

Water exchange process and bulk composition regulate slab dynamics and deep earthquakes

Corresponding Author: Dr Takayuki Ishii

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)

Review of « Dehydration-hydration reactions and bulk composition control slab dynamics, deep earthquakes, and water cycling » by Jintao Zhu et al.

This manuscript presents a very thorough investigation of the phase diagram of the two systems $\text{Mg}_2\text{SiO}_4 + 2 \text{ wt\% H}_2\text{O}$ and $50\% \text{Mg}_2\text{SiO}_4 + 50\% \text{MgSiO}_3 + 2 \text{ wt\% H}_2\text{O}$ at pressures of 8 to 28 GPa and temperatures of 800 to 1500°C. They report about 47 x 2 experiments, which is very impressive.

The measurements of phase texture, phase characterization and water contents is presented in detail. The figures are of very good quality and the English is impeccable. I find that this is an excellent manuscript that brings interesting and important observations, it should be published after some corrections. I have a few comments to help improve the manuscript, especially the discussion and comparison with reports on natural compositions.

The interesting take-home message is that (L.210) “namely, the water content in the bulk composition does not significantly alter the complete dehydration temperature of these hydrous minerals...” Well, compared to literature data using more complex compositions, the dehydration temperatures are higher here, especially at 8-10 GPa. In Supplementary Figure 8 the comparison with previous data is made mostly with experiments performed in the MSH system but containing more water. However, in the mantle portion of the slab, aluminum is very important, especially in stabilizing Phase E at the expense of Phase A as shown by Kawamoto (2004) EPSL. Especially, the phase assemblage of aluminous Phase E + enstatite + olivine can carry 2 wt% H₂O, exactly the water content that the authors decided to use here. A few words acknowledging that would be welcome.

The authors conclude that “hydrous minerals gradually dehydrate with increasing temperature in the mantle transition zone, progressively hydrating NAMs such as wadsleyite and ringwoodite, while the cold slab core remains dry.” While it has been known since Poli and Schmidt (1998) that hydrous minerals dehydrate progressively, the progressive hydration of transition zone mantle NAMS is nicely shown here.

In figure 1: there is important information that is not explained nor mentioned in the text such as the Schreinemaker analysis.

It is not clear why “highly hydrated wadsleyite/ringwoodite” were used. Does the system still corresponds to the same bulk as the other samples, and what was the purpose ?

Figure 1a and b: the lines delimiting the phase stability seem to be very arbitrary: for example: at 8 GPa, if you locate the boundary between the sample with Phase A and the sample without phase A, why you don't do the same at 10 GPa ? You draw the boundary on the sample that still contains phase A. Your experiments seem to show steeper phase boundary. Same for the enstatite-bearing starting composition.

L. 159: “The presence of less hydrated wadsleyite and ringwoodite coexisting with ? hydrous fluid or melt at high temperatures was also confirmed by FTIR ($\text{CH}_2\text{O}=0.7\text{--}1.5 \text{ wt\%}$)”. To what phases does this later range corresponds to ?

L. 172: “...suggesting that compositions of hydrous minerals are constant regardless of H₂O activity.” At least this could be a

little bit explained in the caption of supplementary Figure 7: what is the dashed region representing ? I guess it corresponds to the range of compositions observed in this study ?

L. 174. Volume fractions of hydrous minerals decreased with increasing temperature when they coexisted with wadsleyite or ringwoodite (Fig. 3, Supplementary Table 1).” How did you determine the volume fraction of minerals ? By image J analysis of the surface proportion of each of the phases, ok, but this is said in the supplementary. This should be said in the caption of Figure 3 (a) and (b).

Supplementary Figure 7 should be linked to the supplementary note in its caption, otherwise the figure cannot be understood.

Reviewer #2

(Remarks to the Author)

The authors conducted high-pressure and high-temperature experiments on the MSH system with limited H₂O across a wide range of pressure-temperature conditions to simulate subducted slabs at the mantle transition zone. They found that hydrous minerals gradually dehydrate during subduction while wadsleyite and ringwoodite become hydrated. Meanwhile, the core of MOW remains dry due to the presence of hydrous minerals. Furthermore, they suggested that the deepest deep-focus earthquakes occur due to the dehydration of hydrous minerals at the top of the lower mantle, because the water solubility of bridgmanite and periclase is low, causing excess fluid to be generated. Similarly, the low solubility of forsterite means that dehydration of phase A triggers deep-focus earthquakes at 300–400 km depth. This manuscript is valuable in systematically demonstrating the behavior of hydrous minerals under limited water conditions and their relationship to deep-focus earthquakes. However, the paper is somewhat difficult to read, and I suggest some improvements before publication.

1. The authors performed experiments on Mg₂SiO₄ + 2 wt% H₂O and Mg_{1.3}SiO_{3.3} + 2 wt% H₂O systems to simulate the compositional variations of ultramafic rocks. Although the authors show the variations in stable minerals depending on the Mg/Si ratio (p. 11), the discussion of how the Mg/Si ratio influences the stability field of hydrous minerals in subducted slabs and the occurrence of deep-focus earthquakes is limited (only mentioning that the harzburgite layer has a greater capacity to transport hydrous minerals into the deep mantle). I recommend expanding this discussion, for example by elaborating on the relationship between Fig. 1 and Fig. 4.

2. The explanation referring to Fig. 4 in the main text is insufficient. Fig. 4 provides a good summary of the implications for subducted slabs, but readers must search through the text to connect the discussion to the figure, as Fig. 4 is rarely cited in the main text. Since the relevant details are already well explained, it would be sufficient to add citations to Fig. 4 at the appropriate places throughout the text.

Minor comment

P8, l56 N the other hand->On the other hand

Reviewer #3

(Remarks to the Author)

This manuscript reports phase-relation experiments in hydrous MgO–SiO₂ systems under water-undersaturated conditions (2 wt% H₂O), using two starting compositions with different Mg/Si ratios. The main contribution is the broader P–T coverage and the systematic Mg/Si comparison, following essentially the same experimental approach as earlier limited-water studies (multi-anvil experiments with FTIR constraints).

The phase-equilibrium dataset appears internally consistent and provides useful constraints on the stability of DHMS phases (PhA, PhE, sPhB, PhD) and on the low H₂O contents of coexisting NAMs at low temperatures. The manuscript then extends these results to a broad geophysical narrative based on dry olivine and inferred slow olivine → wadsleyite/ringwoodite transformation. However, most of these implications follow the same framework as previous studies (Ishii and Ohtani 2021 *Nature Geosci.*; Ishii et al., 2025 *EPSL*), and the present dataset does not add new constraints that would strongly test or revise that framework. In particular, the paper does not present direct kinetic data (e.g., transformation rates), although the main story depends on kinetics. In addition, the proposed slab-scale hydration-gradient narrative is difficult to justify at cold-slab temperatures without a clear transport mechanism and quantitative timescale estimates. Overall, this is a solid phase-equilibrium contribution of interest to specialists, but the conceptual advance for a broad readership is not clearly demonstrated.

Specific comments

1. P66–: Some sentences read as if water-undersaturated systems are still largely unexplored. This may mislead readers. Please clearly position this study as an extension of the existing limited-water framework.

2. P246–: The meaning of “kinetically dry” is unclear. Under limited-water conditions, low H₂O in olivine can already be explained by equilibrium partitioning into DHMS. If a kinetic argument is intended, please specify which process is rate-limiting. Otherwise, “dry” may be sufficient, because olivine is expected to be dry in equilibrium at low temperatures as shown in this and previous studies.

3. Estimating H₂O in fine-grained wadsleyite/ringwoodite from EPMA Mg/Si is an interesting approach. Please provide calculated H₂O contents (with uncertainties) for the relevant runs. For higher-temperature runs where FTIR is feasible, please also report EPMA-based H₂O for the same phases and show consistency with FTIR.

