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Daniel R. Neuville

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Contributions to Mineralogy and Petrology

In situ XANES study of the influence of varying temperature and oxygen fugacity on iron oxidation state and coordination in a phonolitic melt --Manuscript Draft--

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Abstract:	<p>Iron oxidation state and environment in magmas affect their phase diagram and their properties, including viscosity and density, which determine magma mobility and eruptive potential. In turn, magma composition, pressure, temperature and oxygen fugacity affect iron oxidation state and coordination, potentially leading to complex feedbacks associated with magma ascent, degassing and eruption. While equilibrium experiments and models have led to a deep understanding of the role of iron in melts, our knowledge of the effects of disequilibrium processes on iron oxidation state and its structural role in lavas and magmas remains limited. Accordingly, we performed a series of dynamic disequilibrium experiments on a natural melt composition (a phonolite lava from Erebus volcano, Antarctica) at atmospheric pressure, in which oxygen fugacity and temperature were controlled and varied. During the experiments, we continuously measured iron oxidation and coordination using Fe K-edge dispersive X-ray Absorption Spectroscopy (XAS). We found that iron oxidation state changes in the phonolite melt are reversible and well reproduced by existing models. Changes in iron oxidation state are driven by joint diffusion of alkali cations and oxygen anions at magmatic temperatures (~1000 °C for Erebus phonolite). However, redox diffusion timescales are too slow for any significant oxygen exchange with the atmosphere at the lava/air interface or via air entrainment. Turning to iron coordination, while Fe²⁺ and Fe³⁺ are present mostly in an average five-fold coordination, complex</p>	

and of his color. For the reported experiments, the XANES signal was stable, we checked (when possible) after the runs that the Raman spectra of the quenched melt were in good agreement with that of the original material, and we systematically visually inspected, using a microscope, the samples to check that no nuggets of iron were present in the glass.

We observed iron loss to the wire in most experiments with Ar-H₂, a very reducing gas. We also observed iron precipitation as metal nanonuggets in such experiments. We systematically excluded those experiments.

We need to say that we actually excluded more than half of the experiments we performed because we were not sure about the quality of the signal and that the sample composition was not modified during the run (to the best of our knowledge because microprobe analysis were not possible to perform, see text). No iron loss to the wire or precipitation of iron metal was observed in more oxidising conditions (N₂ and Air), in agreement with previous experiments performed with this setup by Magnien, Cochain, Neuville, Cicconi and co.

Editor comment:

From an editorial point of view, I would ask you to ensure upon revision that the formatting of the manuscript is consistent with this journal. For example, there should be no numbering of headings and subheadings and journal titles in the reference list should be abbreviated.

Author's reply:

Of course, the revised version now matches the formatting of CMP.

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Reviewer #1

Reviewer's comment:

The paper is well written and clearly structured; the abstract contains some language problems that should be looked at. Overall, the results and the analysis are well documented and do constrain most of the interpretations, unless stated otherwise below.

Authors reply:

Sorry about the abstract. We realised it was probably the result of a bad copy-paste of an older version as some sections were not supposed to be like this. We revised the abstract in the new manuscript, and we hope that those revisions solve this problem.

Reviewer's comment:

As outlined below, the cited literature is strongly biased and should be adopted to represent the work that has been done in that field.

Authors reply:

Excuse us about such bias, we tried solving this in the revised version, paying more attention to the references and citing more various sources of references from the works of Giuli, Wilke, O'Neill, Berry, Cicconi, Fiege, Cottrell, Zhang... We believe this solves the problem.

Reviewer's comment:

The authors use the pre-edge centroid as a figure of merit to trace the changes in oxidation state, without converting to actual values of Fe³⁺/Fe²⁺. This is fully

acceptable to analyze the dynamics of the reaction. Still they do plot pre-edge intensity and centroid on the diagram of Wilke 2001 and start interpreting the intensity in terms of site symmetry in a quantitative manner. The authors have not shown at all that their data reduction is consistent with the values of that diagram. This needs to be checked by known samples, e.g. known glasses or model compounds.

Authors reply:

We understand the concern of the reviewer. Indeed, we originally have not shown the reference diagram implemented in our laboratory with our data reduction protocol. We cited the thesis of Cochain, but we understand this is not enough.

As a consequence, we added the spectra of the reference compounds as well as the reference diagram in Supplementary Figure 2. The data reduction protocol is better presented in the Material and Methods section, as well as the establishment of this reference diagram with the used data reduction protocol.

We hope those changes will fulfil the reviewer expectations, and solve this problem. Thanks for pointing this weakness!

Reviewer's comment:

Given the quality of the data presented in Fig. 1b, I suspect that the very low pre-edge intensity observed for samples in N₂-gas is an artifact of the treatment. In fact the pre-edge intensity in figure 1b is quite low, which looks weird. Other in-situ measurements have not shown this (Wilke et al. 2007, Magnien et al. 2004, 2008). Especially, extracted pre-edges in the first two look pretty similar and different to those here.

Authors reply:

It is normal that our integrated intensities do not match those of Wilke or Magnien, as our data reduction protocol is not the same. Again, we take that into account by implementing a revised version of the centroid vs μ diagram that was made using our protocol.

The pre-edge intensity in Figure 1b for the N₂ sample just reflect the fact that this spectrum contains a mixture of Fe³⁺/Fe²⁺. Actually, the two contributions are fairly visible, and the intensity is coherent with what it should be. Also, the Ar-H₂ spectrum is more noisy due to Ar absorbing a significant portion of the X-rays at ~ 7114 eV.

Reviewer's comment:

The authors need to prove that their data treatment is consistent with plotting it on this diagram. Otherwise, just don't use it and cut out all considerations regarding the site symmetry (coordination) of Fe. Analysis of the dynamics and extraction of the transport parameters should not be affected by this, as it directly uses the centroid.

Authors reply:

We believe that this problem is now solve with the addition of all the details mentioned above.

Reviewer's comment:

Line 43 ff.: The overview on the literature does not give a comprehensive picture on the work that has been done on Fe in melt. Furthermore, it is strongly biased on work of the group, i.e. Neuville and friends. Wilke et al. 2001 is the basis for this XANES work, but the paper on quenched glass is Wilke et al. 2004. Anyway, there is further work to be cited in the XANES business! The sentence line 49-50 is even wrong by content. That Fe³⁺/Fe²⁺ partitioning is driven by the mentioned parameters is known way longer than those papers cited at this position. Please, correct this and provide a fair overview on the current status of the literature Fe in melts as well as the XANES approach.

Authors reply:

We believe the new version should avoid such citation caveat, and corrected this sentence. See the new introduction, lines 71-86.

Reviewer's comment:

Line 60: Again literature is not complete. The in situ study of Wilke et al. 2007 (AmMin 92, pages 44-56) is missing, as well as the one of Drewitt et al. 2013 Phys Rev B 87, 224201 (2013). There is even a short paper that describes a very similar experiment as the one here (Wilke et al. 2007, AIP Conf. Proc., 882, 293-295). Those data are very consistent to these presented here.

Authors reply: Thanks, we added those papers.

Reviewer's comment:

Line 67: What is meant by Fe³⁺/Fe^{tot} data are available for this composition and what is meant by parametrization? Please, specify in more detail. If this is so well known, why don't we find any comparison in the text? It would be really helpful to see what oxidation state can be expected for the used conditions.

Authors reply: This sentence was actually clumsy and thus removed from the new version. The reviewer will also appreciate that the comparison is now provided in Figure 5.

Reviewer's comment:

Line 102: The units of the oxygen fugacity are missing. Bars? Only log fO₂ has no units. Please, correct!

Authors reply: Corrected !

Reviewer's comment:

Line 119: How can the composition of a glass be determined by Raman spectroscopy? This is non-sense, for the composition you would need to use microprobe or a SEM with EDX. In any case, provide a correct statement. Specify whether you really looked at the composition after the experiment by an appropriate method. If not then discuss the potential errors on the composition.

Authors reply:

It is very difficult to embed a full platinum wire in an epoxy ring for EMPA measurements. Plus we don't want to do that because Pt wires are expensive, have a time-consuming T-I calibration, and thus they are meant to be cleaned in HF and re-used for performing other experiments. So we had to check that sample composition was not affected during the experiments by other means.

There were little details on this part in the previous manuscript. In the revised version, we added more details on the protocol we adopted to prevent compositional changes or iron precipitation/alloying, and on the steps we took to detect such changes.

Instead of going in details there, we invite the reviewer to have a look at the new Material and Methods section, lines 197-233. All elements are present to reply to this comment.

Just a precision: appropriately calibrated, Raman spectra can be used to determine the composition of a glass to within 0.5 to 1 mol%, depending on the element (see Di Genova et al. 2015 Journal of Raman Spectroscopy 46: 1235-1244 for an attempt on experimental glasses, and more particularly for a real application on MORB glasses Le Losq et al. 2019 American Mineralogist 104:1032-1049). Indeed, Raman spectroscopy is very sensitive to changes in the glass structure, which is driven by glass

composition. This is why, with some experiences performed at conditions similar to that of the original glass synthesis, we can check that Raman spectra of starting materials and of the glass from the experiments match. No differences indicates no change of glass composition in a quite tight chemical domain.

Reviewer's comment:

At reducing conditions Fe may be easily lost to the Pt-wire, as documented by many studies.

Authors reply:

Yes, we had trouble for a fair number of experiments that showed significant changes in Raman spectra as well as optical changes as checked with the microscope. Those experiments were discarded, and are not reported in this publication as indicated in the Materials and Methods section.

To be honest, most experiments in Ar-H₂ were affected by this effect and are not reported. Experiments in Air or N₂ were not affected by this phenomenon, explaining why reported dynamic runs were made under those fO₂ conditions.

Ar-H₂ runs were not informative as, except at the beginning of the experiment were a few spectra can be acquired (the spectrum in Fig. 1B was acquired after 10 minutes of equilibration at the beginning of a run for instance), iron precipitated in most cases. This is why no dynamic runs under the Ar-H₂ atmosphere are reported.

We must say that on 7 successfully performed "dynamic" runs, only three were really good as they met strict criteria indicating no crystallisation, no iron loss, no chemical change in the sample. In the other runs, we sometime tried to introduce Ar-H₂ that resulted in Fe loss, we also set temperature at values too low resulting in a crystallisation visible on the XANES spectra and optically after the experiments, or simply the run went fine but the post-experiment Raman spectra looked odd (see Supplementary Materials for examples).

Again, we tried to better report on this in the Material and Methods section, so we invite the reviewer to have another read. We hope the new version will give a better overview of the performed work, and of the measures we took to be sure that sample chemical composition changes are negligible.

Reviewer's comment:

Line 135: Using the diagram of Wilke et al. 2001,2004 means that the authors have to prove that their data treatment is consistent with the one used to construct the diagram. This could be easily done with a few measurements on glasses with known oxidation state.

Authors reply:

We were not be very clear in the previous version of the manuscript, but the data treatment for constructing the centroid versus intensity diagram is the same as the one used for the glasses. Indeed, the Wilke diagram had to be adapted to the results obtained with our data reduction protocol. To clarify this, the new version of the manuscript presents in Supplementary Figure 2 the reference materials used for reconstructing the centroid versus intensity diagram, and this is now much better presented in the new manuscript (see Lines 235-270).

Reviewer's comment:

Figure 1: The quality of the data measured in air seems great. However, those in Fig. 1b are much worse. I am completely disturbed by the low pre-edge intensity of the N₂-spectrum. With such data it seems questionable that the analysed centroid and intensity values can be directly compared to the centroid diagram without further proof.

Authors reply:

The pre-edge intensity of the N2 spectrum is not low, it is actually bimodal with a clear separation between Fe²⁺ and Fe³⁺ contributions. We want to remind the reviewer that Fe²⁺ contribution is much less intense than the Fe³⁺ contribution (see intensity versus centroid diagrams).

The integrated intensity of this signal agrees with the trend $[5]Fe^{2+} - [5]Fe^{3+}$ reported in figure 2 for instance.

The higher noise under the Ar-H₂ atmosphere is due to the higher absorption of X-Rays by Ar than by air, O₂ or N₂.

Reviewer's comment:

I am not questioning that the values do reflect the state and dynamics of the oxidation state. I only question that you can compare them to the diagram. Since the systematics of the oxidation state in this melt system are known (see above), the authors could provide info what the expected oxidation state is for the given conditions. This way one could document how the centroid position on the diagram reflects the oxidation state.

Authors reply:

Thanks for this comment. We originally thought this would not bring something to the discussion, but you made us realize that this will be better with the comparison!

This is now performed, see Results section lines 325 – 356 and new Figure 5.

Reviewer's comment:

Line 195: I have never seen such a trend on the centroid diagram. Data of the in-situ study of Wilke et al. 2007 plot very similar to the trend known for glasses from many other XANES studies. This is a further indicator that the authors should first prove that their data treatment is consistent with this diagram. What are the expected oxidation state values for the presented conditions? E.g. by Schuessler et al. 2008, Kilinc et al. or the Moretti model?

Authors reply:

Please again see new Figure 5 for the oxidation state of iron.

Yes, we also never saw such a trend. But to our knowledge, nobody really reported trends in this diagram during dynamic in situ experiments... The dynamic Wilke experiments do not report data in the centroid versus integrated intensity diagram as they only acquired a very limited portion of the signal (actually at one given energy). Therefore, the lack of systematic records of in situ XAS spectra during iron redox changes in melts may explain why this has never really been reported previously.

There is no problem with the oxidation state of the melts, see Figure 5 where equilibrium data from all experiments presented in Figures 1 to 4 are reported.

Thus, with changes in redox coherent with expectation, we have changes in Fe CN that are happening during the dynamic experiments. At the moment, we have no real answer about the factor controlling such changes. This will be the topic of new experiments in the upcoming years.

Reviewer's comment:

Line 222: This is a completely unconstrained statement. How can the authors detect ionic couplings with surrounding oxygens by XANES?

Authors reply: Wrong choice of word, this was deleted.

Reviewer's comment:

The pre-edge reflects the average site symmetry, nothing more.

Authors reply:

Yes, we just meant that by detecting Fe3 in CN 4-5 via XAS and coupling this information with the theory, this implies Fe3+ as a network former unit in FeO4 and FeO5 polyhedra. But again, wrong choice of word, and the discussion of the new version changed significantly for improved clarity. We invite the reviewer to have another look at the discussion.

Reviewer's comment:

If well calibrated the authors may turn this into information on the average coordination polyhedron. I am missing the calibration!

Authors reply:

Again, we understood this point and as commented several time above, we provide such data now. Please see Material and Methods, Supplementary Figure 2 and the new Results section.

Reviewer's comment:

Line 345: It has been shown that the Fe oxidation state may be easily changed at temperatures just above the glass transition (e.g. 600°C), Burkhard 2001, J Petrology 42, 507-527. So, this final statement seems to be rather arbitrary. Further, the whole paragraph does not mention at what temperature the scenario is discussed. Please, rewrite.

Authors reply:

The lava lake size is of 40*80 meters, with a depth that probably scales in the ~ tens of meter value. Typical residence time of the magma is of the order of ~ 5-10 minutes (see reference in the manuscript), so even with diffusion at Tg (much slower than at 1100 °C !) you would have only a very limited diffusion front and would not modify the bulk redox state of the magma.

This is actually what is happening because the redox state of the magma is more reduced at surface that in the deep part of the conduit. Please see Oppenheimer et al. (2009) for details and Discussion in this paper.

