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Structural-controlled isotopic fractionation during sorption of boron onto humic acids and oxides (Fe - Mn)

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Boron isotopes have been widely used in the last decade to constrain surface processes such as continental silicates weathering, or past ocean pH variations. Their uses are based on boron isotopic fractionation during water/rock interactions, such as adsorption and coprecipitation. It is now well established that the light isotope (^{10}B) is preferentially uptake by solids, whereas the solutions are enriched in heavy isotope (^{11}B). However, the exact mechanisms that control this isotopic fractionation are poorly known. In this study, we performed boron sorption experiments to investigate the relationship between boron isotopic fractionation and the steric structures of its surface complexes. Boron was adsorbed at the surface of three well-characterized solids: a flocculated humic acid, a synthetic goethite (Sikovit 10E172) and a home-synthesized birnessite. Adsorption partition coefficients and isotopic fractionation factors were determined as function of pH. The structures of surface complexes were determined via ^{11}B NMR and DRIFT spectroscopy and adsorption curves were modelled in the framework of surface complexation models. Finally, isotopic fractionation variations with pH were used to calculate isotopic compositions of each B surface complex which then were related to steric parameters.

Our experimental results show that boron is strongly complexed at the surface of the studied solids, with a maximum of the partition coefficient (Kd = $[B]_{adsorbed}/[B]_{solution})$ nearly equal to 40 between pH 8 to 10. This adsorption in-

duces an isotopic fractionation at low pH, with the light isotope (^{10}B) enriched at the surface of solids relative to the solution (Δ^{11}B = (^{11}B/^{10}B)$_{solid}$-(^{11}B/^{10}B)$_{solution}$ = -45 per mil for goethite, -16 per mil for birnessite, and -25 per mil for humic acid). Moreover, the isotopic fractionation decreases with increasing pH: it is equal to zero at pH $>$10 for adsorption at the surface of humic acid and goethite, whereas in the case of the adsorption at the surface of birnessite, an ^{11}B enrichment of adsorbed boron is observed at pH$>$10 with Δ^{11}B = +23 per mil at pH =11.

The comparison between B surface speciation models, determined structures and calculated isotopic compositions of B surface complexes showed that boron isotopic fractionation during adsorption strongly depends of the steric strains applied on surfacic boron. Actually, the higher isotopic fractionations are observed when adsorbed boron is strongly distorted (OBO angle is higher than in solute boron complexes).

Then, our results show that i) an important ^{11}B enrichment is expected in waters in equilibrium with organic matter and iron or manganese oxides and ii) this enrichment is a function of pH (that modifies boron speciation in solution and at solid surfaces). Boron adsorption in soils could thus induce an important increase of boron isotopic composition of continental waters. Moreover, in ocean, adsorption on oxide surfaces and on organic rich sediments appears to be an important process affecting the boron marine cycle.