

Contamination of evaporite in the formation of magnetite-apatite deposits in Ningwu district, eastern China: Constraints from tourmaline geochemistry

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Over 30 iron-oxide-apatite deposits are hosted within the Cretaceous Ningwu volcanic basin, eastern China. Most of the ore bodies are located at the top of the diorite intrusions and/or along their contact zone with overlying equivalent volcanic rocks and subordinately sedimentary strata. The sources of ore fluids responsible for formation of these IOA deposits, however, have long been debated. Key models include a dominantly magmatic origin and significant involvement of evaporite-derived brines. Tourmaline boron isotope geochemistry provides an approach to discern the sources of ore fluids in IOA systems. The Taocun deposit is a typical IOA deposit in the central Ningwu district. Tourmaline is minor but widespread in this deposit. It formed in the four stages of mineralization and alteration, including pre-mineralization sodic alteration (stage I) in both volcanic rocks and intrusions, actinolite-magnetite mineralization (stage II), Ca alteration (Act, Ep, Chl etc., stage III), and waning quartz-sulfide or carbonate veins (stage IV).

All investigated tourmaline belongs to the alkali group and plot along the “oxy-dravite”-povondraite join with a kinked trend of Fe/Al ratios from stage I to stage IV. The obtained $\delta^{11}\text{B}$ values conducted by LA-MC-ICPMS show considerable variations from -6.3‰ to +5.4‰ (n=116), and display systematic differences among different samples or even within a single generation. The sample representing the extreme albitization yields the lowest values. Tourmaline from albitized trachyandesite with well-defined chemical zonation display noteworthy isotopic zonation. The cores give isotopic range similar to tourmaline from albitized diorite, whereas the rims show consistently higher values relative to corresponding cores. Tourmaline II from disseminated ores has overall range of $\delta^{11}\text{B}$ values from -0.7‰ to +1.2‰. Tourmaline III from the massive iron ores gives a slightly elevated but homogeneous range from +3.6‰ to +4.3‰. Finally, Tourmaline IV from the pyrite veins covers ranges of -5.7‰ to -2.7‰, showing significant shift from those of tourmaline from mineralized samples.

The formation temperatures for initial fluid are extremely high and have been estimated at 600-800°C according to fluids inclusion studies and isotopic equilibrium thermometer. Tourmaline I compositions therefore yield an inferred $\delta^{11}\text{B}$ values of the initial fluid of around -4.5‰. The variations of $\delta^{11}\text{B}$ values of tourmaline I from less albitized samples and tourmaline II can be ascribed to Rayleigh fractionation coupled with cooling. If assuming the ore fluids are initially constant, the elevated values of tourmaline III (approximately 300-440 °C) indicate that the fluids responsible for tourmaline III have notable deviation (~11‰) from the initial magmatic fluids, which is too large to be caused by Rayleigh fractionation alone. The simplest interpretation hence is that there was fluid mixing between magmatic fluids and externally cooler sulfate-rich fluid. Shift of B isotopes is contemporaneous with extensive magnetite precipitation. The B-isotopic composition of stage IV fluid is attributed to recharge of another pulse of

magmatic fluids. Our study highlights that evaporite or evaporate-derived brines were involved in the magmatic fluid system of IOA deposit.