We modified the paragraph to include the temperatures (they were in Figure 6). This statement is not arbitrary but results from a logical deduction, so we did not modify it.

Reviewer's comment:

Line 354: I think the statement on the structural role is completely unconstrained, which is based on the defined reactions used for thermodynamical analysis. Even a 4-fold coordinated Fe2+ cannot be regarded as network-modifier due the low field-strength of this cation.

Authors reply:

We guess the reviewer meant that Fe2+ in four fold coordination cannot be regarded as a network former, and we agree. We modified the manuscript and our equations to take that into account.

Reviewer's comment:

One could rather consider it as a strong network modifier.

Authors reply: Yes, we agree.

Reviewer's comment:

If there is really 4-fold coordinated Fe²⁺ then this rather indicates the shortcoming of our simple picture of silicate melts. Mg²⁺ shows a very similar structural role as Fe²⁺, no one would ever consider it as network former.

Authors reply:

This is a valid point, indeed. We did not really consider Fe²⁺ in CN₄ as a network former unit in the same way as Si for instance, but rather wanted to point that Fe²⁺ in CN₄ may have properties very different from other CNs... In any case, it is unlikely to find Fe²⁺ in CN₄ given our data. We thus rewrote this part to clarify things.

Reviewer's comment:

Please, rewrite all these assignments in an appropriate way, so that it is constrained by the data. I do admit though that Fe³⁺ may be found in both structural roles, similar to Al³⁺.

Authors reply: Done, please see the new version of the discussion, and in particular lines 388-410.

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Reviewer #2

Reviewer's comment:

Line 18: Missing 'of' before iron.

Authors reply: Corrected.

Reviewer's comment:

Line 30: I would suggest to change 'hence on how they associate' to 'associating' (and 'releasing') to simplify the sentence.

Authors reply: The abstract has changed, we hope the new version will fulfil the reviewer's expectations.

Reviewer's comment:

Line 47: Can the authors give one or two examples of how iron oxidation state affect the physico-chemical properties of melts?

Authors reply: Examples are now provided, please see the new introduction.

Reviewer's comment:

Lines 59-60 and 65-66: Simplify/Reorganize by saying 'can however be studied in-situ (i.e., at high temperature in the liquid state) using [...XANES] spectroscopy' and 'In this study, we used in-situ Fe K-edge XANES spectroscopy to investigate the coordination'.

Authors reply: Done, thanks.

Reviewer's comment:

Line 70: Signal without s?

Authors reply: Corrected.

Reviewer's comment:

Line 80-81: can the authors briefly mention what kind of method they used to prepare the crystal free starting material? It's only few extra words, but it helps the reader not to have to go and check in previous papers...The reference to Le Losq et al. should however be kept.

Authors reply: Yes, good point. We added a whole paragraph and kept the reference for details.

Reviewer's comment:

Line 89: I would suggest using 'in-situ XANES measurements' rather than 'experiments by XANES spectroscopy'.

Authors reply: Done.

Reviewer's comment:

Line 98: specify 'intensity on the Pt wire'.

Authors reply: Done.

Reviewer's comment:

Line 99: 'and temperature was monitored during measurements with an optical pyrometer' - I think this formulation would be clearer for non experimentalist?

Authors reply: Yes, corrected.

Reviewer's comment:

Line 125: The authors had just finished describing Raman spectra, so I would advise to say XANES spectra here, so that the sentence is clearer for the reader.

Authors reply: Yes, thanks, corrected.

Reviewer's comment:

Line 138: 'the Fe K-edge edge' - to correct.
I would also advise to replace 'constant fO2' by 'air fO2'. Or even just mention 'in air (fO2=0.21)'.
Authors reply: Corrected

Authors reply: Corrected

Reviewer's comment:

Line 144: 'varying fO2 (air, N2, ArH2)'

Authors reply: Corrected.

Reviewer's comment:

Line 144-147: I suggest to change to 'clearly showing the reduction of Fe, until Fe2+ dominates under ArH2 fO2 (10-15)' to shorten the sentences.

Authors reply: Thanks, modified.

Reviewer's comment:

Line 195: the Authors mention Fe3+ in CN4. Is that for air (ie., not shown in Figure 2 or 3)? Please explain.

Authors reply: We deleted this sentence, it was not right and not very informative. This helped improve this part.

Reviewer's comment:

Lines 215-217: Why using the prime notation and not FeIIIFeIII?

Indeed, the FeII FeIII notation will be more coherent with e.g. Moretti 2005 for instance.

Authors reply: Yes, thanks, this is a good point, and we modified the text to follow the notation introduced in Moretti (2005)

Reviewer's comment:

Line 222-223: remove nevertheless

Authors reply: Corrected.

Reviewer's comment:

Line 227: Missing space between these and phonolites

Authors reply: Corrected.

Reviewer's comment:

Line 309 and 331: The authors give two slightly different water contents for the Erebus lavas. Is the 0.2wt% also based on Moussalam et al?

Authors reply:

The mean value in the superficial plumbing system is of 0.2 wt%, and the most hydrous phonolites (at depth) present a water content that can reach 0.6 wt%. This is implied as in the first case we clearly speak of the lava lake, and in the second case of the tephriphonolite to phonolite evolution trend. All values were published in the cited papers.

We modified the text to reflect this and make things clearer.

Reviewer's comment:

Figure 5: The authors report D_i from rhyolitic compositions. Can the authors precise how different they may be for a phonolitic composition?

Authors reply:

We did not find lots of data regarding diffusion experiments. Most of them were done on rhyolites, a few on basalts, and also on simplified compositions. Rhyolites are richer in silica and depleted in alkaline-earth elements compared to phonolites. However, both present an important fraction of alkali elements, which drive redox exchanges at temperatures close to T_g . This is why we have chosen to plot D values from rhyolites in this case (also because D values on phonolites do not exist...)

We added a comment to clarify such choice in the text, see lines 493-504.

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Reviewer # 3

Reviewer's comment:

My main request is to have more detail on the experimental and analytical set-up, and for supplementary data to be provided.

Authors reply:

We thank the reviewer for the comments that helped improving this part of the manuscript.

The new version of the manuscript comes with an updated Material and Methods section, supplementary figures presenting the XANES standard for the centroid versus integrated intensity diagram, examples of Raman spectra of starting materials and of successful runs and failed experiments, and examples of pre-edge modelling. We hope that those new pieces of information will fulfil the reviewer expectation.

Reviewer's comment:

"Iron redox and environment" – title, L24, L36

The term "environment" is here used as a way to summarize the variables of temperature and atmospheric gas composition, both of which are controlled in the experiment set-up. I think the title is a little misleading: as it is worded, it implies that the paper is a dynamic study of environment, but actually the "environment" variables are being controlled and what is being studied is the response to the changing environment in iron redox and co-ordination number. Could the title and phrasing in L24, L36 be modified slightly to reflect this? E.g. L24 "In such cases, little is known about the behaviour of iron redox in response to a rapidly changing magmatic environment".

Authors reply:

We understand that the term "environment" leads to some confusion as it could refer to T-fO₂ as stated by the reviewer, but by iron environment we actually meant iron molecular environment.

This is now clarified by the new version of the title, where we replaced environment by coordination. This was also changed in the abstract.

Reviewer's comment:

I'd consider pressure to be an "environmental" variable relevant to natural magmatic systems. Please add a sentence somewhere near the beginning explaining that P is an intensive variable that does change in natural systems, even though this particular study is conducted at constant P. Do the authors expect that pressure would also have some effect on iron speciation and co-ordination number? It would be interesting for the authors to comment on what effect (or not) pressure might be expected to have. The biggest pressure effect might be outgassing of redox-sensitive volatiles like sulfur, so this could usefully be added to the discussion section around L340.

Authors reply:

The effect of pressure is actually known for iron: it promotes higher coordinated species (e.g. see Sanloup 2016 *Chemical Geology* 429:51 and references cited therein) and forces iron to go in a 2+ valence as pressure increases (e.g. O'Neill et al., 2006, *American Min.* 91:404).

However, you have to go to the GPa range to see effects, at pressure higher than those of the superficial Erebus plumbing system. Furthermore, we just cannot perform the same experiments under pressure. This is why all the discussion is geared toward the lava lake and the superficial plumbing system.

We included a paragraph on the effect of pressure in the Discussion (see lines 530-539), thanks for the wise suggestion.

Reviewer's comment:

Experimental methods

I would like to see a brief summary of the preparation of the starting material. Is it prepared by crushing the bulk sample including the 30 vol.% anorthoclase phenocrysts?

[Click here to view linked References](#)

1 ***In situ* XANES study of the influence of varying temperature and oxygen**
2 **fugacity on iron oxidation state and coordination in a phonolitic melt**

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20 Abstract

21
22 Iron oxidation state and environment in magmas affect their phase diagram and their properties,
23 including viscosity and density, which determine magma mobility and eruptive potential. In turn,
24 magma composition, pressure, temperature and oxygen fugacity affect iron oxidation state and
25 coordination, potentially leading to complex feedbacks associated with magma ascent, degassing
26 and eruption. While equilibrium experiments and models have led to a deep understanding of the
27 role of iron in melts, our knowledge of the effects of disequilibrium processes on iron oxidation
28 state and its structural role in lavas and magmas remains limited. Accordingly, we performed a
29 series of dynamic disequilibrium experiments on a natural melt composition (a phonolite lava from
30 Erebus volcano, Antarctica) at atmospheric pressure, in which oxygen fugacity and temperature
31 were controlled and varied. During the experiments, we continuously measured iron oxidation and
32 coordination using Fe K-edge dispersive X-ray Absorption Spectroscopy (XAS). We found that iron
33 oxidation state changes in the phonolite melt are reversible and well reproduced by existing models.
34 Changes in iron oxidation state are driven by joint diffusion of alkali cations and oxygen anions at
35 magmatic temperatures (~1000 °C for Erebus phonolite). However, redox diffusion timescales are
36 too slow for any significant oxygen exchange with the atmosphere at the lava/air interface or via air
37 entrainment. Turning to iron coordination, while Fe²⁺ and Fe³⁺ are present mostly in an average
38 five-fold coordination, complex coordination variations decoupled from redox changes were
39 detected. The data suggest transitions between Fe³⁺ in four-fold and six-fold coordination prior to
40 reduction or as a consequence of oxidation. This questions the possible implication of Fe
41 coordination changes in triggering crystallisation of magnetite nanolites upon magma ascent, and,
42 through such crystallisation events, in promoting magma explosivity.

43
44 **Keywords:** magmas, iron, oxidation state, coordination, XANES spectroscopy, volcano

45
46 **Declarations**

47
48
49 **Funding**

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155 **Conflicts of interest/Competing interests**

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3 56 Not applicable

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8 58 **Availability of data and material**

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11 59 All data are available in this manuscript and in Supplementary Materials. Raw data are available
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13 60 upon request to the corresponding author.

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17 62 **Code availability**

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25 65 **Authors' contributions**

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27 66 CO collected the samples for analysis. CLL, RM, CO and DN designed the study. CLL, RM, FB
28
29 67 and DN performed the XANES experiments. CLL processed the data and drafted the manuscript.

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31 68 All authors contributed to the final version of the manuscript.

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69 Introduction

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271 The importance of iron in magmatic systems has prompted many studies concerning its
372 environment and oxidation state in lavas and magmas (e.g. Berry et al., 2003; Wilke et al., 2004;
472 O'Neill et al., 2006; Cottrell et al., 2009; Giuli et al., 2012; Zhang et al., 2018; Berry et al., 2018,
573 O'Neill et al., 2018), its effects on their rheology (e.g. Dingwell and Virgo, 1987; Dingwell, 1991;
674 Cottrell et al., 2013, 2014) and its structural role in melts and glasses (e.g. Fox et al., 1982; Mysen
775 et al., 1985; Cooney and Sharma, 1990; Wang et al., 1995; Magnien et al., 2004, 2006, 2008;
876 Cicconi et al., 2015a,b). Iron can exist in melts in two valence states (Fe^{2+} and Fe^{3+}) that have
977 different effects on melt physico-chemical properties. In particular, iron affects the density and
1078 viscosity of silicate melts. For instance, increasing the relative fraction of Fe^{2+} in an iron-bearing
1179 sodium silicate melt decreases viscosity by nearly an order of magnitude at constant temperature
1280 (Dingwell and Virgo, 1988). Changes in iron oxidation state also affect melt density because of the
1381 different partial molar volumes of FeO and Fe_2O_3 , thereby influencing magma mobility and
1482 explosivity (see the reviews of Gonnermann et al., 2013; Gonnermann 2015; and Le Losq et al.,
1583 2020 and references cited therein).

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1886 Previous studies of iron redox state in quenched glasses (e.g. Kilinc et al., 1983; Kress and
1987 Carmichael, 1991; Sack et al., 1980; Wilke et al., 2001, 2004, Berry et al., 2003; O'Neill et al. 2006;
2088 Cottrell et al., 2009; Giuli et al., 2012; Cicconi et al., 2015a) or, more recently, in silicate melts via
2189 high temperature X-ray Absorption (XAS) spectroscopy (Magnien et al., 2004, 2006, 2008; Métrich
2290 et al., 2006; Wilke et al., 2007a,b; Cochain et al., 2013; Drewitt et al., 2013; Cicconi et al. 2015b;
2391 Alderman et al., 2017; Bidegaray et al., 2018) have shown that the iron oxidation state in silicate
2492 melts is driven by temperature, oxygen fugacity, pressure and melt chemical composition.
2593 Accordingly, the effects of iron on the structure and properties of silicate melts are complex
2694 functions of those parameters.

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2896 Both parametric (e.g. Kress and Carmichael, 1991; Jayasurika et al., 2004; Borisov et al., 2018) and
2997 thermochemical (Ottonello et al., 2001; Moretti, 2005) models permit estimation of the iron redox
3098 state, hereafter expressed as $\text{Fe}^{3+}/\text{Fe}^{\text{TOT}}$ where $\text{Fe}^{\text{TOT}} = \text{Fe}^{2+} + \text{Fe}^{3+}$, as a function of temperature,
3199 oxygen fugacity and melt chemical composition. Such models are mostly based on analyses of
32100 experimental glasses formed by quenching silicate melts equilibrated at given conditions (e.g. Kress
33101 and Carmichael, 1991). However, such data do not provide insights into dynamic changes likely to
34102 be occurring at high temperature in the molten state in magmatic systems. Such processes can
35103 however be studied *in situ* (i.e, at high temperature in the liquid state) through Fe K-edge X-Ray

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104 Absorption Near Edge Structure (XANES) spectroscopy (Magnien et al., 2004, 2006; Métrich et al.,
105 2006; Wilke et al. 2007a,b; Magnien et al. 2008; Cochain et al., 2013; Cicconi et al. 2015a,
106 Bidegaray et al., 2018). This approach can shed light on how iron oxidation state and coordination
107 number (CN) are affected by dynamic changes in intensive variables in natural lavas. Furthermore,
108 *in situ* XANES experiments avoid the problem of photoreduction of iron (Gonçalves Ferreira et al.,
109 2013), which may compromise data acquired on glasses at room temperature (Gonçalves Ferreira et
110 al., 2013; Cottrell et al., 2018)

111
112 In this study, we leverage the dispersive setup of the ODE beamline at SOLEIL to obtain “snapshot”
113 Fe K-edge XANES spectra of an aluminosilicate melt of phonolitic composition from a natural
114 sample (a lava bomb) collected near the summit of Mt Erebus, Antarctica, *in situ* at high
115 temperature. As the only volcano presently erupting phonolitic lavas, and with an extensive body of
116 studies of its magmatic differentiation (e.g., Kyle et al., 1992; Oppenheimer et al., 2011; Iacovino et
117 al., 2016), degassing (e.g., Oppenheimer et al., 2008) and eruptive style (e.g., Aster et al., 2003;
118 Peters et al., 2018), Erebus serves as something of an archetype for alkaline magmatism. Because of
119 this and as alkali diffusion becomes an important process in iron redox mechanisms in silicate melts
120 below liquidus temperatures, the Erebus phonolite composition appeared to be particularly suited
121 and interesting for performing the *in situ* experiments. We acquired spectra continuously with
122 timesteps of hundreds of ms to 2 s enabling us to track the influence of changes in temperature or
123 oxygen fugacity. Our primary aim is to improve understanding of how dynamically-changing
124 intensive variables influence the Fe oxidation state and CN.

