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## Boron isotope characterization to design a frame of hydrogeological functioning of a wetland system (Massif Central, France)

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### Abstract

Multi-isotopic approaches (Li, Sr, O, H), combined with hydrological tools, have been already applied for tracing the water and dissolved-element fluxes in a peatland in Central France. Here, we applied B isotopes. The  $\delta^{11}\text{B}$  ratios increase from river draining basalts ( $\sim 0\text{‰}$ ) up to springs bordering the peatland ( $> +25\text{‰}$ ). Peatland groundwaters have intermediate  $\delta^{11}\text{B}$ : 7.8 to 19.4‰. This range is accompanied by an increase in the Ca contents between the river draining basalts and water in the peatland. In a  $\delta^{11}\text{B}$  vs. Ca/B diagram, the role of water rock interaction and present day fertilizer inputs is evidenced, as for Sr isotopes.

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*Keywords:* peat land; groundwater; B isotopes; Massif Central

### 1. Introduction

Lands that are seasonally or permanently covered by shallow water, including lands where the water table is at or close to the surface are considered as wetlands. Among the different types, marshes, swamps, bogs, fens, and shallow open waters are the most common ones. The presence of abundant water causes the formation of hydric soils and favors the dominance of water-tolerant plants. Even if considerable scientific knowledge and technical experience have been gained in the diverse aspects of wetland science and management including hydrology, biogeochemistry, ecology, socio-economic valuation and policy analysis, the results of research and management experience were still often too fragmentary and not sufficiently orientated to problem-solving. As the main water fluxes involved in the water status of wetlands are rainwater input, surface run-off, evapotranspiration, input/output

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of stream water, and input/output of groundwater<sup>1</sup>, this means that hydrology is the most important factor in establishing and maintaining wetlands, as the storage capacity of a wetland plays an important role in the dynamics and water balance of such ecosystems

Peat land ecosystems generally correspond to wetlands where an organic production excess can accumulate as peat due to low-energy conditions. The Narces de la Sauvetat peat land (Fig.1), located in the French Massif Central, which is the main volcanic province in France, occupies a maar depression with lapilli tuff deposited on the flanks. Recent coring showed around 6 m of peat deposits in the site and revealed the heterogeneity of the peat in the maar. The limit between the saturated and unsaturated zones lies around -1.5 m in piezometer well Q1 and -0.5 m in piezometer Q2, and the aquifer is unconfined. The Narces de la Sauvetat is drained by a small stream, which represents the outlet of the area. Several diffusive springs occur around the maar but most of them emerge on the western side, reflecting the basal level of a basaltic aquifer<sup>2,3</sup>.

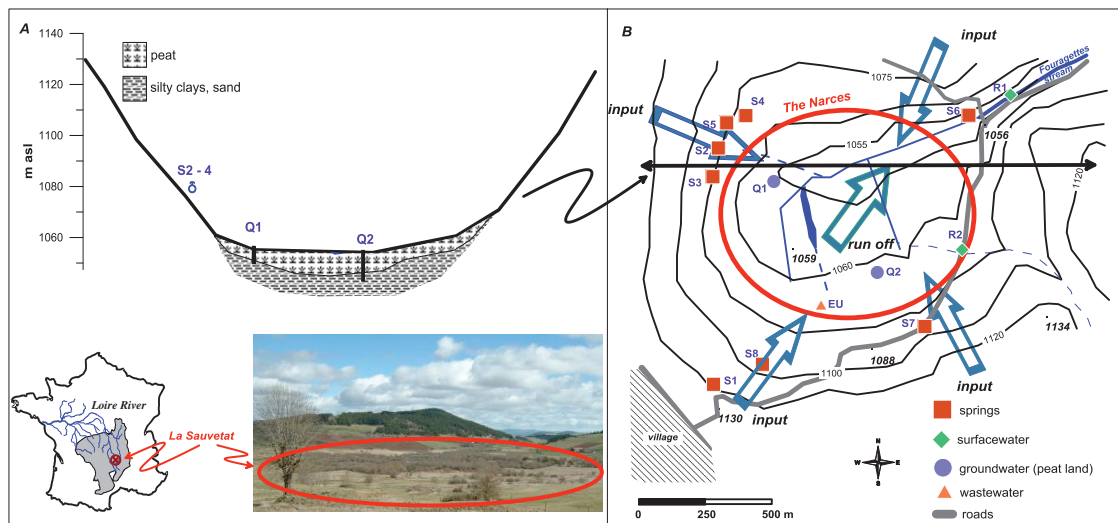


Fig. 1. From ref. 2. (a) Location of the Narces de la Sauvetat peat land in the Massif Central (France), cross section in the peat land with the two boreholes locations (vertical axis not at scale for the peatland), (b) topographic map of the peatland with location of boreholes springs and surface water identified on the site and illustration of flowpaths,

