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

14th Mar 23

Dear Dr Schettino,

I hope you are well?

Your manuscript titled "Mantle-to-crust metal transfer by nanomelts" has now been seen by 3 reviewers, and I include their comments at the end of this message. They find your work of interest, but some important points are raised. We are interested in the possibility of publishing your study in *Communications Earth & Environment*, but would like to consider your responses to these concerns and assess a revised manuscript before we make a final decision on publication.

We therefore invite you to revise and resubmit your manuscript, along with a point-by-point response that takes into account the points raised. Please highlight all changes in the manuscript text file. In addition to the reviewers' comments, please consider the following editorial thresholds when preparing your revised manuscript:

- Provide compelling evidence that immiscibility between metal-rich nanomelts and sulfide liquids modulates mantle to crust metal transport, and highlight clearly how this provides an advance in knowledge beyond previously published work.

- Present a logical narrative by reconsidering the structure of the results and discussion sections to more clearly separate description from interpretation.

- Provide sufficient justification for all mineral identifications, including relevant analytical data.

We are committed to providing a fair and constructive peer-review process. Please don't hesitate to contact us if you wish to discuss the revision in more detail. I would like to note that the tone of one of the reviews is bordering on what I would consider unacceptable, despite making relevant points, I apologise for this and if you would like to discuss this further then please do let me know.

Please use the following link to submit your revised manuscript, point-by-point response to the referees' comments (which should be in a separate document to any cover letter) and the completed checklist:

[link redacted]

** This url links to your confidential home page and associated information about manuscripts you may have submitted or be reviewing for us. If you wish to forward this email to co-authors, please delete the link to your homepage first **

We hope to receive your revised paper within six weeks; please let us know if you aren't able to submit it within this time so that we can discuss how best to proceed. If we don't hear from you, and the revision process takes significantly longer, we may close your file. In this event, we will still 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 understand that due to the current global situation, the time required for revision may be longer than usual. We would appreciate it if you could keep us informed about an estimated timescale for resubmission, to facilitate our planning. Of course, if you are unable to estimate, we are happy to accommodate necessary extensions nevertheless.

Please do not hesitate to contact me if you have any questions or would like to discuss these revisions further. We look forward to seeing the revised manuscript and thank you for the opportunity to review your work.

Best regards,

Emma Liu, PhD

Editorial Board Member

Communications Earth & Environment

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Joe Aslin

Senior Editor

Communications Earth & Environment

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and also in our style and formatting guide [Communications Earth & Environment formatting guide](https://www.nature.com/documents/commsj-phys-style-formatting-guide-accept.pdf) .

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REVIEWER COMMENTS:

Reviewer #1 (Remarks to the Author):

Dear Editor

This manuscript is a documentation of galena (PbS) nanoparticles in sulfide droplets hosted in pyroxenes from mantle xenoliths and lamproite dykes from the Neogene Volcanic Province ^[1] of Eastern Betics SE Spain. The authors used textural observations on the nano scale to conclude that the galena nanoparticles were originally incorporated in the sulfide droplets as immiscible Pb-rich nano melt droplets. The authors assume that this is the first ever geologic evidence of the existence of nano melt droplets in the mantle and suggest a new mechanism of metal transfer from the lithosphere to the crust. The claimed novel idea presented by the authors in this manuscript is that metals; like Pb, are transported from the mantle to the crust as nano immiscible melts, not as cations.

The idea that metals are transported from the mantle to the crust as nano particles has been suggested before in many publications (even by the same authors). The authors went in details (nano scale) inside the micron sized sulfide melt droplets to prove that another immiscible melt droplet exist to prove their

idea, although the micron-sized sulfide melt droplet itself is also immiscible in the silicate melt and transfers also metal from lithosphere to crust!! The conclusion about physical rather than chemical transport/behavior of metals has also been suggested before, even by the same authors. Due to these reasons, I recommend “reject” this manuscript; it is not suitable for publication in Communications Earth & Environment.

Below are some detailed comments.

Detailed comments

Lines 23-24, which minerals? you only mentioned galena.

Lines 24-28, why should that change the classical way of metal transport? I am not saying that this theory is wrong, but you do not present a solid evidence for that! you mentioned in lines (17 and 18) that chemical equilibrium partitioning controls metal transport! nothing change then, the sulfide melt is still there (the sulfide droplet) and the silicate melt as well; the new thing is that you only suggest the presence of another metal-rich immiscible melt! If it is really a melt, it will do the same job done by the immiscible sulfide melt!

^{[L}_{SEP]} Lines 63-66, that is not totally correct, for example many studies reported submicron-sized metal-rich sulfide droplets in xenoliths. Jose Maria González-Jiménez et al (2019) (a co-author) described magmatic platinum nanoparticles in metasomatic silicate glasses and sulfides from Patagonian mantle xenoliths. The same authors also reported platinum nanoparticles in mantle peridotite xenoliths (one plagioclase-bearing) hosted in alkaline basalts from Tallante (southeast Spain).

Lines 83-85: how genetically related, a reference is needed here

Lines 100-105, better do not mix results with interpretations. You state in the supplementary that trace element signatures of sulfide-bearing clinopyroxene record silicate metasomatism by Miocene subalkaline subduction-related magmas; could the sulfides be the result of the reaction of the Cpx with the fluids because you also state that the sulfide droplets were trapped during the early stages of magmatic differentiation of the ascending lamproite melt!

Was the “Pb-rich immiscible melt” present in the mantle or introduced to the sulfide droplet during pyroxene metasomatism?

Lines 102-105 You can not attribute the lack of pyrrhotite to the rapid rate of cooling, pyrrhotite does not exsolve, pentlandite is the mineral to exsolve leaving pyrrhotite as a matrix; either the sulfide

droplet was Cu-Ni-rich and S poor, where no pyrrhotite formed or, pyrrhotite is present in a part of the sphere which is not exposed in the polished section.

Lines 111-115: which characteristics? and why should these characteristics suggest the fast uplift and exsolution only of pentlandite and chalcopyrite?

Lines 117-125: you published some of these data before! In your recent studies you (co-authors) described sub-micron noble metal grains inside the sulfide inclusions and in the same metasomatic pyroxenes, I wonder why you did not make the story you are presenting here based on the noble metals, it is more realistic to convince the readers that the PGM (also crystallizes from melts) nucleated before the sulfide droplet formed and were trapped and lifted up to the crust by the alkaline magma

Lines 120-121: why is Pb nanoparticles so significant than Au (and PGM) to suggest that the metals are transported from the mantle to the crust as nano-immiscible melts?

Lines 140-144: what is the significance of galena crystallizing before the solidification of the host sulfide melt? in the literature (including publication by the same authors) there are many cases where crystallization of platinum-group minerals prior to the solidification of the host sulfide have been reported. If galena crystallized before the solidification of the sulfide melt, why insisting that Pb is transported as immiscible nano melt?

Lines 173-199: what is the significance of this section in the story?

Lines 200-205: why not? precious metals could have been dissolved in the sulfide liquid and nucleated before the sulfide liquid solidified! if not dissolved in the sulfide liquid, which mechanism do you suggest to introduce them to the sulfide liquid?

Lines 210-213: not all minerals exsolve as flames from MSS!

Lines 214-217: indeed, the lack of pyrite (commonly associated with galena in nature) in the sulfide droplets and the formation of bornite suggest deficiency in S in the sulfide liquid droplets.

Lines 235-237: this is not an evidence; an immiscible melt droplet can also be formed in the center of a larger melt droplet.

Lines 273-276: what is the difference between the “assumed” Pb-rich melt droplet and the host sulfide droplet? both do the same job, transferring metals from the lithosphere to the crust!

Lines 256-257: you insisted in the text that galena crystallized from immiscible melt droplets, now it is metal clusters!!

Lines 259-261: you can not justify that! if Pb metal clusters are not dissolved originally in the sulfide liquid, why should these metal clusters be collected by sulfide droplets then? take in account that Pb has a high (sulfide melt/silicate melt) partition coefficient .

Lines 261-262: the listed references did not suggest that! both discuss crystalline phases.

Lines 262-263: these references are not relevant; they examine different mixtures doped with different metals.

Reviewer #2 (Remarks to the Author):

Review Report

Comments to Author

This manuscript presents an exciting view of how metallic nanoparticles (NPs) hosted in sulfide mineral inclusions might prove a crucial vector in transporting base metals and metalloids from the mantle to the crust. Given the growing prominence of NPs in economic geology research in recent years, their results provide a novel window into the conditions that can produce these metallic clusters in natural geological environments. While I am not qualified to comment on some of the specific techniques used to analyze the NPs in this study, I have several general comments I would like to offer to the authors that can improve their reader’s understanding of their manuscript. If these changes are made, I believe the paper will be suitable for publication in Communications Earth & Environment.

(1) Line 42 – there is a typo or a grammatical error. I believe the word “yet” should be replaced by the word “and”

(2) In lines 104-105, the authors comment on how quickly the Tallante xenoliths were brought to the surface. Later in the paper, they discuss timescales generally, referencing average magma ascent rate in subduction zones (Turner and Costa 2007). Have the authors performed any chemical measurements on magmatic phases hosting these xenoliths to determine how quickly these xenolith-hosting melts ascended to the surface? I am thinking of something akin to diffusion chronometry. If not, how do the authors know these lavas were brought quickly to the surface? It would be useful for the authors to spend some time discussing these timescales in more detail. A related question that relates to this ascent rate issue is whether we would expect lavas in other convergent margins - perhaps those that lack the structural complexity of the Betics - to be able to achieve similar ascent rates and thus preserve cpx-hosted NPs? With this question I am imagining convergent margins that lack the kind of STEP faults that access the SCLM in the same way the unique tectonics of Iberia allow magmas to access the SCLM.