125

126 **Material and Methods**

127

128 **Samples**

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130 The starting material was prepared from a lava bomb sampled on the flanks of Erebus volcano,
131 Antarctica, renowned for its long-lived lava lake. The phonolitic lava contains around 30 vol%
132 phenocrystals of anorthoclase and minor (less than a few %) microlites of olivine, clinopyroxene,
133 magnetite and apatite, all held within a glassy matrix. Such a texture is typical of the lava bombs
134 ejected from the crater by the sporadic rupture of large gas bubbles at the lava lake surface.

135

136 Preparation of the crystal-free starting material is detailed in Le Losq et al. (2015), which focused
137 on evaluation of the viscosity of the Erebus phonolite magma. Briefly, we examined whole rock
138 samples. A representative portion of ~ 100 g of the sample was selected, and then cleaned in an

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139 ultrasonic ethanol bath for 1 h. The sample was then crushed in an agate mortar and heated for 12 h
140 at 473 K. The resulting powder was weighed, and then melted in a platinum crucible at 1470 K. The
141 crucible was quenched in water and weighed in order to determine the water loss between 473 and
142 1470 K. Samples were next heated at 1800 K. The melts were quenched in water and the resulting
143 glasses were weighed again to quantify any further losses between 1470 and 1870 K. The obtained
144 glass was crushed in an agate mortar for 1 h, and heated again in the crucible at 1870 K. This
145 procedure was repeated a further two times.

146
147 Finally, four successive melting, quenching and grinding operations were performed in order to
148 obtain an homogeneous glass. The glass density ($2.534(6) \text{ g cm}^{-3}$) was measured using Archimedes'
149 principle using toluene, and its chemical composition was determined using a Cameca SX50
150 electron microprobe, with a $10 \mu\text{m}$ beam diameter, 40 nA current, 15 kV acceleration voltage, and 5
151 s counting time. The composition of the starting glass is 57.4(4) wt% SiO_2 , 0.96(13) wt% TiO_2 ,
152 19.8(2) wt% Al_2O_3 , 5.3(2) wt% FeO , 0.2(2) wt% MnO , 0.89(5) wt% MgO , 2.6(1) wt% CaO , 7.0(3)
153 wt% Na_2O and 4.6(2) wt% K_2O (numbers in parentheses are 1σ analytical errors).

154 155 ***In situ* XANES spectroscopy at the iron K-edge**

156 *In situ* XANES measurements at the iron K-edge were performed on the energy-dispersive ODE
157 beamline at the SOLEIL synchrotron facility, France. This bending magnet beamline is equipped
158 with primary vertical focussing bent specular mirror and a horizontal focussing bent crystalline Si
159 (311) polychromator. The detector is a Princeton CCD camera of 400×1240 pixels. With a 500 mA
160 stored current the flux on the sample is around 2×10^7 photon/ s/eV. This setup allows acquisition
161 of Fe K-edge absorption spectra between 7080 and 7250 eV with a resolution of ± 0.2 eV in a single
162 shot in less than 2 s. Data acquisition timesteps were adjusted to optimise the observed signal to
163 noise ration and varied between 250 ms and 2 s. Beam size was approximately $30 \mu\text{m}$ by $30 \mu\text{m}$
164 FWHM. Energy calibration of the monochromator was made with a metallic iron reference foil,
165 setting the first inflexion point in the Fe K-edge spectrum to 7112 eV. Reference spectra on this
166 material were acquired before and after each run to correct for any drift.

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168 Samples were heated using a platinum wire, following the idea of Mysen and Frantz (1992). The
169 relationship between the electrical current intensity in the Pt wire, I , and the wire temperature, T ,
170 was predetermined through melting salts of known fusion temperatures: KNO_3 (337 °C), $\text{Ba}(\text{NO}_3)_2$
171 (592 °C), Li_2CO_3 (723 °C), NaCl (801 °C), K_2SO_4 (1069 °C), Li_2SiO_3 (1204 °C), $\text{CaMgSi}_2\text{O}_7$
172 (1391 °C), and CaSiO_3 (1544 °C). Temperature was further monitored during experiments with an
173 optical pyrometer. With this setup, temperature could be varied from 500 K up to 2000 K with a

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174 precision of ± 10 K (Neuville et al., 2014 and references therein). The furnace was equipped with an
175 enclosure and a gas-flow system to control oxygen fugacity by fluxing different gases, i.e. O_2 ($fO_2 =$
176 1 bar), air ($fO_2 = 0.21$ bar), N_2 ($fO_2 \sim 10^{-6}$ bar) and ArH_2 ($fO_2 \sim 10^{-15}$ bar). With this setup, desired
177 temperatures were reached within seconds, while fO_2 in the furnace enclosure could be varied from
178 one equilibrium gas to another in less than $\sim 2-3$ min, as the furnace volume is ~ 0.25 dm³ and the
179 gas flux a few L min⁻¹. Accordingly, temperature and fO_2 variations can be considered instantaneous
180 with respect to the typical times, of a few minutes to several hours, required to vary Fe^{3+}/Fe^{TOT} and
181 Fe coordination number (CN) in the melts.

182
183 The goal of the experiments was to observe changes in the Fe K-edge XANES spectra following
184 variations in temperature and fO_2 . We did so by recording spectra through time for different runs
185 during which T and/or fO_2 were varied. Each run involved loading powder of the starting glass
186 material in the hole of the platinum wire. Then, the sample was first heated for more than 10 min
187 above 1600 °C in air to ensure removal of any crystals that could form upon initial heating. We
188 acquired a spectrum at those initial conditions, then adjusted the temperature to the desired starting
189 value. The sample was held at the desired starting temperature for more than 30 min to ensure
190 attainment of equilibrium. Then, each dynamic experiment was initiated by suddenly varying T
191 and/or fO_2 , and spectra were recorded continuously through time (i.e. a spectrum was acquired
192 every 250 ms to 2 s depending on the initial chosen data acquisition setup). All runs were
193 terminated by acquiring a spectrum at 1600 °C in air, in order to detect any change in the Fe K-edge
194 XANES signal that would indicate changes in the iron chemical composition of the melt (e.g.,
195 precipitation of Fe, crystallization, etc.).

196
197 During such high temperature experiments, two main problems can occur: loss of alkali elements
198 and metallic iron precipitation on the Pt wire under a reducing atmosphere like that imposed by the
199 Ar-H₂ gas. It is thus necessary to analyse the melts after quench. However, in the present case,
200 microprobe analysis was impossible to perform because the quenched samples were contained in
201 the platinum wires that are re-used for other experiments (after cleaning in HF). To circumvent this
202 problem, we adopted the following strategy:

- 203 - We monitored the edge absorption value during data acquisition since iron loss is directly evident
204 in XAS spectra as a decrease of the edge intensity.;
- 205 - Noisy XAS signals with intermittent high-frequency features are characteristic of crystallisation.
206 In parallel with the edge absorption value, we thus monitored the appearance of such beyond the
207 edge during experiments;
- 208 - Unfortunately, loss of alkalis is not detectable during the XAS analysis but we limited the

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209 likelihood of it occurring by working mostly below 1550 °C, a temperature very close to that of the
210 synthesis of the original glass at which alkali loss was not observed, and keeping the time at
211 temperatures above 1550 °C as short as necessary (10–15 min).

212 - After the experiments, optical and Raman analyses were performed on the glasses as an additional
213 check further for iron precipitation, crystallisation and chemical changes (e.g. Le Losq et al. 2019).

214
215 Here, we report only experiments for which, (i) XAS signals show no visible signs of iron loss or
216 nano-crystallisation, and (ii) post-experimental observations are consistent with the initial glass
217 optical quality and Raman signal (see Supplementary Figure 1). We encountered systematic
218 problems after ~15 min in the Ar-H₂ atmosphere, with precipitation of Fe and/or crystallisation.
219 Accordingly, we limit our presentation of results to those that used air or N₂. Unfortunately, no
220 viable results for the dynamic experiments with the Ar-H₂ gas can be reported (except single-shot
221 spectra taken quickly after heating and iron reduction, as shown in Fig. 1B).

222
223 Fe precipitation was also detected at temperatures above ~1550 °C for some of the experiments in
224 the N₂ atmosphere. However, no Fe precipitation was observed in air, even after heating the samples
225 at 1630 °C for 15–20 min (Fig. 1A). More generally, above 1120 °C, no crystallisation was
226 observed in the melts. Furthermore, after heating samples for 30 min at 1550 °C in air, the Raman
227 spectra remain similar to those of the initial glass (Supplementary Figure 1), indicating that no
228 significant chemical change has occurred. Consequently, we further focus on reporting long-
229 duration experiments performed at temperatures below 1550 °C, as alkali loss should be very
230 limited under such conditions. Among seven runs that were performed, three meet the
231 aforementioned criteria and are reported below.

232 233 **XANES data reduction protocol**

234
235 The aim of this study is to calculate precisely the centroid (or ‘energy barycenter’) and integrated
236 intensity (area under the curve) of the iron XAS pre-edge near 7114 eV, corrected from a
237 background, as these variables can be used to determine iron oxidation state and speciation in
238 glasses and melts (Wilke et al., 2001, 2004; Berry et al., 2003; Magnien et al., 2004; Cottrell et al.,
239 2009; Cicconi et al., 2015a; Fiege et al., 2017). Indeed, Wilke et al. (2001) established a centroid
240 versus integrated intensity (CII) diagram using mineral standards, which permits evaluation of the
241 mean coordination numbers of Fe²⁺ and Fe³⁺ in minerals. In the CII diagram (see Supplementary
242 Figure 2), reference points are indicated and correspond to the values for Fe²⁺ and Fe³⁺ in CN 4 to 6,
243 and the trends observed when changing the oxidation state of iron between those values are

244 represented by dashed lines. The CII diagram of Wilke et al. (2001) was originally implemented for
245 minerals, and then revised by Wilke et al. (2004) for glasses using appropriate standards.
246 Alternative data reduction protocols have also been developed (e.g. Giuli et al., 2012).

247
248 Choice of protocol (in particular the selection of the pre-edge baseline) is important since it affects
249 the numerical values of centroids and integrated intensities. Here, we apply the data reduction
250 protocol implemented by Cochain (2009; see also Cochain et al., 2009, 2013, and description
251 below). Spectra of Fe²⁺ (Gillepsite, Grandidierite, Kirschteinite, Hedenbergite) and Fe³⁺
252 (Orthoclase, Yoderite, Hematite, Epidote) mineral standards from Cochain (2009) were processed
253 using the scheme described below in order to implement an updated CII diagram (Supplementary
254 Figure 2).

255
256 To determine pre-edge centroid and integrated intensity with precision, we modelled the pre-edge as
257 the sum of a background and two pseudo-voigt functions as developed by Cochain (2009) and also
258 presented in Cochain et al. (2009, 2013). For the background, an exponential function of the type y
259 $= A \exp(B(e - e_0))$ is chosen. The two pseudo-voigt functions are fitted to the observed signal with
260 an equal full-width-at-half-maximum and a fixed energy difference of 1.5 eV, in agreement with
261 recommendations from Wilke et al. (2001) and Berry et al. (2018). This ensures robustness and
262 reproducibility of the peak fitting protocol. An example of fit is provided in Supplementary Figure
263 3, together with histograms of the posterior probability distribution for the calculated pre-edge
264 centroid and integrated intensity. From the fits of six spectra of the melts with a Hamiltonian Monte
265 Carlo algorithm, covering the full encountered range of redox conditions, the maximum standard
266 deviations of the calculated centroid and integrated intensity follow gaussian distributions and are
267 systematically lower than 0.05 eV and 2 % at the 1 σ confidence interval, respectively. This fitting
268 protocol thus has the advantage of being robust and highly reproducible, which is desirable for *in*
269 *situ* data that can present variable signal-to-noise ratios within a single run. Systematic fits of data
270 series (composed of hundreds to thousands of spectra) were performed with a MATLAB script
271 using the *lsqcurvefit* function (for non-linear least square fits) with the same starting conditions.

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272 Results

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274 Before reporting the results of the dynamic runs, we introduce the spectra acquired in air at
 275 equilibrium conditions. These illustrate how the Fe K-edge XANES signal changes with changing
 276 temperature at air fO_2 , and, hence iron oxidation state in the melt. At air fO_2 , the Fe K-edge in
 277 XANES spectra shift towards lower energy with increasing temperature (Fig. 1A), a variation
 278 typical of iron reduction in aluminosilicate melts (e.g. Berry et al., 2003; Wilke et al., 2004). The
 279 shape of the pre-edge also changes with increasing T from 1100 °C to 1630 °C at air fO_2 (insert in
 280 Fig. 1A), indicating variations in the melt Fe^{3+}/Fe^{TOT} . For the conditions reported in Fig. 1A, since
 281 the Fe^{3+} pre-edge has a greater integrated intensity than the Fe^{2+} pre-edge, the dominant Fe valence
 282 in the melt must have been 3. At constant T but varying fO_2 (air, N_2 , Ar- H_2), the pre-edge shape
 283 changes strongly (Fig. 1B), with the appearance of a contribution near 7113 eV that clearly
 284 indicates the reduction of Fe, until Fe^{2+} dominates under Ar- H_2 atmosphere ($fO_2 \sim 10^{-15}$).

285

286 Fig. 2 shows how the pre-edge integrated intensity and centroid change with time after a sudden
 287 increase in T from 1100 °C to 1420 °C at constant fO_2 , in a N_2 atmosphere ($fO_2 \sim 3.5 \times 10^{-6}$). This
 288 sudden increase in T leads to a logarithmic decrease in the pre-edge centroid, indicating a
 289 logarithmic decrease in Fe^{3+}/Fe^{TOT} with time (Fig. 2B; Wilke et al., 2001). The CII diagram
 290 suggests that the mean CNs of Fe^{2+} and Fe^{3+} are ~ 5 , and do not change significantly with T , hence
 291 Fe^{3+}/Fe^{TOT} .

