PALEOFLUID CHEMISTRY OF OROGENIC GOLD DEPOSITS: NOVEL ANALYTICAL METHODS AND CASE STUDIES FROM THE BOHEMIAN MASSIF

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Abstract of the Ph.D. Thesis

Fluid inclusions represent a unique tool for understanding the processes leading to the formation of mineral deposits and fluid–rock interactions in general. Orogenic gold deposits in the central part of the Bohemian Massif (Libčice and Kasejovice deposits) were studied in order to provide a better understanding of their genesis. A multifaceted approach was adopted including a broad spectrum of micro-analytical methods.

While traditional methods were used as the basis of this study (e.g., microthermometry, SEM and optical microscopy), the application and improvement/development of modern analytical methods (e.g., LA-ICP-MS and Raman spectroscopy) or introduction of alternative innovative techniques (CLSM, Nano-tomography, QEMSCAN) constituted a significant part of this study.

This study reveals the importance of the HCO_3^- species in hydrothermal fluids (i.e., >100 °C to ~350 °C). Previously, the prevalence of Cl^- and other anions was reported for hydrothermal paleofluids and the majority of studies suggested acidic to neutral rather than the alkaline nature of fluids. This study shows that the presence of bicarbonate ions in some environments is potentially more important than it was previously thought.

Raman spectroscopy appeared to be a promising method for the identification of HCO_3^- species in paleofluids and for the estimation of pH in fluid inclusions containing bicarbonate. This is based on the pH-controlled equilibria of $(HCO_3^-)/(CO_3^{2-})$, where the concentration of the individual species can be deduced from their characteristic Raman peaks at about 1017 cm^{-1} and 1064 cm^{-1}, respectively. Our results suggest the estimated pH of paleofluids at the Libčice gold deposit at pH between 7 and 8.5. Bicarbonate-rich paleofluids were recorded for the first time by direct HCO_3^- measurement by Raman spectroscopy in an orogenic gold environment.

This thesis also stresses the role of post-entrapment modification of fluid inclusions properties due to thermal, pressure and chemical gradients associated with contact metamorphism. The role of H_2 diffusion into the inclusions was proved and the dependence of diffusion processes duration on temperature was modeled. The diffusion of H_2 through the quartz host was demonstrated as a key factor for the observed intra-grain CO_2/CH_4 zoning in fluid inclusions from the Libčice gold deposit.

It was found that the complex interaction of local lithologies and paleofluids played an important role in the formation of unusually bicarbonate-rich paleofluids containing nahcolite, H_2 (up to 6 mol%) and ethane (up to 0.2 mol%). The presence of organic matter-bearing sediments in combination with the thermal impact of the intrusion of granitoids of the Central Bohemian Plutonic Complex are considered key factors in the formation of the observed variability in paleofluid composition.

Finally, it is demonstrated that fluid chemistry can be reliably determined by the combination of analytical methods and thermodynamic modeling. CLSM and X-ray nano-tomography were shown to be promising techniques for future efforts in single fluid inclusion volume and 3D shape reconstructions. QEMSCAN technology was proved to provide invaluable automated quantitative mineralogical and petrological data.