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Web links to the author's journal account have been redacted from the decision letters as indicated to maintain confidentiality

27th Nov 23

Dear Professor Nicholas,

Your manuscript titled "Detection of Thin Film Phase Transformations at High-Pressure and High-Temperature in a Diamond Anvil Cell" has now been seen by 2 reviewers, and we include their comments at the end of this message. They find your work of interest, but some important points are raised. We are interested in the possibility of publishing your study in Communications Earth & Environment, but would like to consider your responses to these concerns and assess a revised manuscript before we make a final decision on publication.

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

* Present a robust and compelling interpretation for your experimental results of a change in temperature for the wadsleyite-ringwoodite transition and account for alternative potential explanations.

We therefore invite you to revise and resubmit your manuscript, along with a point-by-point response that takes into account the points raised. Please highlight all changes in the manuscript text file.

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

Please use the following link to submit your revised manuscript, point-by-point response to the referees' comments (which should be in a separate document to any cover letter), a tracked-changes version of the manuscript (as a PDF file) and the completed checklist:

[link redacted]

** This url links to your confidential home page and associated information about manuscripts you may have submitted or be reviewing for us. If you wish to forward this email to co-authors, please delete the link to your homepage first **

We hope to receive your revised paper within six weeks; please let us know if you aren't able to submit it within this time so that we can discuss how best to proceed. If we don't hear from you, and the revision process takes significantly longer, we may close your file. In this event, we will still be happy to reconsider your paper at a later date, as long as nothing similar has been accepted for publication at Communications Earth & Environment or published elsewhere in the meantime.

Please do not hesitate to contact us if you have any questions or would like to discuss these revisions further. We look forward to seeing the revised manuscript and thank you for the opportunity to review your work.

Best regards,

Joe Aslin

Senior Editor,

Communications Earth & Environment
<https://www.nature.com/commsenv/>
Twitter: @CommsEarth

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and also in our style and formatting guide [Communications Earth & Environment formatting guide](https://www.nature.com/documents/commsj-phys-style-formatting-guide-accept.pdf) .

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- If applicable, a statement regarding data available with restrictions
- If a dataset has a Digital Object Identifier (DOI) as its unique identifier, we strongly encourage including this in the Reference list and citing the dataset in the Data Availability Statement.

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If a community resource is unavailable, data can be submitted to generalist repositories such as [figshare](https://figshare.com/) or [Dryad Digital Repository](http://datadryad.org/). Please provide a unique identifier for the data (for example a DOI or a permanent URL) in the data availability statement, if possible. If the repository does not provide identifiers, we encourage authors to supply the search terms that will return the data. For data that have been obtained from publically available sources, please provide a URL and the specific data product name in the data availability statement. Data with a DOI should be further cited in the methods reference section.

Please refer to our data policies at <http://www.nature.com/authors/policies/availability.html>.

REVIEWER COMMENTS:

Reviewer #1 (Remarks to the Author):

Review of original paper "Detection of Thin Film Phase Transformations at High-Pressure and High-Temperature in a Diamond Anvil Cell by Berrada et al.

While the equilibrium phase transitions between olivine, wadsleyite, ringwoodite, and the bridgmanite + periclase have been widely studied in bulk samples, and assigned to seismic discontinuities, little is known about the impact of grain size and/or deviatoric stress on the thermodynamic stability of these polymorphs. The present paper addresses this knowledge gap by investigating crystalline Mg_2SiO_4 thin films by X-ray diffraction in the laser heated diamond anvil cell. Indeed, epitaxial films develop large intrinsic stress during their growth which can be tuned to control biaxial deviatoric stress and grain size. The use of thin film samples in DAC experiments therefore represents a promising approach to study geologically relevant phase relationships under extreme stress conditions. The authors have taken an important step in this direction by synthesizing ~400 nm thick Mg_2SiO_4 films made up of ~30 nm sized grains on MgO substrates, and performing X-ray measurements in the DAC. This represents a major experimental achievement that paves the way to exciting new studies in the mineral physics community.

