

ISOTOPIC AND FLUID INCLUSION CONSTRAINS ON THE EVOLUTION OF HYDROTHERMAL FLUIDS IN THE BARRA DO ITAPIRAPUÃ CARBONATITE, SOUTHERN BRAZIL

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The Barra do Itapirapuã carbonatite belongs to the Cretaceous Ponta Grossa alkaline-carbonatitic province, related to the opening of the South Atlantic. The carbonatite is emplaced in the Proterozoic Três Córregos granite, and composed of plutonic magnesio- and ferrocarnatite, with smaller amounts of subvolcanic magnesiocarbonatite. The whole complex experienced extensive late- to post-magmatic hydrothermal alteration. Hydrothermally overprinted carbonatite contains cavities filled with a mineral assemblage of quartz, apatite, fluorite, RE-fluorocarbonates, barite, sulfides, and Fe-oxides.

Two types of overprinted carbonatites can be distinguished: type I containing quartz and RE-fluorocarbonates, enriched in LREE and with ΣREE of up to 3 wt %; and type II containing mainly apatite, and enriched in HREE. Their ε_{Nd} is non-radiogenic, indicating a carbonatite-related source for the REE mineralization. Distinct REE patterns in type I and type II overprinted carbonatite probably reflect differences in the stability of REE complexes. LREE form complexes preferentially with F and CO₃²⁻, while HREE form complexes with PO₄³⁻, the latter being stable at lower temperatures. With decreasing temperature, LREE complexes destabilize first to form the RE-fluorocarbonates (type I), followed by destabilization of HREE complexes (type II).

Coeval fluid inclusions in quartz present a wide range of densities, from high salinity aqueous inclusions to inclusions filled mostly with gas, indicating the existence of a two-phase hydrothermal fluid during quartz crystallization. Variation in filling composition causes a spread in homogenization temperatures (Th) from 100 to 340°C; decrepitation often follows homogenization of nahcolite, prior to total homogenization. Varying degrees of fillings may be related to boiling or post-entrapment necking-down. A sudden drop in pressure probably triggered boiling when the high-temperature fluid entered the corrosion cavities, with the pressure regime changing from lithospheric to hydrospheric. Boiling led to a decrease in temperature and a rise in pH, reducing REE solubility. Fluorite formed later than quartz, and its fluid inclusions have lower salinity and lower Th (~100°C), indicating a groundwater influx at the final hydrothermal stage.

δ³⁴S are negative for early-formed sulfides and positive for late-formed barite. Sulfides and sulfates from surrounding base-metal deposits hosted by Proterozoic marbles have positive δ³⁴S, precluding crustal contamination as an explanation for negative δ³⁴S in the carbonatite sulfides. The negative δ³⁴S values of the sulfides in the carbonatite indicate low crystallization temperatures at high fO₂, in hydrothermal rather than magmatic conditions, while S-isotope geothermometry for the pyrite-galena pair yield temperature of 250°C. The shift from negative δ³⁴S in sulfides to positive values in sulfate may be caused by H₂S loss during degassing and sulfide crystallization, both enhancing ³⁴S in the remaining solution.

According to our results, the mineralizing fluids comprised both residual magmatic and heated groundwater. The magmatic fluids were probably derived from deeper parts of the crystallizing magma chamber, and magmatic heat acted upon groundwater that eventually mixed with the residual magmatic fluid.