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REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

Review of “Hyper-enrichment of silver by the transportation and aggregation of silver sulfide nanoparticles” by Chai et al

Thank you for giving me the opportunity to review this manuscript. It is well written and reports interesting and innovative findings. Central to the manuscript, the discovery of Ag and AgS nanoparticles (NPs) hosted in calcite may represent a leap forward the understanding of high-grade Ag mineralisation. More broadly, this study feeds the increasing recognition of metallic NPs in ore systems and the role they may play during mineralisation. I believe that we will keep finding more examples around the world and as such, the present study is an important contribution.

I offer below some comments and recommendations to improve the manuscript that I hope the authors will find useful:

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Denis Fougereuse, Perth 25-01-24

Reviewer #2 (Remarks to the Author):

Ms. Ref. No.: 475253_0

Title: Hyper-enrichment of silver by the transportation and aggregation of silver sulfide nanoparticles.

Authors: Mingchun Chai, Anthony E. Williams-Jones, Wei Fu, Jianwei Li and Cheng Xu.

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After careful evaluation of this manuscript, I believe that the manuscript "Hyper-enrichment of silver by the transportation and aggregation of silver sulfide nanoparticles" by Mingchun Chai et al can be suitable for publication in journal "Nature Communications" after minor revision and additions.

Major remark:

The crystal structure of silver sulfide nanoparticles observed in the studied ore should be clarified using X-ray microanalysis. Three references to X-ray determinations of the crystal structure of acanthite should be added to the manuscript:

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I recommend refining the silver sulfide structure using the correct space group P2₁/c (see JCPDS card No. C75-1061 - R. Sadanaga, S. Sueno. Mineralog. J. Japan. 1967. V.5. No 2. P.124-148.). It should be noted that nanosized silver sulfide is nonstoichiometric with small deficiency of silver and has Ag_{1.93}S composition. The correct crystal structure of nanocrystalline silver sulfide is described in study [S.I. Sadovnikov, A.I. Gusev, A.A. Rempel. Nonstoichiometry of nanocrystalline monoclinic silver sulfide. Physical Chemistry Chemical Physics. 2015. V.17. No 19. P.12466-12471] (see also ESI files for this paper, DOI: 10.1039/c5cp00650c).

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I will gladly recommend the revised manuscript for publication.

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January 16, 2024

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4- Line 146: “However, the low concentration of silver in such hydrothermal fluids (<30 ppm; ref. 6), rules out the possibility that the Poshan silver ores, which have grades exceeding 1000g/t Ag and locally up to weight-percent levels of Ag, could have formed by direct precipitation.”

Here is a jump in logic. The low solubility does not rule out the hydrothermal transport process. More fluids would be necessary. Is there evidence to disregard large quantities of fluid during mineralisation? On the same subject, during the experimental formation

of Ag and AgS NPs, what concentrations were NPs produced? Can you use this to provide a range of Ag concentration being transported in the hydrothermal fluid as NPs (and a volume of fluid)?

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6- Line 160: “deposit, we propose that silver sulfide nanoparticles can be transported mechanically by fluids in a manner similar to that of gold and electrum.”

Be more specific. Over what distance and what evidence to support this statement?

Denis Fougrouse, Perth 25-01-24

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After careful evaluation of this manuscript, I believe that the manuscript “Hyper-enrichment of silver by the transportation and aggregation of silver sulfide nanoparticles” by Mingchun Chai et al can be suitable for publication in journal “Nature

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2. I recommend refining the silver sulfide structure using the correct space group P21/c (see JCPDS card No. C75-1061 - R. Sadanaga, S. Sueno. *Mineralog. J. Japan*. 1967. V.5. No 2. P.124-148.). It should be noted that nanosized silver sulfide is nonstoichiometric with small deficiency of silver and has Ag_{1.93}S composition. The correct crystal structure of nanocrystalline silver sulfide is described in study [S.I. Sadovnikov, A.I. Gusev, A.A. Rempel. Nonstoichiometry of nanocrystalline monoclinic silver sulfide. *Physical Chemistry Chemical Physics*. 2015. V.17. No 19. P.12466-12471] (see also ESI files for this paper, DOI: 10.1039/c5cp00650c).