292

293 The ability to change T and fO_2 either simultaneously or consecutively during experiments allowed
 294 us to perform more complex, dynamic experiments. Figure 3 illustrates an experiment with a path
 295 composed of multiple T - fO_2 combinations. We first started with a melt in equilibrium with O_2 gas at
 296 1115 °C ($fO_2 \approx 1$), and then, in step (1) suddenly increased T to 1330 °C and decreased fO_2 to that of
 297 N_2 gas ($fO_2 \sim 3.5 \times 10^{-6}$). We see a non-linear decay of the pre-edge centroid, indicating a reduction
 298 of the melt, as expected. A second step (2) was made, in which T was decreased to 1120 °C and fO_2
 299 switched to that of O_2 gas ($fO_2 \approx 1$). In this case, the pre-edge centroid increases, describing a
 300 logarithmic trend with time (Fig. 3B). Step 3 consisted of increasing T to 1400 °C while changing
 301 fO_2 from that of O_2 gas to that imposed by N_2 gas. A sudden decrease of the pre-edge centroid is
 302 observed (Fig. 3B). During step 4, we kept fO_2 to that of N_2 but increased T to 1500 °C; a small and
 303 rapid decrease of the pre-edge centroid is observed, which then quickly stabilized around 7113.6 eV
 304 (Fig. 3B). Finally (step 5), we decreased T to 1130 °C at fO_2 imposed by pure N_2 , resulting in a
 305 progressive increase of the pre-edge centroid, indicating a final oxidation of Fe at this lower
 306 temperature. We notice that this step 5 is characterized by a slow change of the pre-edge centroid,

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307 describing a logarithmic trend again, but a plateau was not attained indicating that the experiment
308 was concluded before reaching equilibrium.

309
310 The integrated intensity of the pre-edge changed in tandem with the centroid during the multi-step
311 run presented in Fig. 3. Variations in steps 1 and 2 fall on a mean Fe^{2+} CN5 – Fe^{3+} CN5 trend in the
312 CII diagram (Fig. 3A). Variations in steps 3, 4 and 5 depart from this trend and indicate the
313 occurrence of Fe^{2+} and Fe^{3+} in CN6. In particular, at the beginning of step 4 (pink symbols in Fig.
314 3A), measurements in the CII diagram fall on the Fe^{2+} CN6 – Fe^{3+} CN6. This changes with time
315 during step 4, and measurements at the beginning of step 5 fall back on a Fe^{2+} CN5 – Fe^{3+} CN5
316 trend. They evolve again toward a Fe^{2+} CN6 – Fe^{3+} CN6 trend upon oxidation in step 5 (Fig. 3A).

317
318 A final successful run allowed us to acquire data following a simple T decrease from 1550 °C to
319 1150 °C at constant $f\text{O}_2$ (0.21; on air). During this run, we observed a logarithmic increase of the
320 pre-edge centroid with time, and a non-linear evolution of the integrated intensity versus centroid
321 relationship (Fig. 4). This indicates that, while $\text{Fe}^{3+}/\text{Fe}^{\text{TOT}}$ is slowly increasing following the
322 temperature change (Fig. 4B), Fe coordination changes rapidly at first and then stabilizes after some
323 time (Fig. 4A). These data suggest that the Fe^{3+} mean coordination is slightly less than 5, while the
324 Fe^{2+} mean CN lies between 5 and 6.

325
326 Data obtained at equilibrium conditions and reported in Figures 1 to 4 can be used to estimate the
327 oxidation state of iron. Several methods are reported in the literature (e.g. see Berry et al., 2004;
328 Wilke et al., 2004; Cottrell et al. 2009; Fiege et al., 2017; Berry et al., 2018; Zhang et al., 2018).
329 Most methods rely on the use of fully oxidized and reduced standards for precision (e.g. Berry et
330 al., 2018, Zhang et al., 2018 and references cited therein). However, this was neither practical nor
331 pertinent in our case as during *in situ* experiments, the signal changes slightly with temperature
332 (Wilke et al., 2007a). Furthermore, even if we have signals from nearly fully oxidized and reduced
333 melts, we cannot assert that a linear combination of the XANES data, for instance, would provide
334 reliable results. Indeed, as we acquire XANES signals continuously, every 250 ms to 2 s depending
335 on the run, the signal to noise ratio varies with acquisition conditions. In particular, Ar absorbs part
336 of the X-ray signal, such that spectra acquired under Ar- H_2 conditions are quite noisy (Fig. 1B).
337 Fortunately, the pre-edge is barely affected by temperature (Wilke et al., 2007a) and its centroid
338 remains easy to measure with precision in noisy data (see experimental methods).

339
340 Wilke et al. (2004) proposed an equation relating the variations of the pre-edge centroid to changes
341 in iron oxidation state in basaltic glasses, where Fe^{2+} and Fe^{3+} were found in CN5. Such a method

342 was reviewed by Fiege et al. (2017), who found that Fe oxidation state determination using the pre-
343 edge centroid position is reliable to within $\pm 6\%$. As Fe^{2+} and Fe^{3+} tend to be generally in CN5 in
344 our system (Figs. 2, 3, 4), we estimated iron redox in our melts using the equation provided by
345 Wilke et al. (2004). Figure 5 presents the results of this exercise. The iron redox state values
346 calculated from the pre-edge centroid agree well with the predictions from the parametric model of
347 Kress and Carmichael (1991), used in the MELTS software (Ghiorso and Sack, 1995), and from the
348 thermodynamic model of Moretti (2005). We only notice a slight shift for the model of Moretti
349 (2005) from data at air $f\text{O}_2$; the Kress and Carmichael (1991) model fits well the data at air $f\text{O}_2$, and
350 both models agree well with data at N_2 $f\text{O}_2$. Both the Kress and Carmichael (1991) and Moretti
351 (2005) models were already tested by Schuessler et al. (2008) and shown to be accurate for
352 phonolites. Therefore, the estimates of the iron redox in the phonolite melts calculated from the pre-
353 edge centroid and the equation provided by Wilke et al. (2004) are reliable, despite differences in
354 melt compositions, the fact that we are dealing with *in situ* data on melts, and the potential presence
355 of 6-fold coordinated iron species in our melts (Fig. 3). The standard deviation between the Kress
356 and Carmichael (1991) model (closest to all data) and measured values is equal to 0.04 (1σ , rounded
357 up value); it provides an estimate of the analytical error affecting redox data presented in Figure 5.

359 Discussion

361 Chemical mechanisms of iron speciation and redox behaviour

363 Our observations confirm that changes in $\text{Fe}^{3+}/\text{Fe}^{\text{TOT}}$ in phonolite melts are entirely reversible
364 following variations in T and $f\text{O}_2$, in agreement with previous findings from high temperature redox
365 measurements on different melt compositions (Wilke et al., 2007a,b, Magnien et al. 2008, Cicconi
366 et al. 2015b). Furthermore, iron oxidation state in phonolite melts is well described by existing
367 models (Figure 5), consistent with Schuessler et al. (2008). However, the data reveal that changes in
368 CN are more complex, and not systematically related to oxidation or reduction phenomena (Figs.
369 2A, 3A, 4A). The reported changes agree, in general, with the studies of Wilke et al. (2007),
370 Cicconi et al. (2015b) or Stabile et al. (2017) that revealed variations in the CII diagram following a
371 Fe^{3+} CN 4-5 and Fe^{2+} CN 5 pathway. But looking more closely, complex but subtle changes in CN
372 are evident (Fig. 4A), together with the possible occurrence of Fe in CN 6 (Fig. 3A).

374 The discrepancies may arise from the fact that previous studies mostly reported equilibrium values
375 in the CII diagram. Indeed, the dynamic studies of Magnien et al. (2006, 2008), Wilke et al.
376 (2007b), Cochain et al. (2009, 2013) or Bidegaray et al. (2018) did not report data in the CII

377 diagram. To the best of our knowledge, no previous study reported out-of-equilibrium results from
378 dynamic experiments in the CII diagram. Dynamic studies may reveal changes in term of iron CN
379 that were not foreseen from equilibrium experiments. Indeed, while in the first reported run (Fig.
380 2A), no change in CN accompanies the redox change following T increase at constant fO_2 , in runs 2
381 and 3, changes in Fe^{2+} and Fe^{3+} CNs are detected and appear to be complex. In one case, decreasing
382 temperature in air is related to a slight but non-linear increase in Fe^{3+} CN (Fig. 4A), suggestive of a
383 decoupling of redox and CN changes under dynamic conditions. In the other case, changing
384 temperature in a N_2 atmosphere can be accompanied by a general change of both Fe^{3+} and Fe^{2+} CNs
385 from 5 to 6 (Fig. 3A). Unfortunately, while revealing intriguing trends, the experiments are
386 insufficient to define the underlying mechanisms. We hope they will stimulate future *in situ*, high
387 temperature experiments.

388
389 Our experimental data indicate Fe^{3+} at a mean CN of ~ 5 , but this value will be sensitive to the
390 magmatic environment and any other dynamic redox processes (Figs. 2, 3, 4). Knowledge of how
391 Fe^{3+} CN varies with intensive and extensive parameters is important because the structural role of
392 Fe^{3+} , and hence its influence on magmatic properties, will depend on its CN. Indeed, while Fe^{3+} in
393 CN4 and 5 acts as a weak network former role, entering the silicate melt polyhedral network, Fe^{3+}
394 in CN6 may be considered as a network modifier that disrupts the melt structure. Consequently,
395 Fe^{3+} influence on melt properties is expected to vary with its CN. In the Erebus lava, Fe^{3+} mean CN
396 may reflect mostly five-folded Fe^{3+} (network former) with lesser amounts of four-folded (network
397 former) and six-folded (network modifier) Fe^{3+} , or from a mixture of four-folded and six-folded
398 Fe^{3+} . By performing high temperature *in situ* XAS experiments on $(Fe_xCa_{1-x}O)_y(SiO_2)_{1-y}$ melts,
399 Drewitt et al. (2013) showed that, in such melts, a mixture of 4-fold and 6-fold coordination is en-
400 tirely plausible. This agrees with previous findings from Mysen et al. (1985), who analysed CaO-
401 MgO-Al₂O₃-SiO₂-FeO glasses with Mössbauer spectroscopy. If this remains valid for phonolites,
402 our study demonstrates that it is possible that Fe^{3+} becomes purely a network modifier under reduc-
403 ing conditions, as proposed by Mysen et al. (1985). Indeed, those authors proposed that the coordi-
404 nation of Fe^{3+} changed with iron oxidation state, Fe^{3+} in CN4 being promoted under oxidized condi-
405 tions and in CN 6 under reduced conditions. This would be consistent with the findings of Drewitt
406 et al. (2013) as already discussed. It would further explain why, under reducing conditions, it is pos-
407 sible to lose the contribution of Fe^{3+} in CN4 as seen in Figure 3A, or, upon oxidation, it is possible
408 to gain a contribution from Fe^{3+} in CN4 as suggested by the trend apparent in Figure 4A. Turning to
409 divalent iron, Fe^{2+} appears five- and even six-fold coordinated in these phonolite melts (Figs. 2-4A).
410 Similar results have been found for basaltic compositions (e.g., Galois et al. 2001; Wilke et al.
411 2004) and phonolitic glasses (Giuli et al. 2012).

412

413 Considering the aforementioned changes in coordination as T and fO_2 vary, different iron-bearing
 414 complexes thus participate in redox exchanges in the melts. These can be polyhedra of trivalent iron
 415 in four-fold and five-fold coordination, $Fe^{III}O_4^{5-}$, $Fe^{III}O_5^{7-}$, and cationic species Fe^{3+} and Fe^{2+} (note
 416 that henceforth we will use III to indicate the valence state in anionic complexes and avoid confu-
 417 sion with Fe^{2+} and Fe^{3+} cations). $Fe^{III}O_4^{5-}$ and $Fe^{III}O_5^{7-}$ anionic complexes are true coordination
 418 polyhedra of iron in the sense of Pauling (1960), that is, effective chemical species in which Fe-O
 419 bonds are strongly covalent. For this reason, iron in these anionic complexes behaves as a network
 420 former (Ottonello et al., 2001; Moretti, 2005, 2020). On the other hand, due to their low ionic field
 421 strengths, Fe^{3+} in CN 6 and Fe^{2+} in CN 4 to 6 do not form true polyhedra, but ionic couplings with
 422 surrounding oxygens. In this case, iron behaves as a network modifier. Using the notations, several
 423 reactions can be written, all presenting different implications for iron redox and melt structure:



426 For redox exchanges involving the cationic species Fe^{3+} and Fe^{2+} acting as network modifiers (e.g.
 427 in CN 6), we have:



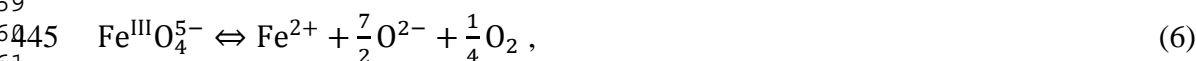
429 These reactions must be coupled with the so-called ‘oxygen electrode’ (Ottonello et al., 2001;
 430 Moretti, 2005, Moretti and Ottonello, 2005, 2020; Cicconi et al., 2020):



432 which links oxygen fugacity to the structural state of the melt through the activity of O^{2-} (oxide
 433 ions, or so-called free oxygens; Fincham and Richardson, 1954; Toop and Samis, 1962; Fraser,
 434 1975; Ottonello et al., 2001; Moretti, 2005; Nesbitt et al., 2015). Free oxygens represent all oxygen
 435 anions not associated with the silicate network, i.e., not part of coordination polyhedra around net-
 436 work formers (e.g., Si^{4+} , Al^{3+} ...). They are considered coupled to network modifying cations (Mg^{2+} ,
 437 Ca^{2+} , Na^+ , K^+ ...) via ionic bonds (e.g. Nesbitt et al., 2015), and measure the system basicity (Moret-
 438 ti, 2005, 2020).

439

440 It must be noted that the adoption of the oxygen electrode is not only required by the theory of apro-
 441 tic, oxide-based solvents (e.g. Flood and Forland, 1947; Jørgensen, 1969), but, in the context of our
 442 experiments, there is no other redox couple able to establish a mutual redox interaction with iron
 443 species. Combining this redox couple to reactions 1 to 4, we can write the following redox equilib-
 444 ria (see also Moretti, 2005):



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448 According to existing thermodynamic data, these reactions are such that the higher oxidation state is
 449 favoured by decreasing temperature (see also Ottonello et al., 2001), consistent with our experi-
 450 mental results (Figure 5). At constant temperature, based on Le Chatelier's principle, reactions 6
 451 and 7 imply that increasing the activity of O^{2-} increases the iron oxidation state at constant oxygen
 452 fugacity (since O_2 and O^{2-} are both on the right side of the equations). This effect has been well
 453 known in the glass industry since the 1960s (e.g. Paul and Douglas, 1965; Moretti, 2005, 2020 and
 454 references therein): it was observed upon addition of alkali oxides to glass batches, with consequent
 455 decrease of silica and melt polymerization, and increase of free oxygens. However, if reaction (8)
 456 becomes dominant, iron reduction at constant oxygen fugacity occurs because O_2 and O^{2-} appear on
 457 the opposite sides of those equations.

458
 459 This contrasting behaviour implies that the iron oxidation state is related to melt polymerization in a
 460 non-linear way, because Fe^{3+} may play an amphoteric role, being a network former or network
 461 modifier depending on its speciation (see also Ottonello et al., 2001; Moretti, 2005, 2020; Moretti
 462 and Ottonello 2005). This amphoteric behaviour is strictly related to bulk melt composition, thus to
 463 the chemical differentiation specific to every system, most often driven by fractional crystallization
 464 and/or degassing. Therefore, iron redox patterns in magmatic systems may be difficult to interpret
 465 because of the combination of contributions from the evolving melt composition and from associat-
 466 ed variations in oxygen fugacities. In the case of Erebus, this implies that, in addition to redox
 467 changes at constant composition, the basanite to phonolite magmatic differentiation trend should
 468 influence the bulk iron redox state of the magma as proposed by Oppenheimer et al. (2011), in addi-
 469 tion to other suspected controls such as magnetite precipitation (Oppenheimer et al., 2011) and pos-
 470 sibly sulfur degassing (Moussallam et al., 2014) in the shallow regions of the magmatic system.

