

Review of “Yttrium speciation in subduction zone fluids from ab initio molecular dynamics simulations” by Johannes Stefanski and Sandro Jahn

This manuscript presents a theoretical study of Y complexation using intensive ab initio MD simulations. The authors performed MD runs to describe the geometries and coordination of Y complexes, and used the thermodynamic integration method to calculate the free energy surface of Y-Cl/F reactions. These results have been used to calculate the thermodynamic properties at 800°C and high pressure. This study provides valuable knowledge of Y-Cl/F complexation under extreme high T-P conditions, which has significant implication in understanding Y and REE under conditions such as subduction zone. The computational methods are well documented and easy to follow. Overall it is a well-organised study, and the manuscript is very informative. It is worth to be published after revisions as noted.

Fig 2. Add constraint distance label for Fig2d.

Fig4: The x-axis is “AIMD run”, which has no meanings... The authors could try to group runs with the same box to see the trend of changes.

I found the unconstraint MD part (section 3.1) is hard to follow. I understand it is challenge to put together large amount of data, especially for Y complexes whose geometry and coordinates are very disordered and complicated compare to some other elements. The data listed in Table 1,3,4 are heavily overlapped, and it's hard to cross check those tables during reading. I suggest the authors consider to merge those Tables to one or two, and put relevant data in the one table.

One major information from the MD is the dissociation of  $H^+$  during the simulation. As shown in Fig3, the difference of Y-O distances for  $Y-OH^-$  and  $Y-OH_2$  are very distinguishable. I suggest in Fig3, label the bond distances of each peak (or in the text); and in Table 3, show the  $Y-OH^-$  and  $Y-OH_2$  distances separately.

In practical, monitoring the change of Y-O distances helps us to identify the H dissociation during the dynamic run. For example, in Fig7, the authors can also add a dynamic distance plot to show the change of Y-O distance during the proton transfer.

The authors mentioned Na-Cl association in some MD runs. Please provide more details of the criteria of Na-Cl association (e.g., CN cutoff).

AIMD of run#5: The whole run looks like the “meta-stable” stage. As run#5 and #4 share the same box size and particles and just started with different initial configuration. The last formed structure of run #5 turned to be the first formed structure of run #4 (Table4). Can you discuss on this?

Line 235: “In #1, the highest amount of hydroxide is formed...”. How about run #6?  $Y-OH^-$  is 1 in run #6 (Table 3). It's not clear which runs# are discussed in this paragraph.

Fig5: This figure is very informative, but hard to read. A main confusion is the definition of “Y-OH formation” and “Occurrence of the initial complex”. As when proton dissociated and Y-OH formed, it is not the “initial complex” anymore. The Y-Na formation could be

recognised as the 2<sup>nd</sup> shell interaction, but in the 1<sup>st</sup> shell, the number of hydration water changed in some calculations (e.g., #17), and the Y-OH<sub>2</sub> and Y-OH<sup>-</sup> are totally distinctive bond (as we can see from the bond distance), which shouldn't be classified as "Occurrence of the initial complex", unless change the definition to "initial Y-halide complex". Another suggestion is to move the legend to the top or bottom, so the figure can be larger in the published version.

Line 280-285: hydrated halide ions. What's the CN cutoff for Cl-/F- hydration? The hydration number of 4-5 at that density looks smaller compare to previous studies (e.g., Sherman 2007, Mei et al., 2018).

Fig7. Looks like the green curve are the running average of the constraint force. Can you show the dynamic force (e.g., Fig2(III)) to see how much difference is?

Line 319: "For the 4.5 GPa runs, the dissociation energies of the Y chloride complexes significantly decrease." Please specify the "significantly decrease". As shown in Table5, TI-1 is -36.1, TI-4 is -29.6, not significant decrease.

Line 325: "TI-5 yields the lowest dissociation energy of 8.5 kJ mol<sup>-1</sup>". I wouldn't say "lowest" here. As you didn't calculate the TI of reaction  $[YCl_3]_{aq} = [YCl_2]^+ + Cl^-$ , which would give lower FES.

Line 328: "For  $[YCl_3(H_2O)_5]_{aq}$  it was not possible to derive a dissociation energy because the initial complex dissociated at short Y-Cl constraint distances within the first picosecond of each simulation." That's **incorrect**. It is possible to calculate the FES of this reaction, by restraint two of the Y-Cl at equilibrium bond distances (e.g., Fig1 of Mei et al., GCA, 179 (2016) 32-52). You would expect a low dissociation FES for that reaction as YCl<sub>3</sub> is not preferred complexes.

Line 335-340: "In the latter case at a constant distance of 2.6Å one of unconstrained fluorides separates from the initial complex. However, this behavior is not reproducible." Again, you can restraint the Y-F pair to keep F around the equilibrium bond distance.

Fig8: For those chemical reactions, why using "→" in Fig8 but "=" in other tables? Please keep consistent.

Fig10: No Y-axes label in Fig10a.