

Sulfide Minerals bear witness to impacts across the Solar System

Corresponding Author: Dr Michelle Thompson

Parts of this Peer Review File have been redacted as indicated to remove third-party material.

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

Summary: The authors present a synthesis of iron sulfide nano-whiskers, analogous to space weathering features found on regolith grains returned from the Moon and multiple asteroids. Remarkably, these whiskers are reproduced by rapidly heating and cooling the sulfide grain, simulating the heat from a micrometeoroid impact, rather than previously-invoked mechanisms involving solar wind ion irradiation. In-situ characterization of the lab-grown whiskers using EDS, FIB-TEM, and electron diffraction demonstrates close similarity with those found in regolith samples. The authors propose a novel whisker growth mechanism, in which the rapidly melted surface of the sulfide grain loses sulfur to space by diffusion, exsolving FeNi metal which contracts faster than the underlying sulfide as it quenches, resulting in compression-driven whisker growth similar to metallic thin films. Sulfide mineral grains may thus record planetary impact histories to an extent not previously understood.

Significance: I have been looking forward to a paper like this ever since Matsumoto and colleagues first reported iron nano-whiskers in Itokawa grains five years ago. To my knowledge, this is the first attempt to replicate nano-whiskers in the laboratory using temperature, and the results are quite compelling. It would be one thing if an experiment like this simply produced whisker-like growths that appear similar to sulfide regolith particles under microscope imaging, but far more relevant is the detailed microstructural analysis showing the chemical variation of the whiskers from base to tip and the presence of crystalline defects, both of which evidence the proposed formation mechanism as a diffusive and thermo-mechanical process. I suspect the planetary materials community would take interest in both the specific mechanism described, as well as the broader use of thin films and synthetic alloys as analogs for nano- and micro-scale processes in the space environment, as we continue finding more diverse mineral systems to be useful indicators of planetary surface evolution.

Soundness: I do not find any faults in the methodology, data analysis, or interpretations of this paper. I expect another laboratory capable of rapidly heating and cooling a grain with in-situ microanalysis tools would be able to replicate the procedures the authors employ, although I would be curious to see how results might differ if an alternate heating mechanism were employed, e.g. pulsed laser irradiation. The images provided in both the main and supplemental documents clearly show the features described in the body of the text, enhanced by minimal but nonetheless effective annotations and descriptive captions. In discussing their findings, the authors suggest an extraordinary whisker formation mechanism, but are careful to do so only after thoroughly assessing the shortcomings of alternative hypotheses, and maintain focus on the proposed mechanism's consistency with observed chemical, microstructural, and morphological features of the whiskers. Overall, I find that the conclusions are well-supported by the empirical evidence presented.

In summary, I believe this work meets the expected standards for Nature Communications, and am pleased to recommend it for publication. I would like to congratulate the authors on their success, and look forward to future work expanding on their ideas.

Reviewer #2

(Remarks to the Author)

This study conducts in-situ heating experiments to simulate micrometeorite bombardment on pentlandite grains, and concludes that Fe-whisker formation could be driven by impact events rather than primarily solar wind irradiation as previously thought. The methods are technically sound, the data is of a high quality, and the results are presented in detail. It is clear to see obvious whiskers forming after a single thermal pulse to 1100 °C, followed by a degradation of whiskers with subsequent thermal pulses. The formation mechanism of Fe-whiskers via thermal events is well explained. The conclusions of this manuscript are well supported by the data shown, and are highly relevant for both past and future missions to sulfide/metal-rich bodies.

Comments:

My only substantial comment/question is: Why was pentlandite used in the experiments rather than troilite/pyrrhotite? I'm not very familiar with the Fe-whisker literature, but from what I've seen the whiskers are usually Ni-poor and form around pyrrhotite grains? It would be good to justify the use of pentlandite in the experiments. Also, it would be useful to add in a few speculative comments somewhere to state whether the same mechanism of whisker formation from a pentlandite grain would also apply to a pyrrhotite grain (how does the melting point of pyrrhotite and thermal expansion properties of pyrrhotite compare to pentlandite? Would the starting composition make any difference to the whiskers? How might whisker formation rates and morphologies from a Ni-poor grain be different to a Ni-rich grain, if at all?). It would then be clearer whether this mechanism could form the Ni-poor Fe-whiskers observed in Itokawa (Matsumoto et al., 2020).

