nature portfolio

Peer Review File

A chemical threshold controls nanocrystallization and degassing behaviour in basalt magmas

Web links to the author's journal account have been redacted from the decision letters as indicated to maintain confidentiality

This manuscript has been previously reviewed at another Nature Portfolio journal. This document only contains reviewer comments and rebuttal letters for versions considered at Communications Earth & Environment.

13th Sep 22

Dear Dr Scarani,

Please allow me to sincerely apologise for the long delay in sending a decision on your manuscript titled "Nanocrystallization in basalts: a chemical threshold between magmas from Mt. Etna and Stromboli". It has now been seen by three reviewers, whose comments appear below. In light of their advice I am delighted to say that we are happy, in principle, to publish a suitably revised version in Communications Earth & Environment under the open access CC BY license (Creative Commons Attribution v4.0 International License).

We therefore invite you to revise your paper one last time to address the remaining concerns of our reviewers. At the same time we ask that you edit your manuscript to comply with our format requirements and to maximise the accessibility and therefore the impact of your work.

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We hope to hear from you within two weeks; please let us know if you need more time.

Best regards,

Joe Aslin

Locum Chief Editor,
Communications Earth & Environment
https://www.nature.com/commsenv/
Twitter: @CommsEarth

REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

This paper should be published essentiall as it is. I have 3 comments for improvement of the manuscript.
This paper addresses the problem we have with nano-crystals growing during viscosity measurements. The authors address the compositional source of this problem. The paper is innovative, new and addresses the topic of nano-crytsal growth as a function of composition. This is one of the cutting edge advancements in our understanding of the evolution of the melt/crystal conditions of our samples as we perform low temperature measurements.
I have 3 suggestions for improvement of the paper.
1. The word "permanance" is not a good choice. You can replace it with "dwell" at each point in the text and it will be better understood.
2. line 189-190. We all write that we calibrate the dilatometer, but that is not correct. The viscosity measurements are absolute measurements and as such the machine is not something that you can calibrate (except for the temperature). You can cailbrate the LVDT. I suggest that "We confirmed the measurement accuracy by determining the viscosity of the standard glass DGG1.W . The certified.....
3. Line 486-487 "This occurs due to the compositional evolution of the residual melt, the formation of highly viscous amorphous nanoshells and possibly the agglomeration of nanocrystals"
I do not think that you have shown this in this manuscript. The words "assume" or "presume" or "probably" need to be added to this sentence. Or reference papers in which this was shown to be the case.

Reviewer #2 (Remarks to the Author):

Dear Editor
Please find the review of the manuscript _6541263_rbtssh “Nanocrystallization in basalts: a chemical threshold between magmas from Mt. Etna and Stromboli” submitted to Communications Earth & Environment.
Authors: Alex Scarani, Alessio Zandonà, Fabrizio Di Fiore, Pedro Antonio Valdivia Munoz, Nobuyoshi Miyajima, Hansjörg Bornhöft, Alessandro Vona, Joachim Deubener, Claudia Romano, Danilo Di Genova

