

New Mexico Bureau of Geology & Mineral Resources

A DIVISION OF THE NEW MEXICO INSTITUTE OF MINING & TECHNOLOGY

MINERALOGICAL MUSEUM

801 Leroy Place

Socorro, NM 87801

Phone: 575-835-7625

<https://geoinfo.nmt.edu/museum/>

Evaluation of PhD Thesis

Ph.D. Candidate: Bartosz Puzio MSc, Eng.

Supervisor: prof. Maciej Manecki, Department of Mineralogy, Petrography, and Geochemistry,
Faculty of Geology, Geophysics and Environmental Protection, AGH University of Kraków, Poland.

Title of a PhD Thesis: New method for prediction of thermodynamic functions for apatites

Professor John Rakovan, State Mineralogist for New Mexico, New Mexico Bureau of Geology and Mineral Resources, New Mexico Institute of Mining and Technology, and Professor at the Department of Geology and Environmental Earth Science, Miami University, Oxford, Ohio.

Thesis evaluation

This dissertation clearly indicates a broad and in depth understanding of thermodynamics and mineralogy by the author, Ph.D. Candidate, Bartosz Puzio. This is evidenced by the in depth review of thermodynamic knowledge of apatite supergroup minerals and the methods by which thermodynamic properties are measured or calculated. The review helps frame the significance of the original research results presented in the dissertation. This is especially true in the comparison of discrepancies between the values of estimated thermodynamic properties, by the different methods reviewed, and measured values when available. For example, the algorithm proposed in this

dissertation for the prediction for enthalpies of formation from elements and for standard entropies predicted values for these properties with higher precision than any other method proposed to date.

The Ph.D. Candidate, Bartosz Puzio, has shown through the work presented in this dissertation the ability to independently conduct scientific work.

This dissertation clearly represents an original solution to the scientific problem of determining the thermodynamic properties necessary to understand and model the behavior of the myriad apatite supergroup minerals and synthetic compounds with the apatite crystal structure. The apatite supergroup and its synthetic analogs is of importance in a greater variety of fields than virtually any other mineral group. It is of particular significance in Earth science, life science, and material science. The foundation of this significance is the apatite structure and its resulting properties. The structure of apatite allows for numerous substitutions, including a multitude of metal cations, anionic complexes, and anions (especially the halogens). Indeed, apatite incorporates half the periodic chart in its atomic arrangement. This complex and variable chemistry has great implications, and is utilized in all areas of apatite research. Because of this, there is a great need to determine the thermodynamic properties of a wide variety of apatite compositions. This dissertation presents a new methodology for the prediction of many thermodynamic properties, including enthalpies of formation from elements and for standard entropies using linear regression of existing experimental data. These in turn allow for calculation of other related thermodynamic functions including the Gibbs Free Energy of formation and the solubility product. Most importantly, the method proposed for the first time in this dissertation results in higher precision in calculated values of many thermodynamic properties than any other method proposed to date. Furthermore, this method can be applied to a wider range of apatites than other estimation methods.

Specific comments

Page 13: *“Therefore, Drouet (2015) calibrated each of the g_i and h_i parameters separately using the least-squares method based on experimental data collected only for apatite and inorganic materials corresponding to its symmetry class.”*

Was it symmetry class or structure class? It seems to me that the former is not correct. Please comment.

Also on page 13th: *“This is, of course, reflected in the measured enthalpies of formation. In addition, a very common apatite impurity, especially in synthetic analogs, is carbonate CO₃²⁻, which significantly stabilizes the apatite structure and thus lower the $\Delta H^{\circ}_{f,el}$ of apatite itself causing deviation when consider this data for pure HAP.”*

This seems odd to me. Carbonate increases the solubility of apatite. I would thus expect this to be a destabilization. Is this correct? E.g.

<https://www.sciencedirect.com/topics/chemistry/apatite#:~:text=B%2Dtype%20carbonate%20apatite%20is,Barralet%20et%20al.>

Please comment on this issue.

Page 53: *“A peculiarity is also apparent: in all cases, the projection of fluoride apatite deviates from the linear trend set by the other apatite. This is probably since the value of the entropy of formation for the F⁻ ion -13 (J/mol·K) is much lower than the entropy of formation of the ions of the other halides.”*

Could this be the result of F sitting on the mirror plane, which decreases the freedom of its disorder, but all of the other X position elements sit off of the mirror and are free to shift their positions?

Please comment.

Final remarks

In my opinion the reviewed PhD thesis 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.**

At the same time, in recognition of a valuable, original approach and quality of research results, I recommend awarding the thesis with an appropriate prize.

August 29, 2023

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date

A handwritten signature in black ink, appearing to read "John Puzio", with a long horizontal line extending to the right.

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Reviewer's signature