

Peer Review File

Metastable liquid immiscibility in the 2018-2021 Fani Maoré lavas: new insights for volcanic nanolite formation



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13th Jul 23

Dear Dr Thivet,

Please allow us to apologise for the delay in sending a decision on your manuscript titled "Nanoscale liquid immiscibility in the 2018-2021 Fani Maoré submarine lavas: new insights for volcanic nanolite formation". It has now been seen by 3 reviewers, whose comments are appended below. You will see that they find your work of some potential interest. However, they have raised quite substantial concerns that must be addressed. In light of these comments, we cannot accept the manuscript for publication, but would be interested in considering a revised version that fully addresses these serious concerns.

On the basis of reviewers comments we recommend in particular to:

- * Present a compelling new mechanism for nanolite formation which is supported by robust and fully qualified observations and modelling.
- * Re-formulate your thermal model in order to account for the influence of latent heat of crystallization.
- * Fully discuss the potential role of metastable nanoscale immiscibility and that of volatiles in your crystallization model and either compellingly exclude these or caveat your conclusions to accommodate it.

The other comments by the reviewers should also be addressed.

We hope you will find the reviewers' comments useful as you decide how to proceed. Should additional work allow you to address these criticisms, we would be happy to look at a substantially revised manuscript. If you choose to take up this option, please either highlight all changes in the manuscript text file, or provide a list of the changes to the manuscript with your responses to the reviewers.

Please bear in mind that we will be reluctant to approach the reviewers again in the absence of substantial revisions.

If the revision process takes significantly longer than three months, we will be happy to reconsider your paper at a later date, as long as nothing similar has been accepted for publication at Communications Earth & Environment or published elsewhere in the meantime.

We are committed to providing a fair and constructive peer-review process. Please do not hesitate to contact us if you wish to discuss the revision in more detail.

Please use the following link to submit your revised manuscript, point-by-point response to the reviewers' comments with a list of your changes to the manuscript text (which should be in a separate document to any cover letter), a tracked-changes version of the manuscript (as a PDF file) and any completed checklist:

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Please do not hesitate to contact us if you have any questions or would like to discuss the required revisions further. Thank you for the opportunity to review your work.

Best regards,

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REVIEWER COMMENTS:

Reviewer #1 (Remarks to the Author):

This paper presents an interesting study of nanoscale silicate liquid immiscibility and crystallisation in rapidly cooled rims of basanitic lava from a submarine eruption in the Indian ocean. The study documents important observations showing that crystal nucleation within a few centimetres from the contact with ocean water was preceded, and probably assisted, by metastable silicate liquid immiscibility. Kinetic relationships between crystallisation and liquid immiscibility have been extensively studied in material science partly because complex interplay between the processes is key for manufacturing some important composite materials such as glass ceramics. In contrast, detailed studies of rapidly quenched magmatic glasses and finely crystallised metastable products of disequilibrium phase transitions in natural lavas have been rare in geological literature. This is a welcome contribution but the importance and novelty of the observations probably require a more detailed discussion, which may be better served by a different paper format.

Major comments.

(1) I am not convinced that the simplified cooling model ignoring latent heat of crystallisation is adequate for calculation of the cooling rates. Yes, there was not much crystallisation within the outermost 1 or 2 cm of the rim but just a few centimetres deeper, at 5 cm from the contact with water and further inside, the lava is fully crystallised (lines 261-263). Latent heat of crystallisation of common natural silicates is about 300 times greater than the heat capacity of silicate melts. Therefore, crystallisation must be an important contributor to the heat budget and may increase it by 40-50%.

(2) Because NBO/T is broadly used in the paper as a measure of melt polymerization and a proxy for melt viscosity, I would ask the authors to check their calculations and better characterize

compositional evolution of the melt in the interior of the lava flow, at low cooling rates and conditions close to equilibrium. NBO/T values at 0.6-0.7 for the original basanite (line 90) look strange. According to Mysen et al. (Amer. Min. 65, 1980, p.708), basanites and picrites have NBO/T between 1 and 2. Figure 6a is too schematic and kind of dubious. I understand why binodal and spinodal curves are poorly defined in the temperature-composition coordinates but one can do better with melt evolution by fractional crystallization (the blue curve to the left of the binodal). For example, one could use MELTs modelling to better constrain the melt evolution path, or use microprobe analyses of interstitial glasses in strongly crystallised inner parts of the lava flows.

(3) The general pattern of liquid-liquid element partitioning and mineralogy of "nanolites" in zone 2 need more discussion and at least some explanations. It makes perfect sense that pre-eruptive micro-phenocrysts in zone 2 are represented by olivine and magnetite. I can also understand why Ti-magnetite nanolites nucleated in the immiscible Fe-Ca-Ti rich liquid droplets. But why biotite, such a compositionally complex, hydrated mineral is the only nanolite nucleating in the Si-Al rich matrix glass? Why not an alkali feldspar? Furthermore, why Mg did not concentrate in the immiscible Fe-Ca-Ti rich droplets, as it should have done, according to its ionic properties and equilibrium liquid-liquid distribution coefficient? I can imagine that slowly diffusing P₂O₅ component might not have enough time to concentrate in the droplets, but why are fast-diffusing alkalis and Mg not properly distributed between the immiscible liquids?

(4) Why did the formation of binodal and spinodal exsolutions precede nucleation of the nano-crystals? Is it because the low liquid-liquid interfacial energy, or a greater compositional flexibility of non-stoichiometric liquid phases? Some discussion would be appropriate here.

(5) Crystal nucleation on stable and metastable immiscible liquid droplets has been thoroughly studied and broadly used in material science. However, if metastable immiscibility in the natural basanitic lava requires very high cooling rates, somewhere between 1 and 500 degrees C per second, and is restricted to a centimetre-thick rim at the surface of the lava flow, it seems that the phenomenon does not have much relevance for large-scale magma dynamics. Apparently, there are no traces of liquid immiscibility left in the strongly crystallized zone 3 of the lava flow. But did immiscibility exist as a transit phenomenon and a trigger for crystallisation at the very start of crystal nucleation? Any thoughts on that?

(6) Concentrations of components in immiscible liquids are different but the activities (line 319) should be the same. At least, this is what thermodynamics demands. Thermodynamic driving force acts towards equilibrating activities in all the coexisting phases.

(7) According to Zanotto (2020), whom you cite, the effects of heterogeneous crystal nucleation on liquid-liquid interfaces are negligible (contrary to what is implied in lines 46 and 340-341).

Minor comments and corrections.

Lines 42-43: what is "macro-t"?

Line 45: "immiscible system" vs. "miscible" is confusing. I would write emulsion vs. homogenous liquid instead.

Line 52: what do you mean by "high surface density"? Is it large surface area per volume unit?

Line 220: "images... highlight" (plural).

Line 230: What are "quenching microlites"? Do you mean pre-eruptive micro-phenocrysts or quenching nanolites?

Reviewer #2 (Remarks to the Author):

The manuscript by Thivet and coauthors is a well-written and very interesting report on the occurrence of nanoscale metastable liquid immiscibility in natural magmatic products of submarine origin. The identification of syneruptive metastable immiscibility is valuable for earth scientists and volcanologists examining eruption dynamics, especially considering the increasing interest for the possible role of nanolites in determining eruptive styles. Consequently, I strongly recommend the publication of this article on "communications earth & environment". Before that, I suggest however some major improvements to the present version:

-The authors could extend the discussion of volcanological implications (for instance in the last section "Potential impacts of quenching immiscibility in magmas") by specifying how the phase separation observed in samples recovered from a submarine lava flow would be expected to practically induce fragmentation and therefore shift the eruptive style towards explosivity.