Communications Earth & Environment requires several general criteria for a manuscript to be accepted and finally published such as: the conclusions are novel - the paper provides strong evidence for the main conclusions - it represents an advance in understanding which may influence thinking in the field.
This manuscript accomplished several of the above criteria, the writing is fluent and I appreciate reading it. On one hand it does not represent, to my opinion, a novelty in the sense that, at presents, as the authors have noted, there are a conspicuous number of publications investigating the nanocrystal impact on rheology of magmatic systems. On the other hand, it highlights the fact that slight change in chemistry of the starting material has the potentiality to change rheological behavior of basaltic melts. Thus, this work could, after an upgrade, be significant for further understanding of magmatic/volcanic behaviors not only for the studied Italian volcanoes but for global basaltic volcanism. That’s why I suggest to further improve the discussion to other volcanic system than Etna and Stromboli, comparing chemistry and relative eruption styles. In fact, as the authors emphasized, 2w% Δ FeO between the Etna and Stromboli chemistry is considered as trigger mechanism for nanocrystal to occur and, as consequence, change the rheological behavior of Etna melt. Now, to which extend nanocrystallization occurs? In other worlds, can the authors volumetrically quantify the occurrence of nanocrystals and their relative evolution with time?
The authors present anhydrous experimental data that are, somehow, far from natural scenarios. Being volatiles the key for the evolution magmatic and volcanic processes, I would like to read on the occurrence of nanocrystals and their impact on rheology of hydrous silicate melts. In fact, the authors state that…. “Stromboli paroxysmal explosions are typically short-lived events driven by the eruption of a volatile- rich magma undergoing closed system degassing.” But volatiles are also present in Etna volcanic system.
Considering that novel experimental facilities couples with in situ observations are challenging and not easy to access, one could consider to use classical high pressure high temperature technics and perform identical study as for measurements performed in this work. Being aware that those measurements are demanding and time consuming, an attempt in reproducing nano-crystallization on hydrous melts would broad up discussions and conclusions and reveal more on real geological scenarios. Why the authors choose to work only on anhydrous melts? Hydrous melts have the potentiality to shed new light on volatiles influence on the possible occurrence of nanocrystals in melts and will represent, I think, the novelty. This request could be partially accomplished with further and much depth discussion on this important point.
On this concern, I, also, encourage authors to emphasize possible future studies and techniques and approaches to be used in order to further understand such important process. This is partially written in the last for lines of discussion and could be a good starting point to better evidence the importance of this work.

Finally, I suggest moderate revision.

I report in the attached Pdf few change and suggestion and references that could possibly broad up discussion.

Sincerely

Reviewer #3 (Remarks to the Author):

I found the paper very interesting and well written.
I think that the addressed problem of the presence of nanocrystals impacts not only laboratory measurements, but also modeling and interpretation of volcanic phenomena.
From this point of view the paper is of wide interest. I appreciated the check-list for a best practice in viscosity measurements reported in Section 3.2.
The descriptions of the measurement procedures seem sufficiently detailed to allow the reproducibility of the experiments in well-equipped laboratories.

I can suggest just few minor corrections:

- Line 66: for a better readability of the paper, please define T_g here (was defined at line 230)
- Line 148: length: you mean the total length of the bar or the length of the bar wetted by the melt during the measurement?
- lines 228-231: can you provide typical values of T_g and m found for Etna and Stromboli?
- Is eq.(1), with the found parameters, also a result of your work? In this case, can you provide the parameters and the range of applicability of eq.(1) for Etna and Stromboli?
- Probably the figures should be numbered 1, 2, 3, 4, etc., instead of 1, S1, 2, S2, 3, 4, S3, etc. Same for the tables.

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Authors: Alex Scarani, Alessio Zandonà, Fabrizio Di Fiore, Pedro Antonio Valdivia Munoz, Nobuyoshi Miyajima, Hansjörg Bornhöft, Alessandro Vona, Joachim Deubener, Claudia Romano, Danilo Di Genova

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Considering that novel experimental facilities couples with in situ observations are challenging and not easy to access, one could consider to use classical high pressure high temperature technics and perform identical study as for measurements performed in this work. Being aware that those measurements are demanding and time consuming, an attempt in reproducing nano-crystallization on hydrous melts would broad up discussions and conclusions and reveal more on real geological scenarios. Why the authors choose to work only on anhydrous melts? Hydrous melts have the potentiality to shed new light on volatiles influence on the possible occurrence of nanocrystals in melts and will represent, I think, the novelty. This request could be partially accomplished with further and much depth discussion on this important point.
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Finally, I suggest moderate revision.

I report below few changes and suggestions and references that could possibly broad up discussion.

Sincerely

Introduction

Lines 32-33 not all eruption have destructive behaviour… please rephrase maybe with …and some potentially could have destructive…..

Lines 56: think to change *post mortem* term and rephrase throughout the manuscript.

Lines 77: I don't think Figure 1 is really necessary. It is enough to stress this point into the introduction as, so far, has been done.

