

## The flotation of magmatic sulfides transfers Cu-Au from magmas to seafloor massive sulfide deposits

Corresponding Author: Dr Aurélien Jeanvoine

Figures originally included in the author's rebuttal have been redacted from this file.

Version 0:

Decision Letter:

\*\* Please ensure you delete the link to your author home page in this e-mail if you wish to forward it to your coauthors \*\*

Dear Dr Jeanvoine,

Your manuscript titled "The Flotation of Magmatic Sulfides: A Source of Cu-Au for Seafloor Massive Sulfide Deposits?" has now been seen by 2 reviewers, whose comments are appended below. You will see that they find your work of some potential interest. However, they have raised quite substantial concerns that must be addressed. In light of these comments, we cannot accept the manuscript for publication, but would be interested in considering a revised version that fully addresses these serious concerns.

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

\*\*\*\*\*

In particular, please ensure that the revised manuscript meets the following editorial thresholds:

\*\*\*\* Provide firm and sufficient evidence for demonstrating that the bubble flotation of droplets process is necessary for explaining your observations.

\*\*\*\* Discuss in detail all physical and chemical principles involved in the process of bubble transportation, including a Stokes-Law analysis for your droplet size and composition.

\*\*\*\* Compellingly justify your claims of novelty in your observations of droplet-bubble pairs, given previous observations as listed by Reviewer #1, or caveat and tone down your claims.

\*\*\*\*\*

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

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

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

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

version of the manuscript (as a PDF file) and any completed checklist:

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

Best regards,

Carolina Ortiz Guerrero  
Associate Editor  
Communications Earth & Environment

## EDITORIAL POLICIES AND FORMAT

If you decide to resubmit your paper, please ensure that your manuscript complies with our editorial policies and complete and upload the checklist below as a Related Manuscript file type with the revised article:

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## REVIEWER COMMENTS:

Reviewer #1 (Remarks to the Author):

There is some good data in this paper, which is well written and illustrated and has a lot to commend it. However, like many dominantly geochemical papers, it has a significant flaw in that it doesn't pay enough attention to the basic physics. The key question is whether bubble flotation of droplets is actually necessary to explain the observations, and whether it's physically plausible. Heinrich and Connolly argue that no such mechanism is necessary because small sulfide droplets will be entrained in most magmas anyway. If it can't be shown that bubble flotation is required, then there still an interesting paper to be published, but the main thrust of the argument would need to change, and there is nothing really novel to be said.

For this reason I can't see how it meets the criteria for publication in a Nature-family journal.

The main issue is to do with viscosity and settling/floating rates. You are claiming that sulfides are effectively transported to the surface by rafting on bubbles, but the droplets you are looking at are tiny, only a few tens of microns. You need to do a Stokes Law calculation using estimated viscosities for your lavas to see what the likely droplet settling rates would be. You'll be alarmed at how small they are – for a typical wet dacite, viscosity of  $10^8$  Pas (well on the low side) a 100 micron sulfide droplet settles at about  $10^{-12}$  m/s. That's order of 1 mm per hundred years. For a ten micron droplet it's 100 times less. Similar numbers apply to upward flotation of bubbles. For an andesite with viscosity 10000 Pas, you're up into the 10s of m per year range for a 100 micron droplet, so it's significant. So for your model to make sense, the process needs to be happening very early in the differentiation process when your magmas are still no more evolved than andesite. The efficiency of the process drops really fast as the temperatures drop and the magmas get stickier. For dacites, I don't think it works, unless they are very wet and/or strongly superheated to bring the viscosities down. I suggest that you work out your likely liquid compositions, use your assumed water contents, and calculate viscosities using the Giordano et al calculator at <https://www.eoas.ubc.ca/~krussell/VISCOSITY/grdViscosity.html> then do the Stokes Law calculation (strictly you should use the Hadamard–Rybczynski version of the Stokes equation for droplets, but it only make about a factor of 2 difference and we're talking multiple orders of magnitude).

Detailed points

Line 47 "sulfide-bubble compound drops observed in natural settings are either preserved in inclusions ... or significantly altered within silicate liquids or xenoliths" – that may be true in felsic-intermediate settings but there are numerous examples in mafic and komatiitic settings – see (Barnes et al., 2019), particularly section "Other examples of segregation vesicles in cumulates". The claim that this is the first observation of droplet-bubble pairs in nature is wrong.

Line 59 it would be helpful to give more info on the petrology of the samples that were actually studied, and also their silica contents. We've only got MgO and trace elements to look at. Viscosity is an important variable here so we need a better idea of what these magmas actually were and whether they represent liquids or liquid-crystal mixtures – that's important because most andesites are porphyritic. A plot of SiO<sub>2</sub> vs MgO and a table of short rock descriptions (subdivided into group 1A and 1B) are both needed.

Line 77 – not immediately clear - so you're saying you didn't analyse Au, and you're extrapolating between Cu and Pd when discussing its distribution?

88 – "nucleate over each other" – this phrase doesn't really make sense. It's not really clear from experimental or natural

observations what nucleates on what. It may be that the bubbles nucleate first, then the droplets heterogeneously nucleate on them, or vice versa, or they both nucleate independently then stick together when they collide. Better to be non-specific and just say that they are known to have a strong surface affinity that makes them stick together.

119 – after MSS crystallisation from the sulfide liquid. Your terminology gets a bit confusing, partly due to the way you use the term “exsolution”. Exsolution means formation of a new phase in the solid state from the breakdown of a solid solution. The sequence of events in magmatic sulfide droplets is that 1) they form from the magma by the process of liquation (like crystallisation, but applying to an immiscible liquid). The sulfide liquid then (2) crystallises to form the solid phase, MSS, with a residual Cu-rich liquid that goes on to form ISS then (usually) chalcopyrite. The MSS then (3) inverts to pyrrhotite at low temperature, exsolving pentlandite along the way. In volcanic rocks, the cooling rate is too high for (3) to happen, so the sulfides typically quench in the high-T MSS. Where it might start getting complicated here is that where you are dealing with dacites and temperatures below 1000C, depending on the Cu content you might be below the solidus of the sulfide, so you might be crystallising MSS directly from the silicate melt without forming a sulfide liquid.

There's a very important but overlooked paper by Ripley (Ripley et al., 2002) that showed that if a magma hits sulfide saturation late when its Cu content is high it saturates not in FeS but in CuS, so you get a very Cu-rich liquid with very low Fe. (This may be the origin of the strange Cu-Pd ores in the Skaergaard intrusion). I don't think you're seeing this but it's something to look for.

So, the point of this is that you need to be aware of these complexities, and make sure you are clear in your use of terminology. The bubble-droplet pair mechanism applies specifically to sulfide liquids and gas bubbles. You need to make the point that your sulfides look like spherical droplets, and the MSS is a crystallisation product of that sulfide liquid.

This is nit-picking somewhat, but it's important to be clear.

126 – aqueous fluid in the form of bubbles.

Figure 2. The reader will find it hard to work out exactly what's going on here. Better to put little boxes in the insets to show exactly where the enlarged area is in the main image, and also put scales on the insets. I can't quite make sense of D – presumably the main image is looking into the curved inner surface of the bubble? Consider rewriting the caption to improve the clarity.

Figure 3 – why not put the important chemical map(s) in the figure? Hardly anybody looks at supplementary figures.

181 – these numbers will then limit the viscosities of your magmas

195 but your figure 2 is showing bubbles in 1A magmas. So if this conclusion is right then presumably these must have formed at low pressure close to eruption? If so then the sulfide droplet attachment might be happening at this stage, as in the lacono-Marziano experiments?

202 “coupled with assimilation of a felsic magma generated by partial melting of the local altered oceanic crust” – this is not something I'd expect you to address, but you should think about how realistic this type of model is. How would you extract a partial melt out of wall rocks in the sea floor? Assimilation can only really happen by physical incorporation of lumps of wall rocks into the magma, followed by melting of the xenolith. (That's because of the slow rate of heat transfer into the country rock, and the consequence distribution of temperatures – the T at the contact is the average of the ambient temperature of the country rock and the T of the magma, so there is at most a very limited zone where the country rock is hot enough to melt – if the country is basalt, there is no such zone – see Robertson (Robertson et al., 2015) et al for a discussion of this). Are there any other possible contaminants that could supply Th?

204, another nitpick, but this would be a lot easier to follow if you used VE5,4,3,2 to denote 5,4,3 and 2% water. And add the water content beside the VE labels into the figure 4 legend to explain it.

Fig 4 – 1000C seems hot for a rhyolite?

222, this nugget effect would affect Cu in the same way, presumably. Mungall et al 2015 quantified this (for mantle nodules, but the maths is the same).

229 (Kiseeva & Wood, 2015) is the best reference for this.

294, “such high apparent compatibility for Pd requires the fractionation of Cu-rich sulfide liquids in these magmas” – not following the logic here. There's no reason to think that Pd is more compatible in Cu-rich sulfide liquids. Or am I misunderstanding your point? Is the “experimental evidence” here the Ripley paper I mentioned above? If so here's where the reference should go.

306, again I don't follow the argument here. How do you go from a Cu rich sulfide to a Cu poor sulfide? What do you mean by “exsolution” here? This para needs a rewrite.

334 – here's where the argument about viscosities and settling rates needs to come in. Henrich and Connolly go into this (but they assume a VERY wet dacite with 10% water to get the viscosity down). More specifically, what they say is that the settling velocities of small droplets are less than upward transport velocities, so they will be entrained, without the need for bubble flotation.

356 – but only if the droplets were a lot bigger than the ones you're seeing in the erupted lavas.

366 – again, nitpicking, but they are only MSS rich when they solidify, at which point they are no longer droplets...better to say, Cu-poor.

372 – here you need to make some estimates on how fast this might happen. Looks like your bubbles go up to ~250 microns, based on Figure 2. I'm estimating flotation rates no more than mm per year for a moderately wet dacite. If we make it a 500 micron droplet in an andesite, then you can get up to ~ 10m/yr. Pushing it...

419, maybe if you are talking about felsic-intermediate magmas only, otherwise this isn't correct – see point above.

427, specifically, the ferric iron content, which cause Fe<sup>3/2</sup> to change, which causes reduction of dissolved sulfate to sulfide.

Barnes, S. J., Le Vaillant, M., Godel, B. & Leshner, C. M. (2019). Droplets and bubbles: solidification of sulphide-rich vapour-saturated orthocumulates in the Noril'sk-Talnakh Ni-Cu-PGE ore-bearing intrusions *Journal of Petrology* 60, 269-300.

doi:10.1093/petrology/egy114

Kiseeva, E. S. & Wood, B. J. (2015). The effects of composition and temperature on chalcophile and lithophile element partitioning into magmatic sulphides. *Earth and Planetary Science Letters* 424, 280-294.

doi:http://dx.doi.org/10.1016/j.epsl.2015.05.012

Ripley, E. M., Brophy, J. G. & Li, C. (2002). Copper solubility in a basaltic melt and sulfide liquid/silicate melt partition coefficients of Cu and Fe. *Geochimica et Cosmochimica Acta* 66, 2791-2800.

Robertson, J. C., Ripley, E. M., Barnes, S. J. & Li, C. (2015). Sulfur Liberation from Country Rocks and Incorporation in Mafic Magmas. *Economic Geology* 110, 1111-1123. doi:10.2113/econgeo.110.4.1111

Reviewer #2 (Remarks to the Author):

This paper presents observations that demonstrate the simultaneous occurrence of sulfide liquid and hydrothermal thermal in magmas from an intra-oceanic subduction zone. The textures shown in the photomicrographs are beautiful. The association of sulfide droplets with hydrothermal fluid 'bubbles' is novel and will help to resolve the ongoing controversy about whether sulfide flotation is a viable geologic process. This topic has been the focus on experimental and theoretical studies, but the submitted manuscript is the first to my knowledge that shows clearly in natural samples the process of sulfide bubble flotation. The observations and modeling presented in the manuscript appear to be robust and clearly communicate the role for sulfide droplets to concentrate chalcophile metals in the apical portions of magma bodies. The manuscript presents first-of-its-kind observations and I predict will be well received by the community and highly cited. I have only a few comments and recommend that the paper be published with minor revisions.

Regarding sulfide saturation discussed on lines 93-96, could pressure play a role considering the strong relationship between increasing sulfur concentration at sulfide saturation (SCSS) and decreasing pressure?

Regarding Cu in the exsolved hydrothermal fluid on lines 151-152, does this track with increasing Cl content of the melt and partitioning of Cl to the fluid?

The oxidization of sulfide caused by degassing has been described in porphyry systems, as discussed in Audétat, A. and Simon, A.C. (2012) Magmatic controls on porphyry Cu genesis. In: *Economic Geology Monograph in honor of Richard Sillitoe*. Eds. J.W. Hedenquist, M. Harris, F. Camus, Society of Economic Geologists Special Publication Number 16, 553-572 (<https://app.ingemmet.gob.pe/biblioteca/pdf/SEG-SP16-553.pdf>) See Figure 8 in this paper.

Here are some small things to fix.

L8: change "texture" to "textural observations"

L31: change "like" to "such as"

L238: I would not use the term "nuggets", but rather refer to these as "sulfide liquid droplets"

L285: do not capitalize the S C S S when spelling out the words

L331: I would not use "dense sulfide blebs", but rather refer to these as "sulfide liquid"

L335: Do you have an estimate of the crystallinity of the magma at the time of sulfide liquid saturation? Is crystallinity low enough to permit settling of sulfide liquid? I know this process is often invoked, but I have only seen compelling evidence for sulfide sinking in high-temperature mafic magmas at low crystallinity.

