Review

of the PhD Thesis of Mgr. Tomáš Hrstka with the title: „Paleofluid chemistry of orogenic gold deposits: novel analytical methods and case studies from the Bohemian Massif“

The submitted Thesis represents a compilation of several articles, focused mostly on development of new analytical techniques in ore deposit studies. The Thesis has the following structure: it contains two introductory chapters, one published article, two articles in preparation, two published proceedings from conferences and a short conclusion chapter. Appendix contains another four short conference abstracts. Most of the articles, but not all, are somehow related to the main topic of the Thesis which is paleofluid chemistry of orogenic gold deposits in Bohemian Massif. Articles connected in this way represent rather scattered pieces of information, giving a reader an impression of a very broad field of study area of the applicant, probably related to his past activities in various labs and institutes across the world. Introductory and conclusion chapters aim to connect together the various type of data present in articles.

The first chapter Introduction gives basic information about gold deposits in metamorphic terrenes and in central part of Bohemian Massif, about related paleofluids and analytical methods in fluid inclusion research. Generally well written chapter gives much more attention to the methods than geological background for the advanced studies. I was missing more information about ore deposits in Bohemian Massif, especially geological setting, metamorphic and magmatic history and metalogeny of the study area. Also most abbreviations related to geological units were used here without explaining what do they mean (e.g. CBPC, CBMZ - used from p. 3).

Methods and Instrumentation chapter gives more details about methods used in analysis of paleofluids. Major part of this chapter describes various aspects and procedures related to Raman spectroscopy which is the essential method used in the first two articles. General principles of LA-ICP-MS, cathodoluminescence, quantitative evaluation of minerals using SEM (QEMSCAN), confocal laser scanning microscopy (CLSM) and 3D-nano-tomography are also explained in detail. This chapter provides evidence that author of the Thesis has a deep knowledge about his field of study, further confirmed by numerous recent and earlier references. However, results of some of the methods are for some reason not presented later in the Thesis (LA-ICP-MS, CLSM).

First article is the principal work of the applicant published in Chemical Geology in 2011. It presents results of fluid inclusion study in the Libčice orogenic Au deposit using Laser Raman spectroscopy, combined with microthermometry and SEM cathodoluminiscence. Unique results include evidence about unusual bicarbonate-rich fluid inclusions and variation of CO_2/CH_4 ratio in fluids due to hydrogen diffusion into inclusions, which was probably related to influence of organic mater-bearing sediments and postmineralisation granitoid intrusions. This work contributes to general

understanding of fluid processes in orogenic-type deposits and possible post-entrapment reactions in the C-O-H fluid system. It contains the first ever direct measurement of HCO_3^- in fluid inclusion from this type of deposit.

Second article deals with potential concentration measurements of HCO_3^- and related pH estimates in fluid inclusions by Raman spectroscopy. Most suitable strategies are proposed here to calibrate the quantitative Raman analyses at room and at elevated temperatures. The research described in this article has surely a big potential to further develop interpretation of Raman spectroscopy of fluid inclusions. However, I was not able to entirely evaluate the calculated pH of paleofluid at the Libčice deposit as the method of calculation was not fully described, just referenced from not easily accessible publications.

Article number 3 describes results of QEMSCAN analysis of rocks from the Libčice deposit as an automated method of search for Na-bearing phases in various rock samples that could correlate with the bicarbonate nature of paleofluids. However, nahcolite was not found in any of the studied rocks, while Na was mostly attributed to Na-feldspars. In fact, major outcome of this article is the testing of reproducibility and repeatability of QEMSCAN on various types of rocks. Exact original modal composition of rocks was based on optical mineralogy, but it is not clear where this information is presented – perhaps in figure 5.4? Relative proportions of minerals was also checked by XRD data, however, they were based just on peak height of individual minerals. This may not be correct due to variable intensity of signals from various minerals which should have been also taken into account. Unclear to me was also construction of figure 5.3 – which mineral or minerals are plotted here. Equations on p.93 need some clarification.

Article no. 4 is related to a similar topic – reproducibility of QEMSCAN analyses, but in this case not for rocks but heavy mineral sand samples in relationship to the way of sample preparation. In this article I could not find any relationship to paleofluid chemistry of orogenic gold deposits which is the title of the Thesis. I was also missing any information about the origin of analysed material, but I doubt it was from the Libčice deposit. Other comments: Figure 6.1 is quite unclear, missing any legend or explanation. What represent individual sections in table 6.2? I am not sure that PMA and BMA type of measurements have the same reproducibility and repeatability as claimed on p. 104 – at least it is not clear from the table 6.2.

The last article no. 5 is in fact an extended abstract devoted to X-ray nanotomography of fluid inclusions. It presents first ever attempt to visualize inclusions in minerals in this way in order to reconstruct volume of inclusions for precise calculation of composition of aqueous carbonic fluid inclusions. There is claimed a potential of this method, but there are still some restrictions related to limited visualization of materials with low density difference.

Abstracts in the Appendix provide evidence about presentation of the data from Thesis on foreign conferences.

The Thesis is written in very good English and contains only a small number of typographic errors. Most of the figures and tables are of good quality. Minor formal mistakes include missing explanations of some abbreviations used in the text and a few missing references in the list of references (e.g. Goldfarb, 2000 in Hedenquist eds. on p. 4). Exceptionally extensive list of references has some minor errors such as repeated references, incorrect order of references and different ways of formatting.

In summary, the submitted Thesis represents a compilation of high quality, original scientific results, with methodological developments of broad usage worldwide. It gives a strong impression that the applicant has not only outstanding skills in various novel techniques, but that he is also able to use the data to successfully interpret geological processes. The developments have been apparently achieved thanks to many years of work in various leading foreign labs. I recommend to accept the submitted Thesis and after successful defence of the Thesis to award the applicant the title PhD. The unpublished artictles should be finished soon.

Questions to applicant:

1. What was the way to construct isochors of P/T conditions at the Libčice deposit (Fig.3.12)?
2. Why higher numbers of relative concentration of HCO_3^- represent lower bicarbonate concentrations? (p. 73)
3. How is calculated pH from Raman data? (p.76)
4. Can you explain why the presence of nahcolite daughter mineral does not have any effect on bicarbonate concentrations in fluid inclusions (p. 79)?
5. Which of the two methods of 3D visualization of fluid inclusions (CLSM and 3D Nano-tomography) do you consider for more applicable in practice in terms of availability, price and quality of results ?

Bratislava, 28. 8. 2012

Doc. Mgr. Peter Koděra, PhD

Doc. Mgr. Peter Koděra PhD
Comenius University
Dept. of Geology of Mineral Deposits
Faculty of Natural Sciences
Mlynská dolina
Bratislava 842 15
Slovak Republic