4. The proposed hydration-gradient story seems to require long-range redistribution across a large fraction of slab thickness. At cold-slab temperatures, it is not obvious that such transport is efficient on geological timescales. Please clarify what transport mechanism is assumed (e.g., solid-state diffusion, grain-boundary transport, transient interconnected fluid films) and provide order-of-magnitude timescale/length-scale estimates with appropriate references. Existing experimental constraints on hydrogen diffusivity in wadsleyite (e.g., Hae et al., 2006) were obtained at much higher temperatures (900–

1200 °C) and represent effective diffusivities in polycrystalline aggregates. Extrapolating such Arrhenius relations to cold-slab temperatures implies substantially slower transport, so km-scale redistribution by diffusion alone may be difficult unless an additional fast pathway is demonstrated.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

I consider that the authors have answered all comments.
The manuscript can be published without further corrections.

Best regards.

Reviewer #2

(Remarks to the Author)

I believe my comments have been adequately addressed, and the manuscript is now suitable for publication.

Reviewer #3

(Remarks to the Author)

I appreciate the substantial effort the authors have made in revising the manuscript.

Overall, I consider that this phase-equilibrium study provides useful constraints over a broad P–T range. Although the compositions are simpler than natural systems, the phase relations involving DHMSs and NAMs are clearly demonstrated for different bulk compositions. The revision has made the discussion more cautious and scientifically solid, but in my view this also makes the broader impact appear more limited. I therefore remain uncertain whether the broader interpretive framework is sufficiently distinct from previous studies for this journal.

The revised manuscript also raises an additional question regarding the newly proposed model. The authors state that hydrogen can be fully homogenized at grain-size scales (on the order of millimeters to centimeters), while long-range redistribution is limited. This itself suggests that hydrogen mobility may be significant at local scales under the relevant coexistence conditions. Equilibrium partitioning does not imply absence of hydrogen mobility; rather, it reflects balanced exchange fluxes between coexisting phases. Therefore, even if bulk H₂O contents in olivine remain low, hydrogen transfer between hydrous phases and adjacent NAMs may still influence local reaction environments, especially at grain boundaries or phase interfaces where transformation is initiated. This may complicate the direct application of previously reported dry olivine transformation kinetics to the present coexistence conditions.

This issue appears particularly important because the applicability of dry olivine transformation kinetics under hydrous phase-bearing coexistence conditions forms a central part of the conceptual framework proposed by this research line since 2022 (Nature Geoscience). However, subsequent studies seem to have focused mainly on partitioning and phase relations, and direct support for this key kinetic assumption still appears limited. Therefore, I am uncertain that this aspect constitutes a clearly distinct conceptual advance.

The revised manuscript provides a more convincing and logically coherent explanation for slab-scale water redistribution than the original version. In particular, fluid/melt transport associated with dehydration is physically more reasonable than relying on long-range hydrogen diffusion. However, this improvement also makes the proposed model closer to previously discussed slab dehydration and fluid-migration frameworks. Thus, while the revision strengthens the internal logic of the model, it also makes the degree of novelty appear more limited.

More broadly, the interpretation still appears to be built largely on concepts that have already been established in previous studies: strong H₂O partitioning into NAMS, dry olivine in the cold slab interior, deep-focus earthquake mechanisms, and water redistribution related to dehydration reactions. In the rebuttal letter, the authors highlight temperature-dependent H₂O partitioning between NAMs and coexisting hydrous phases as an important new element of the revised model. However, similar discussions of increasing H₂O contents in NAMs with temperature appear in the recent 2025 study (EPSL).

Version 2:

Reviewer comments:

Reviewer #3

(Remarks to the Author)

I appreciate the detailed revisions. Although my concerns regarding novelty, the applicability of dry olivine kinetics, and the related implications remain, I have no further major comments.

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Reviewer #1 (Remarks to the Author):

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The measurements of phase texture, phase characterization and water contents is presented in detail. The figures are of very good quality and the English is impeccable. I find that this is an excellent manuscript that brings interesting and important observations, it should be published after some corrections. I have a few comments to help improve the manuscript, especially the discussion and comparison with reports on natural compositions.

Response

We sincerely thank the reviewer for the positive and encouraging evaluation of our manuscript. Following your comments, we have carefully revised the manuscript to improve the interpretation of our results.

The interesting take-home message is that (L.210) “namely, the water content in the bulk composition does not significantly alter the complete dehydration temperature of these hydrous minerals...” Well, compared to literature data using more complex compositions, the dehydration temperatures are higher here, especially at 8-10 GPa. In Supplementary Figure 8 the comparison with previous data is made mostly with experiments performed in the MSH system but containing more water. However, in the mantle portion of the slab, aluminum is very important, especially in stabilizing Phase E at the expense of Phase A as shown by Kawamoto (2004) EPSL. Especially, the phase assemblage of aluminous Phase E + enstatite + olivine can carry 2 wt% H_2O , exactly the water content that the authors decided to use here. A few words acknowledging that would be welcome.

Response

Thank you for your suggestion about the alumina effect on the stability of hydrous minerals, we have added the context as follows:

“In a study of water-saturated peridotite (13.6 wt% H_2O)⁴⁸, Al_2O_3 stabilized PhE, which coexisted with PhA, chondrodite and NAMs (e.g., garnet) at 9.3–10.3 GPa. At 14 GPa, PhE formed alongside garnet and clinoenstatite but decomposed at 1200 °C.”

The authors conclude that “hydrous minerals gradually dehydrate with increasing temperature in the mantle transition zone, progressively hydrating NAMs such as wadsleyite and ringwoodite, while the cold slab core remains dry.” While it has been known since Poli and Schmidt (1998) that hydrous minerals dehydrate progressively, the progressive hydration of transition zone mantle NAMS is nicely shown here.

Response

Thank you for your comment on our study about the progressive dehydration of hydrous minerals in the mantle transition zone. We cited Schmidt and Poli EPSL (1998) in the manuscript and added some statement to show the comparison between our study and their study:

“We note that, although the progressive dehydration in the MTZ is analogous to dehydration of hydrous minerals (e.g., phengite) at sub-arc depth that explains arc magma generation⁴³, no fluid/melt will be generated in the MTZ progressive dehydration of DHMSs due to the high-water storage capacity of wadsleyite and ringwoodite as mentioned above. Such solid-state reactions and mineral transformation can drive short-range redistribution of hydrogen between DHMSs and NAMs in the slab interior (Fig. 4).”

In figure 1: there is important information that is not explained nor mentioned in the text such as the Schreinemakers analysis.

Response

We added “Phase relations and Schreinemakers analysis of reactions were shown in Fig. 1.” In the beginning of the Section “Phase relation of $\text{Mg}_2\text{SiO}_4+2\text{wt}\% \text{H}_2\text{O}$ system”.

It is not clear why “highly hydrated wadsleyite/ringwoodite” were used. Does the system still corresponds to the same bulk as the other samples, and what was the purpose ?

Response

Experiments using highly hydrated wadsleyite/ringwoodite were performed to confirm the stability of hydrous minerals coexisting with NAMs and the degree of water content in wadsleyite and ringwoodite through the observation of the decomposition of the starting hydrous NAMs into hydrous minerals together with these NAMs. The bulk compositions of highly hydrated wadsleyite (~2 wt%) /ringwoodite (~1.6 wt%) are identical or close to that of $\text{Mg}_2\text{SiO}_4+2\text{wt}\%\text{H}_2\text{O}$ system. Therefore, we used these experiments as reversal runs against forward ones using hydrous oxide mixture although the bulk composition of hydrous ringwoodite is not consistent with that of the starting material from the hydrous oxide mixture. We observed decompositions of highly hydrous wadsleyite and ringwoodite to hydrous minerals + NAMs including wadsleyite and ringwoodite. This indicates that highly hydrous wadsleyite and ringwoodite are unstable and water contents of wadsleyite and ringwoodite at these conditions should be lower due to decomposition to hydrous minerals and NAMs. These experiments support our conclusion of the progressive dehydration-hydration process.