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Misiti V., Vetere F., Mangiacapra A., Behrens H., Cavallo A., Scarlato P. Dingwell D. (2009) Viscosity of high-K basalt from the 5th April 2003 Stromboli paroxysmal explosion. Chemical Geology, 260, 278-285.

Viscometry

Lines 140-161: Please add thermocouples type or number of thermocouples used to monitor temperature throughout the sample and their position near the crucible.

Line 153: Please add the quenching rate by using this method and the volume of the quenched melts (amount of melt in the crucible).

2.3. Differential scanning calorimetry

Why don't you show directly ETN and STR experiments instead of the well know DGG1 curve evolution? Could it be moved in supplementary material (Figure S1)?

Line 226 : (Eq. 1, ref.[144] → (Eq. 1, ref.[144])

Line 232: The viscosity limit for silicate melts – 2.9 ± 0.3 is far from the value - 4.31 ± 0.74 proposed by Russel et al. (2003). Please cite and discuss this point.

Russel, J.K., Girdano, D., Dingwell, D.B., 2003. High-temperature limits on viscosity of non-Arrhenian silicate melts. American Mineralogist 88, 1390–1394.

Low-temperature viscosity

Line 163: could the sapphire sphere used in the low-temperature viscosity determination speed up the nucleation and growth processes and somehow enhance nanocrystals?

Line 462…Before the end of the discussion I would like to read on the possible nanocrystal occurrence in hydrous melts and possibly speculate that nanocrystal could occur also in partially crystallized system making the system rheologically much more instable.

Figure 3 and 4

Highlight with an arrow nano-crystallization peaks

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Response to the referees

We thank the reviewers for the positive feedback on our work and their constructive comments. We have followed their suggestions and improved the quality of our manuscript, in which changes are highlighted in **green and bold**. Here, we use the same formatting to provide a point-by-point response to each of the three reviewers.

Reviewer #1 (Remarks to the Author)
I have 3 suggestions for improvement of the paper.

The word "permanance" is not a good choice. You can replace it with "dwell" at each point in the text and it will be better understood.
Done.

line 189-190. We all write that we calibrate the dilatometer, but that is not correct. The viscosity measurements are absolute measurements and as such the machine is not something that you can calibrate (except for the temperature). You can cailbrate the LVDT. I suggest that "We confirmed the measurement accuracy by determining the viscosity of the standard glass DGG1.W. The certified.....
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Done.

Reviewer #2 (Remarks to the Author)

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We agree with reviewer that, although our work was focused on Etna and Stromboli, our results speak of broader range of volcanoes. From line 464 of the first version of manuscript, we stated:

"Because relatively high iron and titanium content also appears to be a common feature of several highly explosive basaltic eruptions, we propose that the chemical composition can play a role in the dynamics of explosive volcanism not only for the cases studies in this work".

As such, we proposed that highly explosive eruptions of Masaya triple layer and Fontana lapilli (Nicaragua), Etna 122 BC, Tarawera (New Zealand) and Llaima volcano (Chile) involved basalts rich in iron and titanium, namely their sum is > 10 wt.% with TiO_2 systematically >1 wt.%.

We now list these volcanoes in the revised version of the manuscript from line 291.

In fact, as the authors emphasized, 2w% D FeO between the Etna and Stromboli chemistry is considered as trigger mechanism for nanocrystal to occur and, as consequence, change the rheological behavior of Etna melt. Now, to which extend nanocrystallization occurs? In other worlds, can the authors volumetrically quantify the occurrence of nanocrystals and their relative evolution with time?

We understand the point of the referee here. However, we avoided to estimate volume content of nanolite in our samples for two reasons: 1) the error of estimation using TEM imaging can be significant and 2) it does not improve the interpretation of results. Let us assume that 100% of iron and titanium (~10 wt.%) is extracted from the melt structure to form nanocrystals. Because the higher density of crystals compared to the melt one, the volume fraction of crystals must be <10 wt.% and probably somewhat around 7 vol.%. This is a very low volume that cannot impact alone the magma viscosity. What instead increases dramatically the viscosity of our samples is the compositional evolution of the residual melt, the formation of highly viscous amorphous nanoshells (see Fig. 6) and possibly the agglomeration of nanocrystals. This was discussed in line 479 of the first version of the manuscript.