In fact, I reviewed a previous version of this article, submitted to Nature Communications, a few weeks ago. I was very enthusiastic about the experimental approach, but had few remarks about the phase diagram of Mg_2SiO_4 and the application to deep focus earthquakes. This new version has been rewritten, and is now more focused on the methodology and technical part than on the results on the phase diagram of olivine. I think this refocusing is a good idea, as the application to deep earthquakes was perhaps less advanced. Several of my previous remarks, particularly regarding P&T metrology, have been considered. Nevertheless, there remain few points to be clarified before publication:

- I encourage the authors to discuss the state of stress in the films under high P-T, and after transformation. The olivine polymorphic reaction mechanisms lead to a significant reduction in volume and grain size. I therefore wonder how it affects the stress/ overpressure state in the film? and if a biaxial stress is actually maintained in the film?
- I'm also wondering whether it would be possible to perform a multi-grain analysis from the TF-DAC X-ray diffraction data, and what current limitations prevent such an analysis? The improvements in nano positioning and beam size brought by the APS upgrade should help in this direction...

I look forward to seeing this work published in Communication Earth & Environment once these points have been addressed.

Reviewer #2 (Remarks to the Author):

Review of "Detection of Thin Film Phase Transformations at High-Pressure and High-Temperature in a Diamond Anvil Cell" by Berrada et al.

General comments

In this manuscript, the authors demonstrate an in-situ high-pressure and high-temperature X-ray diffraction study of thin film samples of nano-grained (~30 nm) Mg_2SiO_4 olivine using a laser-heated diamond anvil cell. They report that the transformation temperature between wadsleyite and ringwoodite at 18 GPa is ~500 K higher than in previous phase equilibrium studies, while other phase transformations in Mg_2SiO_4 are consistent with the phase equilibria. I think this study is an interesting experimental approach to high pressure mineral physics and may provide some insights into polymorphic phase transformations in the fields of earth and material sciences. However, I have some concerns about the discussion of the manuscript, as described below:

- (1) I am confused by the definition of ΔP in the case of the thin film sample compressed in a diamond anvil cell. My understanding is that ΔP , which is given by the Young-Laplace equation, is the pressure difference at the interface between nano-grained olivine particles and Ne pressure medium/MgO substrate/Pt foil. There is a need to explain the values of ΔP more clearly.
- (2) In fact, the olivine nanoparticles experienced a higher pressure than that estimated by the platinum equation of state, as explained by the Young-LaPlace equation. This does not seem to imply a shift in the thermodynamic phase boundary due to the grain size effect, but simply seems to show the difference in effective pressures between the olivine nanograins and the platinum pressure maker.
- (3) If the extremely small grain size of the starting material causes excess pressure (ΔP) on the grains, all phase boundaries in Mg_2SiO_4 may shift to lower pressures compared to those in the previous phase diagrams. In reality, however, such a shift is limited to the wadsleyite-ringwoodite phase boundary. How can the experimental results be explained?
- (4) How were the sample temperatures measured and what is the uncertainty in the temperature measurements during laser heating? Is the error in the temperature measurements small enough to ensure a higher temperature for the wadsleyite-ringwoodite transformation than in the previous phase equilibrium studies?
- (5) As shown in Fig.1b and Fig.1c, both wadsleyite and ringwoodite have some crystallographic preferred orientation (CPO). I wonder if characteristic diffraction rings (spots) of the wadsleyite structure were not seen in some XRD patterns due to CPO. This would cause an apparent shift of the wadsleyite-ringwoodite boundary toward higher temperature.

(6) Grain size is likely to affect the kinetics of polymorphic phase transitions. Can the authors discuss this point?

Because of the above concerns, it is difficult for me to recommend the manuscript for publication in Communications Earth & Environment in its current form. I hope the manuscript may be improved after clearly addressing the above concerns.

Minor comments

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Page 18, line 1–2: What was the duration of laser heating?

Fig. 1, Fig. 2, Fig. S1, Fig. S2: The X-ray diffraction spots must be represented by the Laue indices, but not by the Miller indices. Therefore, all parentheses for the indices should be removed. (e.g. "020" instead of "(020)")

REVIEWER COMMENTS:

Reviewer #1 (Remarks to the Author):

Review of original paper “Detection of Thin Film Phase Transformations at High-Pressure and High-Temperature in a Diamond Anvil Cell by Berrada et al.

