## Composition and evolution of fluids forming the Baiyinnuo'er Zn-Pb skarn deposit in NE China

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The Baiyinnuo'er skarn deposit is one of the largest Zn-Pb deposits in northeastern China, with 32.74 Mt resources averaging 5.44% Zn, 2.02% Pb and 31.36 g/t Ag. The deposit formed in three stages: the pre-ore stage (prograde skarn minerals with minor magnetite), the syn-ore stage (sulfides and retrograde skarn minerals including calcite and quartz), and the post-ore stage (late calcite-dominated veins; cutting the above mineral assemblages). In this study we analyzed the composition of single fluid inclusions using laser ablation-inductively coupled plasma-mass spectrometry, to determine the composition of the fluids and the evolution through the stages, infer the fluid and metal sources and explore the metal deposition mechanisms.

The pre-ore fluids trapped in pyroxene have higher homogenization temperatures (432–504 °C), higher salinity (36.5–46.1 wt % NaCl equiv), and higher concentrations of Zn (~0.9 wt %), Pb (~1.4 wt %), and other elements than syn-ore mineralizing fluids (<370 °C, <10 wt % NaCl equiv, ~450 ppm Zn and ~290 ppm Pb). The post-ore fluids show lower temperatures (<250 °C) and a rather dilute composition (<4 wt % NaCl equiv, Zn ~33 ppm and Pb ~24 ppm). Geochemically, the fluids of all paragenetic stages in Baiyinnuo'er have magmatic signatures, which are distinctively different from basinal brines. Inclusion fluids in pre-ore stage show little variation in composition between ~510 °C and ~430 °C, indicative of a closed cooling system. In contrast, the major components of the syn- and post-ore fluids including Cl, Na and K decrease and correlate with a drop of homogenization temperatures from ~370 °C to ~200 °C, indicating a dilution by mixing with groundwater. The Baiyinnuo'er mineralizing fluids have higher Ca/K mass ratios (averaging ~0.78) than other proximal magmatic hydrothermal systems (0.06–0.52) but lower than that of the distal El Mochito skarn (averaging ~6.4), probably reflecting a gradually weakened magmatic signal away from the causative intrusions.

The metal contents in pre-ore fluids are significantly higher than those in syn-ore fluids, but no mineralization occurred. This confirms that the early fluids were, although enriched in metals, not responsible for ore precipitation, likely due to their high temperature and high salinity. One important factor controlling Zn-Pb mineralization was mixing with groundwater, which resulted in temperature decrease and dilution that significantly reduced the metal solubility, thereby promoting metal deposition. Another main driving force was the interaction with carbonate wallrock that buffered the acidity generated during the breakdown of Zn and (Pb)–Cl complexes and the precipitation of sulfides. Phase separation occurred in both the pre-ore and the early part of the syn-ore stages, but no evidence indicated that it caused metal deposition.

The prograde and retrograde minerals (including ore minerals) coexisting in the same samples could have been caused by two (or more) successive pulses of hydrothermal fluids released from residual melts of a progressively downward crystallizing magma. Each fluid produced a series of proximal high-temperature prograde to distal low-temperature assemblages, with the lower

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temperature assemblages of later fluids overprinting the higher temperature assemblages at most locations.