-The authors seem to disregard the possible effects of water and volatiles on the observed metastable immiscibility. How do they expect these melt components to respond to a nanostructural evolution as the ones shown in Fig. 3, 4 and 5? Is their solubility the same in Si-enriched and Fe-enriched melts? Water is known to influence viscosity and also crystal nucleation ([https://doi.org/10.1016/S0022-3093\(97\)00252-4](https://doi.org/10.1016/S0022-3093(97)00252-4)), so a different water content may interplay with the cooling rate in determining whether immiscible liquids are formed or not.

-Similarly, a possible influence of oxyreduction on the immiscibility and crystallization path should at least be mentioned. How different are oxidation conditions expected to be between outer, inner rim and interior? How would this affect liquidus temperatures? And the tendency to unmix?

-Have the authors considered that metastable nanoscale immiscibility could also represent a key stage of the crystallization sequence of the lava interior (possibly its starting point), being then obliterated by the massive crystal nucleation and growth? Or was this hypothesis discarded on the base of some data/assumptions?

-There seem to be some problems with the supplementary materials. Either some files are absent from the present submission, or they have been renamed without updating the manuscript. I tried to signal below this problem, any time a file/figure/table is recalled without being available in the supplementary materials.

-Please write the units of inverse seconds as s⁻¹, instead of /s

-Line 43: macro- to micrometer-scales

-Lines 45-47: in analogy with the section "Why does liquid immiscibility favor crystallization?" of the discussion and considering reference 57, the authors should highlight the importance of compositional variations with respect to the parent homogeneous melt already at this stage.

-Lines 52-53: "However, nanolite clustering as well as changes in residual melt compositions during nanolite formation, can lead to drastic increases in magma viscosity²⁰⁻²³." There are at least two papers by Di Genova and coauthors which specifically analyse the effect of nanolite formation on the chemical composition and viscosity of the residual melt: <https://doi.org/10.1016/j.jnoncrysol.2020.120248> and <https://doi.org/10.1038/s43247-022-00615-2>. They should be included when introducing previous literature on the topic.

-Lines 52-55: "Further, the high surface density implied by the presence of nanolites is likely to play a role in supporting further heterogeneous nucleation processes such as bubble nucleation, with their consequences for magma fragmentation and, in turn, eruption dynamics²⁴." The effect of nanolites on decompression-driven degassing and bubble formation is demonstrated (in the lab) and discussed also in <https://doi.org/10.1038/s43247-022-00615-2>. Please add this reference at this point as well.

-Line 128: matric -> matrix

-Line 133 and following: "presence of the Boson peak at ca. 75 cm⁻¹ which is a typical signature of the glassy state⁴⁷ that tends to disappear in the presence of significant crystalline phases⁴⁸." It is difficult to identify the position of the Boson peak from uncorrected spectra. The authors should clarify whether 75 cm⁻¹ is the position identified through careful spectral analysis (and in this case provide the details of this analysis) or whether it is generally referring to literature. Indeed, the position of the Boson peak is dependent, among others, on the chemical composition of the glass. The authors may complement their literature references with some more recent sources dealing with volcanic melts and glasses: <https://doi.org/10.1002/jrs.6298>, <https://doi.org/10.1016/j.saa.2023.122430>, <https://doi.org/10.1038/s41598-021-92407-5> If the authors cannot or do not wish to perform a complete spectral treatment to extract the exact position of the Boson peak, they should modify their text in order to make clear that they are only performing a qualitative spectral analysis. In this case, the changes in the low-wavenumber intensity (in the vicinity of the Rayleigh line) can be certainly interpreted as possibly arising from a shift/intensity change of the Boson peak, but this interpretation should be clearly distinct from observation and analysis. This applies to also to other sections dealing with low-wavenumber features (e.g. line 207).

-Line 139: "In addition, a slight rise of the Raman spectrum between 600 and 700 cm⁻¹ suggests the presence of one or more iron-bearing nanolite phases." As clearly shown in <https://doi.org/10.1038/s43247-022-00615-2>, intensity contributions related to Fe clustering can be observed between 600 and 700 already in the amorphous state, i.e. before the actual formation of objects definable as nanocrystals (or nanolites). A Raman spectrum cannot unequivocally distinguish between amorphous and crystalline states. As such, the authors should amend their text to avoid misleading formulations.

-Line 148: I did not find any File S2 in the supplementary materials (it is not listed either), so there may be a type-o here.

-Line 155: I did not find any Table S3 in the supplementary materials (it is not listed either), so there may be a type-o here.

-Line 157: "microlite- and nanolite free (i.e., ca. < 20 μm)" if 20 μm is the threshold below which the authors are not able to analyse the materials (at least at this stage of the manuscript), they should not write "nanolite-free". Did the authors perform any TEM analysis of the outer rim, to confirm (i) its fully amorphous state and (ii) its complete mesoscopic homogeneity? At the moment, only SEM and Raman data are shown; it would be beneficial to see some (S)TEM micrographs, at least as supplementary materials.

-Line 168: again, I could not find Table S3 in the supplementary materials

-Lines 164-199: Have the authors tested the amorphous state of the two immiscible phases by electron diffraction? Can they provide, in the main text or in the supplementary materials, results exemplifying amorphous diffraction patterns for both immiscible phases?

-Line 204: again, I could not find Table S3 in the supplementary materials

-Line 229: no file S2 available

-Line 236: "bimodal" should be "binodal"

-Line 231-239: considering that microlites tend to be aluminosilicates, the residual melt will probably be enriched in Fe and Ti with respect to the parent homogeneous melt, possibly for this reason transitioning from spinodal to binodal behavior. As such, the authors may discuss these compositional changes more specifically, also taking into account the limited solubility of Fe and Ti in silicate melts, which has been recently advocated as a main driving force towards the formation of amorphous heterogeneities and nanolites (in the lab): <https://doi.org/10.1038/s43247-022-00615-2>.

-Line 250: again, I could not find Table S3 in the supplementary materials

-Line 263: no File S2 is available

-Line 264: "quenching liquid immiscibility" is more typically expressed as "metastable immiscibility" in the literature (see for instance <https://doi.org/10.1111/j.1151-2916.1977.tb15525.x>), which immediately clarifies the different nature of this phenomenon as compared to thermodynamically stable (superliquidus) immiscibility. The authors may adopt this terminology (instead of "quenching liquid immiscibility") when describing the binodal and spinoidal nanostructures in their samples.

-Lines 272-286: In fact, the authors could refer already here (and not only further down in the text) to concepts such as the undercooling experienced by the melt (in combination to the quenching rate) to explain why the driving force towards crystallization is different between case 1, 2 and 3, and therefore the crystallization path experienced by the melt.

-Line 306: the Einstein-Stokes equation provides a good approximation of ion mobility in melts that undergo near-stoichiometric crystal nucleation at relatively high temperature. However, the authors should mention that decoupling between viscosity and diffusion has been observed at deeper undercooling (see for instance: <https://doi.org/10.1016/j.jnoncrysol.2015.08.027>). For systems undergoing nanoscale compositional reorganization and non-isochemical nucleation, chemical diffusion provides probably a more representative picture than viscosity. This view may be also included in lines 325-338.

-Line 317: please remove one of the "that".