Figure 1a and b: the lines delimiting the phase stability seem to be very arbitrary: for example: at 8 GPa, if you locate the boundary between the sample with Phase A and the sample without phase A, why you don't do the same at 10 GPa ? You draw the boundary on the sample that still contains phase A. Your experiments seem to show

steeper phase boundary. Same for the enstatite-bearing starting composition.

Response

Thank you for concerns about the phase boundary in Fig. 1. We have constructed the phase boundary based on the principles of Schreinemaker's analysis and the observed phase assemblage. We have simplified some points and lines because the whole petrogenetic grid of the MgO-SiO₂-H₂O system is complex, as illustrated by the calculated results of Komabayashi and Mori (2006).

We did not draw the phase boundary on samples that still contain phase A. Because the data points of specific P-T conditions are enlarged in the figure, it may appear that the phase boundary is located at the P-T condition where the phase assemblage contains PhA. The slight positive slope of the phase boundary is adopted to be consistent with the chemical reaction $\text{PhA} + \text{Cen} = \text{PhE} + \text{Wad}$. If the boundary of the PhA decomposition were placed far from PhA-bearing P-T condition, the reaction $\text{PhA} + \text{Cen} = \text{PhE} + \text{Wad}$ would exhibit an extremely steep slope, which is not suitable.

L. 159: "The presence of less hydrated wadsleyite and ringwoodite coexisting with ? hydrous fluid or melt at high temperatures was also confirmed by FTIR (CH₂O=0.7–1.5 wt%)". To what phases does this later range corresponds to ?

Response

The water contents of wadsleyite and ringwoodite coexisting with hydrous fluid or melt at high temperatures were measured by FTIR. We attached the detailed information in Supplementary Table 6. The variations of water contents are due to the different pressure-temperature conditions and the changes of coexisting phases (e.g., 0.98 wt% of ringwoodite coexisting with akimotoite and melt at 22 GPa, 1400°C vs. 1.33 wt% of ringwoodite coexisting with hydrous melt at 20 GPa, 1400 °C. We have added the following statement to clarify:

"The variation of CH₂O results from different phase assemblages and changes of P-T conditions".

L. 172: "...suggesting that compositions of hydrous minerals are constant regardless of H₂O activity." At least this could be a little bit explained in the caption of supplementary Figure 7: what is the dashed region representing ? I guess it corresponds to the range of compositions observed in this study ?

Response

The dashed regions correspond to the compositional variations of PhE and PhD, summarized by Litasov and Ohtani (2007).

We explained it in the revised caption: "The circles denote the compositions of phase A (PhA) and superhydrous phase B (sPhB), which are derived from their ideal chemical formulas, Mg₇Si₂O₈(OH)₆, Mg₁₀Si₃O₁₄(OH)₄, respectively. The striped fields represent the broad compositional variations of phase E (PhE) and phase D (PhD) reported in previous studies on MgO-SiO₂-H₂O systems (See Ref. 9)"

L. 174. Volume fractions of hydrous minerals decreased with increasing temperature when they coexisted with wadsleyite or ringwoodite (Fig. 3, Supplementary Table 1)."

How did you determine the volume fraction of minerals ? By image J analysis of the surface proportion of each of the phases, ok, but this is said in the supplementary. This should be said in the caption of Figure 3 (a) and (b).

Response

Yes, we used ImageJ software to determine the volume fraction of hydrous minerals.

We have revised the caption of Figure 3 (a) and (b) to “Volume fractions of DHMSs with increasing temperature. DHMSs were manually marked in BSE images and their volume fractions were determined by the ImageJ software.”

Supplementary Figure 7 should be linked to the supplementary note in its caption, otherwise the figure cannot be understood.

Response

We added “See more information in Supplementary Note 1 about the effect of Mg/Si ratio on the stability of hydrous minerals” in the caption of Supplementary Figure 7.

Reviewer #2 (Remarks to the Author):

The authors conducted high-pressure and high-temperature experiments on the MSH system with limited H₂O across a wide range of pressure-temperature conditions to simulate subducted slabs at the mantle transition zone. They found that hydrous minerals gradually dehydrate during subduction while wadsleyite and ringwoodite become hydrated. Meanwhile, the core of MOW remains dry due to the presence of hydrous minerals. Furthermore, they suggested that the deepest deep-focus earthquakes occur due to the dehydration of hydrous minerals at the top of the lower mantle, because the water solubility of bridgmanite and periclase is low, causing excess fluid to be generated. Similarly, the low solubility of forsterite means that dehydration of phase A triggers deep-focus earthquakes at 300–400 km depth. This manuscript is valuable in systematically demonstrating the behavior of hydrous minerals under limited water conditions and their relationship to deep-focus earthquakes. However, the paper is somewhat difficult to read, and I suggest some improvements before publication.

Response

We sincerely thank the reviewer for the thorough and constructive comment. We acknowledge that some parts of the manuscript were not sufficiently clear in the original version. Following your suggestion, we revised the manuscript to improve the readability.

1. The authors performed experiments on Mg₂SiO₄ + 2 wt% H₂O and Mg_{1.3}SiO_{3.3} + 2 wt% H₂O systems to simulate the compositional variations of ultramafic rocks. Although the authors show the variations in stable minerals depending on the Mg/Si ratio (p. 11), the discussion of how the Mg/Si ratio influences the stability field of hydrous minerals in subducted slabs and the occurrence of deep-focus earthquakes is limited (only mentioning that the harzburgite layer has a greater capacity to transport

hydrous minerals into the deep mantle). I recommend expanding this discussion, for example by elaborating on the relationship between Fig. 1 and Fig. 4.

Response

Thank you for the thoughtful comment. Owing to the word limit, we have added a statement in the main text referring to Supplementary Note 1, where the effects of the Mg/Si ratio on the stability of hydrous minerals are discussed in detail.

Different Mg/Si molar ratios yield distinct phase relations and the stability of hydrous minerals. The Mg-rich composition prefers the formation of high Mg/Si phases (e.g., PhA, sPhB) while the Si-rich composition expands the stability of low Mg/Si phases (e.g., PhE). In this study, at 12 GPa and 1000–1100 °C, a three-phase assemblage of hydrous wadsleyite, clinoenstatite and PhE appeared in the system of Mg/Si=1.3. By contrast, a two-phase assemblage of hydrous wadsleyite and PhA formed in the system of Mg/Si=2, owing to the bulk composition being situated on the PhA-hydrous wadsleyite tie-line (Supplementary Fig. 7a). Consequently, the thermal stability of PhA decreased while that of PhE gets expanded in the system with low Mg/Si ratio, although the general dehydration temperature at 8–12 GPa remain constant in the two systems (Fig. 1).

At 14–18 GPa and 1000–1200 °C, hydrous wadsleyite and sPhB formed in Mg/Si=2 system while hydrous wadsleyite and clinoenstatite or stishovite were observed in the Mg/Si=1.3 system, which could be explained by hydrous wadsleyite-sPhB tie-line and hydrous wadsleyite-clinoenstatite/stishovite tie-lines (Supplementary Fig. 7b). As a result, the dehydration temperatures of sPhB are by ~100 °C higher in Mg₂SiO₄ + 2 wt% H₂O system than those in Mg_{1.3}SiO_{3.3} + 2wt% H₂O system at 14–18 GPa. Thermal stability of sPhB under water-saturated conditions also tends to be larger in high Mg/Si ratio systems^{13,17,18} (Supplementary Fig. 8).

