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Evaluation report (4 pages) of Bartosz Puzio's PhD thesis

Based on the analysis of the manuscript entitled "*New method for prediction of thermodynamic functions for apatites*" prepared at the University of Kraków, Poland

PhD Candidate: Bartosz Puzio MSc, Eng.

Supervisor: Prof. Maciej Manecki,

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PhD title: New method for prediction of thermodynamic functions for apatites

Reviewer: Prof. Christophe Drouet, CNRS Senior Scientist, CIRIMAT Institute, University of Toulouse, France

Introduction - General structure of the thesis

The presented thesis manuscript gives a general overview of the existing methods for predicting the thermodynamic properties of apatite compounds, and then develops a specific data analysis methodology based on compositional subgroups. The thesis is clearly written, in a good English with very few typos. The topic is relevant to various domains and disciplinary fields where apatitic compounds are involved such as Earth and extraterrestrial mineralogy, hydrometallurgy, nuclear and environmental sciences, among others.

The manuscript in itself is composed of 82 pages (without references and annexes) and is divided into several sections, often based on the thermodynamic function that is addressed (enthalpy of formation, entropy, Gibbs free energy, solubility product…). This is concluded by a discussion section. Notations used throughout the text are self-comprehensive and consistent. The reference section (and therefore the citations listed in the text) gives a broad and quite exhaustive overview of the relevant scientific literature on the topic addressed in this thesis work.

Thesis evaluation

I have read this PhD thesis work with pleasure and attention, as it totally fits my research interests and activities since I have developed in 2014 the ThermAP (Applied Predictive thermodynamics) additive method to predict the thermodynamic properties of complex oxides – developed so far on phosphates like phosphate apatites as well as Jahnsites/whiteites. In this work, the candidate brings his point of view and critical analysis on the prediction of thermodynamic properties of the apatite supergroup of compounds, and more specifically by addressing and comparing data relevant to apatite endmembers, through the development of an analytical methodology based on the observed vicinity of behavior among apatite composition subgroups.

The thesis manuscript shows that the PhD candidate has a good understanding of the existing methods to predict thermodynamic properties of apatite compounds, and a good knowledge of the relevant literature through a critical scientific eye. In particular, the SSA, VBT, ThermAP, and Latimer methods are cited and considered in this study, for example in subsections from 2.1.3.2 to 2.1.3.5, with the goal to compare the thesis predicted results to some of these methods' outcomes. This is also illustrated for example in Table 1 and section 4.7. Possible inputs from machine learning and artificial intelligence are also addressed rapidly in the text (e.g. in subsection 2.1.3.6) as well as some *ab initio* calculations (see for example section 2.1.2 and some of the data listed in Table AX1 in annex). The theoretical background is well stated by the candidate, e.g. through equations listed and discussed in the text (e.g. page 10 to 14). Through the adequate analysis of the preexisting methods and thermodynamic assessments made in the manuscript, the candidate thus shows that he ***masters the necessary general knowledge for a doctoral degree in Earth sciences and related environmental sciences***.

In the dissertation, the candidate analyzes step-by-step the main thermodynamic properties of formation and of dissolution of various apatite endmembers. This encompasses a variety of compositions with typically members of the three main phosphate/vanadate/arsenate series, in which he addresses endmembers involving the cations Pb^{2+}, Ca^{2+}, Sr^{2+}, Cd^{2+}, Ba^{2+} and the monovalent anions F^-, Cl^-, I^-, Br^- and OH^-. The data of the literature are analyzed by the candidate using a dedicated subgroup-specific approach, and he shows clear linear-like correlations in most cases, indicating that the energetics of formation of apatite endmembers can be drawn/validated/compared via this type of correlation graphs. For such endmembers, this approach generally led to higher accuracy than other existing predictive methods to-date. Although this type of subgroup correlations has been sporadically reported in the literature for some apatites, the candidate shows that he was able to develop an analytical methodology of his own and leading, for key compositional endmembers, to accurate predicted data. A demonstration of this ability is given on Table 14 that summarizes the overall proposed methodology addressing all of the main thermodynamic properties (at room temperature). The

question of temperature is more specifically addressed toward the end of the manuscript (in section 7.8): only very few data are however available to-date in the literature, impeding one to develop today a robust database for developing predictions at temperatures other than RT. On the other hand, the room temperature data (T = 298.15 K) should anyway be the starting point of any such development, and the gain of developing such predictive methods is still very obvious. The global progression of the manuscript and methodology exemplification therefore demonstrate that ***the candidate is able to independently conduct a scientific research work***, which is also a prerequisite for doctoral validation.

