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Review Report made out by: Dr. Alfons van den Kerkhof
Geowissenschaftliches Zentrum der Georg-August-Universität Göttingen, Dept. Applied Geology, Goldschmidtstr. 3, 37 077 Göttingen (Germany)

for a Ph.D. Thesis submitted to the
Charles University in Prague, Faculty of Science, Institute of Geochemistry, Mineralogy and Mineral Recources

Title: Paleofluid chemistry of orogenic gold deposits: Novel analytical methods and case studies from the Bohemian Massif

Author: Tomáš Hrstka

Dear Prof. Bohuslav Gaš, Dean

I kindly accept the invitation of review on the Ph.D. thesis above submitted by Tomáš Hrstka and submit herein the review report to provide 1) general comments, 2) specific comments followed by 3) final evaluation statement.

I. General Comments:

The submitted thesis presents a combined multidisciplinary study of selected gold deposits in the Bohemian Massif, mainly focusing on fluid inclusions and related micro-structures. A number of analytical methods like microthermometry and Raman spectroscopy have been applied. In respect to Raman analysis a set of new standard samples were made for better calibration and therewith a very useful contribution was made also for other users of this analytical method. A highly interesting and -to my knowledge- novel part of the work considers the pH determination from Raman properties of solutes trapped in fluid inclusions. This part of the work is perhaps the most significant achievement. Besides, the author tested a number of micro-analytical methods for the study of fluid inclusions like confocal Laser scanning microscopy (CLSM), 3D nanotomography and electron scanning microscope-based techniques like cathodoluminescence (SEM-CL), and QEMSCAN analysis, i.e.quantitative evaluation of minerals by scanning electron microscopy. These methods were checked for their practicability in rock fluid studies, with more or less success. Unfortunately not all these methods have been integrated in the gold deposit study (and left for future work). Nevertheless the information and experience presented in the thesis make a valuable contribution to petrography and ore geology. The data presented are all of good quality.

II Specific comments

(1) The work does not include a map of the study area. This would be useful for the reader who is not familiar with the topic. Does this show that the author concentrates on the analytical aspects more than the application to the studied ore deposits?

(2) p.15-16. I understand that the Raman probe was calibrated with standards containing CO_2-CO-N_2 and CH_4-N_2-H_2 gas mixtures in order to determine relative Raman cross-sections and the instrumental factor for measuring gas components. How did you make the standards? What is the estimated pressure of the standard samples? Comparing the table of correction factors published by Burke (2001) differences are evident, notably for H_2, even when this compound is not very common in fluid inclusions (except for the present ones!).
How can these differences be explained? Are the differences due to the "instrumental factor (LabRam)" only? Can you recommend to use of these correction factors better than the ones published before?

(3) p.21. Fig. 2.3 shows cathodoluminescence (SEM-CL) images of the main (V1) and late (V2) quartz veins from Kasejovice. However, no further details on these images are given. Cathodoluminescence techniques are not much discussed anyway, neither the CL data presented in the work.

The V1 veins seems strongly altered with healed fractures and a complex pattern of secondary quartz, whereas quartz in the V2 vein shows growth zoning. What are the consequences of this observation for the fluid inclusion inventory? Can the fluid inclusion types be correlated with the microstructures in CL? Are fluid inclusions in the V1 vein secondary and in V2 primary?

(4) p.27. The illustration of three 2D sections of a fluid plate is not very convincing here: details can be (hardly) observed and the scale is missing. Nevertheless this looks a highly promising method for micro-structural analysis.

(5) Chapter 3. The presence of nahcolite as a daughter mineral as well as hydrogen and bicarbonate ions in fluid inclusions are interesting observations. Hydrogen diffusion is probably responsible for the fluid compositional variation (notably in respect to X_{CH4}). The interesting question may rise if there is any relation with the gold? Can one of these parameters be used as a prospective parameter for gold?

(6) Cracking of alkanes by circulating fluids in the Libcice sediments is most probably responsible for the forming of the hydrogen. Do you have any information on the character and quantities of the original organic material at other places, away from the zone of contact metamorphism?

You mention that the Raman D/O ratio can be used for characterizing organic /graphitic material. Do have data for the Libcice deposit? If so, do they reflect variation in formation temperatures?

(7) Chapter 4. Determining pH of fluid inclusions from the Raman spectra for bicarbonate and carbonate ions in solute is one of the most advantageous parts of this work. Even when standards have not (yet) been made to go in more detail and better accuracy, the present results show that the methods seems to work. The present samples however contain extremely high bicarbonate concentration. Is this method generally applicable for aqueous-carbonic inclusions from other locations? Or is it only applicable to this special case with extreme compositions?

(8) Chapter 5. QEMSCAN analysis has been tested for fine-grained phases like nahcolite or graphite, but after all was not very successful, as I understand it right. Except for modal mineralogical applications do you think that the method is useful for fine-grained samples, or

for micro-analysis? Even when you state at the end of the chapter that the method has potential, I do not see any advantage for the present investigations (i.e. the Libcice deposit). Am I wrong?

(9) Chapter 7. X-ray nanotomography was tested for fluid inclusions studies, i.e. for estimating the bubble volume fractions in aqueous-gaseous inclusions and micro-structural analysis of fluid inclusion trails (partly healed fractions). As a result it appeared to be impossible to visualize the fluid inclusions in the host mineral, but phase boundaries within the inclusions cannot be seen. Results for measuring structural elements like healed fractures (as promised) are not given. Is application of the universal stage or spindle stage still the best option for this type of studies?

(10) A method with somewhat similar expectations as for X-ray nanotomography is Confocal Laser Scanning Microscopy and already mentioned on p. 25. This method seems to be more successful in applications to fluid inclusion studies. However so far only in the case of fluorescing material (fluid or host) good results have been achieved. Are there any examples for the present gold-bearing veins where this method was successful?

III Evaluation

This work can be considered an important contribution to the methodology of analyzing fluid inclusions. It is very well written and meets a high standard. The data are of good quality and worked out well. The main conclusions convince and the author sufficiently refers to the literature on the different topics.

The thesis -in my opinion- by far fulfills the criteria for PhD defense and is **acceptable** in its present form. Therefore, I recommend awarding Tomáš Hrstka with the Ph.D. degree after successful defense. The remarks and questions listed above can be commented by the candidate during the defense.

Please feel free to contact me if you have any question or concern on the review report.

Sincerely,

Alfons van den Kerkhof