

## Response to Referee#1- Dan Smith

*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:** I felt that the comparison between the volcanic centres was too narrowly focussed on the sulfide inclusions and didn't consider them in the context of the silicate host

**Reply:** Thank you for this suggestion. The main focus of this study is indeed to provide a background on the sulfide occurrence and chemistry between the different study areas. Regarding the sulfide host minerals, you are right, in the present study we only mention the percentages of the main host minerals for the different study areas, (see line 179). This is due to the fact that in our previous work (Georgatou et al., 2018) we realised a detailed petrographic study as well as EPMA analysis on the silicate sulfide hosts for the case of Ecuador. The results obtained indicated that the sulfide occurrence within the host did not seem to coincide with any chemical anomaly in the zonation of the crystal (amphiboles, pyroxenes and plagioclases). In addition, sulfides were found before, within and after recharge zones in plagioclase hosts.

In this study we have observed a correlation between the sulfide composition (Ni/Cu content) and the nature of the host mineral (sequence of crystallisation) as we mention in line 314 and in the legend of Fig.6. In addition, although we have not shown these data because we are at an initial stage, we have conducted EPMA analysis (single points and profiles) on both silicates and oxides and we have not observed any systematic chemical correlation between the host's major element and the sulfide presence, as in the case of Ecuador. However, because in some cases detectable/determinable Cu amounts were measured in the host, we intend to investigate in detail by analysing both silicate and oxide host minerals with LA-ICP-MS for their trace element composition in order to check whether these Cu spikes are caused by nano-inclusions or possibly Cu diffusion.

**Comment:** in my opinion some of the conclusions made around post-subduction metal budgets draw too much from a small sample set.

**Reply:** We are aware that, despite the efforts made in this study to investigate a large number of thin sections, the population studied remains likely under sampled. However, the aim of this work is to evaluate first order variations in the textural and compositional characteristics of magmatic sulfides collected from different geodynamic contexts and it is likely that the investigated population is able to provide this. Moreover, we understand that this is a 'pilot' study and by investigating a limited number of volcanoes/samples we cannot generalise for all volcanic centers characterised by the same geodynamic setting.

We would like to clarify that the study areas characterised by a post-subduction setting are; the Usak basin including three volcanic centers (Beydagi, Itecektepe and Elmadag) and the Konya volcanic belt. Although, for the area of Konya, as also mentioned in the text, both subduction and post-subduction geodynamic settings have been suggested in the past, according to a very recent study by Rabayrol et al. (2019), the results show clearly that Konya represents a post-subduction rather than a subduction setting. Based on those findings we consider Konya one of the areas characterised by a post-subduction geodynamic regime.

**Change:** We have added a section in the end of Supplementary 2 discussing the limitations of the methods including the fact that this is a 'pilot' study and by investigating a limited number of volcanoes/samples we cannot generalise for all volcanic centers characterised by the same geodynamic setting. In addition, we have re-phrased and corrected transitional setting by post-

subduction setting adding this recent study (Rabayrol et al., 2019) in line 91 and 96. We have also changed the descriptor ‘transitional’ wherever needed.

If by ‘some of the conclusions’ the reviewer refers to a similar and more specific comment regarding our findings on similar initial metal abundances of the different study areas based on ImageJ modal abundances of the relative proportions of the mss and iss, please see our answer below for comment/Line415 (which now reads 482).

**Comment:** One issue that isn’t discussed in detail here is whether total metal abundance is actually a component of fertility. Although it’s a logical assumption that more copper = more copper deposits, that isn’t really supported by data on e.g. arc magmas. They very rarely (if ever) show Cu contents outside of a narrow band, and typically have sub-MORB concentrations of Cu. Cline and Bodnar’s 1991 paper argued that the key to forming a porphyry was the mass of magma, rather than any remarkable pre-ore enrichment of Cu – which has hitherto not been observed.

Reply: In order to be able to discuss in detail total metal abundances, a degree of modelling would be required, which goes beyond the purpose of the present study. Nevertheless, we agree with the comment, there is indeed a debate between studies suggesting that one can make deposits from normal or even “depleted” Cu magmas (Cline and Bodnar, Chiaradia and Caricchi) and others that claim that metal enrichment is a fertility asset (Core et al. 2006; Stern et al., 2007; Park et al., 2015 etc.). In order to emphasize more the importance of the volume of magma vs the total metal abundances as the referee suggested, we have made the following changes;

Changes: We have re-phrased and extended in the discussion the section dedicated to the implications for ore formation adding also in line 454, the paragraph below:

‘Cline and Bodnar (1991) and more recently Chiaradia and Caricchi (2017) and Chelle-Michou et al. (2017) have shown that there is a correlation between the size of the magma reservoirs providing metals and fluids to the ore system and the size of the deposit and that also the duration of the ore process might play a role in this sense.’

### Answers to Specific comments

**Comment/Line 52/Now reads 58:** describes porphyries as being associated with Andean-type subduction, then contrasts post-subduction. I would strike the descriptor “Andean-type”. It’s too narrow to be correct. There is porphyry-type mineralisation associated with the Laramide orogeny – not exactly analogous to the Andes – and significant deposits elsewhere in the Pacific Rim that are associated with non-Andean, intraoceanic arc settings. I would leave the distinction between syn-subduction and post-subduction.

Reply: Thank you for the suggestion.

Change: the descriptor “Andean-type” has been removed and replaced by syn-subduction. In addition as suggested we have used everywhere the distinction syn- and post- subduction to discriminate the two environments.

**Comment/Line 347/Now reads 385:** Konya anhydrite inclusions – possibility of water saturation dismissed – why? On what basis? Some of the Konya samples are evolved compositions (dacites) and water saturation is entirely feasible. Sulphur speciation and hence mineral stability is also modified by pressure (see Matjushkin et al 2016).

Reply: Thank you for this interesting observation, it is something that we had to consider as well. Indeed the iss-only/Cu-rich Type-4 sulfides co-existing with anhydrite are mostly seen in evolved samples (andesites and dacites, median SiO<sub>2</sub>>60 wt%, see Tabs.1-2). This sulfate-sulfide co-existence

itself does not necessarily point out solely to an either water saturated or water-under saturated system since anhydrite can crystallise in both environments. However, if the system was indeed water saturated we probably wouldn't be seeing any magmatic sulfides, since the metals would have been mostly scavenged by the hydrothermal fluid, we would rather find hydrothermal sulphides. Whereas if the system reached sulfide saturation prior to fluid exsolution we would expect for the metals to partition mostly in the sulfide phase. These Type-4 sulfides co-exist in the same magnetite host with melt inclusions and apatite crystals. In addition their angular shape indicates that the solution was trapped initially as a Cu-rich liquid which solidified following the host mineral crystallisation planes and later unmixed. Nonetheless, as we mention in line 431 what we may be seeing here is the initial state of a magma saturating in water. The increased presence of vesicles in contact with the anhydrite-sulfide pairs, may be an additional fact for the above statement. We are currently working on the apatite and magnetite chemistry in order to investigate this possibility.

**Change:** We have added this reason in line 380, the sentence now reads;

'In addition, the system is not expected to be already water saturated since we would expect for the metals to partition into the fluid phase and result in hydrothermal and not magmatic sulfides, and therefore the temperature ranges in which anhydrite will be stable can differ.'

**Comment/Line 385/Now reads 429:** Various authors argue that the Cu is "lost" during arc magma differentiation, but not within continental crust (see Cin-Ty Lee et al 2012, Jenner's work on the topic too, esp. Nat Geoscience 2017). A more common argument is that the continental crust is Cu depleted - more so than expected - and that this occurs through deep fractionation and periodic delamination of Cu-rich cumulates. Both of these authors have invoked those Cu-enriched lithologies being reworked to produce porphyries, but this is at odds with the body of data on Cu-enrichment in arc magmas (we don't really see "failed porphyries" with anomalous Cu – arc andesites are all typically lower Cu than MORB). Richards (2009, Geology) argued that copper is lost to cumulates with other metals, and that reworking of cumulates could effectively enrich resulting deposits in those metals – but not particularly the Cu. This seems to be supported by the data from Howell et al 2019 (Nat Comms). Post-subduction systems show an enrichment in Au and Te, but Cu is similar to syn-subduction.

**Reply:** We agree with the extended explanation and scientific content of the above references mentioned. However, since with the present study we do not have any quantitative and precise restraints on the pressure (and therefore depth) we have removed the phrase "within the continental crust". Our ongoing work on pressure, temperature of sulfide saturation in enclaves and their host rock should help answer this question.

**Change:** We have removed the phrase "within the continental crust" as requested.

**Comment/Line 400/Now reads 519:** An alternative implication is that porphyries are associated with intermediate rocks, and iss-inclusions are also found in intermediate rocks. The formation of iss and saturation of dense, Cu rich phase is unlikely to have a positive impact on "fertility" - and many authors link Cu compatibility during petrogenesis to the *rarity* of porphyries rather than their formation. My view is that porphyry-forming magmas need to be reasonably evolved in order to saturate with water, which subsequently extracts the metals. The degree of evolution required to reach water saturation would also be sufficient for iss stability / dominance.

**Reply:** Thank you for the suggestion.

**Change:** We have included the felsic nature of the lithologies as a possible contributing factor to ore forming process in lines 512 and 490.

**Comment/Line 415/Now reads 482:** I'm not sure that I would conclude that post-subduction systems have the same initial metal budgets based on these data. Kula is intraplate, the text states that Konya has both syn- and post-subduction complexes, and Ecuador is arc related. Using Table 2 for the reconstructed and summarised inclusions, if Beydagi is the clearest example of post-subduction magmatism, then its stats are poor (low N), but it has only one mss-rich inclusion, and rather more that are iss-rich. This is the opposite of the other locations. Given the weak stats on Beydagi, I don't think you can confidently say that post-subduction magmas start with the same metal balance as the others. If this argument is being made by restricting the comparison to type 2 inclusions, then it's a circular argument. Type 2 sulfides are by definition, mss>iss, so the predominance of Ni over Cu in Type inclusions is expected.

Reply: Thank you for your comment, we realise that the method was not sufficiently explained in addition there was a mistake in line 256 that read '100' instead of 126 sulfides. The statement regarding similar initial metal magma contents between the different study areas is a result mainly based on the comparison of the relative proportions of the mss and iss composing Type-2 sulfide inclusions (Fig.9) and to a lesser degree on the bulk area reconstruction (Tab.2). We agree with the referee that it would be a circular argument to compare the Ni and Cu values between mss and iss and this is why we have not applied this method. For details regarding the methodology as well as similar results obtained from other studies which applied the same methodology, please see answer to first general comment of referee#2.

In total 163 sulfides (of all sulfide types) were processed by ImageJ in order to obtain the modal abundances (area %) of the mineral phases composing the sulfide inclusions. Of those (163), 126 corresponded to Type-2 sulfides (see Tab.4 and 5 in doi:10.6084/m9.Figshare.8230787) and 84 account for the post-subduction setting specifically, (Beydagi-12, Itecektepe-16, Elmadag-10 and Konya-26/which is considered post-subduction rather syn-subduction, see answer to 2<sup>nd</sup> general comment above). Between them all those areas show similar mss area % (and iss area %), Beydagi=86.9±3.2 %, Itecektepe =84.8±4.9 %, Elmadag=86.9±4.8 % and Konya=88.1±2.6 %. As also stated in lines 251-254, the mss area % for the Kula/Intraplate-OIB and for the Ecuador/Subduction setting are also similar corresponding to 82.0±7.4 % and 82.0±4.8%, respectively. In total 126 Type-2 sulfides present relative proportions of mss= 84.2 and iss=15.7 with 2se=± 2.2.

Change: We have re-phrased, in the discussion (lines 463), the paragraph dedicated to the source fertility and the argument for initial metal contents of the different magmas, in order to state clearer the main results on which we are basing our argument. In addition we have extended the methodology part of ImageJ of the Supplementary 2 (as requested by referee#2) and we have added the number of sulfides considered for their mss and iss relative proportions in box-plot Fig.9. The value '100' has been corrected since the total number of Type-2 sulfides that have been processed by ImageJ is 126 as shown also in Tables 4 and 5 in doi:10.6084/m9.Figshare.8230787. Please see text for changes.

**Comment/Line 425/Now reads 500:** This is a comparison between basic (Kula) and intermediate (Konya) suites), rather than a like-for-like comparison of subduction vs. OIB. A more direct comparison between suites with equivalent amounts of differentiation would better support the argument here. ISS-rich inclusions are perhaps better considered a phase associated with lower temperatures and more evolved magmas – indirectly associated with water and the subduction setting (given that water-rich melts have a lower liquidus and subduction magmas have more protracted crustal histories). What would happen if you compared the highly evolved phonolites of the Canary Islands? Does comparing an OIB with similar % crystallisation to a dacite yield ISS? As per fig 10 it should: the sulphide sequence is controlled by P and T.

Reply: We agree with the reviewer. Please see answers to specific comments of line 400 (which now reads) and comment in lines 393-395 (which now read 512) from referee#1 regarding similar argument on the importance of lithology/melt evolution.

Change: We have removed the part of the sentence referencing Kula.

**Comment/**Fig.7: Inclusion of SEM data with Cu below detection limits does not seem appropriate to me. They cannot be plotted appropriately on the axes, and this may be a consequence of the analytical technique rather than a fundamental mineral chemical control (i.e. detection limit for Cu by SEM-EDS is probably closer to 1 wt% than 0.01 wt%). I would rather the extreme Ni/Cu SEM-derived points are just removed.

Reply: We understand that the SEM values are not quantitative and since we could not calibrate our SEM (because of software problems with JEOL) we may as well indeed have an error close to 1 wt%.

Change: We have removed the data from the graph as requested.

#### Answers to Specific comments marked on main text by Dan Smith

*The comments/answers below have been also posted directly on the main text of the manuscript*

**Comments/**Lines 96 and 116/**Now read 110 and 130:** This should be tonnes of ore @ Au g/t. These numbers need checking. The resource should be expressed in tonnes or million tonnes, grade in g/t.

Reply: Thank you for the observation.

Change: The grades have been converted from Moz to tonnes. Please see text.

**Comment/**Line 157/**Now reads 173:** The statement isn't wrong, but I don't think the decreasing Sr should really be listed as a defining feature. In a number of post-subduction suites worldwide, anomalously high Sr is a notable feature (as mentioned in intro for Ecuador).

Reply: We agree with the comment.

Change: We have removed the element "Sr" from the sentence as requested.