L362: Use "addition" instead of "adjunction"

L371-2: "...via sulfide bubble flotation."

Adam Simon, 3 January 2023

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If you experience problems in linking your ORCID, please contact the [Platform Support Helpdesk](http://platformsupport.nature.com/).

Author Rebuttal letter:

Rebutal letter for the manuscript "The Flotation of Magmatic Sulfides: A Source of Cu-Au for Seafloor Massive Sulfide Deposits?"

Introduction

We are deeply honored to receive your feedback on our manuscript titled "The Flotation of Magmatic Sulfides: A Source of Cu-Au for Seafloor Massive Sulfide Deposits?" Your insightful review is greatly appreciated, and we would like to express our sincere gratitude for your meticulous attention to detail. In this letter, we aim to address how we have adjusted our argument in response to your valuable concerns. Beyond detailed comments, four main areas of concern were raised through the reviewing process of our manuscript. Firstly, the discussion regarding the physical processes facilitating sulfide flotation was noted. Secondly, the necessity of sulfide flotation in explaining the Cu-Au-rich nature of associated ore deposits was questioned. Thirdly, an inaccuracy in our portrayal of the physico-chemical processes related to the formation and composition of sulfide droplets was highlighted. Lastly, the novelty of identifying sulfide-bubble aggregates in natural settings was discussed. We acknowledge these concerns and have taken diligent steps to address them accordingly.

In the next section, answers to your remarks are provided (p.3). References to Part I to Part IV are made in this section. These refer to in-depth and detailed answers related to the four concerns stated above, as follows:

â€ Part I: Detailed discussion of the physical processes of sulfide transportation. p.15

â€ Part II: Firm and sufficient evidence for demonstrating that the bubble flotation of droplets is necessary for explaining the observations. p.26

â€ Part III: Detailed discussion of the chemical evolution of sulfide compositions. p.31

â€ Part IV: Justification of the claims of novelty in the observations of droplet-bubble pairs given previous observations. p.34

In Part I and Part II, we utilize physical modeling of sulfide growth within magmas, incorporating sulfide convection and sulfur diffusion, alongside realistic timescales of magma storage within the crust, to demonstrate that isolated sulfides are sinking faster than magmas ascend, whether magmas are basaltic, andesitic or dacitic. Based on the Hadamard-Rybczynski version of the Stokes equation, we also show that compound drops identified within Fatu Kapa magmas are either positively (multiple compound drops) or neutrally (simple compound drops) buoyant. This finding underscores the significant role of sulfide flotation in facilitating the transfer of Cu and Au from magmas to ore deposits within intra-oceanic settings. Furthermore, our study presents a counterargument to the viewpoint put forth by Heinrich and Connolly in their 2022 publication, which suggests that sulfide flotation is unnecessary for physically transporting magmatic sulfides to the surface.

In Part III, we align our terminology with the widely accepted understanding of magmatic sulfide formation. We acknowledge that our previous reference to "exsolved MSS" actually pertains to sulfides liquefied within the FeS system, while our mention of "sulfide liquid" refers to sulfides liquefied within the CuS system. These refined designations are consistent with the terminology outlined in Ripley's (2002) paper, graciously provided by Reviewer 1, as well as with geochemically oriented studies such as the one by Li et al. (2021). The latter was instrumental in extracting partition coefficients between sulfides and silicate melts for chalcophile elements.

In Part IV, we conduct a comprehensive review of sulfide-bubble associations previously documented in natural settings. We adopt a cautious tone in our manuscript regarding the novelty of sulfide-bubble associations, acknowledging that several compound drop remnants have been previously identified. However, we emphasize two key points. Firstly, we believe that our study represents the first instance where we can unequivocally demonstrate, through the comparison

between groups 1A and 1B(a), that compound drops systematically form when a magma is both S-saturated and volatile-saturated. Secondly, we highlight in previous studies the absence of preserved sulfide-bubble associations directly within the silicate liquid in natural systems that closely resemble the experimental runs conducted by Mungall et al. (2015). Furthermore, we emphasize that the unique textural preservation of these compound drops allows us, thanks to the reviewer's remarks, to physically demonstrate that sulfide flotation is required to explain the Cu-Au endowment of the associated ores.

In summarizing the updates made to our manuscript, we humbly maintain our main argument that sulfide flotation plays a crucial role in facilitating the transfer of Cu-Au from magmas to ore deposits at Fatu Kapa. This assertion is grounded in our physical modeling of isolated sulfide sinking velocities across a range of magmatic compositions, as well as in the estimated ascending velocities for compound drops, and the consideration of realistic timescales for mafic magmas to evolve toward felsic compositions. We acknowledge the initial formation of sulfide melts in the CuS system, transitioning to the FeS system as Cu concentrations within the silicate liquid decrease below ~100 ppm. We humbly acknowledge that while we do not intend to suggest that we are the first to observe sulfide-bubble aggregates, we still recognize the exceptional nature of these examples due to their preservation. This preservation allows for the identification of rare textures, such as multiple compound drops, and enables the estimation of compound drop densities. Additionally, we emphasize the importance of the systematic association of sulfides with aqueous fluid bubbles in magmas that are both sulfur and volatile saturated, compared to those that are sulfur saturated only.

In closing, we extend our heartfelt appreciation for the constructive critique provided. Their valuable insights have guided us in refining our manuscript with humility and care. We are grateful for the opportunity to engage in this collaborative process. We approach the revisions with a commitment to humility and a dedication to improving the clarity and integrity of our work. We sincerely hope that our efforts contribute positively to the ongoing discourse in our field.

Comments and answers

#### Reviewer 1

There is some good data in this paper, which is well written and illustrated and has a lot to commend it. However, like many dominantly geochemical papers, it has a significant flaw in that it doesn't pay enough attention to the basic physics. The key question is whether bubble flotation of droplets is actually necessary to explain the observations, and whether it's physically plausible. Heinrich and Connolly argue that no such mechanism is necessary because small sulfide droplets will be entrained in most magmas anyway. If it can't be shown that bubble flotation is required, then there still an interesting paper to be published, but the main thrust of the argument would need to change, and there is nothing really novel to be said.

For this reason I can't see how it meets the criteria for publication in a Nature-family journal.

The main issue is to do with viscosity and settling/floating rates. You are claiming that sulfides are effectively transported to the surface by rafting on bubbles, but the droplets you are looking at are tiny, only a few tens of microns. You need to do a Stokes Law calculation using estimated viscosities for your lavas to see what the likely droplet settling rates would be. You'll be alarmed at how small they are for a typical wet dacite, viscosity of  $10^8$  Pas (well on the low side) a 100 micron sulfide droplet settles at about  $10^{-12}$  m/s. That's order of 1 mm per hundred years. For a ten micron droplet it's 100 times less. Similar numbers apply to upward flotation of bubbles. For an andesite with viscosity 10000 Pas, you're up into the 10s of m per year range for a 100 micron droplet, so it's significant. So for your model to make sense, the process needs to be happening very early in the differentiation process when your magmas are still no more evolved than andesite. The efficiency of the process drops really fast as the temperatures drop and the magmas get stickier. For dacites, I don't think it works, unless they are very wet and/or strongly superheated to bring the viscosities down. I suggest that you work out your likely liquid compositions, use your assumed water contents, and calculate viscosities using the Giordano et al calculator at <https://www.eoas.ubc.ca/~krussell/VISCOSITY/grdViscosity.html> then do the Stokes Law calculation (strictly you should use the Hadamard-Rybczynski version of the Stokes equation for droplets, but it only make about a factor of 2 difference and we're talking multiple orders of magnitude).

To address the concern regarding the physical processes involved, we used the Giordano et al. (2008) calculator to estimate the viscosity of five representative magmas erupted at Fatu Kapa. Our estimations yielded a viscosity for dacitic magmas of approximately ~103.5 Pa.s, which differs from the value proposed by Reviewer 1 (~108 Pa.s). This variation can be attributed to the relatively low SiO<sub>2</sub> concentration of dacites that places them near the andesitic area on a TAS diagram, their water content (~2.1 wt.% H<sub>2</sub>O), and their relatively high temperature (~1000°C). Furthermore, we conducted physical modeling to simulate sulfide growth and sulfide sinking velocities within three of these magmas: basalts, trachyandesites (where compound drops are

expected to form), and trachydacites (where compound drops are observed). This modeling, adapted from Zhang (2015) and slightly modified by Yao and Mungall (2020), uses the Hadamard-Rybczynski version of the Stokes equation to estimate sinking velocities. Our models tailored to Fatu Kapa magmas reveal that sulfides, starting from a nanometric size at nucleation, attain a diameter of 300 to 400 Åµm within less than one year. Consequently, isolated sulfides exhibit sinking velocities of approximately ~100 m/year, ~10 m/year, and ~1 to 2 m/year in basaltic, trachyandesitic, and trachydacitic magmas, respectively. Therefore, we attribute the small size of the observed droplets to the fact that they are the few that formed shortly before eruption. Moreover, we estimated the ascent velocities of compound drops using the Hadamard-Rybczynski version of the Stokes equation. In andesitic magmas, both multiple compound drops (one wide bubble with numerous sulfides) and single compound drops (one small bubble with one sulfide) ascend at velocities of approximately ~50 m/year and ~1 m/year, respectively. In dacitic magmas, the ascent velocities for multiple and single compound drops are approximately ~5 m/year and ~0.2 m/year, respectively. To facilitate comparison, we have included Figure 7 in the main manuscript, depicting these values graphically. In the revised manuscript, a brief explanation of these models and their outcomes is provided alongside the figure. Further discussion regarding these results is expounded upon below.

According to Heinrich and Connolly (2022), direct application of Stokes' law to sulfides with diameters of 10 and 100 Åµm suggests that a significant portion of sulfide blebs, especially within intermediate and felsic systems, are entrained by upwelling magmas without necessitating bubble attachment and subsequent flotation. We identify two potential flaws in this reasoning. Firstly, the assumption that every magmatic system on Earth, spanning from mafic to felsic magmas, ascends in the crust at rates exceeding 10 m/year may raise some concerns. As highlighted by Turner and Costa (2007) and Costa et al. (2020), timescales of mafic to felsic differentiation range from 10,000 to 100,000 years. Secondly, the study overlooks the rate at which sulfides grow (and consequently sink) in magmatic systems. As outlined above, sulfides rapidly (< 1 year) reach diameters of ~200 Åµm to ~400 Åµm in both mafic and felsic magmas. Our models indicate that sulfides sink at a similar rate as magma upwells in mafic systems. In dacitic magmas, sulfides reach depths of 1 km within ~500 years, strongly suggesting that they settle in systems that take thousands of years to evolve. Comparative analysis suggests that sinking is the predominant behavior of isolated sulfides within Fatu Kapa magmas, thereby hindering their transfer to the SMS ores. Conversely, our textural observations indicate that most sulfides become associated with an aqueous fluid bubble when magmas are both sulfur and volatile saturated (group 1B(a)). Application of the Stokes law to these compound drops reveals that they either ascend quickly (multiple compound drops) or ascend slowly/are neutrally buoyant (simple compound drops), thereby providing a mechanism for the transfer of Cu and Au to the ore deposits. We discussed these points in more details in the final parts of 'Transfer of Cu and Au from Fatu Kapa magmas to the surface' of our revised manuscript. Finally, we conducted a model of isolated sulfide sinking within Niuatahi-Motutahi dacites (intra-oceanic subduction). Dacites found in this setting are Cu-rich, volatile and sulfur saturated, and we propose that flotation must participate in the Cu-Au transfer in this setting.

#### Detailed points

Line 47 'sulfide-bubble compound drops observed in natural settings are either preserved in inclusions or significantly altered within silicate liquids or xenoliths' that may be true in felsic-intermediate settings but there are numerous examples in mafic and komatiitic settings - see (Barnes et al., 2019), particularly section 'Other examples of segregation vesicles in cumulates'. The claim that this is the first observation of droplet-bubble pairs in nature is wrong.

In response to the reviewer's remarks, we have conducted a thorough re-evaluation of the identification of sulfide-bubble aggregates in natural magmas. This process involved a meticulous review of the study authored by Barnes et al. (2019), which we approached with keen interest. You may find a detailed overview of this review in Part IV, where each reference studied is compiled in a summary table. This table covers various aspects including location, geological setting, host phase, magmatic composition, and secondary processes encompassed by the identified sulfide-bubble aggregates. Additionally, we have included a relevant Figure that highlights the distinctions between these compound drops observed in natural systems and those generated through experimental runs.

In light of this research, we have categorized observations of sulfide-bubble aggregates in natural systems into three distinct cases: (1) sulfide-bubble aggregates trapped within melt inclusions; (2) sulfide occurrences intertwined with carbonates in mantle xenoliths, as well as within lower and middle crust rock assemblages - these carbonates are construed as residual bubbles hosting predominantly CO<sub>2</sub> as the primary volatile species at such depths; (3) sulfides associated with silica caps, where these caps are interpreted as aqueous fluid bubbles that have been filled with late-stage silicate liquids due to pressure increase during solidification,

associated with gas filter pressing.