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I will gladly recommend the revised manuscript for publication.

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January 16, 2024

Response to Reviewers

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We appreciate the assessment of Reviewer #1 that our work “reports interesting and innovative findings” and that it “may represent a leap forward in the understanding of high-grade Ag mineralization”.

In the following, we address the reviewer’s criticisms:

1. One could criticise that the model presented is based on the investigation of only one Ag deposit. I don’t think that is a problem because it is still important to explain the current observations.

We agree. Although our study is based on a silver deposit, to the best of our knowledge, it provides the first example in which the existence of silver sulfide nanoparticles have been documented in nature. We hope that this study will prompt the search for further examples.

2. It would be valuable to add SEM/FIB images of the petrographic location of the TEM foils. The petrographic context is often key to interpret nanoscale observations. I suggest to have these information in the main body of the paper.

To provide the requested petrographic context, we have added the location of the foil schematically (not to scale) to Figure 2d, the only image in which it would be helpful and not interfere with other features of the image.

3. Petrella et al 2022 (Nat Comms) also reports AgO₂ NPs – This is currently omitted from the manuscript

The AgO₂ NPs (Petrella et al., 2022) were recognized from gold ores, and their relations to silver mineralization and high-grade silver ores remain unclear. In addition, AgO₂ has rarely been documented in a hydrothermal silver deposit.

4. Line 146: “However, the low concentration of silver in such hydrothermal fluids (<30 ppm; ref. 6), rules out the possibility that the Poshan silver ores, which have grades exceeding 1000g/t Ag and locally up to weight-percent levels of Ag, could have formed by direct precipitation.”

Here is a jump in logic. The low solubility does not rule out the hydrothermal transport process. More fluids would be necessary. Is there evidence to disregard large quantities of fluid during mineralisation? On the same subject, during the experimental formation of Ag and AgS NPs, what concentrations were NPs produced? Can you use this to provide a range of Ag concentration being transported in the hydrothermal fluid as NPs (and a volume of fluid)?

We agree that the low solubility of silver does not preclude the formation of silver deposits by direct precipitation of silver from hydrothermal fluids. However, the volume of fluid required to precipitate silver in concentrations exceeding 1000 g/t in a single vein would require the passage of unrealistically large volumes of fluid through the corresponding fracture, given flow rates realistic for epithermal systems and the small amount of time that the fractures remain open.

We don't believe that it is possible to translate the information from the published experiments to estimate the concentrations of silver sulfide nanoparticles that can be transported in hydrothermal fluids. The range in the concentration of silver that can be transported as these nanoparticles is likely to be very large and will be determined by their availability and the physical ability of the fluid to transport them; a high flow rate and low temperature (greater fluid density) would enable the transport of a higher concentration of silver as nanoparticles.

5. Line 152: “silver was transported mechanically as silver sulfide nanoparticles”

Not the only explanation. It is conceivable, and likely, that the NPs precipitated in close proximity of the deposition site. The evidence for transport has not been demonstrated.

We agree. The sentence, however, makes no statement about the distance over which the silver sulfide nanoparticles are transported.

6. Line 160: “deposit, we propose that silver sulfide nanoparticles can be transported mechanically by fluids in a manner similar to that of gold and electrum.”

Be more specific. Over what distance and what evidence to support this statement?

We have revised the sentence by adding “nanoparticles” after “electrum”. Although the existence of gold nanoparticles in ore deposits has been well-documented and evidence has been provided for their transport via images of nano-veinlets containing gold nanoparticles (McLeish et al., 2021), to our knowledge there has been no attempt to estimate the distances over which gold nanoparticles have been transported in these systems. The only insight that we have on this issue has been provided by the discovery of gold nanoparticles in black smoker fluids from the seafloor hydrothermal systems (Gartman et al., 2018). In these systems, the nano-particles are transported on a scale of at least tens of centimeters to meters.

