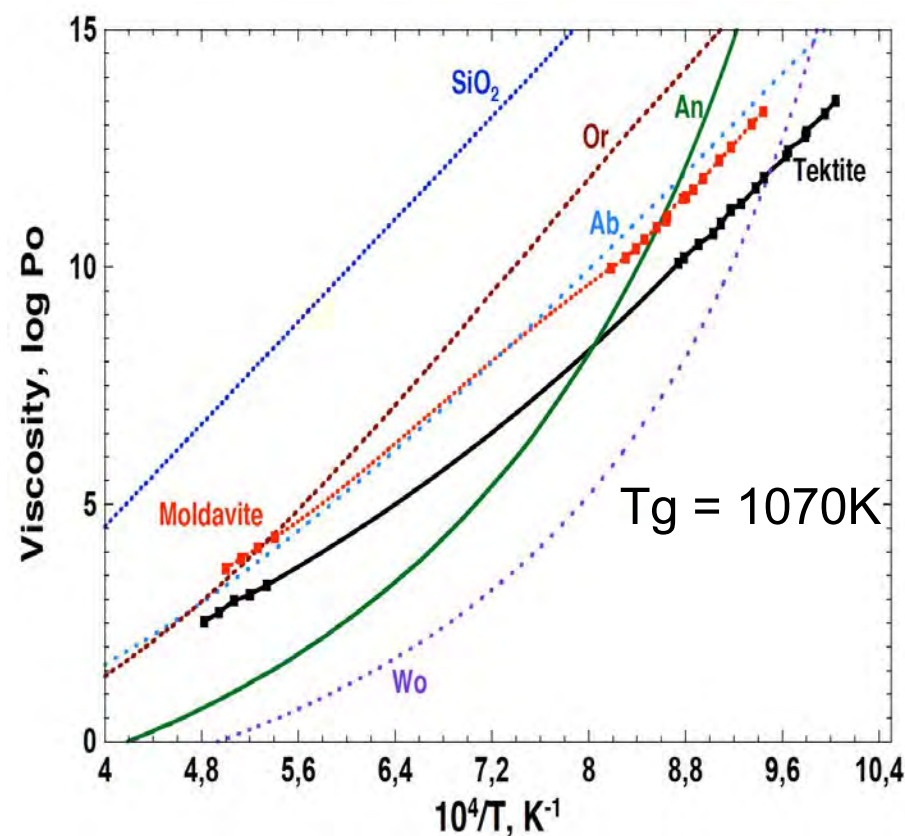
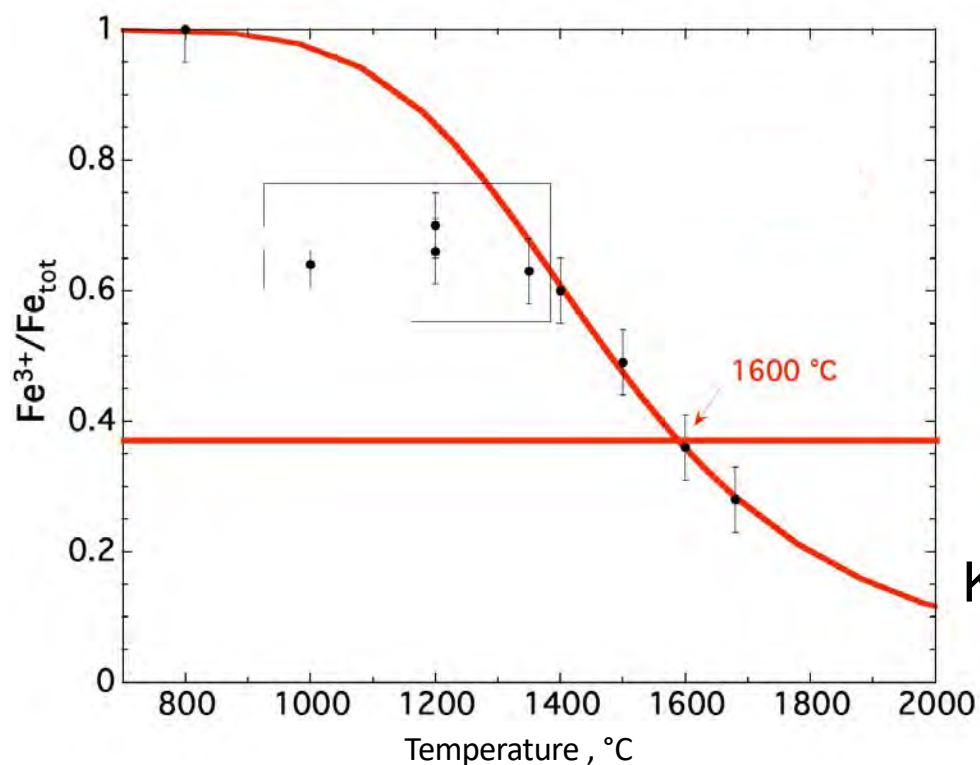
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Drewitt J.W.E, Barnes, A.C., Jahn S., Brooker R., Hennet L., Neuville D.R., Fisher H.E. (2023) Direct measurement of iron coordination in levitated liquid FeAl_2O_4 using neutron diffraction with isotope substitution. Philosophical Transaction of the Royal Society A. <https://doi.org/10.1098/rsta.2022.0351>

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)

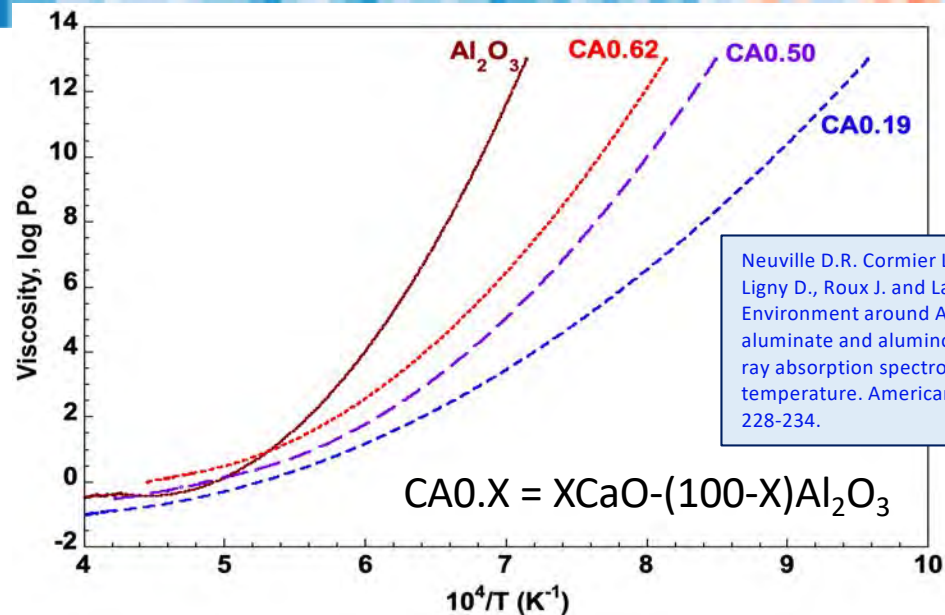
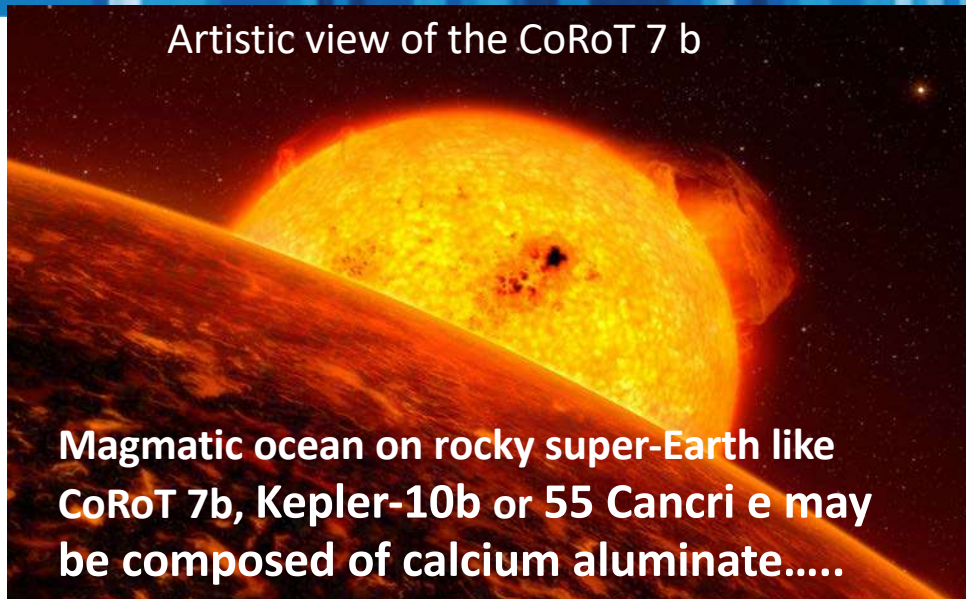


← Redox of the tektite

Kress&Carmichael redox curve

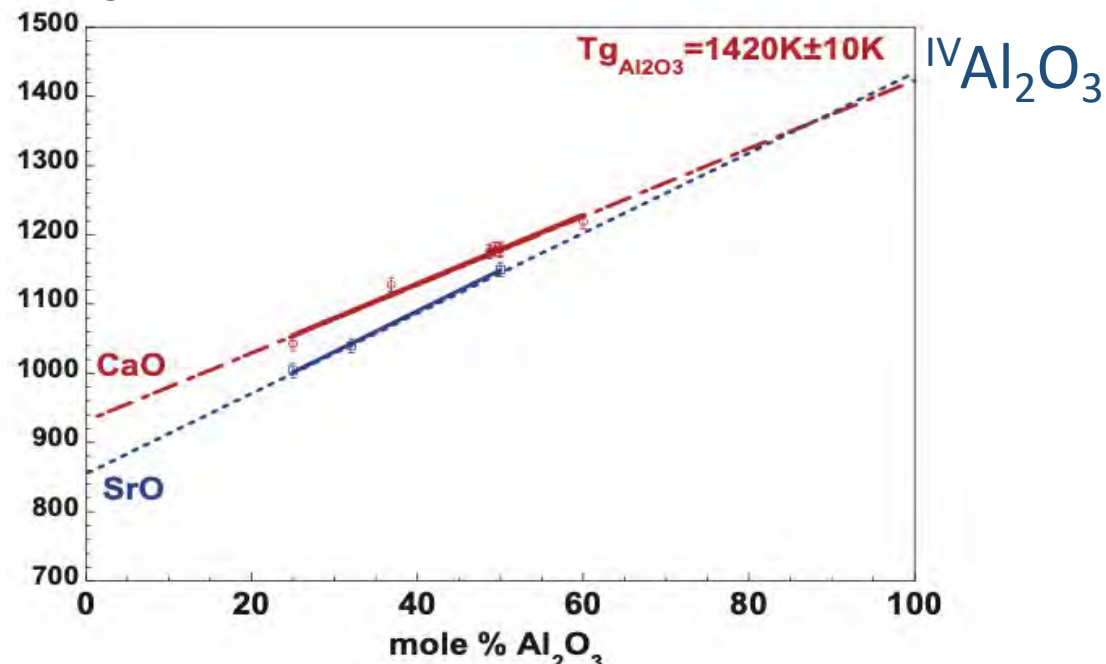
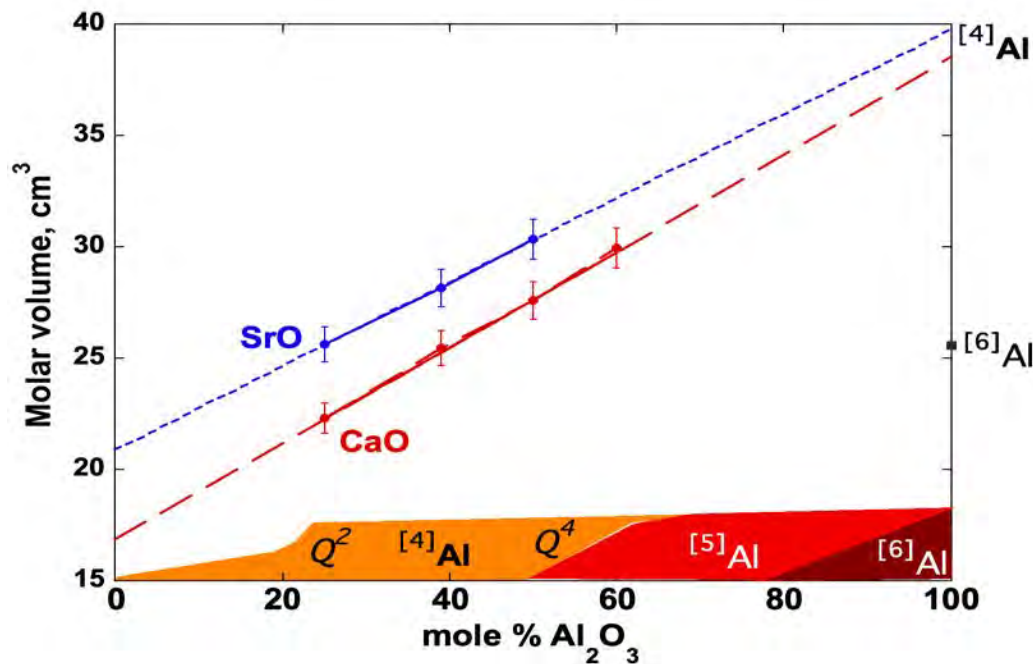
Cicconi M.R., Neuville D.R. (2019) Natural glasses. Springer Handbook of Glass. 771-804 – DOI 10.1007/978-3-319-93728-1

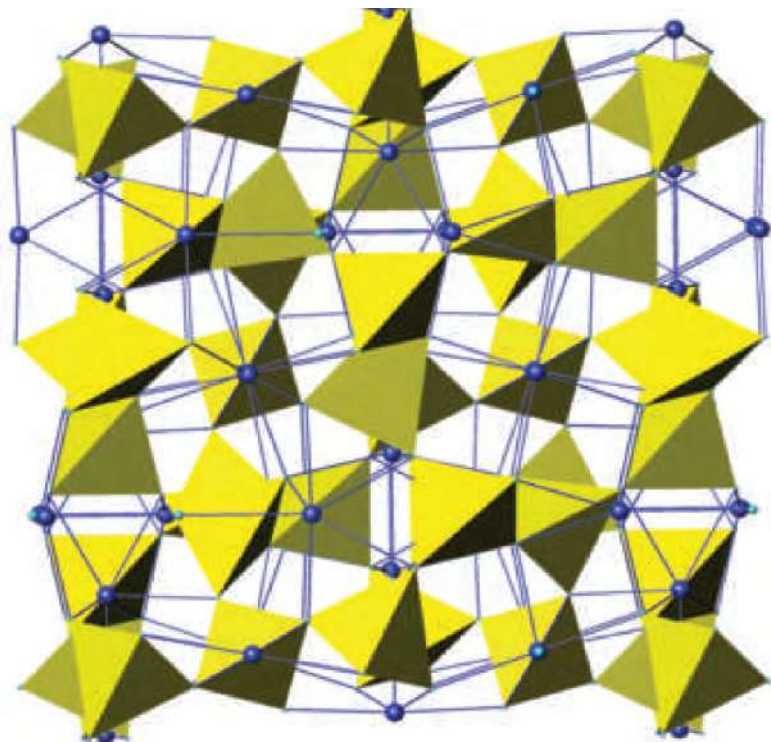
Iron in calcium aluminate melts



Neuville D.R. Cormier L., Flank AM, de Ligny D., Roux J. and Lagarde P. (2008) Environment around Al, Si and Ca in aluminate and aluminosilicate melts by X-ray absorption spectroscopy at high temperature. American Mineralogist, 93, 228-234.

CaO- Al_2O_3



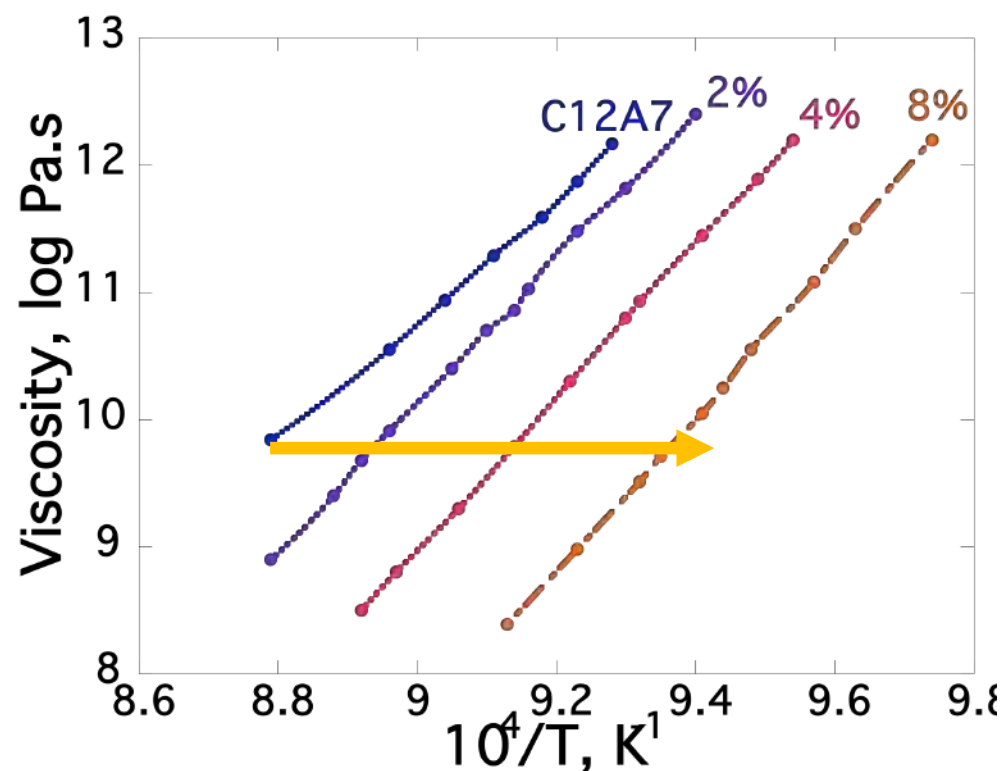


Neuvillle D.R., Henderson G.S., Cormier L., Massiot D. (2010) Structure of CaO-Al₂O₃ crystal, glasses and liquids, using X-ray absorption at Al L and K edges and NMR spectroscopy. American Mineralogist, 95, 1580-1589.

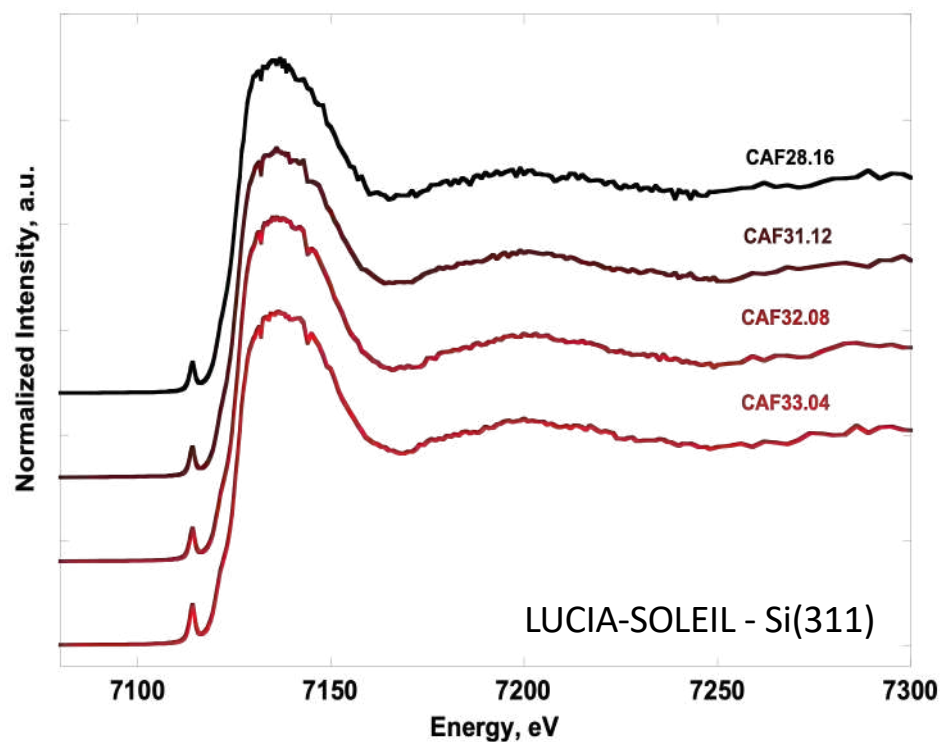
Glasses	%CaO	%Al ₂ O ₃	%Fe ₂ O ₃	Density	T _g (K)
CAF37.00	48.8(0.9)	51.2(1.0)	0.0	2.909(5)	1117.5
CAF35.00	52.1(1.0)	46.2(0.9)	0.0	2.907(3)	1087.0
CAF35.02	46.5(0.9)	47.8(0.9)	3.9(0.0)	2.940(4)	1091.4
CAF33.04	45.7(0.9)	44.3((0.9)	8.7(0.2)	2.987(2)	1060.6
CAF32.08	41.8(0.8)	40.5(0.8)	16.7(0.3)	3.067(5)	1033.9
CAF31.12	37.2(0.7)	38.0(0.8)	23.5(0.5)	3.160(5)	1018.9
CAF28.16	34.7(0.7)	33.3(0.7)	30.2(0.6)	3.232(4)	991.2

El Hayek R., Ferey F., Florian P., Pisch A. and Neuvillle D.R. (2017) Structure and properties of lime alumino-borate glasses and melts. Chemical Geology, 461, 75-81.