(3) Equation 1 on Line 189 has a slightly different form to the version of the Stokes equation used in more recent sulfide-silicate melt settling papers like Roberston et al. 2015, and Yao and Mungall 2022. Specifically, these other authors use the Hadamard-Rybcznski solution to the Stokes equations, which has a slightly different form compared to the version used here. Speaking as someone who does not regularly perform fluid dynamics calculations, can the authors justify why they use this particular form of the equation, compared to the form used by Robertson et al. and Yao & Mungall?

(4) The authors description of the phase immiscibility processes leading to the segregation of Pb-rich NPs in Tallande and Fortuna NPs needs to be better linked to their diagram (Figure 5). Specifically, I ask the authors better annotate and link the red & blue stars in the Figure with the processes they describe in the main text. As it stands it is hard to understand. Furthermore, a shortened version of their description of events from lines 225 through 256 needs to be provide din the caption for Figure 5, along with additional annotations that note which events (blue vs. red star, yellow vs. orange vs. blue fields) occur first. At the moment, it is hard to visualize the processes they describe from lines 225 onwards.

(5) The authors comment on line 256 raises an important point of discussion. This argument assumes the mass fraction of metals like Pb carried by NPs is large enough to make a difference in the overall budget of Pb transported my magmas from the mantle to the crust. Can the authors perform a simple mass balance trying to account for the chemistry & mass of the sulfide hosts of these NPs, compared the chemistry & mass of the NPs, and try to work out a back-of-the-envelope budget for how much potential metallic flux these NPs could deliver in this region?

(6) The conclusion of this article leaves me wanting more. How significantly would this understanding, as described on line 267-270 change our models of ore development in convergent margins? Will the NPs be able to pass along their metals to hydrothermal fluids at similar P/T/X within similar time frames compared to their corresponding host sulfides, or will there be a significant difference in how metals are cycled from metallic NPs to hydrothermal fluids comapred to sulfides? More importantly, is there some “missing reservoir” of metals that has been identified in the literature that is not presently accounted for by equilibrium sulfide stability and sulfide/silicate melt partitioning models of ore development? If current sulfide-dominated models do a good job explaing the abundance of metals we see in the crust, it doesn't seem to me these NPs are an economically crucial component of ore-forming systems (thoguh they are of course mineralogically fascinating). In order to make the importance of their work clearer, I

ask the authors to more specifically address what knowledge gap their understanding of metallic NPs fills.

If these corrections are addressed this paper should be suitable for publication.

Papers I referenced in this report:

Robertson, Jesse C., Stephen J. Barnes, and Margaux Le Vaillant. "Dynamics of magmatic sulphide droplets during transport in silicate melts and implications for magmatic sulphide ore formation." *Journal of Petrology* 56.12 (2015): 2445-2472.

Yao, Zhuosen, and James E. Mungall. "Transport and deposition of immiscible sulfide liquid during lateral magma flow." *Earth-Science Reviews* 227 (2022): 103964.

Signed:

Nicholas D. Barber, PhD

Reviewer #3 (Remarks to the Author):

The study presents an interesting new model for the transport of metals in the crust based on petrographic observation of galena nano-inclusions in sulfide droplets preserved in magmatic rocks. The textural relationship between the mineral phases appear to suggest that a Pb(-Cu)-rich nanomelts was present as an immiscible phase in the sulfide droplets challenging the established model of metal transport in silicate magmas.

The model proposed by this study is interesting, novel and well aligned with recent discoveries and evolving understanding of metal transport within the crust. The methodology is adequate using state-of-the-art instruments and the samples selected for addressing the problem are very relevant.

The context of the study is very well presented in the introduction and show the importance of the study.

The results section however, is very difficult to read and confusing. It is poorly structured and contains more interpretation of the results than results description. I suggest restructuring this section by describing in greater details and more systematically the data.

The nanoinclusions observed in sulfide droplets in both localities studied are referred to in the text as “galena nanoinclusions” or “Pb-rich nanoparticles” or “Pb-Cu-rich nanoparticles” or as “nanosized Pb-Cu-S domain” or “Cu-bearing galena nanoinclusion”. This is confusing. I think the authors should choose one name and use it consistently throughout the manuscript. I am actually still unsure if all these names are referring to the same phase.

It is rather unclear in the text (and only explained at the end of the discussion) of why the above-mentioned nanoparticles are all interpreted as being galena. It appears to be based on selected area electron diffraction (SAED) patterns only. However, the EDS elemental maps presented in Figs 2 and 3 clearly show the unequivocal presence of Cu in these nanoparticles. This is an important observation that is not mentioned in the manuscript until the end of the discussion. Without knowing the relative proportion of Pb and Cu in the phase, SAED patterns alone is not sufficient to identify the phase as galena. Would it be possible to extract quantitative or semi-quantitative measurement of this phase from the EDS data collected? The software used to process EDS images is not mentioned in the method sections, could it be used to estimate the relative proportion of Pb and Cu? But regardless, the fact that Cu is present in the nanoinclusions is important and should be mentioned in the Results section when describing the phase. Moreover, it should be discussed why the mineral is named galena when its composition does not correspond to galena.

Overall, the lack of details and the poor presentation of the data detracts from the importance of the observations made in the study.

Minor comments:

L96 – 98: belongs to introduction or discussion

L102 – 105: an interpretation on a mineral texture (or lack of) is presented but the texture itself is not described. Idem in l140, 164, 167

L111-115: this is an interpretation of the results that belong in the discussion. Same in l140-144, l151-155, l163-170

L122-125: this belongs to the methods section.

L192-194: this interpretation is unclear

L 206-208: please rework the sentence. It is unclear

L218: a new name is introduced "Cu-bearing galena nanoinclusion" and this is confusing. Are all the nanoparticles interpreted as being of the same composition? This is never clearly explained in the manuscript and all the different names makes it very confusing.

L266-269: interesting but bold statement that should take into consideration how such particles may be stabilised at high pressure in hydrothermal solutions.

Supplementary material: extra TEM and EDS images of presumably the same samples are presented but without any explanation. Please carefully describe where the foils are coming from and what do they represent. Some foils point towards nanoparticles which are not visible on the images presented.

Reviewer #1 (Remarks to the Author):

Dear Editor

This manuscript is a documentation of galena (PbS) nanoparticles in sulfide droplets hosted in pyroxenes from mantle xenoliths and lamproite dykes from the Neogene Volcanic Province of Eastern Betics SE Spain. The authors used textural observations on the nano scale to conclude that the galena nanoparticles were originally incorporated in the sulfide droplets as immiscible Pb-rich nano melt droplets. The authors assume that this is the first ever geologic evidence of the existence of nano melt droplets in the mantle and suggest a new mechanism of metal transfer from the lithosphere to the crust. The claimed novel idea presented by the authors in this manuscript is that metals; like Pb, are transported from the mantle to the crust as nano immiscible melts, not as cations.

The idea that metals are transported from the mantle to the crust as nano particles has been suggested before in many publications (even by the same authors). The authors went in details (nano scale) inside the micron sized sulfide melt droplets to prove that another immiscible melt droplet exist to prove their idea, although the micron-sized sulfide melt droplet itself is also immiscible in the silicate melt and transfers also metal from lithosphere to crust!! The conclusion about physical rather than chemical transport/behavior of metals has also been suggested before, even by the same authors. Due to these reasons, I recommend reject this manuscript; it is not suitable for publication in Communications Earth & Environment.

Below are some detailed comments.

We acknowledge the reviewer's comments, which provided us with the opportunity to better clarify the originality and relevance of the outcomes of this work. So far, the existence of immiscible metal-rich nanomelts in magmas, even at concentrations below their solubility limit, had been only experimentally documented but never observed in natural settings (Helmy et al., 2013; Anenburg and Mavrogenes, 2020). Despite this experimentally supported concept had been borrowed by González-Jiménez et al. (2020) to address specific mineralogic observations, no study so far had clearly demonstrated the existence of immiscible metal-rich nanomelts in natural magmas through an integrated mineral-chemical and crystallographic approach as presented here. In addition, this work provides direct evidence that metal-rich nanomelts may not only exist, but also persist as immiscible droplets in magmas across their lithospheric-scale journey, from the source region in the mantle to the volcanic outputs at surface. To the extent of our knowledge, this is the first-ever suggestion that metal-rich

nanomelts may persist in magmas ascending throughout the whole lithospheric column, with the additional result that we document this transport process in an ore-productive sector of continental lithosphere. We thank the reviewer for raising this concern, and we hope to have successfully outlined the importance of the new outcomes in the revised version of the manuscript.

Detailed comments

Lines 23-24, which minerals? you only mentioned galena.

Sentence reworded according to the reviewer's suggestion (lines 24-25 in the revised version of the manuscript).

Lines 24-28, why should that change the classical way of metal transport? I am not saying that this theory is wrong, but you do not present a solid evidence for that! you mentioned in lines (17 and 18) that chemical equilibrium partitioning controls metal transport! nothing change then, the sulfide melt is still there (the sulfide droplet) and the silicate melt as well; the new thing is that you only suggest the presence of another metal-rich immiscible melt! If it is really a melt, it will do the same job done by the immiscible sulfide melt!