While the equilibrium phase transitions between olivine, wadsleyite, ringwoodite, and the bridgmanite + periclase have been widely studied in bulk samples, and assigned to seismic discontinuities, little is known about the impact of grain size and/or deviatoric stress on the thermodynamic stability of these polymorphs. The present paper addresses this knowledge gap by investigating crystalline Mg_2SiO_4 thin films by X-ray diffraction in the laser heated diamond anvil cell. Indeed, epitaxial films develop large intrinsic stress during their growth which can be tuned to control biaxial deviatoric stress and grain size. The use of thin film samples in DAC experiments therefore represents a promising approach to study geologically relevant phase relationships under extreme stress conditions. The authors have taken an important step in this direction by synthesizing ~400 nm thick Mg_2SiO_4 films made up of ~30 nm sized grains on MgO substrates, and performing X-ray measurements in the DAC. This represents a major experimental achievement that paves the way to exciting new studies in the mineral physics community.

In fact, I reviewed a previous version of this article, submitted to Nature Communications, a few weeks ago. I was very enthusiastic about the experimental approach, but had a few remarks about the phase diagram of Mg_2SiO_4 and the application to deep focus earthquakes. This new version has been rewritten, and is now more focused on the methodology and technical part than on the results on the phase diagram of olivine. I think this refocusing is a good idea, as the application to deep earthquakes was perhaps less advanced. Several of my previous remarks, particularly regarding P&T metrology, have been considered. Nevertheless, there remain few points to be clarified before publication:

- I encourage the authors to discuss the state of stress in the films under high P-T, and after transformation. The olivine polymorphic reaction mechanisms lead to a significant reduction in volume and grain size. I therefore wonder how it affects the stress/ overpressure state in the film? and if a biaxial stress is actually maintained in the film?

Response: We are grateful to this reviewer for not only appreciating the importance of this work, but also for reviewing multiple versions of this manuscript. Thank you!

Thank you also for this insightful comment. We also wish we would have been able to comment on the *in-situ* film stress/overpressure state at various points in our high P-T experiments. Unfortunately, we were not able to reliably measure the *in-situ* film stress because of XRD signal blocking from the DACs used here. Specifically, in order to use X-ray Diffraction to reliably determine the in-plane stress of polycrystalline, non-epitaxial thin films like those produced here, one must know 1) the thin film material’s elastic tensor, 2) the crystallographic orientation distribution of the various film grains, and 3) the variation in film grain d-spacing strain as a function of lattice plane inclination to the plane of the film. The need to measure the film strain at various angles of inclination to the plane of the film is caused by the fact that the

film is mostly clamped by the substrate in the plane of the film (i.e. in the x-y plane) but is mostly free to strain in the out-of-plane (i.e. in the z-direction). Unfortunately, XRD signal blocking caused by the small opening angles of the DACs used here prevented characterization of the film strain at incoming XRD beams at various inclination angles to the film xy-plane. To make this clear to readers, we have added the following sentence to the revised manuscript:

“Unfortunately, low film XRD signal-to-noise ratios, the low angular openings of the DACs used here, and the non-spherical diamond anvils used here prevented reliable and complete XRD characterization of the in situ anisotropic film strain, anisotropic film stress, and film crystallographic orientation distribution.”

To remedy this in our future experiments, we intend to utilize Boehler-Almax DACs, or similar DACs which have larger opening angles, to collect XRD signals after various amounts of DAC rotation. Since past literature studies have shown that the elastic constants of materials with grain sizes larger than ~10 nm are similar to those found in bulk materials ([https://doi.org/10.1016/S0965-9773\(99\)00052-5](https://doi.org/10.1016/S0965-9773(99)00052-5)), and the films here had ~30 nm grain sizes, we should be able to use thin film Mechanics Theory (like that in our previous publication <https://doi.org/10.1039/d1ma00842k>) to convert the measured anisotropic *in-situ* film strains into anisotropic *in-situ* film stresses.

All that being said, even without reporting numerical values of the thin film stress, we think that the novel experimental method demonstrated here warrants publication of this manuscript. This is especially true because, in our past attempts to get this work funded, we experienced significant skepticism from the scientific community that well-resolved thin film signals could even be obtained AT ALL inside a diamond anvil cell. In addition, we believe that this manuscript deserves publication because it outlines the promise of, and vision for, a thin film-DAC approach that we believe will advance the field of Mineral Physics, and others.

- I'm also wondering whether it would be possible to perform a multi-grain analysis from the TF-DAC X-ray diffraction data, and what current limitations prevent such an analysis? The improvements in nano positioning and beam size brought by the APS upgrade should help in this direction...

