Review of PhD thesis of: Agnieszka Arabas

"Reconstruction of the Jurassic environment of the Pieniny Klippen Basin using carbon and oxygen isotope composition of bulk carbonates and belemnite rostra"

Author indicates that the Pieniny Klippen Basin is rarely studied northern part of the Tethys Ocean. This basin, in contrast to most of basins located in a western and north-western part of the Tethys Ocean, was in the Jurassic an open marine basin, in which local factors have a negligible significance on water composition, temperature and other environmental conditions. The chemical signatures of the studied rocks suggest that they have recorded the original variations of the ancient sea-water chemistry. If the carbonate are well preserved, high resolution $\delta^{13}C$ isotope record of bulk carbonate together with $\delta^{13}C$ and $\delta^{18}O$ data of the belemnite rostra are optimal to document global carbon cycle or/and global climatic changes in the ancient carbonates. Isotope investigation of the belemnite rostra is a well-established method for the paleoclimate reconstruction and is frequently used.

Presented PhD. dissertation concerning reconstruction of the Jurassic environment of the Pieniny Klippen Basin is a highly actual topic and its results can be widely applied in various geological correlation projects and are interesting for various specialists.

The thesis contains Abstract in English and Polish, Outline of the thesis in Polish, Chapters 1-3 and Appendix 1-4. The outline of the thesis in Polish is not identical with the outline in English, because there are summarized methods and field works. The introduction (Chapter 1) has 16 pages and is divided to four sub-chapters - Main objectives and general outline of the Thesis, Pieniny Klippen Basin (PKBb) and Pieniny Klippen Belt (PKBt), Historical background of isotope studies, Carbon and oxygen isotopes and their application in paleoenvironmental studies and References.

Main objectives of the thesis concerning the evolution of environmental condition in the PKBb are formulated in five points and can be expressed as:

- to highlight Jurassic palaeoclimatic conditions of the open marine basin of the northern Tethys Ocean

- to determine variation in C and O stable isotope composition of the bulk rock and belemnite rostra and changes in the sea-water temperature inferred from $\delta^{18}O$ of belemnite rostra
- to compare the obtained results with results from published studies, mainly from epicontinental basins of Europe
- to contribute new data to regional and global palaeoreconstruction
- to improve the existing Jurassic stratigraphy of the PKBt based on the carbon-isotope stratigraphy

The "geological background" of the Pieniny Klippe Basins resp. Pieniny Klippen Belt sub-chapter is comprehensive and is sufficiently supported by earlier published data.

The sub-chapter 1.3 (Historical background of isotope studies) summarizes principles of stable isotope chemistry which had been given at the beginning of the last century. Thank to Urey et al. (1948, 1951), Craig (1953, 1965) and other pioneer studies the new knowledge was applied in the geology. As is indicated in the thesis the "historical period" lasted to about 1990 when C and O stable isotope methods have been verified and standardized including sample screening procedures. In that time it was documented (by extensive organic matter studies of black shale, hydrocarbon reservoirs and others materials) that organic matter production and accumulation processes are tightly connected with (palaeo)environmental conditions resulting in C isotope fractionation in inorganic carbon reservoir of the oceans. Equilibrium isotope signatures of ancient sea-water can be recorded in calcite – a stable polymorph of $CaCO_3$ including micrite-limestone or belemnite rostra. However, other processes or factors (e.g. vital effect, carbonate diagenesis) could modify equilibrium stable C and O isotope ratios of ancient $CaCO_3$ and may limit environmental application of the stable isotope methods, especially $\delta^{18}O$ paleotemperature method used in the global palaeoclimatic studies. Subchapter dealing with oxygen isotopes is simplified and a traditional form of paleotemperature equation of Anderson and Arthur (1983) is there only presented. Used methods are not critically commented in this part of the thesis (however they are commented in the Polish outline and in the published "articles"). References are listed separately in the both language versions and are formally correct.