We wholeheartedly concur with the reviewer's remark that this is not the first instance of sulfide-bubble aggregates being discerned in natural systems. We acknowledge that the sentences highlighted by Reviewer 1 may have conveyed this idea awkwardly, and we express our full acknowledgment of this possibility. Our intention was rather to emphasize that the identification of preserved compound drops akin to those observed in experiments remains relatively rare in comparison to previously identified remnants of compound drops (refer to Figure 6 of this letter for illustrative examples), facilitating the identification of novel features such as multiple compound drops (see Figure 2.d of the main manuscript). Such preservation also facilitates the estimation of the density of these compound drops, a crucial aspect in addressing the hypotheses posited by Heinrich and Connolly (2022). Additionally, we respectfully posit that another noteworthy finding of our study, stemming from the comparison between group 1A and group 1B(a) magmas, is the nearly ubiquitous association of sulfides with aqueous fluid bubbles when the magma is both sulfur and volatile-saturated. We have revised the sentences flagged by the reviewer that may have conveyed the erroneous notion of this being the first observation of sulfide-bubble aggregates in natural settings. Furthermore, we have incorporated the new bibliographic references graciously provided by the reviewer to enhance the introduction section.

Line 59 it would be helpful to give more info on the petrology of the samples that were actually studied, and also their silica contents. We've only got MgO and trace elements to look at. Viscosity is an important variable here so we need a better idea of what these magmas actually were and whether they represent liquids or liquid-crystal mixtures - that's important because most andesites are porphyritic. A plot of SiO<sub>2</sub> vs MgO and a table of short rock descriptions (subdivided into group 1A and 1B) are both needed.

We totally agree. We added Table 1, in which measured major element concentrations, estimated H<sub>2</sub>O content and temperatures, and texture of three lavas representative of those sampled in the Fatu Kapa area are provided (the mafic basalt from groups 1A and 1B(a), an andesite in group 1B(a) where compound drops are expected to form in agreement with our geochemical modelling, and a dacite from group 1B(a) where compound drops are firmly identified). To ease reader's comprehension, we also added the viscosity calculated with the Giordano et al. (2008) calculator, an estimation of the ascending velocities of compound drops with the HR version of the Stokes equation, and the results of our sinking velocity models for isolated sulfide blebs within these three magmas. In Figure 1, we added a MgO versus SiO<sub>2</sub> diagram (Figure 1.b of the main manuscript).

Line 77 - not immediately clear - so you're saying you didn't analyse Au, and you're extrapolating between Cu and Pd when discussing its distribution?

Indeed. We rewrote it to make it clearer: We did not measure Au but, similarly with previous studies (Park et al., 2021; Park and Campbell, 2021; Hao et al., 2021), we relied on the fact that the affinity of this element for sulfides falls between that of Cu and Pd (Mungall et al., 2014; Liu et al., 2015; Li et al., 2021) to extrapolate its behavior when discussing its contribution.

88 - nucleate over each other - this phrase doesn't really make sense. It's not really clear from experimental or natural observations what nucleates on what. It may be that the bubbles nucleate first, then the droplets heterogeneously nucleate on them, or vice versa, or they both nucleate independently then stick together when they collide. Better to be non-specific and just say that they are known to have a strong surface affinity that makes them stick together.

We changed it accordingly. We also changed it in the introduction (in the paragraph - an experimental study conducted by Mungall et al. (2015)...).

119 - after MSS crystallisation from the sulfide liquid. Your terminology gets a bit confusing, partly due to the way you use the term 'exsolution'. Exsolution means formation of a new phase in the solid state from the breakdown of a solid solution. The sequence of events in magmatic sulfide droplets is that 1) they form from the magma by the process of liquation (like crystallisation, but applying to an immiscible liquid). The sulfide liquid then (2) crystallises to form the solid phase, MSS, with a residual Cu-rich liquid that goes on to form ISS then (usually) chalcopyrite. The MSS then (3) inverts to



pyrrhotite at low temperature, exsolving pentlandite along the way. In volcanic rocks, the cooling rate is too high for (3) to happen, so the sulfides typically quench in the high-T MSS. Where it might start getting complicated here is that where you are dealing with dacites and temperatures below 1000C, depending on the Cu content you might be below the solidus of the sulfide, so you might be crystallising MSS directly from the silicate melt without forming a sulfide liquid.

There's a very important but overlooked paper by Ripley (Ripley et al., 2002) that showed that if a magma hits sulfide saturation late when its Cu content is high it saturates not in FeS but in CuS, so you get a very Cu-rich liquid with very low Fe. (This may be the origin of the strange Cu-Pd ores in the Skaergaard intrusion). I don't think you're seeing this but it's something to look for.

So, the point of this is that you need to be aware of these complexities, and make sure you are clear in your use of terminology. The bubble-droplet pair mechanism applies specifically to sulfide liquids and gas bubbles. You need to make the point that your sulfides look like spherical droplets, and the MSS is a crystallisation product of that sulfide liquid.

This is nit-picking somewhat, but it's important to be clear.

We concur with the reviewer's remarks regarding the inaccuracy of our terminology and acknowledge that the sulfide phase formed from Fatu Kapa magmas is always liquid. Experimental studies partly reproduced the work of Ripley et al. (2002) in analysing the composition of sulfides formed from magmas displaying different Cu concentrations (Li et al., 2021), in order to calculate partition coefficients. In the study of Li et al. (2021), sulfides formed above 100 ppm Cu are almost entirely Cu-rich, while those formed from lower Cu concentrations are a mixture of Cu-rich and pyrrhotitic sulfides. These authors, in line with others in the geochemical community, acknowledged that the pyrrhotitic sulfides are crystalline when they form, while the Cu-rich sulfides are liquids. Consistent with Ripley et al. (2002), we acknowledge that both sulfides are liquids, in agreement with their blebby shape. Furthermore, we note that Li et al. (2021) observed differences in partition coefficients related to silicate liquid for chalcophile elements between pyrrhotitic and Cu-rich phases. Although Pd partition coefficients were not estimated for these phases in the study by Li et al. (2021), Costa et al. (2021) demonstrated that Pd is efficiently extracted from magmas where Cu-rich sulfides are present (refer to Part III for more details). With this information, we believe that the observed two-stage behavior of Pd, and to a lesser extent Cu, in Fatu Kapa magmas (see inset in Figure 5.a.b) is linked to a change in the nature of the formed sulfide phases (here, a switch in the CuS:FeS proportions), which correlates with the Cu content of the magma. Specifically, when the silicate melt Cu content exceeds 100 ppm, the formed sulfide liquid primarily consists of CuS. Conversely, when the Cu content falls below 100 ppm, the formed sulfide liquid primarily consists of FeS. These findings align well with the modeling of chalcophile element concentrations in magmas conducted by Li et al. (2021) for both thin arcs (exhibiting magmas with Cu contents exceeding 100 ppm, wherein the liquefied sulfide predominantly comprises CuS) and thick arcs (displaying magmas with Cu contents below 100 ppm, wherein the liquefied sulfide primarily comprises FeS) (refer to Part III). In our manuscript, we have revised our terminology to align with that suggested by Reviewer 1. For instance, L115 "Individual sulfides are predominantly composed of pyrrhotite, which forms after the cooling of monosulfide solid solutions (MSS)." became: "Individual sulfides are predominantly composed of pyrrhotite, which forms upon exsolution of monosulfide solid solutions (MSS) that crystallized from FeS sulfide liquids."; all the unappropriated "exsolution" became "liquation" for sulfides and "formation" for aqueous fluids (since it is uncertain whether the aqueous fluid phase is liquid or gaseous); "SL:MSS proportions" became "CuS:FeS proportions", etc. We also rewrote the paragraph related to the nature of the formed sulfide phase.

126 aqueous fluid in the form of bubbles.

We changed it.

Figure 2. The reader will find it hard to work out exactly what's going on here. Better to put little boxes in the insets to show exactly where the enlarged area is in the main image, and also put scales on the insets. I can't quite make sense of D - presumably the main image is looking into the curved inner surface of the bubble? Consider rewriting the caption to improve the clarity.

We added boxes and scales in the inset images. We believe that Reviewer 1 was probably talking about C. rather than D. Would it please be possible to confirm? We added the sentence to the caption C to ease clarity.

Figure 3 – why not put the important chemical map(s) in the figure? Hardly anybody looks at supplementary figures.

– We added S (for recognizing sulfides) and Cu (which is the important element to watch here) chemical maps in d. We changed the caption accordingly.

181 – these numbers will then limit the viscosities of your magmas

– They do indeed. Please kindly refer to our answer to your first comment and to Part I.

195 but your figure 2 is showing bubbles in 1A magmas. So if this conclusion is right then presumably these must have formed at low pressure close to eruption? If so then the sulfide droplet attachment might be happening at this stage, as in the Iacono-Marziano experiments?

– Indeed, the bubbles in 1A lavas are likely formed during eruption within the conduit (syn-eruptive). We discuss it in the “Transfer of Cu and Au from Fatu Kapa magmas to the surface” part. Here, we added “before eruption”.

202 – coupled with assimilation of a felsic magma generated by partial melting of the local altered oceanic crust – this is not something I’d expect you to address, but you should think about how realistic this type of model is. How would you extract a partial melt out of wall rocks in the sea floor? Assimilation can only really happen by physical incorporation of lumps of wall rocks into the magma, followed by melting of the xenolith. (That’s because of the slow rate of heat transfer into the country rock, and the consequent distribution of temperatures – the T at the contact is the average of the ambient temperature of the country rock and the T of the magma, so there is at most a very limited zone where the country rock is hot enough to melt – if the country is basalt, there is no such zone – see Robertson (Robertson et al., 2015) et al for a discussion of this). Are there any other possible contaminants that could supply Th?

– Felsic lavas in the Fatu Kapa area exhibit significant enrichment not only in Th but also in other incompatible elements such as REE. From a geochemist perspective, melts resulting from partial melting of the surrounding wallrock are necessary to account for these pronounced Th and REE enrichments. Additionally, partial melting, rather than complete melting, of these wallrocks is necessary to increase the concentration of these incompatible elements in the assimilated endmember. It is worth noting that our partial melting–assimilation model (referred to as FC-PMA) perfectly reproduces all of these elements, as demonstrated in Supplementary Figure 10. These models effectively elucidate the shifts in REE and Th trends, as depicted in Figure 1. Moreover, compatible elements like Co are well accounted for by this model. From a geophysicist perspective, we concur with Reviewer 1 that assimilation of these lavas likely involves the incorporation of centimetre to meter-scale xenoliths, as demonstrated by Robertson et al. (2015) and observed in magmatic chamber outcrops, such as the komatiites found at Silver Swan (Dowling et al., 2004) (Western Australia). While we do not observe these xenoliths in the vitreous felsic lavas of Fatu Kapa, their absence does not negate the existence of this process, especially if the xenoliths are incorporated from the footwall, as evidenced by outcrops, while lavas likely erupt from the apical part of the magmatic chamber. Robertson et al. (2015) demonstrate that this melting–assimilation process is favored by a relatively low melting point, as is the case for felsic xenoliths rather than basaltic ones. In our chemical model, the assimilated “wallrock” has an andesitic composition rather than basaltic. Finally, the remaining question pertains to how it is possible to produce partial melts when physical calculations indicate that these xenoliths can be melted in mere seconds (in komatiites) or minutes (in basalts) for centimeter-scale xenoliths, or in hours (in komatiites) or several days (in basalts) for meter-sized xenoliths (Robertson et al., 2015). An answer to this question, as outlined in Robertson et al. (2015), lies in the dynamics of the magma reservoir. Numerous natural outcrops demonstrate the identification of partially melted xenoliths. For example, felsic xenolith plumes pervade upward in massive sulfides hosted by komatiites in the Silver Swan deposit (Dowling et al., 2004). These xenoliths may display skeletal plagioclase phenocrysts resulting from partial melting, while others exhibit preserved inner cores. In the Duluth Complex (USA), centimeter to meter-sized xenoliths suggestive of footwall delamination are identified. These xenoliths display strong evidence of partial melting, with the initial footwall composition (low-grade chlorite-

muscovite-quartz-plagioclase-pyrite-kerogen) preserved in the core (Ripley et al., 2007). Small but abundant xenoliths are identified in the Basal Breccia sequence of the Voisey's Bay Intrusion (Li and Naldrett, 2000). The total exhaustion of sulfides in these xenoliths compared to the footwall lithology suggests that partial melting was more vigorous compared to those of the Duluth Complex (Robertson et al., 2015), but the fact that these xenoliths are still identifiable in magmas suggests that the melting process was also incomplete. These examples imply that partial melting, as opposed to complete melting, is the norm rather than the exception.

Therefore, it is likely that delamination and incorporation of andesitic footwall xenoliths, followed by their partial melting, represent the plausible physical mechanism that explains the high concentrations of Th and REE in 1B(a) magmas.

204, another nitpick, but this would be a lot easier to follow if you used VE5,4,3,2 to denote 5,4,3 and 2% water. And add the water content beside the VE labels into the figure 4 legend to explain it.

â We do agree. We changed it in the text. We changed the labels and added the water content beside the VE labels in Figure 4.

Fig 4 â 1000C seems hot for a rhyolite?

â We changed it to 850oC. We also changed basalts from 1000oC to 1150oC.

222, this nugget effect would affect Cu in the same way, presumably. Mungall et al 2015 quantified this (for mantle nodules, but the maths is the same).

â We did not duplicate our Cu analyses, but we can see on Figure 5 that Cu data may display different measured values at similar Th concentrations. On the other hand, it may be because magmas follow the VE4 or VE3 trend.