Response: Thank you for this suggestion. Multigrain analysis requires the 3D reconstruction of peak positions in reciprocal space (so that the XRD peaks can be assigned to different grains), which requires DAC rotation during diffraction. Unfortunately, as noted in our previous comment, the style of DAC we used in the present work blocked much of the signal at larger two theta angles, preventing us from harvesting a large number of unique diffraction peaks from different grains, as required for a multigrain analysis. The flat diamonds used in the present study, and the high index of refraction of diamond, would also have conspired to physically separate the laser-heated spot and the XRD-sampled spot during sample rotation (had we attempted a high temperature multigrain analysis using the DACs and diamonds employed here). In future studies, we intend to use spherical diamonds, and spherical-diamond-compatible wide-angle DACs (such as those available at <https://www.dactools.com/diamond-cells>) to ensure that we are able to capture a wide angular range of XRD peaks and we are able to keep the XRD focal position and the laser-heating focal position aligned during high-temperature sample rotation.

I look forward to seeing this work published in Communication Earth & Environment once these points have been addressed.

Response: Thanks, so do we! We hope we have responded to your comments/inquiries adequately.

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Reviewer #2 (Remarks to the Author):

Review of "Detection of Thin Film Phase Transformations at High-Pressure and High-Temperature in a Diamond Anvil Cell" by Berrada et al.

General comments

In this manuscript, the authors demonstrate an in-situ high-pressure and high-temperature X-ray diffraction study of thin film samples of nano-grained (~30 nm) Mg_2SiO_4 olivine using a laser-heated diamond anvil cell. They report that the transformation temperature between wadsleyite and ringwoodite at 18 GPa is ~500 K higher than in previous phase equilibrium studies, while other phase transformations in Mg_2SiO_4 are consistent with the phase equilibria. I think this study is an interesting experimental approach to high pressure mineral physics and may provide some insights into polymorphic phase transformations in the fields of earth and material sciences.

Response: Thanks for the comment. We are delighted that we were able to convey our enthusiasm for the new and potentially-powerful thin-film-DAC approach.

However, I have some concerns about the discussion of the manuscript, as described below:

(1) I am confused by the definition of ΔP in the case of the thin film sample compressed in a diamond anvil cell. My understanding is that ΔP , which is given by the Young-Laplace equation, is the pressure difference at the interface between nano-grained olivine particles and Ne pressure medium/MgO substrate/Pt foil. There is a need to explain the values of ΔP more clearly.

Response: Thank you for this constructive comment. ΔP is not the pressure difference at the interface between nano-grained olivine particles and Ne pressure medium/MgO substrate/Pt foil. As shown in the cited references (Ref 38-39) and in more recent derivations of the Young-Laplace equation such as that in Chapter 12 of Robert DeHoff's 2006 Thermodynamics in Materials Science textbook, <https://doi.org/10.1201/9781420005851>, ΔP is the excess pressure that a nano-particle (even one outside of a DAC or not part of a thin film) experiences because of the large curvature of small particles (i.e., dangling bonds on the surface of the particle produce a surface energy, which results in a "surface tension" that compresses the particle).

To make it clear that the ΔP is not the pressure difference at the interface between nano-grained olivine particles and Ne pressure medium/MgO substrate/Pt foil, we have added a citation to DeHoff's derivation and edited the description of ΔP so that the relevant section of the manuscript now reads:

“Specifically, the impact of grain size on thermodynamic stability can be approximated by the Young-LaPlace equation:

$$\Delta P = 2\Gamma/r \quad [1]$$

which shows that, on account of the surface energy (Γ), spherical particles of a given radius (r) (even those outside a DAC or thin film) experience an additional pressure (ΔP) compared to that experienced by infinitely large particles under the same surrounding pressure and temperature conditions. ³⁸⁻⁴⁰”

(2) In fact, the olivine nanoparticles experienced a higher pressure than that estimated by the platinum equation of state, as explained by the Young-LaPlace equation. This does not seem to imply a shift in the thermodynamic phase boundary due to the grain size effect, but simply seems to show the difference in effective pressures between the olivine nanograins and the platinum pressure maker.