-Line 330: "and can also present 4-, 5-, and 6-fold coordination⁵⁹⁻⁶⁰." The authors should refer to the seminal works of Farges et al., for instance: [https://doi.org/10.1016/S0016-7037\(97\)00050-1](https://doi.org/10.1016/S0016-7037(97)00050-1)

-Lines 325-338: the authors discuss the difference in crystal content between the two observed melt phases in terms of viscosity and therefore ion mobility. In an alternative view, they could take into account the different glass forming ability of the two melts, which is a complex property only partially correlating to viscosity (other factors play a role, such as intrinsic crystal nucleation rate). Aluminosilicate melts are known to be better glass formers than Fe- and Ti-rich silicate melts, being therefore more resilient against crystallization at a given cooling rate. Note that Fe and Ti are added to glass-ceramics as seed formers for this reason, so the authors may include some citations from the domain of manmade silicate melts and glasses to support the easier crystal nucleation of the Fe- and Ti-rich melt.

-Lines 339-352: this section results less clear than the two previous ones and should be improved. The authors refer to a lowering of the alpha parameter due to the presence of an interface; however, the source 57 of the manuscript clearly states that the energetic contribution of the interface to nucleation is most likely negligible, so this view should be reported correctly. When describing chemical gradients around the interface, instead, the authors are implicitly going back to the reasons already described in lines 317-324. Note that nanoscale chemical gradients have been shown to

facilitate/affect nucleation in a plethora of studies in the materials science community. For some examples see: <https://doi.org/10.1021/cg9009898>, <https://doi.org/10.1063/1.3610557>, <https://doi.org/10.1111/jace.17822> and DOI: 10.5802/crphys.150

-Line 365: remove enhancing

-Lines 392-398: Could the authors specify the instrumental setup and measurement routine used to acquire the spectra, in particular with respect to the low-wavenumber region? Are they sure their instrument allows recording of the Boson peak without truncation? What kind of edge filter does the spectrometer mount? Ref. 49 published spectra above 100 cm^{-1} , so I expect that instrument and procedures should have been adapted to facilitate acquisition at low wavenumber.

-Line 411: Figure S4 is not listed in the supplementary materials, I suspect it should be S2.

-Line 432: no Table S5 is available as supplementary material.

-Figure 2, caption: "Grey areas 1 and 2 correspond to the theoretical occurrence areas of the Boson peak and of the iron-bearing nanolite phases, respectively." Please complement the caption with the citations from which these conclusions are drawn, especially in absence of an analytical extraction of the position of the Boson peak. Iron-bearing phases (nanolite or not) exhibit several Raman bands; only the most intense is located in the grey area 2; it is the signature of these phases that occurs in the spectra, not the phases themselves. Please correct the sentence to take this into account, also considering that spectral contributions in this area may refer to clustering of Fe in the amorphous phase, prior to the formation of crystalline nanolites (see above). Please correct similar expressions used in the supplementary materials.

-Figure 3: "e) Crystal Size Distribution (CSD) performed" should probably be modified as "e) Crystal Size Distribution (CSD) analysis performed".

-Figure 6: I find some features of the sketch misleading, so the authors should consider to modify this figure and/or specify its description. It combines thermodynamics and kinetics and can therefore result confusing. For instance, the final temperature of the three cooling paths should invariably reach the same value at the end (RT); it is the duration of the permanence of the melt in each phase field (and not temperature itself) that determines whether the materials stays homogeneous, unmixed or crystallizes. It is unclear whether the dashed line labelled with "crystallization" corresponds to the thermodynamic onset of a crystallization driving force (liquidus) or to the kinetically controlled first observation of crystals. Why does it decrease towards the composition of melt B?

Reviewer #3 (Remarks to the Author):

The study by Thivet et al. is a detailed description of nano-scale textures with immiscible melts and micro-crystals in lavas from the 2018-2021 Fani Maoré eruption. Such textures have already been documented in a recent paper by the same authors (Thivet, S., Hess, K.-U., Dingwell, D.B., Berthod, C., Gurioli, L., Di Muro, A., Lacombe, T. and Komorowski, J.-C. (2023) Volatiles of the active Mayotte volcanic chain: STA & EGA-MS analysis of volcanic products. *Chemical Geology* 618, 121297.) The new aspect of this paper is the proposal that "The occurrence of liquid immiscibility at eruptive conditions must strongly control all physicochemical characteristics of the nanolites as well as residual melt compositions. Such immiscibility likely represents a common yet frequently unobserved feature of such submarine eruptions, with the potential for major impacts on syn-eruptive magma degassing and rheology." Quenching rates are shown to have a strong control on the development of these textures. This was already identified in the previous study of Thivet et al. (2023) in *Chemical Geology*. It is not clear to me that the major impacts of immiscibility on syn-eruptive magma degassing and rheology is shown in this study. Also, it is not true that nanoscale description of immiscible have not been

documented previously. See for example the following references: Veksler, I.V., Dorfman, A.M., Borisov, A.A., Wirth, R. and Dingwell, D.B. (2007) Liquid immiscibility and the evolution of basaltic magma. *Journal of Petrology* 48, 2187-2210 or Honour, V.C., Holness, M.B., Charlier, B., Piazzolo, S.C., Namur, O., Prosa, T.J., Martin, I., Helz, R.T., MacLennan, J. and Jean, M.M. (2019) Compositional boundary layers trigger liquid unmixing in a basaltic crystal mush. *Nature Communications* 10, 4821.

My feeling is that the authors have tried to oversell their study. The description of the textures is of high-quality and the interpretation of their origin is clear (quenching rate). However the interpretation of their implication on eruptive process, degassing, rheology, fragmentation, explosivity is mainly qualitative and fails at getting beyond current understanding of the immiscibility process and nanolite formation.

Reviewer #1 (Remarks to the Author):

This paper presents an interesting study of nanoscale silicate liquid immiscibility and crystallisation in rapidly cooled rims of basanitic lava from a submarine eruption in the Indian ocean. The study documents important observations showing that crystal nucleation within a few centimetres from the contact with ocean water was preceded, and probably assisted, by metastable silicate liquid immiscibility. Kinetic relationships between crystallisation and liquid immiscibility have been extensively studied in material science partly because complex interplay between the processes is key for manufacturing some important composite materials such as glass ceramics. In contrast, detailed studies of rapidly quenched magmatic glasses and finely crystallised metastable products of disequilibrium phase transitions in natural lavas have been rare in geological literature. This is a welcome contribution but the importance and novelty of the observations probably require a more detailed discussion, which may be better served by a different paper format.

We are glad that the importance of our work has been understood and well-recognized. We fully agree that the observations made deserve a more detailed discussion/conclusion, as this kind of mechanism must indeed involve important magmatic processes. You will find more details in the revised manuscript, also trying to be not so much speculative as the main goal of this article is to characterize and describe this nanolite generation mechanism. Also, probably other studies, especially experimental ones, will be needed to better understand in which conditions (i.e., compositions, pressure, and temperature evolutions) this mechanism happens, and to better quantify the effect on magma degassing, and rheology (and *in fine* eruptive dynamics).

Major comments

(1) I am not convinced that the simplified cooling model ignoring latent heat of crystallisation is adequate for calculation of the cooling rates. Yes, there was not much crystallisation within the outermost 1 or 2 cm of the rim but just a few centimetres deeper, at 5 cm from the contact with water and further inside, the lava is fully crystallised (lines 261-263). Latent heat of crystallisation of common natural silicates is about 300 times greater than the heat capacity of silicate melts. Therefore, crystallisation must be an important contributor to the heat budget and may increase it by 40-50%.