**Comment/**Line 277/**Now reads 308:** Do you mean "There are two main stage of sulphide evolution observed..."

Reply: Yes this is what we meant to say.

Changes: After recommendation also from the referee#2 we have changed the sentence as follows, "Two main stages of sulfide evolution were observed in this study".

**Comment/**Line 205/**Now reads 219:** A simple table would better summarise the inclusions types, their mineral hosts, and the volcanic centre hosts (and their classification with regards to syn-/ post-subduction). Perhaps expand fig 4?

Reply: We would rather keep the textural information of the figure and expand as suggested.

Change: We have expanded figure 4, which now besides the study area, the sulfide type with their mineral host also depicts the geodynamic setting at the top.

**Comment/Line 387/Now reads 430:** This content is covered in the background sections. I think you can cut this paragraph.

**Reply:** We agree with the reviewer.

**Change:** We have removed the indicated paragraph.

**Comment/Line 393-395/Now reads 512:** How much of this is because the samples from other areas (e.g. Kula) are in lithologies typically excluded from porphyry exploration programmes - mostly for being too primitive? Are we really seeing implications for ore formation, or are both the sulphide assemblage and presence of mineralization a consequence of the melt evolution stage?

**Reply:** Thank you for the suggestion.

**Change:** We have included the evolved nature of the lithologies as a possible factor for ore forming process and have re-phrased, in the discussion, the paragraph dedicated to the source fertility. Please see text.

**Comment/Line 418-421/Now reads 486:** This needs rephrasing. It reads as if magmas with insufficient water to strip metals are infertile - when logically, that cannot be correct. A porphyry deposit is a hydrothermal feature - the stripping of metals by a fluid is a vital part of the process. A magma with insufficient water will be copper rich yet still infertile.

**Reply:** Thank you for noticing.

**Change:** We have re-phrased as requested. Please see paragraph dedicated to water as a contributing factor for ore formation.

**Comment/Line 427/Now reads 459:** Key reference here is Richards 2009 (for post-subduction). Lee et al. 2012 (Science) argue similarly for normal arcs. I don't really see any good examples of Cu-rich magmas (representing recycled magmas that would be parental to porphyries) in compilations like Georoc.

**Reply:** Thank you for the suggestions.

**Change:** We have added both references.

**Comment/Line 471/Now reads 571:** Does it really suggest Cu enrichment? Is this not just Ni depletion? Fig 3 doesn't support Konya being Cu-enriched (one sample above 30 ppm whole rock).

**Reply:** We agree with the comment, indeed the sentence needed re-phrasing, since the implication does not mean Cu-enrichment in the whole rock, rather in the sulphides.

**Change:** We have re-phrased accordingly.

**Comment/Line 487/Now reads 594:** Many author entries in the reference list only have one initial - despite them actually having more than one.

Reply: Thank you for the observation.

Change: After checking the journal's reference format, we have added the second initial wherever needed.



## 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  $81 \pm 7$  and  $19 \pm 7$ , 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 ( $82.0 \pm 7.4$  %), Itecktepe ( $84.8 \pm 4.9$  %), Elmadag ( $86.9 \pm 4.8$  %), Beydagi ( $86.9 \pm 3.2$  %), Konya ( $88.1 \pm 2.6$  %)' . Ecuador gave similar results with the mss area % being  $82.0 \pm 4.8$ . 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 SiO<sub>2</sub> (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.

# Magmatic sulfides in high-K calc-alkaline to shoshonitic and alkaline rocks

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**Abstract.** We investigate ~~in both mineralised and barren systems~~ the occurrence and chemistry of magmatic sulfides and their chalcophile metal cargo behaviour during the evolution of compositionally different magmas ~~in~~ from diverse geodynamic settings both in mineralised and barren systems. The investigated areas are: (a) the Miocene Konya magmatic province (hosting the Doganbey Cu-Mo porphyry and Inlice Au-epithermal deposits/Post-Subduction) and (b) the Miocene Usak basin (Elmadag, Itecektepe and Beydagi volcanoes, the latter associated with the Kisladag Au porphyry, in Western Turkey/Post-Subduction). For comparison we also investigate (c) the barren intraplate Plio-Quaternary Kula volcanic field, west of Usak. ~~Antraplate and finally,~~ we discuss and compare all the above areas with the already studied (d) Quaternary Ecuadorian volcanic arc (host to the Miocene Llurimagua Cu-Mo and Cascabel Cu-Au porphyry deposits/Subduction). The volcanism of the newly studied areas ranges from basalts to andesites/dacites and from high K-calc-alkaline to shoshonitic series. Multiphase magmatic sulfides occur in different amounts in rocks of all investigated areas, and, based on textural and compositional differences, they can be classified into different types, ~~which crystallised according to their crystallisation~~ at different times/stages of magma evolution (early versus late saturation). Our results suggest that independently of the magma composition, geodynamic setting and whether or not the system has generated an ore deposit on the surface, sulfide saturation occurred in variable degrees in all studied areas and investigated magmatic systems. Those systems present and is characterised by a similar initial metal contents of the magmas. However not all studied areas present all sulfide types and the sulfide composition is dependent depends on the nature of the host mineral. A decrease in the sulfide Ni/Cu (proxy for mss-monosulfide solid solution/iss-intermediate solid solution) ratio is noted with magmatic evolution. At an early stage, Ni-rich/Cu-poorer sulfides are hosted by early crystallising minerals, e.g., olivine/pyroxene, whereas, at a later stage, Cu-rich sulfides are hosted by magnetite. The most common sulfide type ~~resulting from the~~ early saturation stage is composed of a Cu-poor/Ni-rich (pyrrhotite/mss) and one/two Cu-rich (cubanite, chalcopyrite/iss) phases making up ~84 and ~16 area % of the sulfide, respectively. ~~Our results suggest that independently of the magma composition, geodynamic setting and whether or not the system has generated an ore deposit on the surface, sulfide saturation occurred in variable degrees in all studied areas and magmatic systems and is characterised by a similar initial metal content of the magmas. However not all studied areas present all sulfide types and the sulfide composition is dependent on the nature of the host mineral. In particular s~~ Sulfides resulting from the late stage, consisting of Cu-rich phases (chalcopyrite, bornite, digenite/iss), are hosted exclusively by magnetite and are found only in evolved rocks (andesites and dacites) of magmatic provinces associated with porphyry Cu (Konya and Ecuador) and porphyry Au (Beydagi) deposits.

## Commented [AAG1]:

After the comment of Referee#1-Dan Smith:

Co: Move highlighted text to here

R: We accepted the suggestions.

Ch: We moved the paragraph where indicated.



## 1. Introduction

Historically, petrographic and mineral chemistry studies of magmatic sulfides have been carried out on magmatic sulfides associated with orthomagmatic Ni-Cu-PGE mineralised systems (e.g., Barnes et al., 2017, Mungall and Brenan, 2014). Recent studies, however, highlight the growing interest of research towards magmatic sulfides in porphyry ore-associated magma (e.g. Halter et al., 2005, Brennecke, 2006, Zhang and Audétat, 2017) and in barren volcanic arc provinces (e.g., Nadeau et al., 2010, Park et al., 2015, Fulignati et al., 2018, Zelenski et al., 2017, Keith et al., 2017, Savelyev et al., 2018) in order to track processes affecting the fertility of these systems. In fact, it is still unclear how sulfide saturation affects the process of magmatic-hydrothermal ore formation. On one hand early sulfide saturation will strip off chalcophile and siderophile elements from the melt rendering the residual melt less fertile. On the other hand magmatic sulfide- and metal-rich cumulates may represent a temporary storage, which subsequently releases chalcophile metals to the magmatic hydrothermal system (e.g. Nadeau et al., 2010, Wilkinson, 2013, Fontboté et al., 2017).

Georgatou et al. (2018) described the occurrence, texture and composition of magmatic sulfides in relation to the whole rock chemistry of Quaternary Ecuadorian volcanic rocks. Sulfides were found in all rocks ranging in composition from basalts to dacites, occurring as polymineralic inclusions composed of Fe-rich/Cu-poor and Cu-rich phases. The inclusions, of variable size (mostly 1-30  $\mu\text{m}$ ) and shape (globular, ellipsoidal, angular and irregular), were hosted mostly by Fe-oxides (magnetite-45%) and, to a lesser extent, by silicates (amphibole-27%, plagioclase-16% and pyroxene-12% and plagioclase). The Quaternary Ecuadorian volcanism represents a typical example of high Sr/Y calc-alkaline magmas (with  $\text{SiO}_2 = 50\text{-}67$  wt%) occurring in a subduction geodynamic setting potentially related (Loucks, 2014, Chiaradia and Caricchi, 2017) to porphyry-type and epithermal deposits (e.g. Junin, the Llurimagua Cu-Mo and the Cascabel Cu-Au Tertiary (Scütte et al., 2012) porphyry deposits and the El Corazon high sulphidation Au Miocene epithermal deposit).

Although the majority of porphyry Cu ( $\pm$  Au) deposits are formed in association with Andean-type subduction-related magmas (e.g. Sillitoe, 1972, Cooke et al., 2005) there is a growing evidence that numerous porphyry deposits are also related to post-subduction magmatism (Richards, 2009). The porphyry deposits found in both these settings present similarities in terms of mineralisation and alteration styles but also differences concerning petrogenesis and geochemistry of associated magmas (Shafiei et al., 2009, Richards, 2009, Hou et al., 2011). By comparing the occurrence and composition of magmatic sulfides found in volcanic rocks from different geodynamic settings (which may host porphyry and epithermal deposits, Fig.1), it is possible to trace the chalcophile element evolution in those magmas and investigate the role of magmatic sulfide saturation with respect to the fertility of the ore forming systems (e.g., Park et al., 2019, Blundy et al., 2015, Wilkinson, 2013, Audétat and Simon, 2012, Nadeau et al., 2010, Jenner et al., 2010).

In order to investigate the magmatic sulfide occurrence in volcanic rocks characterised by post-subduction geodynamic setting, we focus our study on three volcanic areas located in Western Anatolia (Turkey), namely the Konya volcanic belt, the Usak Basin (Elmadag, Itecktepe and Beydagi volcanoes) and the Kula volcanic field (Fig.2). The investigated areas represent a suitable integration of and comparison to the Ecuadorian study (Georgatou et al., 2018) for the following reasons: (i) the wide range of  $\text{SiO}_2$  content (43-70 wt%) and alkalinity (from high-K calc-alkaline to shoshonitic and alkaline affinities) characterising the volcanic rocks, (ii) the occurrence of both Cu and Au-rich porphyry, and epithermal-type deposits (Doganbey Cu-porphyry and Inlice Au-epithermal in Konya and Kisladag Au-porphyry in Beydagi) temporally associated with magmatic rocks of

**Commented [AAG2]:** Ch: We have added the host mineral percentages in order to emphasise the importance of magnetite as a sulfide host mineral for the case of Ecuador/syn-subduction.

**Commented [AAG3]:**  
After the comment of Referee#1-Dan Smith:

Co: describes porphyries as being associated with Andean-type subduction, then contrasts post-subduction. I would strike the descriptor "Andean-type". It's too narrow to be correct. There is porphyry-type mineralisation associated with the Laramide orogeny – not exactly analogous to the Andes – and significant deposits elsewhere in the Pacific Rim that are associated with non-Andean, intraoceanic arc settings. I would leave the distinction between syn-subduction and post-subduction.

R: Thank you for the suggestion.

Ch: The descriptor "Andean-type" has been removed and replaced by syn-subduction. In addition as suggested we have used throughout the text the distinction syn- and post-subduction to discriminate the two environments.

these areas, and (iii) the inclusion of the intraplate mafic alkaline volcanic field of Kula which is not associated with any type of mineralisation.

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. Compared to the majority of previous studies, focusing which focused only on uncovered sulfides hosted in transparent/semi-transparent host minerals, by investigating uncovered sulfides we are able to 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.

## 2. Geology, Magmatism and Mineralisation in Western Anatolia

The geodynamic regime in Western Anatolia switched from a subduction setting during the Upper Cretaceous to a collisional setting in the Late Paleocene, resulting in post-collisional extension in the Eocene (Delibaş et al., 2016, 2017; Rabayrol et al., 2019; see Figure 2-a for the general geodynamic setting). Several volcano (-plutonic) complexes of Mio-Pliocene age occur in NE-SW-trending extensional basins and are post-orogenic extensional in nature. They have been divided into three regions (Fig.2b,c); (i) the Konya region, for which both subduction (Doglioni et al., 2009; Innocenti et al., 2010) and post-subduction (Pe-piper et al., 2001; Dilek and Altunkaynak, 2007) geodynamic regimes have been suggested, is here taken to represent a ~~transitional post-subduction~~ geodynamic regime as supported by recent evidence presented by Rabayrol et al. (2019) (from subduction to post-subduction), (ii) the Usak-Güre Basin, including three volcanic centers (Elmadag, Itecektepe and Beydagi), corresponds to a post-subduction, locally extensional setting (Prelević et al., 2012, Ersoy et al., 2010), and (iii) the Kula volcanic field results from asthenospheric upwelling associated with extension in a post-subduction setting (Tokçaeç et al., 2005, Alici et al., 2002).

### 2.1 Konya

The Konya volcanic belt is located S-SW of the city of Konya (Fig.2b). It is composed of volcanic domes and ignimbrites of Mid-Miocene to Pliocene age (Keller et al., 1977, Temel 2001). The basement includes Permian metamorphic rocks, Triassic limestone and shales, Jurassic ophiolites, radiolarites and limestones, Cretaceous sandstones and quartzites (Temel et al., 1998). The erupted products are andesites to dacites with high-K calc-alkaline affinity. According to K/Ar ages obtained by Keller et al. (1997) a southwestern migration of magmatism is observed with time, starting with the oldest unit, the Sille volcanics (11.45 Ma – 11.9 Ma), located in the northeastern part of the Konya volcanic and ending with the Fasillar and Gevrekli domes, in the SW of the volcanic belt, which show Pliocene ages (3.75 Ma and 3.35 Ma respectively).

The Konya volcanic belt hosts the Miocene Au-epithermal high sulphidation deposit of Inlice (~~59.600oz1.68t @ 2.36 g/t Au, mining-atlas.com, 2015~~) located in the Erenkaya dome and the Miocene-Pliocene Doganbey Cu porphyry deposit (drilling of 273.90m @ 0.13g/t Au, Stratex International Plc, 2018), ~~situated in the Karadag-Doganbey dome~~, both shown in Figure 2b. Two other prospects (Karacaoren and the Oglakci) have been

#### Commented [AAG4]:

After the comment of Referee#2-Jonathan Naden:

C: Why is this threefold approach important?