Response: Thank you for this comment. On some levels, we sympathize with your notion that the olivine is just acting as it always acts, in response to pressure. However, when plotting up phase stability as a function of thermodynamic state variables (such as the externally-applied hydrostatic pressure, absolute temperature and composition), nanosized particles exhibit shifts in their chemical potentials, relative to the bulk, and hence also exhibit what are considered to be shifts in the thermodynamic phase boundaries. This can be seen on page 438 of DeHoff’s Thermodynamics in Materials Science textbook (<https://doi.org/10.1201/9781420005851>), where he accounts for how the curvature changes of small particles affect chemical potential (Note, this simplistic approach does not take into other nano-size effects such as changes in point defect concentrations caused by space-charge overlap, electron-in-a-box changes to the electronic structure/entropy, nano-particle faceting, etc, but it is still a useful approximation). Specifically, DeHoff writes that “The shifts in composition at constant temperature given in Equation 12.94 and Equation 12.97 may be computed at each temperature along a phase boundary. The result may be viewed as a shift in the phase boundaries of the α and β phases [as shown in], Figure 12.13.”

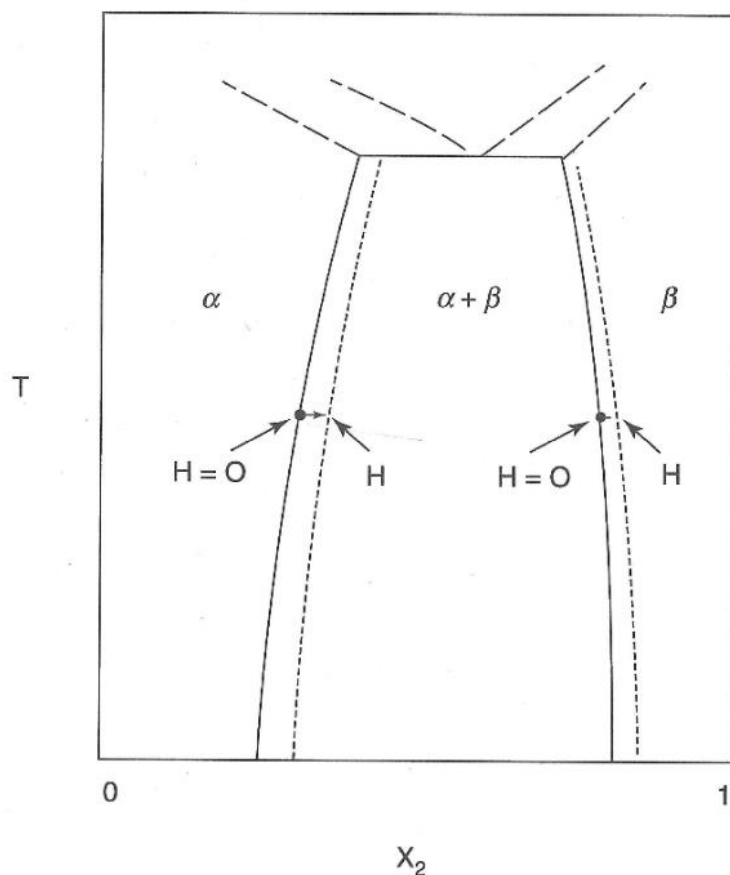


FIGURE 12.13 Effect of curvature of the $\alpha\beta$ interface upon the equilibrium composition of the α and β phases.

(Note how in Figure 12.13, the nano-sized particles possess dashed lines to indicate the edge of the $\alpha + \beta$ field that are shifted to the right, compared to those of identical bulk materials.) To lead interested readers to this derivation, we have added the following sentence to the revised manuscript:

“Second, past thermodynamic derivations demonstrate how grain size reductions can shift phase boundaries.”³⁸

(3) If the extremely small grain size of the starting material causes excess pressure (ΔP) on the grains, all phase boundaries in Mg_2SiO_4 may shift to lower pressures compared to those in the previous phase diagrams. In reality, however, such a shift is limited to the wadsleyite-ringwoodite phase boundary. How can the experimental results be explained?

Response: This is an excellent question, the answer to which is unfortunately beyond the scope of the present study. It is completely possible that the curvature changes, point defect concentration changes, etc. induced by nano-sizing may impact the chemical potential of some phases more than others. To acknowledge this possibility without identifying a specific mechanism, we have added the following statement to the end of the discussion section:

“Although future work is needed to confirm the present results and identify the active mechanisms, the phase boundary shifts observed here are consistent with the thin film forsterite

and wadsleyite having their chemical potentials by a similar, large amount (relative to the other phases found in the Mg_2SiO_4 system). ”

(4) How were the sample temperatures measured and what is the uncertainty in the temperature measurements during laser heating? Is the error in the temperature measurements small enough to ensure a higher temperature for the wadsleyite-ringwoodite transformation than in the previous phase equilibrium studies?