This is a very pertinent remark. Despite the main goal of this article is not focused on thermal calculations in order to estimate precise cooling/quenching rates of our samples in function of lava depth, we fully agree that we have to check more precisely the effect of latent heat of crystallization on our estimations. Thus, we executed additional Differential Scanning Calorimetry (DSC) on representative samples from the Fani Maoré eruption, in order to obtain the latent heat linked to crystallization (we add the contribution of a new co-author). Based on these data, along with additional heat transfer calculations, we evaluated the contribution of latent heat of crystallization in our heat transfer model. This total heat associated with extensive crystallization was only 5 % of the aforementioned total exchanged heat during cooling. Thus, we could conclude that the released heat linked to crystallization was not significant when compared to the total heat exchanged during cooling from the eruptive temperature to the glass transition temperature, especially for the outer (case 1) and inner (case 2) lava rims, which are largely less crystallized than in the DSC experiments, and which the most interesting sample parts for our case study. Therefore, we confidently neglected this contribution in the heat transfer calculations, which would not change the absolute values of the estimated quenching/cooling rates. This estimation based on new experiments and theoretical calculations is fully detailed within the file S2 of the supplementary material (new supplementary file). Also note that such transient heat conduction model is well-recognized and used to estimate natural cooling rates of volcanic products (e.g. Jones et al. 2022, <https://doi.org/10.1038/s41467-022-30501-6>; Honour et al. 2019, <https://doi.org/10.1180/mgm.2019.71>; Poritt et al. 2012, <https://doi.org/10.1016/j.epsl.2012.03.031>; Holness et al. 2012, <https://doi.org/10.1130/G33119.1>). Beside these additional insights, we better describe and recalibrate the initial calculations with more relevant parameters (cf. method part), leading to slightly different quenching/cooling rates for the interface between outer (case 1) and outer (case 2) lava flow rims. Note that, our estimated values are fully coherent with already estimated values on submarine basaltic shards using the geospeedometry technique (Potuzak et al. 2008, <https://doi.org/10.1016/j.epsl.2008.03.018>). We also better explain and compare these values in the results part.

In detail, we have now estimations of ca. 1000 °C s⁻¹ at 500 µm from the lava margin, ca. 1 °C s⁻¹ at 1 cm, and ca. 0,1 °C s⁻¹ at 5 cm where the lava tends to be fully crystallized (which are consistent values regarding the literature and the crystallinity of the samples).

(2) Because NBO/T is broadly used in the paper as a measure of melt polymerization and a proxy for melt viscosity, I would ask the authors to check their calculations and better characterize compositional evolution of the melt in the interior of the lava flow, at low cooling rates and conditions close to equilibrium. NBO/T values at 0.6-0.7 for the original basanite (line 90) look strange. According to Mysen et al. (Amer. Min. 65, 1980, p.708), basanites and picrites have NBO/T between 1 and 2.

We checked again our NBO/T values and add a new supplementary file S1 to support them. Our calculations are based on equations and parameters defined by Mysen et al. 1982 (<https://doi.org/10.1029/RG020i003p00353>) and Middlemost 1989 ([https://doi.org/10.1016/0009-2541\(89\)90011-9](https://doi.org/10.1016/0009-2541(89)90011-9)). As stated in the manuscript, our estimated values are slightly higher than those found recently by Verdurme et al. 2023 (<https://doi.org/10.1016/j.chemgeo.2023.121326>) because these authors were considering all Fe as oxidised. Also, our values typically fall in the range of basanite bulk rock compositions. We checked the paper of Mysen et al. 1980 that deal only with experimental and simplified compositions with NBO/Si and without any relevant values for Al-rich basanites, like we have at Fani Maoré. Mysen et al. 1980 is also showing NBO/T values for tholeiite of 0.66, which is at the end quite coherent with our values between 0.7 and 0.8.

Figure 6a is too schematic and kind of dubious. I understand why binodal and spinodal curves are poorly defined in the temperature-composition coordinates but one can do better with melt evolution by fractional crystallization (the blue curve to the left of the binodal). For example, one could use MELTs modelling to better constrain the melt evolution path, or use microprobe analyses of interstitial glasses in strongly crystallised inner parts of the lava flows.

Thanks for your remark on Fig. 6. Also considering the second reviewer's comments, we rethink the way we wanted to show and summarize the main mechanism shown in this paper. We mostly reconsider the paths shown in the figure, which in fact combined thermodynamics and dynamics. We defined the temperature limits and also specified a new NBO/T value. A value of NBO/T of 0.5 for partially crystallized areas is calculated from residual glass compositions from microprobe analyses performed by Berthod et al. 2022 (<https://doi.org/10.1016/j.epsl.2021.117085>) in lava interiors. This calculation is also added in the new supplementary file S1, and mentioned in the results part. Note that after a crystallization of ca. 50% is not possible to get suitable microprobe analyses of the residual glasses because of the too narrow glass areas (< 10 µm) and the ubiquity of small crystals in the matrix. Also, we want to remind here that the final Fig.6 is not meant to represent precise data, as our study do not pretend to bring the exact conditions in which liquid immiscibility is happening (we add a statement in the conclusion part that highlights the necessity of experimental studies to do so), but do summarize and present a compelling new mechanism for nanolite mechanism, as requested as the very main point of this review.

(3) The general pattern of liquid-liquid element partitioning and mineralogy of "nanolites" in zone 2 need more discussion and at least some explanations. It makes perfect sense that pre-eruptive micro-phenocrysts in zone 2 are represented by olivine and magnetite. I can also understand why Ti-magnetite nanolites nucleated in the immiscible Fe-Ca-Ti rich liquid droplets. But why biotite, such a compositionally complex, hydrated mineral is the only nanolite nucleating in the Si-Al rich matrix glass? Why not an alkali feldspar? Furthermore, why Mg did not concentrate in the immiscible Fe-Ca-Ti rich droplets, as it should have done, according to its ionic properties and equilibrium liquid-liquid distribution coefficient? I can imagine that slowly diffusing P2O5 component might not have enough time to concentrate in the droplets, but why are fast-diffusing alkalis and Mg not properly distributed between the immiscible liquids?

We agree that our observations on the mineralogy must be supported by some discussion, which we added in the manuscript. We basically present in this paper what our results showed to us. We are mostly talking here about TEM results, which were acquired and interpreted in a very confident way (cf. Figs. 3, 4, 5). Also following reviewer 2's comment, we add some arguments in the manuscript that show that volatiles indeed tend to migrate and concentrate in the Si- and Al-rich matrix, with respect to the Ca-, Fe-, and Ti-rich one. That is probably also why phlogopite (volatile-containing phase) is preferentially formed, with no evidence, from our TEM observations, of other phases such as alkali feldspar. We also highlighted that H₂O is known to play a role on nucleation kinetics and sometimes change the expected nucleation processes with respect to dry conditions. Concerning the liquid-liquid element partitioning, we do not have any further insights or explanation why Na, K, Mn, and Mg are not preferentially distributed.

(4) Why did the formation of binodal and spinodal exsolutions precede nucleation of the nano-crystals? Is it because the low liquid-liquid interfacial energy, or a greater compositional flexibility of non-stoichiometric liquid phases? Some discussion would be appropriate here.

Your remark is very interesting and we add a small discussion on this point in the manuscript. We do have the evidence of micro-crystallization before the liquid immiscibility occurrence by the presence of these laths of biotite. Then, the low liquid-liquid interfacial energy is indeed a reason for the rapid formation of immiscibility but we also add other arguments (e.g., Fe and Ti clustering in the matrix around the biotites) that can favour the formation of immiscibility before nanolite formation. The fact that nanolites have a specific mineralogy and texture compare to where no immiscibility occurs, also proves that immiscibility precedes nanolite crystallization in the inner lava rims.

