

Response to Referee#2- Jonathan Naden

*Comments by the reviewers have been indicated with **black***

*Replies by the authors have been indicated with **blue***

*Changes by authors have been indicated with **red***

Answers to General comments

Comment: it is not clear how the modelled sulfide inclusion compositions (Table 2), which all subsequent discussion and conclusions are based on, are derived from the primary analytical data. Fig. 4 shows that the analysed sulfide inclusions are heterogeneous and comprise multiple phases. In addition, other than “The reconstruction of the bulk sulphide composition was based on area (%) of mineral modal abundances calculated by an image analysis software (ImageJ©1.38) and on EPMA analysis” [from the supplementary information], there is no description as to how this heterogeneity is accounted for in Table 2. Furthermore, a single microprobe analysis will only be a sub sample of the bulk composition and will be heavily reliant on the area selected for analysis, for example, in Fig 4. vi, dependent on placement of the EPMA beam, it is possible to get a range of “sulfide melt” analyses from a pure pyrrhotite to almost a pure chalcopyrite. The authors don’t state how the EPMA analyses of the sulfide droplets were undertaken – for example, do the reported data represent a single point, or are they the “best attempt” at ascertaining the bulk composition of the sulfide droplet?. I don’t feel that the methodology as described in the paper and the supplementary materials is sufficient. The authors need to be more critical of the limitations of the methodological approach. The statement [lines 242-244] “One could question that this approach may yield biased results (because of cut effects and crystal orientation), but averaged out over a large number of sulphides we think we obtain a significant first-order estimate.” is not really adequate to address the somewhat complex problem that original sulfide melts have now crystallised, are now heterogeneous and it is not clear what the EPMA analyses represent. Also, estimating the composition from the area occupied by mineral phases will be dependent on the section that is cut through the sulfide droplet – there are methods, such as stereology, to enable 3D volumes to be calculated from 2D sections –the authors do not state if these are appropriate or used, and if they are not appropriate, then how they justify their approach...I think the above criticism can be dealt with by some clear worked examples of how the sulfide droplet compositions were modelled as supplementary information plus a more in depth critique of the limitations of the method in the main text. The sulfide droplet samples depicted in Fig. 4 would be good cases for worked examples and would link the supplementary information directly to the main text.

Reply: Thank you for the extended explanation and for your recommendations. We agree with the referee regarding the existing analytical limitations when it comes to analysing multiphase sulfide inclusions. We have separated our answer in three parts, on the EPMA analysis, on the ImageJ-modal abundances and on the bulk area reconstruction;

EPMA analysis: Each EPMA value reported in this study (Tab.1 of the main text, Tab.4 in doi:10.6084/m9.Figshare.8230787, Figs.7 and 8) corresponds to a single analysis point of a single mineral phase composing a sulfide inclusion. Only sulfide phases that were big enough ($>2\ \mu\text{m}$, which is the maximum excitation volume of the EPMA beam) were analysed, making sure the beam was carefully placed on a single mineral phase. Since in some cases, as the referee has well pointed out, some of the mineral phases composing an inclusion were too small ($<2\ \mu\text{m}$) and did not result in reliable EPMA values, in Tab.1 and Fig.8 we have also added the petrographic observation indicating the type of sulphide analysed. We also agree with the referee that in some cases a measurement corresponds to a range of composition (see line 232) between for example chalcopyrite and pyrrhotite, this however it is not an analytical artefact but rather the result of a solid solution phase as seen in Fig.7a.

Change: We have inserted additional details as requested in the EPMA methodology part of the supplementary material. In addition we added the common mineral phase's stoichiometry in Fig.8 in order for the readers to make easier the connection as well as in Fig.10 as requested by the referee#1.