Response: The temperature and pressure uncertainty estimates are displayed as dimmed-out error bars in Figure 3, and are much smaller than the observed shifts in the wadsleyite to ringwoodite phase boundary. To make this more apparent, in the revised manuscript we have included a revised version of Figure 3a with darker pressure and temperature error bars. The pre-existing Figure 3 caption also provides information on the error bars with the statement:

“The pressure uncertainty bars are due to uncertainty in the volume of platinum. The temperature uncertainty bars are due to the deviation between the temperatures recorded during LH on each side of the sample.”

(5) As shown in Fig.1b and Fig.1c, both wadsleyite and ringwoodite have some crystallographic preferred orientation (CPO). I wonder if characteristic diffraction rings (spots) of the wadsleyite structure were not seen in some XRD patterns due to CPO. This would cause an apparent shift of the wadsleyite-ringwoodite boundary toward higher temperature.

Response: Thank you for this constructive comment. CPO can only eliminate X-ray reflections one would otherwise see in a randomly-oriented polycrystal. Hence, it makes detecting phase transformations more difficult. However, if one is still successful in observing strong x-ray reflections that are unique to the phases on either side of a phase transition, one can still detect that phase transformation. As shown in Figure S2 of the Supplemental materials, that is exactly what has been achieved here. Specifically, Figure S2 shows that at 18.2 GPa, we observe the disappearance of the ringwoodite peaks at 1849 K, and appearance of the wadsleyite peaks at 1910 K. This means that the ringwoodite to wadsleyite phase transition definitely occurred somewhere between 1849 K and 1910 K at 18.2 GPa in the thin film samples (i.e. well above the 1475 K transition temperature reported for this phase transformation in bulk materials).

(6) Grain size is likely to affect the kinetics of polymorphic phase transitions. Can the authors discuss this point?

Response: Thank you for this comment. As already indicated in the manuscript with comments like “perhaps not surprising due to the fast kinetics enabled by a small ~30 nm mean grain size providing many nucleation sites,” we believe that nano-sizing either speeds up, or has no effect on reaction kinetics. Speeding up of the reaction kinetics could occur by having the material switch its phase reaction mechanism from an intra-crystalline to inter-crystalline mechanism. We note this possibility in the introduction where we say that the ““inter-crystalline” mechanism (so named because the phase transformation starts “between the grains” due to the lower nucleation barrier for second-phase nucleation at the grain boundaries compared to the grain interior) is favored at small reactant grain sizes”. Hence, one of the benefits of analyzing samples with small grain sizes, such as those in thin films samples, is that, compared to studies on large-grained

samples, slow phase reaction kinetics are less likely to lead to incorrect determinations of phase boundary locations.

Because of the above concerns, it is difficult for me to recommend the manuscript for publication in Communications Earth & Environment in its current form. I hope the manuscript may be improved after clearly addressing the above concerns.

Minor comments

Page2, line 6: What does "impact water" mean?

Response: As detailed in the references provided at the end of the sentence in question (Refs 13-16), water has been shown to enhance the kinetics of the olivine to wadsleyite, and olivine to ringwoodite phase transformations. To make the sentence in question clearer, we have now added a "that" so that this sentence now reads:

"Some of this controversy has focused on subducting slab water contents and the impact that water has on (Mg,Fe)₂SiO₄ phase stability, transformation kinetics, and transformation mechanisms.¹³⁻¹⁶"

Page 4, line 20: "These results" instead of "This results".

Response: Here, the word "results" is used as a verb. However, since some readers may get confused by treating "results" as a noun in this sentence, we have replaced the sentence:

"This results in an epitaxial film stress that can be up to several gigapascals in magnitude⁴⁴"

with the sentence:

"This leads to an epitaxial film stress that can be up to several gigapascals in magnitude⁴⁴"

Page 11, line 15–17 (As shown by... the original forsterite film): The XRD pattern in Fig. S1 shows strong CPO. However, the text states that the olivine in Fig. S1 is a randomly oriented polycrystal. What do you mean by this?