C12A7 glass : Al in only Q⁴ species and Ca in 6 fold coordination

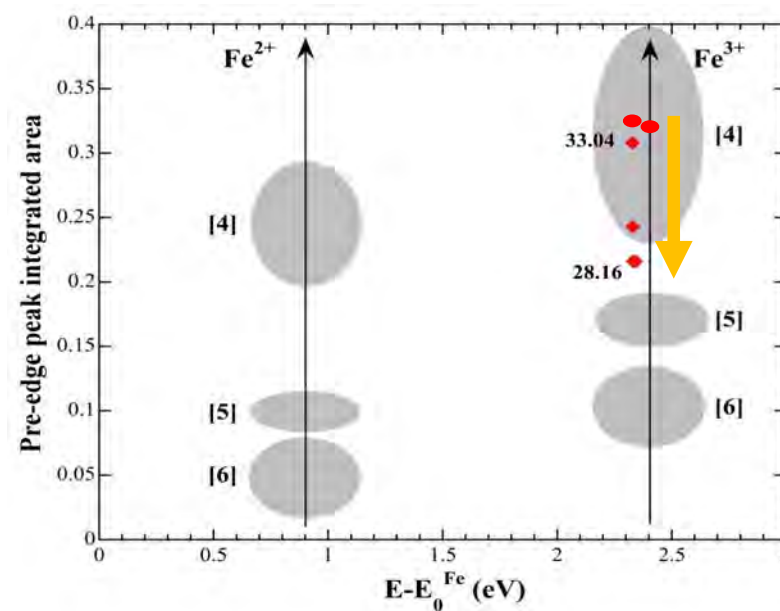
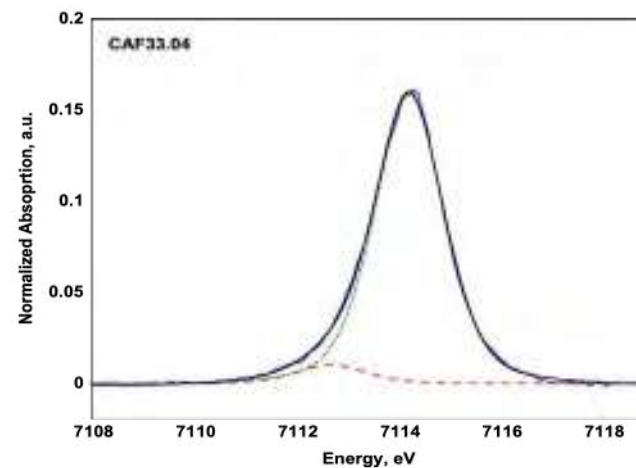


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CAF31.12	37.2(0.7)	38.0(0.8)	23.5(0.5)	3.160(5)	1018.9
CAF28.16	34.7(0.7)	33.3(0.7)	30.2(0.6)	3.232(4)	991.2

El Hayek R., Ferey F., Florian P., Pisch A. and Neuville D.R. (2017) Structure and properties of lime aluminoborate glasses and melts. *Chemical Geology*, 461, 75-81.

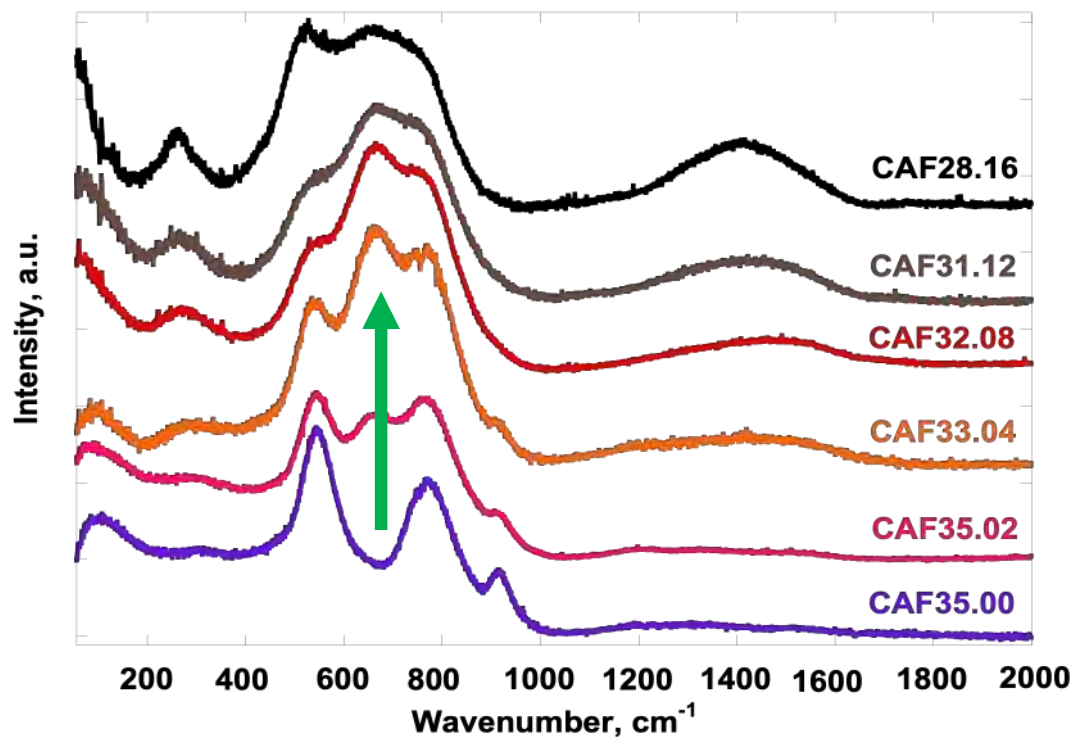


CN of Fe³⁺ increases with Fe^{tot}

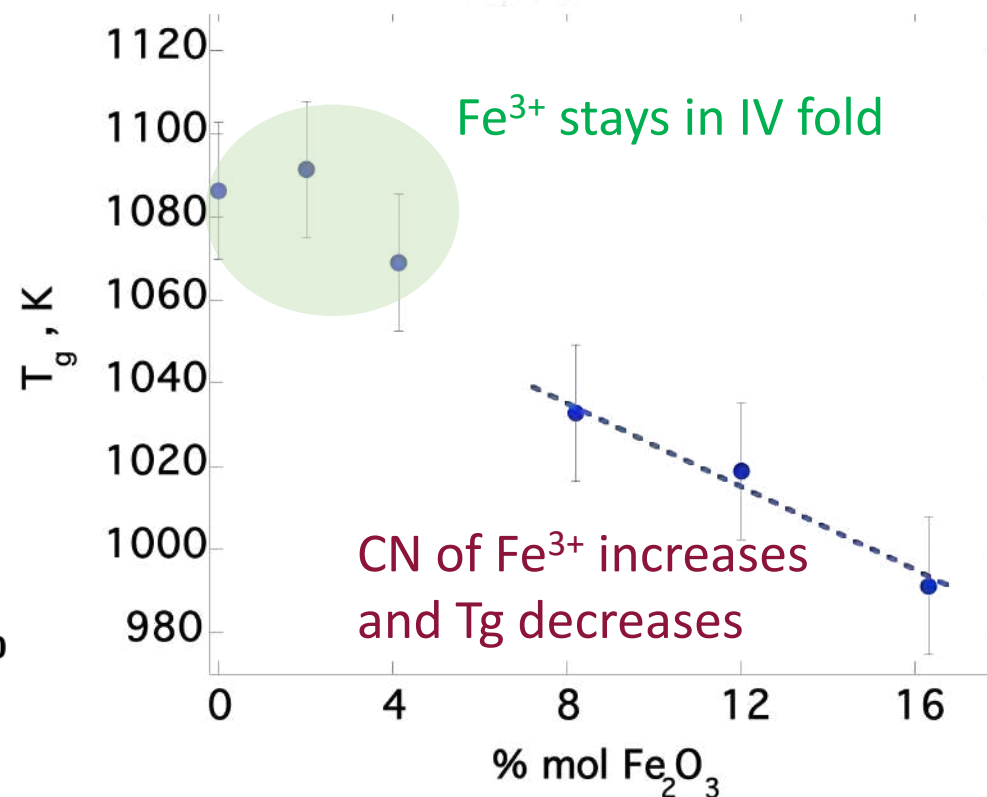
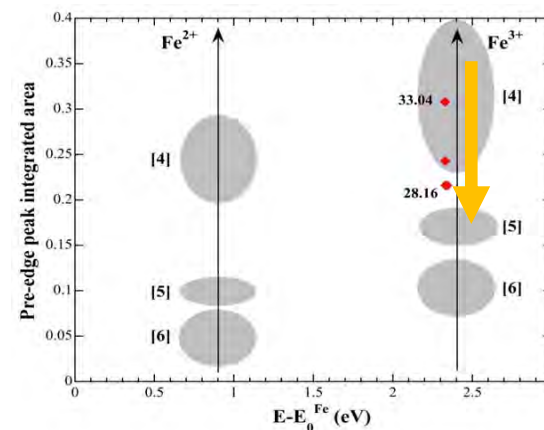
El Hayek, Cicconi, Ferey, Pisch, Vantelon and Neuville (2026) Role of iron on calcium aluminate glasses and melts. *Glass Europe*

Iron in calcium aluminate melts

Glasses	%CaO	%Al ₂ O ₃	%Fe ₂ O ₃	Density	T _g (K)
CAF37.00	48.8(0.9)	51.2(1.0)	0.0	2.909(5)	1117.5
CAF35.00	52.1(1.0)	46.2(0.9)	0.0	2.907(3)	1087.0
CAF35.02	46.5(0.9)	47.8(0.9)	3.9(0.0)	2.940(4)	1091.4
CAF33.04	45.7(0.9)	44.3((0.9)	8.7(0.2)	2.987(2)	1060.6
CAF32.08	41.8(0.8)	40.5(0.8)	16.7(0.3)	3.067(5)	1033.9
CAF31.12	37.2(0.7)	38.0(0.8)	23.5(0.5)	3.160(5)	1018.9
CAF28.16	34.7(0.7)	33.3(0.7)	30.2(0.6)	3.232(4)	991.2

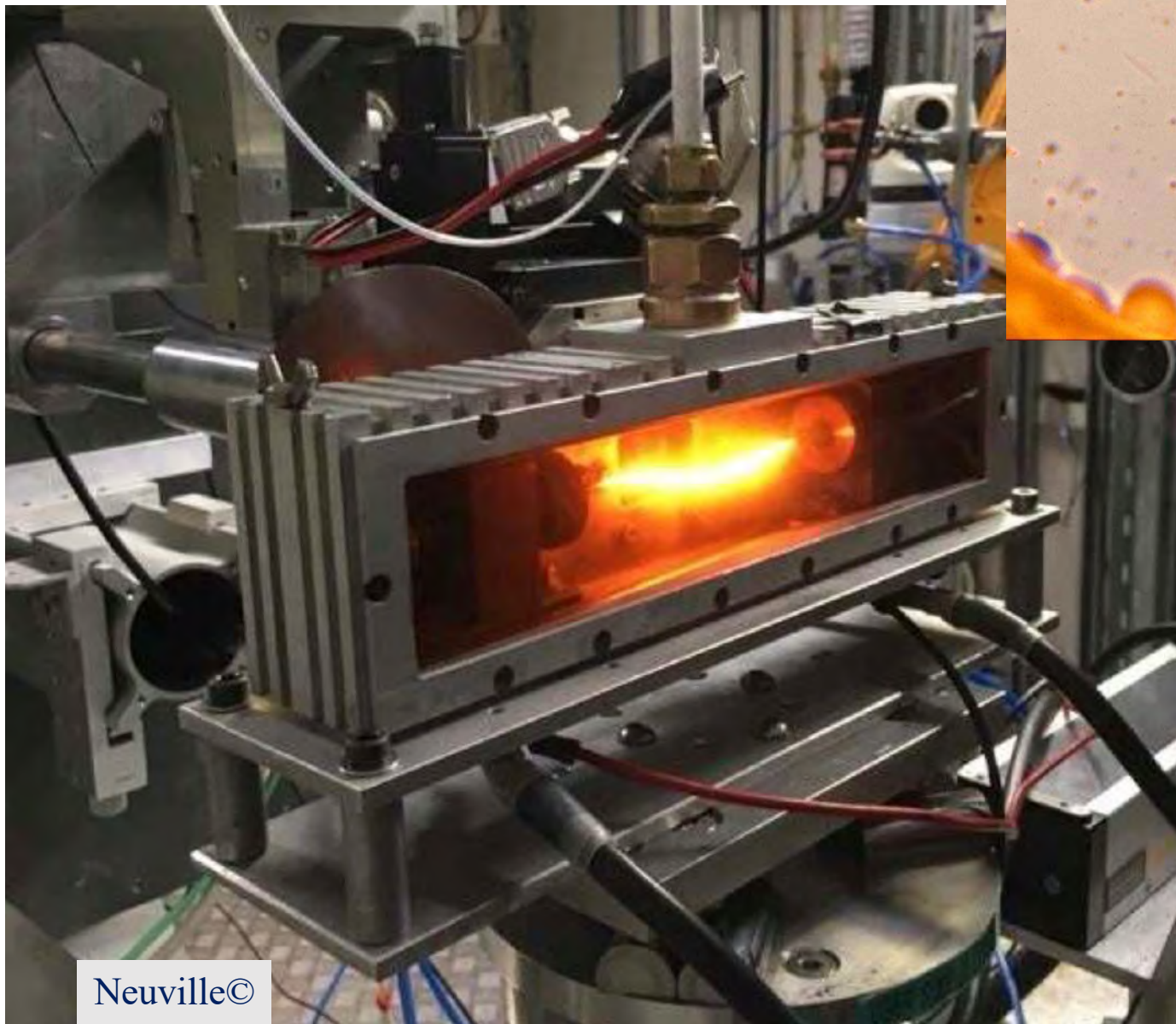


IV Fe³⁺ bands near 700cm⁻¹ in an 3D aluminate network



El Hayek, Cicconi, Ferey, Pisch, Vantelon and Neuville (2026) Role of iron on calcium aluminate glasses and melts. Glass Europe

In situ experiment



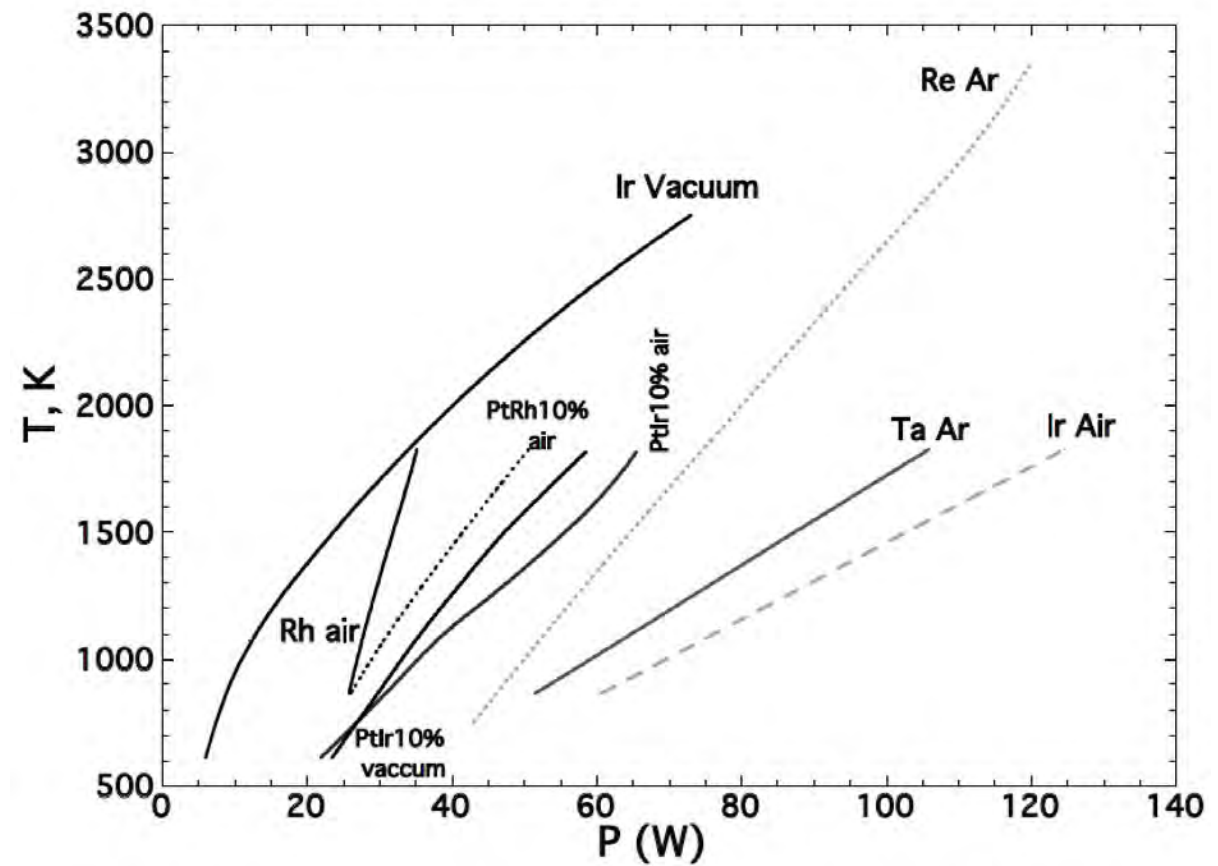
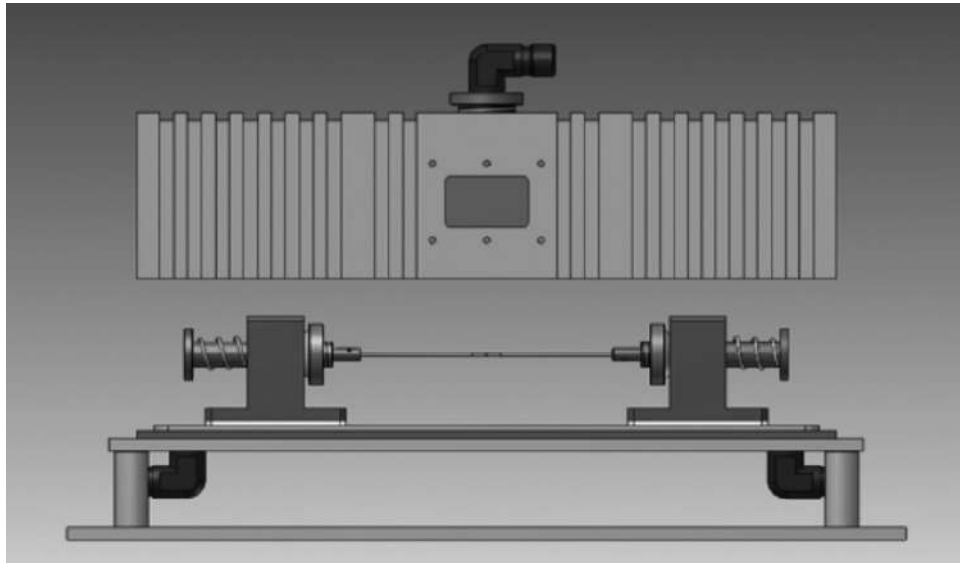
- In situ redox
measurements,
XANES at the Fe K-edge

- in situ nucleation and
growth
WAXS and SAXS

Neuvill©

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.

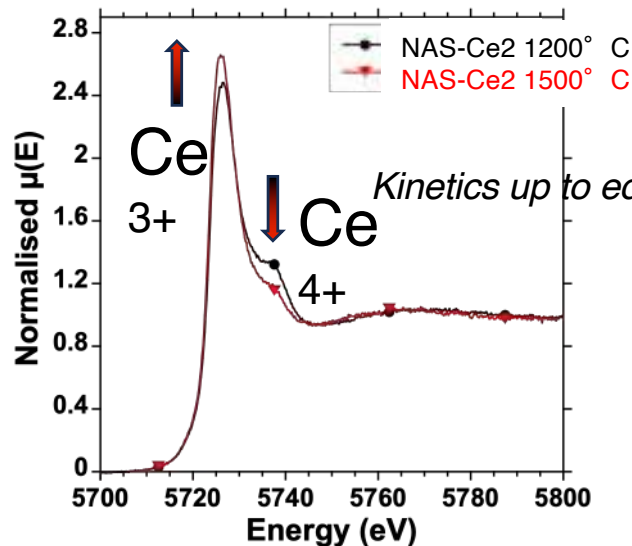
In situ experiment



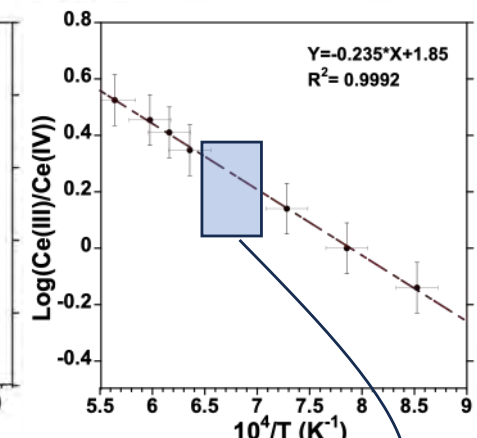
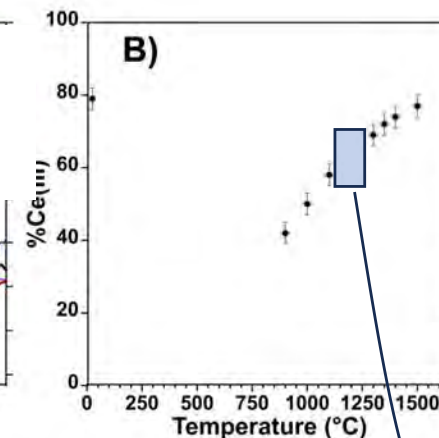
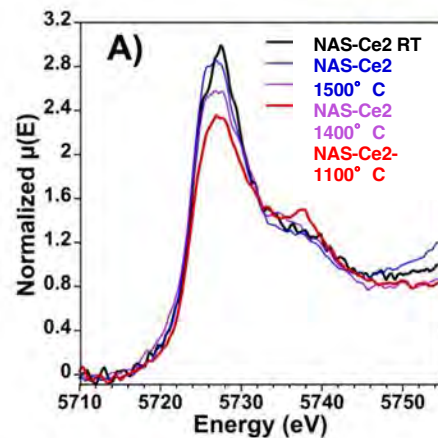
Neuville D.R., Hennet L., Florian P., de Ligny D. (2014) In situ high temperature experiment. In Henderson G.S, Neuville D.R., Down B. (2014) "Spectroscopic methods in Mineralogy and Material Sciences" Review in Mineralogy and Geochemistry, Vol 78, 779-800.