Studies conducted worldwide showed the diversity and complexity of the hydrological processes involved in these ecosystems<sup>4</sup>. Over the past decades, geochemical investigations of peat lands mostly focused on trace- and major-metal concentrations in peat profiles for investigating nutrient cycling, atmospheric input, pollution and the influence of vegetation on wetlands<sup>5</sup>. More recently, isotopes of the water molecule and/or isotopes of solutes within the water were introduced to better constrain the water status and hydrological functioning of wetland ecosystems<sup>2,3</sup>. In the Narces de la Sauvetat peat land we used chemical and multi-isotopic (Li, Sr, O, H) effectiveness approaches, combined with hydrological tools, for tracing the water and dissolved-element fluxes in a peat land in Central France<sup>2,3</sup>. In the present study, we applied B isotopes in the same site in order to provide a complementary view for confirming the different origin of dissolved elements and water involved in the water balance of the peat land.

## 2. Upshot of strontium and lithium isotopes

Brenot et al.<sup>3</sup> suggested the influence of three end-members using the Sr isotope systematics, in combination with cation ratios. It is worth noting that the use of a Ca/Na ratio rather than absolute concentrations alone avoids variations due to dilution or concentration effects. In addition, the <sup>87</sup>Sr/<sup>86</sup>Sr isotopes may help to better constrain the end-members. Three mixing lines can be calculated between three end-members as illustrated in Fig. 2a. The first end-member corresponds to Sr inputs from rainwater contribution modified after run-off. The second end-member corresponds to Sr released from water/rock interactions with lithology expected to be local basaltic rocks. The last

end-member requires a high molar Ca/Na ratio (close to 12) and high  $^{87}\text{Sr}/^{86}\text{Sr}$  ( $>0.708$ ), which are in the range of expected values for carbonate weathering. However, as no carbonate outcrops are evidenced in the area, the unique possible source for such ratios is the carbonate amendments used in local agriculture. The main results are that at least three strong groundwater fluxes with distinct chemical and isotopic signatures supply water to the peat land (regarding Sr isotopes) and water volume flowing out is almost negligible.