R: These three factors allow us to include sulfides hosted by magnetite while still maintaining the textural relations.

Ch: We have re-phrased the sentence as seen in order to emphasize the importance of magnetite.

#### Commented [AAG5]: Ch: We have re-phrased and

corrected transitional setting by post-subduction setting adding this recent study (Rabayrol et al., 2019) in line 90. We have also changed the descriptor 'transitional' wherever needed.

#### Commented [AAG6]:

After the comment of Referee#1-Dan Smith:

C: This should be tonnes of ore @ Au g/t

R: Thank you for the observation.

Ch: We have converted from Moz to tonnes.

discovered by Stratex International in the Konya volcanic belt. [For details on the mentioned economic deposits, please see Zürcher et al. \(2015\) for Inlice and Redwood \(2006\) and Hall et al. \(2007\) for Doganbey.](#)

## 2.2. Usak-Güre basin

The Usak-Güre basin, situated 300 km west of the Konya volcanic belt is composed of (i) the Menders Massif, including a metamorphic core composed of metagranites and gneiss (Proterozoic) overlain by Paleozoic schists and Mesozoic marbles and of (ii) the Upper Cretaceous Ophiolitic mélange of the Izmir-Ankara zone including unmetamorphosed ultramafic rocks, radiolarites and altered silicic rocks (Ercan et al., 1978, Cemen et al., 2006).

Syn-extensional sedimentation and volcanism associated with the metamorphic complex of the Menders Massif are recorded in detail within the basin. From Early- to Mid-Miocene the basin contains three sequences: the Hacibekir Group, the Inay Group and the Asartepe formation, represented by volcanic and metamorphic rocks (Cemen et al., 2006, [KaraogluKaraoglu et al., 2010](#)). The Cenozoic volcanism in the Usak-Güre basin occurs in three NE-SW trending belts where the volcanic edifices are aligned. According to the ages obtained by [KaraogluKaraoglu et al. \(2010\)](#) and Seyitoglu (1997) it appears that the volcanism migrated from north to south with time: (i) Elmadag (17.29 Ma), (ii) Itecektepe (15.04 Ma) and (iii) Beydagi (12.15Ma) (see Figure 2c). Volcanic products includes shoshonites, latites and rhyolitic lavas followed by dacitic and andesitic pyroclastic deposits. All three volcanoes are composed of dacitic ignimbrites formed by the collapse of their caldera and overlying lava flows.

Among all the volcanic complexes situated in the Usak-Güre basin only the Beydagi complex is ~~recognised as~~ mineralised hosting the Kisladag Au-porphyry (~~255t~~ @ 0.61 g/t Au and ~~119 t @ 0.4 g/t Au~~ of total indicated ~~and inferred~~ resources, [respectively, Baker et al., 2016](#), with cut-off grade 0.3 g/t, [www.eldoradogold.com](#)-last update on 30.9.18 and up to 327 ppm of Mo, Sillitoe, 2002).

## 2.3 Kula volcanic field

The Kula volcanic field is situated west of the Usak province (Fig.2c) and its volcanic products are late Pliocene to late Quaternary in age (Ercan and Oztunali, 1983; Ercan et al., 1983, Richardson-~~Bunbury~~, 1996, Innocenti et al., 2005, Aldanmaz, 2002, Westaway et al., 2004). The rocks include lava flows and tephra deposits of varying mafic alkaline composition (basanite, phonolitic tephrite and trachybasalt). Kula represents an intraplate OIB-like alkali-basaltic volcanic center with an asthenospheric mantle signature and no subduction-related inputs (e.g. Agostini et al., 2007, Alici et al., 2002, ~~TokcaerTokcaer et al., 2005~~).

## 3. Analytical Methods

After a preliminary screening for magmatic sulfides in 108 thin sections from all investigated volcanic centres, a total number of 93 thin polished sections were studied in detail under a petrographic microscope both in transmitted and reflected light (Table S1 in Supplementary 1). Thin sections that had both hydrothermal and magmatic sulfides were excluded from this study due to the difficulty in some cases to distinguish between these two types of sulfides ([see distinguishing criteria in Supplementary 2](#)). For this reason, unless stated otherwise, sulfides referred to herein are always meant to be magmatic sulfides. Microphotographs and identification of mineral phases were obtained using a Scanning Electron Microscope (SEM) JEOL JSM7001F digital with 15kV

### Commented [AAG7]:

After the comment of Referee#1-Dan Smith:

C: These numbers need checking. The resource should be expressed in tonnes or million tonnes, grade in g/t.

R: Thank you for the observation.

Ch: We have corrected the grade and converted to tonnes. We have also added the inferred resources.

accelerating potential and 1 nA absorbed current, at the University of Geneva, Switzerland. Whole-rock samples were analysed for major and minor elements by X-ray fluorescence analysis (XRF) using a PANalytical Axiom AX spectrometer and for trace elements by a Laser Ablation Inductively Coupled Mass Spectrometer (LA-ICPMS Agilent 7700), at the University of Lausanne, Switzerland (Tables 1-3 in doi:10.6084/m9.Figshare.8230787). In situ chemical analysis of sulfides (Table 1) was carried out using a JEOL 8200 Probe Micro-Analyser (EPMA) at the University of Geneva, Switzerland (for complete dataset see Table 4 in doi:10.6084/m9.Figshare.8230787). An iImage analysis software (ImageJ©1.38 software) was used to obtain modal abundances of the phases composing each sulfide in order to reconstruct the bulk (area %) sulfide composition (for complete dataset see Table 5 in doi:10.6084/m9.Figshare.8230787). For details on analytical methods ~~(and their limitations), on whole rock and mineral chemistry~~ see Supplementary 2.

#### 4. Results

##### 4.1. Whole rock geochemistry

The ~~volcanism-volcanic rocks~~ of the studied areas displays a wide range of SiO<sub>2</sub> and alkali element concentrations ranging from basalts to andesites/dacites ~~and from with high-K- calc-alkaline~~ to shoshonitic ~~series-affinity~~ (Fig.3a,b). The Konya volcanic belt is characterised by volcanic products ~~with a high-K calc-alkaline affinity~~ ranging from andesitic to dacitic in composition ~~with a high-K calc-alkaline affinity~~. In the Usak basin, the Elmadag volcanic complex is composed mostly of shoshonitic trachyandesites, the Itecktepe volcanic unit is characterised by high-K-~~calc-alkaline~~ rocks, mostly andesitic in composition, and the Beydagi volcanic edifice contains ~~high-K calc-alkaline to shoshonitic~~ rocks ranging from andesites to trachyandesites ~~with high-K calc-alkaline to shoshonitic affinity~~. Finally the Kula Quaternary volcano presents the most alkaline and mafic compositions, ranging from tephrites/basanites to phonotephrites. All rocks present a negative correlation ~~between of TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> and with SiO<sub>2</sub>~~, with Kula being more enriched in TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> than the rest.

In terms of trace element concentrations all rocks show a decrease of Cu and Ni with increase of SiO<sub>2</sub> (Fig.3e-f), indicating a compatible behaviour of these elements during magmatic evolution. In addition all rocks show an enrichment of LREE relative to HREE with decreasing Nb, Ta, ~~Sr~~ and Ni passing from intraplate volcanism (Kula) to post-subduction (Elmadag, Itecktepe, Beydagi, ~~Konya~~), ~~and finally to a transitional subduction to post-subduction regime (Konya)~~.

##### 4.2. Sample petrography

All studied samples are volcanic rocks with porphyritic textures. Phenocrysts are usually plagioclase, amphibole, pyroxene (mostly clinopyroxene) and, depending on the volcanic centre, olivine, biotite and to a lesser extent Fe-Ti oxides (mostly Ti-magnetite). The matrix is aphanitic, mostly composed of microlitic plagioclase (<1 mm) and sometimes amphibole and pyroxene microcrystals. Apatite and anhydrite can also be found as inclusions in pyroxene and Fe-Ti oxide phenocrysts.

##### 4.3. Sulfide petrography and chemistry

Rocks of all study areas contain magmatic sulfides, ~~h~~ However, depending on the volcanic centre, sulfides are present in variable amounts, size, shape and composition. A comparison of the sulfide occurrences ~~between among~~

**Commented [AAG8]:** Ch: We have added a section in the end of the Supplementary 2 dedicated to the limitations of the method and the approach.

**Commented [AAG9]:**  
After the comment of Referee#1-Dan Smith:

C: Sr is a bit more subtle than just a decrease though - the Sr "anomaly" actually increases from Kula to Konya - although there's less, there is actually more than expected (based on the slope between neighbouring elements). The statement isn't wrong, but I don't think the decreasing Sr should really be listed as a defining feature. In a number of post-subduction suites worldwide, anomalously high Sr is a notable feature (as mentioned in intro for Ecuador).

R: We agree with the comment.

Ch: We have deleted Sr from the sentence.

185 the different volcanic centers (corresponding also to different geodynamic settings) is given in Figure 4. In all  
studied samples sulfides occur inside phenocrysts and not in the groundmass (Fig.5), with the exception of the  
Kula volcano that presents sulfides also as aggregates with oxides and micro-sized silicates in the groundmass  
(Figs.4e,ii,5e) and a few cases in Beydagi (Fig.4xi). The main host phenocryst for sulfides is magnetite for Konya  
and Beydagi (42% and 31% respectively), amphibole for Itecektepe and Kula (85% and 39%), and pyroxene for  
190 Elmadag (87%). Sulfides are also hosted in plagioclase (Fig.5b). The common occurrence of  
voids/~~vesicles~~bubbles in contact with the sulfide phases is noteworthy (e.g. Figs. 4ii, 5g).

Based on petrographic observations and SEM mineral analysis we distinguished six main types of magmatic  
sulfides: 1) Type-1 sulfides containing two to three distinct phases, namely a Cu-poor and Ni-rich phase  
(pyrrhotite), a Ni-rich phase (pentlandite), and rarely a Cu-rich phase (cubanite) (Fig.4a); 2) Type-2 sulfides  
195 containing two to four distinct phases, namely a Cu-poor (pyrrhotite), one/two Cu-rich (chalcopyrite  $\pm$  cubanite)  
and sometimes a Ni-rich (pentlandite) phase (Fig.4b); 3) Type-3 sulfides containing a Cu-rich phase (chalcopyrite  
or chalcocite) and an Fe-rich phase (pyrite/Fig.4c); 4) Type-4 sulfides containing only Cu-rich phase/s  
(chalcopyrite,  $\pm$  cubanite,  $\pm$  bornite), occasionally in contact with anhydrite (Fig.4d); and 5) Type-5 sulfides  
containing aggregates of a Cu-poor and Ni-rich (pyrrhotite) sulfide phase and one or more Al-rich oxide phases  
200 (magnetite, magnetite/ilmenite and secondary goethite) (Fig.4e). Finally Type-6 sulfides, the so-called “daughter  
sulfides” (e.g., Savelyev et al., 2018, Fig.5h), were only observed in three cases in this study, within olivine  
phenocrysts of rocks from Kula. From SEM analysis this latter sulfide type it is composed only ~~out~~ of pyrrhotite  
 $\pm$  pentlandite, however due to their small size ( $<0.5 \mu\text{m}$ ) they ~~were~~could not ~~be~~ analysed with the EPMA.

Type-1 sulfides are only hosted by olivine, they are generally small ( $<30 \mu\text{m}$ ), round and show pentlandite  
205 exsolution flames in pyrrhotite (Fig.4i). Type-2 sulfides, the most common, are hosted by different phenocrysts  
(pyroxene, amphibole, magnetite and plagioclase), presenting a range of sizes (up to  $70 \mu\text{m}$ ) and having mostly  
ellipsoidal to rounded shape (Fig.4ii-vii). The pentlandite phase in this sulfide type can occur either as an  
exsolution in the pyrrhotite and/or as an individual phase inside the Ni-rich pyrrhotite (Fig.4vi), whereas cubanite  
is mostly present when the sulfide is hosted in amphibole, forming complex exsolution textures with chalcopyrite  
210 and presenting irregular rounded-resorbed shapes (Fig.5d). Type-3 and -4 sulfides are only hosted by magnetite  
phenocrysts occurring in smaller sizes ( $<30 \mu\text{m}$  and  $<20 \mu\text{m}$ ) and presenting ellipsoidal and angular shapes,  
respectively (Fig.4viii,ix,x). Type-4 sulfides ~~in particular~~ have been observed in some cases in contact with  
anhydrite and with zircon inclusions (usually  $<20 \mu\text{m}$ ) all hosted by the same magnetite crystal (Fig.6). Finally  
Type-5 consists of sulfide aggregates with variable size (up to  $600 \mu\text{m}$ ), which may carry rounded oxide inclusions  
215 and sometimes are in sharp contact with surrounding silicate phases (Figs.4xi,xii,5e). Although all study areas  
present Type-2 sulfides, from the volcanic centers situated in the Usak basin, only Beydagi shows sulfide Type-3  
and -5, whereas only Kula and Konya present sulfide Type-1 and -4, respectively.

Electron microprobe analysis: ~~corresponding to of single mineral phases analysis composing a multi-phase sulfide~~  
inclusion; confirms the above petrographic observations and SEM analysis. Sulfides belonging to Konya and to  
220 the volcanic areas of the Usak-Güre basin (Beydagi, Elmadag and Itecektepe) have compositions typical of the  
Cu-Fe-S system whereas sulfides observed in Kula (intraplate OIB-like volcanism) extend into the Cu-Fe-Ni  
system as well (Fig.7a,b). Sulfides from all areas present a range of compositions between pyrrhotite and cubanite-  
chalcopyrite (Type-2 and -5) hosted by different phenocrysts (mostly amphibole, pyroxene and magnetite, Fig.7a).

**Commented [AAG10]:**

After the **comment of Referee#1**-Dan Smith:

C: A simple table would better summarise the inclusions types, their mineral hosts, and the volcanic centre hosts (and their classification with regards to syn-/ post-subduction). Perhaps expand fig 4?

R: Thank you for the recommendation.

Ch: We have expanded figure 4, which now besides the study area, the sulfide type with their mineral host also depicts the geodynamic setting at the top.