Redox state evolution at high temperature

In situ XANES measurements

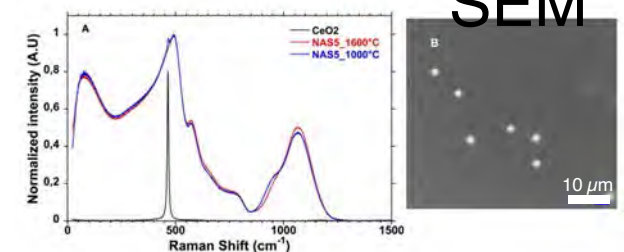


FAME-ESRF; *in situ*



Increase in
temperature
→ **Reduction**

Able to quantify Ce
redox equilibrium at
different temperatures

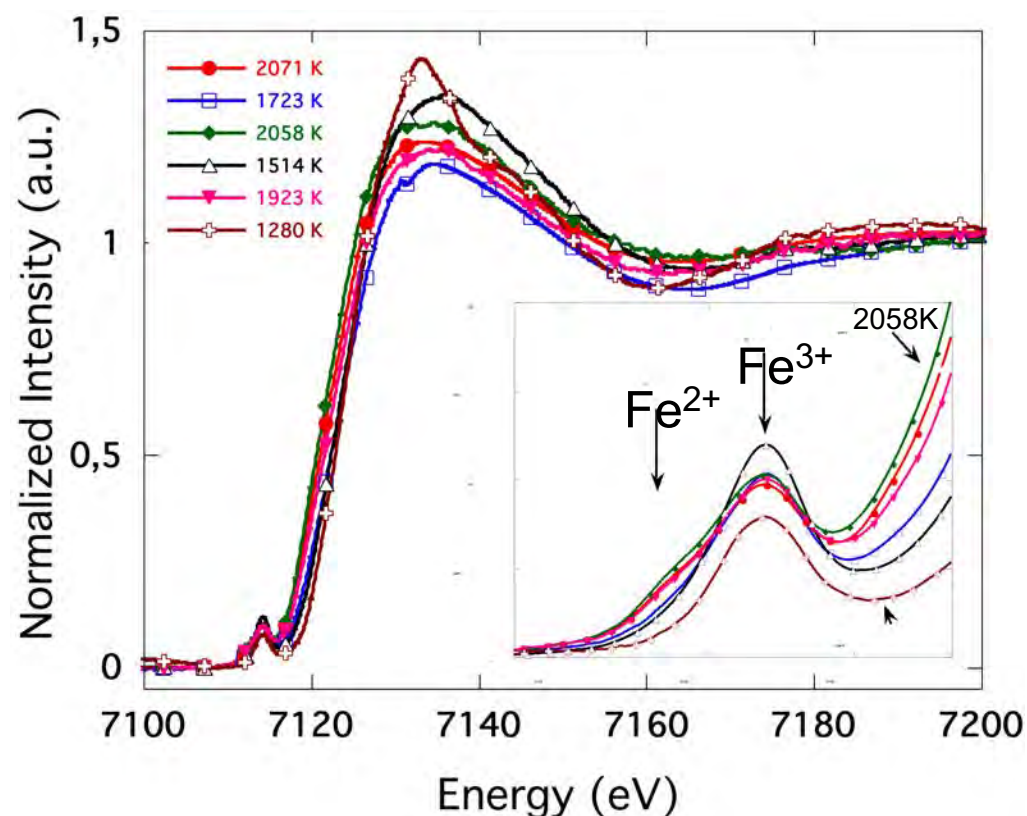


Raman spectroscopy

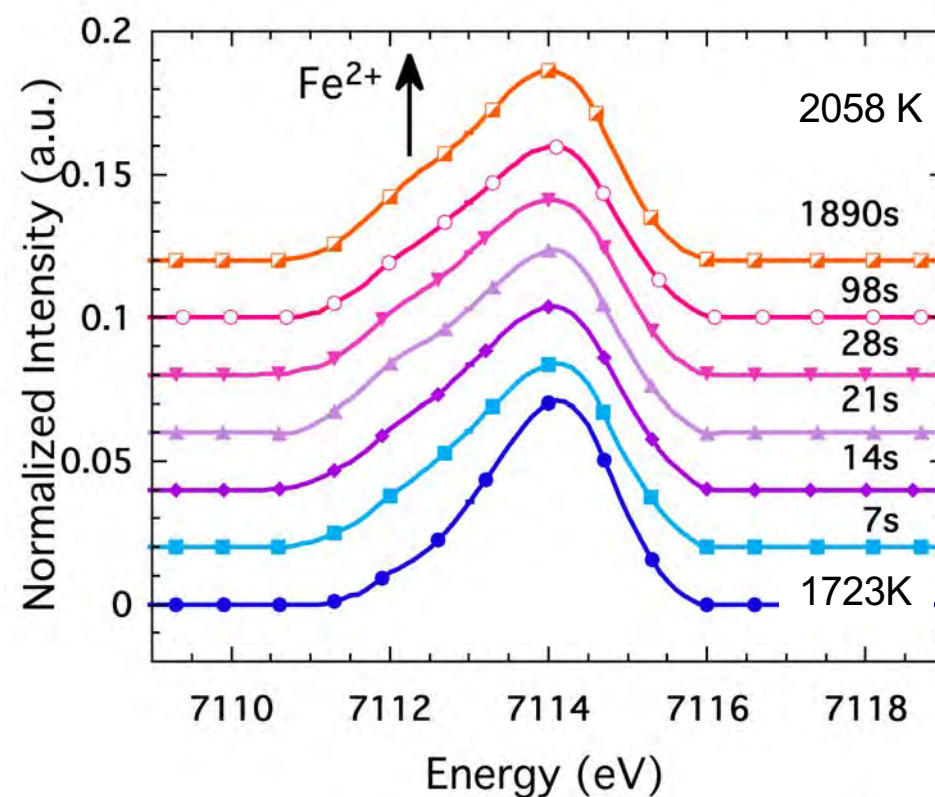
Crystallization of CeO₂
1100-1300° C

XANES versus temperature or time

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



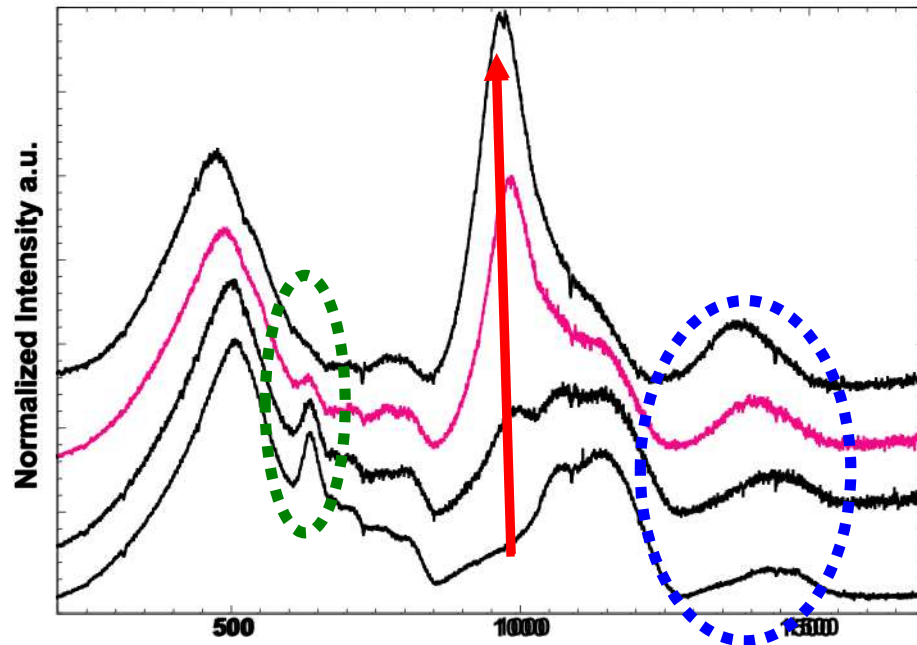
Time dependence during reduction in air at 2058 K of a Pyrox sample previously equilibrated at 1723 K



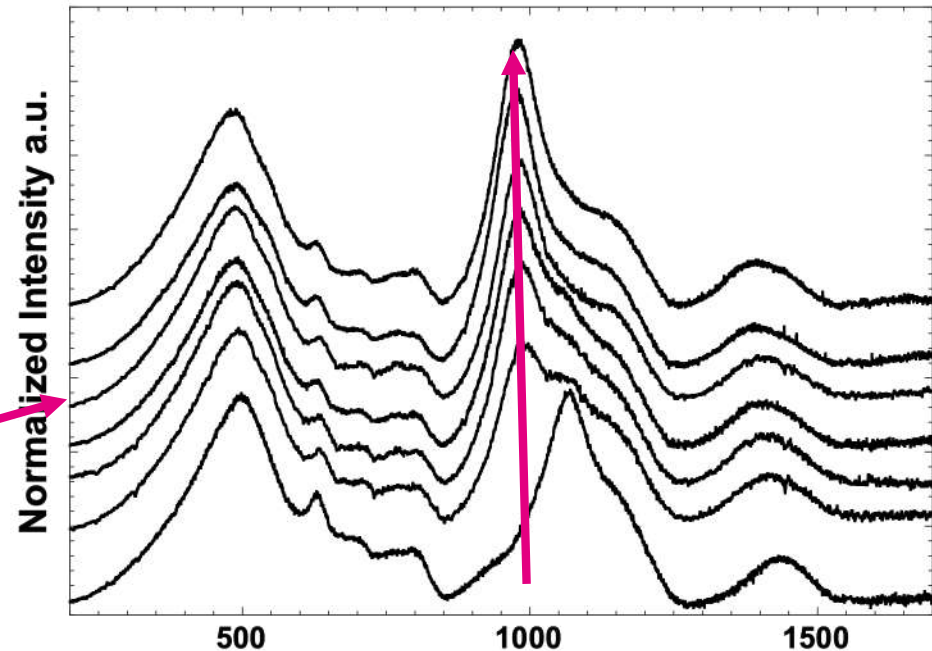
Magnien V., Neuville D.R., Cormier L., Mysen B.O..... (2004) Kinetics of iron oxidation in silicate melts: A preliminary XANES study. *Chem. Geol.*, 213, 253-263

Raman spectroscopy

Borosilicate NBF67.18.x glass with increasing FeO content



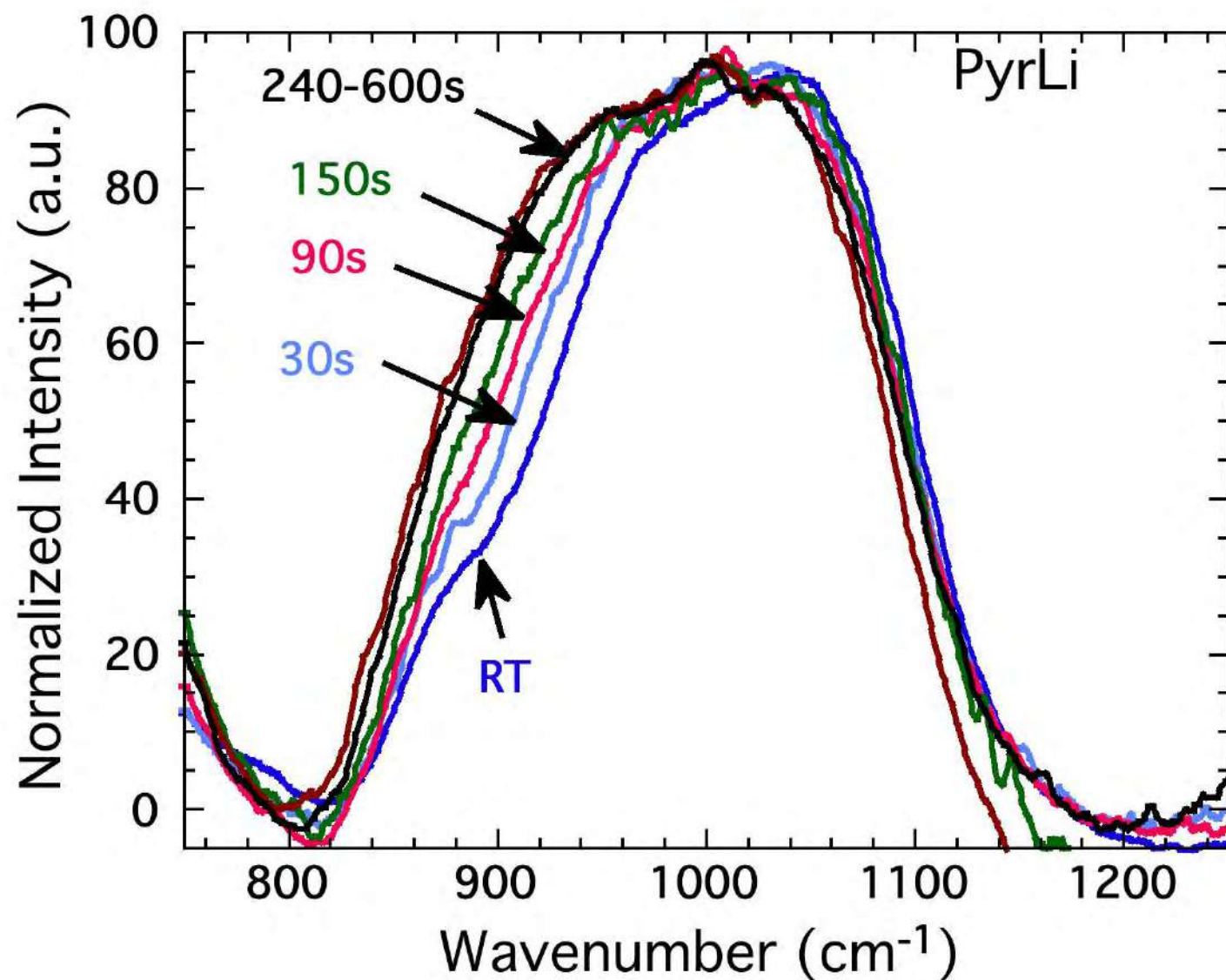
Borosilicate NBF67.18.5 glass with increasing Fe³⁺ content



Increasing **FeO content** at constant redox ratio + inscreasing **Fe³⁺ content**:

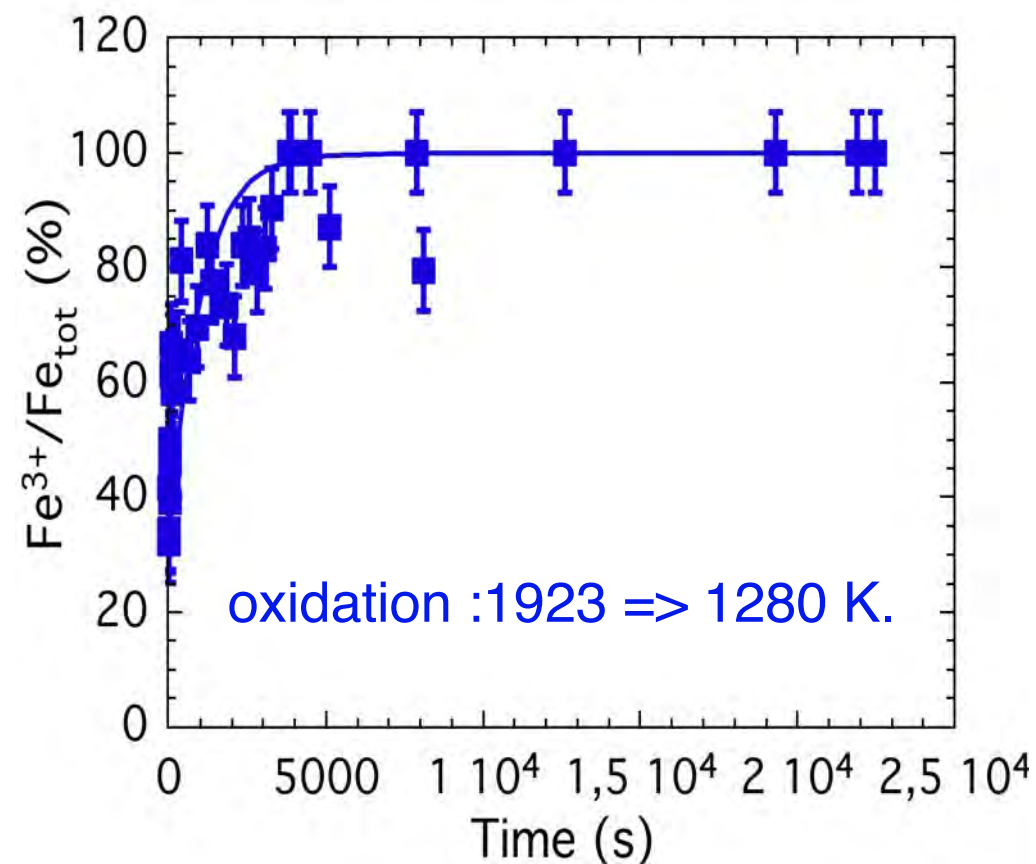
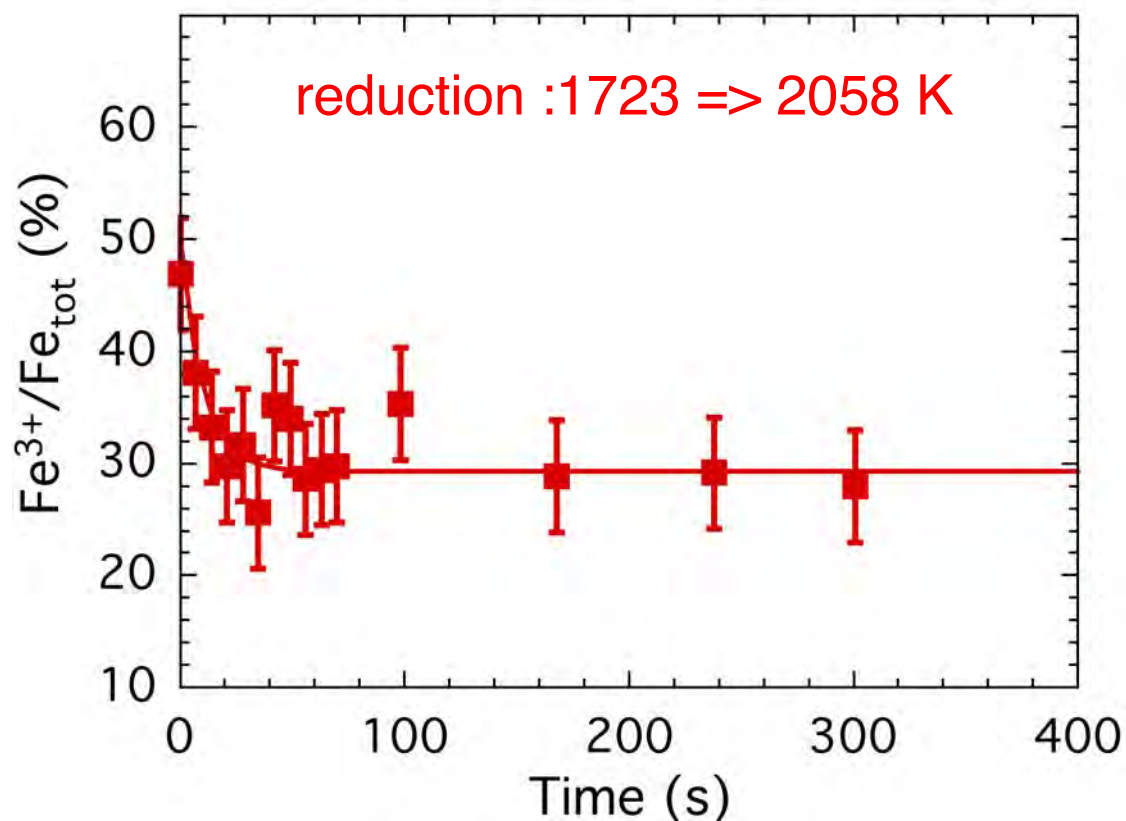
- Increasing band at 980cm⁻¹ in borosilicates
- Shift to lower frequency of the 980 cm⁻¹ band => [⁴]Fe³⁺-O bonds shared with Si
- **BO₃/BO₄ modification**
- Decreasing danburite like rings band ($2\text{SiO}_2-2\text{BO}_4-\text{Na}_2\text{O}$)

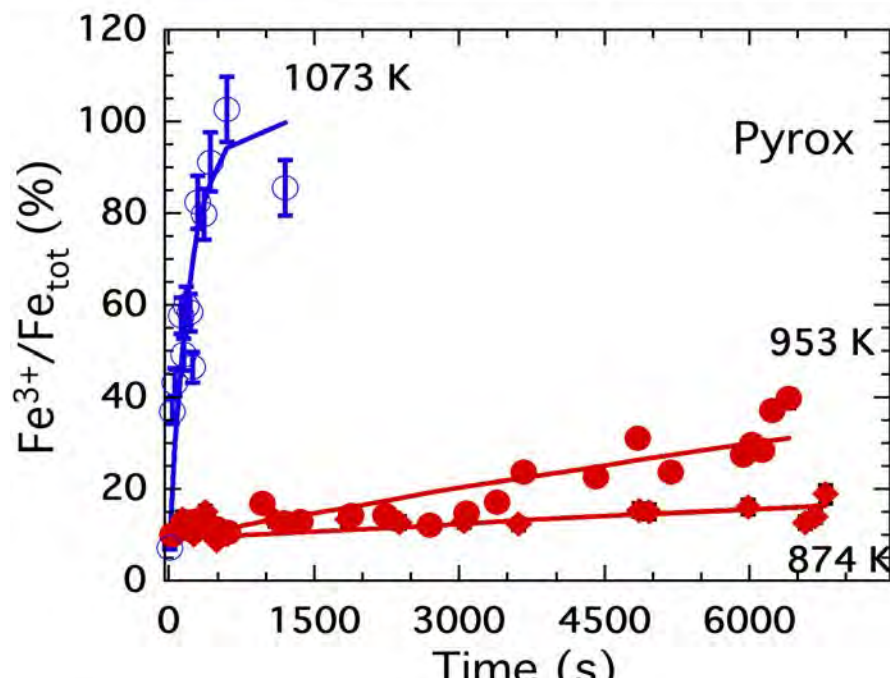
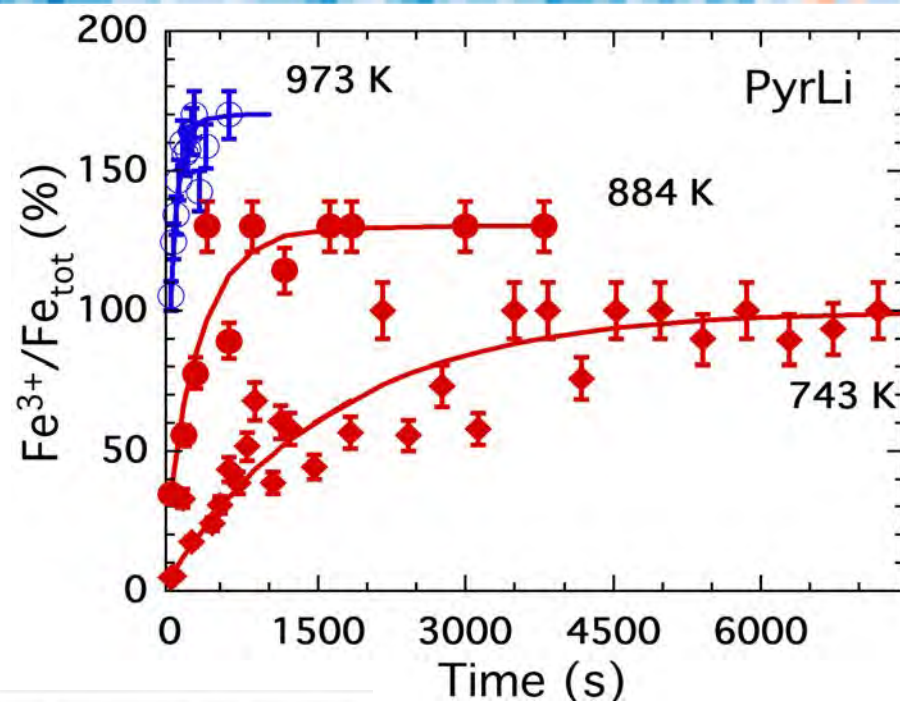
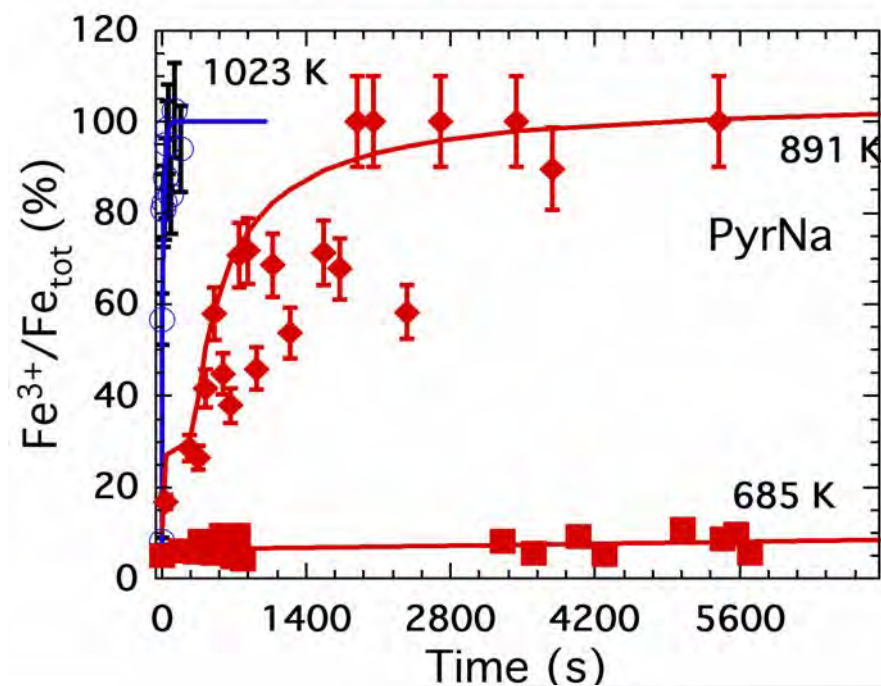
Cochain B., Neuville D. R., Henderson G. S., McCammon C., Pinet O. and P. Richet (2012) Iron content, redox state and structure of sodium borosilicate glasses: A Raman, Mössbauer and boron K-edge XANES spectroscopy study. Journal of the American Ceramics Society, 94, 1-12



