Referee comment on Chen et al, “Hydrogen solubility of stishovite provides insights into water transportation to deep Earth.”

General Comment

The Authors present an empirical equation about the water solubility in Al-bearing stishovite that is based on literature data provided by experimental studies. The equation is used to model the water concentrations of Stv and bulk MORB crust along a subduction geotherm, showing that the water capacity increases till the base of the transition zone and then sharply declines.

There are a few important issues (detailed below) that need to be addressed. The most important ones are an insufficient discussion on the derivation of the equation and its limits, and the missing discussion on the presence of molecular water in stishovite.

The manuscript is well-structured and mostly clearly understandable, although it appears a bit superficial. This contradicts the authors' claim to present a “comprehensive review”. While indeed many important papers are cited, I feel that the work *with* the papers is rather shallow. A comprehensive review needs a more in-depth analysis and more critical data assessment.

The new aspect of the manuscript is the abovementioned equation. Similar models exist (e.g. work of Lin and coworkers cited in the manuscript), and I am unsure if the presented work provides significant new insights.

I think a more thorough revision is required.

Kind regards

Technical and specific comments:

Chapter 1

Line 22 – “Explicitly and implicitly”. While the meaning is explained, these terms are not usually used in the field (and not further in the manuscript) and remain somewhat ambiguous. I would suggest finding a different phrasing or description, e.g., molecular and structurally bound water.

Line 34 - “Although….” sentence needs references.
Line 61 – “preservation conditions of Stishovite are very harsch …”, the word “harsh” is a bit odd and not very descriptive. I suggest rephrasing it to something like “Stv is unstable and easily transforms to lower pressure SiO_2 polymorphs.”

Figure 1 - While cited correctly, this figure is the original figure of Litasov & Ohtani (2007), simply cropped to smaller dimensions. It’s not “after”, which would imply redrawing or significant modifications. I don’t think that is okay, as it implies own artwork.

Chapter 3 – Water solubility and incorporation mechanisms in stishovite.

Generally, for a review, I found this section very superficial. A more in-depth literature study would be beneficial.

Section 3.1

Line 90 – "As shown in Table 1, …". Table 1 lists literature values on synthesis conditions and water contents. Other than stated, it is not directly apparent from the table that correlations exist between water concentration and experimental and chemical parameters. This needs to be elaborated in more detail and displayed in figures (as it has been shown for Al and H_2O concentrations in Fig 5). I don't find Fig 4 very helpful, as it compresses (at least) 4 variables into one plot.

Line 91 – "…differ by more than one order of magnitude". Kueter et al 2023 (CMP) discuss discrepancies in the water content between Al-free and Al-bearing Stv, as well as for Al-free Stv synthesized in DAC and Multi Anvil setups. This review should note & discuss this as well.

Table 1 – The table would benefit from additional information about the synthesis method (e.g., Multi Anvil, Diamond anvil cell). Please also specify "other methods" annotated with an asterisk. Please add the most recent work as well.

Section 3.2

This section is about the hydrogen incorporation mechanism in Stv. Two mechanisms are mentioned, i.e., hydrogarnet and Al-H substitutions. Recent studies also found evidence for molecular water (H_2O) in the stishovite (Lin et al, 2020 & 2022; Kueter et al 2023; Li et al 2023). I think the Authors briefly mention H_2O as "explicit water" in the introduction (if I understand this correctly), but it's not further discussed. The apparent presence of molecular water is important and should be discussed as well. Particularly the Li et al 2023 study is interesting, as it suggests that water is not homogeneously distributed but aligns in one-dimensional SiO_2-H2O superclusters.

Chapter 4

L 117 – "Numerous..". I don't think the sentence is necessary. It contains no information.

L123 – "melt proportions". Please give a few details about Litasov experiments. What kind of melt?

Section 4.1

The effect of water solubility of Stv to CaCl2-structured Stv should be discussed here as well (e.g. Ishii et al 2022). The DAC experiments and models of Lin (2020, 2022) should also be considered.

Section 4.2.

As mentioned above, Al content seems to have a positive correlation with H_2O content in the 100 to 1000th ppm level. However, Al-free Stv incorporates wt% amounts of H_2O; something that's not readily seen with Al-bearing Stv. The manuscript would benefit from discussing this a bit more. See, for example, Kueter et al 2023.