225 Beydagi shows additional compositions between chalcopyrite (sometimes chalcocite) and close or equal to  
magmatic pyrite (Type-3) and Konya presents sulfides ranging from chalcopyrite to bornite compositions (Type-  
4). The latter types are only hosted by magnetite. In the case of Kula ~~a number of sulfides~~ (Type-1 and some Type-  
2) ~~sulfides~~ are Ni-rich, ranging from pyrrhotite to pentlandite (Fig.7b). ~~A general decrease in the sulfide Ni/Cu  
ratio versus Fe/S ratio can be noted switching from Ni-rich sulfide phases (pentlandite) hosted by olivine to Cu-  
rich (bornite) hosted by magnetite (Fig.7c).~~

230 EPMA sulfide compositions often correspond to variable nonstoichiometric atomic ratios of major components  
different from the typical expected base metal composition of the sulfide phase observed, resulting into  
intermediate values characteristic of a solid solution mostly between two end members (e.g. cubanite and  
chalcopyrite and bornite; Figs.6, 7). In addition in some cases sulfides are characterised by a sulphur deficiency,  
which, according to previous studies, may be a result of the replacement of sulphur by oxygen that is not directly  
235 measured by EPMA (e.g. Larocque et al., 2000, Keith et al., 1997). These latter cases show usually lower totals  
than those resulting from Cu-rich Type-4 sulfide analysis (see Table 4 in doi:10.6084/m9.Figshare.8230787).

A sulfide comparison for each area in terms of Cu and Ni contents, determined by EPMA, is shown in Figure 8.  
Konya presents the most Cu-rich sulfides (Type-4, Cu median= 56 wt %) and Kula the most Ni-rich sulfides  
(Type-1, Ni median = 4.2 wt %). In the Usak basin Beydagi shows the most Cu-rich sulfides (Type-3, Cu median=  
240 32 wt %), followed by Elmadag (Type-2, Cu median= 0.14 wt %) and then by Itecektepe (Type-2, Cu median=  
0.03 wt %). In addition to Cu, Fe, Ni and S, sulfides were also analysed for As, Se, Zn, Ag and Au (see Table C.1  
for determination limits.). For all locations As and Se are generally lower than 0.1 wt %. Zn concentrations were  
obtained only for Konya and Kula, showing, for Type-2 sulfides, Zn median= 0.03 and 0.04 wt%, respectively.  
Out of 503 Ag and 196 Au sulfide measurements obtained, only 82 and 31 values, respectively, resulted in  
245 concentrations above detection/determination limit. Ag varies between 0.01-0.07 wt % with a maximum amount  
of 0.11 wt % (in Konya) whereas Au is higher showing higher values in the Usak-Güre basin (Au median=0.14-  
0.24 wt %) compared to the rest (Au median=0.04-0.05 wt %). These unusually high sporadic values of Ag and  
Au have been attributed by previous studies to clustering and nugget effects of noble metals (e.g. Savelyev et al.,  
2018, Zelenski et al., 2017, Holwell et al., 2015, Holwell and McDonald, 2010). A possible Au nugget occurrence  
250 is shown in Figure 4viii for Type-3 sulfides of Beydagi. Although the phase is too small (<0.5 µm) to obtain  
quantitative values by EPMA, detectable Au was measured by SEM near and on this high reflectance micro-  
phase.

Since ~~all~~ sulfide ~~inclusions of all~~ types are composed ~~of by~~ more than one mineral phase ~~(e.g., pyrrhotite and  
chalcopyrite) and therefore a single sulfide may correspond to more than one EPMA value~~, the sulfide composition  
255 data ~~has been~~ presented ~~here and discussed~~ in two different ways: (a) as individual microprobe measurements  
~~of mineral phases within~~ for each ~~multi-phase~~ sulfide type ~~observed in from~~ the different study areas (Table 1,  
Figs.7,8) and (b) as ~~reconstructed~~ bulk compositions of the sulfide ~~inclusion reconstructed~~ by considering the  
modal abundance (area %) and the EPMA concentrations for each phase composing the ~~multi-phase~~ sulfide (see  
Table 2, Figs. 9,10 ~~and examples of the reconstruction methods in Supplementary 2~~).

260 Calculating the area % ~~in-occupied plan-view of by~~ each mineral composing the sulfide ~~in the 2-dimension space~~  
(and therefore the mss/iss initial proportions) allows us to ~~get-obtain~~ an indirect ~~qualitativequantitative~~ information

**Commented [AAG11]:**

After the comment of Referee#2-Jonathan Naden:

C: 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.

R: Thank you for the observation. In terms of our use of the analytical precision of the EPMA please see our comment Supplementary 2.



on the initial metal ~~contents~~budget of the silicate melt from which the sulfide melt was exsolved in the different study areas. ~~This is because the areas characterising the mss and iss phases are proportional to the metal amounts that have partitioned into these phases. Although, due to cut effects, crystal orientation and other limitations of this method (see Supplementary 2),~~ Whereasne could question that this approach may yield biased results ~~(because of cut effects and crystal orientation), but due to cut effects, crystal orientation and other limitations of this method (see Supplementary 2),~~ averaged out over a large number of sulfide ~~inclusions~~ we think we obtain a significant first-order estimate. The mean proportions of mss and iss in area% are shown with the box plot of Figure 9 and in Table 2. 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 $\pm$ 7.4 %), Itecektepe (84.8 $\pm$ 4.9 %), Elmadag (86.9 $\pm$ 4.8 %), Beydagi (86.9 $\pm$ 3.2 %), Konya (88.1 $\pm$ 2.6 %). A reconstruction of the bulk mss and iss in area (%) composition of the sulfides was realised in this study also for the case of Ecuador for comparative purposes, resulting in mss area% of 82.0 $\pm$ 4.8. When ~~considered all together~~ (Type-2 sulfides from all investigated areas), for a total of ~~126~~100 sulfides ~~are considered together~~, all study areas present similar proportions of Fe-rich/mss (84.2%) and Cu-rich/iss (15.7%) phases within error (2se =  $\pm$  2.2).

## 5. Discussion

### 5.1. Sulfide melt evolution

The evolution of sulfide melt has been studied through experiments considering the sulfide globules as closed systems that differentiate with decreasing T (e.g. Kullerud et al., 1969, Calibri, 1973, Naldrett and Gasparini, 1971, Cabri, 1973, Craig and Scott, 1974, Tsujimura and Kitakaze, 2004, Holwell and McDonald, 2010, Naldrett, 2013 and references therein). Nonetheless, there is a difficulty to correlate the different phase stability fields for the complete range of temperatures, i.e., 1200-100°C. This is due to the fact that the Fe-Ni-Cu-S system is a complex system characterised by a number of solid solutions and unquenched phases. In addition, the mineral assemblage composing the sulfides depends, among other factors ( $f\text{O}_2$  and  $f\text{S}_2$ ), on the initial metal budget of the silicate melt, and therefore on the metal contents of the exsolving sulfide melt, as well as on the P and T conditions under which this melt solidifies. A compilation of isothermal sections of the Cu-Fe-S system resulting from a number of experimental studies realised at different temperatures is presented in Figure 10. For this study it is important to note at which approximate temperature intervals mineral phases can coexist and therefore a summary of the experimental findings, only focused on the mineral phases observed in this study, ~~has been added~~is presented below.

The general agreement is that above 1200°C the system is composed of ~~two immiscible liquids~~, a metal (Cu, Au)-rich liquid and a sulphur (+Fe, Ni)-rich liquid (Craig and Kullerud, 1969). An Fe, Ni-rich/Cu-poor monosulfide solid solution (mss) and a Cu, Au-rich/Ni-poor intermediate solid solution (iss) exsolve around 1192°C (Jensen, 1942) and 960°C (Kullerud et al., 1969), respectively (Fig.10a-b and 10c). The pair mss-iss is stable only starting from 935°C and until 590°C (Fig.10c-e), below which temperature these two phases cannot coexist. Around 930°C a high temperature-bornite solid solution (bnss-h) and iss become stable (Fig.10c). With further cooling ( $\sim$ 610°C, Fig.10e) the mss converts to pyrrhotite (po), through exsolution of a high temperature pentlandite (pn-h) (e.g. Stone et al., 1989). Subsequently at 590°C the iss unmixes into chalcopyrite (cp) and cubanite (cb) (Fig.10f, e.g. Yund and Kullerud, 1966). Pyrite (py) appears at 743°C and becomes stable with iss at 739°C and with cp at 600°C (Fig.10e). The pair cp-py coexists until at least 200°C (Craig and Scott, 1974). A low temperature

**Commented [AAG12]:** Ch: The value '100' has been corrected since the total number of Type-2 sulfides that have been processed by ImageJ is 126 as shown also in Table 5 of Supplementary 2. The number 100 corresponds to all sulfides of all types for which a bulk area reconstruction method combining these mss and iss relative proportions and the EPMA wt% compositions.

300 pentlandite (pn) appears at 610°C and becomes stable with cp at 572°C. Finally the bnss-h breaks down to chalcocite (cc) and digenite (dg)-bnss pair at 430°C (Fig.10g). At 334°C pyrrhotite becomes stable with chalcopyrite and with further cooling at 330°C the digenite-bnss pair breaks down to digenite and bornite (bn, Fig.10g-h).

305 Two main stages of sulfide evolution were observed in this study confirming the experimental temperature range windows, for specific mineral pairs, as well as conclusions from previous research ~~by~~ (Hattori, 1999, Parat et al., 2011, Du et al., 2014, Agangi et al., 2016). The first stage accounts for the more primitive sulfide types (Type-1 and -2) including mss-rich±iss and mss+iss sulfide melt, now represented by compositions (shown from both individual mineral analysis-Fig.7 and reconstructed area compositions-Fig.10) close to pyrrhotite (±pentlandite, cubanite) and pyrrhotite + chalcopyrite (±cubanite), respectively. Their shape (round-ellipsoidal) and host mineral  
310 (olivine for Type-1 and, amphibole, pyroxene, plagioclase and magnetite for Type-2) confirm their origin as Fe-Ni (±Cu) - rich sulfide melts. The second stage consists of Type 4 sulfides, characterised by iss-only and a Cu-rich sulfide liquid (as all the Ni has been exhausted), which now comprises chalcopyrite and bornite (±digenite). This sulfide type occurs only within Fe-oxides, mostly in Ti-rich magnetite with displaying occasional ilmenite exsolution lamellae. Their angular shape indicates that the solution was trapped initially as a Cu-rich liquid (Chang and Audétat, 2018) which solidified into an iss following the host mineral crystallisation planes and later unmixed (see also Georgatou et al., 2018, Holwell et al., 2015). In addition to the relatively low temperature ranges compared to the first stage sulfides (<330°C, see Fig.10), other petrographic and compositional arguments for considering this as a later stage are the following: (i) the unique occurrence in magnetite, a late crystallising mineral relative to olivine and pyroxene (hosting the first stage sulfide Type-1 and -2) and (ii) the more common  
315 occurrence of voids/vesicles around the Cu-rich sulfides accounting for higher mean portions of the inclusions (up to 23 area %, see tables 2.C.2) compared to Type-2 sulfides (<10 area%). The contact between each sulfide inclusion and these vesicles is smooth, indicating these voids could account for the presence of a pre-existing fluid phase which exsolved from the silicate melt before entrapment in the magnetite crystal (Table 2).

325 Sulfide Type-3 and -5 are more difficult to interpret. Type-3 presents both ellipsoidal and rectangular shapes indicating entrapment as a liquid/~~melt~~. The temperature range that corresponds to the mineral assemblage of chalcopyrite (±chalcocite) + pyrite is 600-200°C, suggesting a later timing than the first stage sulfides. Finally Type-5 sulfide aggregates are similar to the first stage sulfides (Type-2) and seem to have originated from an mss and Fe-rich system, producing immiscibility textures of the rounded oxide inclusions into the pyrrhotite, which have later aggregated with silicates.

330 In this study, no early and late sulfides co-hosted by the same mineral were observed. This suggests two distinct sulfide saturation stages, where the system has to ~~first~~ undergo magnetite crystallisation to reach the second stage. However, it is still not clear whether these stages are indeed distinct and independent one ~~to of another~~ other, or if they may directly follow one another, through a continuous process of sulfide saturation, whose products change chemistry due to the chemical evolution of the melt. Nonetheless, according to the sulfide types  
335 observed in these two stages, the Ni/Cu (proxy for mss/iss) decreases with magmatic evolution (Fig.7c), starting from an mss-rich sulfide melt (Type-1), followed by an mss and iss-melt (Type-2 and -5) and finally (and uniquely for some settings) by iss-rich/iss-only sulfides (Type-3 and -4). Although, this decrease in Ni/Cu has been noted previously by other researchers (e.g. Hattori, 1999, Du et al., 2014, Keith et al., 2017, Savelyev et al., 2018) for

the early sulfides, until now, there has not been a systematic study on the later stage, iss-only sulfides. The reason for this is most likely the fact that the majority of past studies on sulfides have focussed on silicate mineral separates, in order to be able to locate and analyse the bulk chemistry of entrapped sulfides. This not only prevents necessary observations on textural mineral relations but also the study of non-transparent/opaque minerals, which, as it was shown here, host the Cu-rich and iss-only sulfides.

## 5.2. Sulfide-Textural and compositional comparison of sulfides within Western Anatolia study areas

Volcanic rocks from all study areas contain sulfides and therefore have reached magmatic sulfide saturation at some stage during the lifespan of the magmatic system; however, there are significant textural and compositional differences, which are described below.

### 5.2.1. Kula volcanic field

In Kula, where rocks correspond to more primitive compositions (tephrites/basanites to phonotephrites), we observe sulfide ~~types~~ (Type-1, -2 and -5) representing the most primary Ni-rich and Cu-poor magmatic products resulting from an initial, mostly mss-rich sulfide melt exsolving from a silicate melt. These sulfide types are similar to those found in MORBs (e.g. Patten et al., 2012, Keith et al., 2017, Savelyev et al., 2018 and references therein) and represent only at the first stage of sulfide saturation. From textural evidence, e.g., decompression rims in amphibole (Fig.5c), complex textures of cubanite-chalcopyrite resulting from rapid unmixing of iss due to temperature drop (Fig.5d, Type-3) as well as the intact sulfide aggregates found in the groundmass (Fig.5e, Type-6), the magma in Kula seems to have ascended rapidly from depth (e.g. ~~TokcaerTokcaer~~ et al., 2005). This implies a short residence time in the crust, which in turn explains the minimum crustal contamination (e.g. Dilek and Altunkaynak, 2007, Alici et al., 2002) and the mafic rock composition.