(5) Crystal nucleation on stable and metastable immiscible liquid droplets has been thoroughly studied and broadly used in material science. However, if metastable immiscibility in the natural basanitic lava requires very high cooling rates, somewhere between 1 and 500 degrees C per second, and is restricted to a centimetre-thick rim at the surface of the lava flow, it seems that the phenomenon does not have much relevance for large-scale magma dynamics. Apparently, there are no traces of liquid immiscibility left in the strongly crystallized zone 3 of the lava flow.

We totally agree with this comment. This paper only pretends to present and characterize this new mechanism that has not been clearly described in natural volcanic products (cf. article title). As perspectives, we suggest some potential impacts, as this mechanism could happen in various eruptive conditions (now from ca. 1 to 1000 °C s⁻¹ in term of cooling rates). We also suggest that lower eruptive pressures could be some conditions with more impacts for magma fragmentation (mainly because of the enhancement of H₂O degassing and increase of viscosity that could happen before lava emission in this case). Also, regarding the large lava surface related to this eruption, this 1 cm thick layer of inner lava flow rim could play a role on the secondary fragmentation of small particles into the ocean, with non-negligible impacts for instance for the marine environment. We also added and stated that supplementary studies must be done to better understand in which conditions such mechanisms can happen.

But did immiscibility exist as a transit phenomenon and a trigger for crystallisation at the very start of crystal nucleation? Any thoughts on that?

This is also a very good point, raised also by the second reviewer, that we did not discuss in the first version of our article. We add this discussion because we might indeed lose the signature of liquid immiscibility in the lava interior, despite the fact that we have relatively different crystals (both in terms of mineralogy and texture) between these two areas.

(6) Concentrations of components in immiscible liquids are different but the activities (line 319) should be the same. At least, this is what thermodynamics demands. Thermodynamic driving force acts towards equilibrating activities in all the coexisting phases.

We agree with this comment and the text has been modified accordingly. We focus this part on the thermodynamic driving force for nucleation of crystals, i.e., ΔG_v and not on the activity of these components.

(7) According to Zanotto (2020), whom you cite, the effects of heterogeneous crystal nucleation on liquid-liquid interfaces are negligible (contrary to what is implied in lines 46 and 340-341).

Indeed, the paper of Zanotto 2020 (<https://doi.org/10.1016/j.ceramint.2020.06.305>) considers that the contribution of the droplet-liquid interface is irrelevant due to its low interfacial energy. However, in our case, we could observe that many crystals were nucleated from the interface between the droplets and the external melt. So here, contrary to what was mentioned in this review article, we better explained that in this specific case these liquid-liquid interfaces seem to play a role in the nucleation process. Since this interfacial energy is a function of the available surface area, it can be argued that in our case, since we have nanodroplets, the surface area is high enough to increase the total energy of the system. Besides, we added another reference (Ohlberg et al. 1962) that contrary to Zanotto (2020) also observed crystals being formed at droplet interfaces.

Minor comments and corrections.

Lines 42-43: what is “macro-t”?

Thanks, this was a typo, we corrected it as “macro- to micro-scales”.

Line 45: “immiscible system” vs. “miscible” is confusing. I would write emulsion vs. homogenous liquid instead.

We corrected as mentioned.

Line 52: what do you mean by “high surface density”? Is it large surface area per volume unit?

This was indeed confusing, we corrected it as mentioned with an appropriate reference, latter in the manuscript as we decided to move this statement in the results and discussion part.

Line 220: “images... highlight” (plural).

Done.

Line 230: What are “quenching microlites”? Do you mean pre-eruptive micro-phenocrysts or quenching nanolites?

We specified this better in the sentence. This part indeed mentioned crystalline phases formed during lava quenching.

Reviewer #2 (Remarks to the Author):

The manuscript by Thivet and coauthors is a well-written and very interesting report on the occurrence of nanoscale metastable liquid immiscibility in natural magmatic products of submarine origin. The identification of syneruptive metastable immiscibility is valuable for earth scientists and volcanologists examining eruption dynamics, especially considering the increasing interest for the possible role of nanolites in determining eruptive styles. Consequently, I strongly recommend the publication of this article on "communications earth & environment". Before that, I suggest however some major improvements to the present version:

We thank the reviewer for his comprehensive comments and we are glad that our work has been well-recognized. Below we are following the comments one by one. We believe that they were to a great help improving the quality of the manuscript.

The authors could extend the discussion of volcanological implications (for instance in the last section "Potential impacts of quenching immiscibility in magmas") by specifying how the phase separation observed in samples recovered from a submarine lava flow would be expected to practically induce fragmentation and therefore shift the eruptive style towards explosivity.

As suggested, we emphasized our last discussion on volcanological implications (conclusion part). Our study pretends only to describe this mechanism for nanolite formation, but we tried to give some suggestions and give some insights on the new raised questions in terms of impacts of such mechanism. We also stated that supplementary studies are needed to better constrain in which conditions and which scales this mechanism can happen, and what could be its impact.

The authors seem to disregard the possible effects of water and volatiles on the observed metastable immiscibility. How do they expect these melt components to respond to a nanostructural evolution as the ones shown in Fig. 3, 4 and 5? Is their solubility the same in Si-enriched and Fe-enriched melts? Water is known to influence viscosity and also crystal nucleation ([https://doi.org/10.1016/S0022-3093\(97\)00252-4](https://doi.org/10.1016/S0022-3093(97)00252-4)), so a different water content may interplay with the cooling rate in determining whether immiscible liquids are formed or not.

Thanks for this very interesting comment. We better discussed the role of volatile in the conclusion part considering your suggestions but also the other reviewer's comment. We fully agree that the question of the role of dissolved H₂O on the occurrence of liquid immiscibility is a key question to understand in which condition this mechanism could happen, considering also relevant volcanological conditions. On the other hand, we also add some arguments in the manuscript to suggest that volatiles tend to migrate within the Si- and Al-rich melt as we only observed hydrated minerals there. However, we do not have direct evidence of this volatile partitioning but we better hypothesize and discuss the potential impacts of degassing and rheology in the conclusion part.

Similarly, a possible influence of oxyreduction on the immiscibility and crystallization path should at least be mentioned. How different are oxidation conditions expected to be between outer, inner rim and interior? How would this affect liquidus temperatures? And the tendency to unmix?

Indeed, the redox state of the studied silicate system might also play a role in the discussed processes. It has been mentioned in the conclusion part. Iron reduction, as most of the multivalent elements, is endothermic, meaning that Fe²⁺ is more abundant at higher temperatures. Thus, parts of the system that undergoes fast cooling, such as the external parts, should present higher Fe²⁺ content than the internal ones. Therefore, in the zone 1 and 2, which exhibit relatively high cooling rates, it is expected to observe relatively higher fraction of reduced iron when compared to the internal parts of the material which was cooled relatively slowly. Despite the fact that this information can be raised, to draw a conclusion on it, more analyses should be done. Because of that, we would like to avoid becoming speculative. Also note that the different cooling rates experienced by the lava flow besides playing a role in the redox conditions of the melt and thus on iron speciation, it should also play a role on the liquid temperature. Zones with higher ferrous content are expected to have lower liquidus temperature.

Have the authors considered that metastable nanoscale immiscibility could also represent a key stage of the crystallization sequence of the lava interior (possibly its starting point), being then obliterated by the massive crystal nucleation and growth? Or was this hypothesis discarded on the base of some data/assumptions?

This is a very good point that was also raised by the first reviewer. As mentioned above, we agree that this point must be discussed and it has been added in the manuscript.