Reviewer #2 (Remarks to the Author):

The content of submitted manuscript is sufficiently interest. However, there is minor issue that need to be adequately clarified before considering for its publication.

The main methods used to prove the presence of acanthate in silver ore are scanning and transmission electron microscopy. Experimental studies discovered silver sulfide in the ore in the form of nanoparticles of monoclinic Ag₂S acanthite. The presented experimental electron microscopic results (Fig. 1b, 1c, 1d, 2a-2d, 3c, 3d, 3e in the manuscript) convincingly prove that the accumulation of elemental silver occurs due to the transport of silver sulfide nanoparticles to the sites of deposition and aggregation of Ag₂S nanoparticles with subsequent formation silver.

After careful evaluation of this manuscript, I believe that the manuscript “Hyper-enrichment of silver by the transportation and aggregation of silver sulfide

nanoparticles” by Mingchun Chai et al can be suitable for publication in the journal “Nature Communications” after minor revision and additions.

We gratefully acknowledge the positive comments on our manuscript by Reviewer #2 and the recommendation that it be accepted for publication after minor revision.

Major remark:

The crystal structure of silver sulfide nanoparticles observed in the studied ore should be clarified using X-ray microanalysis. Three references to X-ray determinations of the crystal structure of acanthite should be added to the manuscript:

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In addressing this comment, we would like to emphasize that the focus of this study is not on the crystal structure of silver sulfide and its nanoparticles. Instead, our objective is to show that high-grade silver ores form as a result of the transportation and aggregation of silver sulfide nanoparticles in nature. To conduct an analysis of the crystal structure of the silver sulfide nanoparticles would be well beyond the scope of the study presented in this manuscript and, most importantly, would not impact on its findings. Moreover, it would not be possible to separate silver sulfide nanoparticles for this purpose.

In situ micro XRD analysis, however, which is referred to in the revised manuscript, confirmed that the silver sulfide crystals are acanthite rather than argentite (Supplementary Fig. 2).

I recommend refining the silver sulfide structure using the correct space group P2₁/c (see JCPDS card No. C75-1061 - R. Sadanaga, S. Sueno. Mineralog. J. Japan. 1967. V.5. No 2. P.124-148.). It should be noted that nanosized silver sulfide is nonstoichiometric with small deficiency of silver and has Ag_{1.93}S composition. The

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To refine the structure of the silver sulfide nanoparticles is not only beyond the scope of our study but likely cannot be conducted with our material. See our response to the preceding comment.

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We appreciate the assessment of Reviewer #1 that our work “reports interesting and innovative findings” and that it “may represent a leap forward in the understanding of high-grade Ag mineralization”.

In the following, we address the reviewer’s criticisms:

1. One could criticise that the model presented is based on the investigation of only one Ag deposit. I don’t think that is a problem because it is still important to explain the current observations.

We agree with the reviewer’s comment. Although our study is based on one silver deposit, to the best of our knowledge, it provides the first example in which the existence of silver sulfide nanoparticles have been documented in nature. We hope that this study will prompt the search for further examples.

2. It would be valuable to add SEM/FIB images of the petrographic location of the TEM foils. The petrographic context is often key to interpret nanoscale observations. I suggest to have these information in the main body of the paper.

We thank the reviewer for the insightful suggestions. To provide the requested petrographic context, we have added the location of the foil schematically (not to scale) to Figure 2d, the only image in which it would be helpful and not interfere with other

features of the image.

3. Petrella et al 2022 (Nat Comms) also reports AgO₂ NPs – This is currently omitted from the manuscript

The AgO₂ NPs (Petrella et al., 2022) were recognized from gold ores, and their relations to silver mineralization and high-grade silver ores remain unclear. In addition, AgO₂ has rarely been recognized in a silver deposit as a hydrothermal product. Thus, we dismissed the AgO₂ and did not discuss it in this manuscript.

4. Line 146: “However, the low concentration of silver in such hydrothermal fluids (<30 ppm; ref. 6), rules out the possibility that the Poshan silver ores, which have grades exceeding 1000g/t Ag and locally up to weight-percent levels of Ag, could have formed by direct precipitation.”

