Boron in onshore mud volcanoes: from clay to borate deposit

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Onshore mud volcanoes (MVs) of the Kerch Peninsula (the Caucasus collision zone) emit water and mud with abnormally high B enrichment: 105 to 232 relative to sea water in fluids and up to 6.1 relative to the Oligo-Miocene Maykop source rocks in mud. At the Bulganak MV field, there is a unique accumulation of MV-related non-marine Na borates. B-enrichment of the parent shale and diagenetically-driven smectite illitization and dewatering seems to be main prerequisites for the profound B anomalies. Boron content correlates with the source rocks burial depth and clay mineralogy to be highest (up to ~900-1500 ppm) in illite-domitated mud from large MVs which represent deep endmembers in the Kerch Peninsula (up to 3.5 km). Smectite-dominated mud extruded by small MVs from shallower depths (1-1.5 km) contains 66-250 ppm B. The MV waters of the region have pH = 7.5–9.5 and a HCO_3-Cl/Na and Cl-HCO_3/Na chemistry. Aqueous fluids emitted by large MVs are enriched in ^{18}O (+9.8 to +14.5 ‰ VSMOW) and D (-30 to -4 ‰ VSMOW) isotopes being also rich in boron (average 650 ppm). Waters of small MVs with shallow roots are poorer in both $\delta^{18}O$ (+3.6 to + 6.1 ‰) and B (average 130 ppm). MV aqueous fluids are mainly related to diagenatically altered basinal water diluted by ^{18}O-enriched fresh water released during smectite illitization. The fluid generation temperatures inferred to be $T_{Mg/Li}$ = 34-75°C (small MVs) and 84-117°C (large MVs). Evaporation of MV waters leads to accumulation of Li and B in residual brines with pH > 9 due to stability of Na tetraborates and high solubility of Li salts. The process ends up with crystallization of ulexite, borax, and tincalconite, as well as with Li accumulation in halite-calcite precipitates. The following conditions are essential for the formation of MV-related borate deposits: venting of B-rich MV waters; environment akin to playa lakes; evaporation and ensuing increased boron concentration in shallow close MV pools sourced from the issues of large and deeply rooted MVs; low permeability of mud cover. *The study was supported by the Russian Science Foundation, grant 17-17-01056.*