### 5.2.2. Konya

For the case of Konya, which products range from andesites to dacites, the sulfide types found (Type-2 and -4) represent both stages of sulfide saturation and are less primitive than the ones seen in Kula, with little or no pentlandite present and always a Cu-rich phase (chalcopyrite±bornite). This suggests that the mss and iss-rich sulfide melt started exsolving from the silicate melt at a later stage of magmatic evolution, when the melt was already depleted in Ni and had already a higher amount of iss available, compared to Kula. In fact, Type-4 iss-only sulfide melt of Konya (representing the second/later stage of sulfide saturation) ~~of Konya~~ has sequestered Cu more successfully than at any other location investigated.

Konya is the unique example in this study presenting anhydrite inclusions in contact with a sulfide phase or hosted by the same magnetite phenocryst as the sulfide inclusion (Fig.6). The occurrence of anhydrite either in contact or along with Cu-rich sulfide phases, has been mentioned in the past (e.g., Hattori, 1993, Audétat and Pettke, 2006) and has been suggested to indicate a rapid drop of  $fO_2$  of the system from the sulphate ( $>NNO+1$ ) to the sulfide stability field ( $<NNO$ ) allowing the magma to contain both reduced and oxidized forms of sulphur (Wilke et al., 2011). From experimental constraints for a water saturated system at 150-400 MPa and 1 wt% S added, anhydrite can coexist with pyrrhotite for  $fO_2 = NNO+1$  at 700°C, for  $fO_2 = NNO+1.5$  at 800°C and for  $fO_2 = NNO+2.5$  at 950°C (Parat et al. 2011 and references therein). Therefore, the occasional occurrence of anhydrite in this second stage sulfides (Type-4), would indicate higher temperatures. In addition, the co-existence of sulfide

inclusions, anhydrite, apatite and silicate melt within the same magnetite crystal, would also indicate higher temperatures and a rather magmatic origin of those sulfides. However, in this study the sulfide mineral phases with which anhydrite coexists are Cu-richer/S-poorer (chalcopyrite+bornite±digenite) than pyrrhotite, and are stable at higher fO<sub>2</sub> conditions and lower T. In addition, the system is not expected to be already water saturated since we would expect for that the metals to partition into the fluid phase in such a case and resulting result in hydrothermal and not rather than magmatic sulfides sulphides, and therefore, the temperature ranges in which anhydrite will be stable can differ.

### 5.2.3. Usak-Güre Basin

Beydagi shows slightly more enriched (though similar within error) Cu values in Type-2 sulfide (Cu median= 0.3 wt %) than Elmadag (Cu median= 0.14 wt %) and Itecektepe (Cu median= 0.03 wt %). Additionally, the area (%) of the Cu-phases/iss of Type-2 sulfides found in Elmadag (17.2±4.8), Itecektepe (14.7±4.9) and Beydagi (13.1±3.2) is similar. However, although in terms of bulk chemistry there are not major differences between the three volcanic centers (mostly andesites to trachyandesites), Beydagi is the only volcanic center within the Usak basin which is characterised by two other sulfide types (Type-3 and -5), and at the same is the only mineralised volcanic center. Implications regarding the ore fertility of these systems will be discussed in the following section. Relative to the other investigated areas of Western Anatolia, sulfides in Beydagi show no pentlandite but present in some cases present chalcopyrite (±chalcocite) coexisting with pyrite. This suggests that the iss-rich exsolving sulfide melt was Cu-rich relative to Kula but Cu-depleted relative to Konya.

### 5.3. Comparison of sulfide textures and compositions with-between Western Anatolia systems and Ecuador

Various Miocene large Cu-Mo±Au porphyry deposits (e.g., Junin/Llurimagua Cu–Mo deposit and the Cascabel Cu–Au rich deposit) occur in the frontal arc of Ecuador. Available data on whole rocks indicate that mineralisation is spatially and temporally associated with high Sr/Y porphyritic stocks (Schütte et al., 2012). Investigation of these rocks under a reflected petrographic microscope confirmed previous observations from Schütte et al. (2012) that the rocks contain abundant hydrothermal sulfides, rendering these samples inadequate for the scope of the present study. For this reason, Georgatou et al. (2018) have investigated fresh volcanic rocks from the Quaternary arc of Ecuador. These are intermediate to felsic calc-alkaline magmatic rocks with high Sr/Y values erupted through a crust with a thickness ranging from 50 to 70 km (Feininger and Seguin, 1983, Guillier et al., 2001). Such features are similar to those of magmatic systems typically associated with large porphyry Cu deposits (Loucks, 2014, Chiaradia and Caricchi, 2017) and the temporal and spatial proximity of Miocene deposits to the Quaternary arc rocks investigated lend support to the possibility that processes leading to the formation of porphyry-type deposits under the Quaternary arc of Ecuador could be currently ongoing. Therefore, the Quaternary arc rocks of Ecuador can be used as a proxy of a potentially fertile typical Andean-syn-subduction-related magmatic environment.

In the barren Quaternary volcanics, Georgatou et al. (2018) observed that magmatic sulfides occurred in all studied rocks (from basalt to dacite) of the volcanic arc as polyminerale inclusions composed of Fe-rich/Cu-poor and/or Cu-rich phases, occurring mostly in Fe/Ti oxides and to a lesser extent in silicate minerals. Only sulfide Type-2 and 4 were observed in Ecuador, presenting a remarkable textural and compositional resemblance to the case of

**Commented [AAG13]:** After the comment of Referee#1-Dan Smith:

C: Konya anhydrite inclusions – possibility of water saturation dismissed – why? On what basis? Some of the Konya samples are evolved compositions (dacites) and water saturation is entirely feasible. Sulphur speciation and hence mineral stability is also modified by pressure (see Matjushkin et al 2016).

R: These Type-4 sulfides apart from the anhydrite they also co-exist with apatite and silicate melt inclusions in magnetite which indicates their magmatic nature. If the system was already water saturated we would expect to see hydrothermal sulfides.

Please see our extended reply at the response pdf doc entitled "Response to Referee#1-Dan Smith".

Ch: We have explained the statement by adding the above arguments as seen in the text.

Konya. ~~B~~Rocks from both areas are characterised from both, display first (Type-1 ad -2) and second stage (Type -4) sulfide saturation. Nonetheless, Type 4 sulfides in Konya have sequestered higher amounts of Cu compared to Ecuador. In particular according to EPMA individual mineral analyses of 19 sulfides in Konya and 22 in Ecuador, Cu<sub>max</sub> ranges between 72 and 66 wt %, respectively.

Georgatou et al. (2018) suggested that the negative trend of Cu with magmatic differentiation (e.g., Keith et al., 1997, Chiaradia, 2014) observed in typical ~~syn-subduction~~Andean-type magmatic arcs is a result of a continuous Cu sequestration in magmatic sulfides. A similar Cu decrease with magmatic evolution is observed also in the areas studied here and characterised by post-subduction magmatic rocks some of which are also associated with porphyry and epithermal-type deposits. This suggests that in both settings (~~syn~~-subduction and post-subduction) Cu and other chalcophile metals behave compatibly during magmatic evolution and confirms that these metals are lost on the way to the surface ~~within the continental crust~~.

~~In contrast to Ecuador, the volcanic provinces of Konya and Beydagi are associated with coeval economic deposits. In particular, the Beydagi volcanic center was active from ~16 to 12 Ma and hosts the ~14 Ma Kisladag Au porphyry, whereas the Konya Volcanic Belt is characterised by more or less continuous magmatism between ~12 and 3.3 Ma and hosts the ~7.2 Ma old Doganbey Cu-porphyry (Zürcher et al., 2015) and the Miocene Inlice Au-epithermal deposit (Redwood, 2006, Hall et al., 2007).~~

## 6. Implications for ore formation

~~Konya, Beydagi (Usak basin) and Ecuador are the only areas among those studied, which are associated or potentially associated with economic deposits of the porphyry suite. It is remarkable noteworthy that this feature coincides with the fact that rocks from these areas are the only ones with iss-only (Type 4) and iss-rich (Type 3) sulfides. In particular, Type 4 sulfides (chalcopyrite-bornite+digenite) were observed in areas associated (Konya) or potentially associated (Ecuador) porphyry Cu deposits (e.g. Konya-Doganbey and Ecuador-Casabel/Llurimagua Junin). Beydagi, where Type 3 sulfides (chalcopyrite-pyrite) are seen, is associated with a porphyry Au deposit (Kisladag). The above observation calls for further investigation since the presence of iss-rich and iss-only sulfide types, like in cases 3 and 4, could be used as a proxy for porphyry Cu and porphyry Au type deposits, respectively.~~

Some of the most discussed ~~contributing factors to the fertility of a magmatic system and its potential fertility issues of magmatic systems~~ to produce a porphyry deposit on the surface, involve: (i) metal and volatile contents in the primary magma (e.g. Core et al. 2006;-) fertility, in terms of initial chalcophile and siderophile element concentration, and (ii) metal and volatile element content changes during evolution of the primitive magma to the intermediate-felsic compositions typically associated with porphyry-type deposits (e.g. Richards and Kerrich, 2007)s which is linked to increased water amount in the magma, (iii) magma volume and duration of magmatic-hydrothermal activity (e.g. Chiaradia and Caricchi, 2017), and (iv) later enrichment of the system in chalcophile elements by efficiency of pre-concentration processes of chalcophile and siderophile elements in sulfide-rich zones (e.g. Nadeau et al., 2010).

Fertility issues (iii) and (iv) above have been addressed by various studies. Cline and Bodnar (1991) and more recently Chiaradia and Caricchi (2017) and Chelle-Michou et al. (2017) have shown that there is a correlation

### Commented [AAG14]:

After the comment of Referee#1-Dan Smith:

C: This content is covered in the background sections. I think you can cut this paragraph.

Ch: We have removed the indicated paragraph.

Commented [AAG15]: After the comments of Referee#1-Dan Smith, suggesting to include the importance of evolved lithologies and to discuss total metal abundances and magma volumes as contributing factors for ore genesis.

Ch: We have moved this part further below and have re-structured and re-phrased all the chapter on 'implications for ore formation'.

between the size of the magma reservoir providing metals and fluids to the ore system and the size of the deposit and that also the duration of the ore process might play a role in this sense.

Sulfide pre-concentration in cumulates at depth and a later magmatic recycling through remelting and release of the metals back to the system has been suggested as a possibility by various studies (e.g. Richards, 2009, Lee et al., 2012, Audétat and Simon, 2012, Sillitoe, 2012, Wilkinson, 2013, Chiaradia, 2014, Jenner, 2017, Fontboté et al., 2017). Although we cannot test this hypothesis in the present study, it is possible that the sulphide-silicate-oxide aggregates observed in Kula (Figs. 4xi, 5e) account for those cumulates. However, further investigation to quantify the physico-chemical conditions under which this recycling process may be possible or not is needed.

Below we discuss the fertility issues (i) and (ii) above in the light of our data. For source fertility to play an important role for the ore genesis in terms of metal budget, it would imply an obvious difference in the Cu amount of the sulfides saturating during the first stage as well as different proportions of mss (Cu-poor) and iss (Cu-rich) composing the most primitive sulfides (Type-2) for the different study areas. This would be a result of different metal abundances in the initial silicate melt that would preferentially partition into either the iss (eg. Cu, Au) or the mss (eg. Ni, Fe), respectively. For example, the average area (%) of the Cu-rich/iss phases in sulphide inclusions from Beydagi, Konya and Ecuador, relative to the mss phases composing the same sulfide inclusions, should be larger compared to the area (%) of the iss phases in sulphide inclusions of Kula, Itecektepe and Elmadag. This goes against the results found in this study where inclusions from all regions show similar relative proportions (84.2 and 15.7 (2 standard error =  $\pm 2.2$  area %) of Ni-rich/mss and Cu-rich/iss phases. These values are very similar to the mss-iss proportions of sulfides found in Merapi volcano (mss =  $81 \pm 7$  and iss =  $19 \pm 7$ , respectively; Nadeau et al., 2010). Also according to the study carried out by Chang and Audétat (2018), on arc magmas of Santa Rita and Cherillos (New Mexico) using LA-ICP-MS, the more Cu-rich/iss mineral phases are  $<20$  vol% relative to the Cu-poor/mss. A second argument that supports the contention of similar metal contents in the primitive magmas is that there are no significant differences in the Cu values of Type-2 sulfides neither for the individual EPMA analysis (Cu median = 0.03–1.3 wt %, Tab.1 and Fig.8) nor for the bulk area reconstructed compositions (Cu median = 0.69–6.04 wt %, Tab.2) –among the areas that present iss-only sulfides and are associated with porphyry deposits. All study areas are characterised by similar Cu amount (Cu median = 0.03–1.3 wt %) and proportions (area %) of Ni-rich/mss (84.2) and Cu-rich/iss (15.7) phases within uncertainty (2se =  $\pm 2.2$ ). This observation carries major implications suggesting that independent of the geodynamic setting (subduction, post-subduction and intraplate-OIB like volcanism) the initial metal abundances of the primitive magmas are approximately the same (see also Lee et al., 2012 for similar Cu contents in primitive arc basalts and MORBs).

Concerning the amount of water in the source, it is possible that different water contents of the primitive magmas corresponding to different geodynamic settings may play an important role for both sulfide saturation at depth and ore generation. It is likely that all magmatic systems have the potential to become saturated in Cu-rich/iss-only sulphides, after exhausting all the Ni, as long as there is not enough water to strip out the metals from the melt, rendering a residual magma fertile, leading to the formation of a porphyry deposit. Because H<sub>2</sub>O is incompatible, magma evolution from a primitive basaltic magma will result in increasing concentrations of H<sub>2</sub>O in the residual derivative magmas of intermediate to felsic composition until water saturation may be reached depending mostly on the depth at which magma evolution occurs at surface (e.g. Kelley and Cottrell, 2009, Richards, 2011, Yang et

**Commented [AAG16]:** After the comment of Referee#2-Jonathan Naden:

C: 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.

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

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

**Commented [AAG17]:**  
After recommendation of Referee#1-Dan Smith

We have rephrased this paragraph in order to state clearer the main result (relative proportions of mss and iss from Imaje) on which we are basing our argument that similar initial metal contents of the different areas/magmas are observed.

**Commented [AAG18]:**  
After recommendation of Referee#1-Dan Smith

C: This needs rephrasing. It reads as if magmas with insufficient water to strip metals are infertile - when logically, that cannot be correct. A porphyry deposit is a hydrothermal feature - the stripping of metals by a fluid is a vital part of the process. A magma with insufficient water will be copper rich yet still infertile.

R: Thank you for noticing.