The occurrence of metal-rich nanomelts, immiscible in both sulfide liquids and silicate magmas, dramatically changes the way metals may be transported and concentrated during magmatic processes. In fact, chemical constraints imposed by equilibrium partitioning coefficients and relative volumetric ratios of sulfide and silicate magmas (R-factor) would not impact the magma budget of metallic elements if these reside in metal-rich nanomelts immiscible and mechanically trapped in both silicate magmas and sulfide liquids.

Lines 63-66, that is not totally correct, for example many studies reported submicron-sized metal-rich sulfide droplets in xenoliths. Jose Maria González-Jiménez et al (2019) (a co-author) described magmatic platinum nanoparticles in metasomatic silicate glasses and sulfides from Patagonian mantle xenoliths. The same authors also reported platinum nanoparticles in mantle peridotite xenoliths (one plagioclase-bearing) hosted in alkaline basalts from Tallante (southeast Spain).

All the works mentioned by the reviewer do report the presence of metal-rich nanoparticles in mantle peridotites and associated magmatic rocks. However, none of these studies showd that metal-particles crystallized from a precursor metal-rich nanomelt that was already

immiscible in the sulfide liquid and the silicate magma. For instance, the crystallization of Pt(-As)-rich alloys, dispersed within the glass matrix or in sulfide droplets in the interstitial silicate glass of Patagonian xenoliths (González-Jiménez et al., 2019), was ascribed to lowering oxygen fugacities in the host magma in response to chromite/ilmenite crystallization (Finnigan et al., 2008; Anenburg and Mavrogenes, 2016). A similar interpretation was adopted for explaining the occurrence of Pt-rich and Au-rich nanoparticles hosted in sulfide droplets within metasomatic pyroxenes in the Tallante mantle xenoliths (Schettino et al., 2022), as well as of Os-Ir and Pt-Fe nanoinclusions in Cr-spinel phenocrysts from arc lavas (Kamenetsky et al., 2015; Zelenski et al., 2017; Kamenetsky and Zelenski, 2020). All these studies interpret metal-rich nanoparticles as primary liquidus phases, which crystallized from the silicate magmas as reducing conditions (e.g., during chromite crystallization) promote the saturation in alloys and/or PGM. In contrast, in this study we explore the possibility that many of these metal-rich crystals could be preceded by nanomelts, or non-crystalline precursors, that were already immiscible in the silicate magmas even at concentrations that are lower to their solubility limit. Furthermore, these latter observations provide the first-ever confirmation in nature of experimental results of Helmy et al. (2013) and Anenburg and Mavrogenes (2020). This hypothesis was only evoked by González-Jiménez et al. (2020) but has never been demonstrated in natural systems so far.

Lines 83-85: how genetically related, a reference is needed here

Reference added according to the reviewer's suggestion (line 87 in the revised version of the manuscript).

Lines 100-105, better do not mix results with interpretations. You state in the supplementary that trace element signatures of sulfide-bearing clinopyroxene record silicate metasomatism by Miocene subalkaline subduction-related magmas; could the sulfides be the result of the reaction of the Cpx with the fluids because you also state that the sulfide droplets were trapped during the early stages of magmatic differentiation of the ascending lamproite melt! Was the "Pb-rich immiscible melt" present in the mantle or introduced to the sulfide droplet during pyroxene metasomatism?

The close association of Pb-rich nanomelt with pyroxene-hosted sulfide droplets suggests it was introduced in the mantle during the percolation of Miocene subalkaline magmas that led to pyroxene and sulfide crystallization, as already demonstrated by Schettino et al. (2022). These subalkaline magmas are not associated with the differentiation of lamproite melts,

which were in turn produced during a subsequent stage of partial melting of the subduction-metasomatized SCLM (e.g. Duggen et al., 2005).

Lines 102-105 You can not attribute the lack of pyrrhotite to the rapid rate of cooling, pyrrhotite does not exsolve, pentlandite is the mineral to exsolve leaving pyrrhotite as a matrix; either the sulfide droplet was Cu-Ni-rich and S poor, where no pyrrhotite form or, pyrrhotite is present in a part of the sphere which is not exposed in the polished section.

Sentence removed from the revised version of the manuscript.

Lines 111-115: which characteristics? and why should these characteristics suggest the fast uplift and exsolution only of pentlandite and chalcopyrite?

Sentence removed from the revised version of the manuscript.

Lines 117-125: you published some of these data before! In your recent studies you (co-authors) described sub micron noble metal grains inside the sulfide inclusions and in the same metasomatic pyroxenes, I wonder why you did not make the story you are presenting here based on the noble metals, it is more realistic to convince the readers that the PGM (also crystallizes from melts) nucleated before the sulfide droplet form and were trapped and lifted up to the crust by the alkaline magma.

Gold grains have been already described at both Tallante and Fortuna localities (Toscani et al., 1999; Schettino et al., 2022). Previous studies provided the conceptual framework that was necessary for nanoscale investigation performed in this work. However, former studies did not provide any mineralogical approach to prove that gold precipitated from a precursor immiscible nanomelt, which is the main innovative aspect of this work.

Lines 120-121: why is Pb nanoparticles so significant than Au (and PGM) to suggest that the metals are transported from the mantle to the crust as nano immiscible melts?

There is no particular preference for one element instead of another. Both Pb and Au are metallic elements relevant for ore genesis in the studied metallogenic province and for tracking mantle processes worldwide. The first-ever description of magmatic galena crystallizing in subduction-related melts and their source mantle rocks itself deserves a

detailed argumentation, which may provide relevant insights into the processes controlling the mobility and concentration of metals from the source to the deposition place.

Lines 140-144: what is the significance of galena crystallizing before the solidification of the host sulfide melt? in the literature (including publication by the same authors) there are many cases where crystallization of platinum-group minerals prior to the solidification of the host sulfide have been reported. If galena crystallized before the solidification of the sulfide melt, why insisting that Pb is transported as immiscible nano melt?

The main significance of galena crystallizing before the solidification of the host sulfide melt relies on the fact that, according to solubility criteria, galena should be fully dissolved in the sulfide melt. Experimental studies reported that ternary sulfide liquid at $T > 716$ °C may dissolve up to 60 wt.% Pb, 70 wt.% PbS (Brett & Kullerud, 1967). The average bulk compositions of Tallante sulfide droplets (Pb ranging between 1.58-280 ppm, data included in the Supplementary material) indicate that galena crystallization occurred even at Pb concentrations that were orders of magnitude below those necessary to saturate the sulfide liquid with galena (line 283-288 in the revised version of the manuscript). Moreover, the existence of a precursor immiscible nanomelt is supported by the presence of galena+digenite envelope, as argued in the discussion section.

Lines 173-199: what is the significance of this section in the story?

This section provides the basic constraints to argue for the transport process hypothesized in this work, as it illustrates that the galena-bearing sulfide droplets may have been indeed transported in the lamproite magmas ascending through the continental lithosphere. Without this assumption, the metal transport mechanism proposed here would have been unsupported by the empirical observations.

Lines 200-205: why not? precious metals could have been dissolved in the sulfide liquid and nucleated before the sulfide liquid solidify! if not dissolved in the sulfide liquid, which mechanism you suggest to introduce them to the sulfide liquid?

Throughout the discussion section, we provided arguments for supporting the hypothesis that the sulfide liquid may have collected metals by mechanical processes in the form of immiscible

nanomelts, rather than by conventional dissolution in sulfide liquid by chemical equilibrium partitioning (lines 245-277).

Lines 210-213: not all minerals exsolve as flames from MSS!

Modified according to the reviewer's suggestion.

Lines 214-217: indeed, the lack of pyrite (common associate with galena in nature) in the sulfide droplets and the formation of bornite suggest deficiency in S in the sulfide liquid droplets.

Sentence reworded and clarified (line 298-302 in the revised version of the manuscript).

Lines 235-237: this is not an evidence; an immiscible melt droplet can also be formed in the center of a larger melt droplet.

Sentence removed according to the reviewer's suggestion.

Lines 243-246: what is the difference between the assumed Pb-rich melt droplet and the host sulfide droplet? both do the same job, transferring metals from the lithosphere to the crust!

We believe that the physical collection of metals in the form of nanomelts immiscible in the sulfide liquid twists the budget of metallic elements that can be transported according solely to chemical partitioning and melt mass ratios. This issue has been extensively argued in the discussion section of the revised version of the manuscript (lines 278-293).

Lines 256-257: you insisted in the text that galena crystallized from immiscible melt droplets, now it is metal clusters!!

Sentence reworded according to the reviewer's suggestion.

Lines 259-261: you can not justify that! if Pb metal clusters are not dissolved originally in the sulfide liquid, why should these metal clusters be collected by sulfide droplets then? take in account that Pb has a high (sulfide melt/silicate melt) partition coefficient.

We favor the hypothesis that immiscible nanomelts and sulfide liquid may preferentially agglomerate and coalesce in a silicate magma by surface energy-driven mechanisms (lines 365-372).

Lines 261-262: the listed references did not suggest that! both discuss crystalline phases.

Sentence reworded according to the reviewer's suggestion.

Lines 262-263: these references are not relevant; they examine different mixtures doped with different metals.

The cited references (Helmy et al., 2013; Anenburg and Mavrogenes, 2020) are very relevant as they provide the experimental background for interpreting the nano-inclusions documented in this work.