Although the P-T stability of PhD is nearly identical in two systems studied, it is expanded in the Si-rich composition under water-saturated conditions. At 20–24 GPa and 1000–1200 °C, sPhB, stishovite and fluid was observed in Ohtani et al. (2000)² (Mg/Si=2, H₂O=11 wt%). However, PhD appears alongside sPhB and fluid in Komabayashi and Omori (2006)¹⁸ (Mg/Si=1.4, H₂O=12.2 wt%) at 21.5 GPa and 1000–1200 °C and Irifune et al. (1998)¹⁶ (Mg/Si=1.5, H₂O=13 wt%) under similar P-T conditions. With more silica incorporated, PhD coexists with stishovite and sPhB at 22 GPa and 1200–1400 °C¹² (Mg/Si=0.5, H₂O=10.09 wt%).

Because sPhB is more stable at high Mg/Si ratio at 14–18 GPa, we suggested that high Mg/Si lithology (e.g., harzburgite) has greater capacity for transporting hydrous minerals, considering its thermal structure. Accordingly, we have revised the discussion as follows:

We have also revised Fig. 4 to better illustrate the association of Mg/Si ratio of slabs with stability of hydrous minerals. Specifically, the subducting slab is now divided into MORB, harzburgitic, and peridotitic domains, with their respective stable hydrous mineral assemblages indicated at different depths, based on the phase relations shown in Fig. 1.

“In the upper MTZ, the thermal stability of DHMSs is higher in a high Mg/Si system (Fig. 1), indicating the harzburgitic layer has a greater capacity to transport

surface (Supplementary Note 2). The green stars denote intermediate-depth and deep-focus earthquakes caused by hydrous fluid (FI) or melt (M) (purple droplets) produced by the decomposition of hydrous minerals. The red stars denote the deep-focus earthquakes triggered by grain-size reduction during the dry Ol transformation. The black arrows indicate the transformational fault caused by the Ol transformation. The pink wavy lines indicate low-velocity zones below the 660-km discontinuity. Our proposed water-content gradient model arises from three basic patterns (in blue arrows): (A) the water budget inherited from the shallower depth than 410 km depth; (B) solid-state reactions between DHMSs and NAMs within the interior; (C) FI/M-mediated hydrogen transport near the surface/bottom of the slab.”

We have added the citation of Fig. 4 in Chapter “Deep water exchange between hydrous minerals, NAMs, and hydrous fluid/melt”, “Compositional dependence on the stability of hydrous minerals”, and “Implications for earthquake genesis and slab dynamics”.

Minor comment

P8, l56 N the other hand->On the other hand

Response

We have corrected it.

Reviewer #3 (Remarks to the Author):

This manuscript reports phase-relation experiments in hydrous MgO–SiO₂ systems under water-undersaturated conditions (2 wt% H₂O), using two starting compositions with different Mg/Si ratios. The main contribution is the broader P–T coverage and the systematic Mg/Si comparison, following essentially the same experimental approach as earlier limited-water studies (multi-anvil experiments with FTIR constraints).

The phase-equilibrium dataset appears internally consistent and provides useful constraints on the stability of DHMS phases (PhA, PhE, sPhB, PhD) and on the low H₂O contents of coexisting NAMs at low temperatures. The manuscript then extends these results to a broad geophysical narrative based on dry olivine and inferred slow olivine → wadsleyite/ringwoodite transformation. However, most of these implications follow the same framework as previous studies (Ishii and Ohtani 2021 *Nature Geosci.*; Ishii et al., 2025 *EPSL*), and the present dataset does not add new constraints that would strongly test or revise that framework. In particular, the paper does not present direct kinetic data (e.g., transformation rates), although the main story depends on kinetics. In addition, the proposed slab-scale hydration-gradient narrative is difficult to justify at cold-slab temperatures without a clear transport mechanism and quantitative timescale estimates.

Overall, this is a solid phase-equilibrium contribution of interest to specialists, but the conceptual advance for a broad readership is not clearly demonstrated.

Response

We thank the reviewer for the constructive comments. We are grateful to the reviewer for the evaluation about the significance of our experimental work.

To address the concern about the advances in conception, we have revised the manuscript to classify the novel aspects of this study. As the reviewer commented, our study extended previous limited-water experiments by providing data under broader and fine P–T condition. We found that the dehydration-hydration process between NAMs and hydrous minerals dominantly occur in the mantle transition zone. The previous studies only focused on their water contents at relatively low temperatures around the cold core and how water content develops with temperature (i.e. thermal stability and volume fraction of hydrous minerals determined in this study) was not experimentally clarified. This hampered the detailed model construction of water distribution in a subducting slab. In addition, we identified stable hydrous minerals with depth. The previous studies did not well constrain this point. This constraint allowed us to discuss which hydrous mineral can play an important role on producing the deepest earthquakes. We also determined the effect of Mg/Si ratio on stability of hydrous minerals, newly finding that Mg/Si ratio affects stability of hydrous minerals especially in the mantle transition zone. This allowed us to discuss difference in water-transport property of each slab-constituent layer, which is a completely new finding. We have clarified how these results refine, rather than duplicate, the existing framework.

Regarding kinetics, we agree that our study does not provide direct kinetic measurements. We explicitly frame the discussion of phase transformation and dehydration behaviour as being consistent with, but not directly constraining, kinetic processes.

In response to the concern about the slab-scale hydration-gradient model, we have clarified the underlying mechanism and added more considerations (Supplementary Note 2). In particular, we emphasize that the proposed water-content gradient may be affected by 1) nature of hydration state of slab above 410 km; 2) short-scale water redistribution by the solid-state reactions in the hydrated interior; 3) efficient water redistribution by fluid-involved reactions near the slab surface. Therefore, our model would be enough to support the efficient kilometer-scale water redistribution and does not rely only on limited hydrogen diffusion.

Overall, we have revised the manuscript to better distinguish our new contributions and strengthen the possible development of the hydration-gradient in the slab.

Specific comments

1. P66–: Some sentences read as if water-undersaturated systems are still largely unexplored. This may mislead readers. Please clearly position this study as an extension of the existing limited-water framework.

Response

We thank the reviewer for this important comment. We agree that some sentences in the original manuscript may give the impression that water-undersaturated systems remain largely unexplored, which was not our intention. There are some previous studies trying to study phase relations under fluid-absent condition (e.g., Komabayashi and Omori, 2006) and our previous studies have worked on the water partitioning between NAMs and hydrous minerals at low temperatures under water-undersaturated

condition (Ishii and Ohtani, 2021; Ishii et al., 2025). But they investigated the phase relations of hydrous minerals only at limited experimental *P-T* condition, which restricts the understanding of stability of hydrous minerals under water-undersaturated condition up to the topmost lower mantle.

We accordingly revised the paragraph as follows:

“Previous studies revealed that phase relations of hydrous minerals change with bulk water content. Different types of DHMSs form, or coexist with hydrous fluid or melt in systems with relatively high-water contents^{10,11,15,17}. Hereafter, we define such conditions with a high-water content as water-saturated. However, as dehydration expels most water from hydrous slabs at sub-arc depth, the amount of water reaching the deep mantle is limited³², with a maximum estimated at ~2 wt%^{8,33}. In subducted peridotite and harzburgite in the deep mantle, NAMs coexist with DHMSs in the absence of fluid; we define these conditions with a low-water content as water-undersaturated. The stability of DHMSs under water-undersaturated conditions could differ from that under water-saturated conditions because of their coexistence with NAMs, which allows chemical interactions between NAMs and DHMSs. For example, in the $\text{Mg}_2\text{SiO}_4 + 20 \text{ wt\% H}_2\text{O}$ system, a phase assemblage of PhA + PhD + hydrous fluid forms at 16 GPa and 800 °C, and PhD + brucite + hydrous fluid at 21 GPa and 800 °C¹¹. In contrast, in $\text{Mg}_2\text{SiO}_4 + 2.5\text{--}4.9 \text{ wt\% H}_2\text{O}$ systems, phase assemblages of PhA + clinoenstatite + wadsleyite and sPhB + stishovite + ringwoodite were identified under similar pressure (*P*)-temperature (*T*) conditions, respectively¹²⁻¹⁴. However, these studies¹²⁻¹⁴ investigated the stability of DHMSs only within a limited range of *P-T* conditions, highlighting the need to extend experimental constraints to broader *P-T* regimes.