Ch: We have re-phrased as requested.



al., 2015). It is likely that all magmatic systems have the potential to become saturated in Cu-rich/iss-only sulfides, after exhausting all the Ni, as long as the system does evolve to intermediate-felsic compositions while still not reaching water saturation conditions before sulphide saturation occurs. Based on the textural and chemical evidence from Type-4 sulfides of Konya, and in particular the co-existence of vesicles indicating a pre-existing gas phase in contact with Type-4 sulfides, here we may be able to trace the transition from a sulfide-saturated system to a fluid-saturated system. Indeed only the rather primitive rocks from Kula did not evolve enough in order to reach the second saturation stage. In addition, in this study, only areas that are characterised by a subduction component, and therefore by likely higher water contents in their source, resulted in displaying a Cu-rich sulfide saturation, with the counterexample of the intraplate OIB-like volcanism of Kula.

An additional important factor in order to saturate sulfide Cu-rich phases is magnetite crystallisation. Although it has already been pointed out as an important step for sulfide saturation in general (e.g. Metrich et al., 2009, Jenner et al., 2010) in this study we show that magnetite crystallisation does not seem necessary for the saturation of any sulfide type, but is systematically associated with the iss-rich (chalcopyrite-pyrite) and iss-only (chalcopyrite-bornite/digenite), Cu-rich sulfide types (Type-3 and -4). Only rocks that have undergone magnetite crystallisation present Cu-richer sulfides, with the exception of Kula as well as the cases of Elmadag and Itecektepe which lavas do not include magnetite (Fig.7). These three volcanic centers are not associated with any known economic deposit.

In contrast, Konya, Beydagi (Usak basin) and Ecuador are the only areas among those studied, which present iss-only (Type-4) and iss-richer (Type-3) sulfides. The rocks in which these sulfide types are present correspond to more evolved lithologies (SiO<sub>2</sub>>60 wt %), which are associated or potentially associated with economic deposits of the porphyry suite. It is noteworthy that this feature coincides with the fact that rocks from these areas are the only ones with iss-only (Type-4) and iss-richer (Type-3) sulfides. In particular, Type-4 sulfides (chalcopyrite-bornite+digenite) were observed in areas associated (Konya) or potentially associated (Ecuador) with porphyry Cu deposits (e.g. Konya-Doganbey and Ecuador-Cascabel/Lurimagua-Junin). Beydagi, where Type-3 sulfides (chalcopyrite-pyrite) are seen, is associated with a porphyry Au deposit (Kisladag). The above observation calls for further investigation since the presence of iss-rich and iss-only sulfide types, (like in cases 3 and 4); in felsic volcanic rocks and in particular in magnetite host minerals, could be used as a proxy for porphyry-Cu and porphyry-Au type deposits, respectively.

An additional significant implications based on the correlation between Type-3 and -4 sulfides high in Cu and ore deposits (Beydagi, Konya and Ecuador), combined with the similar initial metal contents of the magmas of these areas, suggests an increase in the Cu contents of the sulfides and in the later hydrothermal ore fluid which has not occurred in the other study areas. We argue that the later sulfide Type-3 and -4 (iss-rich/only, hosted in magnetite) can help us to further understand the transition between a sulfide-saturated system and a fluid-saturated system. In addition, taking into consideration how porphyry deposits in subduction settings are generally Cu-rich whereas those found in post-subduction settings tend to be Au-rich (e.g. Sillitoe, 1993, Li et al, 2006, Richards, 2009), future sulfide trace element LA-ICP-MS analysis including precise Au, Ag and PGE values (which constitute better markers for sulfide saturation identification, see Park et al., 2019, Park et al., 2015, Cocker et al., 2015, Jenner, 2017, Mandon, 2017) will-could help distinguish the conditions of magma fertility for the different geodynamic settings. Finally magmatic sulfide saturation will retain a certain amount of CSEs and deplete the

**Commented [AAG19]:**

After recommendation of Referee#1-Dan Smith

Please see 'Authors response to Referee#1 for entire comment and reply.

Ch: We have removed the part of the sentence referencing Kula.

**Commented [AAG20]:**

After the comment of Referee#1-Dan Smith:

C: How much of this is because the samples from other areas (e.g. Kula) are in lithologies typically excluded from porphyry exploration programmes - mostly for being too primitive? Are we really seeing implications for ore formation, or are both the sulphide assemblage and presence of mineralization a consequence of the melt evolution stage?

R: Thank you for the suggestion.

Ch: We have included the felsic nature of the lithologies as a possible factor for ore forming process. See also lines 412-413.

After the comment of Referee#2-Jonathan Naden:

C: The use of "remarkable" is hyperbole in this context, please rewrite this sentence in more circumspect terms.

Ch: We have rephrased as seen.

residual melt in them. Quantifying this metal loss is crucial in order to understand whether, for the **bigger** ~~picture~~ sake of ore forming processes, this loss is significant or not and may be compensated by other more critical ingredients like an increase of volatiles and magma volumes (Chiaradia and Caricchi, 2017). Modelling combined with experimental results on metal partition coefficients, petrographic observations and data compilation of real case sulfide mineral analysis can aid to solve this question.

## 7. Conclusions

~~There are four main conclusions~~ In this study we have investigated the magmatic sulfide occurrence and chemistry during the evolution of different magma types (from high-K calc-alkaline to shoshonitic series) in study areas characterised by diverse geodynamic settings (post-subduction, syn-subduction and OIB-intraplate volcanism). Our data allow us to draw the following conclusions: (1) Sulfide saturation occurred in magmatic rocks from all study areas, independently of the magma composition, geodynamic regimes and whether or not the system produced an economic deposit. Sulfides were present in all rocks, corresponding to a wide range of composition ( $\text{SiO}_2$  range = 46-68 wt.%, basalts to andesites/dacites and from high K-calc-alkaline to shoshonitic series), characterised by different geodynamic regimes (subduction, post-collision and intraplate OIB volcanism) some of which are associated with economic deposits (porphyry Cu and/or Au and Au epithermal); (2) According to their occurrence and chemical composition, sulfides can be classified in different types ~~and which~~ do not ~~necessarily~~ appear in all study areas. Type-1 sulfides are rare, mostly composed of Cu-poor phases (pyrrhotite, pentlandite-mss), hosted only by olivine phenocrysts and are seen only in Kula. Type-2 sulfides consist of a Cu-poor phase (pyrrhotite,  $\pm$ pentlandite), and a Cu-rich phase (cubanite, chalcopyrite). They are the most abundant type, hosted by different minerals (pyroxene, amphibole, magnetite, and plagioclase) and are found in all study areas. Type-3 sulfides are rare, composed of mostly a Cu-rich phase (chalcopyrite $\pm$ chalcocite) and pyrite, hosted by magnetite and are observed only in Beydagi. Type-4 sulfides are less abundant than Type-2 but more abundant than Type-1 and -3. They are composed of only Cu-rich phases (chalcopyrite-bornite $\pm$ digenite), hosted only by magnetite and observed solely in Konya and Ecuador. Type-5 sulfides are found in the groundmass as sulfide-oxide-silicate aggregates: they are mostly found in Kula and the sulfides are mainly Cu-poor. Type-3 and 4 are the sulfides with the highest Cu contents and are only observed in areas associated with porphyry Au and Cu deposits, respectively, together with epithermal Au deposits. (3) As the sulfide melt evolves, a decrease in Ni/Cu is observed, which is used here as a proxy for the mss/iss ratio. This chemical evolution corresponds to a sulfide melt evolution starting with an mss-rich sulfide melt, switching to an mss and iss-melt and finally (and uniquely for some settings) to iss-only sulfides. This suggests at least two sulfide saturating stages: an early mss-only or mss-rich and a late iss-only or iss-rich stage. Further research needs to address the question whether these stages are distinct or are part of a continuous process of sulfide saturation. (4) The initial metal content of the magma was very similar for all the study areas. This can be inferred from the similar proportions of the mss and iss of the early saturating stage sulfide (Type-2) for all investigated study areas (mss=84.2 and iss=15.7 area%, with  $2\sigma=\pm 2.2$ ). Based on points 2 and 4 above, the correlation between sulfides high in Cu and ore deposits (Beydagi, Konya and Ecuador), combined with the similar mss and iss proportions ~~for in rocks from~~ all study areas, suggests ~~an increase in the~~ that Cu contents of the sulfides and, potentially, of ~~a later Cu enrichment~~ the later hydrothermal ore-forming fluids (e.g., Nadeau et al., 2010); increase concurrently with a Cu ~~deprivation~~ depletion of the residual magma ~~for the cases of Beydagi, Konya and Ecuador.~~ (43) This possibly suggests that metal enrichment in

**Commented [AAG21]:** After the comment of Referee#1-Dan Smith:

C: Does it really suggest Cu enrichment? Is this not just Ni depletion? Fig 3 doesn't support Konya being Cu-enriched (one sample above 30 ppm whole rock).

R: We agree with the comment, indeed the sentence needed re-phrasing, since the implication does not mean Cu-enrichment in the whole rock, rather in the sulphides.  
Ch: We have re-phrased as seen.

derivative magmas is not an essential requirement for the fertility of the latter and that other factors associated with magma evolution (H<sub>2</sub>O content, magma volume: Rohrlach and Loucks, 2005; Chiaradia and Caricchi, 2017) could play a more important role. As the sulfide melt evolves, a decrease in Ni/Cu is observed, which is used here as a proxy for the mss/iss ratio. This chemical evolution corresponds to a sulfide melt evolution starting with an mss-rich sulfide melt, switching to an mss and iss melt and finally (and uniquely for some settings) to iss-only sulfides. This suggests at least two sulfide saturating stages: an early mss only or mss rich and a late iss only or iss rich stage. Further research needs to address the question whether these stages are distinct or are part of a continuous process of sulfide saturation.

## 8. Author Contribution

AG and MC designed the project and methodology. AG carried out petrographical investigation, EPMA sulfide analysis and bulk rock chemical analysis. AG wrote the manuscript with contributions from MC.

## 9. Acknowledgements

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### Tables and Table Captions

Table 1. EPMA summary for individual sulfide analysis (N=number of measurements) corresponding to each sulfide type for every study area. The empty cells (-) correspond to a lack of measurement either because it was below determination limit or not measured. For complete dataset, analytical conditions and detection limits see Table 4 in doi:10.6084/m9.Figshare.8230787.

Area	Type (N)	Whole Rock Chemistry				EPMA Sulfide Chemistry (wt %)								
			Cu ppm	SiO <sub>2</sub> wt%	S	Cu	Fe	Ni	As	Se	Zn	Ag	Au	Tot
Beydağı	2 (17)	med	7	62	38	0.3	55	0.15	0.03	0.2	0.5	0.02	0.22	98
		min	4.2	46	35	0.01	29	0.03	0.03	0.02	0.5	0.01	0.15	-
		max	29	72	53	34	58	0.77	0.03	0.02	0.5	0.02	0.27	-
		av	12	62	40	6.6	49	0.31	0.03	0.02	0.5	0.02	0.22	99
		SD	6.7	3.9	5.7	11	10	0.28	-	-	-	-	0.05	-
	3 (16)	med	18	59	35	32	31	0.12	0.07	0.03	0.98	0.01	0.24	99
		min	6.7	59	33	0.17	31	0.01	0.07	0.03	0.73	0.01	0.24	-
		max	18	63	53	33	58	1.21	0.07	0.03	3	0.02	0.24	-
		av	17	59	38	24	35	0.32	0.07	0.03	1.4	0.01	0.24	99
		SD	2.8	1	6.1	13	7.6	0.43	-	-	0.9	-	-	-
	5 (6)	med	6.7	63	38	0.78	56	0.04	-	-	0.71	0.02	0.14	97
		min	6.7	59	33	0.08	29	0.01	-	-	0.59	0.02	0.14	-
		max	18	63	51	32	58	0.21	-	-	2.4	0.02	0.14	-
		av	10	61	38	11	47	0.07	-	-	1.2	0.02	0.14	97
		SD	5.6	2.1	5.3	15	13	0.07	-	-	1.03	-	-	-
İtecektepe	2 (26)	med	7	62	38	0.03	57	0.1	-	0.04	0.81	0.02	0.18	97
		min	5.1	61	35	0.01	52	0.02	-	0.04	0.57	0.01	0.18	-
		max	13	64	39	6.1	58	0.25	-	0.04	1.5	0.03	0.18	-
		av	7.2	62	38	0.27	57	0.1	-	0.04	0.88	0.02	0.18	97
		SD	1.6	0.85	0.85	1.2	1.3	0.05	-	-	0.34	0.01	-	-
	Elmadag	med	26	61	37	0.14	56	0.26	0.04	-	0.75	0.02	-	96
		min	4.3	56	35	0.01	32	0.04	0.04	-	0.72	0.02	-	-
		max	63	69	39	29	58	1.5	0.04	-	0.79	0.02	-	-
		av	26	61	37	4.2	53	0.4	0.04	-	0.75	0.02	-	96
		SD	12	2.9	1.29	11	8.73	0.47	-	-	0.05	-	-	-
Kula	1 (10)	med	29	47	38	0.05	56	4.2	0.04	0.02	-	-	0.04	98
		min	29	47	36	0.03	45	3	0.03	0.02	-	-	0.04	-
		max	30	48	39	0.34	57	14	0.06	0.03	-	-	0.04	-
		av	29	48	38	0.15	54	6	0.04	0.02	-	-	0.04	98
		SD	0.25	0.35	0.76	0.14	4.4	4.3	0.01	-	-	-	-	-
	2 (190)	med	29	47	38	0.1	58	0.77	0.04	0.04	0.03	0.02	0.05	98
		min	23	37	38	0.01	5.8	0.01	0.02	0.02	0.02	0.01	0.03	-
		max	61	66	40	32	62	41	0.1	0.08	0.16	0.04	0.22	-
		av	30	47	36	2.4	54	2.9	0.05	0.04	0.05	0.02	0.06	98
		SD	4.2	1.7	5.9	6.3	10	7.3	0.02	0.01	0.04	0.01	0.04	-
	5 (35)	med	29	47	37	0.45	59	0.78	0.05	0.03	0.03	0.02	0.04	98
		min	28	47	33	0.01	35	0.04	0.02	0.02	0.02	0.01	0.03	-
		max	35	48	40	26	61	22	0.08	0.06	0.16	0.05	0.11	-