ImageJ modal abundances: We agree with the referee's comment ('estimating the composition from the area occupied by mineral phases will be dependent on the section that is cut through the sulfide droplet – there are methods, such as stereology, to enable 3D volumes to be calculated from 2D sections') and this is what we meant by stating in line 268 the comment 'One could question that this approach may yield biased results (because of cut effects and crystal orientation), but averaged out over a large number of sulphides we think we obtain a significant first-order estimate that cutting and crystal orientation can indeed affect the results'.

As mentioned in line 473, this method has been applied before by Nadeau et al., 2010 (investigating the Merapi volcano) on 5 sulfides resulting in mss and iss proportions of 81 ± 7 and 19 ± 7 , respectively. In addition, Chang et al., 2018 while investigating what seems to be Type-2 sulfides (in arc magmas of Santa Rita and Cherillos/New Mexico), their LA-ICP-MS results indicate that the more Cu-rich/iss mineral phases take less than/equal to 20 vol% relative to the Cu-poor/mss. Finally and even though this is a more qualitative information the review written by Parat et al., 2011, states that the mss is more abundant than the iss.

Our results agree with the results mentioned above. In this study a total of 163 sulfides were processed by ImageJ of which 126 (Kula=25, Itecktepe=16, Elmadag=10, Beydagi=15, Konya=25, Ecuador=35) were classified as Type-2 sulfides corresponding to different study areas. All areas revealed very similar if not the same relative proportions of mss and iss. As stated in lines 251-254: 'The mss area % ($=\text{mss}/(\text{mss}+\text{iss}) \times 100$) and the 2 standard error for each study area are as follows: Kula (82.0 ± 7.4 %), Itecktepe (84.8 ± 4.9 %), Elmadag (86.9 ± 4.8 %), Beydagi (86.9 ± 3.2 %), Konya (88.1 ± 2.6 %)' . Ecuador gave similar results with the mss area % being 82.0 ± 4.8 . In total 126 Type-2 sulfides present relative proportions of mss= 84.2 and iss=15.7 with $2\text{se}=\pm 2.2$.

For details on the role of ImageJ for the bulk reconstruction please see our answer below.

Change: We have extended the methodology part of ImageJ of the supplementary material, where we also added the result of Nadeau et al., 2010 and Chang et al, 2018.

Bulk area composition: We are aware that EPMA mineral analysis will not give representative bulk (volume) metal contents compared to LA-ICP-MS analysis. However considering that the majority of the sulfide inclusions are hosted by magnetite/opaque mineral phase, a method like LA-ICP-MS, which targets uncovered/not exposed sulfides in transparent minerals wouldn't be applicable. For this reason in this study we have combined the ImageJ area (%) results weighed by the EPMA (wt%) contents in an attempt to best quantify the bulk area composition of the sulfides. This method has been applied before by Greau et al., 2013 working on sulfides in eclogites (Roberts Victor/South Africa) and by Shaw, 1997 working on sulfides in mantle xenoliths (West Eifel volcanics/Germany). For the cases where one of the mineral phases composing the sulfide inclusion was smaller than $2 \mu\text{m}$ and a reliable EPMA value could not be obtained an SEM value was used instead in order to get a qualitative information on the metal contents. These SEM values used in this study correspond only to 9 sulphides and had only been used for Fig.7c, which after Referee's #1 recommendation, we have removed the values from the graph and in the bulk area reconstruction in Tab.2 and Fig.10.

Change: We have inserted an extensive explanation on the bulk area reconstruction of the supplementary material, adding also examples with microphotographs from Fig.4 as suggested by the referee as well as the references of the two mentioned studies applying the same technique (Greau's et al., 2013 and Shaw, 1997).

General comments on style and English usage

We have asked from a third person (native English speaker) to check the manuscript and correct any possible mistakes we may have missed. We have made the corrections with 'track changes' mode on.

Comment: The correct IUAPC spelling of “sulphides” is “sulfides” – see: <https://www.nature.com/articles/nchem.301>. Please amend throughout.

Reply: Thank you for this comment.

Change: We have corrected the “ph” in sulphides by “f”, which now reads sulfides.

