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Comparison of fluid processes in coexisting wolframite and quartz from a giant vein-type tungsten deposit, South China: Insights from detailed petrography and LA-ICP-MS analysis of fluid inclusions

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Abstract

Granite-related wolframite-quartz veins are the world's most important tungsten mineralization and production resource. Recent progress in revealing their hydrothermal processes has been greatly facilitated by the use of infrared microscopy and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) analysis of both quartz- and wolframite-hosted fluid inclusions. However, owing to the paucity of detailed petrography, previous fluid inclusion studies on coexisting wolframite and quartz are associated with a certain degree of ambiguity. To better understand the fluid processes forming these two minerals, free-grown crystals of intergrown wolframite and quartz from the giant Yaogangxian W deposit in South China were studied using integrated in situ analytical methods including cathodoluminescence (CL) imaging, infrared microthermometry, Raman microspectroscopy, and fluid inclusion LA-ICP-MS analysis. Detailed crystal-scale petrography with critical help from CL imaging shows repetition of quartz, wolframite, and muscovite in the depositional sequence, which comprises a paragenesis far more complex than previous comparable studies. The reconstruction of fluid history in coexisting wolframite and quartz recognizes at least four successive fluid inclusion generations, two of which were entrapped concurrently with wolframite deposition.

Fluctuations of fluid temperature and salinity during precipitation of coexisting wolframite and quartz are reflected by our microthermometry results, according to which wolframite-hosted fluid inclusions do not display higher homogenization temperature or salinity than those in quartz. However, LA-ICP-MS analysis shows that both primary fluid inclusions in wolframite and quartz-hosted fluid inclusions associated intimately with wolframite deposition are characterized by strong enrichment in Sr and depletion in B and As compared to quartz-hosted fluid inclusions that are not associated with wolframite deposition. The chemical similarity between the two fluid inclusion generations associated with wolframite deposition implies episodic tungsten mineralization derived from fluids exhibiting distinct chemical signatures. Multiple chemical criteria including incompatible elements and Br/Cl ratios of fluid inclusions in both minerals suggest a magmatic-sourced fluid with the possible addition of sedimentary and meteoric water. Combined with microthermometry and Raman results, fluid chemical evolution in terms of B, As, S, Sr, W, Mn, Fe, and carbonic volatiles collectively imply fluid phase separation and mixing with sedimentary fluid may have played important roles in wolframite deposition, whereas fluid cooling and addition of Fe and Mn do not appear to be the major driving factor.

This study also shows that fluid inclusions in both wolframite and coexisting quartz may contain a substantial amount of carbonic volatiles ($CO_2 \pm CH_4$) and H_3BO_3. Ignoring the occurrence of these components can result in significant overestimation of apparent salinity and miscalculation of LA-ICP-MS elemental concentrations. We suggest that these effects should be considered critically to avoid misinterpretation of fluid inclusion data, especially for granite-related tungsten-tin deposits.

Keywords: Wolframite-quartz vein, fluid inclusion petrography, LA-ICP-MS, SEM-CL, infrared microscopy, fluid geochemistry, metallogenic mechanism; Applications of Fluid, Mineral, and Melt Inclusions