Line 144 – "Statistically compiling…" I don't understand the wording. Figure 5 does not show any statistics or statistical breakdown of the data. It's a summary plot of available data. Also, please cite the literature shown in Fig 5. I would recommend being more quantitative as well: Maybe you can provide a regression of the data and plot it in Fig 5 (similar to what Litasov et al. 2007 did).

Line 167 onward - The fO2 part of section 4.2 is too vague and qualitative. There is no real information gain from it. I would recommend to discussing it in more detail, or (less recommended) omitting it.

Chapter 5 – Water solubility…

The following is, in my opinion, the most important issue that has to be addressed:
This chapter is the core of the study and subsequent models rely on equation 2 given in it. Consequently, Eqn 2 needs to be carefully derived and explained:

It is important to

- discuss the dismissal and use of literature experimental data in more detail
- show a plot that displays the data and the fits from which Eqn 2 has been derived
- make a thorough error/uncertainty analysis of the fit
- discuss the obtained fitting parameters (are they realistic, do they compare with literature?)
- discuss limits of the fitting method (e.g. boundaries, uncertainties)

I further would recommend providing at least one example calculation (main text or appendix). This helps the reader tremendously to comprehend and reproduce the data & models. Also, please provide the exact literature data in the appendix that you used for the fitting.

Since the study focuses on Al-Stv only, it is ok to omit the high H_2O experiments of Al-free Stv, but it would be good to mention this in the text and give reasons for it.

Last but not least: Eqn 2 has a typo ("epx", same in the conclusion part)

Chapter 6

The second half of the first paragraph should also cite Walter (2021, Natl Sci Rev, 2021, Vol. 8).

Fig. 6 - I am not really sure what Fig. 6a is based on. Also, range is 800-1400 °C, caption says 1000-1400 °C). 6b – the curve maxima are basically the Stv to CaCl2-Stv phase transitions? Please explain in more detail. Maybe mark the transition interval in the diagram.

L 224 – Please refer to fig. 7.

L 225 – "Consequently, Stishovite…" The statement in this sentence is correct, but not very new. Several previous studies concluded this, e.g. Walter 2021 and refs within. That should be cited accordingly.

L 228 – "Taking into …" Please elaborate on the melts and outline your reasoning a bit more in detail.

Figure 7 – "Yin and Kang, 2023 (in preparation). I disagree with citing non-peer reviewed work. Is there an alternative?

Paper mentioned:

Walter, M. J. (2021). Water transport to the core–mantle boundary. *National Science Review*, *8*(4), nwab007.

Nisr, C., Chen, H., Leinenweber, K., Chizmeshya, A., Prakapenka, V. B., Prescher, C., ... & Shim, S. H. (2020). Large H2O solubility in dense silica and its implications for the interiors of water-rich planets. *Proceedings of the National Academy of Sciences*, *117*(18), 9747-9754.

Li, J., Lin, Y., Meier, T., Liu, Z., Yang, W., Mao, H. K., ... & Hu, Q. (2023). Silica-water superstructure and one-dimensional superionic conduit in Earth's mantle. *Science Advances*, *9*(35), eadh3784.

Litasov, K. D., Kagi, H., Shatskiy, A., Ohtani, E., Lakshtanov, D. L., Bass, J. D., & Ito, E. (2007). High hydrogen solubility in Al-rich stishovite and water transport in the lower mantle. *Earth and Planetary Science Letters*, *262*(3-4), 620-634.

Lin, Y., Hu, Q., Meng, Y., Walter, M., & Mao, H. K. (2020). Evidence for the stability of ultrahydrous stishovite in Earth's lower mantle. *Proceedings of the National Academy of Sciences*, *117*(1), 184-189.

Lin, Y., Hu, Q., Walter, M. J., Yang, J., Meng, Y., Feng, X., ... & Mao, H. K. (2022). Hydrous SiO2 in subducted oceanic crust and H2O transport to the core-mantle boundary. *Earth and Planetary Science Letters*, *594*, 117708.

Kueter, N., Brugman, K., Miozzi, F., Cody, G. D., Yang, J., Strobel, T. A., & Walter, M. J. (2023). Water speciation and hydrogen isotopes in hydrous stishovite: implications for the deep Earth water cycle. *Contributions to Mineralogy and Petrology*, *178*(8), 48.

Ishii, T., Criniti, G., Ohtani, E., Purevjav, N., Fei, H., Katsura, T., & Mao, H. K. (2022). Superhydrous aluminous silica phases as major water hosts in high-temperature lower mantle. *Proceedings of the National Academy of Sciences*, *119*(44), e2211243119.