Konya	2 (187)	av	30	47	37	4.7	55	1.8	0.05	0.04	0.05	0.02	0.05	98
		SD	2.6	0.31	1.8	8.5	8.3	4.1	0.01	0.01	0.04	0.01	0.02	-
		med	12	61	38	0.09	58	0.11	0.04	0.02	0.04	0.05	-	97
		min	4.6	46	26	0.01	15	0.01	0.02	0.01	0.01	0.01	-	-
		max	50	70	48	69	60	9.4	0.08	0.05	0.23	0.11	-	-
		av	13	62	37	4.2	55	0.23	0.04	0.02	0.04	0.05	-	96
	4 (19)	SD	4.8	2.9	3.2	11	8.7	0.79	0.02	0.01	0.04	0.03	-	-
		med	13	62	26	56	16	0.01	0.05	0.02	0.06	0.06	-	99
		min	12	61	22	38	5.6	0.01	0.02	0.02	0.06	0.04	-	-
		max	21	62	33	72	29	0.11	0.06	0.02	0.06	0.07	-	-
		av	14	62	27	54	18	0.02	0.04	0.02	0.06	0.06	-	99
		SD	3.5	0.33	3.1	11	7.1	0.02	0.02	-	-	0.01	-	-
Ecuador	2 (172)	med	23	62	39	1.27	58	0.4	0.04	-	0.02	-	-	98
		min	6	48	20	0.01	17	0.01	0.01	-	0.02	-	-	-
		max	105	77	53	36	65	10	45	-	0.02	-	-	-
		av	27	62	38	11	52	0.68	1.18	-	0.02	-	-	98
		SD	15	3.3	3.2	14	11	1.14	7.01	-	-	-	-	-
		med	32	60	27	56	17	0.39	0.08	-	-	0.02	-	100
	4 (22)	min	16	58	25	40	14	0.23	0.01	-	-	0.01	-	-
		max	38	64	32	66	27	0.56	0.32	-	-	0.02	-	-
		av	31	60	27	55	18	0.39	0.08	-	-	0.02	-	100
		SD	4.8	1.8	1.9	7.4	4.1	0.23	0.08	-	-	-	-	-

860 Table 2. Summary composition of 100 reconstructed sulfides belonging to different sulfide types (N=number of sulfides reconstructed) observed in every study area except Itecektepe and Elmadag where the Cu-rich phase was too small to analyse with the EPMA. The empty cells (-) correspond to a lack of measurement either because it was below determination limit or not measured. For complete dataset (including mss/iss area% of Itecektepe and Elmadag) see Table 5 in doi:10.6084/m9.Figshare.8230787.

		Whole Rock med		Area med%				EPMA med wt% Reconstruction										
Area	Type (N)	Cu ppm	SiO <sub>2</sub>	mss	iss	void	S	Cu	Fe	Ni	As	Se	Zn	Ag	Au	Tot		
Beydağı	2(1)	17.85	58.67	95.5	4.5	16.7	38.77	0.69	56.67	0.73	-	-	-	-	0.08	97		
	3(8)	17.85	58.67	34.5	65.5	2.8	39.53	23.02	34.24	0.05	0.02	0.11	-	0.02	0.09	97		
	1 (4)	28.8	47.42	99.5	0.5	0	37.84	0.1	55.35	4.42	0.05	-	-	-	0.03	99		
Kula	2(25)	28.8	47.42	88.7	11.2	0.7	37.93	2.57	56.66	0.73	0.04	-	0.02	0.02	0.03	99		
	5(8)	29	47.64	86.8	13.1	-	36.03	3.46	57.3	1.03	0.04	0.02	0.02	0.01	-	98		
Konya	2(26)	11.71	61.27	89.5	10.8	0.4	38.66	2.73	56.78	0.11	0.03	0.03	0.03	0.03	0.02	98		
	4(8)	12.68	61.82	0	100	21.2	28.31	48.44	23.09	0.02	0.02	0.02	0.04	0.04	-	99		
	2(10)	19	62.27	78.5	21.5	16.9	37.7	6.04	53.47	1.71	0.02	-	-	-	-	98		
Ecuador	4(10)	32	59.66	0	100	5.65	28.09	51.71	21.05	0.37	0.11	-	-	-	-	100		

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## Figure Captions

Figure 1. World distribution of arc-related metallogenic belts showing the biggest Cu and/or Au porphyry deposits, modified from Richards, 2013 and Cooke et al., 2005. References of previous studies on magmatic sulfides are depicted with black stars whereas the areas considered in this study are shown with a red bigger star.

Figure 2. Tectonic (a) and geological maps (b-c) of the studied areas and associated Au epithermal and Cu, Au porphyry deposits in Western Anatolia. The investigated Miocene volcano-plutonic complexes are Konya (b) and the volcanoes of Usak basin (Elmadag, Itecektepe and Beydagi-c) as well as the Quaternary Kula volcano (c). The geological maps have been modified after; (b) Keller et al., 1977 and (c) Karaoğlu et al., 2010.

Figure 3. Major (a-d) and trace (e-h) element variations with SiO<sub>2</sub> for the different study areas, illustrated by a different shape and colour. Smaller in size symbols correspond to datasets obtained from other studies (Beydagi-Karaoğlu, 2010, Kula-Alici et al., 2002, Aldanmaz et al., 2002, 2015, Dilek et al., 2010, Ercan et al., 1985, Konya-Temel et al., 1998, Korkmaz et al., 2017). For comparison purposes whole rock chemistry from Ecuador has been illustrated as a field in the graphs (a-f). Spider graph-g showing the solid mean trace element distribution for the different study areas. For dataset see Tables 1-3 in doi:10.6084/m9.Figshare.8230787

Figure 4. Sulfide types observed in the different study areas [characterise by diverse geodynamic settings](#). The abbreviations stand for: pyrrhotite-po, pentlandite-pn, chalcopyrite-cp, chalcocite-cc, cubanite-cb, pyrite-py, bornite-bn, digenite-dg, anhydrite-anhy, apatite-apt, magnetite-mt, monosulfide solid solution-mss and intermediate solid solution-iss. The scale bar corresponds to 5 µm unless stated otherwise.

Figure 5. BSE (a-f,h) and SEI (g) microphotographs of sulfides, their host and accessory mineral phases. Important things to note: a) the common occurrence of apatite inclusions observed together with the sulfide and hosted by the same mineral (px in a and mt in b,f); b) the lack of sulfides in the biotite phenocrysts, even in the cases where the biotite itself includes a magnetite that hosts sulfides; c) the usual sulfide presence in the amphibole destabilised rim, where amphibole is being replaced by clinopyroxene, plagioclase and rhönite, characterising the Kula volcano (also seen by Grutzner et al., 2013); d) resorbed sulfide found in amphibole in (c) showing a rapid unmixing of the cp-cb (iss); e) unusually big (up to 600 µm) sulfide aggregate composed of mostly Cu-poor sulfides, magnetite and micro-sized silicates, found in Kula; f) partly dissolved sulfide hosted by magnetite that shows ilmenite exsolution lamellae, g) trail of bubbles of silicate melt and ~~vesicles~~ associated with the sulfide and h) daughter sulfide (<0.5 µm), composed mostly po found in re-crystallised melt inclusion hosted by olivine, observed in Kula. [For abbreviation see legend in Fig.4](#). The scale bar corresponds to 100 µm unless stated otherwise.

Figure 6. BSE (a,b-i,c-i,e,f) and SEI (b-ii,c-ii,d,e) microphotographs of anhydrite occurrences in magnetite phenocrysts, as individual phases or found together with Cu-rich sulfides and occasionally with zircons. Apatite and silicate melt are often hosted by the same magnetite phenocrysts as well. Note that the anhydrite; (b-i,f) in BSE is not visible unless seen in SEI (b-ii), it can be partly (d,e) or completely (c) dissolved. In image-e BSE and

SEI imaging have been merged in order to make both sulfide and sulphate, respectively visible. [For abbreviation see legend in Fig.4.](#) The scale bar corresponds to 2  $\mu\text{m}$  unless stated otherwise.

Figure 7. Sulfide composition in the Cu-Fe-S system and Ni-Fe-Cu from individual [mineral](#) analyses by EPMA. The colour shows the study area and the shape indicates the host mineral in which magmatic sulfides were found. Note the progressive Ni/Cu depletion as we switch from more mafic suites (e.g. Kula) and early crystallising host minerals (olivine, pyroxene and amphibole) to more evolved (e.g. Konya) and later crystallising mineral phases (magnetite). The grey fields correspond to analysis that resulted in Ni or Cu below determination limit equal to 0.01 wt% that however for discussion purposes have been shown here. ~~The measurements depicted with an error bar (cross) represent SEM analysis where the mineral phase was too small to analyse by EPMA, the error does not correspond to a quantitative value.~~ For dataset see Table 4 in doi:10.6084/m9.Figshare.8230787.

Figure 8. Box plot comparison of the Cu and Ni content (wt %) [resulting by individual mineral analyses](#) measured by EPMA for the different sulfide types characterising each study area. The central box is in the middle 50% of the data (total number of measurements considered is noted in parenthesis on the x axes). The line and dots in the box represent the median and mean value for each box/sulfide type, respectively (see values in Table 1). The outliers are further than 1.5\*(75th percentile/top of box-25th percentile/bottom of box) and the whiskers are the extreme values that are not outliers. Note that only Beydagi, Konya and Ecuador which are the three areas associated with porphyry deposits display the highest in Cu values of type 3 and 4 sulfides. [The stoichiometry of common sulfide mineral phases has been depicted for Cu and Ni \(wt %\) contents according to mindat.org.](#) For dataset see Table 4 in doi:10.6084/m9.Figshare.8230787.

Figure 9. Box plot comparison of the Cu-rich phase (chalcopyrite = iss) and Ni-rich phase (pyrrhotite±pentlandite = mss) proportions (area %) composing type-2 sulfides, calculated by ImageJ©1.38 software analysis for each study area (-N of [sulfides reconstructed](#)) sample; Kula=25, Itceektepe=16, Elmadag=10, Beydagi=15, Konya=25, Ecuador=35). Average, mean and median values are represented in the graph same as in Figure 8. For dataset see Table 5 in doi:10.6084/m9.Figshare.8230787.

Figure 10. Ternary isothermal sections through the central part of the Cu-Fe-S system according to and modified from (a,b,c) Kullerud et al., 1969, (d) Tsujimura and Kitakaze, 2004, (e) Cabri, 1973, (f,h) Yund and Kullerud 1966, (g) Craig and Scot, 1974. The stability fields and phase-relations at different temperatures are shown for; sulfide liquid-L (brown), bornite solid solution-bnss (purple), monosulfide solid solution-mss (pink), intermediate solid solution-iss (yellow) and digenite solid solution-dgss (blue). The data shown correspond to the bulk (area %) reconstructed sulfide compositions hosted by different phenocrysts/groundmass (shape) observed in every study areas (colour). For dataset see Table 5 in doi:10.6084/m9.Figshare.8230787.

**Commented [AAG22]:**

After the **comment of Referee#1**-Dan Smith:

C: I don't think these data add value. I would rather those that can't be measured in the ratio - particularly when analysed by a different, less sensitive technique - are just omitted.

R: We have removed the data from the graph as requested.