471 472 **The role of diffusive mechanisms**

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 474 Redox reactions in silicate melts are controlled by three different mechanisms involving the diffu-
 475 sion of O^{2-} , of O_2 , and of divalent cations (for details see Goldman and Gupta, 1983; Schreiber,
 476 1986; Cooper et al., 1996a, 1996b; Magnien et al., 2008; Cochain et al., 2013). To distinguish be-
 477 tween these mechanisms, the *in situ* data can be used to calculate the redox diffusivity (Magnien et
 478 al., 2008). Indeed, the evolution of the Fe K-edge XANES centroid at a time t , C_t , can be repro-
 479 duced using expressions of the form (Magnien et al., 2008):

$$C_t = (C_{i0} - C_{eq}) \exp(-t/\tau) + C_{eq}, \quad (9)$$

with C_{i0} the centroid at starting time (before perturbation) and C_{eq} that at equilibrium, and τ a characteristic time. Those parameters can be determined from a least-squares fit of the data presented in Figs. 2b, 3b and 4b. According to Magnien et al. (2008), τ is related to the time t_{eq} necessary to reach 99 % of the equilibrium value C_{eq} , which reflects equilibrium in $\text{Fe}^{3+}/\text{Fe}^{\text{TOT}}$, as:

$$t_{eq} = -\tau \ln(0.01). \quad (10)$$

The redox diffusivity, which characterises the diffusivity of structural species necessary to allow the Fe redox state to change following a variation in intensive parameters, can then be calculated as:

$$D_{Redox} = r^2 / 4t_{eq}, \quad (11)$$

where r is the sample thickness. From Magnien et al. (2008), the thickness of samples in the platinum-wire setup we have used varies at most between 0.1 and 0.5 mm. Taking those values as maximum deviations from a mean around 0.3 mm, and using eqs. 9 to 11, we calculate D_{Redox} with associated errors from the observations made *in situ* and reported in Figs. 2, 3 and 4.

The results are reported in Table 1 and represented in Fig. 6, where D_{Redox} is given as a function of reciprocal T . D_{Redox} for our phonolite melt agrees with previous values reported for an alkali basalt melt (Fig. 6) by Cochain et al. (2009). They show a trend similar to those of the diffusivities of the alkalis Na and K, and possibly of Ca in alkali-rich and silica-rich melts at high temperature (diffusivity values for phonolite melts were not found for the elements of interest, so we consider values for rhyolite melts because they also are alkali-rich melts). In particular, the slopes of D_{Redox} versus T and $D_{Na} / D_K / D_{Ca} / D_{Mg}$ versus T are similar, indicating that the activation energy of the redox diffusivity in phonolite melt is similar to that of metal cation diffusivity in silica-rich melts. On the contrary, D_{Redox} is much higher than D_{O_2} , which can be calculated from the phonolite viscosity $\eta(T)$ estimated by Le Losq et al. (2015). Indeed, as viscosity of silicate melts is governed by exchanges of O atoms between network formers in the melt structure (e.g. Le Losq and Neuville, 2017), D_{O_2} directly relates to the diffusivity of O in the melt, D_O , which can be estimated with the Eyring equation:

$$D_{O_2} = D_O = k_b T / (\eta(T) \lambda), \quad (12)$$

where k_b is the Boltzmann constant and λ the atomic jump distance, taken as 280 pm. As D_{Redox} ranges between D_O and D_{Na} / D_K in the temperature range of our experiments (~ 1100 °C to 1600 °C), and considering the high alkali content of the Erebus magma, redox processes in phonolite melts at such temperatures likely involve mainly cationic and anionic diffusions of O^{2-} , Na^+ and K^+ . This supports previous reports highlighting the importance of metal cation diffusivity for redox exchanges in lavas at magmatic temperatures (e.g. Cooper et al., 1996a,b; Magnien et al., 2008). We

514 infer that, compared with the alkalis, alkaline-earth cations play a secondary role given their low
515 concentrations in the Erebus phonolite magma.

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517 An important caveat to our study is that, in the natural system, the presence of volatiles should also
518 affect D_{Redox} . Water likely plays a limited role because the phonolite in the Erebus lava lake plumb-
519 ing system is water-poor (between 0.2 and 0.6 wt% of water are observed in the tephriphonolite to
520 phonolite series; Oppenheimer et al. 2011; Moussallam et al., 2013; 2014). Furthermore, while
521 changes in S oxidation state can cause significant changes in that of Fe in a magma due to the large
522 numbers of electrons exchanged in the redox reactions involving sulfur, S diffusion is slow and is
523 not expected to be an important process in transferring electrons over large distances. Indeed, in
524 intermediate to silicic anhydrous melts, S diffuses more slowly than metal cations (e.g., Fig. 6 for
525 rhyolite, see also Behrens and Stelling, 2011 and references therein), with SO_4^{2-} (i.e., the S^{6+} -
526 bearing species) diffusing even more slowly than S^{2-} (Behrens and Stelling, 2011; Lierenfeld et al.,
527 2018). Thus, while S degassing accompanied by local redox changes in the melt will cause local
528 changes in iron redox, diffusion of S alone is not an efficient transporter of electrons capable of
529 driving changes in reactions 6 to 10.

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531 This comment on sulphur degassing invites consideration of its cause and the consequences the later
532 has on iron oxidation state and coordination in the melt. Indeed, sulphur degassing arises from the
533 decrease of pressure upon magma ascent. Pressure also influences iron redox and coordination in
534 silicate melts, but this effect is mostly measurable at the GPa scale (e.g. see the works of O'Neill et
535 al., 2006; Sanloup et al., 2013; Zhang et al. 2017). In the case of Erebus magmatic pressure is not so
536 extreme (~0.5 GPa at the deepest part of the magmatic system; Oppenheimer et al., 2011) and is
537 thus unlikely to affect the oxidation state or coordination of iron in the magmas. Other variables like
538 magma composition, crystallinity and variations in temperature and volatile contents are much more
539 likely to be the key parameters controlling the magma oxidation state (Oppenheimer et al., 2011;
540 Moussallam et al., 2014).

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542 Finally, given the low D_{Redox} at estimated magmatic temperatures for Erebus phonolite (Figure 6),
543 which range between ~950 and 1100 °C (different methods have yielded disparate results, see Cal-
544 kins et al., 2008; Burgisser et al., 2012; Moussallam et al., 2013), diffusive processes should be fair-
545 ly ineffective for any redox re-equilibration in the shallow magmatic system of Erebus, particularly
546 at the surface of the lava lake, which is resurfaced on timescales of around 10 min (Oppenheimer et
547 al., 2009). On such a timescale, even if no crust formed at the lake surface (in reality, a crust forms
548 instantaneously on exposure of fresh magmalava at the surface due to the very high radiative heat

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549 losses), an approximate D_{Redox} of $10^{-12} \text{ m}^2 \text{ s}^{-1}$ is estimated for the lava lake (Fig. 6). In this case, re-
550 dox re-equilibration of the lava could not extend more than a few tens of microns within the melt.

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552 Conclusions

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554 Our novel *in situ* dynamic experiments, using XANES spectroscopy to investigate iron oxidation
555 state and coordination numbers in the Erebus phonolite, reveal how diffusive behaviour and iron
556 speciation control the redox evolution of a lava. While Fe^{3+} appears to be in CN 4 and 6 in the
557 phonolite melt, the Fe^{2+} coordination number tends to be mostly equal to 5 to 6. Changes in iron
558 oxidation state are consistent with predictions of thermodynamic and parametric models. Changes
559 in iron coordination number seem more complex under dynamic conditions, when temperature or
560 $f\text{O}_2$ are changed abruptly. A decoupling between changes in iron oxidation state and coordination
561 number is observed under the present dynamic conditions, with Fe^{3+} probably shifting from a CN 4
562 to 6 as iron reduction proceeds. This agrees with previously reported data and confirms that Fe^{3+} is
563 an amphoteric cation that behaves as a network former and modifier in the melt structure. More
564 generally, the melt basicity will control iron redox state. As the basicity of the residual melt will
565 change with magma differentiation, it will be one of the mechanisms influencing the redox
566 evolution of a magma upon differentiation.

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568 Our observations allow determination of the redox diffusivity, which represents the diffusion of a
569 redox front within a melt. Redox diffusion is controlled by alkali counter-diffusion, as shown by the
570 diffusion coefficients (Figure 6). It is of the order of $\sim 10^{-12} \text{ m}^2 \text{ s}^{-1}$ at the temperature of the Erebus
571 lava lake ($\sim 1000 \text{ }^\circ\text{C}$). Re-equilibration of the lava redox by diffusion is thus unlikely in the
572 plumbing system, such that redox changes close to or at the surface should only be controlled by
573 magmatic process such as crystallization and degassing.

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575 Our experimental setup represents a first step towards improving our understanding of magma
576 redox changes under varying conditions, and of the underlying mechanisms. Extending the
577 approach to other compositions will be valuable as we can expect redox timescales to be
578 compositionally-dependent. Knowledge of such redox timescales within the melt promises new
579 understanding of redox variations associated with disequilibrium processes that are driven by
580 rapidly changing intensive parameters and feedbacks associated with dynamic volcanic phenomena
581 such as explosive magma fragmentation. For instance, our study indicates that magma degassing
582 could trigger rapid changes in iron CN and oxidation state. Such rapid change could occur during
583 sulfur degassing for instance, and potentially trigger late nucleation and crystallisation of Fe-

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584 bearing nanolites like magnetite, for instance as Fe³⁺ becomes available in CN6 following local
585 reduction due to sulfur loss. As nanolites appear to play a significant role in increasing the explosive
586 character of magmas through their effect on their rheology (Di Genova et al., 2017), such Fe CN
587 changes could further participate in increasing melt explosivity, in addition to the many other
588 variables at play. This is a hypothesis that remains to be tested, but it highlights the needs for more
589 in situ data to understand iron behaviour under conditions prone to magma crystallisation and
590 degassing, representative of volcanic systems.

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593

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598 References

599

- 600 Alderman OLG, Wilding MC, Tamalonis A, et al (2017) Iron K-edge X-ray absorption near-edge structure
601 spectroscopy of aerodynamically levitated silicate melts and glasses. *Chem. Geol.* 453:169-185.
- 602 Aster, R., Mah, S., Kyle, P., McIntosh, W., Dunbar, N., Johnson, J., Ruiz, M. and McNamara, S., 2003. Very
603 long period oscillations of Mount Erebus Volcano. *Journal of Geophysical Research: Solid Earth*,
604 108(B11).
- 605 Baker LL, Rutherford MJ (1996) Sulfur diffusion in rhyolite melts. *Contrib Mineral Petrol* 123, 335–344.
- 606 Behrens H, Stelling J (2011) Diffusion and redox reactions of sulfur in silicate melts. *Rev Mineral Geochem*
607 73, 79–111.
- 608 Berry AJ, O'Neill HSC, Jayasuriya KD, Campbell SJ, Foran GJ (2003) XANES calibrations for the
609 oxidation state of iron in a silicate glass. *Am Mineral* 88:967–977.
- 610 Berry AJ, Stewart GA, O'Neill HSC, Mallmann G, Mosselmans JFW (2018) A re-assessment of the
611 oxidation state of iron in MORB glasses. *Earth Planet Sc Lett* 483:114–123.
- 612 Bidegaray A-I, Ceglia A, Cicconi MR, et al (2018) An in-situ XANES investigation of the interactions
613 between iron, manganese and antimony in silicate melts. *Journal of Non-Crystalline Solids* 502:227–
614 235.
- 615 Borisov A, Behrens H, Holtz F (2018) Ferric/ferrous ratio in silicate melts: a new model for 1 atm data with
616 special emphasis on the effects of melt composition. *Contrib Mineral Petrol* 173:98.
- 617 Borisov, A., Behrens, H., Holtz, F., 2015. Effects of melt composition on Fe³⁺/Fe²⁺ in silicate melts: a step to
618 model ferric/ferrous ratio in multicomponent systems. *Contrib Mineral Petrol* 169.
- 619 Chevrel MO, Baratoux D, Hess K-U, Dingwell DB (2014) Viscous flow behavior of tholeiitic and alkaline
620 Fe-rich martian basalts. *Geochim Cosmochim Acta* 124:348–365.

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46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
- Chevrel MO, Giordano D, Potuzak M, et al (2013) Physical properties of $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-CaMgSi}_2\text{O}_6\text{-FeO-Fe}_2\text{O}_3$ melts: Analogues for extra-terrestrial basalt. *Chem Geol* 346:93–105.
- Cicconi MR, Giuli G, Ertel-Ingrisch W, et al (2015a) The effect of the $[\text{Na}/(\text{Na}+\text{K})]$ ratio on Fe speciation in phonolitic glasses. *Am Mineral* 100:1610–1619.
- Cicconi MR, Neuville DR, Tannou I, et al (2015b) Competition between two redox states in silicate melts: An in-situ experiment at the Fe K-edge and Eu L3-edge. *Am Mineral* 100:1013–1016.
- Cicconi MR, Moretti R, Neuville DR (2020) Earth's Electrodes, Elements (in press)
- Cochain B (2009) Cinétique et mécanismes d'oxydoréduction dans les silicates fondus (Ph.D.). Pierre et Marie Curie - Paris VI, Paris.
- Cochain B, Neuville DR, de Ligny D, Roux J, Baudelet F, Strukelj E, Richet P (2009) Kinetics of iron redox reaction in silicate melts: A high temperature Xanes study on an alkali basalt. *J Phys Conf Ser* 190:012182.
- Cochain B, Neuville DR, de Ligny D, Malki M, Testemale D, Pinet O, Richet P, 2013. Dynamics of iron-bearing borosilicate melts: effects of melt structure and composition on viscosity, electrical conductivity and kinetics of redox reactions. *J Non-Cryst Solids* 373–374:18–27.
- Cooney, T.F., Sharma, S.K., 1990. Structure of glasses in the systems $\text{Mg}_2\text{SiO}_4\text{-Fe}_2\text{SiO}_4$, $\text{Mn}_2\text{SiO}_4\text{-Fe}_2\text{SiO}_4$, $\text{Mg}_2\text{SiO}_4\text{-CaMgSiO}_4$, and $\text{Mn}_2\text{SiO}_4\text{-CaMnSiO}_4$. *J Non-Cryst Solids* 122, 10–32.
- Cooper, R.F., Fanselow, J.B., Poker, D.B., 1996a. The mechanism of oxidation of a basaltic glass: chemical diffusion of network-modifying cations. *Geochim Cosmoch Acta* 60, 3253–3265.
- Cooper, R.F., Fanselow, J.B., Weber, J.K.R., Merkley, D.R., Poker, D.B., 1996b. Dynamics of oxidation of a Fe^{2+} -bearing aluminosilicate (basaltic) melt. *Science* 274, 1173–1176.
- Cottrell E, Kelley KA, Lanzirotti A, Fischer RA (2009) High-precision determination of iron oxidation state in silicate glasses using XANES. *Chem Geol* 268:167–179.
- Cottrell E, Lanzirotti A, Mysen BO, et al (2018) A Mössbauer-based XANES calibration for hydrous basalt glasses reveals radiation-induced oxidation of Fe. *Am Mineral* 103:489–501.
- Dickenson MP, Hess PC (1982) Redox equilibria and the structural role of iron in alumino-silicate melts. *Contr Mineral Petrol* 78:352–357.
- Di Genova D, Kolzenburg S, Wiesmaier S, et al (2017) A compositional tipping point governing the mobilization and eruption style of rhyolitic magma. *Nature* 552:235-238.
- Dingwell DB (1991) Redox viscometry of some Fe-bearing silicate melts. *Am Mineral* 76:1560–1562.
- Dingwell DB, Brearley M, Dickinson JE (1988) Melt densities in the $\text{Na}_2\text{O-FeO-Fe}_2\text{O}_3\text{-SiO}_2$ system and the partial molar volume of tetrahedrally-coordinated ferric iron in silicate melts. *Geochim Cosmoch Acta* 52:2467–2475.
- Dingwell DB, Virgo D (1988) Viscosities of melts in the $\text{Na}_2\text{O-FeO-Fe}_2\text{O}_3\text{-SiO}_2$ system and factors controlling relative viscosities of fully polymerized silicate melts. *Geochim Cosmoch Acta* 52:395–403.
- Drewitt JWE, Sanloup C, Bytchkov A, Brassamin S, Hennem L (2013) Structure of $(\text{Fe}_x\text{Ca}_{1-x}\text{O})_y(\text{SiO}_2)_{1-y}$ liquids and glasses from high-energy x-ray diffraction: Implications for the structure of natural

basaltic magmas. *Phys. Rev. B - Condens. Matter Mater. Phys.* 87(22):1–10.