229 (Kiseeva & Wood, 2015) is the best reference for this.

â We updated it.

294, âsuch high apparent compatibility for Pd requires the fractionation of Cu-rich sulfide liquids in these magmasâ â not following the logic here. Thereâs no reason to think that Pd is more compatible in Cu-rich sulfide liquids. Or am I misunderstanding your point? Is the âexperimental evidenceâ here the Ripley paper I mentioned above? If so hereâs where the reference should go.

306, again I donât follow the argument here. How do you go from a Cu rich sulfide to a Cu poor sulfide? What do you mean by âexsolutionâ here? This para needs a rewrite.

â We rewrote the whole paragraph, hoping that things are clearer this way. There is experimental evidence that Pd, as a strongly chalcophile element, display higher affinity for CuS sulfides than FeS sulfides (e.g., Liu and Brenan, 2015). Moreover and as described in more details in the discussion above, a change in the nature of the liquified sulfide phase is necessary to account for the two-stage behavior of Pd (critical drop followed by a more gentle decrease). Please kindly refer to the answer we made to your comment above (â119 â after MSS crystallisation from the sulfide liquid. Your terminology...â) and to Part III.

334 â hereâs where the argument about viscosities and settling rates needs to come in. Heinrich and Connolly go into this (but they assume a VERY wet dacite with 10% water to get the viscosity down). More specifically, what they say is that the settling velocities of small droplets are less than upward transport velocities, so they will be entrained, without the need for bubble flotation.

â Please kindly refer to our answer to your first remark and to Part I and Part II below. To summarize, there are two factors that we believe were overlooked by Heinrich and Connolly (2022) regarding felsic systems. Firstly, the rapid growth of sulfides to diameters of 300 â 400 micrometers within a few years. Secondly, the extended ascent of initially mafic magmas originating from mantle depths, which do not transition to felsic compositions upon reaching the surface within a few days to years.

356 – but only if the droplets were a lot bigger than the ones you’re seeing in the erupted lavas.

– Sulfide blebs quickly reach (~1 year) a diameter of 300 – 400 micrometers (see above). The one we are observing are likely the few that were formed briefly before eruption.

366 – again, nitpicking, but they are only MSS rich when they solidify, at which point they are no longer droplets—better to say, Cu-poor.

– We modified it. Here and there, we also wrote “FeS sulfides” rather than “MSS sulfides”. See our longer comment above and Part III.

372 – here you need to make some estimates on how fast this might happen. Looks like your bubbles go up to ~250 microns, based on Figure 2. I’m estimating flotation rates no more than mm per year for a moderately wet dacite. If we make it a 500 micron droplet in an andesite, then you can get up to ~ 10m/yr. Pushing it!

– Based on the estimated viscosities, we determined that multiple compound drops (such as the ~250 microns one depicted in Figure 2.d) exhibit an ascending velocity of approximately 50 m/year in andesitic lavas and approximately 5 m/year in dacitic lavas (see Part I).

419, maybe if you are talking about felsic-intermediate magmas only, otherwise this isn’t correct – see point above.

– See our answer above and Part IV.

427, specifically, the ferric iron content, which cause Fe<sup>3</sup>/2 to change, which causes reduction of dissolved sulfate to sulfide.

– We modified the sentences to make it clearer.

## Reviewer 2

This paper presents observations that demonstrate the simultaneous occurrence of sulfide liquid and hydrothermal thermal in magmas from an intra-oceanic subduction zone. The textures shown in the photomicrographs are beautiful. The association of sulfide droplets with hydrothermal fluid 'bubbles' is novel and will help to resolve the ongoing controversy about whether sulfide flotation is a viable geologic process. This topic has been the focus on experimental and theoretical studies, but the submitted manuscript is the first to my knowledge that shows clearly in natural samples the process of sulfide bubble flotation. The observations and modeling presented in the manuscript appear to be robust and clearly communicate the role for sulfide droplets to concentrate chalcophile metals in the apical portions of magma bodies. The manuscript presents first-of-its-kind observations and I predict will be well received by the community and highly cited. I have only a few comments and recommend that the paper be published with minor revisions.

Regarding sulfide saturation discussed on lines 93-96, could pressure play a role considering the strong relationship between increasing sulfur concentration at sulfide saturation (SCSS) and decreasing pressure?

– Indeed, pressure does play a role. At Fatu Kapa, we attribute the relatively late stage of sulfide saturation compared to MORB (SS occurs at 7 wt.% MgO compared to 9.5 wt.% MgO in MORB) to the more important pressure gradient between the mantle source and the magmatic chamber. It is developed in the discussion: “Given the inverse relation between pressure and sulfur content at sulfide saturation (O’Neill, 2021), magma that undergo deeper melting will become more S-undersaturated when they ascend adiabatically to shallower crustal levels. The isotopic characteristics of the Fatu Kapa magmas strongly suggest an influence from the Samoan hotspot (Jeanvoine et al., 2021). Therefore, we propose that this initial stage of S-undersaturation is linked to a greater depth of partial melting, similar to Lau Basin magmas (Figure 6.a., Figure 6.b.).” However, we stress that the first order parameter that explains the presence of these Cu-Au-rich in intra-oceanic subduction settings is the fO<sub>2</sub> (as developed in

the part of the manuscript), so we did not highlight the pressure parameter in the introduction in order to keep our reasoning as straightforward as possible.

Regarding Cu in the exsolved hydrothermal fluid on lines 151-152, does this track with increasing Cl content of the melt and partitioning of Cl to the fluid?

The oxidization of sulfide caused by degassing has been described in porphyry systems, as discussed in Audétat, A. and Simon, A.C. (2012) Magmatic controls on porphyry Cu genesis. In: Economic Geology Monograph in honor of Richard Sillitoe. Eds. J.W. Hedenquist, M. Harris, F. Camus, Society of Economic Geologists Special Publication Number 16, 553-572 (<https://app.ingemmet.gov.pe/biblioteca/pdf/SEG-SP16-553.pdf>) See Figure 8 in this paper.

â We read the paper kindly provided with keen interest. There are two textural objects mentioned in the remark of Reviewer 2: the sulfides that display Fe-rich rims (Figure 3 of our manuscript) similar to those enclosed within fractured inclusions presented in the Figure 8 of Audétat, A. and Simon, A.C. (2012), and the sulfide-bubble interfaces for which SEM analysis reveal that sulfides may display high Cu concentrations (up to ~20 wt.%, although this is only semi-quantitative). Textural evidence strongly suggests that the latter are formed through direct deposition from the fluid phase contained within the bubble (refer to Figure 3.d for clarification). The former sulfides are identified within group 1A magmas (~5-15 km depth), typically associated with a few sulfides within bubbles (see inset of the new Figure 7), while the latter are found within group 1B(a) magmas (<4 km depth). Our interpretation posits that 1A Fe-rimmed sulfides initially form within the magmatic chamber and are later carried by erupting magmas. Subsequently, syn-eruptive bubbles may nucleate on these sulfides during ascent, and interactions between fluid and sulfide may induce sulfide oxidation during ascent, releasing metals from sulfides into fluids (refer to Figure 7.d to f.). We acknowledge that magmatic degassing is a potential mechanism to form these Fe-rich sulfide rims (Audétat and Simon, 2012). However, we do not see evidence for pre-eruptive fluid formation in these 1A magmas (H<sub>2</sub>O is likely the dominant volatile species at these depths, as stressed in the Audétat and Simon paper, and H<sub>2</sub>O concentrations are significantly above the water solubility curve, as depicted in the Figure 4 of our manuscript), and the few found Fe-rimmed sulfides are typically the few associated with bubbles. On the other hand, the heterogeneously Cu-rich composition of bubble-sulfide compound drop interfaces found in Cl-rich (~5,000 to 6,000 ppm) 1B(a) shallow magmas (< 4 km) may directly reflect the composition of the aqueous fluid contained in the bubble. The high chlorinity of these magmas increases the affinity of Cu for aqueous fluids (Simon et al., 2006), and precipitated sulfides reflect this concentration. To conclude, Fe-rimmed sulfides and Cu-rich sulfide-bubble interfaces are not found in the same magma groups and are therefore probably not related to each other in the specific case of Fatu Kapa. However, we concur that the high chlorinity of 1B(a) felsic melts is important for the partitioning of Cu from silicate melt directly to the aqueous fluids.

Here are some small things to fix.

L8: change "texture" to "textural observations"

â We changed it accordingly.

L31: change "like" to "such as"

â We changed it accordingly.

L238: I would not use the term "nuggets", but rather refer to these as "sulfide liquid droplets"

â We changed it accordingly.

L285: do not capitalize the S C S S when spelling out the words

â We deleted it because the SCSS term is not called elsewhere in our manuscript.

L331: I would not use "dense sulfide blebs", but rather refer to these as "sulfide liquid"

â We rewrote âThroughout most of their evolution, group 1A magmas liquefied sulfidesâ, to also take into account the remarks from reviewer 1 (exsolution vs liquation). Therefore, the âliquidâ aspect is implicitly stated in the sentence.

L335: Do you have an estimate of the crystallinity of the magma at the time of sulfide liquid saturation? Is crystallinity low enough to permit settling of sulfide liquid? I know this process is often invoked, but I have only seen compelling evidence for sulfide sinking in high-temperature mafic magmas at low crystallinity.

â From mafic (where sulfur saturation occurs in group 1A) to andesitic (where sulfur saturation occurs in group 1B(a)) compositions, lavas present a fine-grained matrix with ~<5% to 15% phenocrysts (please refer to the newly added Table 1 of our main manuscript). Therefore, it is likely that the capillary forces remain limited in these magmas, allowing sulfide sinking. Dacitic lavas are mostly aphyric (you may find SEM pictures representative of these lavas in the supplementary Figure 12), so the same reasoning may apply. More information related to the physical processes of sulfide sinking within Fatu Kapa magmas can be found in Part I and Part II of this report.

L362: Use "addition" instead of "adjunction"

â We changed it accordingly.

L371-2: "...via sulfide bubble flotation."

â We changed it accordingly.

l) Detailed discussion of the physical principles of sinking and floating sulfides

Estimated viscosities for Fatu Kapa magmas

We estimated the viscosity of lavas representing basalts, basalt-andesites, and andesites within group 1A, along with andesites and dacites from group 1B(a) using the Giordano et al. (2008) calculator (Table 1). For the major element estimates of these magmas, we relied on microprobe data from glasses when possible. For the most mafic basalts before sulfide saturation, only whole rocks data are available. The H<sub>2</sub>O concentrations align with those in the manuscript, determined through plagioclase-silicate melt equilibrium. Andesites from group 1B(a) were not directly sampled, and we assumed a similar concentration in major elements compared to 1A andesites. Since fluid exsolution is presumed to occur at the andesitic stage in 1B(a) magmas, we assumed a H<sub>2</sub>O concentration equal to the solubility of water (i.e., 2.1 wt.%) for these 1B(a) andesites. The selected temperatures are the averaged temperatures within each group as estimated with plagioclase-silicate-melt equilibrium (i.e., 1170oC for basalts, 1150oC for basalt-andesites, 1070oC for andesites, and 1000oC for dacites).

The viscosities range from ~101.5 to 102.5 Pa.s from basalts to andesites within group 1A. The viscosity of 1B(a) dacites is estimated to be ~103.5 Pa.s. This viscosity is significantly lower than the averaged viscosity of ~108 Pa.s presented by Reviewer 1. This difference can be attributed to the relatively high-water concentrations (2.1 wt.%) and temperatures (1000oC) estimated for Fatu Kapa dacites. The fact that these dacites display relatively low SiO<sub>2</sub> concentrations that put them close to the andesite area in a TAS diagram can also explain their relatively low viscosity. When compared with a dry dacite with the same composition in major elements (Table 1), the viscosity at 1000oC reaches ~105.8 Pa.s, and at 900oC, it reaches ~107.2 Pa.s, falling within the range of the value proposed by Reviewer 1.

Lava 1A basalt 1A basalt- 1A andesite 1Ba andesite 1Ba dacite 1Ba dry  
andesitic dacite

Sample FU2-DR26-02 FU3-DR01-08 FU3-DR13-05 FU3-DR13- FU3-PL03-03 FU3-PL03-05+H2O 03

Sample type WR GL GL GL GL GL

SiO<sub>2</sub> 49.69 52.30 56.80 56.80 63.30 63.30

Al<sub>2</sub>O<sub>3</sub> 14.84 14.21 14.30 14.30 13.31 13.31

MgO 6.99 3.91 2.30 2.30 0.99 0.99

CaO 11.99 8.13 5.58 5.58 3.25 3.25

FeOtot 11.54 12.73 11.10 11.10 7.16 7.16

TiO<sub>2</sub> 1.65 2.51 1.79 1.79 1.02 1.02

Na2O 2.82 4.12 4.20 4.20 5.95 5.95  
 K2O 0.49 0.75 1.32 1.32 2.06 2.06  
 Total without H2O 100.17 98.67 97.37 97.37 97.04 97.04  
 H2O 0.40 0.50 1.10 2.10 2.10 0.00  
 T (oC) 1160-1180 1150 1070 1070 980 - 1020 980 - 1020  
 log  $\hat{\eta}$  (Pa.s)<sub>900</sub> 4.03 4.59 4.56 3.94 4.34 7.13  
 log  $\hat{\eta}$  (Pa.s)<sub>950</sub> 3.40 3.98 4.03 3.47 3.90 6.41  
 log  $\hat{\eta}$  (Pa.s)<sub>1000</sub> 2.85 3.44 3.55 3.05 3.51 5.78  
 log  $\hat{\eta}$  (Pa.s)<sub>1070</sub> 2.20 2.80 2.97 2.53 3.01 5.01  
 log  $\hat{\eta}$  (Pa.s)<sub>1150</sub> 1.59 2.18 2.41 2.01 2.52 4.26  
 log  $\hat{\eta}$  (Pa.s)<sub>1170</sub> 1.45 2.04 2.28 1.90 2.40 4.09  
 $\hat{\eta}$  (Pa.s) selected 28.36 149.63 942.75 335.77 3223.97 604806.84

Table 1: Concentrations of major elements, estimated water concentrations, and estimated viscosities for representative lavas of basalts, basalt-andesites, and andesites within group 1A, along with dacites from group 1B(a). Andesites from group 1B(a) were not sampled, and a similar concentration in major elements is assumed when compared to 1A andesites. Since fluid exsolution is presumed to occur at the andesitic stage in 1B(a) magmas, a H2O concentration equal to the solubility of water (i.e., 2.1 wt.%) is assumed. Viscosities are computed for a dry dacite in group 1B(a) magmas. Temperatures are estimated with the plagioclase-silicate liquid equilibrium.