Introduction is followed by "Outline of the publications" (Chapter 2, two pages) and Conclusion (Chapter 3, one page, in English). Two complete manuscripts (one already peer - reviewed published, other in print paper) are presented as Appendix 1 and as Appendix 2. Supplementary data to publication – Arabas et al. (in press): Early Jurassic carbon and oxygen isotope records and seawater temperature variations: Insights from marine carbonate and belemnite rostra

(Pieniny Klippen Belt, Carpathians) are given in the Appendix 3 and supplementary data to Arabas (2016) : Middle–Upper Jurassic stable isotope records and seawater temperature variations: New palaeoclimate data from marine carbonate and belemnite rostra (Pieniny Klippen Belt, Carpathians) are given in the Appendix 4.

Both articles have been revised, carefully corrected and controlled before their publication in the prestige journal (Palaeogeography, Palaeoclimatology, Palaeoecology). Therefore, I would only highlight major contributions of the papers and formally indicate achievement of the dissertation aims:

1. New results of carbon and oxygen stable isotope analyses of 151 belemnite rostra and 593 bulk carbonate samples from the Lower Jurassic and analyses of 44 belemnite rostra and 236 bulk carbonate samples from the Middle–Upper Jurassic from an open-marine environment of the Pieniny Klippen Belt, Carpathians, which constitute an extensive database for future investigation.
2. The obtained high resolution $\delta^{13}C$ data through the Jurassic of the Pieniny Klippen Belt have enabled documentation of the most important (global carbon) events in palaeoenvironmental history of the basin, which are properly interpreted (- Late Pliensbachian event points to enhancement of the carbon burial under redox condition, - prominent Lower Toarcian event corresponds to the global post-TOAE, trend when accelerated sequestration of organic matter and stabilization of global carbon cycle after the TOAE took place, etc.).
3. Presented stable isotope data from the deep, open-marine Pieniny Klippen Basin mostly corroborate previous palaeoenvironmental interpretations based on published data derived from the restricted, epicontinental basins of the peri-Tethyans areas.
4. Temperatures inferred from the $\delta^{18}O$ values of well-preserved belemnite rostra suggest the Early Jurassic climate instability. Furthermore, the comparison of obtained results with previously published data from other peri-Tethyan basins enables recognition of the most important changes in the Early Jurassic environment of the northern part of the Tethys Ocean.
5. The carbon isotope data enable improvement of the existing stratigraphy of the studied succession of the PKBn.

Presented results generated questions which are discussed in the dissertation. However, some matter needs further explanation.

1. The paleotemperature equation (Anderson and Arthur, 1983) used in the thesis is well-established, but the interpretation of the reconstructed palaeotemperature variations can be limited. Some authors prefer interpretation of only relative temperature changes, especially

when determined water temperature cannot be supported by ecology of the biota. The author should comment this problem.

2. Critical value in the paleotemperature equation is the assumed $\delta^{18}O$ of original (Jurrassic) ocean water. It is not explained in the light of the more recent studies (and/or modeled $\delta^{18}O$ values of deep or shallow waters) why the ancient water composition of -1‰ SMOW (Standard Mean Ocean Water, Shackleton and Kennett, 1975) is used. Obtained data are also derived from various intervals and relative wide span of time. The author should, thus, also explain how precise the values of calculated temperature are.

3. It is also not given if new methods based on stable isotope composition of ancient carbonates can be tested or developed for the Jurassic sediments of the Pieniny Klippen Belt.

Conclusion: Identification of the local and global geochemical/isotope signals in the ancient carbonate materials is not a routine or trivial geochemical work. The author uses (from sample selection to isotope analyses interpretation) wide and complex geological methods. The presented PhD thesis and published articles is a novel and original study, which confirms, that Agnieszka Arabas is a fully valuated scientist. PhD dissertation thesis fulfils requirements for this kind of work and therefore, I recommend the acceptance of the dissertation and its admission for public defense.

10th August 2017

prof. Otília Lintnerová