- 1 Fiege A, Ruprecht P, Simon AC, Bell AS, Göttlicher J, Newville M, Lanzirotti T and Moore G (2017).
2 Calibration of Fe XANES for high-precision determination of Fe oxidation state in glasses:
3 Comparison of new and existing results obtained at different synchrotron radiation sources. *Am*
4 *Mineral* 102(2):369–380.
5
6 Fincham CJB, Richardson FD (1954) The behaviour of sulphur in silicate and aluminate melts. *P Roy Soc A:*
7 *Math Phys* 223:40–62.
8
9 Flood H, Förland, T (1947) The acidic and basic properties of oxides. *Acta Chem. Scand*, 1, 592-604.
10
11 Fox KE, Furukawa T, White WB (1982) Transition metal ions in silicate melts. Part 2. Iron in sodium silicate
12 glasses. *Phys Chem Glasses* 23:169–178.
13
14 Fraser DG (1975) Activities of trace elements in silicate melts. *Geochim Cosmoch Acta* 39, 1525–1530.
15
16 Galois L, Calas G, Arrio MA (2001) High-resolution XANES spectra of iron in minerals and glasses:
17 structural information from the pre-edge region. *Chem Geol* 174:307–319.
18
19 Ghiorso MS, Sack RO (1995) Chemical mass transfer in magmatic processes IV. A revised and internally
20 consistent thermodynamic model for the interpolation and extrapolation of liquid-solid equilibria in
21 magmatic systems at elevated temperatures and pressures. *Contrib Mineral Petrol* 119(2-3):197-212.
22
23
24
25 Giuli G, Alonso-Mori R, Cicconi MR, et al (2012) Effect of alkalis on the Fe oxidation state and local
26 environment in peralkaline rhyolitic glasses. *Am Mineral* 97:468–475.
27
28 Goldman DS, Gupta PK (1983) Diffusion-controlled redox kinetics in a glassmelt. *J Am Ceram Soc* 66:188–
29 190.
30
31 Gonçalves Ferreira P, de Ligny D, Lazzari O, et al (2013) Photoreduction of iron by a synchrotron X-ray
32 beam in low iron content soda-lime silicate glasses. *Chem Geol* 346:106–112.
33
34
35 Gonnermann HM (2015) Magma Fragmentation. *Annu Rev Earth Planet Sci* 43:431–458.
36
37 Gonnermann HM, Manga M, Fagents SA (2013) Dynamics of magma ascent in the volcanic conduit. In:
38 Gregg TKP, Lopes RMC (eds). Cambridge University Press, pp 55–84.
39
40 Iacovino, K., Oppenheimer, C., Scaillet, B. and Kyle, P., 2016. Storage and evolution of mafic and
41 intermediate alkaline magmas beneath Ross Island, Antarctica. *Journal of Petrology*, 57(1), pp.93-
42 118.
43
44
45 Jambon A (1982) Tracer Diffusion In Granitic Melts: Experimental Results For Na, K, Rb, Cs, Ca, Sr, Ba,
46 Ce, Eu to 1300 °C and a Model of Calculation. *J. Geophys. Res.* 87:10797–10810.
47
48 Jayasurika KD, O'Neill HStC, Berry AJ, Campbell SJ (2004) A Mössbauer study of the oxidation state of Fe
49 in silicate melts. *Am Mineral* 89:1597–1609
50
51 Jørgensen CK (1969) Oxidation numbers and oxidation states. Springer-Verlag, Berlin.
52
53 Kilinc A, Carmichael ISE, Rivers ML, Sack RO (1983) The Ferric-Ferrous ratio of natural silicate liquids
54 equilibrated in air. *Contrib Mineral Petrol* 83:136–140.
55
56
57 Kress VC, Carmichael IS (1991) The compressibility of silicate liquids containing Fe₂O₃ and the effect of
58 composition, temperature, oxygen fugacity and pressure on their redox states. *Contrib Mineral Petrol*
59 108:82–92.
60
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- Kyle, P.R., Moore, J.A. and Thirlwall, M.F., 1992. Petrologic evolution of anorthoclase phonolite lavas at Mount Erebus, Ross Island, Antarctica. *Journal of Petrology*, 33(4), pp.849-875.
- Le Losq C, Berry AJ, Kendrick MA, Neuville DR, O'Neill HStC (2019) Determination of the oxidation state of iron in Mid-Ocean Ridge basalt glasses by Raman spectroscopy. *Am Mineral* 104:1032–1049.
- Le Losq C, Cicconi MR, Neuville DR (2020) Iron in silicate glasses and melts: implications for volcanological processes, in: AGU Monograph. American Geophysical Union.
- Le Losq C, Neuville DR (2017) Molecular structure, configurational entropy and viscosity of silicate melts: Link through the Adam and Gibbs theory of viscous flow. *J Non-Cryst Solids* 463:175–188.
- Le Losq C, Neuville DR, Moretti R, Kyle, P.R., Oppenheimer, C., 2015. Rheology of phonolitic magmas – the case of the Erebus lava lake. *Earth Planet Sc Lett* 411, 53–61.
- Lierenfeld MB, Zajacz Z, Bachmann O, Ulmer P (2018) Sulfur diffusion in dacitic melt at various oxidation states: Implications for volcanic degassing. *Geochim Cosmoch Acta* 226:50–68.
- Magnien V, Neuville DR, Cormier L, Mysen BO, Briois V, Belin S, Pinet O, Richet P (2004) Kinetics of iron oxidation in silicate melts: a preliminary XANES study. *Chem Geol* 213:253–263.
- Magnien V, Neuville DR, Cormier L, Roux J, Hazemann J-L, de Ligny D, Pascarelli S, Vickridge I, Pinet O, Richet P (2008) Kinetics and mechanisms of iron redox reactions in silicate melts: The effects of temperature and alkali cations. *Geochim Cosmoch Acta* 72:2157–2168.
- Métrich N, Susini J, Foy E, et al (2006) Redox state of iron in peralkaline rhyolitic glass/melt: X-ray absorption micro-spectroscopy experiments at high temperature. *Chem Geol* 231:350–363.
- Moretti R (2005) Polymerisation, basicity, oxidation state and their role in ionic modelling of silicate melts. *Ann Geophys-italy* 48.
- Moretti R (2020) Ionic syntax and equilibrium approach to redox exchanges in melts: basic concepts and the case of iron and sulfur in degassing magmas. In *Magma redox Geochemistry*, AGU Geophysical Monograph (Moretti R, Neuville DR eds.) (submitted)
- Moretti R, Ottonello G (2005) Solubility and speciation of sulfur in silicate melts: The Conjugated Toop-Samis-Flood-Grjotheim (CTSFG) model. *Geochim Cosmoch Acta* 69:801–823.
- Moussallam Y, Oppenheimer C, Scaillet B, Gaillard F, Kyle P, Peters N, Hartley M, Berlo K, Donovan A (2014) Tracking the changing oxidation state of Erebus magmas, from mantle to surface, driven by magma ascent and degassing. *Earth Planet Sc Lett* 393, 200–209.
- Moussallam Y, Oppenheimer C, Scaillet B, Kyle P (2013) Experimental phase equilibrium constraints on the phonolite magmatic system of Erebus volcano, Antarctica. *J Petrol* 54:1285–1307.
- Mysen BO, Frantz JD (1992) Raman spectroscopy of silicate melts at magmatic temperatures: Na₂O-SiO₂, K₂O-SiO₂ and Li₂O-SiO₂ binary compositions in the temperature range 25-1475°C. *Chem Geol* 96, 321–332.
- Mysen BO, Virgo D, Neumann E-R, Seifert FA (1985) Redox equilibria and the structural states of ferric and ferrous iron in melts in the system CaO-MgO-Al₂O₃-SiO₂-Fe-O: relationships between redox equilibria, melt structure and liquidus phase equilibria. *Am Mineral* 70:317–331.
- Nesbitt HW, Bancroft GM, Henderson GS, Sawyer R, Secco RA (2015) Direct and indirect evidence for free

oxygen (O^{2-}) in MO-silicate glasses and melts ($M = Mg, Ca, Pb$). *Am Mineral* 100:2566–2578.

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64
65
- Neuville DR, Hennet L, Florian P, De Ligny D (2014) In situ High-Temperature Experiments, in: *Rev in Mineral Geochem* 78:779–800.
- O'Neill HStC, Berry AJ, Mallmann G (2018) The oxidation state of iron in Mid-Ocean Ridge basaltic (MORB) glasses: implications for their petrogenesis and oxygen fugacities. *Earth Planet Sc Lett* 504:152–162
- O'Neill HStC, Berry AJ, McCammon CC, et al (2006) An experimental determination of the effect of pressure on the $Fe^{3+}/\Sigma Fe$ ratio of an anhydrous silicate melt to 3.0 GPa. *Am Mineral* 91:404–412.
- Oppenheimer C, Lomakina AS, Kyle PR, et al (2009) Pulsatory magma supply to a phonolite lava lake. *Earth Planet Sc Lett* 284:392–398.
- Oppenheimer C, Moretti R, Kyle PR, et al (2011) Mantle to surface degassing of alkalic magmas at Erebus volcano, Antarctica. *Earth Planet Sc Lett* 306:261–271.
- Ottonello G, Moretti R, Marini L, Vetuschi Zuccolini M (2001) Oxidation state of iron in silicate glasses and melts: a thermochemical model. *Chem Geol* 174:157–179.
- Paul A, Douglas RW (1965) Ferrous-ferric equilibrium in binary alkali silicate glasses. *Phys Chem Glasses* 6:207.
- Pauling L (1960) *The Nature of the Chemical Bond*. Cornell University Press.
- Peters, N.J., Oppenheimer, C., Brennan, P., Lok, L.B., Ash, M. and Kyle, P., 2018. Radar altimetry as a robust tool for monitoring the active lava lake at Erebus volcano, Antarctica. *Geophysical Research Letters*, 45(17), pp.8897-8904.
- Ravel B, Newville M (2005) ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J Synchrotron Radiat* 12:537–541.
- Sack RO, Carmichael ISE, Rivers M, Ghiorso MS (1980) Ferric-Ferrous equilibria in natural silicate liquids at 1 bar. *Contrib Mineral Petrol* 75:369–376.
- Sanloup C, Drewitt JWE, Crépeisson C, et al (2013) Structure and density of molten fayalite at high pressure. *Geochim Cosmochim Acta* 118:118–128.
- Schreiber HD (1986) Redox processes in glass-forming melts. *J Non-Cryst Solids* 84:129–141.
- Schuessler JA, Botcharnikov RE, Behrens H, et al (2008) Amorphous Materials: Properties, structure, and Durability: Oxidation state of iron in hydrous phono-tephritic melts. *Am Mineral* 93:1493–1504
- Toop GW, Samis CS (1962) Activities of ions in silicate melts. *Trans Metall AIME* 224:878–887.
- Wang Z, Cooney TF, Sharma SK (1995) In situ structural investigation of iron-containing silicate liquids and glasses. *Geochim Cosmoch Acta* 59:1571–1577.
- Wilke M, Farges F, Partzsch GM, Schmidt C, Behrens H (2007a) Speciation of Fe in silicate glasses and melts by in-situ XANES spectroscopy. *Am Mineral* 92:44–56.
- Wilke M, Farges F, Petit P-E, et al (2001) Oxidation state and coordination of Fe in minerals: An Fe K-XANES spectroscopic study. *Am Mineral* 86:714–730.
- Wilke M, Partzsch GM, Bernhardt R, Lattard D (2004) Determination of the iron oxidation state in basaltic glasses using XANES at the K-edge. *Chem Geol* 213:71–87.

- 606 Wilke M, Partzsch GM, Welter E, Farges F (2007b) Redox reaction in silicate melts monitored by
607 “static” in-situ Fe K-Edge XANES up to 1180°C. *AIP Conf Proc* 882:293–295.
- 1
2
3 Zhang HL, Cottrell E, Solheid PA, Kelley KA, Hirschmann MM (2018) Determination of $\text{Fe}^{3+}/\Sigma\text{Fe}$ of
4 XANES basaltic glass standards by Mössbauer spectroscopy and its application to the oxidation state
5 of iron in MORB. *Chem Geol* 479:166–175.
- 6
7 Zhang HL, Hirschmann MM, Cottrell E, Withers AC (2017) Effect of pressure on $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio in a mafic
8 magma and consequences for magma ocean redox gradients. *Geochim Cosmoch Acta* 204:83–103.
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11 Zhang Y, Ni H, Chen Y (2010) Diffusion Data in Silicate Melts. *Rev Mineral Geochem* 72:311–408.
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608 **Table 1:** Redox diffusivity D_{Redox} calculated from the experiments shown in Figure 2, 3 and 4.

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	T, K	D_{Redox}	Error
		$\log \text{m}^2 \text{s}^{-1}$	
1			
2			
3			
4			
5	1400	-10.9	+0.4 / -0.9
6			
7	1423	-11.2	+0.4 / -0.9
8			
9	1603	-10.5	+0.4 / -0.9
10	1603	-10.3	+0.4 / -0.9
11			
12	1673	-9.9	+0.4 / -0.9
13			
14	1693	-10.1	+0.4 / -0.9
15			
16	1773	-9.3	+0.4 / -0.9

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613 **Figure 1:** Examples of Fe K-edge XANES spectra of the Erebus phonolitic melt (anhydrous, free from
 614 crystals) at (A) air fO_2 but varying T (inset: zoom on the pre-edge of the XANES spectra) and (B) constant T
 615 and different fO_2 conditions. Signals were stable after a few minutes to tens of minutes (depending on T),
 616 indicating the attainment of equilibrium conditions at the reported T and fO_2 . The higher noise of the ArH₂
 617 spectrum results from the higher absorption of X-rays by Argon.

618
 619 **Figure 2:** Pre-edge centroid versus integrated intensity CII diagram (A) and centroid versus time (B) during
 620 a run where T was suddenly increased at $t = 142$ s (shown by the black dashed vertical line in B) from
 621 1100 °C to 1420 °C, at constant fO_2 ($\sim 3.5 \cdot 10^{-6}$). The CII diagram shown in (A) was built from the analysis of
 622 Fe K-edge XAS spectra of reference minerals, see Supplementary Figure 3. In (B), the black line is a fit to
 623 the data using eq. (10), see “Results” section for details. Errors are smaller than symbols and not visible in
 624 these plots.