Systematically determining the stability of DHMSs coexisting with NAMs under water-undersaturated conditions enables a detailed discussion of water distribution in subducted lithosphere with varying Mg/Si ratios³⁴, providing clearer insights into deep-water cycling and dynamic processes. To achieve this, we conducted high *P-T* experiments at pressures ranging from 8 to 28 GPa in MgO-SiO₂-H₂O systems ($\text{Mg}_2\text{SiO}_4 + 2 \text{ wt\% H}_2\text{O}$, Mg/Si=2; $\text{Mg}_{1.3}\text{SiO}_{3.3} + 2 \text{ wt\% H}_2\text{O}$, Mg/Si=1.3), which covers compositional variations of subducting ultramafic layers (Mg/Si ratios of harzburgite and peridotite are ~1.6³⁵ and ~1.3³⁶, respectively) to broaden our understanding towards water cycling under water-undersaturated conditions.”

2. P246–: The meaning of “kinetically dry” is unclear. Under limited-water conditions, low H₂O in olivine can already be explained by equilibrium partitioning into DHMS. If a kinetic argument is intended, please specify which process is rate-limiting. Otherwise, “dry” may be sufficient, because olivine is expected to be dry in equilibrium at low temperatures as shown in this and previous studies.

Response

We thank the reviewer for this careful comment. We agree that the term “kinetically dry” requires clearer definition and may lead to confusion.

Following your suggestion, we have revised the relevant sentence to avoid ambiguity. Specifically, we have removed the expression “kinetically dry” and instead

emphasize that olivine and its high-pressure polymorphs remain effectively dry under cold slab core conditions due to limited H₂O incorporation. Importantly, the phase transformation from olivine to its high-pressure polymorphs is kinetically sluggish due to the low temperature.

The revised sentence now reads:

“Because the descending oceanic lithosphere is thick and a poor thermal conductor, especially under wet conditions⁵², it can remain sufficiently cold, with core temperatures around 500–700 °C, even at the depths of the MTZ^{20,21,24}, leading to kinetically sluggish phase transformation of olivine to its high-pressure polymorphs^{20,21}. As a result, metastable olivine persists in the cold interior of slabs^{20-23,53} (Fig. 4). This region can form even in a wet subducting slab because olivine and its high-pressure polymorphs, which coexist with DHMSs, remain dry enough^{13,14} to drive the olivine transformation³¹ at the cold core temperatures.”

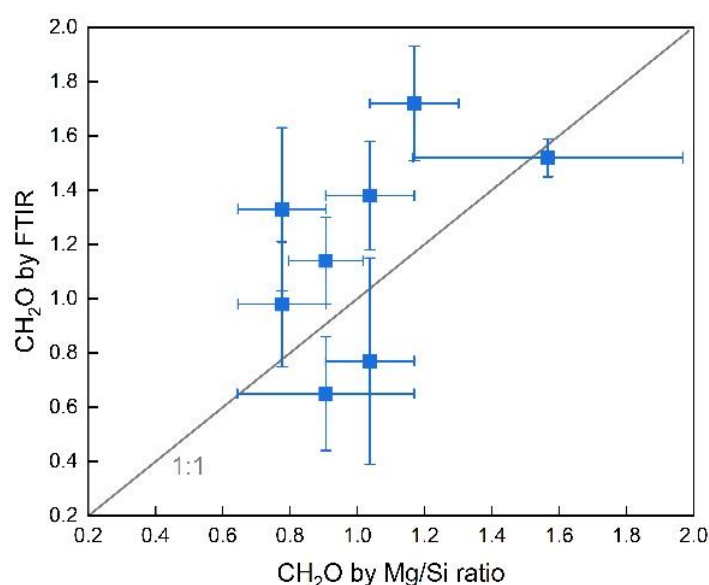
3. Estimating H₂O in fine-grained wadsleyite/ringwoodite from EPMA Mg/Si is an interesting approach. Please provide calculated H₂O contents (with uncertainties) for the relevant runs. For higher-temperature runs where FTIR is feasible, please also report EPMA-based H₂O for the same phases and show consistency with FTIR.

Response

Thank you for the suggestions.

Following this comment, we have calculated the H₂O contents based on EPMA-derived Mg/Si ratios, and the results are now provided in Supplementary Table 6, together with associated uncertainties.

For the runs where FTIR measurements are available, we compared the H₂O contents obtained from FTIR with those estimated from Mg/Si ratios (in chemical formula) in Supplementary Fig. 6. The two approaches show general agreement within analytical uncertainties. This consistency supports the reliability of using Mg/Si ratios as a proxy for estimating H₂O contents in wadsleyite and ringwoodite.



Supplementary Figure 6. Comparison of water contents determined by FTIR (y-axis) and Mg/Si ratios (x-axis) in chemical formula of wadsleyite and ringwoodite.

4. The proposed hydration-gradient story seems to require long-range redistribution across a large fraction of slab thickness. At cold-slab temperatures, it is not obvious that such transport is efficient on geological timescales. Please clarify what transport mechanism is assumed (e.g., solid-state diffusion, grain-boundary transport, transient interconnected fluid films) and provide order-of-magnitude timescale/length-scale estimates with appropriate references. Existing experimental constraints on hydrogen diffusivity in wadsleyite (e.g., Hae et al., 2006) were obtained at much higher temperatures (900–1200 °C) and represent effective diffusivities in polycrystalline aggregates. Extrapolating such Arrhenius relations to cold-slab temperatures implies substantially slower transport, so km-scale redistribution by diffusion alone may be difficult unless an additional fast pathway is demonstrated.

Response

As the reviewer correctly pointed out, hydrogen diffusion from the cold core is not an efficient mechanism for producing a huge water-content gradient within a subducting slab. Previous experimental studies have constrained hydrogen diffusivity in forsterite, wadsleyite, and ringwoodite (Hae et al., 2006; Kudo et al., 2006; Demouchy et al., 2026). These data consistently show that hydrogen mobility is strongly temperature-dependent and becomes significantly reduced under cold-slab conditions. Simple order-of-magnitude estimates therefore suggest that hydrogen diffusion in major NAMs is difficult to permit efficient kilometer-scale redistribution from the cold slab interior to its warmer outer regions over geological timescales. On the other hand, hydrogen can be fully homogenized at grain-size scales (on the order of millimeters to centimeters). In our model, long-range diffusion is not the primary mechanism for generating the suggested water-content gradient. Instead, the hydration–dehydration model we propose arises from short-range redistribution of hydrogen between NAMs and coexisting hydrous minerals, combined with transport by fluids or hydrous melts released just after the complete dehydration of hydrous phases in the warmer portions of the hydrated region. These mechanisms are fundamentally different from long-range diffusion and is consistent with both experimental constraints and geophysical observations. We describe this process in detail below.

During the review process, we also recognized that the original version of Fig. 4 did not accurately reflect these mechanisms. We have revised Fig. 4 to reflect our intention. Below, we outline the assumptions and processes used to construct the revised figure.

An essential assumption underlying the revised Fig. 4 is that the subducting oceanic lithosphere undergoes deep hydration down to the cold core at shallow depths. This is consistent with seismological evidence of bending-fault hydration and hydrated mantle plumes supplying water to the slab mantle (Peacock, 2001; Seno and Yamasaki, 1996; Hirano et al. 2006; Ranero et al. 2003; Cai et al., 2018). Detailed processes are summarized in Ohtani and Ishii (2024). During subduction, these shallow hydrous

minerals (e.g., serpentine) progressively transform into dense hydrous magnesium silicates (DHMS), such as phase A. Consequently, water is stored in a combination of NAMs and DHMSs down to the 410-km discontinuity (Komabayashi et al., *Phys. Earth Planet. Inter.* 2005; Komabayashi and Omori, *Phys. Earth Planet. Inter.* 2006).