Response: Thanks for the question. While the XRD data in Figure S1 is for our as-deposited forsterite films (which indeed displayed lots of CPO), the overlaid index pattern percentages are from the randomly oriented polycrystalline Mg₂SiO₄ sample of PDF#00-004-0768. To make this clearer, we have edited the sentence in question to now read:

*"As shown by comparing the **Figure 2** forsterite peak intensities with those for a randomly oriented polycrystal indicated by the percentage numbers in **Figure S1** of Supplementary Materials, this regenerated forsterite exhibited CPO that was different from the original forsterite film."*

Page 12, line 3–12: The akimotoite+periclase assemblage has not been reported in previous phase equilibrium studies, but Kubo et al. (Geophys. Res. Lett., v.27, 807–810, 2000) reported that the assemblage formed metastably from Mg₂SiO₄ olivine at ~24–28 GPa and ~800–1100 °C. Have you done reversal runs to confirm the equilibrium "akimotoite+periclase" – "bridgmanite+periclase" phase boundary?

Response: Thank you for bringing this to our attention and for the reference to the Kubo paper. To highlight the fact that akimotoite+periclase assemblage has not been reported previously in experimental phase equilibrium studies, we have added the following paragraph:

“Figures 2 and 3 also show that at ~23 GPa and ~1000 K the sample exhibited 1) MgSiO₃ akimotoite XRD peaks and 2) MgO XRD peaks that were likely from both the substrate and from the chemical breakdown of the thin film Mg₂SiO₄. This behavior agreed with Hernandez et al.’s Mg₂SiO₄ simulations,⁷⁰ as did conversion of the akimotoite into bridgmanite observed here at ~1454 K and ~23 GPa. However, the observation of akimotoite+periclase from ~1000 to 1454 K at 23 GPa disagreed with past experimental studies which have either directly-observed⁶⁹ or assumed^{71,80,81} that ringwoodite is stable at these P-T conditions. The results here, along with possible discrepancies in previous studies resulting from the use of Au vs Pt of MgO pressure sensors,⁸¹ the observation of a metastable akimotoite + periclase assemblage near the edges of Hernandez et al.’s akimotoite + periclase stability window,⁸⁹ past suggestions that the akimotoite to bridgmanite transition is seismically relevant,⁹⁰ the possibility of slow kinetics resulting from the larger grain sizes used in previous studies,⁶⁹ and the removal of the MgO nucleation barrier here caused by the use of a MgO substrate, suggest that a previously-unconfirmed, Earth-relevant akimotoite + periclase phase field may exist in the Mg₂SiO₄ phase diagram. However, additional thin film + DAC experiments performed as a function of grain-size, deviatoric-stress, substrate-identity, and water content are needed before firm conclusions can be drawn.”

In addition, we have modified the middle of the Conclusions section to now read:
“The P-T conditions of the thin film Mg₂SiO₄ (akimotoite+periclase)-to-(bridgmanite+periclase) phase transformation, and the thin film Mg₂SiO₄ (akimotoite+periclase) phase stability field, agreed with past simulation results, but disagreed with past experimental results. The P-T conditions of the thin film Mg₂SiO₄ wadsleyite-to-ringwoodite transformation occurred ~300 K lower at ~18 GPa (~1 GPa lower at 1900 K) than previous simulation results, but ~500 K higher at ~18 GPa (~2.5 GPa lower at 1900 K) than previous experimental reports.”

Due to the limited duration of our beamtime sessions, we were prevented from performing phase transformation reversal runs. While we plan to do a whole series of Mg₂SiO₄ reversal runs under various P-T conditions in the future (hopefully as part of a pending NSF Geophysics program proposal), we believe that their exclusion here does not detract from the main message of this paper (which is to 1) demonstrate that well-resolved thin film XRD signals can be obtained within a DAC, and 2) outlining how thin film DAC studies may possibly be able to contribute to major Mineral Physics advances in the future).

Page 18, line 1–2: What was the duration of laser heating?

Response: Thank you for pointing out this oversight. To correct it, we have added the following sentence to the revised manuscript:

“Laser heated lasted between 15-20 minutes, depending on the highest temperature reached and number of measurements taken at each pressure point.”

Fig. 1, Fig. 2, Fig. S1, Fig. S2: The X-ray diffraction spots must be represented by the Laue indices, but not by the Miller indices. Therefore, all parentheses for the indices should be removed. (e.g. "020" instead of "(020)")

Response: Thank you for the comment. In response, we have deleted all the parentheses from the peak labels in Fig 1, Fig 2, and Fig S2 of the revised manuscript. Since the peak labels in Figure S1 are for an overlaid reference pattern taken on randomly-oriented polycrystalline samples, we have retained the peak label parentheses in Figure S1.