Time dependence of the Raman spectrum of PyrLiR at 973 K

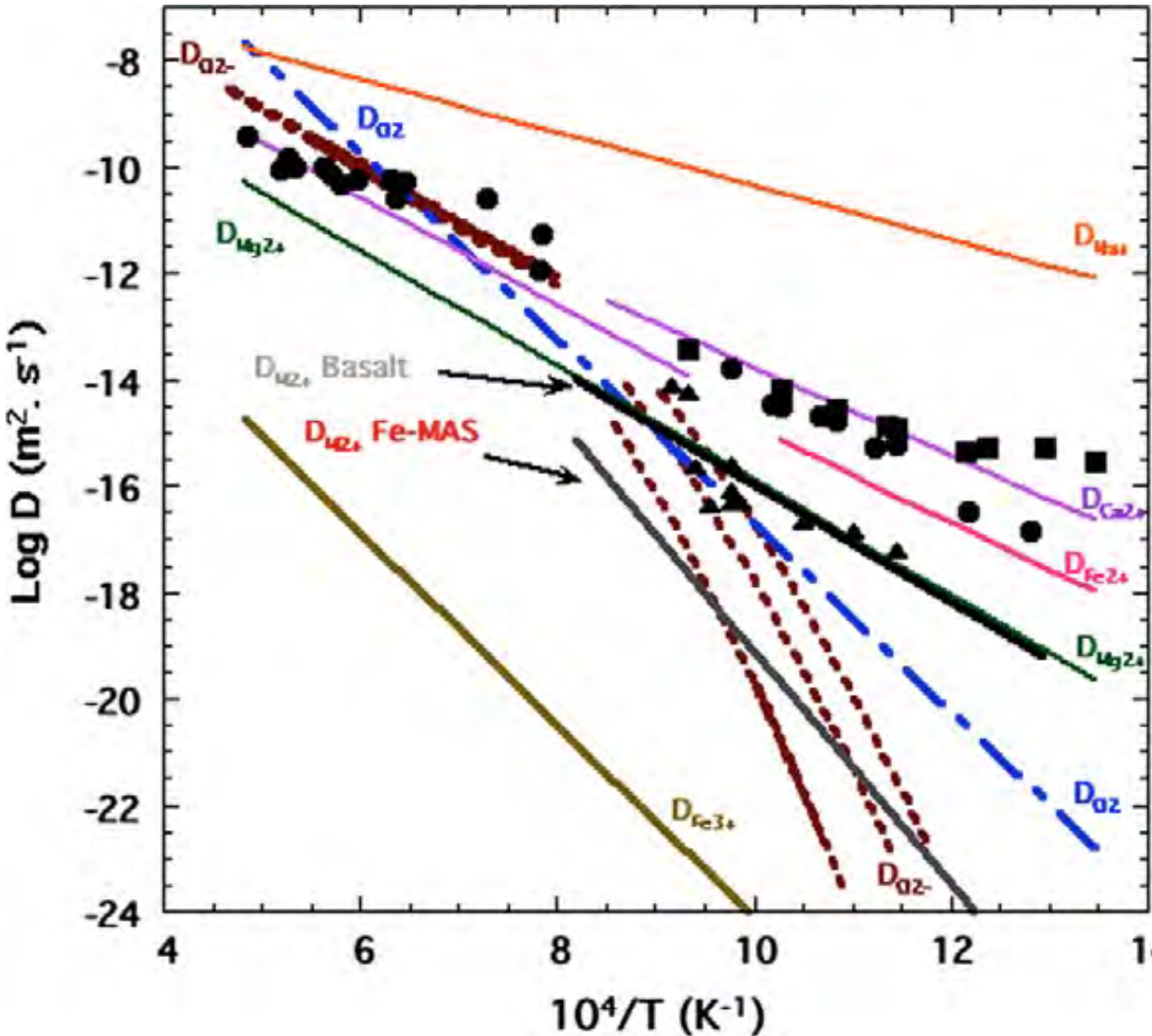
Time dependence of the iron redox ratio of Pyrox





Raman
XANES

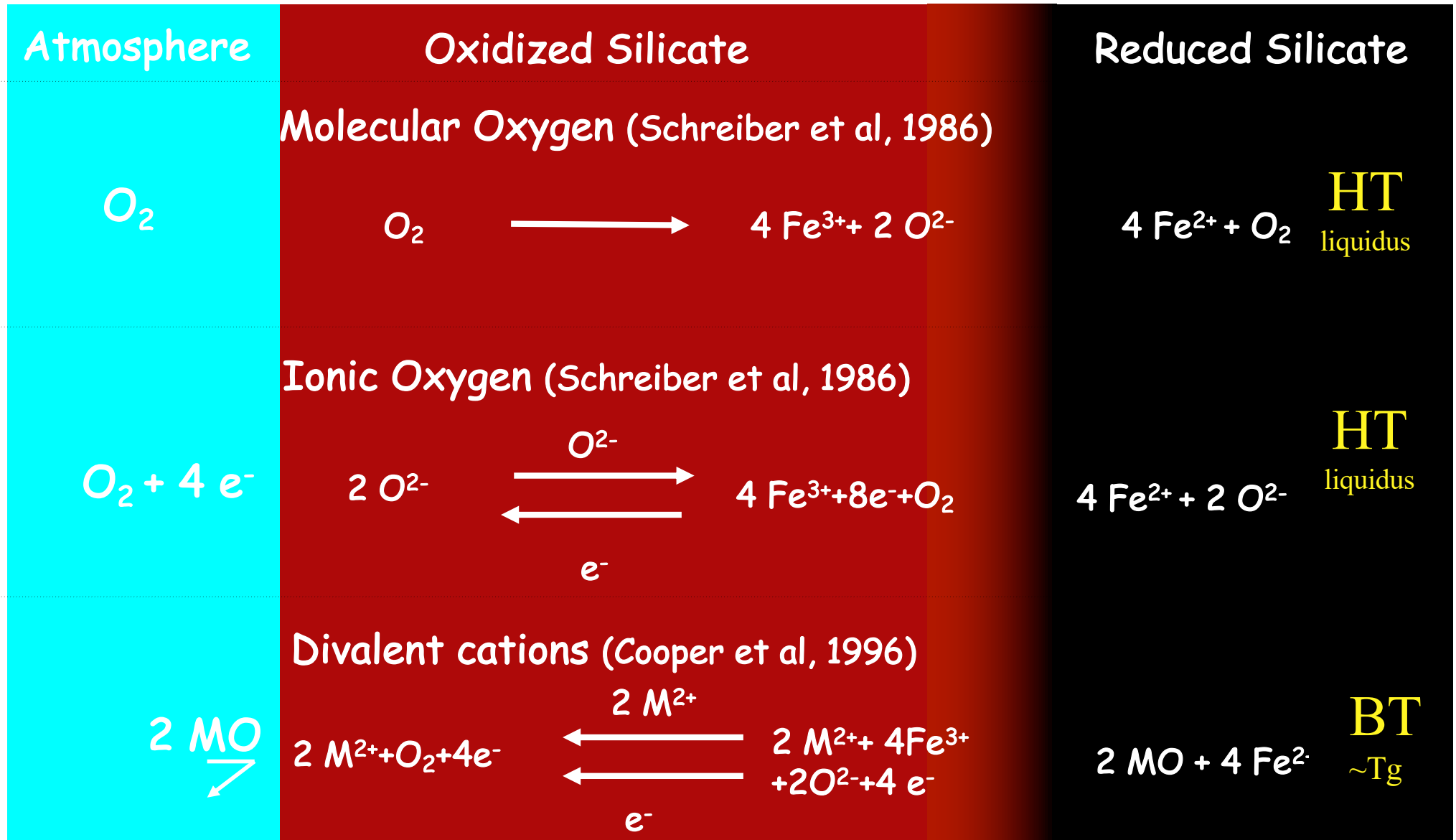
« Redox diffusivity »



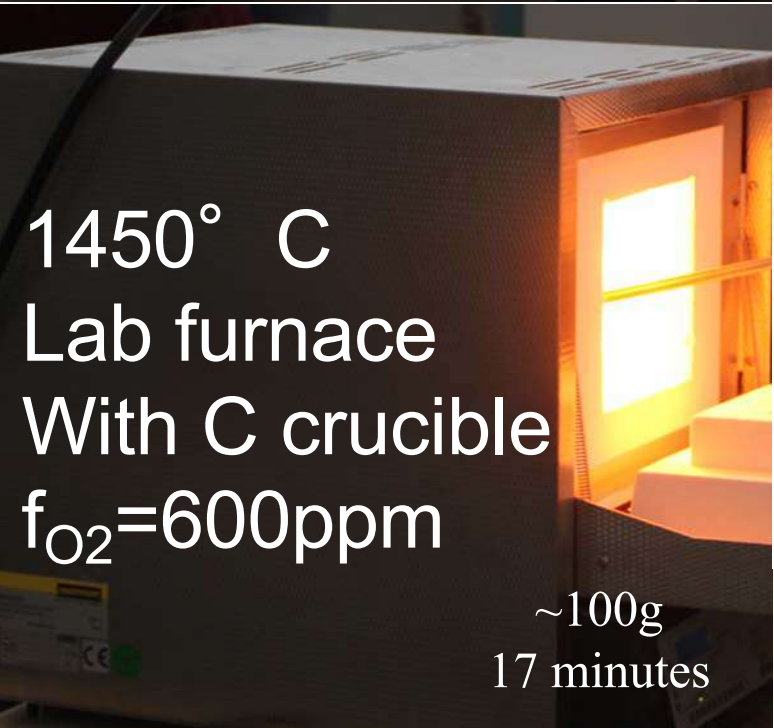
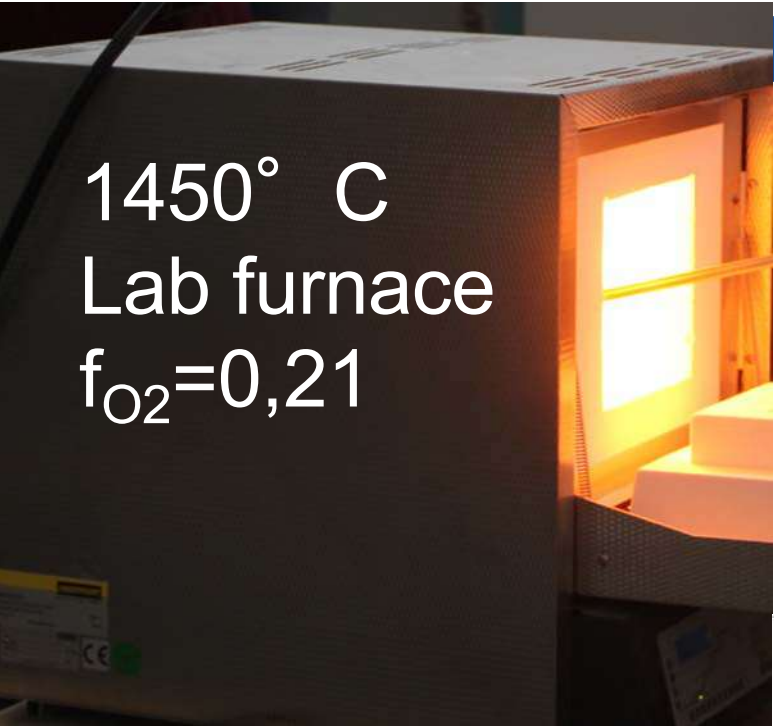
D_{O2} from Semkow and Haskin (1985) for diopside composition; D_{Ca} and D_{Mg} from Jambon and Semet (1977), Roselieb and Jambon (2002) for albite, jadeite or orthoclase compositions; D_{Na} from Jambon and Carron (1976), Lowry et al. (1981) for albite, obsidienne and basaltic compositions ; D_{Fe} from Kohler and Frischat (1978) for Na₂O-FeO-Al₂O₃-SiO₂ compositions and from Henderson et al. (1985) for aluminosilicates; D_{M2+} Basalte et Fe-MAS (MAS= MgO-Al₂O₃-SiO₂ 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.

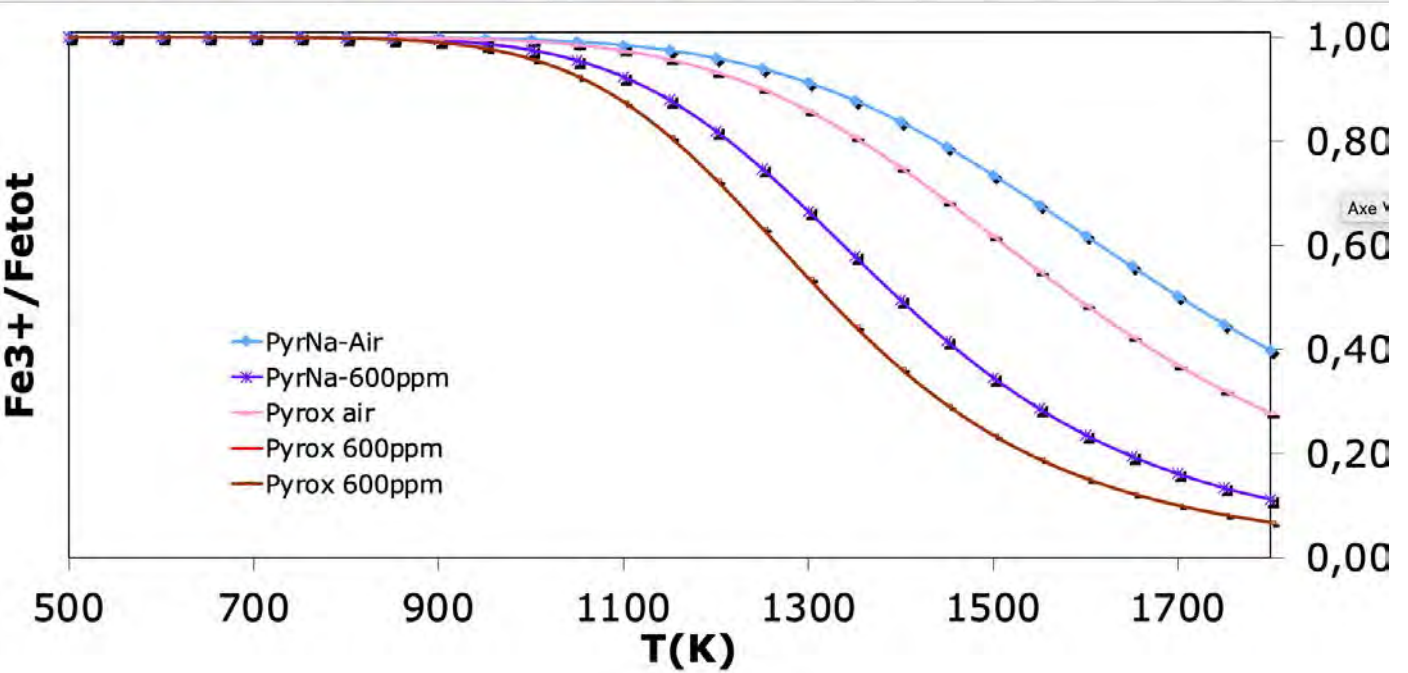
What are the diffusing species? Predominating mechanism $\Rightarrow$ $f(T, \text{composition}, f(O_2))$



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.



	PyrNa	Pyrox
SiO ₂	52,6	53,27
Na ₂ O	5,46	0
MgO	11,98	14,08
CaO	17,01	19,54
FeO	12,83	13,03
Fe ³⁺ /Fe _{tot} air	0,75	0,65
Fe ³⁺ /Fe _{tot} 600ppm	0,09	0,07



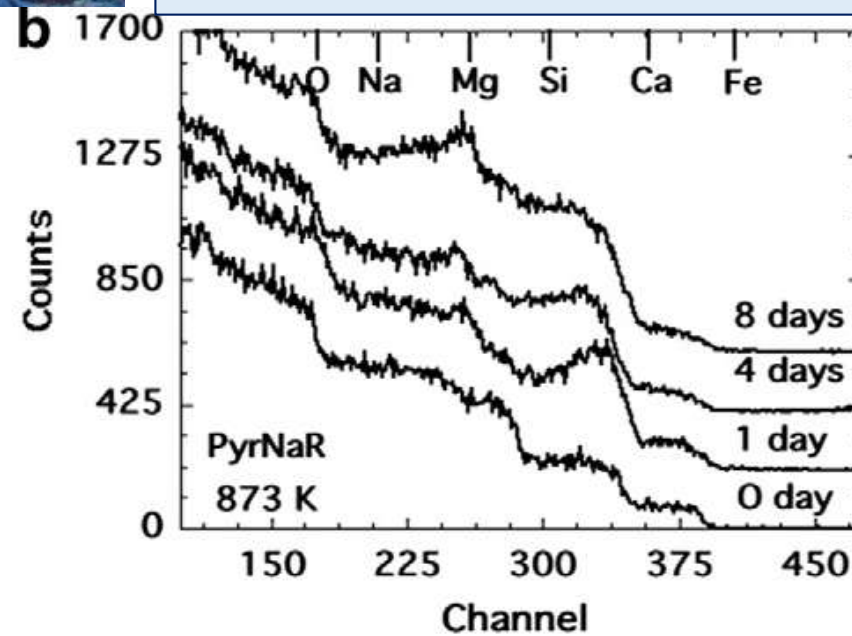
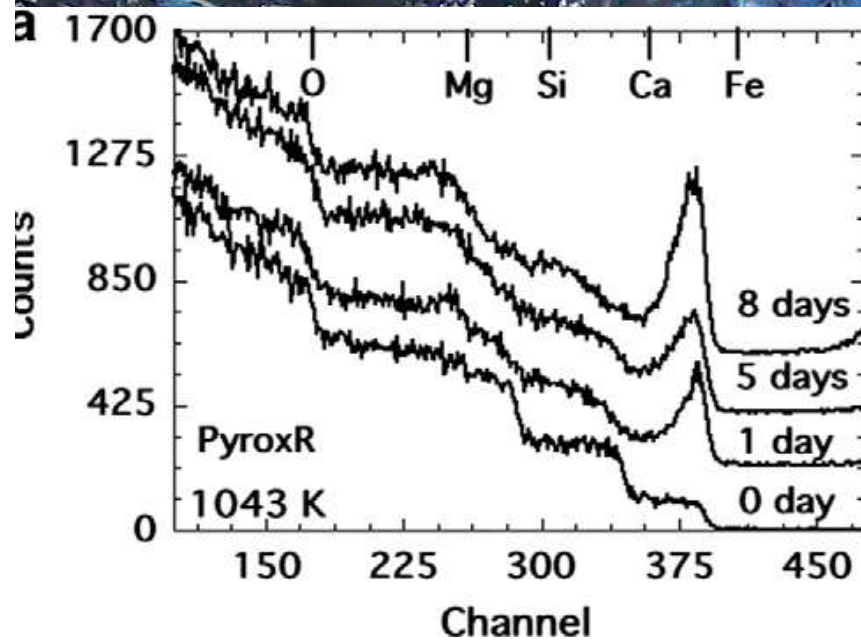
Magnien V, Neuville D.R., Cormier L., Roux J., Hazemann J-L., de Ligny D., Pasquarelli S., Vickridge I., Pinet O. and Richet P. (2008) Kinetics and mechanisms of iron redox reactions in silicate melts: The effects of temperature and alkali cations. *Geochim. Cosmochim. Acta.*, 72, 2157-2168.