Lines 93 – 95: It's great that the whiskers formed after one thermal pulse are morphologically consistent with whiskers observed in samples from Itokawa and the Moon! Are there no naturally produced whisker morphologies in the literature that are consistent with those after multiple experimental thermal pulses? It's strange that this is the case, as you'd expect the sulfides in Itokawa and the Moon would have experienced multiple impacts?

Figure 2: while it is relatively obvious to spot that, for example, C) corresponds to the pink outlined region in A), I think it would be useful to add labels inside the boxes outlined in A) to make it even clearer how the panels correspond to each other (if this change is made here, then similar labels should be added to all other figures where appropriate).

Figure 5: in the caption: "through which whiskers during simulated...", needs changing to "through which whiskers formed during simulated..."?

Open Access This Peer Review File is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

In cases where reviewers are anonymous, credit should be given to 'Anonymous Referee' and the source.

The images or other third party material in this Peer Review File are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this license, visit <https://creativecommons.org/licenses/by/4.0/>

Response to Reviewers

We thank the reviewers for their comments, which have greatly improved the manuscript. We have provided responses to their comments in **green text** below.

REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

Summary: The authors present a synthesis of iron sulfide nano-whiskers, analogous to space weathering features found on regolith grains returned from the Moon and multiple asteroids. Remarkably, these whiskers are reproduced by rapidly heating and cooling the sulfide grain, simulating the heat from a micrometeoroid impact, rather than previously-invoked mechanisms involving solar wind ion irradiation. In-situ characterization of the lab-grown whiskers using EDS, FIB-TEM, and electron diffraction demonstrates close similarity with those found in regolith samples. The authors propose a novel whisker growth mechanism, in which the rapidly melted surface of the sulfide grain loses sulfur to space by diffusion, exsolving FeNi metal which contracts faster than the underlying sulfide as it quenches, resulting in compression-driven whisker growth similar to metallic thin films. Sulfide mineral grains may thus record planetary impact histories to an extent not previously understood.

Significance: I have been looking forward to a paper like this ever since Matsumoto and colleagues first reported iron nano-whiskers in Itokawa grains five years ago. To my knowledge, this is the first attempt to replicate nano-whiskers in the laboratory using temperature, and the results are quite compelling. It would be one thing if an experiment like this simply produced whisker-like growths that appear similar to sulfide regolith particles under microscope imaging, but far more relevant is the detailed microstructural analysis showing the chemical variation of the whiskers from base to tip and the presence of crystalline defects, both of which evidence the proposed formation mechanism as a diffusive and thermo-mechanical process. I suspect the planetary materials community would take interest in both the specific mechanism described, as well as the broader use of thin films and synthetic alloys as analogs for nano- and micro-scale processes in the space environment, as we continue finding more diverse mineral systems to be useful indicators of planetary surface evolution.

We thank the reviewer for their positive commentary.

Soundness: I do not find any faults in the methodology, data analysis, or interpretations of this paper. I expect another laboratory capable of rapidly heating and cooling a grain with in-situ microanalysis tools would be able to replicate the procedures the authors employ, although I would be curious to see how results might differ if an alternate heating mechanism were employed, e.g. pulsed laser irradiation. The images provided in both the main and supplemental documents clearly show the features described in the body of the text, enhanced by minimal but nonetheless effective annotations and descriptive captions. In discussing their findings, the authors suggest an extraordinary whisker formation mechanism, but are careful to do so only after thoroughly assessing the shortcomings of alternative hypotheses, and maintain focus on the

proposed mechanism's consistency with observed chemical, microstructural, and morphological features of the whiskers. Overall, I find that the conclusions are well-supported by the empirical evidence presented.

In summary, I believe this work meets the expected standards for Nature Communications, and am pleased to recommend it for publication. I would like to congratulate the authors on their success, and look forward to future work expanding on their ideas.

We sincerely thank the reviewer for their positive commentary.

Reviewer #2 (Remarks to the Author):

This study conducts in-situ heating experiments to simulate micrometeorite bombardment on pentlandite grains, and concludes that Fe-whisker formation could be driven by impact events rather than primarily solar wind irradiation as previously thought. The methods are technically sound, the data is of a high quality, and the results are presented in detail. It is clear to see obvious whiskers forming after a single thermal pulse to 1100 °C, followed by a degradation of whiskers with subsequent thermal pulses. The formation mechanism of Fe-whiskers via thermal events is well explained. The conclusions of this manuscript are well supported by the data shown, and are highly relevant for both past and future missions to sulfide/metal-rich bodies.