The topic of the thesis, as mentioned above, is relevant to many fields. However, in spite of the ubiquitous character of apatitic compounds in many domains including natural (e.g. Earth, Moon and Mars mineralogy, biomineralizations…) and industrial ones (e.g. remediation of polluting ions, nuclear waste disposal, biomaterials…), there are surprisingly few experimental data on apatites' thermodynamics. Attempts have been made to fill some of these gaps by applying *ab initio* calculations such as DFT, but even in this case the data remain scarce, and the validity of the DFT models used has not always been clearly demonstrated, posing questions as to their actual representation of realistic apatite systems. This is why several of us have been developing different sorts of strategies to predict/compare/verify the values of formation enthalpies, entropies, Gibbs free energies and solubility products of apatitic compounds based on their chemical composition, and with the ultimate goal to predict the energetics of other compositions for which no data exists to far in the literature. It may be noted that each method developed has its own advantages and drawbacks, and shows limitations due to their intrinsic nature. This will be discussed during the final thesis defense with the candidate. In any case, the present thesis dissertation presents a self-consistent piece of work that can be used to address in particular halide-bearing apatite endmembers that are relevant to several domains. The situation with OH-bearing apatites is shown to be somewhat specific, leading for some thermodynamic properties to be outliners of the general tendencies depicted by the halide apatite subgroups. This could, most probably, be linked to the additional H-bonding effect of such hydroxylated apatites, as was stated by the candidate in the dissertation. The candidate has for sure demonstrated his capacity to consider a scientific problem as a whole, to identify the key literature relating to this problem as well as the existing solutions, and to develop a solution of his own to address remaining gaps or to refine the predictions accuracy. Of course, as said before, every predictive methodology without exception is bound to have its own limitations as it is always grounded on hypotheses, but this work undoubtedly shows that the candidate can come into play in the state-of-the-art worldwide discussion on apatite thermodynamics and can ***present an original way to face the problem of predicting the fundamental energetics of apatite compounds of various compositions***. This is evidenced from the reading of the present thesis dissertation, and this is also requested for a doctoral candidate.

Naturally, as in any high-level scientific work, there are some aspects that will be interesting to discuss altogether on the day of the defense. For example, it could have been relevant to show some practical ways to actually "use" the developed methodology, e.g. for other unknown apatite compositions or intermediate solid solutions. Also, in some cases, the comparison with approaches like ThermAP or others has not been shown, e.g. in Tables 3, 5 and 10, and comparison of the data from Tables 3 and 4 could also have been instructive. The distinctive behavior of the alkaline-earth (AE) apatites has been previously reported in the literature typically through the VBT approach, but it was not clearly mentioned in the text: it could have been interesting to mention it more clearly (e.g. Figure 8). On Table 11, it is not clear which set of S° values has been listed in the first column and this could be clarified. Some slight modifications in the text would also be relevant in my opinion. For example, since the absolute

entropy S° is always positive, I would not speak about "absolute value" in this case (page 38). On page 60, it is said that OH^- does not occupy the same z position, but this is also the case for all of the halide apatites compared to F-apatite, so I am not sure this sentence is appropriate here. On page 65, the sentence "it was not possible to obtain experimental data…" should probably be rephrased. Indeed, the author probably means that experimental data are not yet available, but the compositions do not seem 'impossible to prepare' at some point using refined synthesis methodologies and experimental data should be 'possible to get' at some point in my opinion. In some cases, a hypothesis or a preliminary explanation of the observations could have been interesting to add, e.g. on page 65 when saying "F-apatites stand out from the trend": according to the candidate, why is it the case? It is sometimes difficult to assess for sure, but hypotheses regarding ion size, element electronegativity or other considerations could perhaps be added if relevant after crosscheck. On page 69, when stating "higher $\Delta G°_{f,el}$", it would have been more precise to say "less negative" in this case. On page 73, I would replace "K_{sp} is a state function" by "K_{sp} is a thermodynamic property" or "thermodynamic function". Concerning Figure 23, there are 10 compounds listed but there seems to be only 9 curves (or perhaps some are overlapping?), is is possible to check it and/or improve the visibility of the 10 systems? Also, importantly, on this same Figure 23 and on the corresponding Table 13, the data used are in Me_5 apatite notations while the rest of the dissertation concerns Me_{10} notations (which is more relevant think taking into account the current state-of-the-art of the current apatite community). Indeed, while the K_{sp} of $Ca_{10}(PO_4)_6(OH)_2$ for example is around 116-120, here it is only half (around 58-60): please multiply by $\times 2$ these tabulated/plotted data (adding a justification by an asterisk* for example) to be consistent throughout the dissertation and avoid data misuses from non-expert readers of the thesis manuscript once it becomes public.

Despite these comments, and the discussion that will follow the defense, the thesis work is definitely interesting and relevant, and it provides another way to analyze apatite thermodynamics of great interest to the scientific community, as well as tabulated data for use as reference.

Concluding remarks

In my opinion, the reviewed PhD thesis presented by Bartosz Puzio meets all the legal requirements for content, originality, and the form of scientific monographs required for PhD dissertations by Law on higher education and science in Poland (the Act of 14 March 2003 on Academic Degrees and Academic Title and Title in the Arts, Journal of Laws of 2017, item 1789, and the Act of 3 July 2018 Law on higher education and science, Journal of Laws of 2018, item 1669). In view of the above, I hereby apply to the Research Discipline Council of Earth and Related Environmental Sciences of AGH University of Kraków **to admit Mr. Bartosz Puzio, M.Sc., to further stages of the doctoral procedure**.

August 31st, 2023

Reviewer's signature