Estimated sinking velocities of isolated sulfide bleb and ascending velocities of compound drop within Fatu Kapa magmas

In this section, we firstly estimate the sinking velocities of individual sulfides within Fatu Kapa magmas by directly applying the Hadamard-Rybczynski version of the Stokes equation to the sulfide blebs identified. Here, we assume a constant sulfide radius. Secondly, we estimate the velocities of sulfides whose radii are increasing due to S diffusivity as they descend through the magma. Finally, we assess the upward velocities of both single (a single sulfide with a relatively small bubble) and multiple (several sulfides with a relatively large bubble) compound droplets. This section solely addresses physical considerations, while Part II proposes a comparison of the different calculated velocities to determine which phenomenon can account for the Cu-Au endowment of the associated deposits.

Estimation of the sinking velocities of isolated sulfides (case A, constant radius)

We calculated the velocities of sulfide blebs and compound drops in Fatu Kapa magmas using both the Hadamard-Rybczynski version of the Stokes equation (equation 1) and the standard Stokes equation (equation 2) as provided by Heinrich and Connolly (2022).

The constant parameters used for these equations are outlined in Table 2.

$\hat{\rho}_{\text{bleb}}$  4050 kg.m<sup>-3</sup> (Zhang, 2015)

$\hat{\rho}_{\text{CD}}$  400 kg.m<sup>-3</sup>

$\hat{\rho}_{\text{magma}}$  2760 kg.m<sup>-3</sup> (Zhang, 2015)

$\hat{\eta}_{\text{bleb}}$  0.01 Pa.s (Saumur et al., 2015)  
 $g$  10 m.s<sup>-2</sup>

Table 2: Constant parameters used for assessing the velocities of sulfide blebs and compound drops in Fatu Kapa magmas. CD: compound drops.  $\hat{\rho}_{\text{CD}}$  is estimated for Fatu Kapa CD by reporting the measured  $\hat{\eta}_{\text{MV}}$  angle in the abacus displayed in Yao and Mungall (2020).

3

Considering that  $\delta \rightarrow 0$  tends toward zero,  $\delta \gg \delta_0 \sim 2 \delta_0$ . Therefore, using one equation instead of the other does not significantly change the order of magnitude of the estimated velocities. Reviewer 1 outlined three scenarios for which velocity estimates were provided. Before estimating velocities for sulfide blebs and compound drops within Fatu Kapa magmas, we first estimated velocities for these three scenarios to gauge the consistency of our parameters with those of Reviewer 1. These estimates are summarized in Table 3. The alignment between our calculated values and those proposed by Reviewer 1 confirms that the parameters we selected for computing sulfide bleb velocities in Fatu Kapa magmas align with those chosen by Reviewer 1.

Case 1 Case 2 Case 3  
 $r$  [ $\hat{\mu}\text{m}$ ] 1.00E+01 1.00E+02 1.00E+02

$\hat{\eta}$  [Pa.s] 1.00E+08 (dacite) 1.00E+08 (dacite) 1.00E+04 (andesite)

WHR [m/y] 1.37E-07 1.37E-05 1.37E-01

WS [m/y] 9.11E-08 9.11E-06 9.11E-02

WReviewer1 [m/y] 1.00E-07 1.00E-05 1.00E-01

Table 3: Estimation of sulfide bleb velocities for three case studies proposed by Reviewer 1.

The sinking behavior of sulfides is investigated across five types of magmas: basalts from group 1A, basalt-andesites from group 1A, andesites from group 1A, andesites from group 1B(a) (at the onset of compound drop formation), and dacites from group 1B(a). Sulfide blebs were observed in basalt-andesites from group 1A and in dacites from group 1B(a). While sulfide blebs with diameters of up to 65  $\mu\text{m}$  were found within group 1A basalt-andesites, the majority exhibited a diameter of approximately  $\sim 15 \mu\text{m}$ . A similar diameter was noted for most of the sulfide blebs identified within 1B(a) dacites. Velocities were estimated using the Hadamard-Rybczynski version of the Stokes equation (Equation 1), as suggested by Reviewer 1. In group 1A magmas, sinking sulfide velocities for constant radius are approximately  $\sim 1 \cdot 10^1$  m/y in basalts,  $\sim 2 \cdot 10^{-1}$  m/y in basalt-andesites, and  $\sim 3 \cdot 10^{-2}$  m/y in andesites. For group 1B(a) magmas, sinking sulfide bleb velocities were around  $\sim 9 \cdot 10^{-2}$  m/y in andesites and  $\sim 1 \cdot 10^{-2}$  m/y in dacites. These velocities are compiled in Table 4 at the conclusion of this section.

Estimation of the sinking velocity of isolated sulfides (case B, sulfide growth by diffusion and convection)

Zhang (2015) proposed a quantitative model of sulfide growth through sulfur diffusion during particle sinking, aiming to elucidate the formation of gravitational magmatic sulfide deposits. This model was subsequently employed by Yao and Mungall (2020) to evaluate the feasibility of sulfide flotation in magmatic systems. A significant finding discussed in Part II is that micrometric sulfides can attain a radius exceeding 100 micrometers in less than one year. However, their model accounts for evolving viscosities as a function of temperature, making direct comparisons of sinking sulfide velocities between mafic and intermediate/felsic systems challenging, as required for Fatu Kapa. Before delving into our adaptations of this model, we provide a brief overview of its assumptions and equations and reproduce the model proposed by Zhang (2015).

Zhang's (2015) model considers the thermodynamic (sulfide melt supersaturation), kinetic (sulfide droplet growth), and dynamic (sulfide droplet settling) controls of sulfide bleb evolution in magmas. There exists positive feedback between growth and settling: larger sulfide droplets sink faster than smaller ones (Equations 1 and 2), and more rapid settling enhances sulfide growth (increasing sulfur available for sulfide growth and expanding reaction surface) (Figure 1). In this model, sulfide growth is governed by sulfur mass transfer involving both diffusion (with sulfur being the principal equilibrium-determining component due to its lower concentration in the silicate melt compared to iron) and convection (the descent of a sulfide bleb induces convection around it, removing the silicate liquid on the leading or lower side of the droplet). The model simultaneously computes the convective growth rate and the descent velocity at each time step to determine the growth and descent of sulfides. The composition of the sulfide is assumed to be FeS. Magma convection within the magma chamber may influence the movement of individual sulfide droplets. However, because upward flow is counterbalanced by downward flow in a convection cell, the average time for a droplet to sink (as well as its average velocity) would remain relatively constant in the presence of convection within the magma chamber. The vertical temperature gradient within the magma chamber is disregarded. Assuming adiabatic conditions within the magma chamber, the temperature gradient would be approximately 1 K per km (Zhang, 2015, and references therein). The sulfide saturation temperature also exhibits slight dependence on depth, about 3K per km using the equation from Li and Ripley (2009), which can be considered negligible.

Figure 1 : The growth and sinking of a sulfide droplet in a silicate melt. In each panel, the circle represents a spherical sulfide droplet, and the region between the circle and dashed curve represents the compositional boundary layer  $\delta$  (silicate melt) (Zhang, 2015). The heavy solid arrow indicates the falling direction, and the thin dashed arrows indicate mass transfer into the droplet. As it falls from a to b, the droplet grows. A generic single stage exponential cooling history for the magma chamber is assumed (equation 3).  $T_a$  is the ambient temperature (assumed to be 300 K),  $T_0$  is the temperature at which nucleation occurs, and  $\delta$  is the cooling timescale (assumed to be 1,000 years).



The largest uncertainty of the model is the nucleation rate, that is assumed to occur during one single nucleation event leading to  $N$  nuclei per  $m^3$  once the degree of supersaturation reaches  $x$ . The degree of supersaturation  $x$  is defined as equation (4), where  $C$  is the sulfur concentration in the silicate melt and  $S$  is the sulfur solubility in the melt.

The solubility of sulfur in the silicate melt ( $S$ ) is estimated with the model of Li and Ripley (2009) (equation 5), simplified as equation 6 for the case study of magmas from Etna ( $P = 0.5$  GPa, compositions relative to Etna magmas).

From equation (4), given the initial sulfur concentration  $C_0$  and a specified value of  $x$  for nucleation to occur, nucleation occurs at temperature  $T_0$  as written in equation (7).

Given the solubility relation in equation (6) and using equation (7),  $T_0$  can be solved and used in equation (1) for a given value of  $x$ . The nucleus radius is used as the initial radius  $a_0$  of the droplets and is estimated with equation (8), where  $\delta$  is the interface tension between sulfide melt and silicate melt (taken as  $0.5 \text{ N}\cdot\text{m}^{-1}$  in Zhang (2015)),  $\bar{v}$  is the molar volume of an FeS melt, and  $R$  is the universal gas constant.

There are only few studies that constrained the diffusivity of sulfur in silicate melts. More specifically and according to Zhang (2015), there is no general S diffusivity model accounting for the compositional dependence. S diffusivity differs from the Eyring diffusivity model by no more than a factor of 10 for basaltic to andesitic melts, but the difference can be a factor of 106 for rhyolitic melts. Using the experimental data from Freda et al. (2005), sulfur diffusivity in Etna basalt as a function of H<sub>2</sub>O content at 0.5 to 1.0 GPa can be fit by equation (9), where  $D$  is in  $\text{m}^2/\text{s}$ , and  $w$  is H<sub>2</sub>O wt.%.

For estimating the velocity of sinking sulfide blebs, Zhang (2015) used the Stokes equation (2). Because sulfur concentration in the silicate melt is low, meaning that sulfide droplets are typically separated far from each other, coalescence during droplet motion is not considered to be important. The viscosity of magmas in the case of dried Etna magmas is given as a non-Arrhenian function of temperature (equation 10).

The convective growth rate  $u$  is estimated with the equation (11), where  $a$  is the droplet radius,  $\hat{\rho}$  is a compositional parameter and  $\hat{l}$  is the effective thickness of the compositional boundary layer surrounding the droplet.

The compositional parameter  $\hat{\rho}$  is expressed as equation 13, where  $C$  is the mass fraction,  $C_{\text{sulf}}$  is the sulfur concentration in FeS melt (36.47 wt.%),  $C_{\hat{\rho}}$  is the dissolved sulfur concentration in the far-field silicate melt and varies with time, and  $C_{\text{sat}}$  is the sulfur concentration at saturation and depends on the radius of the drop (a small drop has high Gibbs free energy due to  $\delta$  contribution).

Assuming interface equilibrium,  $C_{\text{sat}}$  is the sulfur concentration within the interface silicate melt at  $r = a$  and both can be expressed as equation (14).

$C_{\hat{\rho}}$  decreases with sulfide droplet growth, and is estimated from the initial sulfur concentration minus sulfur that went into sulfide droplets and sulfur deficiency in the boundary layer, as stated in equation (15).  $M_0 = \bar{V}_{\text{sil}}/V_0 = \bar{V}_{\text{sil}}/N$  is the average silicate melt mass per sulfide droplet,  $M_{\text{sulf}} = (4/3)\pi a^3 \bar{V}_{\text{sulf}}$ ,  $C_0$  is the initial sulfur mass fraction in the silicate melt, and  $\Delta M$  is the amount of sulfur depletion in the boundary layer, which is negligible.

These calculations are conducted as follows: time is the varying parameter. For each iteration, the growth rate of sulfide droplets and the settling velocities are calculated. The radius as a function of time is estimated for each iteration by integration of the growth rate. The settling distance as a function of time is calculated by integration of the settling velocity with respect to time.

Prior to adapting this model to the Fatu Kapa magmas, we executed the model for the Dry Etna case outlined in Zhang (2015) (Figure 2). We were able to precisely replicate the calculated temperature at the onset of sulfide saturation, the evolution of sulfide radius over time, and the

progression of settling distance as a function of time.

Figure 2 : Top - The growth and settling of sulfide droplet with time at various degrees of supersaturation  $x$  in the Dry Etna model (Zhang, 2015; Figure 3). Down - Replication of the same model. The calculated radius, temperature at the onset of sulfide saturation, and settling distance accurately match.

