Referee's report for article cg-2020-00589c

Title: Metastable structures of $CaCO_3$ and their role in transformation of calcite to aragonite and post-aragonite

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The manuscript of Gavryushkin et al. shows results of a coupled theoretical and experimental work aimed to study the metastable high pressure (H*P*) polymorphs of aragonite, their relationship with the stable ones, and their role on the (1) aragonite to calcite transformation and (2) calcite to post-aragonite phase transition. The theoretical work was done by means of molecular dynamics simulations and evolutionary metadynamic calculations; whereas, the experimental part was carried out by means of high temperature X-ray powder diffraction (H*T* XRPD) and transmission electron microscopy (TEM). By the above-mentioned methods, the authors revealed the occurrence of metastable polytypes of calcite, namely, two-layered (*hexarag*) and six-layered (*hexite*) close-packing structures. The authors gave an interpretation of the topotactic transformation from aragonite to calcite as a two-stepped mechanism with *hexarag* being the first metastable phase to form followed by its transformation to the 3-layered cp structure of calcite through the series of disordered many layered polytypes. Moreover, the analysis of metastable H*P* polymorphs at room temperature (*T*) and in the *P* range from 2 to 40 GPa allowed the authors (i) to speculate about the mechanism for the phase transition from calcite to post-aragonite and (ii) to explain the reasons for the formation of $CaCO_3$-II, III, IIIb, and VI polymorphs during cold compression of calcite and their absence during compression of aragonite.

I think that the proposed objectives are very interesting and that the authors reached quite well the main objectives of the proposed research. However, I would like to point out some comments and suggestions, as detailed in the following.

General considerations:

- Even if the paper is quite clear in its present form, some grammatical and phrasal errors are present. In the following I will give some examples. However, I do not go into a detailed English revision of the manuscript as it is not my expertise, instead, I suggest the authors to perform a deep English revision during the preparation of the in the revised version of the paper.
    - Abstract, line 28: missing article “the” before “3-layered”. Articles are often missing throughout the manuscript.
    - Page 3 lines 10-11: “revealed theoretically” should be “theoretically revealed” as well as

"synthesized experimentally" should be "experimentally synthesized". These inversions are often needed throughout the manuscript.

  - Page 7 line 24: please replace "transforamtion" with "transformation".
  - Page 8 lines 28-30: please replace "It make" with "It makes" and "The performed calculations shows" with "The performed calculations show".

- In my opinion, a detailed description of the crystal structure of the metastable polymorphs *hexarag* and *hexite* is missing. I would expect the authors to publish details of the optimized geometries, not only cell parameters. Paraphs, a figure of both *hexarag* and *hexite* oriented parallel to (001) might be important to give a graphical visualization of both structures. The Figures 2, 3 and 5 are important to follow the text, however, an additional figure where the 2- and 6-layered polytypism is shown might be important too.
- In general, it is not usual to write "powder X-ray diffraction". Please replace with "X-ray powder diffraction" when needed along the whole text. The correct abbreviation should be H*T* XRPD.
- Please use *italics* when needed: non-English terms (*i.e.*, *in situ*, …), space groups (*R*-3, *R*-3*c*), state variable (e.g. *P*, *T*), cell parameters and interplanar distances (e.g. *a*, *c*, *V*, *d*). In some cases, throughout the text, italics is not correctly applied. Some examples below:
  - Page 2 line 50: replace PT with *P*-*T*.
  - Page 9 line 24: replace PT with *P*-*T*.
- Sometimes the special character " – " is used. However, I do not understand its meaning (e.g. page 3 line 21, Page 6 line 48).

Specific comments:

- Please erase from the abstract the acronyms declaration (HT PXRD) and (TEM) as they are not used along the abstract. Acronyms need to be specified at their first appearance in the text.
- Page 3 line 14: Please rephrase "Calcite is stable modification" with something more appropriate such as "The stable phase of $CaCO_3$ at ambient condition is calcite".
- Page 3 line 19: specify the "cp" acronym as "close packing".
- Page 3 line 26: please replace "about" with "approximately". The same suggestion needs to be applied at Page 11 line 8.
- Page 3 lines 33: please insert a reference relative to the sentence "Metastable at ambient pressure aragonite is stabilised above 2 GPa and remains stable up to 25 GPa.".
- Page 3 lines 45-48: please rephrase.
- Page 4 lines 45-50: Were topological analyses performed at H*P*? At Page 12 the manuscript is focused on the H*P* behaviour of stable and metastable polymorphs. However, no details are given about the

H*P* calculations in the "Methods" section. I think that some details should be given.

- Page 4 lines 50-53: no details are given about the used samples (chemistry, locality, …). Please insert some information together with the value of CoKα.
- Page 5 line 17: are site scattering used for neutral atoms? Please specify.
- Page 5 lines 21-22: please rephrase since the meaning is not clear. Might be something like "…since at higher *T* aragonite is replaced by calcite"?
- Page 5 line 41: does the sentence "In molecular dynamic simulations, aragonite structure is stable up to the temperature of 700-800 K." come out from your work? Or it is maybe taken from literature? Please clarify and, if appropriate, insert a reference.
- Page 7 lines 29-39: The comparison of *hexarag* with other carbonates is quite interesting. However, the discussion might go deeper in explaining the influence of other cation than Ca on the H*T* behaviour of $CaCO_3$-like minerals. In particular:
    - no data on the variation in distribution of Ba/Ca atoms are given. Did the authors perform such calculations? If yes, please give some "quantitative" results. If not, references are needed;
    - in the last sentence, Sr is taken into account. However, it is not clear why the authors introduced Sr. Are there experimental/theoretical evidences to link Sr to the Ba behaviour in $CaCO_3$ crystal structures? Please explain.
- Page 7 lines 51-52, Page 8 line 28: Is the sentence referring to Figure 3? What is "stagger" used for? I do not understand its meaning in this context. This is probably my fault; however, some of other readers might have such a conflict. Please, explain what "two-staggered" represents.
- Page 8 lines 43-45: the final sentence is too qualitative. Please, insert details, e.g. which "specific conditions are necessary for their stabilisations".
- Page 9 line 35-37: Please rephrase the sentence "Calcite, structure with $n = 3$, is the exclusion from this trend.", since its meaning is ambiguous.
- Page 9 Figure 5: please insert the orientation of the crystal structures as well as the meaning of the different colours.
- Page 10 line 48: I think that the authors meant to refer to Table 3 instead of Figure 3. Please correct.
- Page 11 line 11: I do not understand the reason for the sentence "…there is a way to increase this temperature.". The reader expects the authors to give some details in the following of the manuscript. However, no speculations/discussions are given about it. Please, either add some consideration or erase this sentence.
- Page 12 Figure 9: there are almost no discussions related to Figure 9. Moreover, at lines 44 onwards, the authors refer to the *P* range 15-40 GPa that is quite higher that what reported in Figure 9. Please, either make Figure 9 being in accord with the text or *vice versa*.

By the above-mentioned comments, I do recommend the paper to be published in *Crystal Growth and Design* journal after a revision of the manuscript following the proposed suggestions and comments.

Sincerely.