The authors present anhydrous experimental data that are, somehow, far from natural scenarios. Being volatiles the key for the evolution magmatic and volcanic processes, I would like to read on the occurrence of nanocrystals and their impact on rheology of hydrous silicate melts.

From line 239 we report new evidence on the chemical control on nanolite and bubble formation in hydrous basalts.

In fact, the authors state that…. "Stromboli paroxysmal explosions are typically short-lived events driven by the eruption of a volatile- rich magma undergoing closed system degassing." But volatiles are also present in Etna volcanic system.

We meant that Stromboli paroxysmal explosions are fed by a magma richer in volatile with respect to normal activity at the sample volcano. We agree with the reviewer that volatiles are the engine of explosive eruptions at any volcano. The revised version of the manuscript now reads: *"Stromboli paroxysmal explosions are typically short-lived events driven by the eruption of a volatile-richer magma (as compared to the typical low-energy Strombolian activity) undergoing closed system degassing".*

Considering that novel experimental facilities couples with in situ observations are challenging and not easy to access, one could consider to use classical high pressure high temperature technics and perform identical study as for measurements performed in this work. Being aware that those measurements are demanding and time consuming, an attempt in reproducing nano-crystallization on hydrous melts would broad up discussions and conclusions and reveal more on real geological scenarios. Why the authors choose to work only on anhydrous melts? Hydrous melts have the potentiality to shed new light on volatiles influence on the possible occurrence of nanocrystals in melts and will represent, I think, the novelty. This request could be partially accomplished with further and much depth discussion on this important point. On this concern, I, also, encourage authors to emphasize possible future studies and techniques and approaches to be used in order to further understand such important process. This is partially written in the last for lines of discussion and could be a good starting point to better evidence the importance of this work.
We tackled the aspect of hydrous conditions by performing high-temperature and -pressure experiments using Etna and Stromboli basalts. We confirmed that the anhydrous composition is the main factor controlling the occurrence of nanocrystallization, even in hydrous melts. We show SEM images and Raman spectra of quenched samples documenting the importance of nanolite formation for rheology and bubble nucleation. We hope the referee will appreciate our results and discussion from line 239.

Finally, I suggest moderate revision. I report below few changes and suggestions and references that could possibly broad up discussion.

Lines 32-33 not all eruption have destructive behavior… please rephrase maybe with …and some potentially could have destructive...
Done.

Lines 56: think to change post mortem term and rephrase throughout the manuscript.
Done.

Lines 77: I don't think Figure 1 is really necessary. It is enough to stress this point into the introduction as, so far, has been done.
We think that Fig. 1 provides a straightforward message on the importance on the topic of nanocrystal formation in experimental volcanology nowadays. As such, we have decided to keep (and update meanwhile) the figure.

Lines 106: possibly the following reference could be added to the reference list: Misiti V., Vetere F., Mangiacapra A., Behrens H., Cavallo A., Scarlato P. Dingwell D. (2009) Viscosity of high-K basalt from the 5th April 2003 Stromboli paroxysmal explosion. Chemical Geology, 260, 278-285.
Done.

<u>Viscometry</u>
Lines 140-161: Please add thermocouples type or number of thermocouples used to monitor temperature throughout the sample and their position near the crucible.
We specified the thermocouple type and its position. We modified the text as follow: *"Temperature was monitored using a factory calibrated S-type thermocouple (precision of ±2 °C; Di Fiore et al., 2021a) placed near the crucible walls. Accuracy in viscometry measurements was better than 0.06 Log units (Di Fiore et al., 2022).*

Line 153: Please add the quenching rate by using this method and the volume of the quenched melts (amount of melt in the crucible).
We added the measured quenching rate and the volume of extracted melt. We modified the text as follow: *"…and the sample contained in the crucible (volume: ~ 15 cm^3) was allowed to quench in air under continuous water flow to the crucible walls at ~120 °C/min (Di Fiore et al., 2021b)."*

Differential scanning calorimetry
Why don't you show directly ETN and STR experiments instead of the well know DGG1 curve evolution? Could it be moved in supplementary material (Figure S1)?
DSC experiments are already reported in Supplementary Fig. S3, and Fig. 4. What we reported in the Fig. S1 is a DSC upscan of the standard DGG1 glass. We do so as this system is stable, namely it does not crystallize during the measurement. As such, it allows the reader to learn how to estimate the characteristic DSC temperatures used in our study. We thus feel to keep the text as it is.