Rutherford back-scattering spectra



$$f_{O_2} = 0,02$$

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%

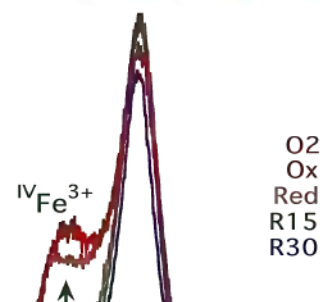
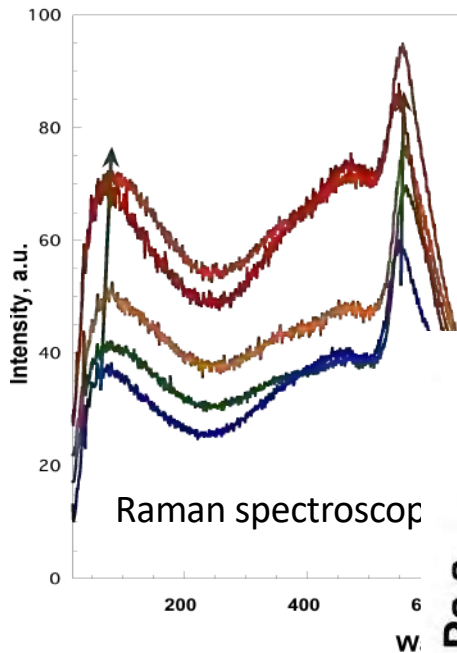
Redox of window glass

--○-- $\text{Fe}^{2+}/(\text{Fe}^{2+}+\text{Fe}^{3+})=0.27$

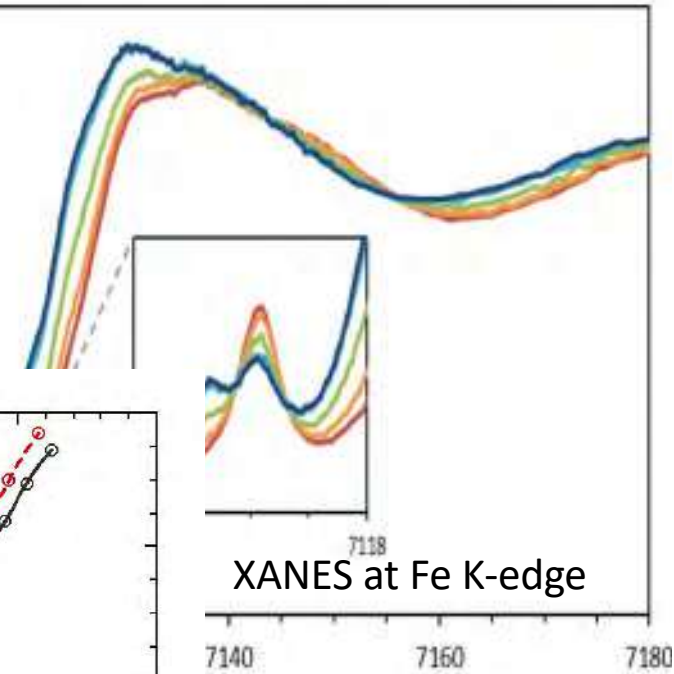
Ox

—○— $\text{Fe}^{2+}/(\text{Fe}^{2+}+\text{Fe}^{3+})=0.60$

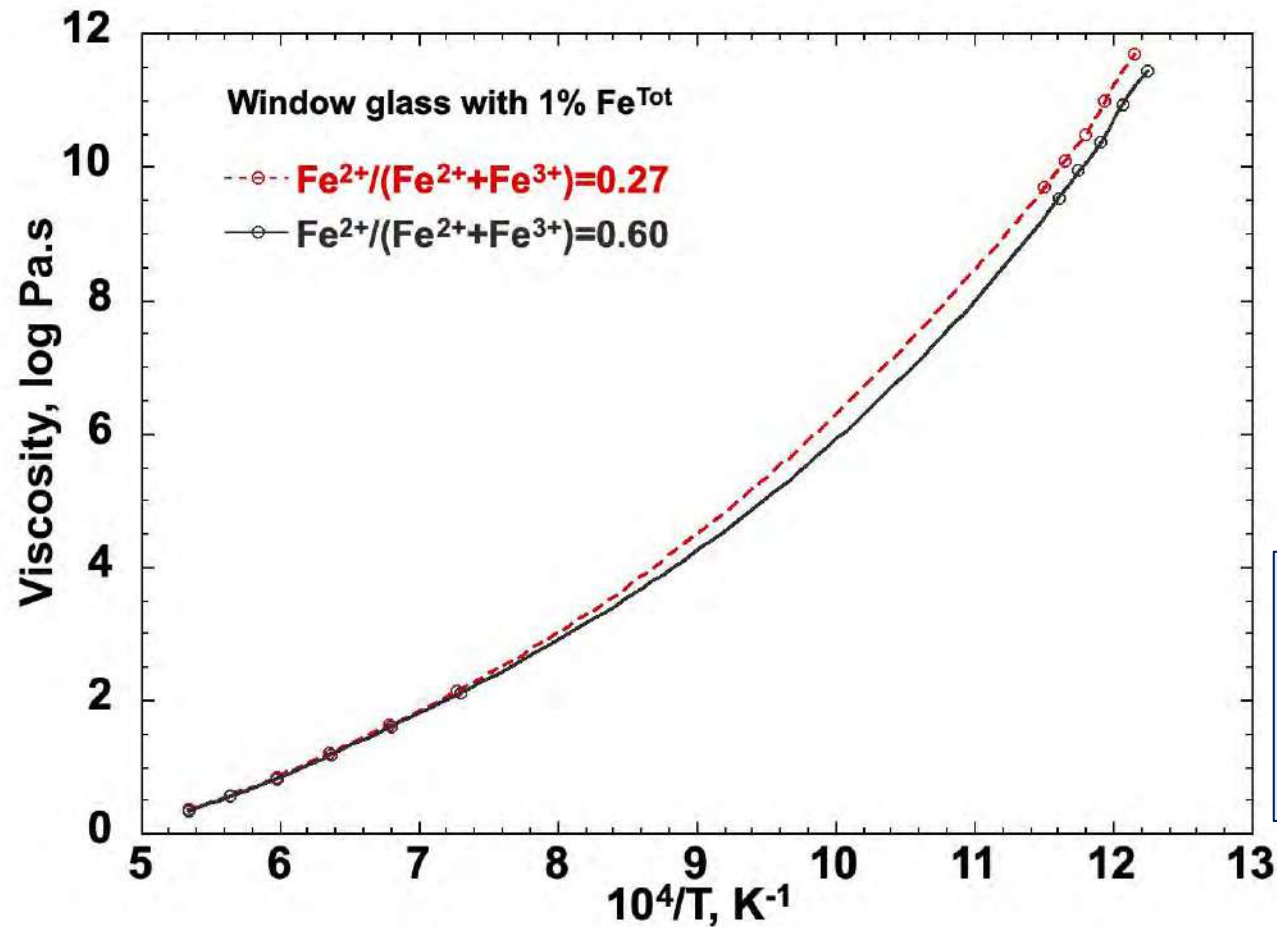
Red



Intensity

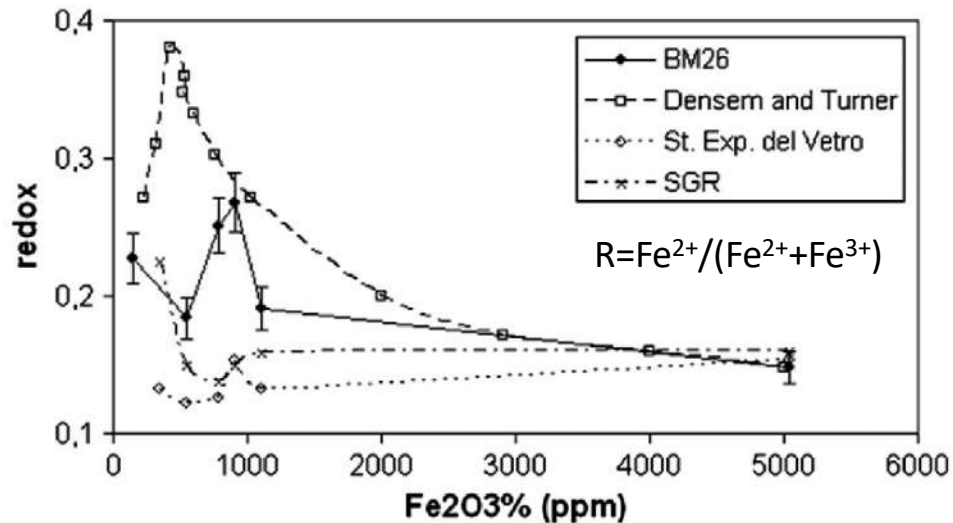
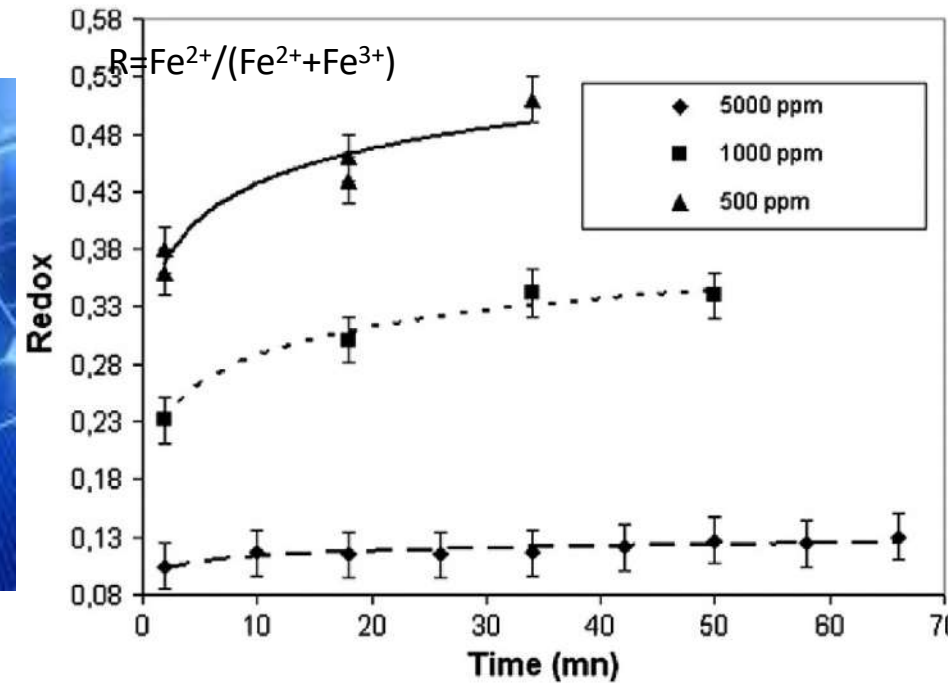
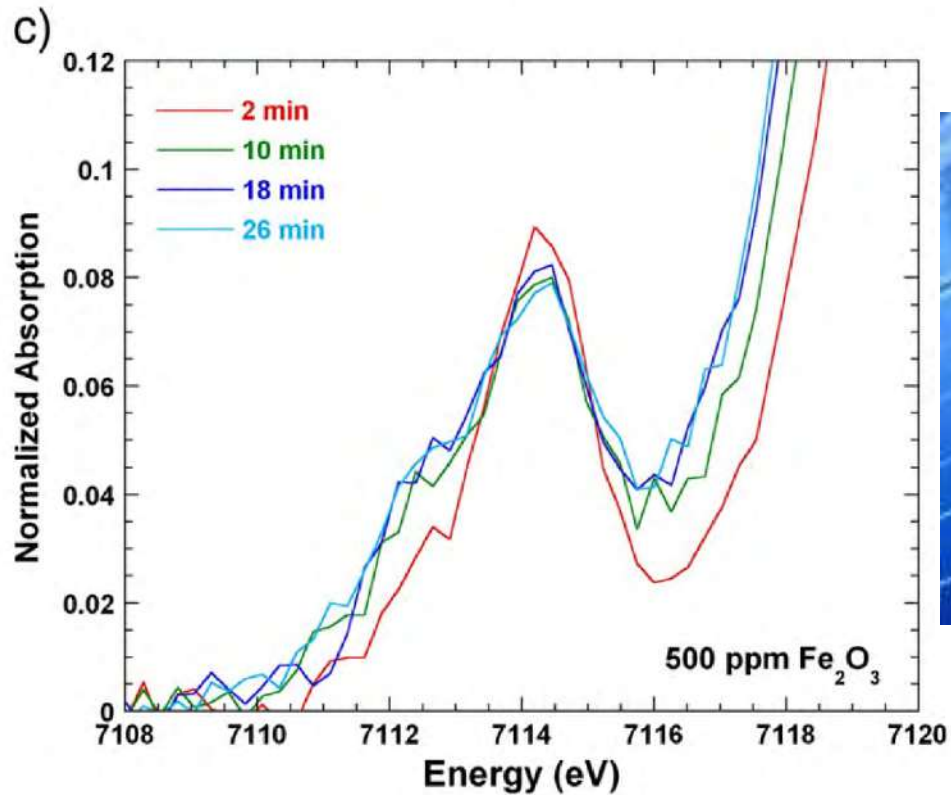


Energy, eV



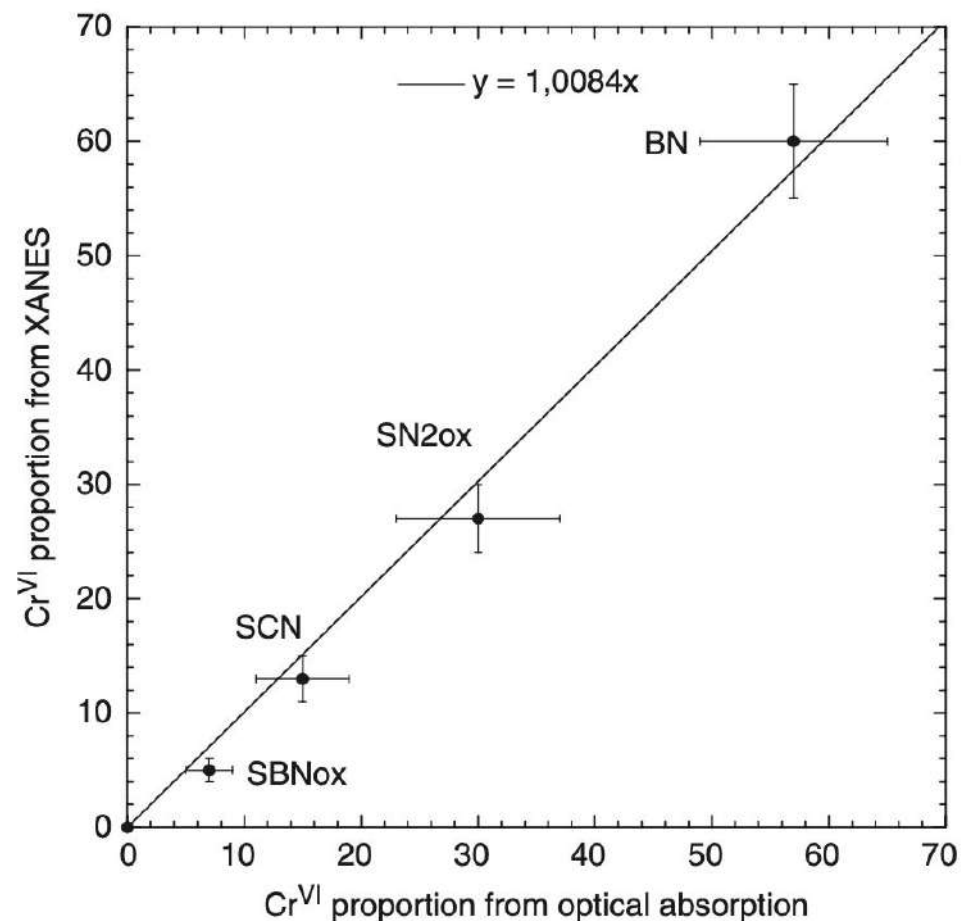
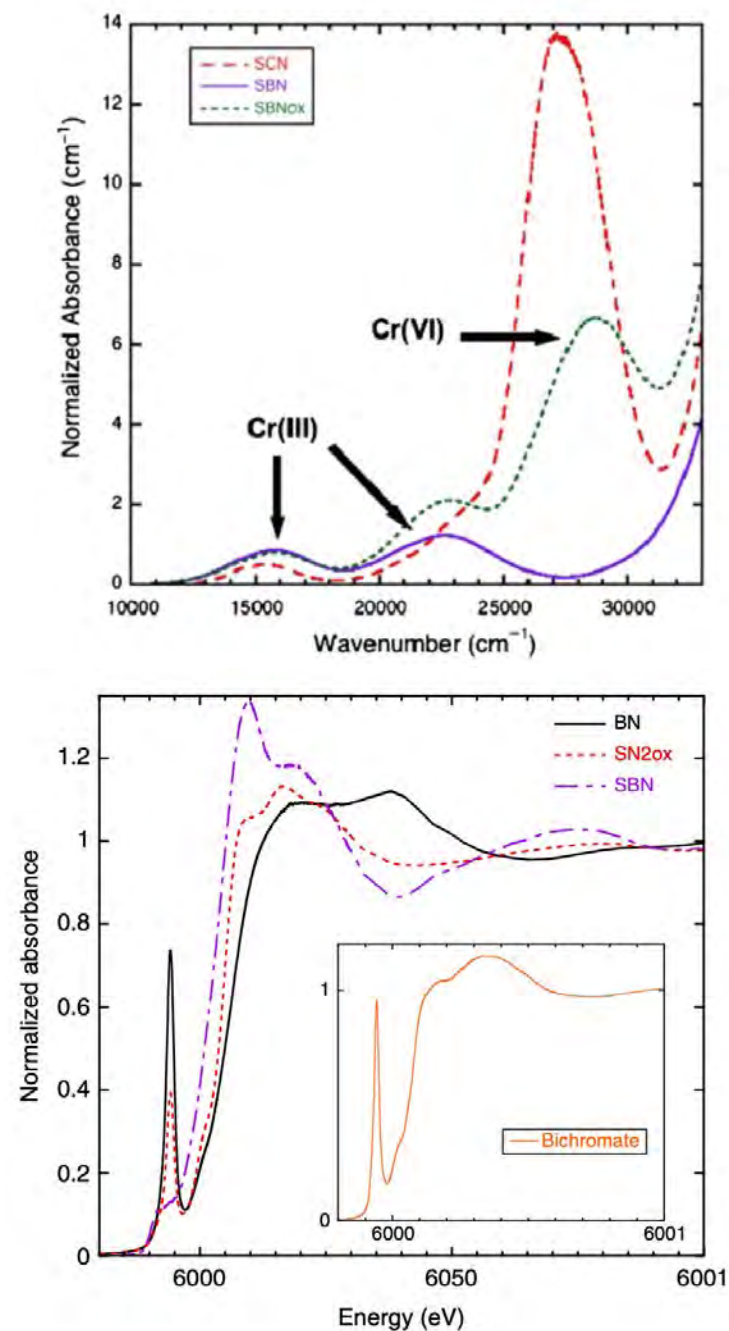
Neuville D.R. and Cormier L. (2024)
Redox variations in glass
manufacturing: effects of oxygen
fugacity and temperature on glass
and melt properties. Material
Letter. DOI:
[10.1016/j.matlet.2024.137821](https://doi.org/10.1016/j.matlet.2024.137821)

Ultra-clear glasses



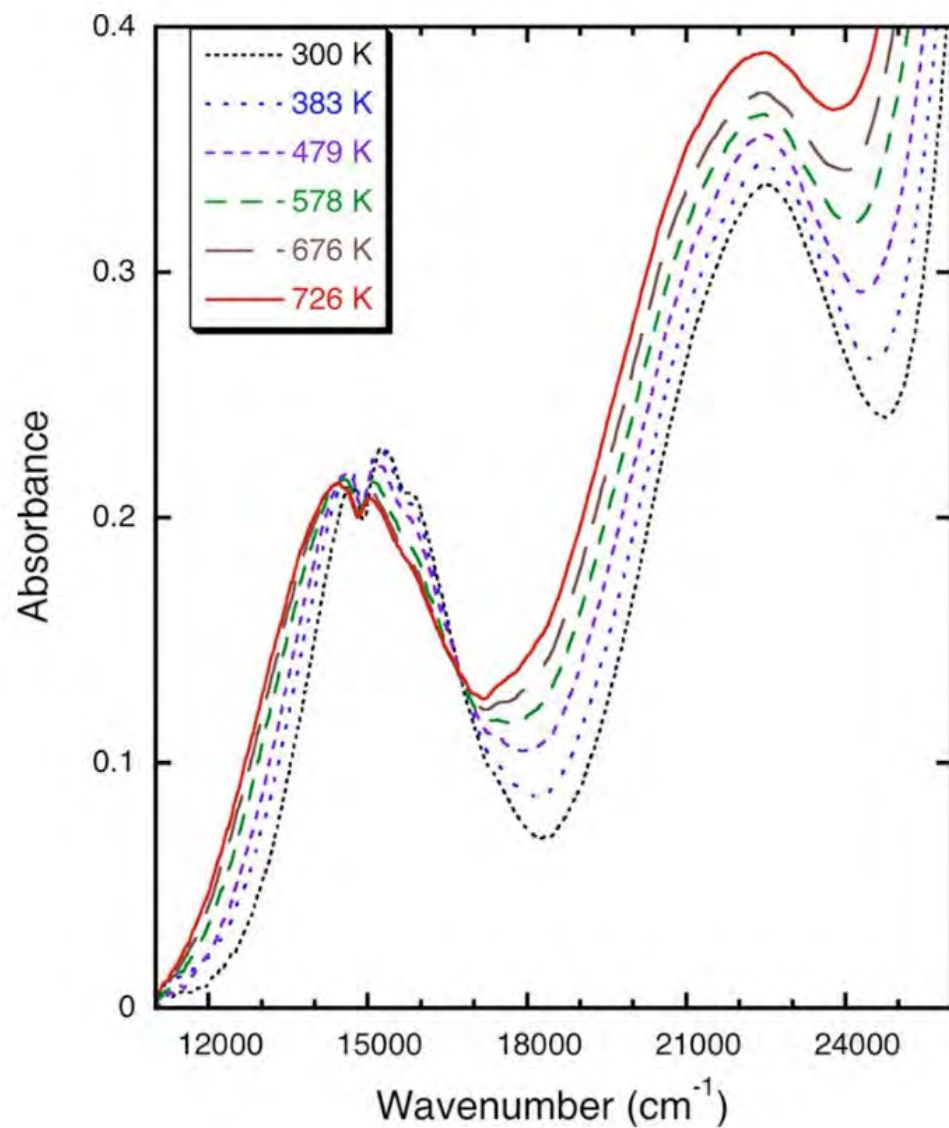
good agreement with Densen and Turner,
the redox of elements in diluted condition
does not follow the expected rules

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

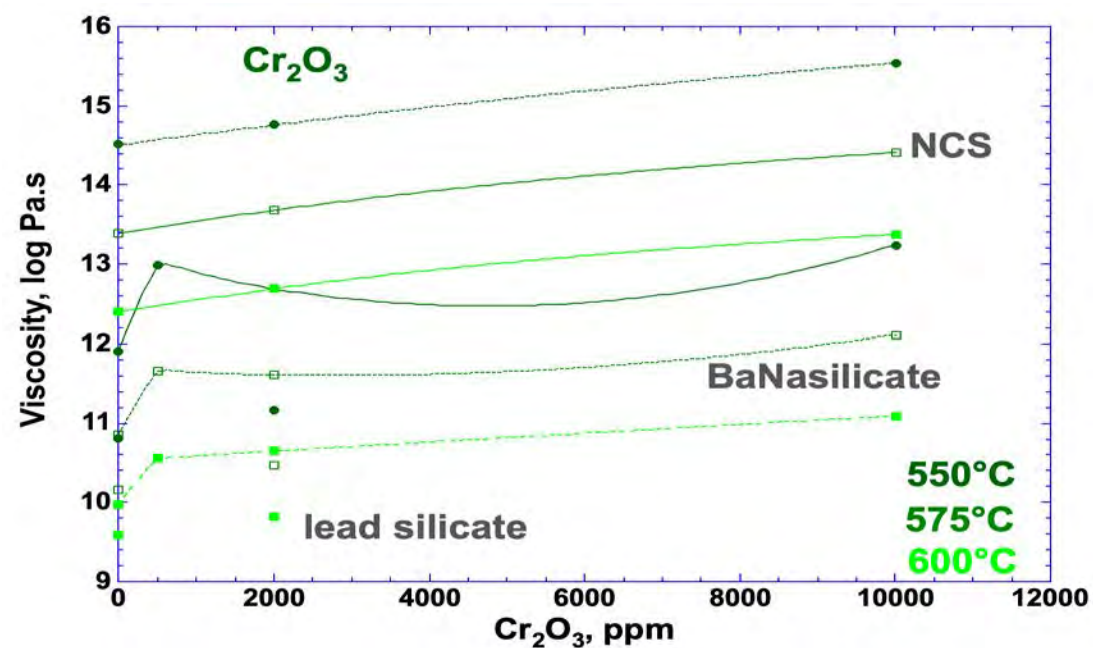
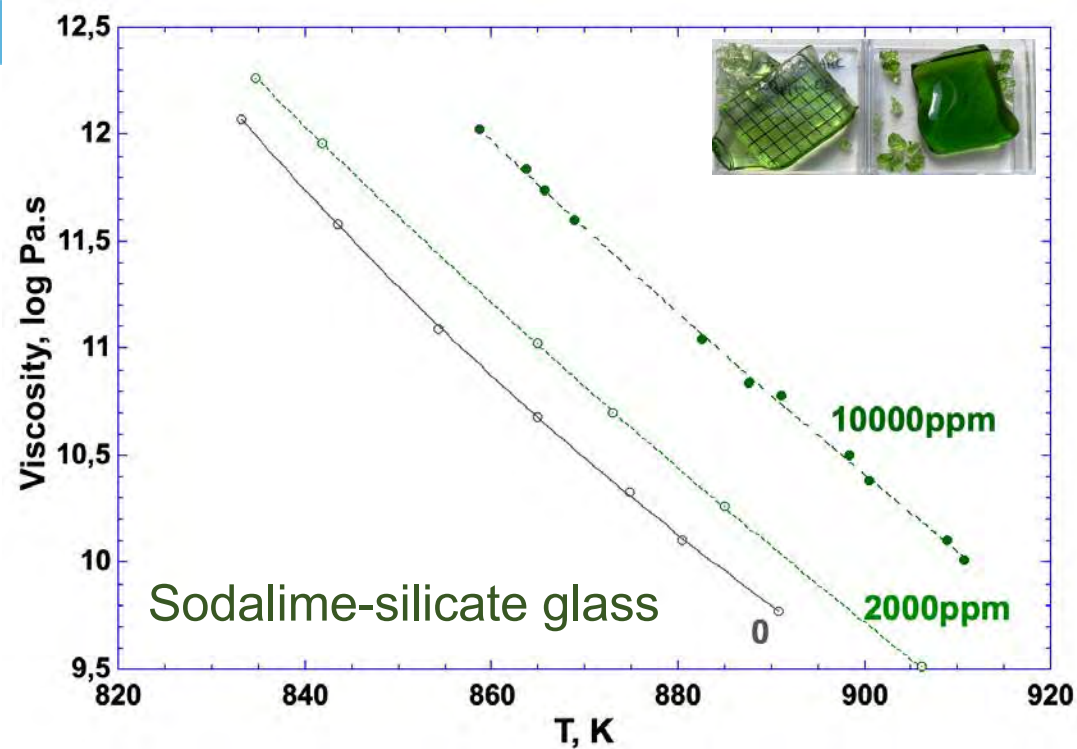