Reviewer #2 (Remarks to the Author):

This manuscript presents an exciting view of how metallic nanoparticles (NPs) hosted in sulfide mineral inclusions might prove a crucial vector in transporting base metals and metalloids from the mantle to the crust. Given the growing prominence of NPs in economic geology research in recent years, their results provide a novel window into the conditions that can produce these metallic

clusters in natural geological environments. While I am not qualified to comment on some of the specific techniques used to analyze the NPs in this study, I have several general comments I would like to offer to the authors that can improve their readers understanding of their manuscript. If these changes are made, I believe the paper will be suitable for publication in Communications Earth & Environment.

We are grateful for the insightful comments of the reviewer and we hope to have fully addressed all the points that have been raised.

(1) Line 42; there is a typo or a grammatical error. I believe the word “yet” should be replaced by the word “and”.

Modified according to the reviewer’s suggestion.

(2) In lines 104-105, the authors comment on how quickly the Tallante xenoliths were brought to the surface. Later in the paper, they discuss timescales generally, referencing average magma ascent rate in subduction zones (Turner and Costa 2007). Have the authors performed any chemical measurements on magmatic phases hosting these xenoliths to determine how quickly these xenolith-hosting melts ascended to the surface? I am thinking of something akin to diffusion chronometry. If not, how do the authors know these lavas were brought quickly to the surface?

Accurate estimates of ascent rates of the alkaline basalts discussed here would require modelling complex hydrogen diffusion profiles in nominally anhydrous minerals determined by in situ nanoSIMS analysis or FTIR spectroscopy, which is far beyond the scope of our research. However, there is a large amount of studies in the literature reporting average ascent rates of alkaline basalts that could be properly adopted for our case study. In general, xenolith-bearing magmas must ascend very rapidly through the lithosphere to be able to carry dense fragments of exotic mantle peridotites (O’Reilly and Griffin, 2010 for a review). Estimates based on mantle xenolith settling velocities and fluid dynamics calculations have provided minimum ascent velocities ranging between 0.1-5 m/s for alkaline basalts to 10-30 m/s for kimberlites (Spera, 1980; 1984). Similar results have been obtained by element diffusion profiles in xenolith minerals, which yielded ascent rates ranging between 0.2-6 m/s for xenolith-bearing alkaline basalts (Demouchy et al., 2006; Peslier and Luhr, 2006) and 5-37 m/s for kimberlite magmas (Kelley and Wartho, 2000; Peslier et al., 2008). All these estimates may be reasonably applied to illustrate the ascent rates of the eruption of the xenolith-bearing alkaline basalts from the Tallante volcanic field. However, this eruptive event does not deal

with the transport process of metals that has been proposed in this work. We envisage that metals were transported from the mantle source (sampled by Tallante peridotite xenolith) within ascending Fortuna lamproites. This metal transport has nothing to do with the entrainment and ascent of Tallante peridotite xenolith, which occurred in a subsequent stage of magmatism (Pliocene). In the model that we propose the Tallante peridotite xenoliths are assumed to be representative of the mantle source region of the magma route. On the other hand, the ascent rate of the lamproite magmas is relevant for this study (see below), as they represent the transport media carrying sulfide droplets and metal-rich nanomelts. Therefore, we would prefer to avoid any reference to ascent rates of xenolith-bearing alkaline basalts, which could make the reader misunderstand or misinterpret the transport process that has been discussed in this study.

It would be useful for the authors to spend some time discussing these timescales in more detail. A related question that relates to this ascent rate issue is whether we would expect lavas in other convergent margins - perhaps those that lack the structural complexity of the Betics - to be able to achieve similar ascent rates and thus preserve cpx-hosted NPs? With this question I am imagining convergent margins that lack the kind of STEP faults that access the SCLM in the same way the unique tectonics of Iberia allow magmas to access the SCLM.

The ascent rates of the lamproite magmas are relevant for the purposes of the process documented in this work. Therefore, we agree with the reviewer's suggestion on better discussing these time scales. Average ascent rates have been estimated by previous work for magmas compositionally and physically akin to the lamproite magmas of SE Spain, and in geotectonic settings similar to that of the western Mediterranean in the Neogene (Turner et al., 2001; Sparks et al., 2006; Wilson and Head, 2007; Turner and Costa, 2007; Ruprecht & Plank, 2013). We believe that all this bibliographic background provides the constraints for describing the ascent of the Fortuna lamproites. Additional paragraphs and related bibliographical references discussing timescales of this magma ascent have been added in the text (lines 172-174) and extensively argued in the Supplementary material.

(3) Equation 1 on Line 189 has a slightly different form to the version of the Stokes equation used in more recent sulfide-silicate melt settling papers like Roberston et al. 2015, and Yao and Mungall 2022. Specifically, these other authors use the Hadamard-Rybcznski solution to the stokes equations, which has a slightly different form compared to the version used here. Speaking as

someone who does not regularly perform fluid dynamics calculations, can the authors justify why they use this particular form of the equation, compared to the form used by Robertson et al. and Yao & Mungall?

The Stokes law formulation employed in this work refers to the Stokes solution for steady creeping flow past a rigid sphere (Clift, 1978). The Hadamard-Rybczynski solution employed by Robertson et al. (2015) and Yao and Mungall (2022) defines the terminal velocity for a fluid sphere, which is expected to be up to 50% higher than that of a rigid sphere of the same size and density. However, it appears that small-sized bubbles and droplets, such as those described in this work, generally tend to obey Stokes law for solid sphere rather than the corresponding Hadamard-Rybczynski solution for a fluid sphere (Clift, 1978). An additional paragraph discussing in detail the formulation of the settling velocity of sulfide melt has been added in the Supplementary material.

(4) The authors description of the phase immiscibility processes leading to the segregation of Pb-rich NPs in Tallande and Fortuna NPs needs to be better linked to their diagram (Figure 5). Specifically, I ask the authors better annotate and link the red & blue stars in the Figure with the processes they describe in the main text. As it stands it is hard to understand. Furthermore, a shortened version of their description of events from lines 225 through 256 needs to be provided in the caption for Figure 5, along with additional annotations that note which events (blue vs. red star, yellow vs. orange vs. blue fields) occur first. At the moment, it is hard to visualize the processes they describe from lines 225 onwards.

Modified according to the reviewer's suggestion.

(5) The authors comment on line 256 raises an important point of discussion. This argument assumes the mass fraction of metals like Pb carried by NPs is large enough to make a difference in the overall budget of Pb transported by magmas from the mantle to the crust. Can the authors perform a simple mass balance trying to account for the chemistry & mass of the sulfide hosts of these NPs, compared the chemistry & mass of the NPs, and try to work out a back-of-the-envelope budget for how much potential metallic flux these NPs could deliver in this region?

In order to determine the potential Pb flux transported by nanoparticles into the sulfide droplets, we have conducted a careful inspection of the time-resolved spectra of laser ablation analysis of sulfide droplets in the Tallante mantle xenoliths. We found out that 43 out of 66 time-resolved spectra show sharp spikes in the Pb signals, which reflect the occurrence of discrete,

Pb-rich nano-to-micrometer-sized inclusions of galena. It is relevant to note that sulfide droplets lacking Pb-rich inclusions display a very narrow range of Pb concentrations varying between 14.4-48.7 ppm (Supplementary table). On the other hand, the presence of galena-bearing sulfide droplets with a much wider scattering in Pb concentrations, spanning from 1.58 to 280 ppm, supports the hypothesis that the mechanical incorporation of Pb-rich nanomelts may significantly upgrade the Pb abundances in the sulfide melts. These observations are consistent with hypothetical mass balance calculations, showing that sulfide droplets of ~ 20 µm diameter incorporating one galena nanoparticle of 100 nm and 1 µm in diameter may concentrate up to 2.16 and 216 ppm of Pb, respectively (Supplementary material). All these considerations have been integrated in the discussion section of the revised version of the manuscript (lines 258-277), as well as in separate tables and figures in the Supplementary material.

(6) The conclusion of this article leaves me wanting more. How significantly would this understanding, as described on line 267-270 change our models of ore development in convergent margins? Will the NPs be able to pass along their metals to hydrothermal fluids at similar P/T/X within similar time frames compared to their corresponding host sulfides, or will there be a significant difference in how metals are cycled from metallic NPs to hydrothermal fluids compared to sulfides? More importantly, is there some missing reservoir of metals that has been identified in the literature that is not presently accounted for by equilibrium sulfide stability and sulfide/silicate melt partitioning models of ore development? If current sulfide-dominated models do a good job explaining the abundance of metals we see in the crust, it doesn't seem to me these NPs are an economically crucial component of ore-forming systems (though they are of course mineralogically fascinating). In order to make the importance of their work clearer, I ask the authors to more specifically address what knowledge gap their understanding of metallic NPs fills.

The physical incorporation of metal-rich nanomelts within sulfide liquids deeply changes our perspective into how ore deposits may form, in continental arc settings and elsewhere. In fact, this transport process provides an additional pathway for upgrading the metallic budget of sulfide melts, beyond values expected through equilibrium chemical partitioning and mass ratios to the host silicate magmas (R-factor). Moreover, ever-growing evidence of metal-rich nanoparticles accumulating in ore-forming hydrothermal fluids pointed out that mechanical transport of metal-rich nanoparticles is closely linked to the ore mineralization process (Petrella et al., 2020, 2022; Hastie et al., 2021; McLeish et al., 2021). These discoveries witness

that the magmatic-hydrothermal transit of nanoparticles may act as a feasible and extremely efficient process for finally concentrating and focusing metals to the site of ore deposition (González-Jiménez et al., 2021; Petrella et al., 2022). An extensive argumentation of the relevance of immiscible nanomelts on controlling the genesis of magmatic and hydrothermal ores has been added in the revised version of the manuscript (lines 278-293).