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We don't believe that it is possible to translate the information from the published

experiments to estimate the concentrations of silver sulfide nanoparticles that can be transported in hydrothermal fluids. The range in the concentration of silver that can be transported as these nanoparticles is likely to be very large and will be determined by their availability and the physical ability of the fluid to transport them; a high flow rate and low temperature (greater fluid density) would enable the transport of a higher concentration of silver as nanoparticles.

5. Line 152: “silver was transported mechanically as silver sulfide nanoparticles”

Not the only explanation. It is conceivable, and likely, that the NPs precipitated in close proximity of the deposition site. The evidence for transport has not been demonstrated.

This is an excellent comment. The only thing we confirmed is that silver sulfide nanoparticles were transported mechanically in fluid during metal formation and were captured by calcite. The exact time of nanoparticle formation and the distance over which these nanoparticles may be transported, however, can not be tightly constrained by the present study; more studies and ample evidence are needed to solve these problems in the future. Here, we rephrased the discussion to make it more clear (lines 158-160).

6. Line 160: “deposit, we propose that silver sulfide nanoparticles can be transported mechanically by fluids in a manner similar to that of gold and electrum.”

Be more specific. Over what distance and what evidence to support this statement?

We have revised the sentence by adding “at least in the time interval of” and “nanoparticles” (lines 169-170). Although the existence of gold nanoparticles in ore deposits has been well-documented and evidence has been provided for their transport via images of nano-veinlets containing gold nanoparticles (McLeish et al., 2021), to our knowledge there has been no attempt to estimate the distances over which gold nanoparticles have been transported in these systems. The only insight that we have on this issue has been provided by the discovery of gold nanoparticles in black smoker fluids from the seafloor hydrothermal systems (Gartman et al., 2018). In these systems, the nano-particles are transported on a scale of at least tens of centimeters to meters. As replied above, the transportation of silver sulfide nanoparticles can be constrained at least to the time interval of metal formation. However, no conclusion can be deduced

from this study to constrain the distance that these nanoparticles could have been transported.

Reviewer #2 (Remarks to the Author):

The content of submitted manuscript is sufficiently interest. However, there is minor issue that need to be adequately clarified before considering for its publication.

The main methods used to prove the presence of acanthate in silver ore are scanning and transmission electron microscopy. Experimental studies discovered silver sulfide in the ore in the form of nanoparticles of monoclinic Ag₂S acanthite. The presented experimental electron microscopic results (Fig. 1b, 1c, 1d, 2a-2d, 3c, 3d, 3e in the manuscript) convincingly prove that the accumulation of elemental silver occurs due to the transport of silver sulfide nanoparticles to the sites of deposition and aggregation of Ag₂S nanoparticles with subsequent formation silver.

After careful evaluation of this manuscript, I believe that the manuscript “Hyper-enrichment of silver by the transportation and aggregation of silver sulfide nanoparticles” by Mingchun Chai et al can be suitable for publication in the journal “Nature Communications” after minor revision and additions.

We gratefully acknowledge the positive comments on our manuscript by Reviewer #2 and the recommendation that it be accepted for publication after minor revision.

Major remark:

The crystal structure of silver sulfide nanoparticles observed in the studied ore should be clarified using X-ray microanalysis. Three references to X-ray determinations of the crystal structure of acanthite should be added to the manuscript:

- 1) R. Sadanaga, S. Sueno. Mineralog. J. Japan. 1967. V.5. No 2. P.124-148.
- 2) Sadovnikov S.I., Gusev A.I., Rempel A.A. Artificial silver sulfide Ag₂S: Crystal structure and particle size in deposited powders. Superlattices and Microstructures. 2015. V.83. P.35-47.
- 3) S.I. Sadovnikov, A.I. Gusev, A.A. Rempel. Nonstoichiometry of nanocrystalline monoclinic silver sulfide. Physical Chemistry Chemical Physics. 2015. V.17. No 19. P.12466-12471] (see also ESI files for this paper, DOI: 10.1039/c5cp00650c).