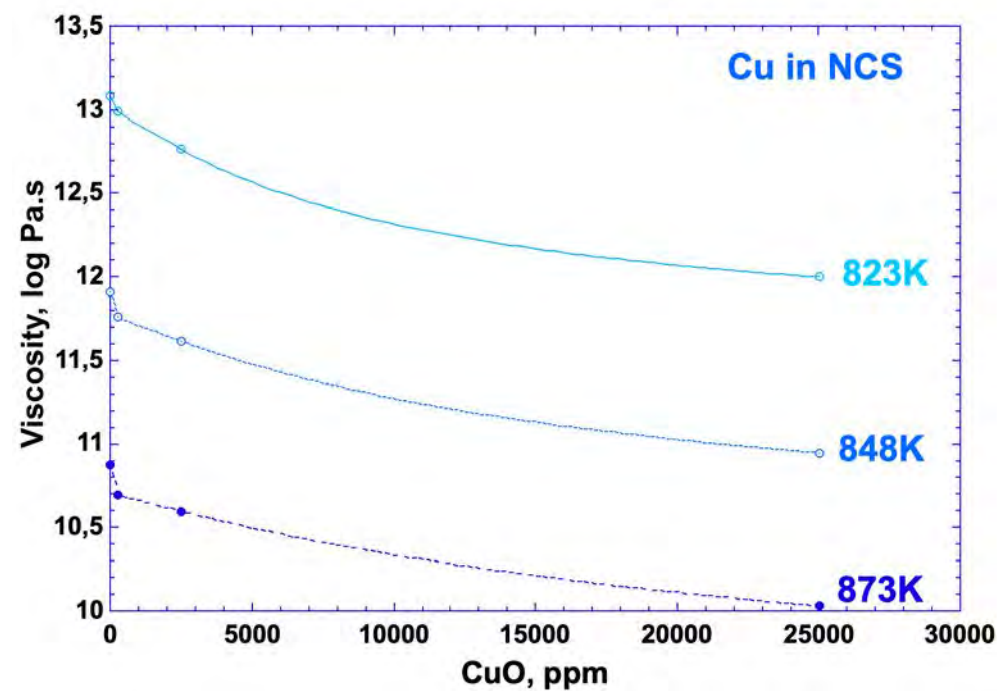
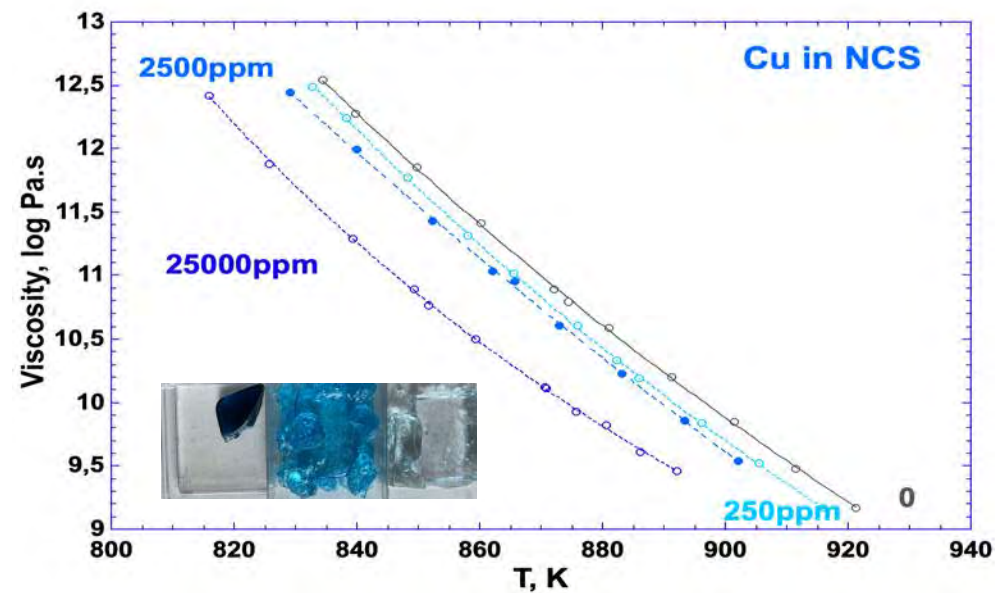
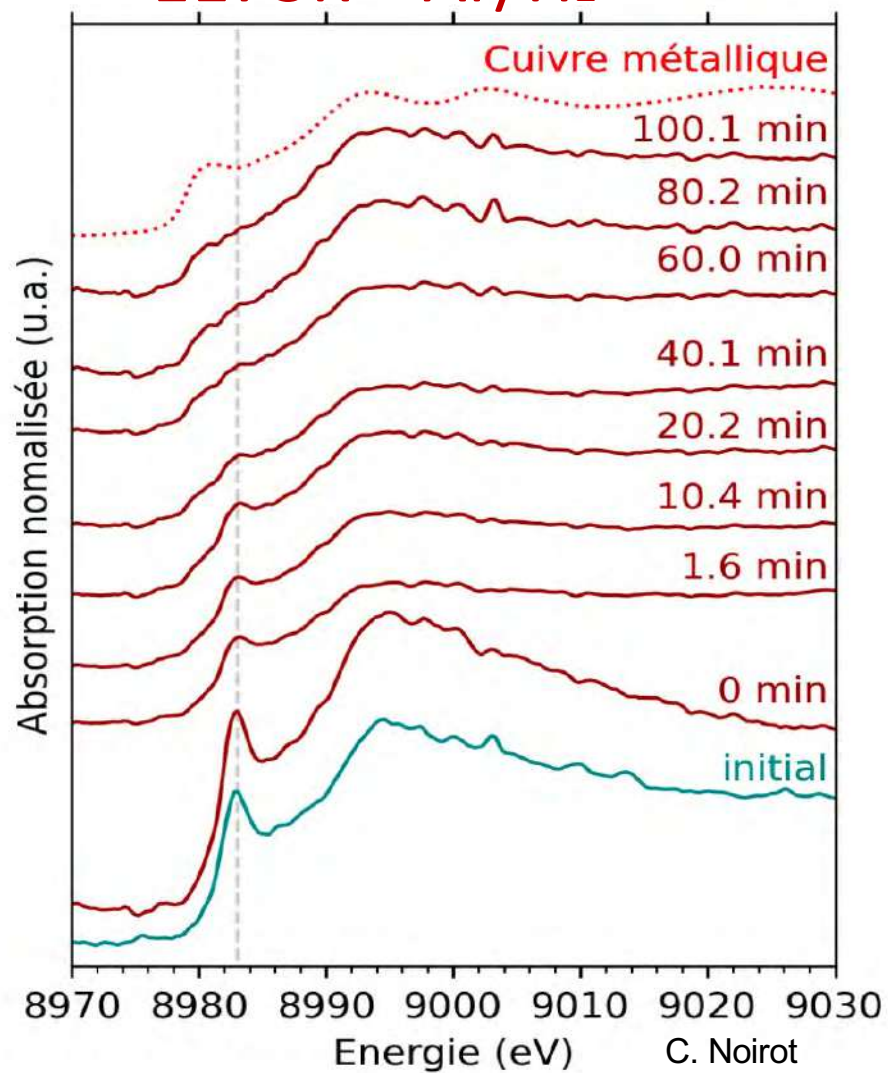
Good correlation between
optic and XANES

Redox Chrome

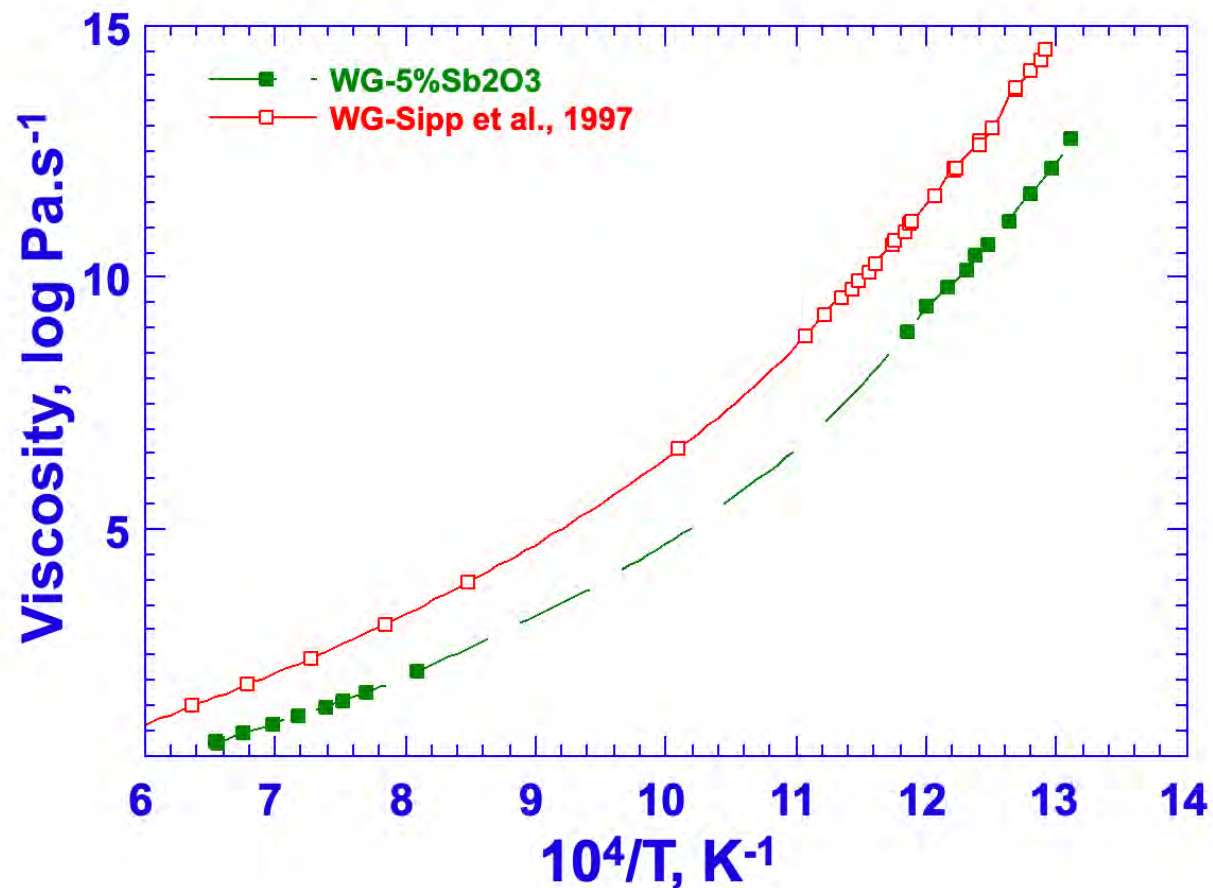


Calas, Majerus, Galois, Cormier (2006) Determination of the thermal expansion of Cr³⁺ sites in glasses. APPLIED PHYSICS LETTERS 88, 121918

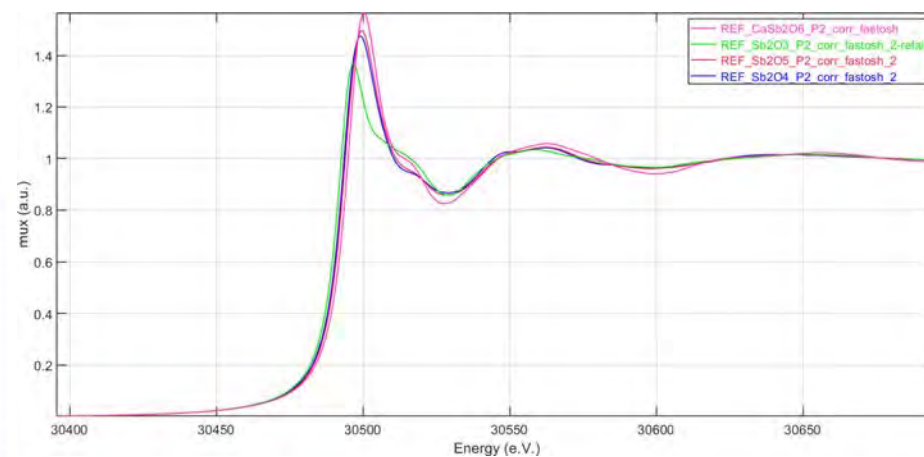


1173K Ar/H₂

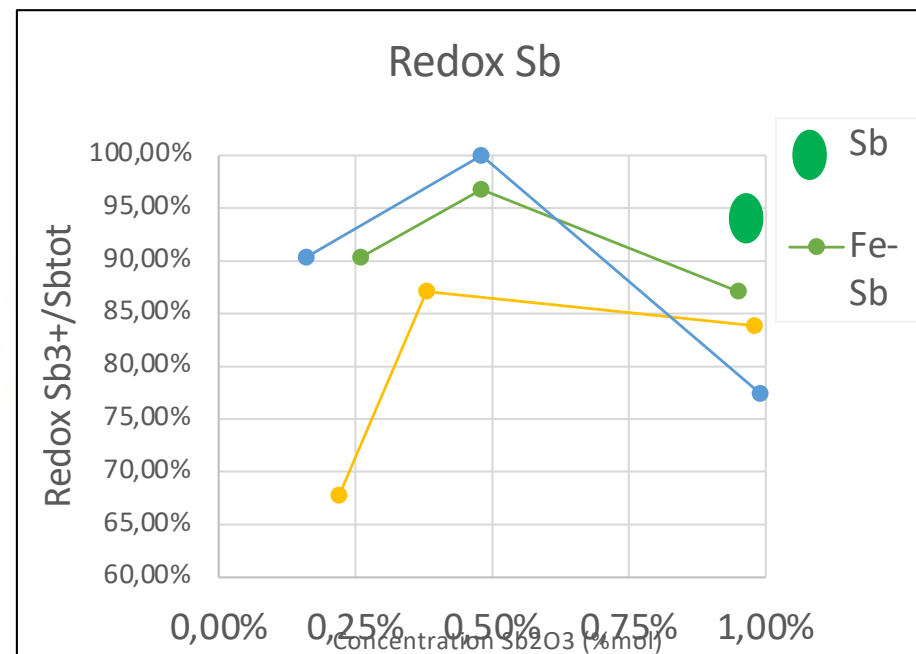
Antimony role?



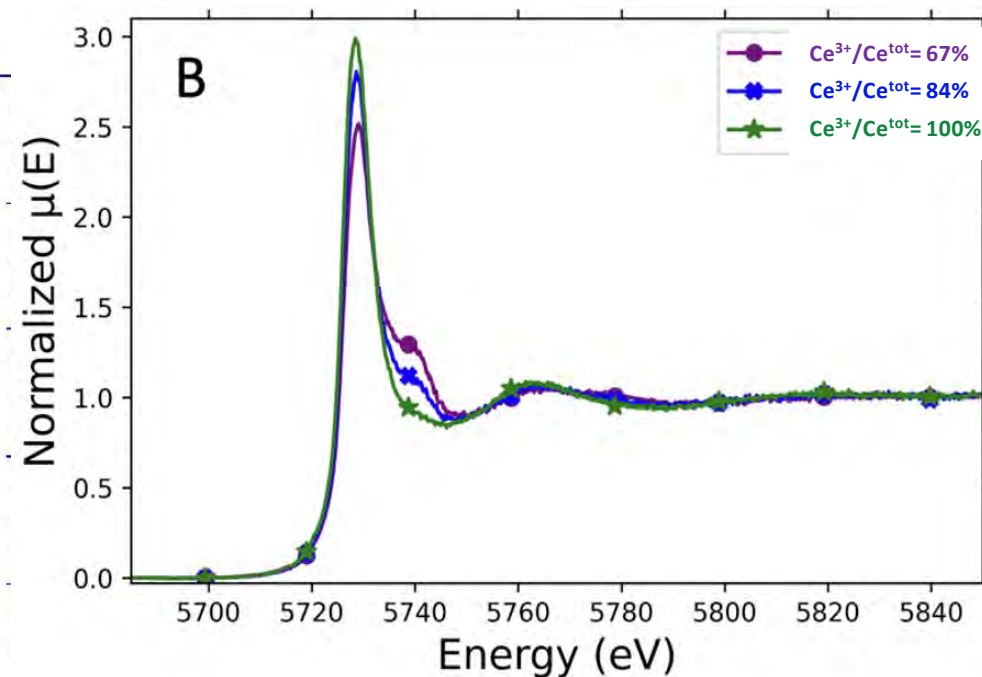
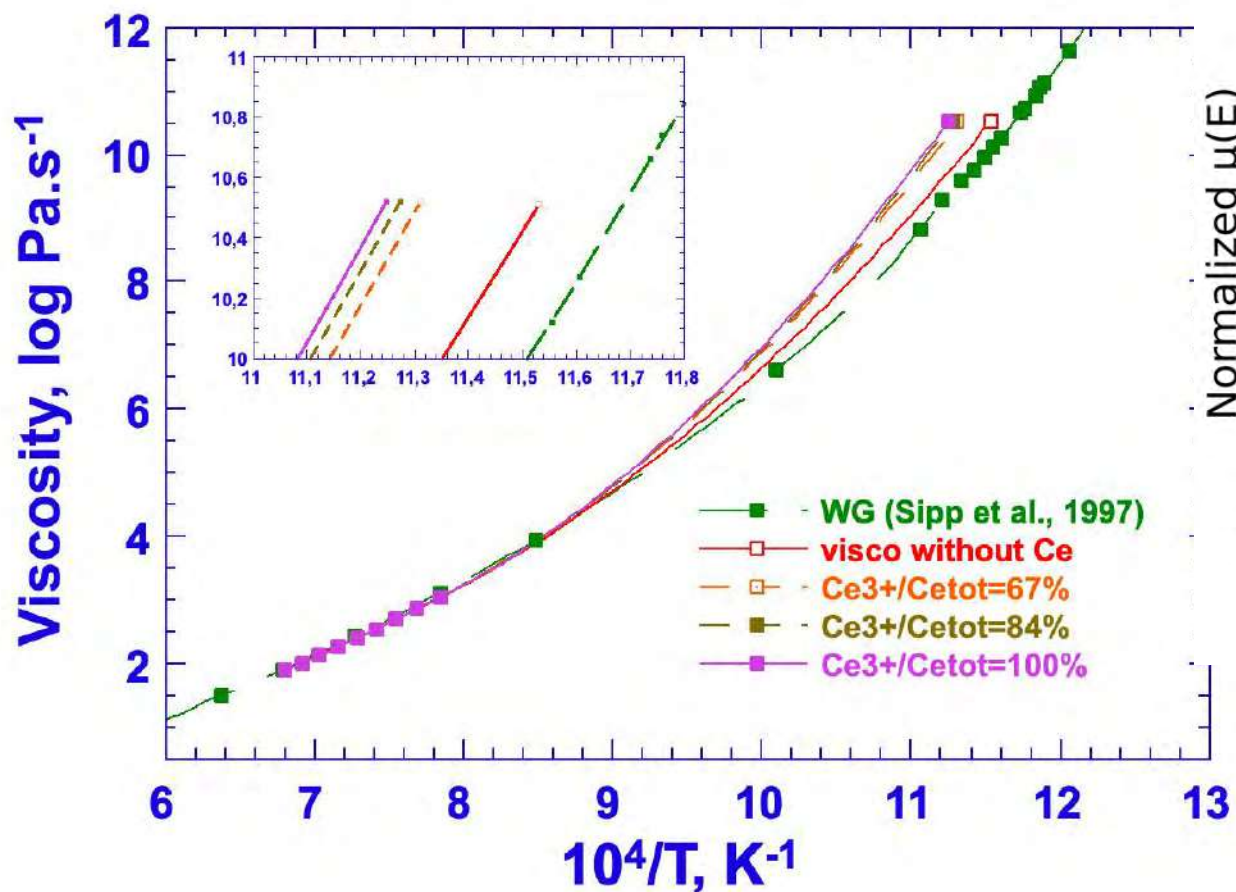
Sb³⁺ decreases viscosity