If these corrections are addressed this paper should be suitable for publication.

Papers I referenced in this report:

Robertson, Jesse C., Stephen J. Barnes, and Margaux Le Vaillant. "Dynamics of magmatic sulphide droplets during transport in silicate melts and implications for magmatic sulphide ore formation." *Journal of Petrology* 56.12 (2015): 2445-2472.

Yao, Zhuosen, and James E. Mungall. "Transport and deposition of immiscible sulfide liquid during lateral magma flow." *Earth-Science Reviews* 227 (2022): 103964.

Signed:

Nicholas D. Barber, PhD

Reviewer #3 (Remarks to the Author):

The study presents an interesting new model for the transport of metals in the crust based on petrographic observation of galena nanoinclusions in sulfide droplets preserved in magmatic rocks. The textural relationship between the mineral phases appear to suggest that a Pb(-Cu)-rich nanomelts was present as an immiscible phase in the sulfide droplets challenging the established model of metal transport in silicate magmas. The model proposed by this study is interesting, novel

and well aligned with recent discoveries and evolving understanding of metal transport within the crust. The methodology is adequate using state-of-the-art instruments and the samples selected for addressing the problem are very relevant. The context of the study is very well presented in the introduction and show the importance of the study. The results section however, is very difficult to read and confusing. It is poorly structured and contains more interpretation of the results than results description. I suggest restructuring this section by describing in greater details and more systematically the data.

We thank the reviewer for the insightful comments and we hope that the revised version of the manuscript accounts satisfactorily for their concerns. In particular, the result section has been re-structured according to a more logical narrative and integrated with a more detailed description of the data (lines 174-240 of the revised version of the manuscript). Most interpretations were moved to the discussion section.

1) The nanoinclusions observed in sulfide droplets in both localities studied are referred to in the text as galena nanoinclusions or Pb-rich nanoparticles or Pb-Cu-rich nanoparticles or as nanosized Pb-Cu-S domain or Cu-bearing galena nanoinclusion. This is confusing. I think the authors should choose one name and use it consistently throughout the manuscript. I am actually still unsure if all these names are referring to the same phase.

We agree with the referee's concern on limiting the range of terminologies to be adopted, and we have changed the text accordingly. Anyway, we would like to maintain the distinction between Pb-rich nanoinclusion (which is a purely descriptive term) and galena nanoinclusion (which is an interpretative term based on crystallographic data).

2) It is rather unclear in the text (and only explained at the end of the discussion) of why the above-mentioned nanoparticles are all interpreted as being galena. It appears to be based on selected area electron diffraction (SAED) patterns only. However, the EDS elemental maps presented in Figs 2 and 3 clearly show the unequivocal presence of Cu in these nanoparticles. This is an important observation that is not mentioned in the manuscript until the end of the discussion. Without knowing the relative proportion of Pb and Cu in the phase, SAED patterns alone is not sufficient to identify the phase as galena. Would it be possible to extract quantitative or semi-quantitative measurement of this phase from the EDS data collected? The software used to process EDS images is not mentioned in the method sections, could it be used to estimate the relative proportion of Pb and Cu? But regardless, the fact that Cu is present in the nanoinclusions is important and should be

mentioned in the Results section when describing the phase. Moreover, it should be discussed why the mineral is named galena when its composition does not correspond to galena.

The TEM-EDS elemental mapping cannot be employed to extrapolate quantitative analysis of the studied minerals. In the Supplementary material of the revised version of the manuscript we provide additional EDS spectra obtained by SEM analysis, which yield qualitative estimates over the relative proportion of Pb and Cu in these minerals. The great difference between Pb and Cu peaks in the EDS spectra highlights the fact that Cu occurs as a minor component in these mineral phases. Anyway, we should remark that galena may accommodate significant amounts of Cu into its crystal lattice (up to ~797 ppm, George et al., 2015), thus behaving as an efficient mineralogical sink for other metalloids through the coupled substitution $(Ag,Cu,Tl)^{++}(Bi,Sb)_3^+ \leftrightarrow 2Pb^{2+}$ (Chutas et al., 2008; Milot et al., 2020). Furthermore, experimental studies demonstrated that galena may dissolve up to 1 wt.% Cu in solid solution (Johyo & Taskien, 2013; Shishin et al., 2020). Therefore, we believe that indexing of crystal lattice parameters by checking data from the American Mineralogist Crystal Structure Database (<http://rruff.geo.arizona.edu/AMS/amcsd.php>), coupled with qualitative compositional estimates by EDS analysis, provided the most reliable method for interpreting all these Pb(-Cu) mineral inclusions as galena crystals. Additional paragraphs discussing the composition of galena have been added in the text in order to clarify this interpretation (lines 108-110, 148-149, 213-215).

Overall, the lack of details and the poor presentation of the data detracts from the importance of the observations made in the study.

Minor comments:

L96-98: belongs to introduction or discussion.

Statement removed according to the reviewer's suggestion.

L102-105: an interpretation on a mineral texture (or lack of) is presented but the texture itself is not described. Idem in 1140, 164, 167.

These interpretations of mineral textures have been removed from the results section, according to the reviewer's suggestion

L111-115: this is an interpretation of the results that belong in the discussion. Same in 1140-144, 1151-155, 1163-170.

The statement in L111-115 of the unrevised version of the manuscript refers to an interpretation already provided by previous work, which is useful to establish a logical narrative for contextualizing the description of the results of this study. The other interpretations mentioned by the reviewer have been removed from the result section according to the reviewer's suggestion.

L122-125: this belongs to the methods section.

Statement removed according to the reviewer's suggestion.

L192-194: this interpretation is unclear.

This sentence has been re-worded (lines 2067-268 in the revised version of the manuscript).

L 206-208: please rework the sentence. It is unclear.

This sentence has been re-worded (lines 286-291 in the revised version of the manuscript).

L218: a new name is introduced Cu-bearing galena nanoinclusion and this is confusing. Are all the nanoparticles interpreted as being of the same composition? This is never clearly explained in the manuscript and all the different names makes it very confusing.

All the nanoparticles described in the study have been interpreted based on crystal-lattice parameters and qualitative chemical compositions as galena crystals, regardless of whether they contain minor amounts of Cu or not. We hope to have clarified this issue in the revised version of the manuscript (lines 108-110, 148-149, 213-215).

L266-269: interesting but bold statement that should take into consideration how such particles may be stabilised at high pressure in hydrothermal solutions.

The statement has been reworded (lines 400-407 in the revised version of the manuscript). By the way, the presence of nanoparticles in hydrothermal solutions has been already

documented by cited works (Petrella et al., 2020, 2022; Hastie et al., 2021; McLeish et al., 2021), and their behavior in such fluids are beyond the scope of this work.

Supplementary material: extra TEM and EDS images of presumably the same samples are presented but without any explanation. Please carefully describe where the foils are coming from and what do they represent. Some foils point towards nanoparticles which are not visible on the images presented.

Additional figures have been added in the Supplementary material, outlining the exact location and orientation of the FIB sections described in this study.

7th Jun 23

Dear Dr Schettino,

Your manuscript titled "Mantle-to-crust metal transfer by nanomelts" has now been seen by our 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 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

Senior Editor,

Communications Earth & Environment

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REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

Dear AE

The authors have made significant changes to the manuscript, they explained all my questions and made all changes I and the other reviewers suggested. In its new version, the manuscript is acceptable for publication in Communications Earth & Environment. No further revisions are needed.

Reviewer #2 (Remarks to the Author):

Following on from my original comments on this manuscript, I am satisfied the authors have addressed my concerns and I am happy to see this article published promptly.

The readability of this manuscript is substantially improved. Both the results and discussion sections are much clearer. More importantly, the authors have made a much more compelling case for the physical viability of nano-melts as a mechanism of metal "upgrading" in sulfide-bearing magmas. Given the growing recognition of PbS nanoparticles occurrence in sulfide systems, this work should prompt exciting future research into the presence and quantity of nano-inclusions in similar magmatic systems.

I am grateful for the opportunity to review this manuscript, and I thank the authors for their thorough response to the reviewer's comments.

-Nicholas D. Barber, PhD

Reviewer #3 (Remarks to the Author):

Dear Authors,

Thank you for replying to and addressing my comments.

I am satisfied with the reply and the modifications made to the manuscript.

I commend the authors on a very interesting study.

I just wanted to add a quick note on the last comment I made in my revision to which you replied: "The statement has been reworded (lines 400-407 in the revised version of the manuscript). By the way, the presence of nanoparticles in hydrothermal solutions has been already documented by cited works (Petrella et al., 2020, 2022; Hastie et al., 2021; McLeish et al., 2021), and their behavior in such fluids are beyond the scope of this work."

I am happy with your reply I just wanted to emphasize that these studies demonstrated the presence of metal NP in hydrothermal fluids but not their transport. NP may have nucleated from the fluid and being deposited directly.

(Also the line numbering indicated is wrong)

Reviewer #1 (Remarks to the Author):

Dear Editor

This manuscript is a documentation of galena (PbS) nanoparticles in sulfide droplets hosted in pyroxenes from mantle xenoliths and lamproite dykes from the Neogene Volcanic Province of Eastern Betics SE Spain. The authors used textural observations on the nano scale to conclude that the galena nanoparticles were originally incorporated in the sulfide droplets as immiscible Pb-rich nano melt droplets. The authors assume that this is the first ever geologic evidence of the existence of nano melt droplets in the mantle and suggest a new mechanism of metal transfer from the lithosphere to the crust. The claimed novel idea presented by the authors in this manuscript is that metals; like Pb, are transported from the mantle to the crust as nano immiscible melts, not as cations.