We thank the reviewer for this insightful comment. In addressing this comment, we would like to emphasize that the focus of this study is not on the crystal structure of silver sulfide and its nanoparticles. Instead, our objective is to show that high-grade silver ores form as a result of the transportation and aggregation of silver sulfide nanoparticles in nature. To conduct an analysis of the crystal structure of the silver sulfide nanoparticles would be well beyond the scope of the study presented in this manuscript and, most importantly, would not impact on its findings. Moreover, it would not be possible to separate silver sulfide nanoparticles for this purpose.

The available XRD data, including the above references, are mainly based on the synthetic silver sulfide powder. The natural acanthite grains, mostly 1–3 mm in diameter in this study, are more malleable, which makes it challenging for traditional XRD analysis of powder samples. The author tried to use Raman to determine the mineral phase of silver sulfide in 2020. Results show that the ablated position becomes a hole without forming a useful spectrum, which, however, indicates that the silver sulfide investigated in this study is most likely the low-temperature phase of monoclinic acanthite, as observed from the mineral grains and further confirmed by TEM analysis. Nevertheless, the author tried again using in situ micro XRD analysis, which is referred to in the revised manuscript, confirming that the silver sulfide crystals are acanthite rather than argentite (Supplementary Fig. 2). We believe that confirmation of the mineral phase of silver sulfides is more important than the structure analysis to this study.

I recommend refining the silver sulfide structure using the correct space group P21/c (see JCPDS card No. C75-1061 - R. Sadanaga, S. Sueno. *Mineralog. J. Japan*. 1967. V.5. No 2. P.124-148.). It should be noted that nanosized silver sulfide is nonstoichiometric with small deficiency of silver and has Ag_{1.93}S composition. The correct crystal structure of nanocrystalline silver sulfide is described in study [S.I. Sadovnikov, A.I. Gusev, A.A. Rempel. *Nonstoichiometry of nanocrystalline monoclinic silver sulfide*. *Physical Chemistry Chemical Physics*. 2015. V.17. No 19. P.12466-12471] (see also ESI files for this paper, DOI: 10.1039/c5cp00650c).

The starting parameters of a monoclinic (space group P21/c) unit cell of silver sulfide and the occupancy degree of its positions with atoms Ag and S, necessary for the quantitative refinement of the experimental XRD pattern, can be found in article [S.I.

Sadovnikov, A.I. Gusev, A.A. Rempel. Physical Chemistry Chemical Physics. 2015.V.17. No 19. P.12466-12471].

We sincerely thank the reviewer for this suggestion. However, to refine the structure of the silver sulfide nanoparticles is not only beyond the scope of our study but likely cannot be conducted with our material. Please see our response to the preceding comment. Thus, we did not follow the suggestion for this time. We are available for further communication if the reviewer considers that it is essential to the present research.

REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

Second review of “Hyper-enrichment of silver by the transportation and aggregation of silver sulfide nanoparticles” by Chai et al.

I reviewed a previous version of this manuscript and was invited to assess whether my comments were addressed appropriately. My opinion has not changed, this is a great study that reports some fundamental processes responsible for ore deposit formation.

However, in response to my previous comments regarding the lacking evidence of mechanical transport of Ag nanoparticles, the authors write in their rebuttal letter “we confirmed that silver sulfide nanoparticles were transported mechanically” and “the distance over which these nanoparticles may be transported, however, can not be tightly constrained”. By a minor change in wording, the authors claim that my comment has been addressed.

Yet, the mechanical transport has not been demonstrated and I think my comment has not been addressed...

The observations are clear: Ag NPs are present in calcite. However, these NPs could have been precipitated at the same time/location as calcite. The authors do not provide evidence in favor of a model, or the other. Transport remains unproven.

Therefore, the statements in the manuscript (lines 112-113) “Our study provides direct evidence for the hypothesis that the transport of silver as silver sulfide nanoparticles” and (lines 189-192) “This study provides compelling evidence that hyper-enriched silver sulfide ores do not form through direct hydrothermal precipitation. Instead, they are the products of the transport of silver sulfide nanoparticles to the sites of deposition...” are not justified.