Line 226: (Eq. 1, ref.144 → (Eq. 1, ref.144)
Done.

Line 232: The viscosity limit for silicate melts – 2.9 ± 0.3 is far from the value - 4.31 ± 0.74 proposed by Russel et al. (2003). Please cite and discuss this point. Russel, J.K., Giordano, D., Dingwell, D.B., 2003. High-temperature limits on viscosity of non-Arrhenian silicate melts. American Mineralogist 88, 1390–1394.
We have recently reviewed the viscosity limit at infinite temperature in a previous publication (see ref. 31 in the original version of the manuscript). In agreement with Russell et al., we showed that the extrapolation of viscosity to the limit of infinite temperature yields different values according to the selected viscosity model (in their work, $10^{-4.3\pm0.74}$ and $10^{-3.2\pm0.66}$ Pa s for the Vogel-Fulcher-Tammann and Adam-Gibbs parameterizations, respectively). For the Mauro-Yue-Ellison-Gupta-Allan (MYEGA) equation used in this work to describe the viscosity of Etna and Stromboli, the best-fitting and widely accepted universal limit of viscosity at infinite temperature is $10^{-2.9\pm0.2}$. We have modified the text and clarified this point at line 134 of the new version.

Low-temperature viscosity
Line 163: could the sapphire sphere used in the low-temperature viscosity determination speed up the nucleation and growth processes and somehow enhance nanocrystals?
Heterogeneous nucleation is always possible, but we invariably checked the samples by Raman spectroscopy after the measurements and never found evidence of enhanced (nano)crystallization within the micropenetration indent. Moreover, our TEM images document that nanocrystallization of Fe-Ti-oxides in our samples was clearly a homogeneous (volume) nucleation process, governed by elemental diffusion within the silicate melt.

Line 462…Before the end of the discussion I would like to read on the possible nanocrystal occurrence in hydrous melts and possibly speculate that nanocrystal could occur also in partially crystallized system making the system rheologically much more instable.
As already presented above, we now tackle the effect of water content on nanocrystallization during decompression experiments described starting from line 239.

Figure 3 and 4 Highlight with an arrow nano-crystallization peaks.
Done.

Reviewer #3 (Remarks to the Author)
I can suggest just few minor corrections:

Line 66: for a better readability of the paper, please define T_g here (was defined at line 230)
Done.

Line 148: length: you mean the total length of the bar or the length of the bar wetted by the melt during the measurement?
We meant the wetted length; we amended the text to correct this imprecision.

Lines 228-231: can you provide typical values of T_g and m found for Etna and Stromboli?
We have added the requested information and modified the text to clarify our fitting procedure, at lines 137-144 of the new version of the manuscript.

Is eq.(1), with the found parameters, also a result of your work? In this case, can you provide the parameters and the range of applicability of eq.(1) for Etna and Stromboli?
The found parameters fitting Eq. (1) are results of our work, here and in a previous study (Cassetta et al., 2021). We now report them in Fig. 2.

Probably the figures should be numbered 1, 2, 3, 4, etc., instead of 1, S1, 2, S2, 3, 4, S3, etc. Same for the tables.
Figures labeled with an S are meant to appear in the online Supplementary Information and were inserted in the main manuscript file only to facilitate the reviewers' reading. They will be removed from the final version of the manuscript, restoring the consecutive figure order. In addition, according to the journal guidelines, we rename in the main text the supplementary figures as fallow: Fig. S1 → Supplementary Fig. 1.