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An isotopic view of rapid exchange reaction and long-term weathering: investigation of reaction pathways and time of water and solutes transfer

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The chemistry of surface and ground waters witnesses chemical reactions that occur at their contact with hosting rocks. The nature and abundance of elements dissolved in continental waters, and sometime their isotopes, are then classicaly used to identify the chemical reactions that occur during rock weathering and the rate at which minerals dissolve or precipitate. Because these reactions are relatively slow they control the water quality over long time scales usualy overpasing time of observation and more generaly reflecting the nature of rocks in contact with water at conditions close to steady state. However, dissolved elements also interact with a very large and reactive pool resulting from complexation reactions occuring at the solid/solution surface. This pool can be one or two orders of magnitude larger in size than the dissolved one and because the complexation reactions are fast, they can drastically and rapidly modify the chemical signature of the dissolved load. Counter-intuitively, the development of mathematical models demonstrates that this rapid exchangeable pool only impacts the water quality in case the rock/system is out of a steady state and, inversely, becomes invisible once the conditions are stable on a period of time long enough to ensure equilibrium. Then, the ion complexation reactions only act as a retardation factor that delays the propagation of a perturbation through a system. In particular, if the water chemistry has changed after modification of the water sources or the weathering

regime, the perturbation immediately affects the exchangeable pool and propagates through the system at a speed depending on the water velocity and the reactivity of elements.

We chose to use boron isotopes to investigate the water/rock interactions because it is mainly released by weathering of silicate rocks and because its adsorption onto mineral surfaces leads to an important isotopic fractionation that can be easily identified. Moreover its partition coefficient between solid and water (5-20 L/kg) is large enough to make significant the fluxes related to adsorption/desorption but is also small enough to not freeze the chemical composition of the system during a loo long period of time. We applied this B isotopic approach to systems of various sizes: from the Mackenzie basin, to a coal bed aquifer in Wyoming and to the top meter of a forest soil. It is then found that the B isotopes are always suitable for investigation of the reactions that affects the water chemistry and to give insights on the time scales over which these reactions occur (melting of the permafrost, pH dependant reaction and biological seasonal activity, respectively).