We employed the same model and equations for simulating sulfide growth, sulfide velocity, and settling distance in Fatu Kapa magmas. We categorized three scenarios:

1. Basaltic compositions representative of the anhydrous mafic magmas from both groups 1A and 1B(a) (fixed viscosity with  $\log(\hat{\eta}) = 1.45$  Pa.s; first column in Table 1).
2. Andesitic composition representative of the magma from group 1B(a) at the onset of compound drop formation (H<sub>2</sub>O concentration of 2.1 wt.%; fixed viscosity with  $\log(\hat{\eta}) = 2.35$  Pa.s; fourth column in Table 1).
3. Dacitic composition representative of the magma from group 1B(a) where compound drops are identified (H<sub>2</sub>O concentration of 2.1 wt.%; fixed viscosity with  $\log(\hat{\eta}) = 3.51$  Pa.s; fifth column in Table 1).

In contrast to Zhang's (2015) model, we utilized an interface tension between sulfide melt and silicate melt equal to 0.21 N.m<sup>-1</sup>, which aligns more closely with values estimated in natural settings (Mungall et al., 2015; Yao and Mungall, 2020). Similar to Yao and Mungall (2020), we conducted our calculations by setting the degree of supersaturation  $x$  to 0.1 and examined three different initial sulfur concentrations of 800, 1200, and 1600 ppm. For each model, the calculation halts when the sulfide droplet reaches 1 km. This distance corresponds to the typical thickness of crustal magma chambers, which range from 0.1 to 10 km with a median value of 1 km (Marsh, 1989; Zhang, 2015).

The findings are presented in the new Figure 7 of the manuscript and in Figure 3 of this document. An important observation, consistent with Zhang (2015) and Yao and Mungall (2020) findings, is that the radius of sulfide blebs initially increases at a rapid pace. For instance, micrometric sulfide blebs sinking in basaltic magmas with initial sulfur concentrations of 1600 ppm and 800 ppm reach diameters of 300 and 400 micrometers, respectively, within a year (Figure 3.b). Following this transient phase, the size of sulfide blebs evolves more slowly (Figure 3.b), as does the sinking velocity (Figure 3.c). Another key result is that sulfides sink faster in mafic magmas compared to andesitic magmas, reaching a depth of 1 kilometer within approximately ten years in basaltic magmas and around a hundred years in andesitic 1B(a) magmas. In dacitic magmas, the depth of 1 kilometer is reached within 400 to 500 years. The viscosity of magmas exerts greater control over sulfide bleb velocities than the initial sulfur concentration: while varying the initial sulfur concentration for a given viscosity changes the sinking velocity by about 20% once the transient phase is surpassed, the viscosity varies by ~one order of magnitude from basalts to wet andesites, and from wet andesites to wet dacites (Figure 3.c). This sinking velocity is  $\sim 1 \times 10^2$  m/y in dry basalts (initial 1A and 1B(a) magmas),  $\sim 1 \times 10^1$  m/y in wet andesites (1B(a) at the expected onset compound drops formation) and is of  $\sim 2 \times 10^0$  m/y in wet dacites (1B(a) where both simple and multiple compound drops are firmly identified) (summarized in Table 4).

Figure 3 : Size and sinking velocity of isolated magmatic sulfides within Fatu Kapa magmas compared to ascending velocities of compound drops and magmas. a. Histogram depicting the distribution of sulfide bleb diameters observed in the magmas of groups 1A and 1B(a). The proportions of sulfides associated with a bubble for groups 1A and 1B(a) are shown in the inset. b. Mean sulfide droplet radius as a function of time for various initial sulfur concentrations estimated with a model of sulfide growth by diffusion and convection (Zhang, 2015).  $\hat{\eta}$  is the cooling timescale,  $N$  is the initial number density of sulfide nuclei,  $x$  is the degree of supersaturation required to form the sulfide nuclei, and  $\hat{\eta}_{MS}$  is the silicate melt-sulfide surface tension. Magma viscosities are estimated via Giordano (2008). Three initial S concentrations (800 ppm, 1,200 ppm, and 1,600 ppm) relevant to those found in natural systems are considered for basaltic, andesitic and dacitic lavas akin to those found at Fatu Kapa. The model stops when the sulfide bleb reaches 1 km depth. The range of sulfide sizes identified in groups 1A and 1B(a) are outlined by the grey rectangle. c. Velocity versus time for isolated sinking sulfides and for ascending compound drops, compared to the ascending rates of mafic magmas within the crust (redish rectangle, Turner and Costa, 2007) and to the velocities estimated from the mafic-silicic differentiation timescale (Turner and Costa, 2007), assuming a crustal section of 25 km (greenish rectangle). Sulfide sinking velocities are estimated with the same model as in b.

Estimation of the ascending velocity of simple and multiple compound drops

The sulfide-bubble association depicted in Figure 2.b. (manuscript) represents what we term as simple compound drops, wherein one sulfide is associated to one bubble. These simple compound drops exhibit similar sizes of sulfides and bubbles among themselves. The diameter of these bubbles is  $\sim 45 \text{ }\mu\text{m}$ . The sulfides-bubble association shown in Figure 2.d. (manuscript) represents what we refer to as multiple compound drops, where numerous sulfides are associated with one bubble. These bubbles exhibit a larger volume compared to those of single compound drops. In the case of Figure 2.d. (manuscript), this volume is  $\sim 260 \text{ }\mu\text{m}^3$ .

We estimated the densities of simple compound drops within Fatu Kapa magmas by reporting the measured  $\hat{\eta}_{MV}$  angle in the abacus displayed in Yao and Mungall (2020) (see Supplementary

Information 2). These densities fall within the range of 351 and 492 kg.m<sup>-3</sup> (16 densities estimated), and we selected a value of 400 kg.m<sup>-3</sup>. We used the same density for multiple compound drops. In our calculations, we simplified the shape of compound drops by assuming a spherical form with a volume equal to that of the bubble. The velocities are estimated with the Hadamard-Rybczynski version of the Stokes equation (equation 1). In magmas representative of 1B(a) andesites (H<sub>2</sub>O concentration of 2.1 wt.%;  $\log(\hat{\eta}) = 2.35$  Pa.s; fourth column in Table 1), the ascending velocity of simple compound drops is  $\sim 1 \times 10^0$  m/y and that of multiple compound drops is  $\sim 5 \times 10^1$  m/y (Figure 3.c). In magmas representative of 1B(a) dacites (H<sub>2</sub>O concentration of 2.1 wt.%;  $\log(\hat{\eta}) = 3.51$  Pa.s; fifth column in Table 1), the ascending velocity of simple compound drops is  $\sim 2 \times 10^{-1}$  m/y and that of multiple compound drops is  $\sim 5 \times 10^0$  m/y (Figure 3.c).

## Summary

The estimated sinking velocities of isolated sulfides, both when their radius is considered constant and when their radius evolves with sinking, along with the ascending velocities of both simple and multiple compound drops, are summarized in Table 4.

1A (B)	1A (BA)	1A (A)	1Ba (A)	1Ba (D)
WHR(bleb, fixed radius)[m/y]	1E+00	2E-01	3E-02	9E-02
WHR(bleb, evolving radius after transient phase)[m/y]	1E+02	-1E+01	2E+00	
WHR(CD45)[m/y]	-1E+00	-2E-01		
WHR(CD260)[m/y]	-5E+01	-5E+00		

Table 4: Velocities of sulfide sinking (first and second line) and of simple and multiple compound drop flotation (third and fourth line) in Fatu Kapa magmas, expressed in m/y. B: basalt; BA: basalt-andesite; A: andesite; D: dacite; CD45: simple compound drops with a volume of 45  $\mu\text{m}^3$ ; CD260: multiple compound drops with a volume of 260  $\mu\text{m}^3$ . Positive values indicate downward movement, negative values indicate upward movement.

II) Firm and sufficient evidence for demonstrating that the bubble flotation of droplets is necessary for explaining the observations

## Summary of the Heinrich and Connolly's (2022) line of reasoning

In their 2022 paper, Heinrich and Connolly estimated the sinking velocity of sulfide blebs with radii of 10 and 100  $\mu\text{m}$  across various viscosities, achieved by varying melt composition, temperature, and water content. According to these authors, these estimations fall within the observed range of sulfide sizes found in magmatic glass or inclusions in phenocrysts, with an upper limit of approximately 300 micrometers, as determined by modeling sulfide growth through diffusion and convection (referred to as diffusion and coalescence in their paper) as per Yao and Mungall (2020). They juxtaposed these sinking velocities with the ascending velocities of upwelling magmas, estimated using U-Th disequilibria and diffusion speedometers, purportedly representing the entire spectrum of upwelling magma velocities worldwide. These ascending velocities span from 10 to 1000 m/year. They found that the only scenario where sulfide sinking velocities surpass magma upwelling velocities is for sulfides with a size of 100 micrometers in hot basaltic magmas. Consequently, they deduced that sulfide buoyancy facilitated by sulfide attachment to bubbles is not imperative for the transportation of chalcophile elements to the surface, as sulfide blebs are typically entrained within upwelling magmas in most cases.

We believe that two potential flaws are apparent in this line of reasoning. Firstly, the authors assume that each magmatic system on Earth, ranging from mafic to felsic magmas, ascends in the crust at rates exceeding 10 m/year. Secondly, they do not consider the pace at which sulfides are growing (and therefore sinking) in magmatic systems.

## Rates of magma upwelling

Two methodologies are commonly employed to ascertain the timescales and rates of magmatic processes: analysis of short-lived radioactive isotopes (generally within zircons), and diffusion modeling of zoning patterns in minerals. The former approach capitalizes on the fact that the secular equilibrium of U-series isotopes can be disrupted towards disequilibrium by the introduction of U or Th concentrations into the system, typically occurring during partial melting. Conversely, the latter method hinges on the re-equilibration of chemical zonation within crystals, allowing the determination of the onset of zonation. A crucial distinction between these methodologies lies in the timescales they record for magmatic processes within the same magmatic system. Notably, when

considering mafic compositions such as MORB or hotspots, the ages yielded by both chronometers are notably congruent. However, in felsic systems, the ages obtained by these methods often exhibit significant discrepancies. Diffusion-based methods typically record timescales ranging from days to a thousand years, contingent upon the specific system chosen, while U-Th disequilibria-based methods yield timescales spanning from ten thousand to a hundred thousand years (e.g., Figure 4.a). This disparity arises from the differing starting points of these chronometers: the U-Th disequilibrium clock commences at the time of mineral formation (Figure 4.b.A), whereas the diffusion clock initiates when the composition of the overlying silicate melt undergoes substantial changes, typically upon the injection of new batches of mafic magmas into the magmatic chamber (Figure 4.b.B). These injections are commonly regarded as triggers for eruption, thus the age recorded by diffusion methods represents the interval between magma mixing and magma eruption. Consequently, it is advisable to employ the U-Th disequilibrium clock when estimating timescales of magma storage within the crust rather than diffusion speedometers.

The rate of magma ascent determined with the U-Th clock in the Heinrich and Connolly paper (2022) is taken from Turner and Costa (2007). The latter serves as a comprehensive review encompassing various timescales associated with magmatic processes, including magma residence and differentiation times, magma assimilation, magma mixing, pluton remobilization, and magma transport rates. Specifically, the magma transport rates referenced in Heinrich and Connolly's work (2022) for U-Th disequilibrium (Figure 4.c) denote the velocity of magma ascent from reservoirs to the surface. As previously mentioned, these rates are particularly applicable to mafic systems for which storage times within the crust are minimal. However, attempting to correlate sulfide sinking velocities in felsic magmas with these ascent rates may lead to erroneous interpretations, given that initially mafic magmas evolve within magmatic chambers to form felsic magmas. To obtain a more accurate estimate of the average rate at which evolving magmas traverse the crust, from the generation of mafic magma at mantle depths to the eruption of felsic magmas, we utilized the timescale of "mafic-silicic differentiation" provided in the same review paper, which typically spans 30,000 to 50,000 years. Subsequently, we calculated the averaged ascent velocity, considering a crustal section of 25 km. For timescales ranging from 30,000 to 50,000 years, the average ascent velocities of these magmas range between 0.83 m/y to 0.50 m/y.

Figure 4: Timescales of magmatic processes a. Diffusion timescales obtained from different minerals in the high-silica rhyolite of the Bishop Tuff (Costa et al., 2020). A comparison with U-Th ages obtained within zircons is shown. b. Interpretation of difference in time information obtained from radioactive isotope and diffusion clocks in the same mineral (Turner and Costa, 2007). A. The system crystallizes and accumulates minerals for 50,000 years. B. A new batch of magma disrupts cumulates and partially reacts with them, creating a new rim much younger than the core. During this event the diffusion clock starts, and shortly after the magma reaches the surface with the eruption triggered by the new magma income. c. Summary of the timescales determined from radioactive isotopes and from diffusion modelling (Turner and Costa, 2007). The timescales employed by Heinrich and Connolly (2022) to infer magma ascent rates are highlighted in red, while the timescales utilized to determine ascent rates for more silicic systems in our study are denoted in blue.

Rates of sulfide sinking

As discussed in Part I, sulfides originating from nanometric nuclei in lavas grow to sizes exceeding 100 micrometers in both mafic (Yao and Mungall, 2020) and felsic (Part I) magmas within less than one year. Based on these modeling outcomes, it can be asserted with confidence that sulfides ranging from 10 to 100 micrometers, identified in glasses or as inclusions in phenocrysts, formed shortly before the onset of eruption, typically within a span of less than one year. Sulfide sizes approaching ~300 micrometers represent an upper threshold, beyond which the velocity of sulfide sinking stabilizes (Figure 3). To facilitate a meaningful comparison between sulfide sinking velocities and magma ascent rates, it is advisable to conduct diffusion and convection modeling of sulfide growth. If such modeling is unfeasible, applying Stokes equations to sulfide blebs measuring approximately ~300 micrometers would be more pertinent than applying them to sizes of 10 or 100 micrometers, notwithstanding textural evidence.