There seem to be some problems with the supplementary materials. Either some files are absent from the present submission, or they have been renamed without updating the manuscript. I tried to signal below this problem, any time a file/figure/table is recalled without being available in the supplementary materials.

We are sorry about this. Indeed, there was an error on the supplementary material nomenclature. But all files were available with appropriate captions. We corrected the nomenclature such as no confusions will occur anymore.

Please write the units of inverse seconds as s⁻¹, instead of /s

Done.

Line 43: macro- to micrometer-scales

Done.

Lines 45-47: in analogy with the section “Why does liquid immiscibility favor crystallization?” of the discussion and considering reference 57, the authors should highlight the importance of compositional variations with respect to the parent homogeneous melt already at this stage.

We agree and we added the importance of compositional variations induced by liquid immiscibility in this introduction part.

Lines 52-53: “However, nanolite clustering as well as changes in residual melt compositions during nanolite formation, can lead to drastic increases in magma viscosity²⁰⁻²³.” There are at least two papers by Di Genova and coauthors which specifically analyse the effect of nanolite formation on the chemical composition and viscosity of the residual melt <https://doi.org/10.1016/j.jnoncrysol.2020.120248> and <https://doi.org/10.1038/s43247-022-00615-2>. They should be included when introducing previous literature on the topic.”

We added these 2 references as suggested.

Lines 52-55: “Further, the high surface density implied by the presence of nanolites is likely to play a role in supporting further heterogeneous nucleation processes such as bubble nucleation, with their consequences for magma fragmentation and, in turn, eruption dynamics²⁴.” The effect of nanolites on decompression-driven degassing and bubble formation is demonstrated (in the lab) and discussed also in <https://doi.org/10.1038/s43247-022-00615-2>. Please add this reference at this point as well.

We added this reference as suggested.

Line 128: *matric* -> *matrix*

Done.

Line 133 and following: *“presence of the Boson peak at ca. 75 cm⁻¹ which is a typical signature of the glassy state⁴⁷ that tends to disappear in the presence of significant crystalline phases⁴⁸.” It is difficult to identify the position of the Boson peak from uncorrected spectra. The authors should clarify whether 75 cm⁻¹ is the position identified through careful spectral analysis (and in this case provide the details of this analysis) or whether it is generally referring to literature. Indeed, the position of the Boson peak is dependent, among others, on the chemical composition of the glass. The authors may complement their literature references with some more recent sources dealing with volcanic melts and glasses: <https://doi.org/10.1002/jrs.6298>, <https://doi.org/10.1016/j.saa.2023.122430>, <https://doi.org/10.1038/s41598-021-92407-5> If the authors cannot or do not wish to perform a complete spectral treatment to extract the exact position of the Boson peak, they should modify their text in order to make clear that they are only performing a qualitative spectral analysis. In this case, the changes in the low-wavenumber intensity (in the vicinity of the Rayleigh line) can be certainly interpreted as possibly arising from a shift/intensity change of the Boson peak, but this interpretation should be clearly distinct from observation and analysis. This applies to also to other sections dealing with low-wavenumber features (e.g. line 207).*

We agree with this comment and changed accordingly the text and associated results interpretations. We now clearly highlight that this is a qualitative Raman spectra analysis and that based on the literature, we interpret the position and presence or not of the Boson peak within the uncorrected Raman spectra. We also added one of the suggested references. We also highlight again in the method section concerning the Raman spectroscopy, that we used a qualitative approach and we better explained the conditions of analysis.

Line 139: *“In addition, a slight rise of the Raman spectrum between 600 and 700 cm⁻¹ suggests the presence of one or more iron-bearing nanolite phases.” As clearly shown in <https://doi.org/10.1038/s43247-022-00615-2>, intensity contributions related to Fe clustering can be observed between 600 and 700 already in the amorphous state, i.e. before the actual formation of objects definable as nanocrystals (or nanolites). A Raman spectrum cannot unequivocally distinguish between amorphous and crystalline states. As such, the authors should amend their text to avoid misleading formulations.*

We also agree with this comment and corrected the manuscript accordingly also with the relevant reference.

Line 148: *I did not find any File S2 in the supplementary materials (it is not listed either), so there may be a typo here.*

Same as above for the comment about the supplementary material.

Line 155: *I did not find any Table S3 in the supplementary materials (it is not listed either), so there may be a typo here.*

Same as above for the comment about the supplementary material.

Line 157: *“microlite- and nanolite free (i.e., ca. < 20 μm)” if 20 μm is the threshold below which the authors are not able to analyse the materials (at least at this stage of the manuscript), they should not write “nanolite-free”. Did the authors perform any TEM analysis of the outer rim, to confirm (i) its fully amorphous state and (ii) its*

complete mesoscopic homogeneity? At the moment, only SEM and Raman data are shown; it would be beneficial to see some (S)TEM micrographs, at least as supplementary materials.

This comment is very relevant. The specified size is confusing here so we just removed it as we discuss in general about visible crystalline phases. So far, with the SEM and Raman, no crystalline phase (apart from the inherited phenocrysts) were identified. Unfortunately, the outer rims were too thin and difficult to work with to make any thin section for the TEM (we had this explanation on the manuscript as well). However, we are pretty much confident that micro- and nano-scaled phases can be at least distinguished with high-magnification SEM images (cf. Fig. 2c). An interesting and supplementary study would be indeed to be able to sample and isolate glassy rims and characterize its mesoscopic parameters with the TEM in order to better understand the transition between case 1 and case 2.

Line 168: again, I could not find Table S3 in the supplementary materials

Same as above for the comment about the supplementary material.

Lines 164-199: Have the authors tested the amorphous state of the two immiscible phases by electron diffraction? Can they provide, in the main text or in the supplementary materials, results exemplifying amorphous diffraction patterns for both immiscible phases?

Each immiscible phase was too narrow to analyse them independently. However, we provide in Fig. 4d an example of an amorphous area which includes both immiscible phases. Then, looking at all associated BF-TEM images we can easily identify by colour contrast where we can find crystalline phases and where the matrix is amorphous. Same with HAADF-STEM, EDXS-STEM, and EF-TEM images. That's the main reason why we do not focus so much on amorphous areas after all with the electron diffraction, which was mainly used to identify and/or confirm the specific mineralogy in each phase and in each case.

Line 204: again, I could not find Table S3 in the supplementary materials

Same as above for the comment about the supplementary material.

Line 229: no file S2 available

Same as above for the comment about the supplementary material.

Line 236: "bimodal" should be "binodal"

Done.

Line 231-239: considering that microlites tend to be aluminosilicates, the residual melt will probably be enriched in Fe and Ti with respect to the parent homogeneous melt, possibly for this reason transitioning from spinodal to binodal behavior. As such, the authors may discuss these compositional changes more specifically, also taking into account the limited solubility of Fe and Ti in silicate melts, which has been recently advocated as a main driving force towards the formation of amorphous heterogeneities and nanolites (in the lab): <https://doi.org/10.1038/s43247-022-00615-2>.

We agree with this point which have been already discuss in the specified paragraph. We also add to this point the fact that Fe and Ti are enriched in the residual melt, more specifically around biotites where we

can see more binodal than spinodal textures. We also add that Fe and Ti have a limited solubility in silicate melts, which can be indeed a main contributor for the occurrence of nanometer-scale Fe and Ti clustering (amorphous and/or crystalline), and *in fine*, the transition from the spinodal to the binodal textures. We also add the associated reference in this part.

Line 250: again, I could not find Table S3 in the supplementary materials

Same as above for the comment about the supplementary material.