Comments:

My only substantial comment/question is: Why was pentlandite used in the experiments rather than troilite/pyrrhotite? I'm not very familiar with the Fe-whisker literature, but from what I've seen the whiskers are usually Ni-poor and form around pyrrhotite grains? It would be good to justify the use of pentlandite in the experiments. Also, it would be useful to add in a few speculative comments somewhere to state whether the same mechanism of whisker formation from a pentlandite grain would also apply to a pyrrhotite grain (how does the melting point of pyrrhotite and thermal expansion properties of pyrrhotite compare to pentlandite? Would the starting composition make any difference to the whiskers? How might whisker formation rates and morphologies from a Ni-poor grain be different to a Ni-rich grain, if at all?). It would then be clearer whether this mechanism could form the Ni-poor Fe-whiskers observed in Itokawa (Matsumoto et al., 2020).

We thank the reviewer for their comments. Using pentlandite as opposed to troilite or pyrrhotite was driven by observations of whiskers features in other returned samples, namely in material from asteroid Bennu collected by the OSIRIS-REx mission (see Keller et al. 2024 Meteoritical Society Abstract #3036). In those samples, the whiskers are FeNi-rich, as opposed to predominantly Fe-rich as has been observed most commonly in samples from Itokawa and the Moon. These are the first whiskers that the authors observed themselves in returned samples, contributing to the motivation for this study.

When comparing whisker formation in pyrrhotite versus pentlandite, we suggest that our proposed mechanism could also drive whisker formation in sulfides with Ni-poor compositions.

From Kellerud (1963; citation 21 in manuscript text) the maximum melting temperature for pyrrhotite is 1190 °C, which is close to the temperature achieved in these in situ heating experiments and is relevant to thermal conditions experienced by sulfide minerals during true micrometeoroid impacts. This melting temperature is still lower than that of Fe-metal, suggesting that pyrrhotite would experience similar conditions to pentlandite, wherein S would preferentially escape from the outer rim of the grain, resulting in quenched Fe-metal shell surrounding a predominantly molten core of pyrrhotite. As a result, the same compressive stresses might develop in the pyrrhotite samples during thermal events, subsequently prompting analogous whisker growth. Without Ni, however, the whiskers would be composed of strictly Fe, as is observed in some samples from Itokawa and the Moon. In terms of thermal expansion, some compositions of pyrrhotite have thermal expansion coefficients that are lower, but within range of measurements made for pentlandite (Rajamani and Prewitt 1975; citation 29 in the manuscript text). Though whisker formation is probable in sulfides with both Ni-rich and Ni-poor compositions, the larger differences in melting temperature and thermal expansion coefficients between pentlandite and FeNi-metal compared to pyrrhotite and Fe-metal suggest that whisker formation might be a more efficient process in Ni-rich sulfides.

We have added several sentences to the discussion section (see green text in manuscript file) to reflect that this would likely be a viable mechanism for the formation of whiskers as observed in pyrrhotite as well.

Lines 93 – 95: It's great that the whiskers formed after one thermal pulse are morphologically consistent with whiskers observed in samples from Itokawa and the Moon! Are there no naturally produced whisker morphologies in the literature that are consistent with those after multiple experimental thermal pulses? It's strange that this is the case, as you'd expect the sulfides in Itokawa and the Moon would have experienced multiple impacts?

There are indeed features in returned samples that appear more similar to the whisker morphologies we see in the samples that experienced multiple thermal pulses in our experiments. In Matsumoto et al. (2020), Figure 1d (copied below) shows some surface features that are more linear in morphology and protrude less from the grain surfaces compared to the more discrete whiskers. These ridge-like features are reminiscent of the degraded whiskers in experimental samples that experienced multiple thermal pulses. This similarity could suggest returned samples are recording the effects of repeated impact processing after all.

We have added a sentence reflecting the similarity in these observations to the discussion section (see green text in the manuscript file).

[REDACTED]

(Matsumoto et al. 2020)

Figure 2: while it is relatively obvious to spot that, for example, C) corresponds to the pink outlined region in A), I think it would be useful to add labels inside the boxes outlined in A) to make it even clearer how the panels correspond to each other (if this change is made here, then similar labels should be added to all other figures where appropriate).

We thank the reviewer for the suggestion. To prevent obscuring some of the features in the figures with superimposed labels, we added text to the captions of Figures 2 and 4 to indicate that colored insets correspond to the location of features identified in subsequent panels.

Figure 5: in the caption: “through which whiskers during simulated...”, needs changing to “through which whiskers formed during simulated...”?

Corrected.