

Formation of the 15 Å phase as the most expanded hydrated mineral in cold subduction zone

Corresponding Author: Professor Yongjae Lee

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)

This contribution addresses the experimental discovery of a new hydrous phase — a super-hydrated 15 Å phase — formed from talc under high-pressure, very low-temperature conditions in the presence of an alkaline fluid modeled by the addition of NaHCO₃.

The results have potential applications in subduction zone environments, provided there is an excess fluid at such low-temperature conditions, suggesting dehydration occurs elsewhere to promote hydration in a potential talc-bearing layer or lithology along the prograde P-T path typical of subducting slabs. Although this is not immediately evident, it should not be considered a major obstacle at this stage, given the discovery of a new hydrous phase.

The results are robust, supported by molecular dynamics modeling, and I believe this contribution merits publication, after major revisions (see criticism below).

The discussion on carbonates and carbon cycling is completely out of context. Observing the formation of a carbonate (magnesite) from hydrous phases (talc) at high CO₂ activities is not new, with basic concepts dating back to Greenwood (1967). The section titled "New insights into the deep carbon cycle from subducting talc" should be entirely omitted, and Figure 3 simplified accordingly.

A secondary issue concerns the use of the term "hydration and carbonation breakdown." This wording is misleading, as any reaction can be considered a "breakdown" of a phase. Additionally, any reaction involving a complex fluid (Na-C-O-H species + solutes) is a continuous reaction, where the appearance/disappearance of a solid is also influenced by the bulk and/or internal/external buffering of fluid composition. This is a lengthy discussion beyond the scope of this work.

Reaction (2) is merely a mass balance, but keep in mind that a C-O-H fluid will form. The description and discussion of fluid speciation are naive and should be improved.

Reviewer #2

(Remarks to the Author)

This paper describes the formation (and decomposition) condition of a 15-Angstrom-layered hydrous silicate structure from talc and H₂O. Its formation only proceeded in a carbonate solution and not in pure water or NaCl solution. The described results of DAC experiments and molecular dynamics simulation in combination may have implications for understanding water transport systematics within Earth. The paper is worth considering for publication in Nature Communication only after several major issues are correctly answered, which are listed below.

(Major issues)

Page 7, line 165: The linear compressibility of a crystal structure is only meaningful when there is no chemical reaction involving the crystal. Thus, the author should demonstrate that there is no water in/out exchange reaction during the compression and decompression of the relevant crystal structure. Is that true? In addition, why is the bulk modulus not calculated, rather than the linear compressibility, when the compressibility of a mineral is compared with the others? It seems a tricky discussion.

Page 8, line 176: Numbers of moles of Mg^{2+} are not equal in this reaction formula.

Page 9, from line 202, Discussion:

The 15-Angstrom structure can only form when talc is directly contacting with enough amount of fluid water. On the other hand, as the slabs are subducting, the pore pressure increases, and the remaining pore fluid in the slabs should be squeezed out and drastically decreased. The author needs a much more careful discussion of this issue to evaluate the water mass carried by the 15-Angstrom structure.

Page 11, starting from line 257: If the dehydration of the 15-Angstrom structure indeed proceeds at the described depth, it should be observable by seismic and/or volcanological studies of the subduction areas. Apparently, a more critical discussion is needed on how to find and evaluate such a process occurring in nature.

(Minor comment)

Three significant digits of water/carbon masses in the discussion are not very meaningful. Two digits should be enough.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

apologies, but i feel i will not have the time for a careful reading of the manuscript.

However, I went through the new version and I think the authors significantly improved the manuscript, first of all omitting the discussion on the "carbon cycle", very loosely related to the experimental results. Furthermore the discussion/speculation on H_2O is now more informative.

I hope this helps somehow.

Reviewer #2

(Remarks to the Author)

Now I found that the major issues had been correctly answered.

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

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

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

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

Response to Reviewers

Dear Reviewers,

We appreciate all of the insightful comments and constructive suggestions for our manuscript to Nature Communications (NCOMMS-24-38789-T) entitled “Formation of the 15 Å phase as the most expanded hydrated mineral in cold subduction zone”. Please find attached our revised version of the paper (all the changes made in the revised manuscript **are marked in red**). Our point-by-point responses to all the comments and criticisms are summarized below (the reviewers’ comments are marked in blue).

Reviewer #1 (Remarks to the Author):

This contribution addresses the experimental discovery of a new hydrous phase — a super-hydrated 15 Å phase — formed from talc under high-pressure, very low-temperature conditions in the presence of an alkaline fluid modeled by the addition of NaHCO₃.

The results have potential applications in subduction zone environments, provided there is an excess fluid at such low-temperature conditions, suggesting dehydration occurs elsewhere to promote hydration in a potential talc-bearing layer or lithology along the prograde P-T path typical of subducting slabs. Although this is not immediately evident, it should not be considered a major obstacle at this stage, given the discovery of a new hydrous phase.