## Figures

Fig.1

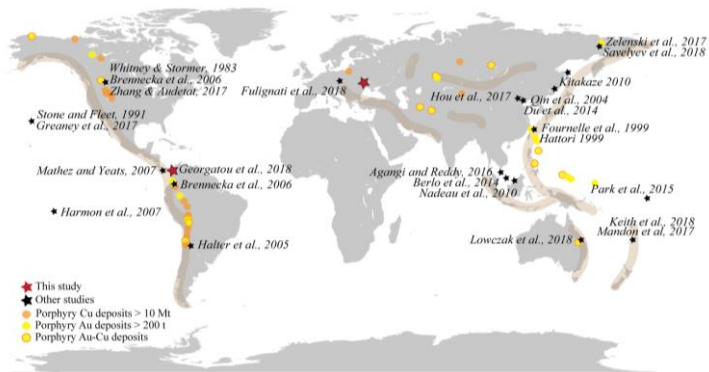
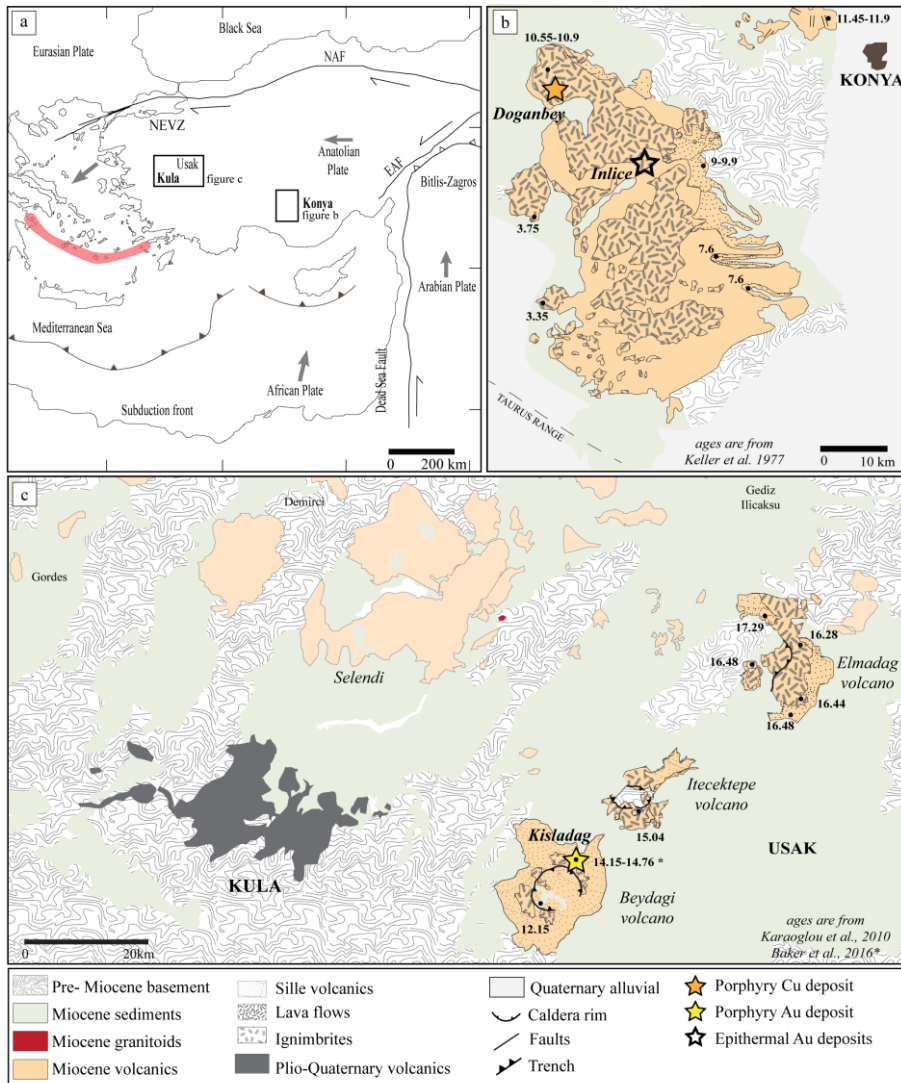
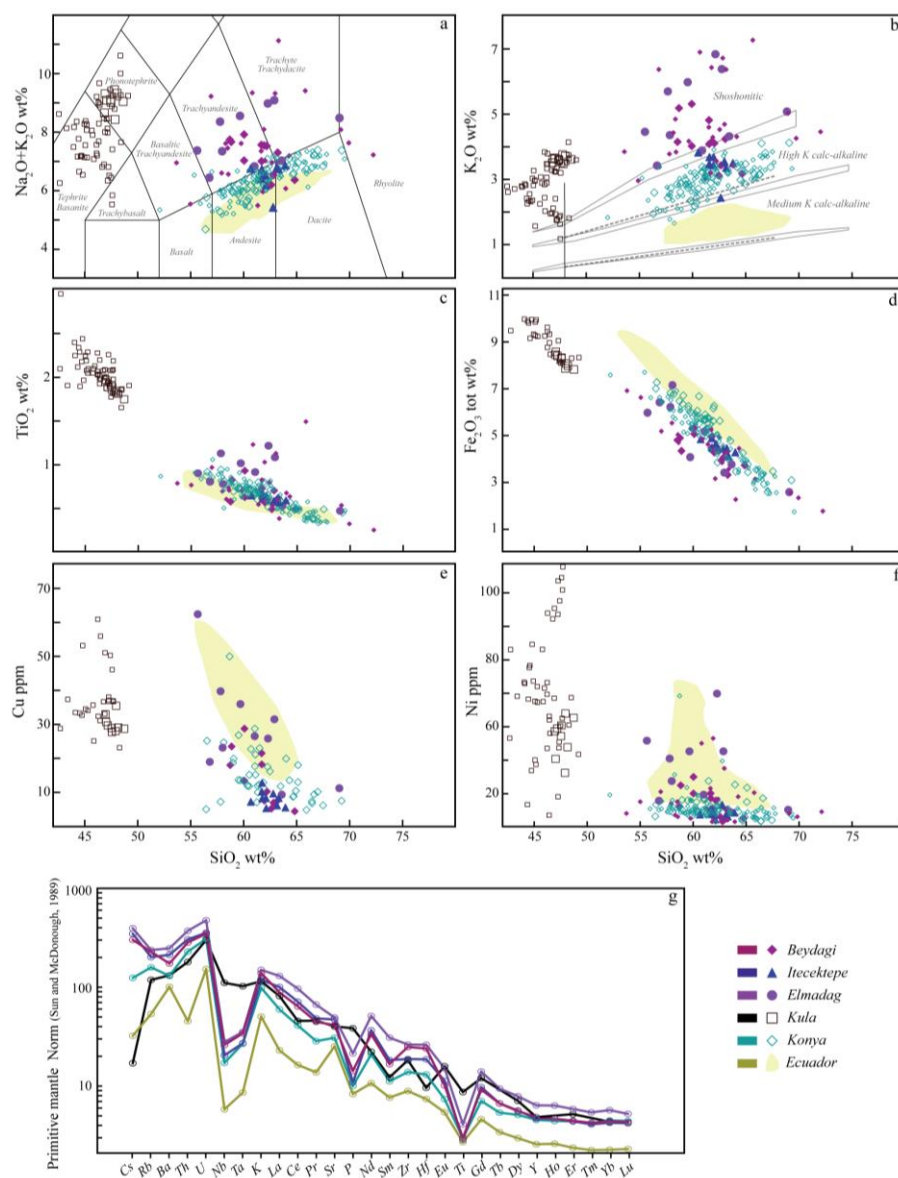




Fig.2



**Fig.3**



**Commented [AAG23]:**

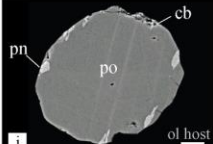
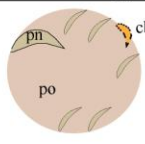
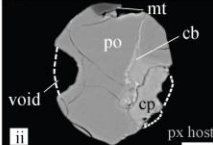
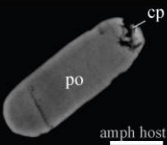
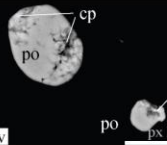
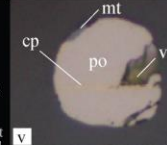
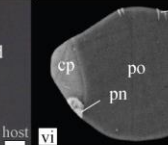
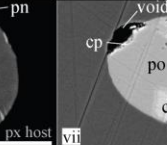
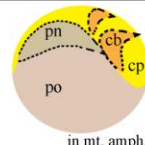
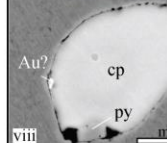
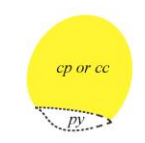
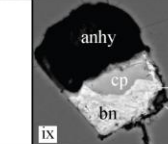
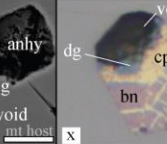

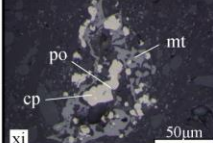
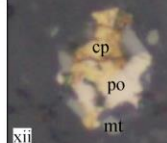
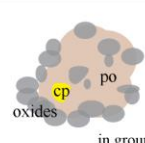
After the comment of Referee#1-Dan Smith:

C: Molecular formulae on axes all need subscripts for stoichiometry.

Ch: We have corrected for subscription, added the ' $\text{SiO}_2$ ' that was missing at the x axes, specified the total for  $\text{Fe}_2\text{O}_3$  and corrected  $\text{TiO}_2$ .

950

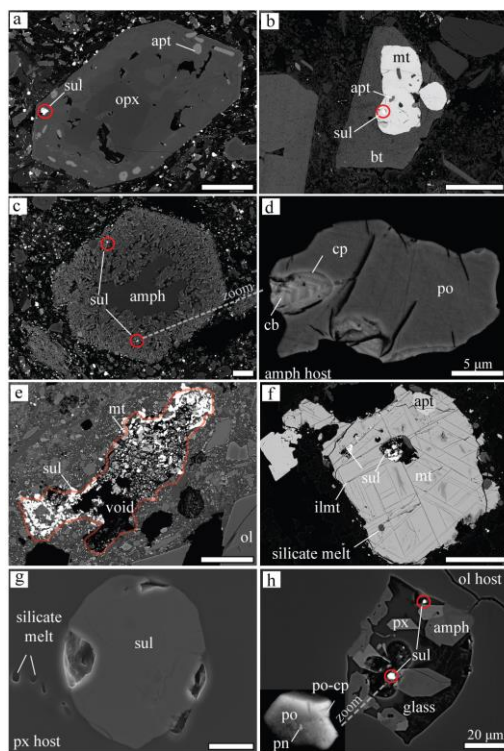
Fig.4

Intraplate-OIB	Post-Subduction				Syn-Subduction	Sulfide types	
KULA	ITECEKTEPE	ELMADAG	BEYDAGI	KONYA	ECUADOR		
 i						 a	1: mss +/- iss
 ii	 iii	 iv	 v	 vi	 vii	 b	2: mss > + iss
			 viii			 c	3: iss > + mss
				 ix	 x	 d	4: iss +/- anhy
 xi			 xii			 e	5: mss + iss + ox
barren	barren	barren	Kisladag Au-Mo porphyry deposit	Doganbey Cu-Au porphyry and Inlice Au epithermal deposit	Cascabel and Llurimagua Cu porphyry and Corazon Au epithermal deposits		ORE

Commented [AAG24]: We have extended the figure by adding the geodynamic setting as requested by Referee#1-Dan Smith. In addition we have changes the 'ph' to 'f' for Sulfide types.

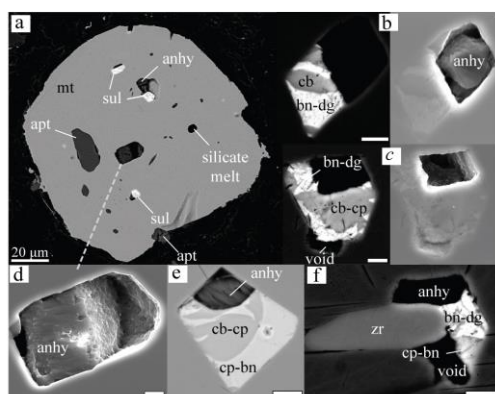
951

952 **Fig.5**



953

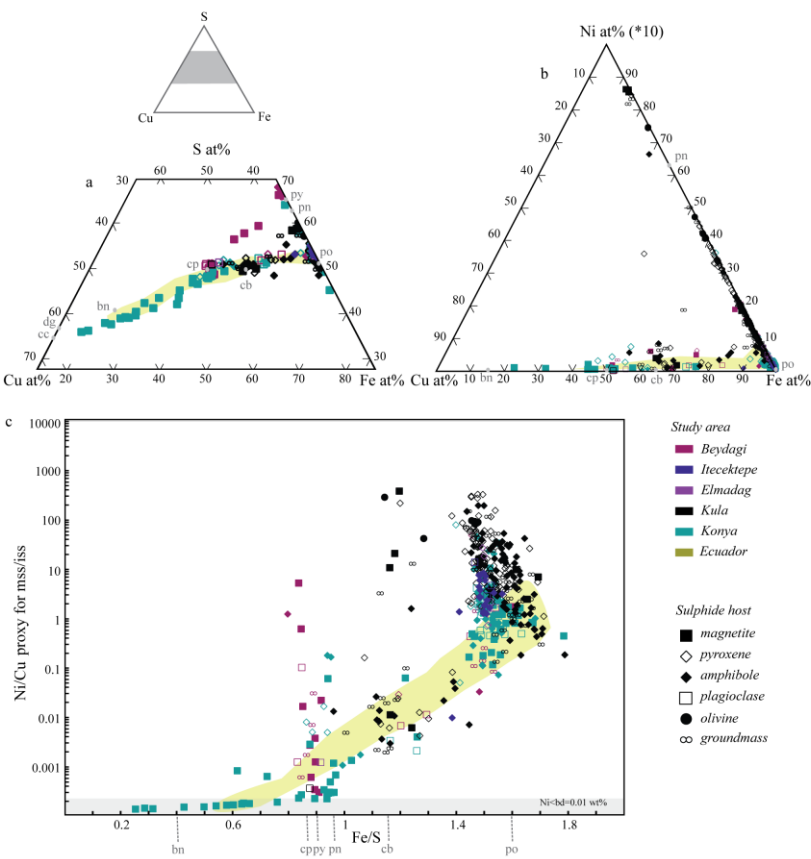
954 **Fig.6**



955

956

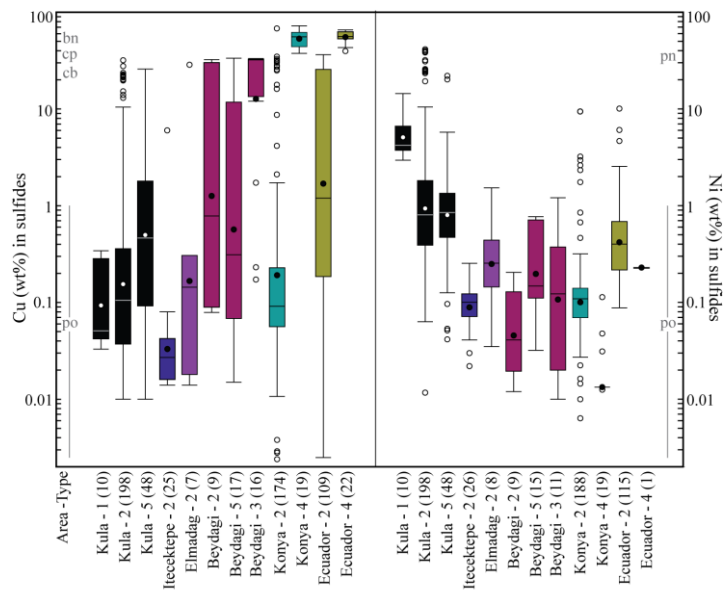
957 **Fig.7**



**Commented [AAG25]:** We have added on the graphs the common mineral phases and we have removed the SEM data from graph-c as requested by Referee#1-Dan Smith

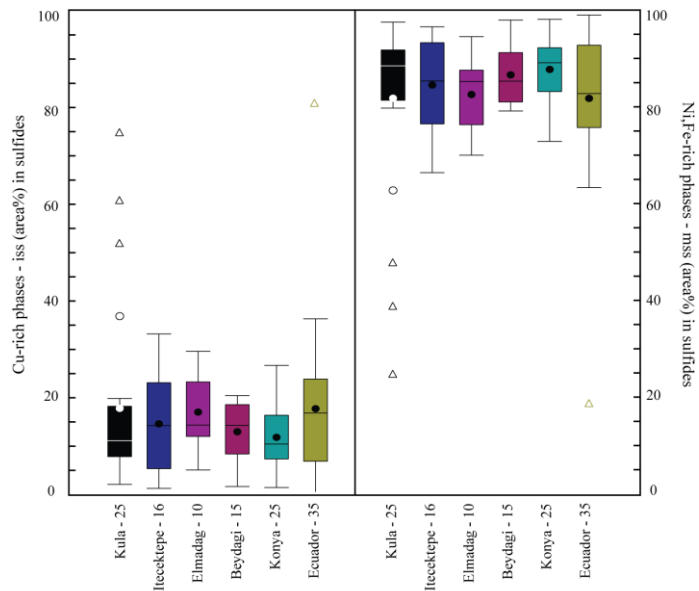
958

959 Fig.8



Commented [AAG26]: We have added the common mineral phases on the axes and changed the 'ph' to 'f' in the word sulfides

960  
961 Fig.9



Commented [AAG27]: Since all sulfides considered in this graph are Type-2 sulfides, which is indicated in the figure legend, we have included the number of sulfides considered for each area on the x axes instead. We also changed the 'ph' to 'f' in the word sulfides

962

