

## Ore Genesis and Hydrothermal Fluid Evolution of the Supergiant Zhuxi W-Cu Skarn Deposit, South China: Evidence from Fluid Inclusions, Oxygen Isotopes, and Scheelite

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The Zhuxi W-Cu deposit (2.86Mt WO<sub>3</sub> at 0.55% and 10Kt Cu at 0.57%), located in the north segment of the Jiangnan Orogen, is the largest tungsten deposit in the world. Skarn and orebodies occur mainly between different units of the Huanglong Formation or within the contact zone between the Mesozoic highly fractionated intrusions and Carboniferous marble.

Four stages of skarn formation and ore deposition have been recognized on the basis of petrographic observations: (1) the prograde skarn stage (garnet-clinopyroxene-scheelite), (2) the retrograde skarn stage (vesuvianite-zoisite-fluorite-actinolite-tremolite-scheelite), (3) the quartz-sulfide stage (quartz-calcite-chlorite-sulfides), and (4) the quartz-calcite stage. The very low Ad compositions in garnet and Mo concentrations in scheelite, high Hd compositions in clinopyroxene indicate the ore-forming fluids are strongly reduced. Microthermometric and Raman spectroscopic analyses of fluid inclusions indicate that the skarn-forming fluids are water-dominant, low in salinity, and methane-bearing. The average salinities are very similar for different ore-forming stages, indicating the decrease of temperature is the major mechanism for scheelite precipitation. The limited coexistence of liquid-rich (L-type) and halite-bearing (S-type) inclusions or liquid-rich (L-type) and vapor-rich (V-type) inclusions in the prograde and retrograde skarn stages indicate that fluid immiscibility occurred under hydrostatic pressures of 97-141 bars (~1.3–2.2 km).

The garnet, clinopyroxene, and scheelite in the prograde skarn gave values of  $\delta^{18}\text{O}_{\text{fluid}}$  from 10.0 to 11.3‰, which are slightly less than those values of magmatic fluid (12.8–13.2‰). The results of apatite and scheelite ( $\delta^{18}\text{O}_{\text{fluid}} = 6.5$  and 8.8‰) represent isotope compositions of fluid in the retrograde skarn stage. The  $\delta^{18}\text{O}_{\text{fluid}}$  values for two quartz samples in the quartz-sulfide stage are 2.0 to 2.5‰. The country rocks of the Shuangqiaoshan Group and the marble from the Huanglong Formation have higher values in the range of 14.8 to 15.5‰ and 11.2 to 19.1‰, respectively. All these observations reveal that the formation of the W-Cu skarn deposit was dominated by a magmatic hydrothermal in the prograde skarn stage, and more meteoric water contributed to the formation of the later retrograde and quartz-sulfide stages.

Scheelites from the Zhuxi deposit show negative Eu anomalies in the prograde skarn stage but positive Eu anomalies in the retrograde skarn stage in the chondrite-normalized REE patterns. The variation of Eu anomalies recorded the ore-forming processes. Considering the closely spatial and temporal relationship between the mineralization and the three highly differentiated granites, we think the negative Eu anomalies were inherited from these granites and the positive ones from the more reduced ore-forming conditions. The scheelites from the Zhuxi deposit are characterized by low  $\epsilon_{\text{Nd}}(t)$  values ( $-7.0 \sim -10.1$ ) and high initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios ( $0.71231 \sim 0.72371$ ), which are different from those scheelites hosted in vein-type Au-W deposits. The Nd-Sr isotopes of scheelites are consistent with the results of the three Mesozoic granites, but the variable Nb/Ta ratios of scheelite indicate the Shuangqiaoshan Group also contributed to the ore-

forming fluids and metals. This is different from a commonly accepted model that the ore-forming fluids and metals were exsolved exclusively from the granite plutons.