The results are robust, supported by molecular dynamics modeling, and I believe this contribution merits publication, after major revisions (see criticism below).

Reply: We appreciate the reviewer #1 for the overall positive appraisal on our work.

The discussion on carbonates and carbon cycling is completely out of context. Observing the formation of a carbonate (magnesite) from hydrous phases (talc) at high CO₂ activities is not new, with basic concepts dating back to Greenwood (1967). The section titled "New insights into the deep carbon cycle from subducting talc" should be entirely omitted, and Figure 3 simplified accordingly.

Reply: As suggested, we have deleted the carbonate section and simplified Figure 3 and Table 1 (plus Supplementary Table S5) accordingly.

A secondary issue concerns the use of the term "hydration and carbonation breakdown." This wording is misleading, as any reaction can be considered a "breakdown" of a phase. Additionally, any reaction involving a complex fluid (Na-C-O-H species + solutes) is a continuous reaction, where the appearance/disappearance of a solid is also influenced by the

bulk and/or internal/external buffering of fluid composition. This is a lengthy discussion beyond the scope of this work.

Reply: As suggested, we have replaced the term “hydration and carbonation breakdown” with “hydration reaction” (lines 101 and 174). We appreciate the comments concerning the reaction pathway involving complex fluid which we will consider in our future studies.

Reaction (2) is merely a mass balance, but keep in mind that a C-O-H fluid will form. The description and discussion of fluid speciation are naive and should be improved.

Reply: We agree to the reviewer #1's point and have added the following sentences with relevant references (lines 191-194).

“Although most carbon-bearing geological fluids in the Earth's mantle (at temperatures above 400 °C) exist as the C-O-H system, including species such as H₂O, CO₂, CH₄, H₂, CO, O₂, and C₂H₆ (ref. 37,38), the reaction conditions (2) in our study would prefer the formation of magnesite (at temperatures below 400 °C), rather than the complex evolution of the fluid system itself.”

Reviewer #2 (Remarks to the Author):

This paper describes the formation (and decomposition) condition of a 15-Angstrom-layered hydrous silicate structure from talc and H₂O. Its formation only proceeded in a carbonate solution and not in pure water or NaCl solution. The described results of DAC experiments and molecular dynamics simulation in combination may have implications for understanding water transport systematics within Earth. The paper is worth considering for publication in Nature Communication only after several major issues are correctly answered, which are listed below.

Reply: We appreciate the reviewer #2 for the overall positive appraisal on our work.

(Major issues)

Page 7, line 165: The linear compressibility of a crystal structure is only meaningful when there is no chemical reaction involving the crystal. Thus, the author should demonstrate that there is no water in/out exchange reaction during the compression and decompression of the relevant crystal structure. Is that true? In addition, why is the bulk modulus not calculated, rather than the linear compressibility, when the compressibility of a mineral is compared with the others? It seems a tricky discussion.

Reply: We confirm that there was no water in/out exchange reaction during the isothermal compression experiment on the quenched 15 Å phase. We have calculated linear compressibility, rather than bulk modulus, as the quality of the XRD data measured during the

isothermal compression was not sufficient to allow whole profile fitting to derive volume data. Therefore, we have fitted individual (*00l*) peaks to estimate axial compressibility across the layers, which was then compared to those of the original talc and its 10 Å phase.

Page 8, line 176: Numbers of moles of Mg²⁺ are not equal in this reaction formula.

Reply: We have revised the reaction formula (1) assuming the mass balance into account (lines 178-179).

Page 9, from line 202, Discussion:

The 15-Angstrom structure can only form when talc is directly contacting with enough amount of fluid water. On the other hand, as the slabs are subducting, the pore pressure increases, and the remaining pore fluid in the slabs should be squeezed out and drastically decreased. The author needs a much more careful discussion of this issue to evaluate the water mass carried by the 15-Angstrom structure.

Reply: To address the issue of the amount of fluid in the subducting slab, we have added a new paragraph with references to showcase various fluid migration pathways in subduction zones that are relevant to the formation of the super-hydrated 15 Å phase (lines 246-263).

Page 11, starting from line 257: If the dehydration of the 15-Angstrom structure indeed proceeds at the described depth, it should be observable by seismic and/or volcanological studies of the subduction areas. Apparently, a more critical discussion is needed on how to find and evaluate such a process occurring in nature.

Reply: We appreciate this insightful suggestion by the reviewer #2 as we have found the correlation between the stability of the super-hydrated 15 Å phase and seismicity and volcanism in the subduction system we modeled in our experimental study. We have added a new paragraph with relevant references plus a new Figure 4 to correlate our results to the distribution of volcanoes as well as the earthquake frequency using available data for the South Mariana subduction systems (lines 284-309).

(Minor comment)

Three significant digits of water/carbon masses in the discussion are not very meaningful. Two digits should be enough.

Reply: As suggested, we have corrected the reported values to two significant digits in the manuscript (lines 269-282). Accordingly, we have also modified Figure 3 and Table 1.