Fatu Kapa

In Part I, we conducted a model of sulfide growth utilizing diffusion and convection principles across three representative magma types akin to those observed at Fatu Kapa: near-anhydrous basalts (representing the initial magma prior to the evolution of 1A and 1B(a) magmas), wet andesites (representing 1B(a) magmas where compound drops begin to form, according to our geochemical modelling), and wet dacites (representing 1B(a) magmas where compound drops are firmly identified).

In basalts, sulfides exhibit a rapid sinking rate of approximately ~100 m/year. This value intersects with the range of estimated ascent velocities for mafic magmas, suggesting that sulfides likely sink within these magmas. As previously mentioned, the observation that sulfides identified within Fatu Kapa magmas typically display diameters of less than 20 micrometers, yet are expected to exceed 100 micrometers within one year, indicates that the only isolated sulfides identified are those

that formed shortly before eruption. While the presence of phenocrysts in these lavas may theoretically decrease the pace of sulfide sinking, phenocrysts are relatively rare, comprising less than 5% of the basaltic lavas (refer to Table 1 appended to the main manuscript, and Jeanvoine et al. (2021)), thus minimizing the reduction in velocity due to capillarity. In dacites, sulfides sink with a velocity of approximately ~2 m/year, slightly surpassing the estimated ascent velocity of felsic magmas (0.5 to 0.8 m/year), implying that isolated sulfides within dacitic lavas would sink. Given that these dacites are predominantly vitreous, capillarity forces do not impede sulfide sinking. In andesites, sulfides sink at a velocity of approximately ~10 m/year, likely sufficiently high compared to ascending rates of andesitic magmas, which were not explicitly estimated. In Group 1A, these andesitic lavas are porphyritic with minor amounts of phenocrysts (~15%). This may marginally decrease sulfide velocity, but not significantly enough to prevent sulfide sinking. In summary, isolated sulfides identified in basaltic to dacitic Fatu Kapa magmas sink at velocities exceeding those of magma ascent, indicating that the budget of Cu, Au, and other chalcophile elements partitioned into isolated sulfides will not be transported toward the surface due to sulfide settlement.

Multiple compound drops identified in dacites ascend with velocities significantly higher (~5 m/year) than those estimated based on the timescale of magmatic evolution from mafic to felsic lavas (0.5 to 0.8 m/year). Similarly, multiple compound drops anticipated to form in S-saturated and volatile-saturated andesitic magmas are projected to rise at approximately ~50 m/year, in the range of the velocities estimated for mafic magmas (Turner and Costa, 2007), and likely exceeding the ascending velocities of andesitic magmas. Hence, it is physically plausible for multiple compound drops to accumulate at the roof of the magmatic chamber, where they can be readily mobilized by new batches of erupting magmas. Simple compound drops exhibit ascending velocities more than one order of magnitude lower than those estimated for multiple compound drops (~1 m/year and ~0.2 m/year in andesitic and dacitic magmas, respectively). While these simple compound drops are either neutrally buoyant or ascend slowly compared to magma ascent rates, they still facilitate the transport of sulfides towards the surface, thereby preventing sulfide settlement. Moreover, these compound drops are likely to form in regions where S- and volatile supersaturation is more pronounced. Considering that the heat of the magma chamber is primarily lost through the upper part of the reservoir, the degree of supersaturation is likely more pronounced in its upper part, where compound drops are consequently more likely to form.

In conclusion, isolated sulfides within Fatu Kapa magmas sink from basaltic to dacitic compositions, excluding entrainment of sulfides by ascending magmas as a plausible mechanism for bringing Cu-Au-rich sulfides to the surface. Conversely, compound drops formed in andesitic and dacitic lavas either ascend faster than magmas (multiple compound drops) or prevent sulfide sinking by being neutrally buoyant (simple compound drops). This line of argument underscores the necessity of sulfide flotation for explaining the Cu-Au endowment of the associated ore deposits.

III) Detailed discussion of the chemical evolution of sulfide compositions

While there is general consensus that sulfides form through liquation from the silicate melt, and that these sulfide liquids follow the sequence proposed by Reviewer 1 upon cooling, studies examining chalcophile element behavior in magmas have prompted several authors to stress the potential formation of crystalline sulfides alongside sulfide liquids. For instance, the constant Cu/Ag ratio in MORB throughout their evolution has been attributed to the liquation of so-called sulfide liquids, whereas the decreasing ratio in evolved back-arc lavas has been attributed to the formation of crystalline Cu-rich sulfides, such as bornite, with which Cu is more compatible than Ag (Jenner et al., 2010; Jenner et al., 2015).

The distinction between crystalline MSS and Cu-rich sulfide liquids, both formed directly from silicate magma, appears widely accepted among various geochemists. An important study in this framework is the paper published by Li et al. (2021). To investigate chalcophile element behavior in arc magmas, they carried out experimental runs of lavas doped with varying amounts of Cu under conditions relevant to arc magma systems (temperatures ranging between 1200°C and 1000°C,  $fO_2 > 1-1.5$  FMQ, and pressure at 0.5 or 1 GPa). They found that quenched lavas displaying Cu concentrations below approximately 100 ppm host sulfides that comprise a mixture of Cu-rich sulfides and Cu-poor sulfides ("sulfide liquid" and "MSS" in Figure 5.1, respectively), while lavas quenched with Cu concentrations higher than 180 ppm form exclusively Cu-rich sulfide liquids. These authors estimated partition coefficients for these two phases (DSL-SM and DMSS-SM, with SL standing for sulfide liquid, SM for silicate melt and MSS for monosulfide solid solution).

A significant finding in their paper is their ability to replicate the trend in chalcophile elements in both thin (intra-oceanic subduction, crustal thickness <20 km) and thick (ocean-continent subduction, crustal thickness >30 km) arc magmas by considering different proportions of "precipitated" (sic) sulfide liquid and crystalline MSS (please note that they consider magmatic temperatures higher than 1000°C, so we are not placed in the scenario described by Reviewer 1 where MSS may be expected to crystallize directly from the silicate melt). The main distinction between these two settings is that sulfide saturation occurs later in intra-oceanic subductions, allowing magmas to reach Cu

concentrations of approximately ~250 ppm at the onset of sulfide saturation (Figure 5.3), whereas the Cu concentration at the onset of sulfide saturation in ocean-continent subductions is below 90 ppm. In alignment with their experimental results (Figure 5.2), the main disparity between their models lies in the SL:MSS proportion, ranging from 50:50 to 90:10 in intra-oceanic subductions (Figure 5.3), while for ocean-continent subductions, this proportion ranges from 20:80 to 0:100 (see their Figures 7 and 8). These results concur with natural observations. For example, Costa et al. (2021a) demonstrated that magmas from La Fossa (Italy, thin crust) have a Cu concentration of approximately ~250 ppm at the onset of sulfide saturation and provided textural evidence that the sulfide melt contains 34-66 wt.% Cu. The Cu concentration of the silicate melt after sulfide saturation decreases significantly below 100 ppm. Subsequently, Cu concentrations decrease more gradually, and the identified sulfide phase is primarily MSS (pyrrhotite). A marked decline in Pd and Rh accompanies the Cu drop (Costa et al., 2021b), attributed to the formation of Cu-rich sulfides, after which these PGE fall below the detection limit.

Figure 5 : Selected figures from Li et al. (2021). In their study, the authors explore the notion that both crystalline MSS and sulfide liquids are precipitated (sic) from magmas. They present an experimental study where starting material are doped with varying Cu concentrations and heated under conditions relevant to arc systems (T ranging between 1200°C and 1000°C,  $fO_2 > 1-1.5$  FMQ, P = 0.5 or 1 GPa). 1. Coexistence of crystalline MSS with Cu-rich sulfide liquid (run at 1200°C, 1GPa, doped with moderate amounts of Cu) (Figure 1.c of Li et al. (2021)). 2. Type of precipitating Fe-Cu-S sulfide as a function of the Cu content of the silicate melt (Figure 6 of Li et al. (2021)). Below 100 ppm, the precipitated sulfides are a mixture of crystalline MSS and of Cu-rich sulfide liquids, akin to the sulfide shown in 1. Above this threshold, sulfides consist solely of Cu-rich sulfide liquids. 3. Modelling the evolution of Cu in intra-oceanic arc magmas (thin crust, <20 km) with Cu partitioning in a mixture of sulfide liquids (SL) and crystalline MSS (Figure 7.c of Li et al. (2021)). The partition coefficients are those determined after laser ablation of the sulfide liquid, MSS and silicate melt phases (pits in the sulfide shown in 1.).

In the context of Fatu Kapa lavas, we observed a similar behavior in Cu and Pd concentrations as observed in La Fossa magmas, with a few notable distinctions. Firstly, sulfide saturation occurs earlier in Fatu Kapa lavas, at 7 wt.% MgO compared to 2 wt.% MgO at La Fossa. Secondly, unlike La Fossa magmas, Pd concentrations in Fatu Kapa lavas are not below the detection limit, allowing for an assessment of its behavior, which, like Cu, decreases more gradually with further magmatic evolution. Importantly, the Cu content of Fatu Kapa lavas at the onset of sulfide saturation is close to 150 ppm. Consequently, we developed a model akin to the one proposed by Li et al. (2021) for intra-oceanic magmas. Initially, the SL:MSS proportions are approximately 90:10 at the onset of sulfide saturation, then transitioning to around 10:90 thereafter. We used the partition coefficients calculated by Li et al. (2021) for Cu, Pb, and Zn for these two phases. Additionally, for Pd, we used a partition coefficient of 8,000 for the "SL" phase and a coefficient equal to 20% of this value for the "precipitated" MSS (Liu and Brenan, 2015). This model successfully replicates the Cu and Pd concentrations of group 1A magmas, as well as those of group 1B(a) magmas when accounting for aqueous fluid formation.

After reading the paper of Ripley et al. (2002), it is our contention that what Li et al. (2021) referred to as "Sulfide Liquid" likely corresponds to sulfide liquids within the CuS system, whereas their designation of "crystalline MSS" probably represents sulfide liquids within the FeS system (Table 5). In both instances, these sulfides are liquified from the silicate melt, as evidenced by the spherical morphology of sulfides containing both FeS and CuS systems in the experimental runs (e.g., Figure 5.1). Therefore, the sulfide evolution model proposed by Li et al. (2021) for thin and thick arc systems is likely accurate, albeit with the clarification that FeS sulfide liquids rather than crystalline MSS are formed. Consequently, the estimated partition coefficients for these two phases are likely accurate once the phases are appropriately named.

In conclusion, our study suggests that the two-stage behavior observed in Pd and Cu concentrations within Fatu Kapa magmas indicates an initial saturation in the CuS system for Cu-rich (>100 ppm) lavas. While we did not directly observe these sulfides, these are not unexpected given the narrow range of evolution during which these Cu-rich sulfides form. Subsequently, once Cu concentrations reach approximately ~100 ppm, the sulfide phase predominantly liquefies within the FeS system, as evidenced by our textural observations indicating that sulfides identified at this stage are primarily composed of pyrrhotite upon cooling. It is important to note that the two-stage evolution of Pd (and to a lower extent Cu) can only be elucidated if a shift in the composition of the liquefied sulfide phase is considered. We believe that our chemical modeling remains valid with only adjustments to reference "sulfide liquids" as "sulfide liquids in the CuS system" and "MSS" as "sulfide liquid in the FeS system" (Table 5). However, we sincerely welcome the opportunity for detailed discussions and remain entirely open to making any adjustments that the reviewers may deem necessary.

How we called the phase in our manuscript What it actually is  
Sulfide liquid (when Pd drops significantly) Sulfide liquid in the CuS system (Ripley et al.,

2002) (attested by the Pd drop, but not identified tecturally).

MSS (when Pd decreases more gently) Sulfide liquid in the FeS system.

Table 5: Changes in the main manuscript related to chemical evolution of magmatic sulfides.

IV) Justification of the claims of novelty in the observations of droplet-bubble pairs given previous observations

In experimental studies, sulfide-bubble compound drops have been observed directly within silicate liquid, with neither sulfide nor aqueous fluid bubble phases being significantly modified by secondary processes such as sulfide dissolution, bubble infilling by silicate liquid or bubble shrinkage (Figure 6.a.b). We examined the occurrences of sulfide-bubble compound drops found in natural settings (Figure 6, Table 6) and classified these into three distinct subgroups.

The first subgroup encompasses sulfide-aqueous fluid bubbles confined within inclusions, exemplified by those observed in lavas originating from the Merapi Volcano (Indonesia) (Nadeau et al., 2010) (Figure 6.c) and The Pleiades Volcanic Field (Antarctica) (Kim et al., 2023) (Figure 6.d). In the case of Merapi, sulfides associated with bubbles exhibit a range of dissolution degrees, from slight to significant, reaching up to 80% of the initial sulfide volume. Notably, this stands as a singular example where such compound droplets are formed from felsic lavas, owing to the high silica content (61-72 wt.% SiO<sub>2</sub> anhydrous) of silicate melt inclusions co-trapped with the compound droplets. Conversely, sulfides within The Pleiades samples appear well-preserved based on visual observations from the figures presented. Due to their entrapment within inclusions, an accurate estimation of the original compound droplet density remains elusive, given the accompanying bubble shrinkage during entrapment.