Above 410 km depths, within the cold core, dry olivine coexists with hydrous phases A or E, which retain most of the slab-bound water. Toward the slab surface, rising temperatures would stabilize slightly hydrated olivine together with the hydrous phases, as shown in our results and recent experimental constraints (Ishii and Ohtani, *Nat. Geosci.* 2021). Although the temperature range of the gradual hydration due to dehydration of hydrous phase A or E seems narrower than those of wadsleyite and ringwoodite, the water content of olivine would gradually increase with temperature and reach a maximum near the dehydration temperatures of phases A or E (900-1200 °C depending on depth). Thus, below these dehydration temperatures, the bulk water remains partitioned between olivine and the DHMSs. Above the dehydration temperatures, i.e., near the surface of the slab, water is stored mainly in olivine, and excess water is released as fluid or hydrous melt due to the limited solubility of water in olivine. Smyth et al. (*Geophys. Res. Lett.* 2006) reported that olivine can incorporate up to ~0.9 wt% H₂O at ~1250 °C, beyond which the solubility of olivine diminishes.

Assuming that this maximum water content corresponds to the olivine water content at the dehydration temperature, the peak water content of NAMs in the revised Fig. 4 (above 410 km) likely lies around the slab surface or within the region between the slab surface and the cold core. The precise location depends on the slab thermal structure (e.g., van Keken et al., *Phys. Earth Planet. Inter.* 2008). An older, colder slab would tend to place the gradient closer to the slab surface, whereas a younger, warmer slab would shift the gradient toward the interior between the surface and the cold core. If the slab temperature near the surface (top of the harzburgite layer) is higher than the complete dehydration temperatures of the hydrous phases, water is primarily redistributed by fluids or hydrous melts produced from dehydration of hydrous minerals due to the above-mentioned temperature dependence of water solubility of olivine.

Below 410 km depths, water is redistributed within the hydrated region described above. Thus, water redistribution in the transition zone follows the same basic pattern as above 410 km depths: (1) efficient transport near the slab surface via fluids/melts (2) short-range redistribution within the hydrous interior via solid-state reactions, rather than long-range diffusion. These conditions can make a water-content gradient structure in the transition zone.

Within the cold core, dry olivine persists because temperatures are insufficient for transformation to wadsleyite or ringwoodite. As temperature increases toward the slab surface, transformed wadsleyite is gradually hydrated through short-range reactions between wadsleyite and DHMSs during the partial dehydration. Approaching the complete dehydration temperatures (Fig. 1), wadsleyite reaches its maximum water content. Near the surface of the slab, hydrous wadsleyite may dehydrate due to reduced solubility when coexisting with fluid or hydrous melt, depending on thermal structure of the slab. This process naturally produces a maximum in water content between the

slab surface and the cold core. Ringwoodite behaves analogously. In the lower mantle, bridgmanite could control slab water storage, following the same mechanism.

In summary, the water gradient in the transition zone arises from (1) the water budget inherited from the depth shallower than 410 km, (2) short-range redistribution associated with mineral transformations within the slab interior, and (3) efficient fluid/melt-mediated transport near the slab surface, combined with the slab thermal structure. In the revised Fig. 4, we drew a possible water gradient structure where a water-content peak in NAMs locates within the region between the surface and the cold core in the transition zone to emphasize our concept of the model. To clarify this conceptual model, we have made explanatory paragraph to the main text and supplementary information.

The main text: “Changes in the hydration state of NAMs are coupled with the progressive dehydration of DHMSs, their reactions with NAMs, and the partitioning of water between NAMs and hydrous fluid/melt, all of which are critically controlled by temperature. At relatively low temperatures below 900 °C, typical of conditions in the slab core, water is primarily accommodated in DHMSs, leaving forsterite, wadsleyite, and ringwoodite that coexist with DHMSs nearly dry^{13,14}(Fig. 4). Rising temperature enhances reactions between DHMSs and NAMs, leading to the progressive incorporation of water into NAMs (Fig. 4). This results in the formation of NAMs with a maximum water content, determined by the bulk water content, at the thermal boundary where the coexisting hydrous minerals disappear. Because wadsleyite and ringwoodite have a much higher water storage capacity than other NAMs such as forsterite and bridgmanite¹⁵⁻¹⁷, the progressive dehydration of hydrous minerals coupled with the continuous hydration of coexisting wadsleyite and ringwoodite produces pronounced water-content variations in the subducting slab under MTZ conditions (Fig. 4). We note that, although the progressive dehydration in the MTZ is analogous to dehydration of hydrous minerals (e.g., phengite) at sub-arc depth that explains arc magma generation⁴³, no fluid/melt will be generated in the MTZ progressive dehydration of DHMSs due to the high-water storage capacity of wadsleyite and ringwoodite as mentioned above. Such solid-state reactions and mineral transformation can drive short-range redistribution of hydrogen between DHMSs and NAMs in the slab interior (Fig. 4).

In contrast, hydrous minerals coexisting with forsterite and bridgmanite tend to decompose more abruptly with increasing temperature. In the olivine region above 410 km depth, the complete dehydration temperature could be near the slab surface when considering its thermal structure⁴⁴ (Fig. 4). In the bridgmanite region below 660 km depth, the complete dehydration of DHMSs would occur at a relatively deeper region between the slab surface and the core due to the stability of DHMSs (Fig. 1) and thermal structure⁴⁴.

Near the slab surface in the MTZ, where temperatures can be higher than the complete dehydration threshold of DHMSs, water solubility in NAMs decreases as a result of hydrous fluid or melt formation (Fig. 4). This process also naturally produces a maximum in water content of wadsleyite or ringwoodite between the slab surface and the cold core, with the precise location depending on the thermal structure⁴⁴. In these

regions, efficient hydrogen transport is facilitated by water partitioning between NAMs and hydrous fluid or melt (Fig. 4). Consequently, a kilometer-scale water-content gradient may develop in the deep lithospheric slab, when taking into account its hydration state inherited at shallow depths and water redistribution in the slab core (Fig. 4) (Supplementary Note 2). ”

Supplementary Note 2: “Supplementary Note 2: Water-content gradient in the subducting slab

Water initially present in the oceanic plate originates from hydration of slab prior to subduction. The seismological evidence indicates that subducting oceanic lithosphere undergoes extensive hydration even down to the cold core or lower portion of slab via bending-fault¹⁹⁻²³ or interactions with hydrated mantle plume^{24,25}. Upon subduction, hydrous minerals (e.g., serpentine) formed at shallow depths progressively transform into DHMSs (e.g., PhA) as the slab descends to the 410-km discontinuity^{13,17,18} when the hydrated lithosphere remains below “choke point”²⁶. The water stored in these DHMSs, in combination with that in NAMs (e.g., olivine), constitutes the primary water budget for subducting lithosphere below 410 km depth.

In the cold interior of a slab, NAMs remain dry, and water is mainly accommodated in hydrous minerals. Within the stability of hydrous minerals, water remained partitioned between hydrous minerals and NAMs. The interactions between hydrous minerals and NAMs with increasing temperature results in progressive hydration of coexisting NAMs and diminishing amounts of DMHSs. Hence, the water-content gradient within the hydrated interior results from solid-state reactions between DHMSs and NAMs via short-range redistribution of hydrogen (Fig. 4).

As temperatures approach the complete dehydration temperature near the slab surface (at the top of harzburgitic layer and the bottom of peridotitic layer), the water contents in NAMs peak. This maximum water content in NAMs can occur near the surface or at the region between the slab surface and the cold core. The precise location depends on the thermal structure. An older, colder slab would tend to place the gradient closer to the slab surface, whereas a younger, warmer slab would shift the gradient toward the interior between the surface and the cold²⁷. If the slab temperature near the surface is above the complete dehydration temperature, water is partitioned between hydrous fluid/melt and NAMs. This water redistribution is enhanced by the transport of hydrous fluid or melt. Thus, the water-content gradient in the vicinity of slab surface is mainly mediated via hydrous fluid or melt (Fig. 4).