The idea that metals are transported from the mantle to the crust as nano particles has been suggested before in many publications (even by the same authors). The authors went in details (nano scale) inside the micron sized sulfide melt droplets to prove that another immiscible melt droplet exist to prove their idea, although the micron-sized sulfide melt droplet itself is also immiscible in the silicate melt and transfers also metal from lithosphere to crust!! The conclusion about physical rather than chemical transport/behavior of metals has also been suggested before, even by the same authors. Due to these reasons, I recommend reject this manuscript; it is not suitable for publication in Communications Earth & Environment.

Below are some detailed comments.

We acknowledge the reviewer's comments, which provided us with the opportunity to better clarify the originality and relevance of the outcomes of this work. So far, the existence of immiscible metal-rich nanomelts in magmas, even at concentrations below their solubility limit, had been only experimentally documented but never observed in natural settings (Helmy et al., 2013; Anenburg and Mavrogenes, 2020). Despite this experimentally supported concept had been borrowed by González-Jiménez et al. (2020) to address specific mineralogic observations, no study so far had clearly demonstrated the existence of immiscible metal-rich nanomelts in natural magmas through an integrated mineral-chemical and crystallographic approach as presented here. In addition, this work provides direct evidence that metal-rich nanomelts may not only exist, but also persist as immiscible droplets in magmas across their lithospheric-scale journey, from the source region in the mantle to the volcanic outputs at surface. To the extent of our knowledge, this is the first-ever suggestion that metal-rich

nanomelts may persist in magmas ascending throughout the whole lithospheric column, with the additional result that we document this transport process in an ore-productive sector of continental lithosphere. We thank the reviewer for raising this concern, and we hope to have successfully outlined the importance of the new outcomes in the revised version of the manuscript.

Detailed comments

Lines 23-24, which minerals? you only mentioned galena.

Sentence reworded according to the reviewer's suggestion (lines 24-25 in the revised version of the manuscript).

Lines 24-28, why should that change the classical way of metal transport? I am not saying that this theory is wrong, but you do not present a solid evidence for that! you mentioned in lines (17 and 18) that chemical equilibrium partitioning controls metal transport! nothing change then, the sulfide melt is still there (the sulfide droplet) and the silicate melt as well; the new thing is that you only suggest the presence of another metal-rich immiscible melt! If it is really a melt, it will do the same job done by the immiscible sulfide melt!

The occurrence of metal-rich nanomelts, immiscible in both sulfide liquids and silicate magmas, dramatically changes the way metals may be transported and concentrated during magmatic processes. In fact, chemical constraints imposed by equilibrium partitioning coefficients and relative volumetric ratios of sulfide and silicate magmas (R-factor) would not impact the magma budget of metallic elements if these reside in metal-rich nanomelts immiscible and mechanically trapped in both silicate magmas and sulfide liquids.

Lines 63-66, that is not totally correct, for example many studies reported submicron-sized metal-rich sulfide droplets in xenoliths. Jose Maria González-Jiménez et al (2019) (a co-author) described magmatic platinum nanoparticles in metasomatic silicate glasses and sulfides from Patagonian mantle xenoliths. The same authors also reported platinum nanoparticles in mantle peridotite xenoliths (one plagioclase-bearing) hosted in alkaline basalts from Tallante (southeast Spain).

All the works mentioned by the reviewer do report the presence of metal-rich nanoparticles in mantle peridotites and associated magmatic rocks. However, none of these studies showd that metal-particles crystallized from a precursor metal-rich nanomelt that was already

immiscible in the sulfide liquid and the silicate magma. For instance, the crystallization of Pt(-As)-rich alloys, dispersed within the glass matrix or in sulfide droplets in the interstitial silicate glass of Patagonian xenoliths (González-Jiménez et al., 2019), was ascribed to lowering oxygen fugacities in the host magma in response to chromite/ilmenite crystallization (Finnigan et al., 2008; Anenburg and Mavrogenes, 2016). A similar interpretation was adopted for explaining the occurrence of Pt-rich and Au-rich nanoparticles hosted in sulfide droplets within metasomatic pyroxenes in the Tallante mantle xenoliths (Schettino et al., 2022), as well as of Os-Ir and Pt-Fe nanoinclusions in Cr-spinel phenocrysts from arc lavas (Kamenetsky et al., 2015; Zelenski et al., 2017; Kamenetsky and Zelenski, 2020). All these studies interpret metal-rich nanoparticles as primary liquidus phases, which crystallized from the silicate magmas as reducing conditions (e.g., during chromite crystallization) promote the saturation in alloys and/or PGM. In contrast, in this study we explore the possibility that many of these metal-rich crystals could be preceded by nanomelts, or non-crystalline precursors, that were already immiscible in the silicate magmas even at concentrations that are lower to their solubility limit. Furthermore, these latter observations provide the first-ever confirmation in nature of experimental results of Helmy et al. (2013) and Anenburg and Mavrogenes (2020). This hypothesis was only evoked by González-Jiménez et al. (2020) but has never been demonstrated in natural systems so far.

Lines 83-85: how genetically related, a reference is needed here

Reference added according to the reviewer's suggestion (line 87 in the revised version of the manuscript).

Lines 100-105, better do not mix results with interpretations. You state in the supplementary that trace element signatures of sulfide-bearing clinopyroxene record silicate metasomatism by Miocene subalkaline subduction-related magmas; could the sulfides be the result of the reaction of the Cpx with the fluids because you also state that the sulfide droplets were trapped during the early stages of magmatic differentiation of the ascending lamproite melt! Was the "Pb-rich immiscible melt" present in the mantle or introduced to the sulfide droplet during pyroxene metasomatism?

The close association of Pb-rich nanomelt with pyroxene-hosted sulfide droplets suggests it was introduced in the mantle during the percolation of Miocene subalkaline magmas that led to pyroxene and sulfide crystallization, as already demonstrated by Schettino et al. (2022). These subalkaline magmas are not associated with the differentiation of lamproite melts,

which were in turn produced during a subsequent stage of partial melting of the subduction-metasomatized SCLM (e.g. Duggen et al., 2005).

Lines 102-105 You can not attribute the lack of pyrrhotite to the rapid rate of cooling, pyrrhotite does not exsolve, pentlandite is the mineral to exsolve leaving pyrrhotite as a matrix; either the sulfide droplet was Cu-Ni-rich and S poor, where no pyrrhotite form or, pyrrhotite is present in a part of the sphere which is not exposed in the polished section.

Sentence removed from the revised version of the manuscript.

Lines 111-115: which characteristics? and why should these characteristics suggest the fast uplift and exsolution only of pentlandite and chalcopyrite?

Sentence removed from the revised version of the manuscript.

Lines 117-125: you published some of these data before! In your recent studies you (co-authors) described sub micron noble metal grains inside the sulfide inclusions and in the same metasomatic pyroxenes, I wonder why you did not make the story you are presenting here based on the noble metals, it is more realistic to convince the readers that the PGM (also crystallizes from melts) nucleated before the sulfide droplet form and were trapped and lifted up to the crust by the alkaline magma.

Gold grains have been already described at both Tallante and Fortuna localities (Toscani et al., 1999; Schettino et al., 2022). Previous studies provided the conceptual framework that was necessary for nanoscale investigation performed in this work. However, former studies did not provide any mineralogical approach to prove that gold precipitated from a precursor immiscible nanomelt, which is the main innovative aspect of this work.

Lines 120-121: why is Pb nanoparticles so significant than Au (and PGM) to suggest that the metals are transported from the mantle to the crust as nano immiscible melts?

There is no particular preference for one element instead of another. Both Pb and Au are metallic elements relevant for ore genesis in the studied metallogenic province and for tracking mantle processes worldwide. The first-ever description of magmatic galena crystallizing in subduction-related melts and their source mantle rocks itself deserves a

detailed argumentation, which may provide relevant insights into the processes controlling the mobility and concentration of metals from the source to the deposition place.

Lines 140-144: what is the significance of galena crystallizing before the solidification of the host sulfide melt? in the literature (including publication by the same authors) there are many cases where crystallization of platinum-group minerals prior to the solidification of the host sulfide have been reported. If galena crystallized before the solidification of the sulfide melt, why insisting that Pb is transported as immiscible nano melt?

The main significance of galena crystallizing before the solidification of the host sulfide melt relies on the fact that, according to solubility criteria, galena should be fully dissolved in the sulfide melt. Experimental studies reported that ternary sulfide liquid at $T > 716$ °C may dissolve up to 60 wt.% Pb, 70 wt.% PbS (Brett & Kullerud, 1967). The average bulk compositions of Tallante sulfide droplets (Pb ranging between 1.58-280 ppm, data included in the Supplementary material) indicate that galena crystallization occurred even at Pb concentrations that were orders of magnitude below those necessary to saturate the sulfide liquid with galena (line 283-288 in the revised version of the manuscript). Moreover, the existence of a precursor immiscible nanomelt is supported by the presence of galena+digenite envelope, as argued in the discussion section.

Lines 173-199: what is the significance of this section in the story?

This section provides the basic constraints to argue for the transport process hypothesized in this work, as it illustrates that the galena-bearing sulfide droplets may have been indeed transported in the lamproite magmas ascending through the continental lithosphere. Without this assumption, the metal transport mechanism proposed here would have been unsupported by the empirical observations.