I tend to agree with the authors models; however, these statements need to be significantly toned down or removed entirely.

Additional minor comments:

Line 54: “Bonanza ores like these have created a paradox that until this study remained unresolved.”
Ores do not create a paradox - rephrase. There is a paradox in explaining how low concentration fluids can create a high concentration of Ag.

Throughout the manuscript, Ag and silver are used. I suggest keeping with Ag throughout.

Figures:

Figure 1: The geological map is not very informative. A geological map without a legend has allegedly no

meaning! I suggest adding a legend and an inset showing the location of the Qinling orogen respective to China. The location of other Ag deposits would also be welcome.

Figure 3b: please label the phase on the right side of the image.

Denis Fougrouse,
Perth, 21-02-24

Reviewer #3 (Remarks to the Author):

The ms entitled: "Hyper-enrichment of silver by the transportation and aggregation of silver sulfide nanoparticles" in the very interesting ms that worths publishing in Nat.Comm, under minor revision. Please see my comments in the ms.

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Response to Reviewers

Reviewer #1 (Remarks to the Author):

1. I reviewed a previous version of this manuscript and was invited to assess whether my comments were addressed appropriately. My opinion has not changed, this is a great study that reports some fundamental processes responsible for ore deposit formation.

Reply: We thank the reviewer for his/her second review of our manuscript and his/her positive assessment of our work.

2. However, in response to my previous comments regarding the lacking evidence of mechanical transport of Ag nanoparticles, the authors write in their rebuttal letter “we confirmed that silver sulfide nanoparticles were transported mechanically” and “the distance over which these nanoparticles may be transported, however, can not be tightly constrained”. By a minor change in wording, the authors claim that my comment has been addressed.

Yet, the mechanical transport has not been demonstrated and I think my comment has not been addressed...

The observations are clear: Ag NPs are present in calcite. However, these NPs could have been precipitated at the same time/location as calcite. The authors do not provide evidence in favor of a model, or the other. Transport remains unproven.

Therefore, the statements in the manuscript (lines 112-113) “Our study provides direct evidence for the hypothesis that the transport of silver as silver sulfide nanoparticles” and (lines 189-192) “This study provides compelling evidence that hyper-enriched silver sulfide ores do not form through direct hydrothermal precipitation. Instead, they are the products of the transport of silver sulfide nanoparticles to the sites of deposition...” are not justified.

I tend to agree with the authors models; however, these statements need to be

significantly toned down or removed entirely.

Reply: We accept the criticism of the reviewer that although we have documented the occurrence of silver sulfide nanoparticles, we have not provided evidence for their mechanical transport. As requested, we therefore have “toned down” our statements on lines 112-113 and 189-192 by eliminating all mention of transport or mechanical transport. These statements now read “Our study provides direct evidence for the hypothesis that the aggregation of silver sulfide nanoparticles was the cause of the hyper-enrichment of silver in some deposits” (lines 112-114) and “This study provides compelling evidence that hyper-enriched or high-grade silver sulfide ores do not form through direct hydrothermal precipitation. Instead, they are the products of the aggregation of silver sulfide nanoparticles.” (lines 189-191).

We have also removed mention of transport from the title, abstract, and main text (i.e., lines 33–35 and 223–225).

3. Line 54: “Bonanza ores like these have created a paradox that until this study remained unresolved.”

Ores do not create a paradox - rephrase. There is a paradox in explaining how low concentration fluids can create a high concentration of Ag.

Reply: The sentence referring to a paradox has been replaced with “How bonanza-grade silver ores can form from ore fluids with such low concentrations of silver remains unknown” (lines 49–51).

4. Throughout the manuscript, Ag and silver are used. I suggest keeping with Ag throughout.

Reply: Except for the chemical formulas and reactions, the word silver is now used throughout the manuscript.

5. Figure 1: The geological map is not very informative. A geological map without a legend has allegedly no meaning! I suggest adding a legend and an inset showing the location of the Qinling orogen relative to China. The location of other Ag deposits

would also be welcome.