We note that the hydrogen diffusion in major NAMs, as determined by previous studies^{27,28}, is difficult to permit efficient kilometer-scale redistribution from the cold slab interior to its warmer outer regions over geological timescales. On the other hand, hydrogen can be fully homogenized at grain-size scale (on the order of millimeters to centimeters). Here we emphasize that our model does not rely on long-range hydrogen diffusion responsible for generating the suggested gradient. Instead, the hydration-dehydration model proposed in this study arises from: 1) the water budget inherited from the initial hydration nature of descending plate shallower than 410 km depths; 2) short-range redistribution relevant to mineral transformation and solid-state reactions

within the hydrated interior; and 3) efficient fluid/melt-mediated transport near the slab surface, alongside the slab thermal structure (Fig. 4).

Reviewer #1 (Remarks to the Author):

I consider that the authors have answered all comments.
The manuscript can be published without further corrections.

Best regards.

Response

We sincerely thank the reviewer for the comments.

Reviewer #2 (Remarks to the Author):

I believe my comments have been adequately addressed, and the manuscript is now suitable for publication.

Response

We sincerely thanks for reviewer's suggestions during revision.

Reviewer #3 (Remarks to the Author):

I appreciate the substantial effort the authors have made in revising the manuscript.

Overall, I consider that this phase-equilibrium study provides useful constraints over a broad P–T range. Although the compositions are simpler than natural systems, the phase relations involving DHMSs and NAMs are clearly demonstrated for different bulk compositions. The revision has made the discussion more cautious and scientifically solid, but in my view this also makes the broader impact appear more limited. I therefore remain uncertain whether the broader interpretive framework is sufficiently distinct from previous studies for this journal.

Response

We thank the reviewer for the constructive comments and appreciate the reviewer's recognition that our phase-equilibrium experiments provide useful constraints on DHMS–NAM phase relations over a broad P–T range and for different bulk compositions, and have a solid discussion.

We acknowledge the reviewer's concern regarding the distinctiveness of the broader interpretive framework relative to previous studies. We have substantially revised the manuscript to more clearly define the scope and conceptual advance of this study. Detailed responses to these issues are provided below.

The revised manuscript also raises an additional question regarding the newly proposed model. The authors state that hydrogen can be fully homogenized at grain-size scales (on the order of millimeters to centimeters), while long-range redistribution is limited. This itself suggests that hydrogen mobility may be significant at local scales under the

relevant coexistence conditions. Equilibrium partitioning does not imply absence of hydrogen mobility; rather, it reflects balanced exchange fluxes between coexisting phases. Therefore, even if bulk H₂O contents in olivine remain low, hydrogen transfer between hydrous phases and adjacent NAMs may still influence local reaction environments, especially at grain boundaries or phase interfaces where transformation is initiated. This may complicate the direct application of previously reported dry olivine transformation kinetics to the present coexistence conditions.

This issue appears particularly important because the applicability of dry olivine transformation kinetics under hydrous phase-bearing coexistence conditions forms a central part of the conceptual framework proposed by this research line since 2022 (Nature Geoscience). However, subsequent studies seem to have focused mainly on partitioning and phase relations, and direct support for this key kinetic assumption still appears limited. Therefore, I am uncertain that this aspect constitutes a clearly distinct conceptual advance.

Response

We agree that equilibrium partitioning between DHMSs and NAMs requires a certain degree of hydrogen mobility over grain-scale distances. However, we emphasize that hydrogen mobility does not necessarily imply olivine hydration, because the thermodynamic driving force strongly favours hydrogen incorporation into DHMSs rather than into NAMs.

A key experimental result supporting this point comes from Ishii and Ohtani Nat. Geosci. (2021). In their study, even when hydrous olivine was used as the starting material, forsterite coexisting with hydrous phase A became effectively anhydrous (<1 ppm H₂O). This is consistent with the reaction:

$$5\text{Mg}_2\text{SiO}_4 \text{ forsterite} + 3\text{H}_2\text{O} \rightarrow \text{Mg}_7\text{Si}_2\text{O}_8(\text{OH})_6 \text{ Phase A} + 3\text{MgSiO}_3 \text{ pyroxene}$$
which demonstrates that DHMSs act as a strong sink for hydrogen, efficiently extracting hydrogen from olivine. Thus, even if transient hydrogen exchange occurs at grain boundaries, the net flux is directed from NAMs to DHMSs. As a result, forsterite coexisting with DHMSs remains thermodynamically dry under the expected cold slab core temperatures.

This point directly addresses the reviewer's concern: although local hydrogen mobility can exist, it would not lead to local hydration of olivine, because the hydrogen chemical potential is buffered by DHMSs. Under these conditions, dry olivine transformation kinetics remain the appropriate first-order approximation.

We have clarified this thermodynamic constraint in the Supplementary Note 2 and now explicitly state that the presence of DHMSs enforces a dry transformation regime in the slab interior, even under hydrous phase-bearing coexistence conditions. We also acknowledge that future kinetic experiments under controlled water-undersaturated conditions would be valuable for further quantifying this behaviour. We have added the following text in the Supplementary Note 2 and "Implications for earthquake genesis, phase transformation, and slab dynamics" Section in the main text

Supplementary Note 2: Water-content gradient in the subducting slab]“We also emphasize that limited hydrogen mobility between NAMs and DHMSs does not imply local hydration of NAMs, nor does it promote metastable olivine transformation through locally hydrated reaction zones. This is because the thermodynamic driving force overwhelmingly favours hydrogen incorporation into DHMSs rather than into NAMs. Indeed, Ishii and Ohtani (2021)²⁸ demonstrated that even when hydrous forsterite was used as the starting material, forsterite coexisting with Phase A became anhydrous (<1 ppm H₂O). This is consistent with the reaction:



which shows that DHMSs act as a strong sink for hydrogen, efficiently extracting hydrogen from forsterite. Therefore, even transient hydrogen exchange at grain boundaries does not lead to meaningful hydration of NAMs through DHMS, and olivine remains effectively dry at cold core temperatures. Several previous studies have specifically investigated the kinetics of phase transformation using pre-hydrated olivine with homogeneous hydrogen distribution²⁹⁻³⁰, which differs fundamentally from the transformation kinetics in hydrous-phase-bearing coexistence systems investigated here and water-partitioning experiments²⁸. Future kinetic experiments under controlled water-undersaturated and hydrous-phase-bearing coexistence conditions would be valuable for further quantifying this behaviour.”

Line 335-352: [Implications for earthquake genesis, phase transformation, and slab dynamics]“This region can form even in the core of an wet subducting slab under water-undersaturated conditions because olivine and its high-pressure polymorphs, which coexist with DHMSs, remain comparatively hydrogen-poor. With increasing depth and excess pressure, metastable olivine wedge eventually disappears at the bottom of the MTZ as the kinetic barrier is overcome (Fig. 4). This process may cause grain-size reduction in the cold core²⁹, resulting in a rheologically weak region that could promote slab deformation and formation of a stagnant slab above the 660-km discontinuity. In contrast, at the outer part of the metastable olivine wedge, higher temperatures promote progressive dehydration of DHMSs, consequential hydration of coexisting NAMs, and efficient hydrogen redistribution. Due to the warmer conditions and enhanced water incorporation, olivine transforms to hydrous wadsleyite or ringwoodite. As slab temperature further increases toward the slab surface owing to heating from the surrounding mantle, water incorporation into hydrous fluid or melt and a water-content gradient formed by hydrated wadsleyite/ringwoodite could exist (Fig. 4).”

The revised manuscript provides a more convincing and logically coherent explanation for slab-scale water redistribution than the original version. In particular, fluid/melt transport associated with dehydration is physically more reasonable than relying on long-range hydrogen diffusion. However, this improvement also makes the proposed model closer to previously discussed slab dehydration and fluid-migration frameworks.