Comment: Check capitalisation of Fig, Figure etc. these are used inconsistently. Make sure that “figure” or “fig.” are in the correct format for the journal – usually they are capitalized and “fig.” always has a full stop to indicate an abbreviation. The same applies for the usage of “tab.” and “table”.

Reply: We have checked the journal’s instruction for author and we have changed accordingly.

Change: We have capitalised “figure” and “fig.” as well as “tab.” and “table”.

Comment: It would be useful in the methods section or supplementary material to state what the criteria for magmatic sulfides are, this is an open source publication and this type of information will be valuable for readers who wish to undertake similar studies.

Reply: Thank you for the recommendation.

Change: We have added in Supplementary 2 (below the analytical methods) a section with the criteria for distinguishing magmatic to hydrothermal sulfides as well as some microphotographs as examples for each case.

Comment: In the text abbreviations for the sulfides are used e.g. pn, po etc – write out in full throughout. Think about having “Type X” being always capitalized – it makes it easier for the reader to see what is being written about – you have classified something so consider making it a proper noun – A proper noun is the name of a particular person, place, organization, or thing. Proper nouns begin with a capital letter. I realise this is a stylistic preference so not necessary to correct.

Reply: Thank you for the observation.

Changes: We have written in full all mineral names within the text and only left the abbreviations (with their explanation) in two points:

-lines 294-307 where it is easier for the reader to read the paragraph and follow the sulfide evolution with decreasing temperatures through all ternary graphs without looking at the legend

-and at the legend of Figure 4, in order for the reader to understand the inscriptions on the microphotographs.

We have also capitalised “Type X” throughout the text.

Comment: Abbreviations used inconsistently. Once defined they are sometimes used in full instead of using the abbreviation e.g. the Konya volcanic belt – I don’t think it is necessary to use abbreviations such as these, and using the full name helps the reader as they don’t have to refer

backwards to see what the abbreviation refers to. The saving on space using abbreviations is minimal and use in full is preferred except for commonly understood abbreviations e.g. EPMA.

Reply: Thank you for the suggestion.

Change: We have checked the text and corrected for inconsistency regarding the usage of abbreviations, including the Konya volcanic belt-KVB, chalcophile siderophile elements-CSE and mineral names (e.g. chalcopyrite-cp).

Answers to Specific comments

The comments/answers below have been also posted directly on the main text of the manuscript. In addition all specific comments realised by Referee#2-Jonathan Naden suggesting or correcting; spelling mistakes, writing style and English usage, have been accepted and corrected directly in the main text.

Comment/Line 70/Now reads 78: Why is this threefold approach important?

Reply: The comment refers to a paragraph that read,

“Contrary to the majority of previous studies, here (i) we do not focus explicitly on transparent/semi-transparent sulfide host minerals, (ii) we do not work with mineral separates, and (iii) we investigate uncovered sulfides. These three factors allow us to include the study of opaque minerals (e.g. magnetite) as hosts of magmatic sulfides and maintain the textural relations not only between the sulfide, its host mineral and the surrounding minerals but also within the sulfide inclusion itself. ”

Although for primitive rocks magnetite does not seem to be the main sulfide host phase (e.g. MORB-Keith et al., 2017, Savelyev et al., 2018, Zelenski et al., 2017) the importance of magnetite for sulfide saturation has been proven in terms of bulk rock geochemistry (‘magnetite crisis’-Jenner et al., 2010). Therefore and since in our study we include a wide range of SiO₂ (basalts to dacites) we consider this approach is very important because these three factors allow us to include sulfides hosted by magnetite (which has been previously noted to be the major sulfide host phase in intermediate-felsic rocks, see line 52-Georgatou et al., 2018) while still maintaining the textural relations. As we mention in line 345, most past studies focus in transparent/silicate sulfide host phases in order to be able to analyse them by LA-ICP-MS, failing to include however magnetite.

