

## Trace element enrichment of Bigadiç Borates deposits, Balıkesir, Türkiye

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In this study, trace element geochemistry of Bigadiç (Balıkesir, Turkey) borates deposits which are the largest colemanite and ulexite deposits in the world, is investigated. The known borate deposits of Turkey were deposited in the lacustrine environment during Miocene when the volcanic activity occurred since Tertiary to Quaternary. All of the Turkish borate deposits are classified as volcanic related deposits. Borat minerals formed in two zones. Tülü and Acep-Simav open mines represented lower borates zone and upper borate zone, respectively (Özpeker, 1969 and Helvacı, 1995).

All samples had analyzed with ICP-MS by ACME analytical laboratories. Trace element contents of colemanites and ulexites were compared with their abundances in earth crust (Krauskopf, 1989), andesite (Schroll, 1975) and freshwater (Abollino *et al.*, 2004). With respect to averages of earth crust and andesite, Li (6,20–6,21 times), Mo (1,93–3,21 times), As (6,56–6,22 times), Sr (17,41–8,16 times) and Se (656,55–656,55 times) are significantly enriched in the Tülü. Li (3,73–3,73 times), Mo (1,80–3,00 times), As (5,61–5,32 times), Sr (24,84–11,64 times) and Se (733,75–733,75 times) are enriched in Simav. In the other hand, the trace elements in Acep samples are enriched as Li (8,88–8,88 times), As (5,40–5,12 times), Sr (10,19–4,77 times) and Se (435,17–435,17 times). Based on freshwater averages were determined to significant increases in all trace elements. Samples show to increase that Tülü are Se (328272,7 times), Sr (130628 times), As (5911,4 times), Li (124154,5 times), Mo (2894,5 times); Acep are Se (217583,3 times), Sr (76392,8 times), As (4862,5 times), Li (177600 times), Mo (506,7 times) and Simav are Se (366875 times), Sr (186360 times), As (5056,25 times), Li (74600 times), Mo (2707 times).

Se is significantly enriched in Bigadiç borates. Sr can be accumulated in volatile-rich solutions (e.g. Cl, F and B) following the solidification of magma, Se together with Ag, Au, As, Sb and Hg might be enriched in epithermal stage and Li is enriched in last stages of magmatic differentiation. Therefore, these elements are thought to be added to the environment in last stages of magmatic differentiation particularly hydrothermal stage.

## Diffusive controls and thermodynamic constraints on reductive biogeochemical reactions

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For any favorable biogeochemical reaction in soils and sediments, microorganisms exploit thermodynamic disequilibrium; as a community, they are generally noted to select and deplete electron acceptors that yield the greatest energy return until the next acceptor becomes more favorable. This usual pattern is often apparent in, or at least perceived for, soils and sediments transitioning from aerobic to anaerobic conditions, leading to progressive reduction of O<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, Fe(III), SO<sub>4</sub><sup>2-</sup>, and CO<sub>2</sub>. For successive electron acceptors, however, variations in reactant/product concentration gradients, as well as speciation, can result in conditions which may alter the expected electron flow (i.e., utilization and depletion of an electron acceptor). Owing to the physical heterogeneity of most natural systems, extreme concentration gradients can be established within diffusively controlled domains that thus alter the expected redox sequence and leads to microscale variation in operative biogeochemical processes.

Iron(III) minerals impart a particularly important variable to the thermodynamic favorability of anaerobic electron acceptors: their redox potentials vary appreciably. Here we provide a detailed account of their thermodynamic variability for anaerobic soils and sediments, revealing the expected preference of electron acceptors—results not always consistent with commonly presumed redox ladders. In support of the thermodynamic analysis, we conducted experiments utilizing reaction cells designed to mimic the interface between diffusive and advective domains within structured soil/sediment media. Diffusive domains were packed with ferrihydrite or hematite-coated gibbsite inoculated with a microbial community collected from a California (USA) rice paddy (capable of Fe(III)<sub>(s)</sub>, SO<sub>4</sub><sup>2-</sup> and CO<sub>2</sub> reduction) and overlain with an advective flow channel consisting of quartz sand. Flow of artificial groundwater containing lactate and acetate was then initiated in the advective domain. Our results demonstrate that the segregation of biogeochemical processes within diffusive domains is highly dependent on the thermodynamic favorability of the Fe (hydr)oxide present, and that thermodynamic disequilibrium results in the co-occurrence of sulfate reduction, methanogenesis, and reduction of hematite.