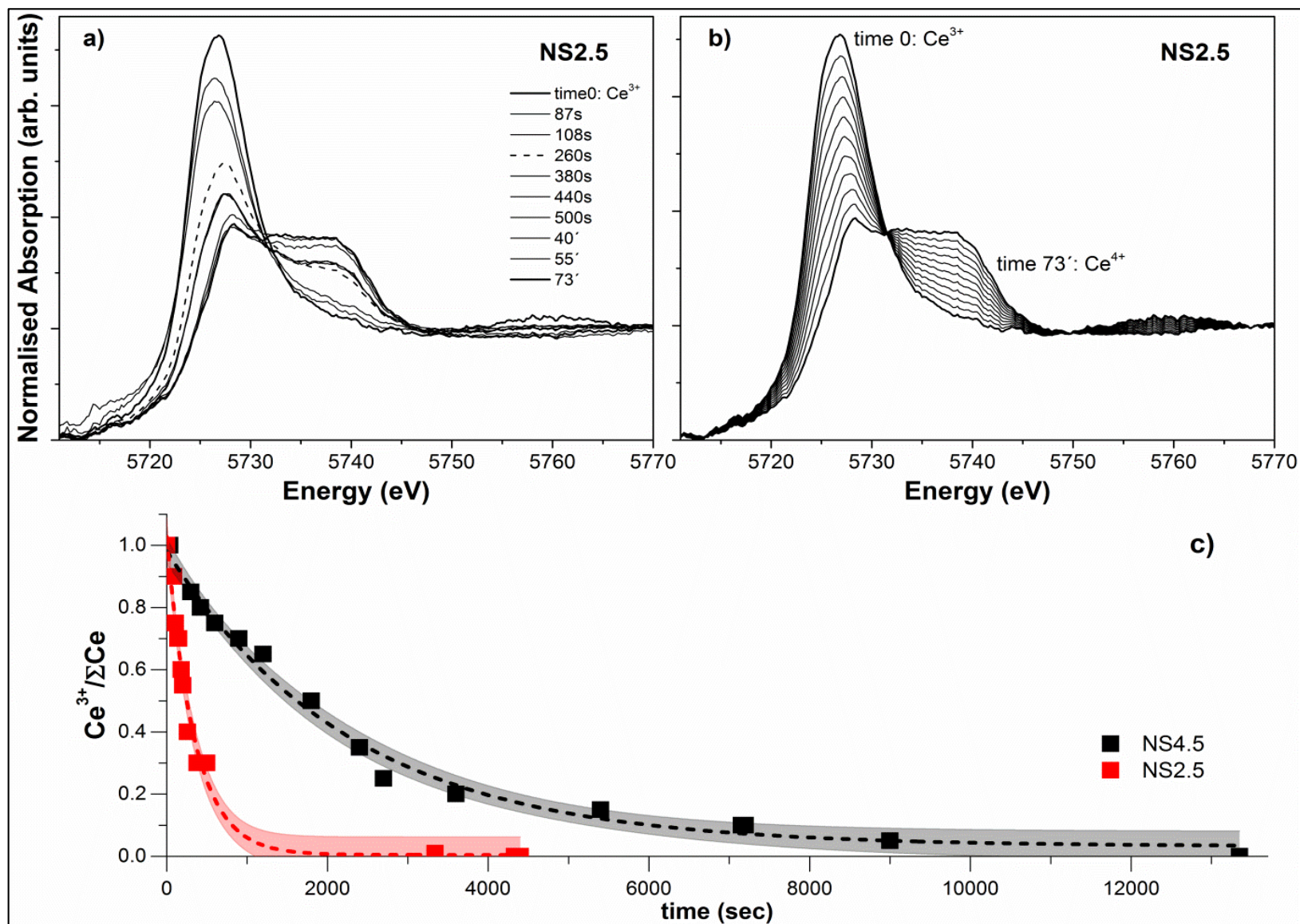
Sb K-edge XANES (Samba, SOLEIL)



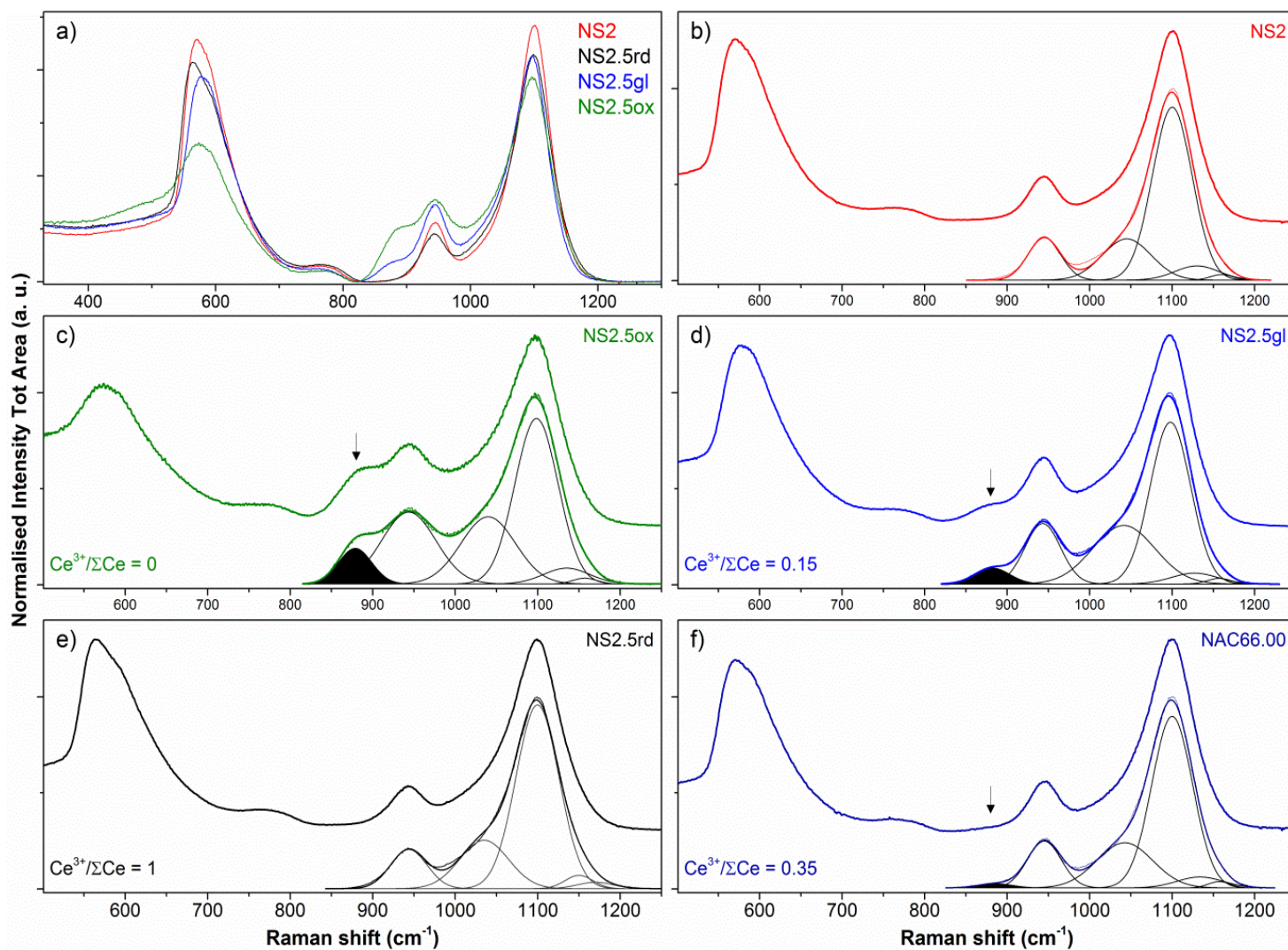
Cerium effect



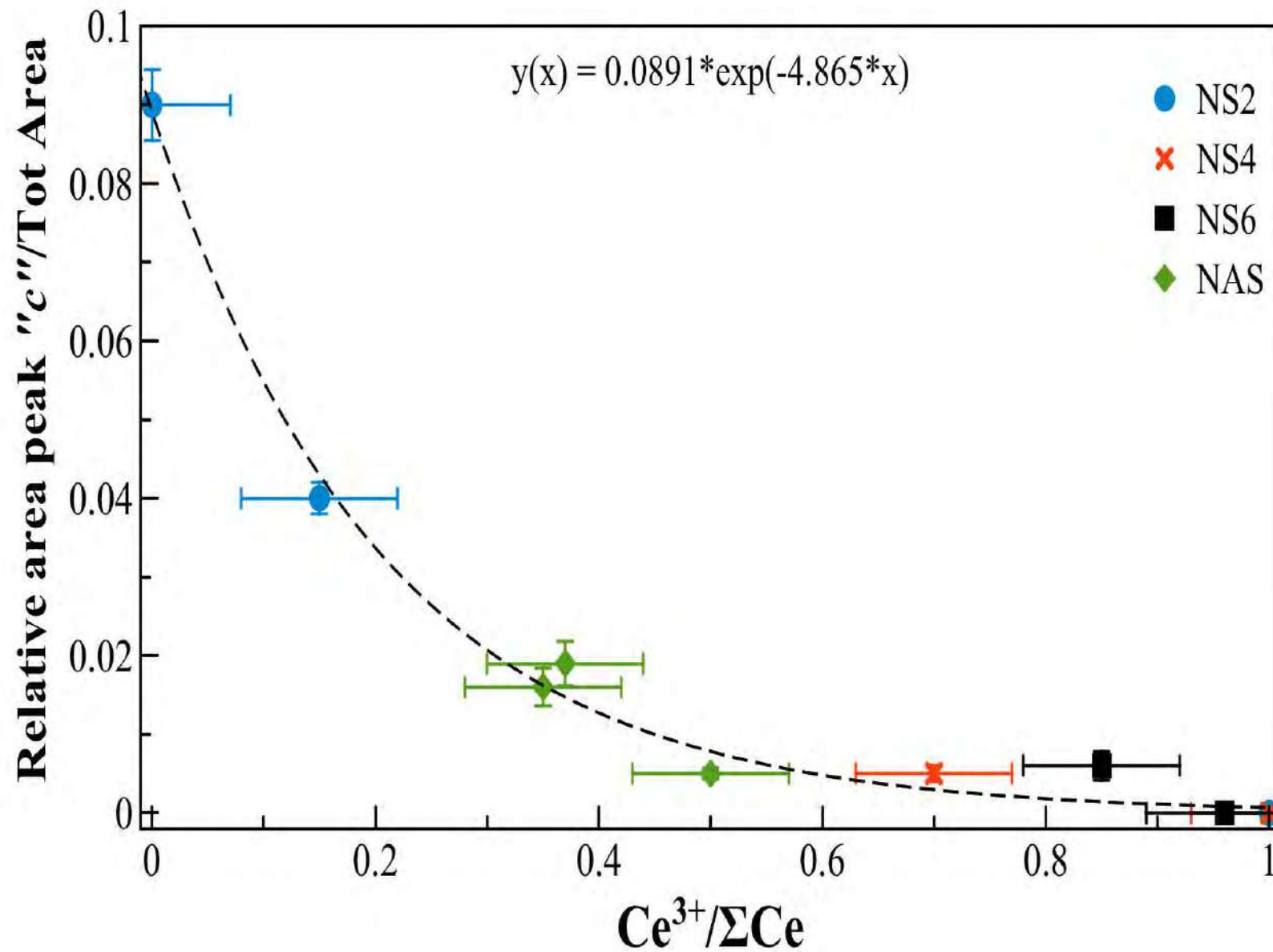
Donatini A., Pereira L., Dingwell D.B., Hess K-U, Müller D., Cormier L., Neuville D.R.
(2024) The effect of cerium addition and redox state on silicate structure and viscosity.
Journal of the American Ceramic Society. submitted



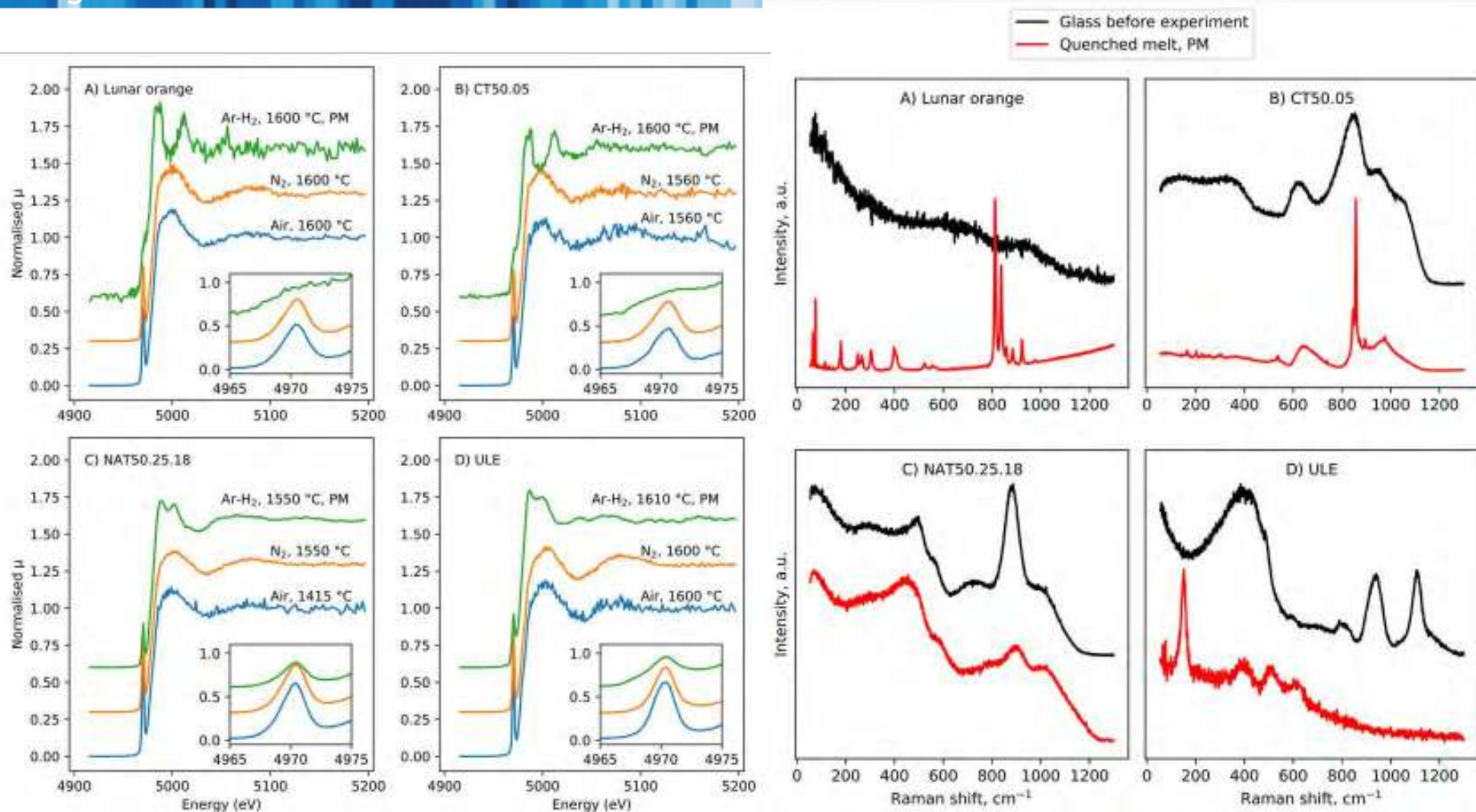
Raman spectroscopy on Ce-NSx silicate glasses



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.



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](https://doi.org/10.1016/j.matlet.2022.132296)

In situ Eu LIII and Fe K-edges ODE Beamline SOLEIL

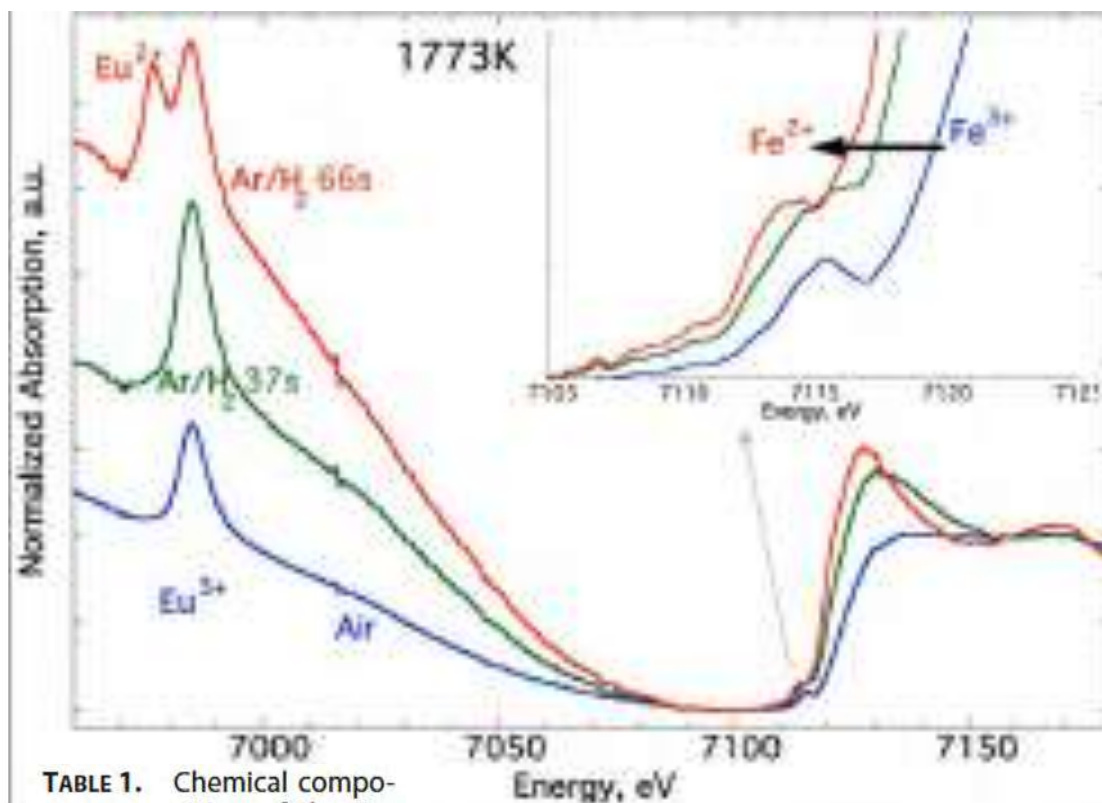
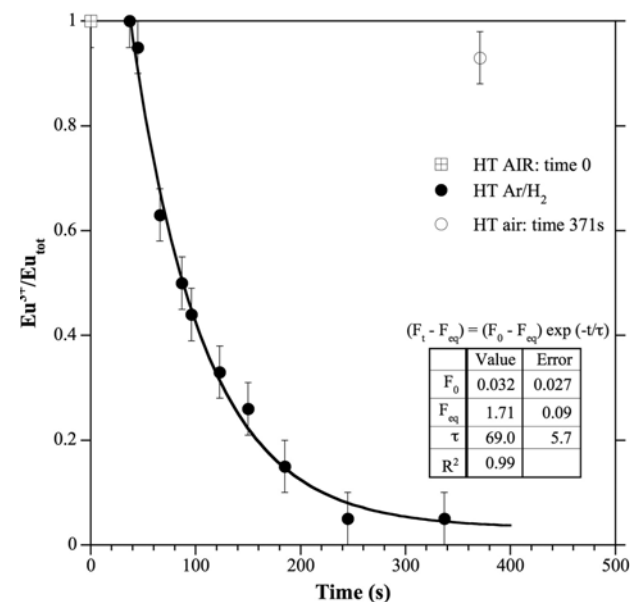
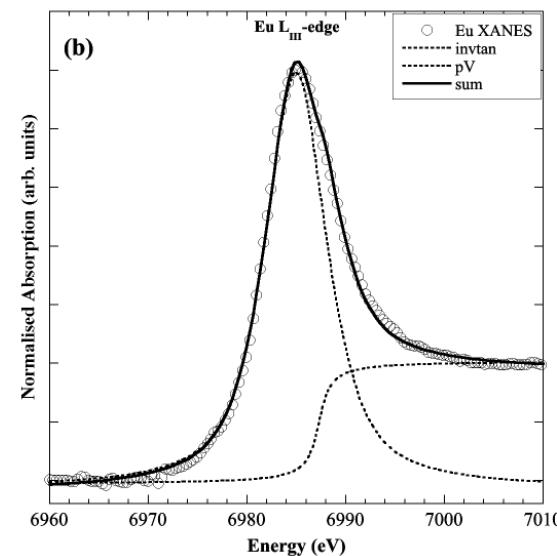


TABLE 1. Chemical composition of the Fe-basalt glass (wt%)

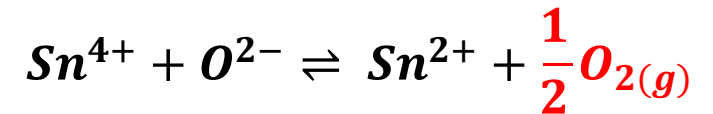
	wt%
SiO ₂	44.12
Al ₂ O ₃	9.90
FeO	15.10
CaO	5.28
MgO	5.39
K ₂ O	4.54
Na ₂ O	3.06
TiO ₂	7.72
Eu ₂ O ₃	4.89
Total	100.01



Cicconi M.R., Neuville D.R., Tannou I., Baudet F., Flouy 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.

