

## **Vegetation regulates dissolved B in forested watershed**

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The mechanisms by which the vegetation influences geochemical fluxes at the catchment scale remain difficult to describe because of a lack of knowledge on their links and feedbacks. In particular, it is still a question to know at what level the nature of the vegetal cover can regulate the river water chemistry or influence the reactivity of soil horizons.

To address these points, we have conducted a comprehensive study of B isotopes in a small-forested watershed (Strengbach, NE France). Water was sampled along the hydrological pathways from rainwaters down to springs via throughfalls and soil solutions in two distinct parcels covered by spruces and beeches.

It comes out that the amount of B yearly cycled by vegetation is about twice the amount of B exported out of the basin. This demonstrates that the biological activity is the key factor that regulates the B geochemical cycle in forested area. Moreover, the B isotopic signature of the vegetation is enriched in <sup>11</sup>B far from any other reservoirs. These two features make B a highly reliable and easy-to-follow element for investigating the mechanisms of geochemical transfert that involve the vegetation cycle.

In soil solutions, there is an exponential-like decrease of the [B] indicating that B mostly originates from throughfalls. Associated with the isotopic analyses, the behavior of B primarily reflects the reactivity of soil horizons in terms of ion exchange intensity. At depth greater than 60 cm, soils developed under spruces and beeches show distinct isotopic composition, each fingerprinting the corresponding spring water. It then strongly suggests that the nature of the vegetal cover directly influences the reactivity of the soil from which it grows and then drives the B isotopic composition of the sub-surface waters.

Overall, this study demonstrates that the geochemical cycle of B isotopes in forested catchment is controlled by vegetation cycling and that B can be used for closer investigation of the relative impact of the biosphere on the mass transfert at regional scale.

## **Sulfate, methane, and the rise in atmospheric oxygen**

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Using two distinct numerical models, we have developed a conceptual picture that implicates sulfate as a key player in ushering in the late Archean global ice age and ultimately leading to complex-life sustaining levels of atmospheric oxygen. We attempt to provide a theoretical framework for understanding the Archean records of increasing mass-dependent sulfur isotope fractionation ( $\delta^{34}\text{S}$ ) concurrent with a decrease in the mass-independent signal  $\Delta^{33}\text{S}$  (MIF-S). Increasing  $\delta^{34}\text{S}$  is commonly linked to increasing oceanic sulfate availability. First, we describe results from a global redox box model which investigates how slight increases in oceanic sulfate concentration could affect anaerobic methanotrophy in the Archean/Proterozoic biosphere. We show that this metabolism enhances a positive feedback on the atmospheric destruction of methane by oxygen, by acting as a throttle for methane fluxes from the seafloor. We next describe results from a 1-D photochemical model which is used to explore the transition between weakly reduced and weakly oxidizing atmospheres. We show that the disappearance of MIF-S is better explained by a decline in atmospheric methane levels, rather than by a rise in oxygen levels. Increasing oceanic sulfate thus hastens a collapse in atmospheric methane to below 10 ppm, which halts the MIF-S signal. These conditions can lead to a global ice age, and are favorable for increasing amounts of free oxygen in the atmosphere. Oxygen levels and climate stabilize in the early Proterozoic once sufficient ozone forms to allow methane to re-rise to levels of approximately 100 ppm.

### **References**

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