Change: We have re-phrased in order to show more clearly the importance of this approach as follows,

‘Compared to the majority of previous studies, focusing only on uncovered sulfides hosted in transparent/semi-transparent host minerals, by investigating uncovered sulfides we include opaque host minerals (e.g. magnetite, which was a major sulfide host phase for the case of Ecuador: Georgatou et al., 2018) while maintaining the textural relations not only between the sulfide, its host mineral and the surrounding minerals but also within the sulfide inclusion itself.’.

Comment/Line 210/Now reads 512: How much of this compositional variability is due to the analysis of multiple phases? E.g., the electron beam excites a phase beneath the surface being analysed. For example, in Fig 4x it would be very difficult to analyse bornite without incorporating some signal from chalcopyrite.

Reply: Thank you for the observation. In terms of our use of the analytical precision of the EPMA please see our answer to the first general comment. Indeed for the case of Fig.4x it was not possible to obtain a reliable EPMA value that only accounted for one individual mineral phase composing the sulfide inclusion. More specifically the metal EPMA contents (wt %) were equal to; S=27.01,

Cu=57.56, Fe=16.23 and As=0.03 whereas the SEM gave for chalcopyrite, S=20.68, Cu=50.63, Fe=28.68, for bornite S=16.32, Cu=67.13, Fe=16.55 and for digenite, S=15.92, Cu=73.57, Fe=10.51. However other Type-4 sulphides were composed of larger mineral phases making it possible to analyse them by EPMA. Please see example of Fig.6e where the damage/size of the beam can be seen on the surface of the mineral after the analysis, as well as the new examples and sulfide microphotographs in table 5 of supplementary material B.

Considering the information mentioned above, the Ni/Cu variability is not an artefact of mixed EPMA signals but it rather corresponds to the different proportions of Ni-rich/Cu-poor/mss phases relative to Ni-poor/Cu-rich/iss phases composing a sulfide inclusion which change with magmatic evolution. Starting with Type-1 sulfides hosted in olivine of the most mafic suite being mss-rich, switching to Type-2 sulfides, hosted by both silicate and oxide minerals, composed of more mss than iss and finally to Type-3 and 4 sulfides hosted only by magnetite and corresponding to more felsic rock suites. The same trend has been observed by other researchers (e.g. Hattori, 1999, Du et al., 2014, Keith et al., 2017, Savelyev et al., 2018) as mentioned in line 342.

Change: We have added a section in the end of Supplementary 2 discussing the limitations of the methods. In addition as already mentioned above as a change for the first general of Referee#1, we have inserted additional details as requested in the EPMA methodology part of the supplementary material. In addition we added the common mineral phase's stoichiometry in Fig.8 in order for the readers to make easier the connection as well as in Fig.10 as requested by the referee#1.

Comment/Line 224/Now reads 245: “detection limits” not “determination limits”?

Reply: Most studies show indeed detection limits, however we find more precise to show determination limits since a value resulting over the detection limit does not necessarily mean that it can be quantified. Only values above both detection and determination limits have been used in this study.

Comment/Line 391/Now reads 430: Reference for the Inlice deposit?

Reply: Thank you for the observation, the sentence was not clearly written.

Change: After a comment from Referee#1 on the same paragraph we have removed the sentence as requested.

Comment/Line 394/Now reads 512: The use of “remarkable” is hyperbole in this context, please rewrite this sentence in more circumspect terms.

Reply: Thank you.

Change: We have replaced ‘remarkable’ by ‘noteworthy’ and have rephrased as requested.

Comment/Line 428/Now reads 461: If you can’t “test the hypothesis in the present study” then it shouldn’t be discussed as it is speculation. Please remove this paragraph and any subsequent discussion that is based on it.

Reply: We consider important to still mention the hypothesis of sulfide pre-concentration in cumulates as it has been suggested by a number of authors (see references). In fact there are currently experimental studies investigating this process (e.g. Virtanen et al., 2019, Goldschmidt presentation).

Change: We have deleted the sentence regarding the aggregates seen in Kula as requested.