Reply: We have added a legend and an inset to show the location of the Qinling orogen within China in Figure 1. This figure also shows the major silver polymetallic deposits in the Qinling orogen and adjacent areas.

6. Figure 3b: please label the phase on the right side of the image.

Reply: We have labeled the phase on the right side in Figure 3b.

Reviewer #3 (Remarks to the Author):

The ms entitled: "Hyper-enrichment of silver by the transportation and aggregation of silver sulfide nanoparticles" in the very interesting ms that worths publishing in Nat.Comm, under minor revision. Please see my comments in the ms.

The authors are grateful to Reviewer #3 for his /her annotation of our manuscript. We have replied to each of the comments in the manuscript file "475253_2_rel_ms_0_sknn1h-Authors reply". Our responses to the main comments are as follows:

1. Please see Tombros and Fitros, 2019, for the real evidence regarding Ag nanoparticles.

Reply: Tombros and Fitros (2019) showed that the particles in the Panormos Bay Ag-Au-Te deposit have $\text{Ag}/(\text{Pb} + \text{Ag} + \text{Cu} + \text{Fe} + \text{Zn})$ ratios ranging from approximately 1% to 6%. These are not native silver particles, but rather alloys or tetrahedrite-freibergite microinclusions. Tobros and Fitros (2019) did not provide direct evidence for the presence of silver nanoparticles.

2. I agree with your thinking. However, what triggered all this mechanism? Cooling?

Reply: The surface and interfacial free energy of nanoparticles are considered to be the

essential factors that influence aggregation-based crystal growth (Penn and Banfield, 1998; Banfield et al., 2000). A reduction in this free energy is conducive to nanoparticle reorientation and coalescence (Theissmann et al., 2008). Additionally, temperature has been shown to influence the gold nanoparticle growth involved in Ostwald ripening (Reich et al., 2006). The redox condition and pH are potential factors regulating nanoparticle aggregation and crystal growth. A discussion of the specific influence of these factors on the formation of silver sulfide crystals is beyond the scope of this study.

3. In this reaction, only the fugacity of oxygen and the activity of hydrogen sulfide (aqueous or gaseous?) are considered as the parameters for the desulfidation of acanthite. Also, what about the pH control? I believe that this reaction should be rewritten.

Reply: The hydrogen sulfide in this reaction is aqueous. This is evident in the use of the term activity. The corresponding term for gaseous H₂S is fugacity. We see no need to rewrite the reaction nor has the reviewer provided one. The formation of abundant calcite and the negative cerium anomalies ($\delta\text{Ce} = 0.67\text{--}1.03$, mean 0.85; unpublished data) of the calcite are consistent with a relatively alkaline fluid (e.g., Himmler et al., 2010), which was likely promoted calcite and acanthite precipitation. However, the role of pH in the replacement of the acanthite by the silver is unknown.

References cited:

- Banfield, J. F., Welch, S. A., Zhang, H., Ebert, T. T. & Penn, R. L. Aggregation-Based Crystal Growth and Microstructure Development in Natural Iron Oxyhydroxide Biomineralization Products. *Science*. 289, 751-754 (2000).
- Himmler, T., Bach, W., Bohrmann, G. & Peckmann, J. Rare earth elements in authigenic methane-seep carbonates as tracers for fluid composition during early diagenesis. *Chem. Geol.* 277, 126-136 (2010).
- Penn, R. L. & Banfield, J. F. Imperfect Oriented Attachment: Dislocation Generation in Defect-Free Nanocrystals. *Science*. 281, 969-971 (1998).
- Reich, M. et al. Thermal behavior of metal nanoparticles in geologic materials. *Geology*. 34, 1033-1036 (2006).
- Theissmann, R. et al. Crystallographic reorientation and nanoparticle coalescence.

Physical Review. B, Condensed Matter and Materials Physics. 78, 205413 (2008).
Tombros, S. F., & Fitros, M. Evidence for vapor transport of the base and precious metals in the Panormos Bay Ag-Au-Te deposit, Tinos Island, Cyclades. *Journal of Geochemical Exploration*, 199, 128-140 (2019).