28th Dec 23

Dear Professor Nicholas,

Your manuscript titled "Detection of Thin Film Phase Transformations at High-Pressure and High-Temperature in a Diamond Anvil Cell" has now been seen by our reviewers, whose comments appear below. In light of their advice we are delighted to say that we are happy, in principle, to publish a suitably revised version in Communications Earth & Environment under the open access CC BY license (Creative Commons Attribution v4.0 International License).

We therefore invite you to revise your paper one last time to address the remaining concerns of our reviewers. At the same time we ask that you edit your manuscript to comply with our format requirements and to maximise the accessibility and therefore the impact of your work.

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We hope to hear from you within two weeks; please let us know if you need more time.

Best regards,

Joe Aslin

Senior Editor,
Communications Earth & Environment
<https://www.nature.com/commsenv/>
Twitter: @CommsEarth

REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

I have carefully read this new version of the article "Detection of Thin Film Phase Transformations at High-Pressure and High-Temperature in a Diamond Anvil Cell" by Berrada et al. The authors have taken my comments into account, detailing the technical limitations (associated with X-ray diffraction in the DAC) that prevented estimation of the stress state in the sample and a multi-grain analysis to explore the microstructure. These additions will be useful to the readers. Areas for improvement and future work are listed in the rebuttal letter, but could advantageously be listed in the main text. (this would be my only request)
I therefore support the publication of this manuscript.

Reviewer #2 (Remarks to the Author):

To Dr. Aslin, Editor, Communications Earth & Environment

I have thoroughly read the revised manuscript "Detection of thin film phase transformations at high-pressure and high-temperature in a diamond anvil cell" by Berrada et al. and the authors' responses to the reviewers. I realized my misunderstanding on the definition of ΔP in the Young-LaPlace equation, and all my concerns about the original manuscript have been addressed in the revised manuscript. I therefore think the revised version of the manuscript is suitable for publication in Communications Earth & Environment.

Minor comments:

There are some typos on mineral names on page 13 of the revised manuscript.

Line 5: "akimotoite" instead of "akimoite"

Line 6: "akimotoite" instead of "akimotiite"

Line 7: "bridgmanite" instead of "bridgemantite"

Response to Reviewer Comments

Reviewer #1 (Remarks to the Author):

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Response: Thanks! We agree.

Areas for improvement and future work are listed in the rebuttal letter, but could advantageously be listed in the main text. (this would be my only request)

Response: We appreciate your comment and agree that some readers may be interested in the specific DAC types we plan to use in future studies, our planned future use of DAC rotation, and the constancy of elastic constants in grains down to 10 nm in diameter mentioned in our previous author rebuttal letter. However, we do not feel that a discussion of these topics should appear in the main manuscript because 1) we believe their inclusion would distract readers from the main accomplishments summarized in the main manuscript, 2) some readers may consider it unprofessional to include unproven future research plans in a peer-reviewed archival journal, and 3) the Communications Earth & Environment policy of publishing author rebuttals alongside manuscripts will provide interested readers with a mechanism to access this information.

I therefore support the publication of this manuscript.

Response: Thank you again for your valuable input on our multiple manuscripts. Your comments have helped us determine how to best present our atypical experiments/results to the Geophysics community.

Reviewer #2 (Remarks to the Author):

To Dr. Aslin, Editor, Communications Earth & Environment

I have thoroughly read the revised manuscript "Detection of thin film phase transformations at high-pressure and high-temperature in a diamond anvil cell" by Berrada et al. and the authors' responses to the reviewers. I realized my misunderstanding on the definition of ΔP in the Young-LaPlace equation, and all my concerns about the original manuscript have been addressed in the revised manuscript. I therefore think the revised version of the manuscript is suitable for publication in Communications Earth & Environment.

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Line 5: "akimotoite" instead of "akimoite"

Line 6: "akimotoite" instead of "akimotiite"

Line 7: "bridgmanite" instead of "bridgemantite"

Response: Thank you for your valuable input on our manuscript. We have made the minor corrections noted here, and we appreciate the time you spent in service to the community reviewing our manuscript.