Thus, while the revision strengthens the internal logic of the model, it also makes the degree of novelty appear more limited.

Response

We would like to clarify how our model differs fundamentally from the previously discussed slab dehydration and fluid-migration frameworks.

The “previously discussed” models referred to in the literature generally involve direct breakdown of hydrous minerals and subsequent fluid/melt migration, either in the shallow mantle (e.g., Schmidt & Poli, 1998) or within the transition zone (e.g., Shirey et al., 2021). These models typically assume that dehydration is controlled primarily by the stability limits of individual hydrous phases, and that the released fluid/melt migrates independently of the hydration state of coexisting NAMs.

In contrast, the novelty of our study lies in demonstrating, through systematic high-pressure experiments, that hydrogen redistribution in the slab is modulated by mineral coexistence, water partitioning, and thermal structure, rather than by hydrous-phase breakdown alone. Our results reveal a spatially heterogeneous hydration structure within the slab, in which the hydration state of NAMs and the stability of DHMSs jointly determine when and where hydrous fluid/melt can form. This coexistence-controlled redistribution mechanism is not captured by previous dehydration/fluid-migration models.

We have revised the manuscript to more clearly distinguish our model from previous general dehydration/fluid-migration models and to emphasize that our advance lies primarily in the experimental constraints and shows a unified picture of slab-scale water redistribution under transition zone conditions.

We have added the following statement in the “Deep water exchange between hydrous minerals, NAMs, and hydrous fluid/melt” Section as follows:

“Unlike previous dehydration models that primarily focused on direct breakdown of individual hydrous minerals and subsequent fluid/melt migration independently of hydration state of coexisting NAMs in the shallow mantle or transition zone^{5,27,28,43}, the occurrence of hydrous fluid/melt in the warmer part of slab is strongly modulated by the hydration state of coexisting NAMs and their water partitioning.”

More broadly, the interpretation still appears to be built largely on concepts that have already been established in previous studies: strong H₂O partitioning into NAMS, dry olivine in the cold slab interior, deep-focus earthquake mechanisms, and water redistribution related to dehydration reactions. In the rebuttal letter, the authors highlight temperature-dependent H₂O partitioning between NAMs and coexisting hydrous phases as an important new element of the revised model. However, similar discussions of increasing H₂O contents in NAMs with temperature appear in the recent 2025 study (EPSL).

Response

In the recent 2025 EPSL paper, the authors conducted water-partitioning experiments between wadsleyite and PhA, and between ringwoodite and sPhB, at 14–16 GPa and 800 °C, and at 21 GPa and 800–900 °C, respectively (see their Table 1 for the experimental conditions). Based on these low-temperature partitioning experiments

together with phase relations in MgO-SiO₂-H₂O systems, they indirectly proposed that water contents in NAMs coexisting with hydrous minerals increase with temperature because the stability field of ringwoodite + sPhB + stishovite is divariant (see Fig. 6 of the paper).

We agree that the concept of temperature-dependent hydration of NAMs was already anticipated in 2025 EPSL paper. However, direct experimental constraints on how NAM hydration and DHMS dehydration evolve continuously with temperature and changing phase assemblages under water-undersaturated transition zone conditions remained limited, particularly between the low-temperature partitioning experiments and the higher-temperature conditions approaching disappearance of hydrous minerals. Importantly, although their results suggest a positive temperature dependence of water contents in NAMs when coexisting with hydrous minerals, other previous studies have also predicted that the water contents of NAMs remain essentially constant with temperature under similar coexistence conditions (e.g., Ohtani et al., *Phys. Chem. Minerals* **27**, 533-544, 2000; Demouchy et al., *Am. Mineral.* **90**, 1084-1091, 2005). Therefore, direct experimental constraints are still required to determine which of these contrasting predictions reflects the actual behaviour of NAMs.

The present study directly demonstrates progressive partial dehydration of DHMSs coupled with gradual hydration of coexisting NAMs as phase assemblages evolve with increasing temperature, thereby ruling out the models for constant water-contents of NAMs coexisting with hydrous minerals. Hydrogen redistribution is therefore experimentally constrained as a continuous process controlled by mineral coexistence and slab thermal structure, rather than being inferred primarily from partition coefficients measured under relatively restricted low-temperature conditions. Moreover, we measured the water content in wadsleyite coexisting with sPhB at 18 GPa and 1200 °C to be ~1.7 wt%, substantially higher than values reported at lower temperatures (e.g., ~244 ppm at 16 GPa and 800 °C in the EPSL paper).

In addition, we conducted a series of high-pressure experiments using highly hydrated wadsleyite (~2.0 wt% H₂O) and ringwoodite (~1.6 wt% H₂O) at significantly higher temperatures (e.g., 1000–1300 °C) than those explored in the EPSL paper (800 °C). These experiments revealed the decomposition of the highly hydrated NAMs to hydrous minerals and less-hydrous NAMs, indicating stabilization of corresponding DHMSs and progressive decreases in water contents of NAMs toward lower temperatures. These results provide direct experimental support for the proposed temperature-dependent dehydration–hydration framework and further constrain how water redistribution evolves across transition-zone conditions.

This study further evaluates the effects of Mg/Si ratio, one of the most important compositional parameters in hydrous systems, on DHMS stability, NAM hydration, and water redistribution pathways, thereby providing additional constraints on spatially heterogeneous water distribution within subducting slabs.

To clarify our contribution, we added context in “Introduction” and “Comparison with previous studies and compositional dependence on the stability of DHMSs” Section as follows:

Lines 61-75: [Introduction] “Recent studies examined water partitioning between NAMs and DHMSs under relatively low-temperature conditions, including forsterite-PhA at 10 GPa and 800 °C¹³, wadsleyite-PhA at 12 GPa and 800–900 °C¹³ and at 14–16 GPa and 800 °C¹⁴, as well as ringwoodite-sPhB at 21 GPa and 800–900 °C¹⁴. They have found strong water partitioning into DHMSs, leaving NAMs nearly dry^{13,14}. The authors further predicted from thermodynamic viewpoints that ringwoodite may become gradually hydrated with increasing temperature due to the partial dehydration of sPhB¹⁴. However, there is currently no direct experimental evidence supporting gradual temperature-dependent hydration of NAMs. We note that other earlier studies reported water contents in NAMs coexisting with DHMSs remain essentially constant with increasing temperatures^{15,33}. Thus, the hydration state of a subducting slab can be more complicated than previously considered. The stability of hydrous minerals is especially critical for understanding the formation of metastable olivine wedges, slab dynamics, slab hydration states, and the origin of deep earthquakes.”

Lines 91-95: “However, these studies¹²⁻¹⁴ investigated the stability of DHMSs only within a limited range of P-T and compositional conditions, and the proposed partial dehydration was inferred on restricted data. This limitation highlights the need to extend experimental constraints to broader P–T regimes.”

Lines 285-297: [Comparison with previous studies and compositional dependence on the stability of DHMSs] “Distinguished from previous studies on MgO-SiO₂-H₂O systems, we have constructed internally consistent phase diagrams at a lower bulk water content (2 wt %), allowing detailed discussion of water distribution within a subducting slab over a broad range of P-T conditions and geological settings, extending into the topmost lower mantle. Importantly, our experiments provide direct evidence for depth- and temperature-dependent dehydration behaviours of hydrous minerals under water-undersaturated conditions, accompanied by evolving phase assemblages, an aspect that has received limited attention in previous works. Thus, we experimentally demonstrate partial dehydration of DHMSs accompanied by progressive hydration of coexisting NAMs with temperature in MTZ, providing constraints on water distribution within slabs and supporting the previously proposed temperature-related dehydration model¹⁴. In addition, the effect of Mg/Si ratios was evaluated, offering further insights into the heterogeneous distribution and transport of water within subducting slabs (see below).”