The second subgroup comprises sulfide occurrences associated with carbonates, discernible within mantle xenoliths or mineral assemblages characteristic of the lower and middle crust (Blanks et al., 2020) (Figure 6.e.f.g). The presence of carbonates is interpreted as vestiges of aqueous fluid bubbles, with carbon dioxide prevailing as the primary volatile species at these depths. Although the quantity of carbonates affiliated with sulfides within mantle xenoliths suggests the potential positive buoyancy of compound droplets, the sparse presence of carbonates alongside sulfides within lower to middle crust assemblages precludes such a deduction. Here again, accurate density estimations of primary compound droplets remain elusive, owing to secondary modifications including bubble shrinkage and carbonate precipitation.

The third example comprises sulfides associated with intercumulus voids that are partially to fully infilled with crystallization products of highly fractionated silicate liquids (silica caps) and/or amygdaloidal linings including for instance anhydrite or calcite (Figure 6.h.i.j.k.l.m) (Keele and Nickel, 1974; Prichard et al., 2004; Stone et al., 1996; Hill et al., 2004; Barnes et al., 2009; Holwell et al., 2012; Le Vaillant et al., 2017; Barnes et al., 2019). These silica caps are interpreted as aqueous fluid bubbles that became infilled with late-stage silicate liquids (Le Vaillant et al., 2017; Barnes et al., 2019) due to pressure increase during solidification coupled with gas filter pressing (Barnes et al., 2019). The association of sulfides with fractionated products have been observed between cumulate crystals formed from the Norilsk-Talnakh flood basalts (Russia) (Le Vaillant et al., 2017; Barnes et al., 2019), between the grains of doleritic dyke margins (Prichard et al., 2004; Holwell et al., 2012), and between cumulate crystals formed from komatiitic flows (Keele and Nickel, 1974; Hill et al., 2004; Barnes et al., 2009) (except for Fredâ Flow (Australia), where this association is found in the silicate liquid between olivine and clinopyroxene crystals (Stone et al., 1996)). Either engulfing of sulfides within the void space or bubble flattening due to increasing pressure within the cumulate preclude accurate density estimations.

Below are the full sentences we've composed regarding the prior identifications of bubble-sulfide pairs that pertain to our observations.

Line 419: "To the best of our knowledge, our study provides the first evidence in a natural setting that floating sulfide-bubble compound drops can form in a magma saturated with both sulfides and volatiles (Mungall et al., 2015; Yao and Mungall, 2020)."

Line 46: "Accordingly, sulfide-bubble compound drops observed in natural settings are either preserved in inclusions (Nadeau et al., 2010; Kim et al., 2023) or significantly altered within silicate liquids or xenoliths. In the latter case, silica spherules and carbonates associated with sulfides have been interpreted as H<sub>2</sub>O-rich bubbles pierced by silicate liquids (Le Vaillant et al., 2017; Iacono-Marziano, 2022), and bubbles from which CO<sub>2</sub>-rich supercritical fluids have sublimated (Blanks et al., 2020), respectively. Limited observations of sulfide-bubble associations in natural settings make it challenging to determine whether sulfide flotation is a viable process for transferring metals from magmas to the surface."

The sentence on Line 419 came across as too assertive. Our intention was not to suggest that the association between sulfides and bubbles had never been observed before. Rather, we aimed to convey that previous observations hindered the calculation of compound drop densities, hindering

our understanding of whether flotation serves as a viable mechanism for transporting Cu and Au from magmas to ore deposits (Line 46). We believe that what makes the sulfide-bubble association found at Fatu Kapa (Figure 2.b of the main manuscript) particularly valuable for the scientific community is its resemblance to those produced by the experimental runs of Mungall et al. (2015) (Figure 6.a of this report) and later by Iacono-Marziano (2022) (Figure 6.b of this report). Specifically, this association is directly observed in the silicate liquid, unlike previous examples where it was identified in phenocryst inclusions (Figure 6.c.d) (Nadeau et al., 2010; Kim et al., 2023), between crystals forming the cumulate pile in volcanic examples (Keele and Nickel, 1974; Stone et al., 1996; Hill et al., 2004; Barnes et al., 2009; Le Vaillant et al., 2017; Barnes et al., 2019) (Figure 6.h.k.l.m of this report), or within crustal joints for doleritic dyke assemblages (Prichard et al., 2004; Holwell et al., 2012) (Figure 6.i.j of this report). The only exception is Fredâs Flow (Australia) (Stone et al., 1996), where amygdules are found within a basaltic flow and, to a lesser extent, within a komatiitic flow. As pointed out by Reviewer 1, an important missing aspect of our initial manuscript was the physical consideration of the flotation process (see Part I and Part II). We acknowledge that estimating the density of sulfide-bubble aggregates previously identified in natural settings is impossible due to shrinkage and/or flattening of the primary bubble resulting from its entrapment within or between phenocrysts formed by fractional crystallization. In contrast, the unique identification of unmodified compound drops after their formation allows for the estimation of their density, which is crucial for discussing arguments presented in the paper by Heinrich and Connolly (see Part II and Figure 3 of this report).

We believe that another crucial point, valuable for the scientific community, is the comparison between groups 1A and 1B(a) regarding the association of sulfides with aqueous fluid bubbles. Our findings reveal that in group 1A magmas, which are S-saturated and volatile unsaturated, only a small percentage of sulfides are associated with aqueous fluid bubbles (only 24%, see inset of Figure 3.a). Conversely, in group 1B(a) lavas, which are both S-saturated and volatile saturated, sulfides are systematically associated with aqueous fluid bubbles (87%, see inset of Figure 3.a). To the best of our knowledge, previous studies displaying examples of remnant compound drops did not consider the point in the magmatic evolution at which the magma became S- and volatile-saturated. This aspect is important because in numerous geochemically oriented papers, the timing of S-saturation relative to the timing of volatile saturation is examined to assess the fertility of magmas. In these papers, which often pay less attention to physical processes, it is commonly assumed that if volatile exsolution occurs before the liquation of dense sinking sulfides, then chalcophile elements will primarily partition into aqueous fluids and ultimately contribute to the endowment of ore deposits. Through geochemical modeling, textural observations, and insights from reviewers, we demonstrate that sulfide flotation occurs quantitatively (i.e., most sulfides are associated with bubbles, as evidenced texturally) when a magma, not overly viscous, is both S- and volatile saturated. This is the point we intended to convey, albeit clumsily, at Line 419 ("To the best of our knowledge, our study provides the first evidence in a natural setting that floating sulfide-bubble compound drops can form in a magma saturated with both sulfides and volatiles"), and we would like to apologize for any misunderstanding.

In conclusion, we want to clarify that our intention was not to suggest that the sulfide-bubble association had never been observed in natural settings (although we realize that our wording may have conveyed that impression). Rather, we aimed to emphasize that unlike previous observations, sulfide-bubble associations are directly identified within the silicate liquid. Furthermore, we highlight that this association is systematically observed when magmas are both S-saturated and volatile-saturated. One of the most notable observations is the striking similarity between experimental runs and well-preserved sulfide-bubble aggregates. This preservation can be attributed to the short path traveled by the aggregates toward the surface and the vitreous nature of the dacitic magmas, resulting in minimal capillary forces exerted on the aggregates.

Location Geological Host phases Magmatic Secondary modifications  
setting composition

Patagonia, Subcontinental Mantle Ultramafic to Sulfides associated with few  
Kimberly (South lithosphere xenoliths, mafic amounts of calcites. Calcites are  
Africa), Vulture (mantle, lower sulfides within interpreted as the remnant of  
(Italy), Valmaggia crust, middle plutonic rocks aqueous fluid-rich bubbles for  
(Switzerland), crust) which the dominant volatile

Sron Garbh species at these depths is CO<sub>2</sub>.

(Scotland), The structure of the compound

Mordor drop is not visible.

(Australia)

(Blanks et al.,

2020)

Merapi Volcano Intra-oceanic Amphibole Mafic to Sulfide are variably dissolved (up

(Indonesia) arc (upper megacrysts felsic melt to 90%) as result of sulfide

(Nadeau et al., crust) inclusions interaction with trapped aqueous

2010) fluid pockets in the megacrysts.



The Pleiades Continental Enclaves within Mafic to -  
 Volcanic Field intraplate kaersutite intermediate  
 (Antarctica) (Kim volcanic system diorites + other  
 et al., 2023) phenocrysts  
 (e.g., augite  
 phenocryst)  
 Norilâsk (Russia) Flood basalt Between Mafic Capped globules: a sulfide globule  
 Le Vaillant et al. primocrysts of with a silica cap. Sulfide attached  
 (2017); Barnes et silicate minerals to bubbles deposited at the  
 al. (2019) forming the cumulus stage and aqueous fluid  
 cumulate pile bubbles get filled by silicate lavas  
 (olivine due to increasing cumulate  
 orthocumulate) pressure to form the silica cap  
 resulting in both bubble  
 shrinkage and gas filter pressing.  
 Kangerlussuaq Dolerite dike Between the Mafic Capped globules similar to those  
 (East Greenland) grains of a observed in Norilâsk magmas.  
 (Holwell et al., doleritic gabbro  
 2012)  
 Uruguayan dike Andesitic dike Between Mafic Capped globules similar to those  
 swarm (Prichard plagioclases and observed in Norilâsk magmas.  
 et al., 2004) clinopyroxenes  
 Black Swan Komatiitic body Cumulate Ultramafic Capped globules similar to those  
 (Barnes et al., (serpentinized observed in Norilâsk magmas.  
 2009; Hill et al., olivine)  
 2004)  
 Otter Shoot Komatiitic body In serpentine- Ultramafic Capped globules similar to those  
 (Kambalda, talc-carbonate observed in Norilâsk magmas.  
 Western host rock Significant exogen alteration.  
 Australia) (Keele  
 and Nickel, 1974)  
 Dundonald Komatiitic body ? (we only found Ultramafic ? Probably capped globules  
 komatiite an abstract similar to those observed in  
 (Eckstrand and related to a Norilâsk magmas.  
 Williamson, 1985) conference for  
 this study)  
 Fredâs Flow Komatiitic and In basaltic flows Mafic Capped globules similar to those  
 (Ontario, Canada) basaltic flow that seems to be observed in Norilâsk magmas.  
 (Stone et al., porphyritic  
 1996)

Table 6: Location, geological setting, host phase, magmatic composition and secondary modification of sulfide-bubble compound drops previously identified within natural magmas.

Figure 6 : Comparison between sulfide-bubble associations formed in the silicate liquid during experimental runs with sulfide-aqueous fluid bubbles trapped in silicate minerals (light gray), sulfide-carbonate associations interpreted as remnant compound drops for which the dominant volatile species was CO<sub>2</sub> (gray), and capped sulfides that formed through filling of the aqueous fluid-bubble by gas-filtering (dark gray) found in natural settings. a. Experimental run from Mungall et al. (2015); b. Experimental run from Iacono-Marziano et al. (2022); c. Sulfide-bubble compound drop associated with a mafic lava in an amphibole megacryst from the Merapi volcano (Indonesia) (Nadeau et al., 2010). d. Heterogeneous inclusion hosted in an augite phenocryst of basanite from The Pleiades Volcanic Field (Antarctica) (Kim et al., 2023). e. Sulfide-carbonate pool in a mantle xenolith from Kimberly (South Africa) (Blanks et al., 2020); f. Sulfide-carbonate association found in a mineralogical assemblage representative of the lower crust found at Valmaggia (Switzerland) (Blanks et al., 2020); g. Sulfide-carbonate assemblage found in a mineralogical assemblage representative of the middle crust found at Mordor (Australia) (Blanks et al., 2020); h. Tornado XRF map of a silica cap in an olivine orthocumulate from Norilâsk (Russia) (Barnes et al., 2019). i. Silica cap between the grains of a doleritic gabbro from a dike at Kangerlussuaq (Greenland) (Holwell et al., 2012); j. Silica cap between plagioclases and clinopyroxenes in an andesitic dike (Uruguay) (Prichard et al., 2004); k. Silica cap in a komatiitic olivine orthocumulate from Black Swan (Barnes et al., 2019); l. Silica caps in komatiitic serpentine-talc-carbonate olivine cumulate from Otter Shoot (Australia); sulfides are in white and silicates in light to dark gray (Keel and Nickel, 1974); m. Sulfide associated with an amygdale mainly made of chlorite within a basaltic magma from Fredâs Flow (Ontario, Canada) (Stone et al., 1996).

Figure 6 (continued).  
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Best regards,

Carolina Ortiz Guerrero, Ph.D.  
Associate Editor  
Communications Earth & Environment

#### REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

I'm satisfied you've given careful consideration to the points I raised and I can't see the need to delay this any further. Well done.

Reviewer #2 (Remarks to the Author):

This revised manuscript is excellent. The authors have satisfactorily addressed all reviewer comments. I recommend accepting this revised manuscript for publication.

Adam Simon

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Author Rebuttal letter:

Title. Author responses for the manuscript titled "The flotation of magmatic sulfides transfers Cu-Au from magmas to seafloor massive sulfide deposits"

Reviewer comments :

Reviewer #1 (Remarks to the Author):

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Adam Simon

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