Lines 200-205: why not? precious metals could have been dissolved in the sulfide liquid and nucleated before the sulfide liquid solidify! if not dissolved in the sulfide liquid, which mechanism you suggest to introduce them to the sulfide liquid?

Throughout the discussion section, we provided arguments for supporting the hypothesis that the sulfide liquid may have collected metals by mechanical processes in the form of immiscible

nanomelts, rather than by conventional dissolution in sulfide liquid by chemical equilibrium partitioning (lines 245-277).

Lines 210-213: not all minerals exsolve as flames from MSS!

Modified according to the reviewer's suggestion.

Lines 214-217: indeed, the lack of pyrite (common associate with galena in nature) in the sulfide droplets and the formation of bornite suggest deficiency in S in the sulfide liquid droplets.

Sentence reworded and clarified (line 298-302 in the revised version of the manuscript).

Lines 235-237: this is not an evidence; an immiscible melt droplet can also be formed in the center of a larger melt droplet.

Sentence removed according to the reviewer's suggestion.

Lines 243-246: what is the difference between the assumed Pb-rich melt droplet and the host sulfide droplet? both do the same job, transferring metals from the lithosphere to the crust!

We believe that the physical collection of metals in the form of nanomelts immiscible in the sulfide liquid twists the budget of metallic elements that can be transported according solely to chemical partitioning and melt mass ratios. This issue has been extensively argued in the discussion section of the revised version of the manuscript (lines 278-293).

Lines 256-257: you insisted in the text that galena crystallized from immiscible melt droplets, now it is metal clusters!!

Sentence reworded according to the reviewer's suggestion.

Lines 259-261: you can not justify that! if Pb metal clusters are not dissolved originally in the sulfide liquid, why should these metal clusters be collected by sulfide droplets then? take in account that Pb has a high (sulfide melt/silicate melt) partition coefficient.

We favor the hypothesis that immiscible nanomelts and sulfide liquid may preferentially agglomerate and coalesce in a silicate magma by surface energy-driven mechanisms (lines 365-372).

Lines 261-262: the listed references did not suggest that! both discuss crystalline phases.

Sentence reworded according to the reviewer's suggestion.

Lines 262-263: these references are not relevant; they examine different mixtures doped with different metals.

The cited references (Helmy et al., 2013; Anenburg and Mavrogenes, 2020) are very relevant as they provide the experimental background for interpreting the nano-inclusions documented in this work.

Reviewer #2 (Remarks to the Author):

This manuscript presents an exciting view of how metallic nanoparticles (NPs) hosted in sulfide mineral inclusions might prove a crucial vector in transporting base metals and metalloids from the mantle to the crust. Given the growing prominence of NPs in economic geology research in recent years, their results provide a novel window into the conditions that can produce these metallic

clusters in natural geological environments. While I am not qualified to comment on some of the specific techniques used to analyze the NPs in this study, I have several general comments I would like to offer to the authors that can improve their readers understanding of their manuscript. If these changes are made, I believe the paper will be suitable for publication in Communications Earth & Environment.

We are grateful for the insightful comments of the reviewer and we hope to have fully addressed all the points that have been raised.

(1) Line 42; there is a typo or a grammatical error. I believe the word “yet” should be replaced by the word “and”.

Modified according to the reviewer’s suggestion.

(2) In lines 104-105, the authors comment on how quickly the Tallante xenoliths were brought to the surface. Later in the paper, they discuss timescales generally, referencing average magma ascent rate in subduction zones (Turner and Costa 2007). Have the authors performed any chemical measurements on magmatic phases hosting these xenoliths to determine how quickly these xenolith-hosting melts ascended to the surface? I am thinking of something akin to diffusion chronometry. If not, how do the authors know these lavas were brought quickly to the surface?

Accurate estimates of ascent rates of the alkaline basalts discussed here would require modelling complex hydrogen diffusion profiles in nominally anhydrous minerals determined by in situ nanoSIMS analysis or FTIR spectroscopy, which is far beyond the scope of our research. However, there is a large amount of studies in the literature reporting average ascent rates of alkaline basalts that could be properly adopted for our case study. In general, xenolith-bearing magmas must ascend very rapidly through the lithosphere to be able to carry dense fragments of exotic mantle peridotites (O’Reilly and Griffin, 2010 for a review). Estimates based on mantle xenolith settling velocities and fluid dynamics calculations have provided minimum ascent velocities ranging between 0.1-5 m/s for alkaline basalts to 10-30 m/s for kimberlites (Spera, 1980; 1984). Similar results have been obtained by element diffusion profiles in xenolith minerals, which yielded ascent rates ranging between 0.2-6 m/s for xenolith-bearing alkaline basalts (Demouchy et al., 2006; Peslier and Luhr, 2006) and 5-37 m/s for kimberlite magmas (Kelley and Wartho, 2000; Peslier et al., 2008). All these estimates may be reasonably applied to illustrate the ascent rates of the eruption of the xenolith-bearing alkaline basalts from the Tallante volcanic field. However, this eruptive event does not deal

with the transport process of metals that has been proposed in this work. We envisage that metals were transported from the mantle source (sampled by Tallante peridotite xenolith) within ascending Fortuna lamproites. This metal transport has nothing to do with the entrainment and ascent of Tallante peridotite xenolith, which occurred in a subsequent stage of magmatism (Pliocene). In the model that we propose the Tallante peridotite xenoliths are assumed to be representative of the mantle source region of the magma route. On the other hand, the ascent rate of the lamproite magmas is relevant for this study (see below), as they represent the transport media carrying sulfide droplets and metal-rich nanomelts. Therefore, we would prefer to avoid any reference to ascent rates of xenolith-bearing alkaline basalts, which could make the reader misunderstand or misinterpret the transport process that has been discussed in this study.

It would be useful for the authors to spend some time discussing these timescales in more detail. A related question that relates to this ascent rate issue is whether we would expect lavas in other convergent margins - perhaps those that lack the structural complexity of the Betics - to be able to achieve similar ascent rates and thus preserve cpx-hosted NPs? With this question I am imagining convergent margins that lack the kind of STEP faults that access the SCLM in the same way the unique tectonics of Iberia allow magmas to access the SCLM.

The ascent rates of the lamproite magmas are relevant for the purposes of the process documented in this work. Therefore, we agree with the reviewer's suggestion on better discussing these time scales. Average ascent rates have been estimated by previous work for magmas compositionally and physically akin to the lamproite magmas of SE Spain, and in geotectonic settings similar to that of the western Mediterranean in the Neogene (Turner et al., 2001; Sparks et al., 2006; Wilson and Head, 2007; Turner and Costa, 2007; Ruprecht & Plank, 2013). We believe that all this bibliographic background provides the constraints for describing the ascent of the Fortuna lamproites. Additional paragraphs and related bibliographical references discussing timescales of this magma ascent have been added in the text (lines 172-174) and extensively argued in the Supplementary material.

(3) Equation 1 on Line 189 has a slightly different form to the version of the Stokes equation used in more recent sulfide-silicate melt settling papers like Roberston et al. 2015, and Yao and Mungall 2022. Specifically, these other authors use the Hadamard-Rybcznski solution to the stokes equations, which has a slightly different form compared to the version used here. Speaking as

someone who does not regularly perform fluid dynamics calculations, can the authors justify why they use this particular form of the equation, compared to the form used by Robertson et al. and Yao & Mungall?

The Stokes law formulation employed in this work refers to the Stokes solution for steady creeping flow past a rigid sphere (Clift, 1978). The Hadamard-Rybczynski solution employed by Robertson et al. (2015) and Yao and Mungall (2022) defines the terminal velocity for a fluid sphere, which is expected to be up to 50% higher than that of a rigid sphere of the same size and density. However, it appears that small-sized bubbles and droplets, such as those described in this work, generally tend to obey Stokes law for solid sphere rather than the corresponding Hadamard-Rybczynski solution for a fluid sphere (Clift, 1978). An additional paragraph discussing in detail the formulation of the settling velocity of sulfide melt has been added in the Supplementary material.

(4) The authors description of the phase immiscibility processes leading to the segregation of Pb-rich NPs in Tallande and Fortuna NPs needs to be better linked to their diagram (Figure 5). Specifically, I ask the authors better annotate and link the red & blue stars in the Figure with the processes they describe in the main text. As it stands it is hard to understand. Furthermore, a shortened version of their description of events from lines 225 through 256 needs to be provided in the caption for Figure 5, along with additional annotations that note which events (blue vs. red star, yellow vs. orange vs. blue fields) occur first. At the moment, it is hard to visualize the processes they describe from lines 225 onwards.

Modified according to the reviewer's suggestion.

(5) The authors comment on line 256 raises an important point of discussion. This argument assumes the mass fraction of metals like Pb carried by NPs is large enough to make a difference in the overall budget of Pb transported by magmas from the mantle to the crust. Can the authors perform a simple mass balance trying to account for the chemistry & mass of the sulfide hosts of these NPs, compared the chemistry & mass of the NPs, and try to work out a back-of-the-envelope budget for how much potential metallic flux these NPs could deliver in this region?