Line 263: no File S2 is available

Same as above for the comment about the supplementary material.

Line 264: “quenching liquid immiscibility” is more typically expressed as “metastable immiscibility” in the literature (see for instance <https://doi.org/10.1111/j.1151-2916.1977.tb15525.x>), which immediately clarifies the different nature of this phenomenon as compared to thermodynamically stable (superliquidus) immiscibility. The authors may adopt this terminology (instead of “quenching liquid immiscibility”) when describing the binodal and spinoidal nanostructures in their samples.

We agree with this and changed the terminology through all the manuscript.

Lines 272-286: In fact, the authors could refer already here (an not only further down in the text) to concepts such as the undercooling experienced by the melt (in combination to the quenching rate) to explain why the driving force towards crystallization is different between case 1, 2 and 3, and therefore the crystallization path experienced by the melt.

We introduce the notion of undercooling at the beginning of the specified paragraph, such as the reader is prepared to the topic of crystallization, which is coming right after.

Line 306: the Einstein-Stokes equation provides a good approximation of ion mobility in melts that undergo near-stoichiometric crystal nucleation at relatively high temperature. However, the authors should mention that decoupling between viscosity and diffusion has been observed at deeper undercooling (see for instance: <https://doi.org/10.1016/j.jnoncrysol.2015.08.027>). For systems undergoing nanoscale compositional reorganization and non-isochemical nucleation, chemical diffusion provides probably a more representative picture than viscosity. This view may be also included in lines 325-338.

We agree with this comment and mentioned that on the discussion part.

Line 317: please remove one of the “that”

Done.

Line 330: “and can also present 4-, 5-, and 6-fold coordination⁵⁹⁻⁶⁰.” The authors should refer to the seminal works of Farges et al., for instance: [https://doi.org/10.1016/S0016-7037\(97\)00050-1](https://doi.org/10.1016/S0016-7037(97)00050-1)

Done.

Lines 325-338: the authors discuss the difference in crystal content between the two observed melt phases in terms of viscosity and therefore ion mobility. In an alternative view, they could take into account the different glass forming ability of the two melts, which is a complex property only partially correlating to viscosity (other factors play a role, such as intrinsic crystal nucleation rate). Aluminosilicate melts are known to be better glass formers than Fe- and Ti-rich silicate melts, being therefore more resilient against crystallization at a given cooling rate. Note that Fe and Ti are added to glass-ceramics as seed formers for this reason, so the authors may include some citations from the domain of manmade silicate melts and glasses to support the easier crystal nucleation of the Fe- and Ti-rich melt.

Indeed, systems containing Fe and/or Ti present lower glass forming ability and therefore are more likely to crystallize under cooling. At the end of the section titled 'Why does liquid immiscibility favor crystallization?' it has been added a short discussion on glass forming ability of systems containing either Fe or/and Ti as well as a phrase mentioning that TiO₂ is also used to promote crystallization, when used as seeds in glass ceramic industry.

Lines 339-352: this section results less clear than the two previous ones and should be improved. The authors refer to a lowering of the alpha parameter due to the presence of an interface; however, the source 57 of the manuscript clearly states that the energetic contribution of the interface to nucleation is most likely negligible, so this view should be reported correctly. When describing chemical gradients around the interface, instead, the authors are implicitly going back to the reasons already described in lines 317-324. Note that nanoscale chemical gradients have been shown to facilitate/affect nucleation in a plethora of studies in the materials science community. For some examples see: <https://doi.org/10.1021/cq9009898>, <https://doi.org/10.1063/1.3610557>, <https://doi.org/10.1111/jace.17822> and DOI: 10.5802/crphys.150

Indeed, the paper by Zanotto 2020 (<https://doi.org/10.1016/j.ceramint.2020.06.305>) considers that the contribution of the droplet-liquid interface is irrelevant due to its low interfacial energy. However, we could observe that many crystals were nucleated from the interface between the droplets and the external melt. So here, contrary to what was mentioned in their review article, we claim that in this specific case these liquid-liquid interfaces do play a role in the nucleation process. Since this interfacial energy is a function of the available surface area, it can be argued that in our case, since we have nanodroplets, the surface area is high enough to become relevant to influence crystal nucleation. Besides, we added another reference paper, that contrary to Zanotto (2020), also observed crystals being formed at droplet interfaces (Ohlberg et al. 1960). The chemical gradient close to interfaces would affect also the driving force for nucleation and would be therefore considered to be the same reason as the chemical modifications previously mentioned. However, we chose to keep this part at the interface section because in this particular case, the interface is causing these chemical changes.

Line 365: remove enhancing

Done.

Lines 392-398: Could the authors specify the instrumental setup and measurement routine used to acquire the spectra, in particular with respect to the low-wavenumber region? Are they sure their instrument allows recording of the Boson peak without truncation? What kind of edge filter does the spectrometer mount? Ref. 49 published spectra above 100 cm⁻¹, so I expect that instrument and procedures should have been adapted to facilitate acquisition at low wavenumber.

The Raman method is better explained especially for the low-wavenumber region. The use of the edge filter was indeed necessary to explain the viability of the analysis of the 50 to 100 cm⁻¹ Raman shift (we also removed the spectra analysis from 20 to 50 cm⁻¹ that was theoretically not suitable for analysis).

Line 411: Figure S4 is not listed in the supplementary materials, I suspect it should be S2.

Same as above for the comment about the supplementary material.

Line 432: no Table S5 is available as supplementary material.

Same as above for the comment about the supplementary material.

Figure 2, caption: "Grey areas 1 and 2 correspond to the theoretical occurrence areas of the Boson peak and of the iron-bearing nanolite phases, respectively." Please complement the caption with the citations from which these conclusions are drawn, especially in absence of an analytical extraction of the position of the Boson peak. Iron-bearing phases (nanolite or not) exhibit several Raman bands; only the most intense is located in the grey area 2; it is the signature of these phases that occurs in the spectra, not the phases themselves. Please correct the sentence to take this into account, also considering that spectral contributions in this area may refer to clustering of Fe in the amorphous phase, prior to the formation of crystalline nanolites (see above). Please correct similar expressions used in the supplementary materials.

We agree again with this comment. Corrections have been done accordingly.

Figure 3: "e) Crystal Size Distribution (CSD) performed" should probably be modified as "e) Crystal Size Distribution (CSD) analysis performed"

Done.

Figure 6: I find some features of the sketch misleading, so the authors should consider to modify this figure and/or specify its description. It combines thermodynamics and kinetics and can therefore result confusing. For instance, the final temperature of the three cooling paths should invariably reach the same value at the end (RT); it is the duration of the permanence of the melt in each phase field (and not temperature itself) that determines whether the materials stays homogeneous, unmixes or crystallizes. It is unclear whether the dashed line labelled with "crystallization" corresponds to the thermodynamic onset of a crystallization driving force (liquidus) or to the kinetically controlled first observation of crystals. Why does it decrease towards the composition of melt B?

We agree that this final figure gather a lot of information, combing thermodynamics and kinetics. The goal of this figure was to summarize the involved processes, and remain clear. The dashed line for crystallization represents the kinetically controlled first observation of crystals. We also agree that the ending of each cooling paths should end in the same temperature position. We tried our best to improve the quality of the figure and also specify important things in the caption following your advices, and also following the first reviewer's comment.

