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Boron isotope systematic of marine hydrothermal fluids: new insights from the Lost City Hydrothermal System (MAR 30[•]N)

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Along mid-ocean ridges, seawater circulates through the oceanic lithosphere, exchanges mass and heat with the country rocks, and is finally expelled at hydrothermal vents as a high-T, chemically modified hydrothermal fluid. When vent fluids exit at the seafloor, their chemical and isotopic composition represents the net result of: 1) low-T water-rock interaction along the down-flow recharge zone; 2) high-T, water-rock interaction and fluid phase separation in the "reaction zone" at depth; and 3) additional high-T water-rock interactions when fluids rise to the seafloor along the discharge zone, with possible mixing with unaltered seawater at shallow levels within this zone.

Boron represents a useful element for tracing the complex water-rock interactions occurred along the hydrothermal path, owing to large differences in speciation, content and isotope composition between seawater and rocks that form the oceanic lithosphere. Seawater has a quite constant B concentration (4.5 ppm) and isotope composition ($\delta^{11}B_{sw}$ = 39.5 permil, while the oceanic crust and upper mantle typically have negative isotopic compositions (-10 to - 5 permil and very low B contents (0.05 to 2 ppm). In settings with a "classic" layered crustal architecture, seawater initially interacts at low-T with basalts and trigonally-coordinated boron in the fluid is partially removed by incorporation in phyllosilicate tetrahedral sites, resulting in significant isotope fractionation. Modelling of altered oceanic basalts indicates that the B con-

tent and δ^{11} B of the resulting fluids decrease down to 4.2 ppm and increase up to 45 permil respectively. Along its flow path, this altered fluid then gains B by quantitative leaching of basalt at high temperatures (>270°C) and very low water/rock ratios in the reaction zone, with negligible isotope fractionation. This simple mixing process between boron of seawater modified at low-T, and subsequent boron leached from MORB at higher T, elegantly explains a very regular array of data points in a δ^{11} B–B diagram, defined by fluids from the Pacific (i.e. fast-spreading ridges). However, hydrothermal fluids at slow-spreading ridges, such as the Mid-Atlantic Ridge (MAR), do not plot on the Pacific array and show systematically lower boron contents and isotope compositions.

Our study of the Lost City Hydrothermal Field (LCHF; MAR 30°N) provides new boron content and isotope data of fluids and brucite-carbonate hydrothermal deposits that shed light on better understanding B systematics of hydrothermal fluids. Endmember fluids at the ultramafic-hosted LCHF are characterised by a high pH (10-11), low T (55-90°C), $\delta^{11}B = 25$ permil and very low boron contents (0.34 ppm) and define the most extremely depleted composition among the MAR hydrothermal fluids. At these pH and T conditions, most of the B is tetrahedrally coordinated in the fluid and only precipitation of a mineral containing trigonal boron can explain the observed isotope fractionation and boron depletion. Our chemical, isotopic and ¹¹B MAS NMR study of brucite-carbonate deposits sampled in the serpentinite substratum of the LCHF indicates that brucite is an efficient sink for B (up to 140 ppm) with a δ^{11} B higher than seawater (up to 53 permil, and incorporates B as a dominantly trigonal species (up to 90%).

The LCHF fluids can thus be regarded as a low-T, end-member fluid composition representative of slow- and ultraslow-spreading ridge environments that are characterised by a heterogeneous architecture with varying proportions of ultramafic and mafic rocks. We propose that the systematically lower B contents and isotope compositions typical of MAR hydrothermal fluids reflect variable reaction with mafic and ultramafic rocks along its flow path at varying temperatures, and the key role of brucite in the boron geochemical cycle of ultramafic-hosted marine hydrothermal systems. These differences in the boron geochemical cycle at slow- and fast-spreading ridges can have strong implications for the secular variations of boron and δ^{11} B of the oceans.