In order to determine the potential Pb flux transported by nanoparticles into the sulfide droplets, we have conducted a careful inspection of the time-resolved spectra of laser ablation analysis of sulfide droplets in the Tallante mantle xenoliths. We found out that 43 out of 66 time-resolved spectra show sharp spikes in the Pb signals, which reflect the occurrence of discrete,

Pb-rich nano-to-micrometer-sized inclusions of galena. It is relevant to note that sulfide droplets lacking Pb-rich inclusions display a very narrow range of Pb concentrations varying between 14.4-48.7 ppm (Supplementary table). On the other hand, the presence of galena-bearing sulfide droplets with a much wider scattering in Pb concentrations, spanning from 1.58 to 280 ppm, supports the hypothesis that the mechanical incorporation of Pb-rich nanomelts may significantly upgrade the Pb abundances in the sulfide melts. These observations are consistent with hypothetical mass balance calculations, showing that sulfide droplets of ~ 20 µm diameter incorporating one galena nanoparticle of 100 nm and 1 µm in diameter may concentrate up to 2.16 and 216 ppm of Pb, respectively (Supplementary material). All these considerations have been integrated in the discussion section of the revised version of the manuscript (lines 258-277), as well as in separate tables and figures in the Supplementary material.

(6) The conclusion of this article leaves me wanting more. How significantly would this understanding, as described on line 267-270 change our models of ore development in convergent margins? Will the NPs be able to pass along their metals to hydrothermal fluids at similar P/T/X within similar time frames compared to their corresponding host sulfides, or will there be a significant difference in how metals are cycled from metallic NPs to hydrothermal fluids compared to sulfides? More importantly, is there some missing reservoir of metals that has been identified in the literature that is not presently accounted for by equilibrium sulfide stability and sulfide/silicate melt partitioning models of ore development? If current sulfide-dominated models do a good job explaining the abundance of metals we see in the crust, it doesn't seem to me these NPs are an economically crucial component of ore-forming systems (though they are of course mineralogically fascinating). In order to make the importance of their work clearer, I ask the authors to more specifically address what knowledge gap their understanding of metallic NPs fills.

The physical incorporation of metal-rich nanomelts within sulfide liquids deeply changes our perspective into how ore deposits may form, in continental arc settings and elsewhere. In fact, this transport process provides an additional pathway for upgrading the metallic budget of sulfide melts, beyond values expected through equilibrium chemical partitioning and mass ratios to the host silicate magmas (R-factor). Moreover, ever-growing evidence of metal-rich nanoparticles accumulating in ore-forming hydrothermal fluids pointed out that mechanical transport of metal-rich nanoparticles is closely linked to the ore mineralization process (Petrella et al., 2020, 2022; Hastie et al., 2021; McLeish et al., 2021). These discoveries witness

that the magmatic-hydrothermal transit of nanoparticles may act as a feasible and extremely efficient process for finally concentrating and focusing metals to the site of ore deposition (González-Jiménez et al., 2021; Petrella et al., 2022). An extensive argumentation of the relevance of immiscible nanomelts on controlling the genesis of magmatic and hydrothermal ores has been added in the revised version of the manuscript (lines 278-293).

If these corrections are addressed this paper should be suitable for publication.

Papers I referenced in this report:

Robertson, Jesse C., Stephen J. Barnes, and Margaux Le Vaillant. "Dynamics of magmatic sulphide droplets during transport in silicate melts and implications for magmatic sulphide ore formation." *Journal of Petrology* 56.12 (2015): 2445-2472.

Yao, Zhuosen, and James E. Mungall. "Transport and deposition of immiscible sulfide liquid during lateral magma flow." *Earth-Science Reviews* 227 (2022): 103964.

Signed:

Nicholas D. Barber, PhD

Reviewer #3 (Remarks to the Author):

The study presents an interesting new model for the transport of metals in the crust based on petrographic observation of galena nanoinclusions in sulfide droplets preserved in magmatic rocks. The textural relationship between the mineral phases appear to suggest that a Pb(-Cu)-rich nanomelts was present as an immiscible phase in the sulfide droplets challenging the established model of metal transport in silicate magmas. The model proposed by this study is interesting, novel

and well aligned with recent discoveries and evolving understanding of metal transport within the crust. The methodology is adequate using state-of-the-art instruments and the samples selected for addressing the problem are very relevant. The context of the study is very well presented in the introduction and show the importance of the study. The results section however, is very difficult to read and confusing. It is poorly structured and contains more interpretation of the results than results description. I suggest restructuring this section by describing in greater details and more systematically the data.

We thank the reviewer for the insightful comments and we hope that the revised version of the manuscript accounts satisfactorily for their concerns. In particular, the result section has been re-structured according to a more logical narrative and integrated with a more detailed description of the data (lines 174-240 of the revised version of the manuscript). Most interpretations were moved to the discussion section.

1) The nanoinclusions observed in sulfide droplets in both localities studied are referred to in the text as galena nanoinclusions or Pb-rich nanoparticles or Pb-Cu-rich nanoparticles or as nanosized Pb-Cu-S domain or Cu-bearing galena nanoinclusion. This is confusing. I think the authors should choose one name and use it consistently throughout the manuscript. I am actually still unsure if all these names are referring to the same phase.

We agree with the referee's concern on limiting the range of terminologies to be adopted, and we have changed the text accordingly. Anyway, we would like to maintain the distinction between Pb-rich nanoinclusion (which is a purely descriptive term) and galena nanoinclusion (which is an interpretative term based on crystallographic data).

2) It is rather unclear in the text (and only explained at the end of the discussion) of why the above-mentioned nanoparticles are all interpreted as being galena. It appears to be based on selected area electron diffraction (SAED) patterns only. However, the EDS elemental maps presented in Figs 2 and 3 clearly show the unequivocal presence of Cu in these nanoparticles. This is an important observation that is not mentioned in the manuscript until the end of the discussion. Without knowing the relative proportion of Pb and Cu in the phase, SAED patterns alone is not sufficient to identify the phase as galena. Would it be possible to extract quantitative or semi-quantitative measurement of this phase from the EDS data collected? The software used to process EDS images is not mentioned in the method sections, could it be used to estimate the relative proportion of Pb and Cu? But regardless, the fact that Cu is present in the nanoinclusions is important and should be

mentioned in the Results section when describing the phase. Moreover, it should be discussed why the mineral is named galena when its composition does not correspond to galena.

The TEM-EDS elemental mapping cannot be employed to extrapolate quantitative analysis of the studied minerals. In the Supplementary material of the revised version of the manuscript we provide additional EDS spectra obtained by SEM analysis, which yield qualitative estimates over the relative proportion of Pb and Cu in these minerals. The great difference between Pb and Cu peaks in the EDS spectra highlights the fact that Cu occurs as a minor component in these mineral phases. Anyway, we should remark that galena may accommodate significant amounts of Cu into its crystal lattice (up to ~797 ppm, George et al., 2015), thus behaving as an efficient mineralogical sink for other metalloids through the coupled substitution $(Ag,Cu,Tl)^{++}(Bi,Sb)_3^+ \leftrightarrow 2Pb^{2+}$ (Chutas et al., 2008; Milot et al., 2020). Furthermore, experimental studies demonstrated that galena may dissolve up to 1 wt.% Cu in solid solution (Johyo & Taskien, 2013; Shishin et al., 2020). Therefore, we believe that indexing of crystal lattice parameters by checking data from the American Mineralogist Crystal Structure Database (<http://rruff.geo.arizona.edu/AMS/amcsd.php>), coupled with qualitative compositional estimates by EDS analysis, provided the most reliable method for interpreting all these Pb(-Cu) mineral inclusions as galena crystals. Additional paragraphs discussing the composition of galena have been added in the text in order to clarify this interpretation (lines 108-110, 148-149, 213-215).

Overall, the lack of details and the poor presentation of the data detracts from the importance of the observations made in the study.

Minor comments:

L96-98: belongs to introduction or discussion.

Statement removed according to the reviewer's suggestion.

L102-105: an interpretation on a mineral texture (or lack of) is presented but the texture itself is not described. Idem in 1140, 164, 167.

These interpretations of mineral textures have been removed from the results section, according to the reviewer's suggestion

L111-115: this is an interpretation of the results that belong in the discussion. Same in 1140-144, 1151-155, 1163-170.

The statement in L111-115 of the unrevised version of the manuscript refers to an interpretation already provided by previous work, which is useful to establish a logical narrative for contextualizing the description of the results of this study. The other interpretations mentioned by the reviewer have been removed from the result section according to the reviewer's suggestion.

L122-125: this belongs to the methods section.

Statement removed according to the reviewer's suggestion.

L192-194: this interpretation is unclear.

This sentence has been re-worded (lines 2067-268 in the revised version of the manuscript).

L 206-208: please rework the sentence. It is unclear.

This sentence has been re-worded (lines 286-291 in the revised version of the manuscript).

L218: a new name is introduced Cu-bearing galena nanoinclusion and this is confusing. Are all the nanoparticles interpreted as being of the same composition? This is never clearly explained in the manuscript and all the different names makes it very confusing.

All the nanoparticles described in the study have been interpreted based on crystal-lattice parameters and qualitative chemical compositions as galena crystals, regardless of whether they contain minor amounts of Cu or not. We hope to have clarified this issue in the revised version of the manuscript (lines 108-110, 148-149, 213-215).

L266-269: interesting but bold statement that should take into consideration how such particles may be stabilised at high pressure in hydrothermal solutions.

The statement has been reworded (lines 400-407 in the revised version of the manuscript). By the way, the presence of nanoparticles in hydrothermal solutions has been already

documented by cited works (Petrella et al., 2020, 2022; Hastie et al., 2021; McLeish et al., 2021), and their behavior in such fluids are beyond the scope of this work.

Supplementary material: extra TEM and EDS images of presumably the same samples are presented but without any explanation. Please carefully describe where the foils are coming from and what do they represent. Some foils point towards nanoparticles which are not visible on the images presented.

Additional figures have been added in the Supplementary material, outlining the exact location and orientation of the FIB sections described in this study.