Predicting redox equilibrium : Ce, Sn and Fe

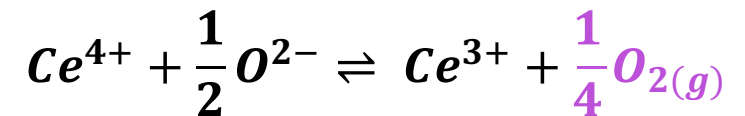
Fining of NAS at 1600° C



Bubble release at
high temperature/low viscosity

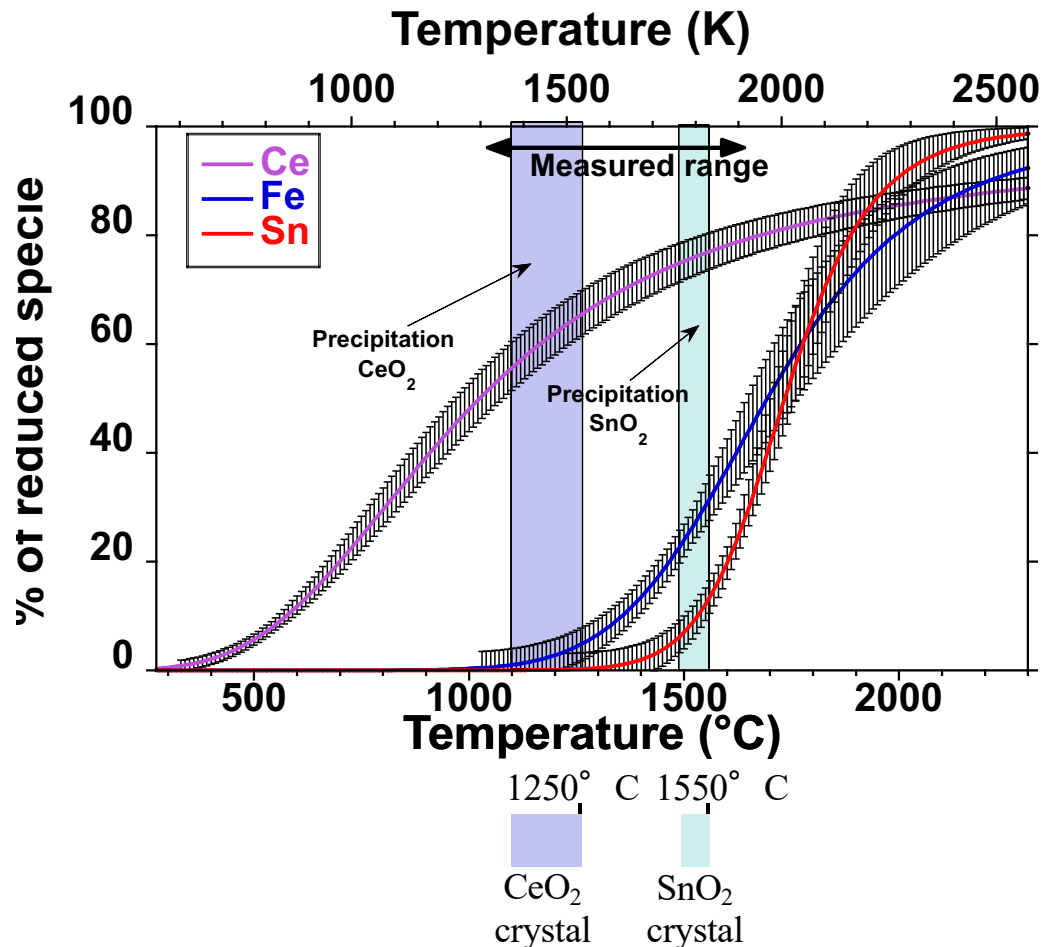
→ SnO₂ is a suitable fining agent for aluminosilicate melts (like NAS)

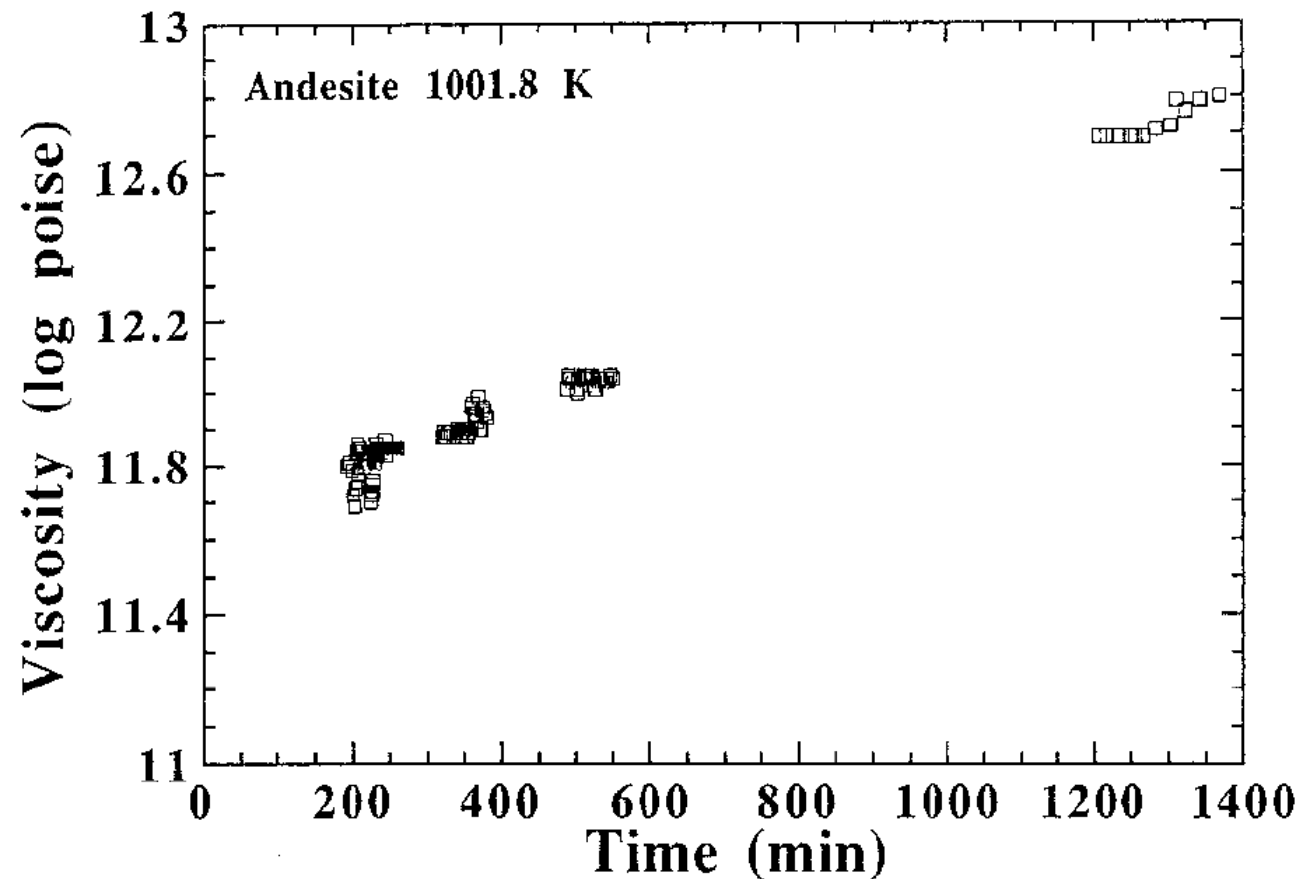
Cerium can be efficient fining agent at low T



Bubble release in NAS melt at
low temperature/high viscosity
→ Bubbles can't escape the melt

But Cerium is efficient fining agent
for window glass





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

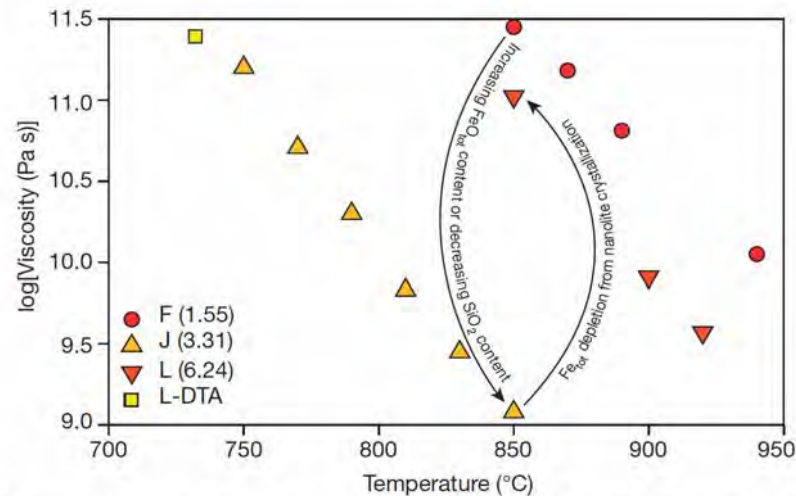
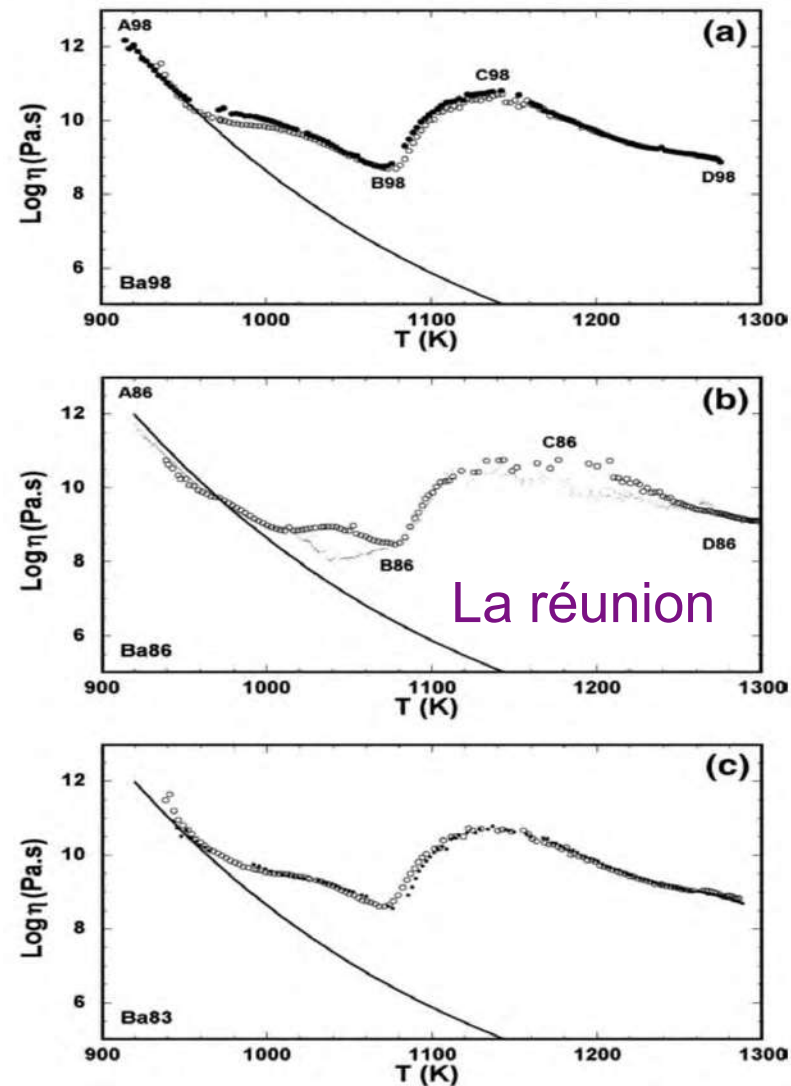


Figure 2 | Measured viscosity at 850°C for samples F, J and L characterized by increasing FeO content. FeO content (in wt%) is given in parentheses; see

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

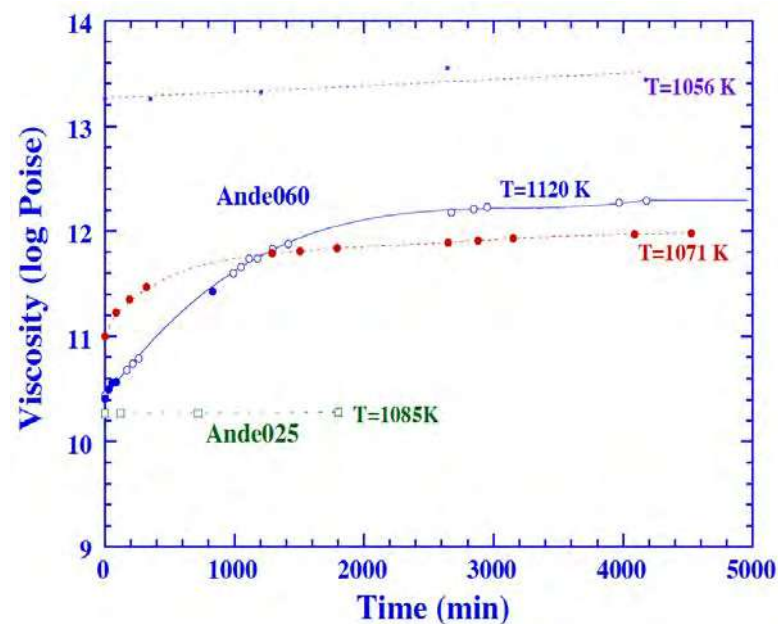
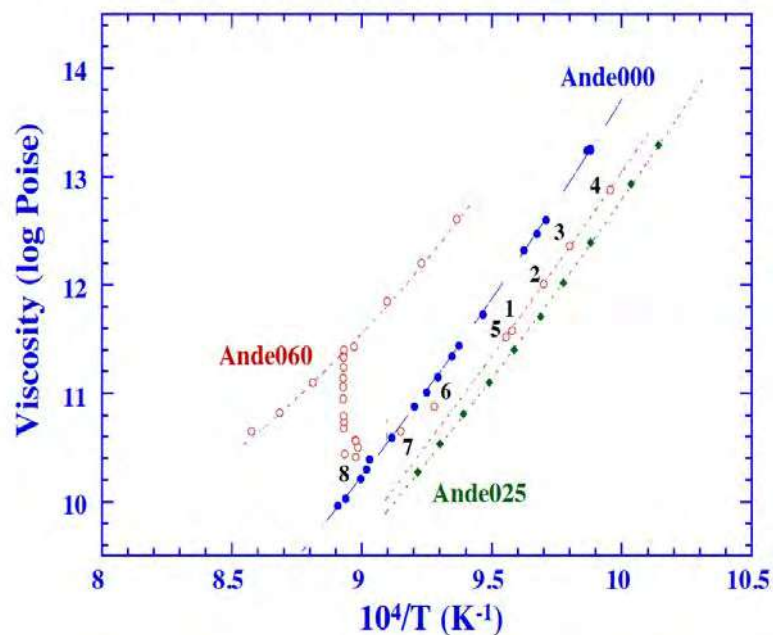
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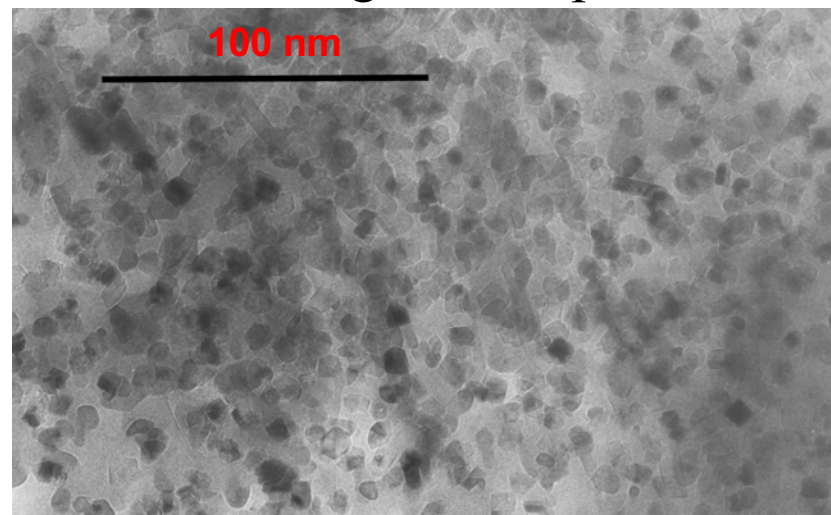
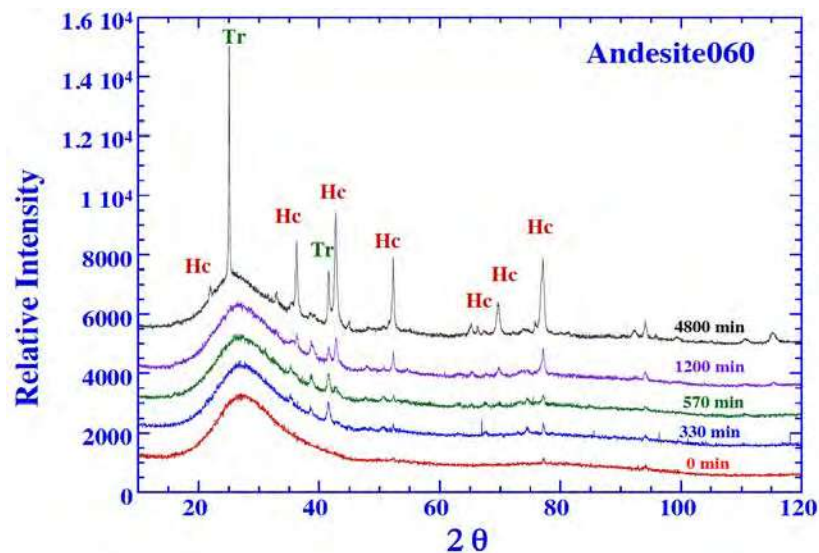


Villeneuve N, Neuville D.R. Boivin P., Bachelery P. (2008) Magma crystallization and viscosity: A study of molten basalts from the Piton de la Fournaise volcano (La Réunion island) *Chemical Geology*, 256, 242-251

Nucleation, effect on viscosity?



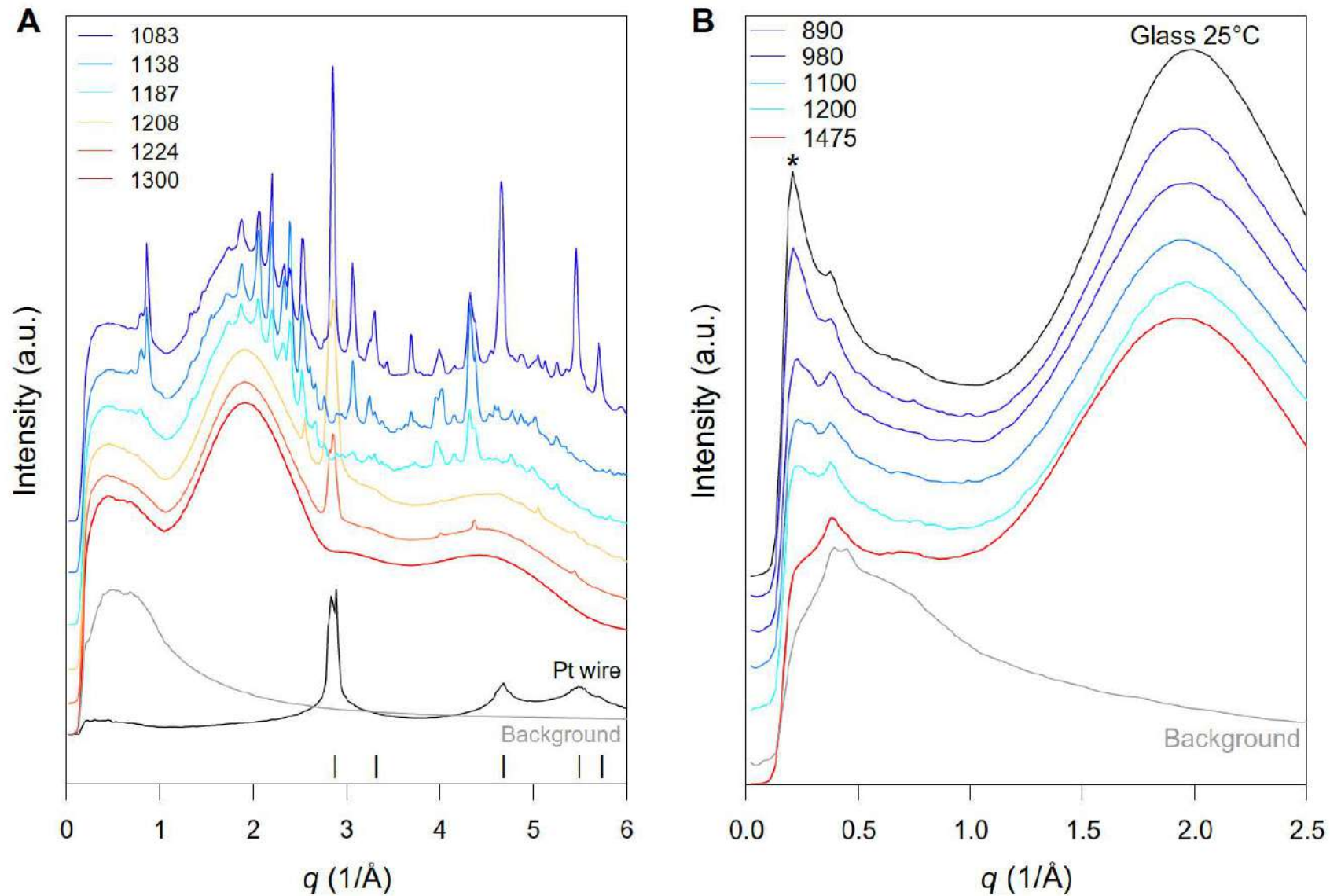
Andesitic glass composition



HR-TEM

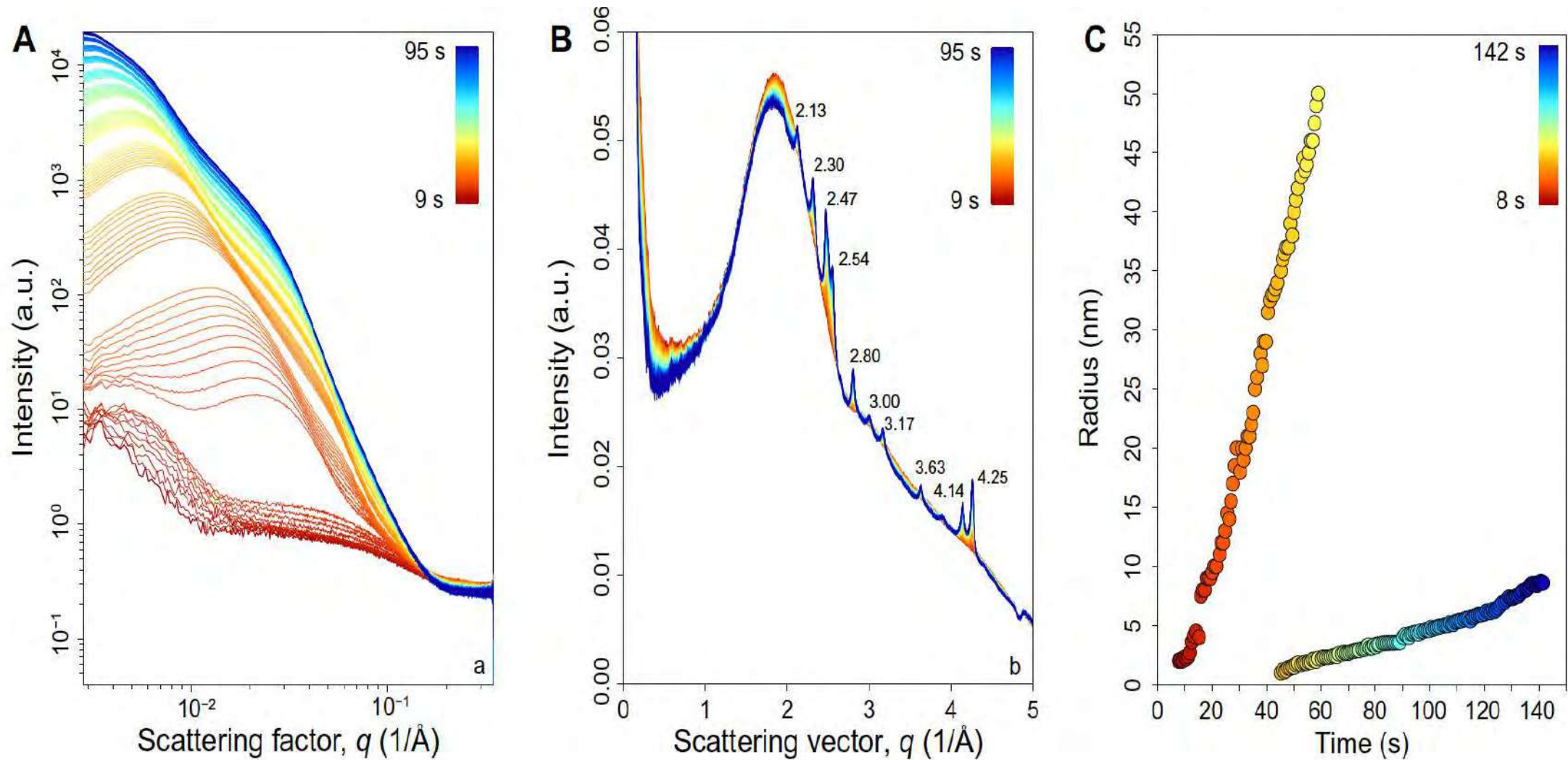
Pereira L., Linard Y., Wadsworth F.B., Vasseur J., Moretti R., Dingwell D.B., Neuville D.R. (2024) non stoichiometric nano-crystallization in magmas: the impact of composition change on viscosity. Journal of Volcanology and Geothermal Research.

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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- ✓ 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 investigate 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.