625
 626 **Figure 3:** Pre-edge centroid versus integrated intensity CII diagram (A) and centroid versus time (B) during
 627 a multi-step run where T and/or fO_2 were changed as indicated for each of five steps of the experiment.
 628 Starting conditions for step i are given by step $i-1$; steps 1 to 5 are indicated in B) along with timings of step
 629 changes (vertical dashed lines). In (B), the black dashed lines are fits to the data at each step using eq. (10),
 630 see “Results” section for details. Errors are smaller than symbols and not visible in these plots.

631
 632 **Figure 4:** Pre-edge centroid versus integrated intensity CII diagram (A) and centroid versus time (B) during
 633 a run where T was suddenly decreased at $t = 0$ from 1550 °C to 1150 °C, at constant fO_2 (air, 0.21). In (B),
 634 the black dashed line is a fit to the data using eq. (10), see “Results” section for details. Errors are smaller
 635 than symbols and not visible in these plots.

636
 637 **Figure 5:** Iron oxidation state, expressed as Fe^{3+}/Fe^{TOT} , as a function of temperature for the Erebus melt at
 638 two different oxygen fugacities: air ($\log fO_2 = 0.67$) and N₂ ($\log fO_2 \sim 3.5 \cdot 10^{-6}$). Symbols are values
 639 calculated from the Fe K-edge XANES pre-edge centroid. Dotted and dashed lines are from the models of
 640 Kress and Carmichael (1991; KC1991 in legend) and Moretti (2005; M2005 in legend), respectively. The
 641 numerical error for each calculation is smaller than the size of symbols.

642
 643 **Figure 6:** Redox diffusivity (D_{Redox}) calculated from eqs. 9-11 and the data presented in figs 2-4 are
 644 represented as a function of reciprocal T as red circles (error bars are represented as small horizontal
 645 dashes above/below the symbols). D_{Redox} values for an alkali basalt from Cochain et al. (2009)
 646 are also reported as grey squares (no error bars are provided from this reference). Lava lake temper-
 647 atures range between 950 and 1100 °C (Calkins et al., 2008; Burgisser et al., 2012; Moussallam et
 648 al., 2013). D_O was calculated from the viscosity of the Erebus phonolite melt using the Eyring equa-
 649 tion (Le Losq et al., 2015) ; D_{Na} and D_K are from (Zhang et al., 2010) for silica rich rhyolite drop-
 650 melts, D_{Ca} and D_S are also for rhyolites from Jambon (1982) and Baker and Rutherford (1996, ex-

651 periments involving a mixture of S species), respectively, and D_{Mg} was calculated for the Erebus
652 composition from eq. 23 in Zhang et al. (2010). All D are for low-pressure anhydrous conditions,
653 representative of that of the Erebus lava lake (water content ~ 0.2 wt%).

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Figure 1

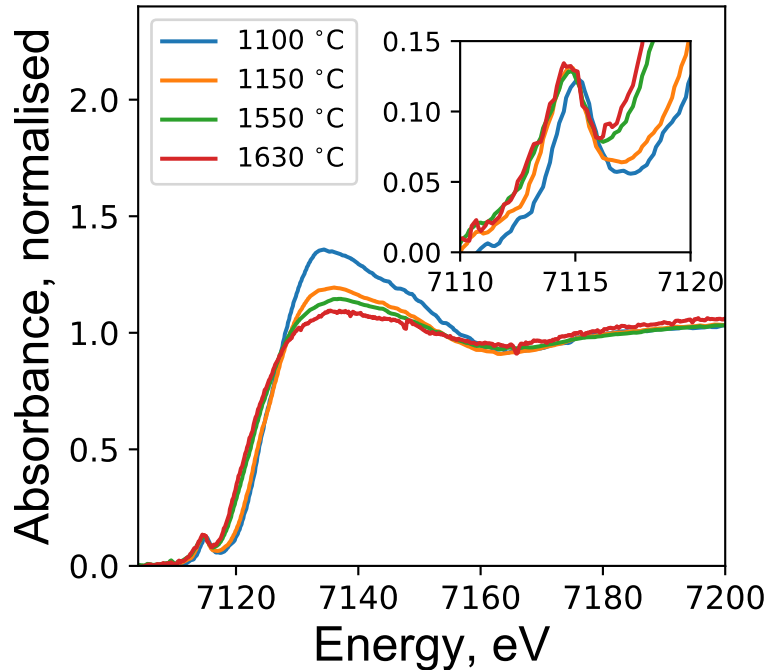
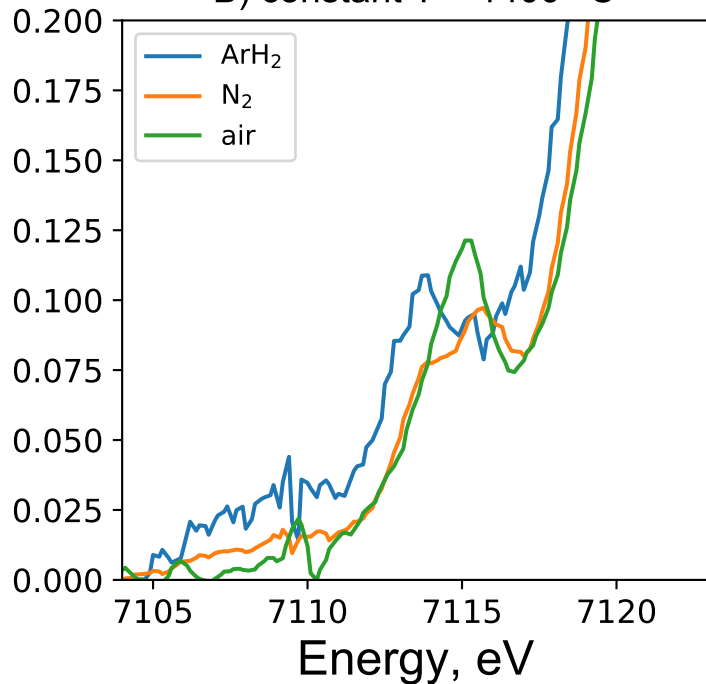
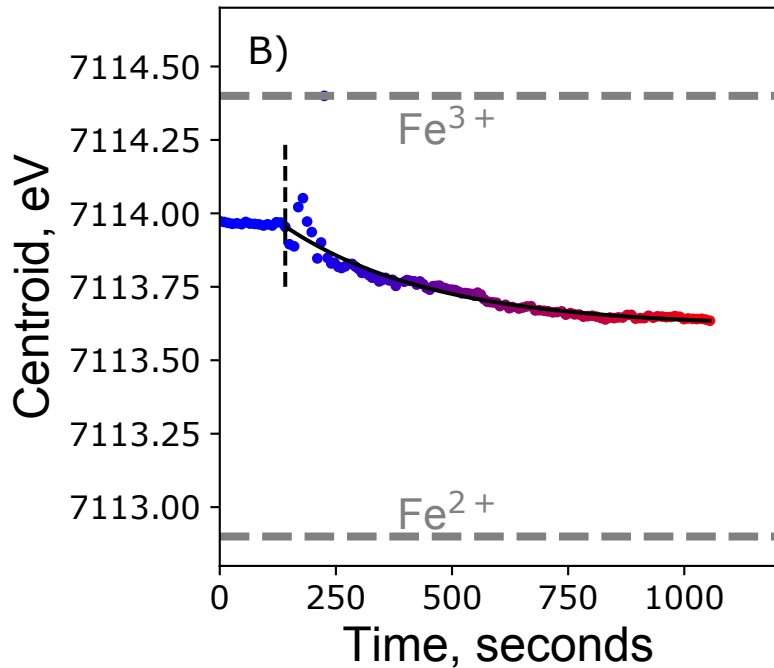
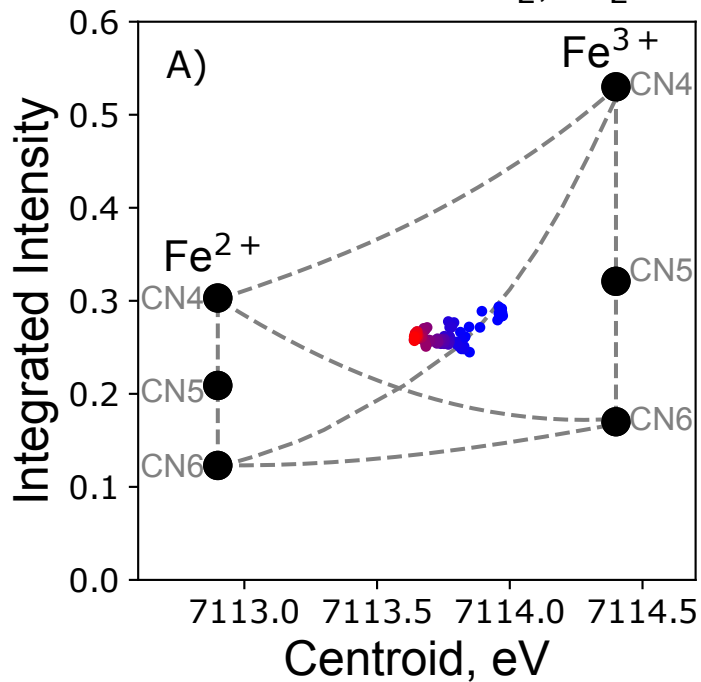
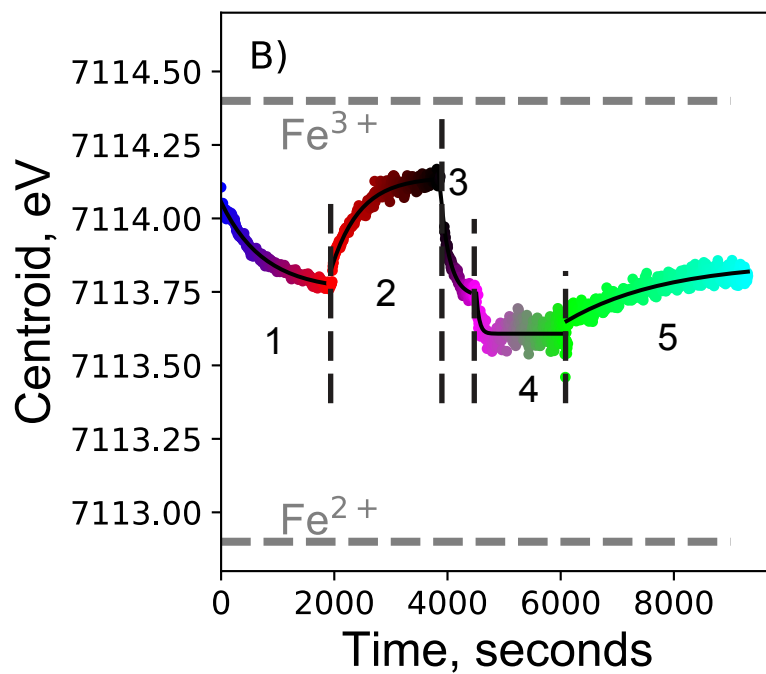
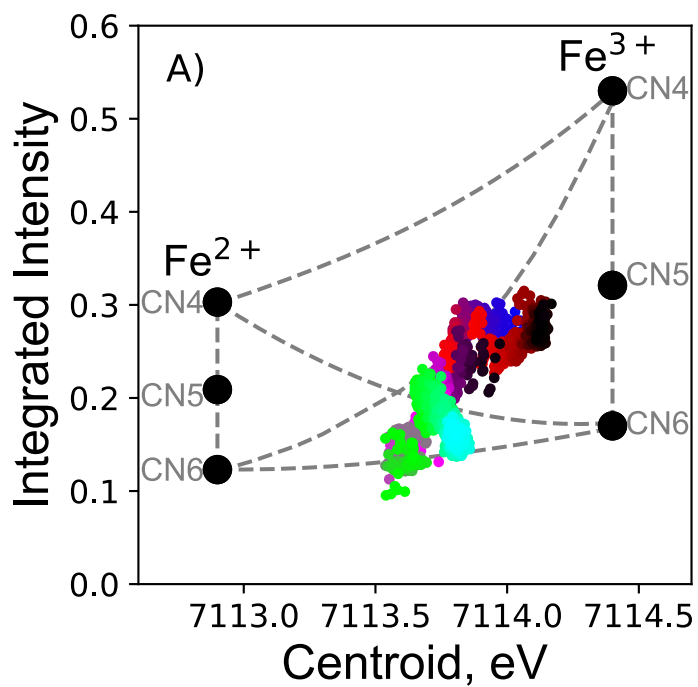
A) constant $fO_2 = 0.21$ (air)[Click here to access/download;Figure:Figure1.pdf](#)B) constant $T = 1400$ °C

Figure 2

Gas N_2 , $fO_2 \sim 10^{-6}$, 1100 to 1420 °C [Click here to access/download;Figure;Figure2.pdf](#)



Starting condition 0: O_2 gas at 1115°C

Step 1: N_2 gas at 1330°C

Step 2: O_2 gas at 1120°C

Step 3: N_2 gas at 1400°C

Step 4: N_2 gas at 1500°C

Step 5: N_2 gas at 1130°C

Figure 4

Air, 1550 to 1150 °C

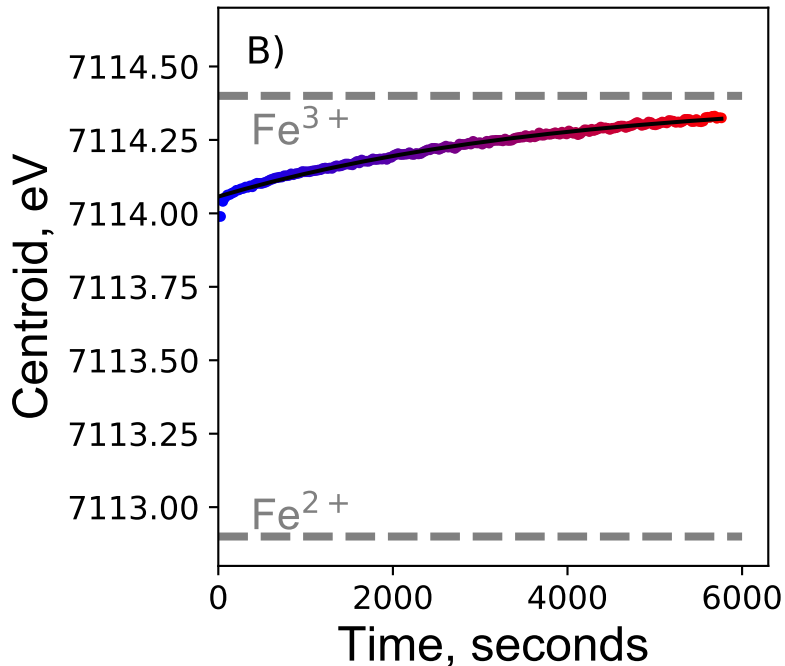
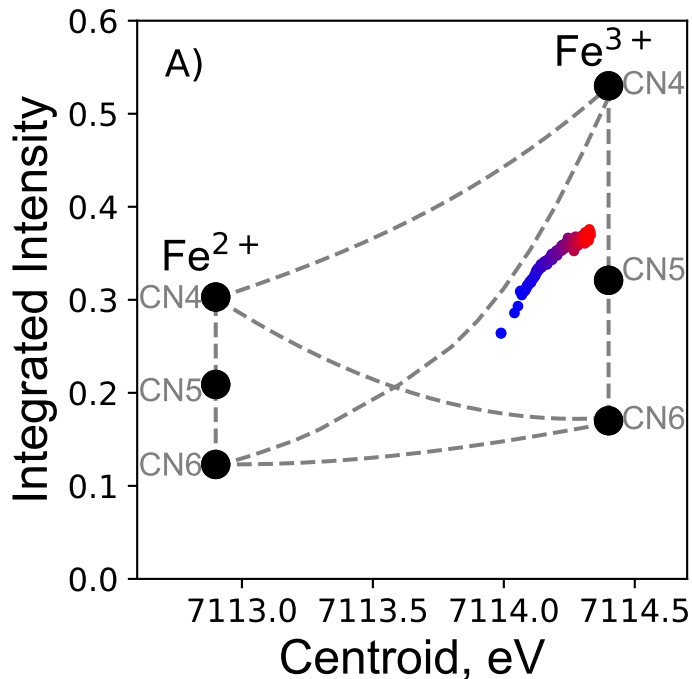
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Figure 5