Reviewer #3 (Remarks to the Author):

The study by Thivet et al. is a detailed description of nano-scale textures with immiscible melts and micro-crystals in lavas from the 2018-2021 Fani Maoré eruption. Such textures have already been documented in a recent paper by the same authors (Thivet, S., Hess, K.-U., Dingwell, D.B., Berthod, C., Gurioli, L., Di Muro, A., Lacombe, T. and Komorowski, J.-C. (2023) Volatiles of the active Mayotte volcanic chain: STA & EGA-MS analysis of volcanic products. Chemical Geology 618, 121297.) The new aspect of this paper is the proposal that “The occurrence of liquid immiscibility at eruptive conditions must strongly control all physicochemical characteristics of the nanolites as well as residual melt compositions. Such immiscibility likely represents a common yet frequently unobserved feature of such submarine eruptions, with the potential for major impacts on syn-eruptive magma degassing and rheology. Quenching rates are shown to have a strong control on the development of these textures. This was already identified in the previous study of Thivet et al. (2023) in Chemical Geology.

Indeed, the main goal of this work is to describe and discuss the occurrence of metastable liquid immiscibility at eruptive conditions, which is affecting the physicochemical characteristics (both mineralogy and texture) of the associated nanolite crystallization. However, the previous paper published in chemical geology (Thivet et al. 2023, <https://doi.org/10.1016/j.chemgeo.2022.121297>) is not at all about this newly described mechanism, but deal with Simultaneous Thermal Analysis conducted by Evolved Gas Analysis (STA-EGA) and the experimental volatile behaviour of submarine samples of the Mayotte’s volcanic chain (Fani Maoré samples among other ones as well). This previous work was an opportunity to describe the behaviour of such volatile-rich sample using STA-EGA and quantify adsorbed vs. magmatic H₂O in these samples. The nanoscale texture was not studied in this case, but only mentioned as a perspective of work. This is only in this present work that we emphasize that, depending on the quenching rate, different textures are observed, especially at nanoscale. They are described with TEM observations, which was not the case in the previous paper. Also, heat transfer calculations were performed to estimate quenching/cooling rates in function of the lava facies (i.e. lava depth from the margin), which was not the case in the previous paper, which was only considering bulk rock analysis on sample chips. In the present study, we highlight the importance of in-situ analysis (especially TEM) as liquid immiscibility and associated crystallization occurred at nanoscale (although widespread in the inner lava rims, which can potentially have a global impact on the studied system). Also note that thanks to previously performed STA-EGA experiments, we could better emphasize the discussion and conclusion about the volatile behaviour within the present study.

It is not clear to me that the major impacts of immiscibility on syn-eruptive magma degassing and rheology is shown in this study.

We substantially changed and upgraded the discussion and conclusion part in order to integrate a discussion on the impact of such mechanism (immiscibility and associated crystallization) on magma degassing and rheology.

“Also, it is not true that nanoscale description of immiscible have not been documented previously. See for example the following references: Veksler, I.V., Dorfman, A.M., Borisov, A.A., Wirth, R. and Dingwell, D.B. (2007) Liquid immiscibility and the evolution of basaltic magma. Journal of Petrology 48, 2187-2210 or Honour, V.C., Holness, M.B., Charlier, B., Piazzolo, S.C., Namur, O., Prosa, T.J., Martin, I., Helz, R.T., MacLennan, J. and Jean, M.M. (2019) Compositional boundary layers trigger liquid unmixing in a basaltic crystal mush. Nature Communications 10, 4821.”

It is true that liquid immiscibility has been already documented for both experimental and natural samples. In our introduction, we now highlight that nanoscale description of emulsions has been rarely documented for natural volcanic products (we use TEM analysis on different facies of submarine lavas), compared to macro- to micro-scaled natural or experimental emulsions (mainly SEM on experiments or on single facies of naturally cooled magmas). Also, we already cited the aforementioned references when it comes to describes experimental charges or natural micro-scale immiscibility. Again, the main goal of our study is to

characterize and understand this new mechanism for natural volcanic nanolite generation, because of the natural occurrence of metastable nanoscale liquid immiscibility. Considering your comment and also other, we rewrote and reorganize the manuscript, and we think that we now give a better and concise conclusion on this new mechanism.

My feeling is that the authors have tried to oversell their study. The description of the textures is of high-quality and the interpretation of their origin is clear (quenching rate). However the interpretation of their implication on eruptive process, degassing, rheology, fragmentation, explosivity is mainly qualitative and fails at getting beyond current understanding of the immiscibility process and nanolite formation.

We are glad that the description of textures and associated discussion were welcome. We want to specify here that their origin is indeed linked to the quenching/cooling rate, but most importantly to the occurrence or not of liquid immiscibility, which ultimately lead to the type 1 or type 2 crystallization. Thus, we remind here that the main goal of this study is to describe the mechanism of volcanic nanolite generation by the occurrence of metastable liquid immiscibility at eruptive condition, which highly contrasts with the classical mechanism already described in the literature within a homogeneous melt. The rewriting and reorganization of the manuscript better now illustrate and explain this mechanism. Also, and based on the other reviewers' comment, we emphasized the discussion and conclusion part in order to better discuss the potential implications of such mechanism for magma properties (on the one hand in term of degassing and on the other hand in term of viscosity) and *in fine* eruptive dynamics. Obviously, supplementary studies will be needed to answer open questions raised by this study, especially to decipher in which realistic conditions relevant for volcanology this mechanism can occur.

18th Oct 23

Dear Dr Thivet,

Your manuscript titled "Nanoscale liquid immiscibility in the 2018-2021 Fani Maoré lavas: new insights for volcanic nanolite formation" has now been seen by our reviewers, whose comments appear below. In light of their advice we are 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.

Please note that it may still be possible for your paper to be published before the end of 2023, but in order to do this we will need you to address these points as quickly as possible so that we can move forward with your paper.

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Best regards,

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Editorial Board Member
Communications Earth & Environment

Joe Aslin
Senior Editor,
Communications Earth & Environment
<https://www.nature.com/commsenv/>
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REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

The revised version of the paper has been greatly improved, all my questions and concerns were properly addressed and I am fully satisfied with the changes in the text and answers in the rebuttal letter. The text may still need some minor technical editing to weed out typos and improve the style of some sentences. For example, "diffusion has may be observed" (lines 372-373) should be corrected this way or another and the expression "nanolites are more present" (line 387 and elsewhere in the text) looks awkward. Please consider changing to "nanolites are more abundant", or something like that.

Reviewer #2 (Remarks to the Author):

I thank the authors for their thorough consideration of my previous comments and corrections; I appreciated in particular the new version of Fig. 6 and the somewhat more precise discussion of immiscibility vs. crystal nucleation. I believe the manuscript could now be suitable for publication in the Journal, with only minor improvements (see below):

- Line 372: "has may be observed" -> choose one of the two forms
- Line 394: reference 63 does not seem very suitable to support this sentence, given that it analyzes the interplay between glass forming ability and viscosity and does not really examine in detail titanium-containing melts (apart from discussing phase diagrams). Reference to literature from the field of materials science (or fundamental glass science), where the role of titanium and iron as nucleating agents has been clearly described, would be more beneficial for the reader.
- Line 594 (Caption Fig. 2): I still find "the theoretical signature of the Boson peak" a misleading expression. I would prefer something like "the range in which the signature of the Boson peak is typically observed". A similar formulation would be more appropriate also in the supplementary file File S5.

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Author response: We corrected the cited sentence and performed a final check of the whole manuscript. Thanks for your comments and advices.

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Author response: We corrected the cited sentences and performed a final check of the whole manuscript, as well as supplementary material. Reference 63 has also been changed as suggested. It suits better now the main point of the associated statement. Thanks for your comments and advices.