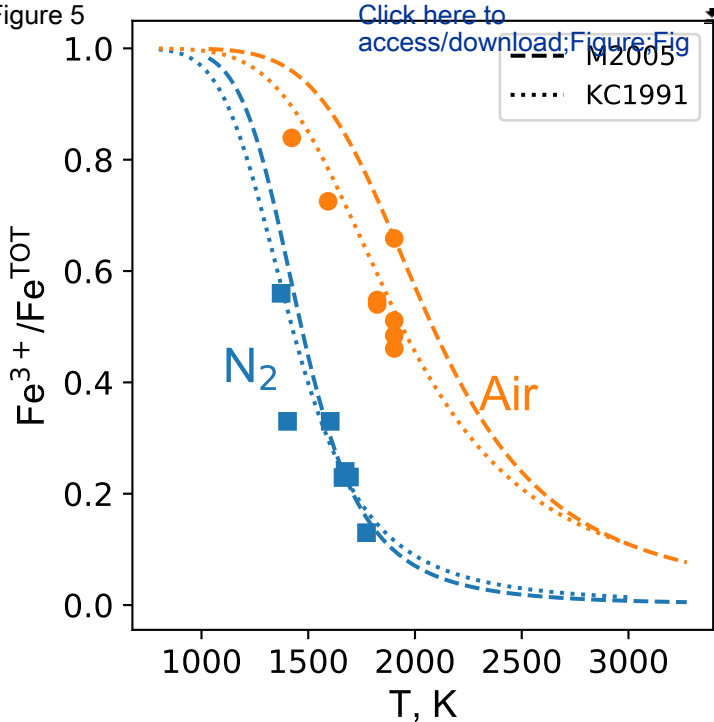
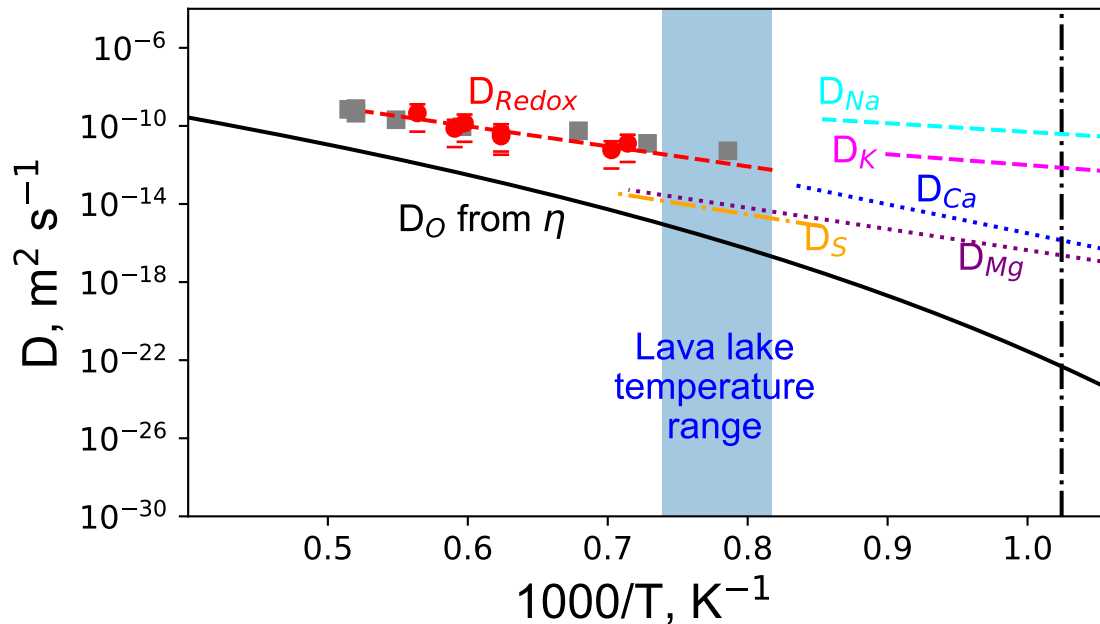


Figure 6

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Supplementary Materials

***In situ* XANES study of the influence of varying temperature and oxygen fugacity on iron oxidation state and coordination in a phonolitic melt**

Charles Le Losq^{1,2*}, Roberto Moretti^{1,3}, Clive Oppenheimer⁴, François Baudelet⁵, Daniel R. Neuville¹

Contributions to Mineralogy and Petrology

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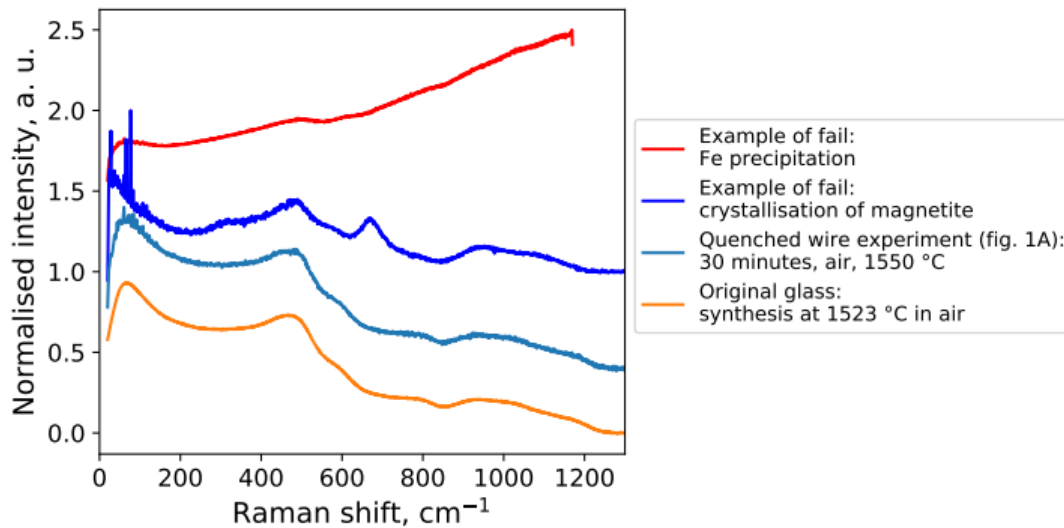
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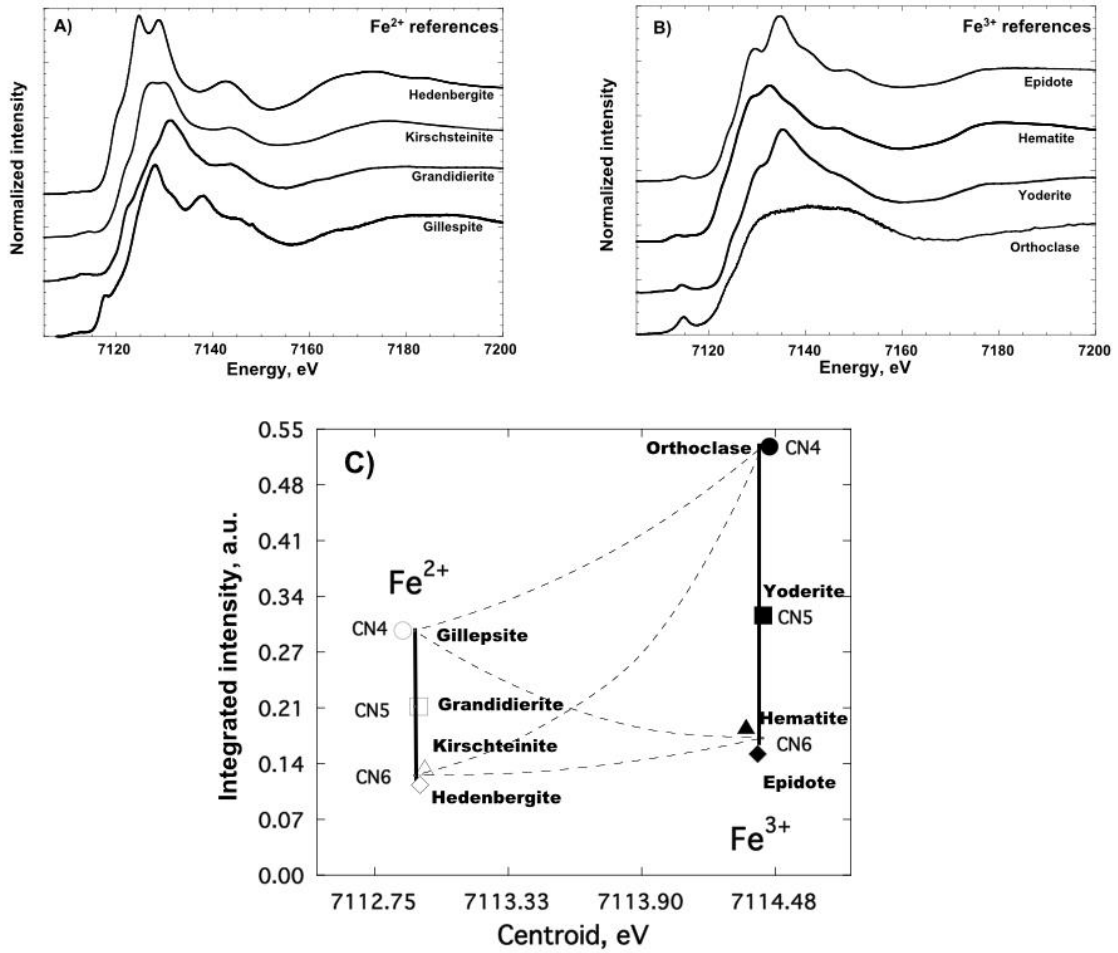
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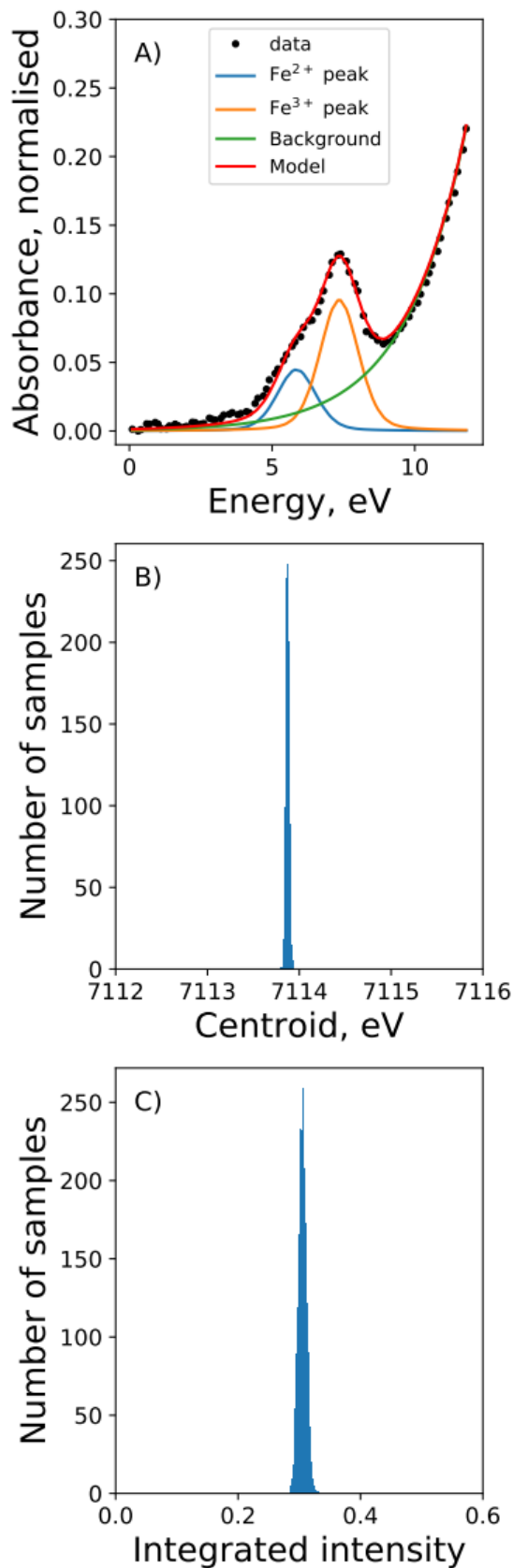
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Supplementary Figure 1: Raman spectra of the original glass, of a glass after an experiment in air (30 minutes at 1550 °C), and of two dynamic runs where iron loss or crystallisation were detected during the runs (via the XAS signals that appears every ~1-2 seconds on the monitoring screen on the beamline). The lack of difference between the initial glass (synthesised in air, at 1523 °C) and that obtained after running 30 minutes in air at 1550 °C indicate that the chemistry of the melt did not change, within the sensitivity of Raman spectroscopy to glass chemistry (~ 1 mol %, e.g. see Le Losq et al. 2019).



Supplementary Figure 2: A) and B) Fe K-edge XANES spectra of Fe²⁺ and Fe³⁺ reference minerals, respectively. C) Pre-edge centroid versus integrated intensity diagram, determined using spectra reported above and the data treatment used in this study (see experimental methods). Data from Cochain (2009).



Supplementary Figure 3: A) Example of a fit of the pre-edge. B) and C) posterior probability distributions for the centroid and integrated intensity calculated from 1000 models sampled on the posterior probability distribution of the problem (PyMC3 library, NUTS algorithm sampling 1000 models after 5000 tuning steps).

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François was the beamline manager at SOLEIL during the experiments. We originally thanked him in the Acknowledgements. Following a recent contact at SOLEIL early March, François took a look at the manuscript and helped us revise it, bringing some important insights and modifications. Considering his help during the experiments and the new comments on the manuscript, we invited him to join the authorboard in this revised version.

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New acknowledgements:

We acknowledge SOLEIL (Gif sur Yvette, France) for provision of synchrotron radiation facilities (proposal 20101038). CLL acknowledges support received from the Australian Research Council Laureate Fellowship (FL130100066) of Hugh St.C. O'Neill as well as from the Chaire d'Excellence of the University of Paris during data processing and manuscript preparation. CO acknowledges support from the Natural Environment Research Council (grant NE/N009312/1).

New Disclosures (financial and non-financial interests, funding):

Not applicable

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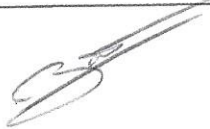
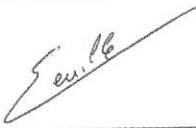
CO collected the samples for analysis. CLL, RM, CO and DN designed the study. CLL, RM, FB and DN performed the XANES experiments. CLL processed the data and drafted the manuscript. All authors contributed to the final version of the manuscript.

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