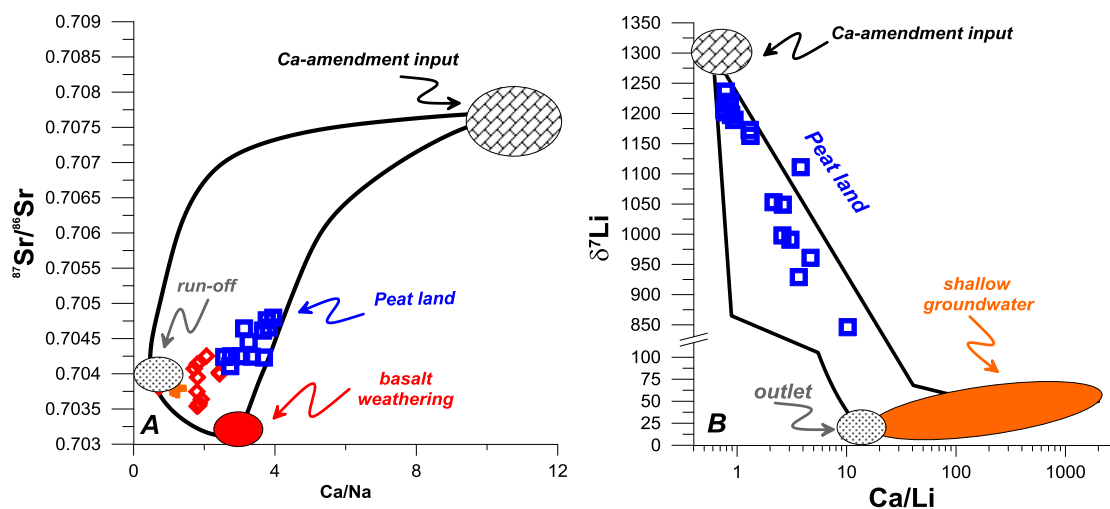


Fig. 2. (a) From Brenot et al.<sup>3</sup>,  $^{87}\text{Sr}/^{86}\text{Sr}$  versus Ca/Na diagram. The three calculated mixing lines between three end-members are represented, including i) the rainwater after run-off ( $^{87}\text{Sr}/^{86}\text{Sr}$  around 0.704 and Ca/Na ratio close to 1), ii) an end-member with very low  $^{87}\text{Sr}/^{86}\text{Sr}$  and Ca/Na ratios corresponding to water/rock interactions with basaltic rocks and iii) an end-member with high  $^{87}\text{Sr}/^{86}\text{Sr}$  and Ca/Na ratios, corresponding to carbonate amendments from agriculture; (b) From Négrel et al.<sup>2</sup>,  $\delta^7\text{Li}$  versus Ca/Li ratios for groundwater from the peat land. Shallow groundwater and surface water at the outlet are represented. One end-member corresponds to the carbonate amendment input. Its location on the graph is assumed to represent the required Ca/Li and Li isotope ratios to take all data into account. Two different mixing lines can be calculated between this end-member, representing the application of carbonate amendment, and two shallow groundwater end-members. Blue squares are the groundwater from the peatland, red diamonds are the springwater around the peatland.

Négrel et al.<sup>2</sup> discussed Li and  $\delta^7\text{Li}$ . They evidenced that low Ca and Li contents are observed for the stream at the outlet whereas, on the contrary, higher Li-Ca contents are observed for groundwater in the peat land, with a significant relationship for Q2 between Li and Ca. The Li-Ca relationship in Q2 groundwater shows low contents for the winter and spring samples and high ones for the summer samples. This indicates the existence of a common source for Li-Ca in the Q1 and Q2 groundwaters, this source being more marked during the summer season. The other spring- and waste-waters have low Li contents with similar Ca contents. Variations in  $\delta^7\text{Li}$  values can be used to distinguish between precipitation, groundwater and anthropogenic inputs in peat lands, providing a unique perspective on the hydrologic dynamics of the system. The primary finding evidenced by Négrel et al.<sup>2</sup> concerned the existence of hugely enriched values for  $\delta^7\text{Li}$  in groundwater from the peat land. Li contents fluctuate significantly and  $\delta^7\text{Li}$  (‰) are extremely variable reaching values up to +1226‰. This high values, never being observed in waters, being explained by an external input due to Ca-amendment, used in local agriculture (Fig. 2). Mixing relationships (Fig. 2b between the  $\delta^7\text{Li}$  and the Ca/Li ratios) indicate that most of the water in the peat land site derives from groundwater from the hill slope. Mixing plots also show that the surface water at the outlet seems to be only controlled by input from other groundwater bodies and strongly suggests that groundwater in the peat land does not play any role in supplying surface-water runoff and may evolve as a stagnant system, being only diluted as the Li contents show.

### 3. New insights from Boron isotopes

The  $\delta^{11}\text{B}$  (‰) shows values increasing from river draining basalts (around 0‰) up to springs bordering the peat land ( $> +25\text{‰}$ ). Peat land groundwaters have intermediate  $\delta^{11}\text{B}$  values from +7.8 to +19.4‰. This range is accompanied by an increase in the Ca contents between the river draining basalts (around 150  $\mu\text{mol/kg}$  Ca) and water in the peat land (300-1150  $\mu\text{mol/kg}$  Ca). Comparing the  $\delta^{11}\text{B}$  with the B contents, the data highlight the role of water rock interaction and present day fertilizer inputs as Sr isotopes did. Reported as  $\delta^{11}\text{B}$  vs. Ca/B ratios (Fig. 3a), the data also highlight the role of water rock interaction and present day fertilizer inputs (as manure form) but discard the role of Ca-amendment on the B isotope systematics as defined by Li-isotopes. Cross interpretation of  $\delta^{11}\text{B}$  and  $\delta^7\text{Li}^2$  (Fig. 3b) confirms the role of water rock interaction and present day fertilizer inputs in the stream and in the springs bordering the peat land. The extremely enriched  $^7\text{Li}$  signature of the groundwaters cannot be explained by an input due to present day Ca-amendment, used in local agriculture, the shift of the  $\delta^{11}\text{B}$  suggests that Li-isotopes possibly trace “old” Ca-fertilizers addition.

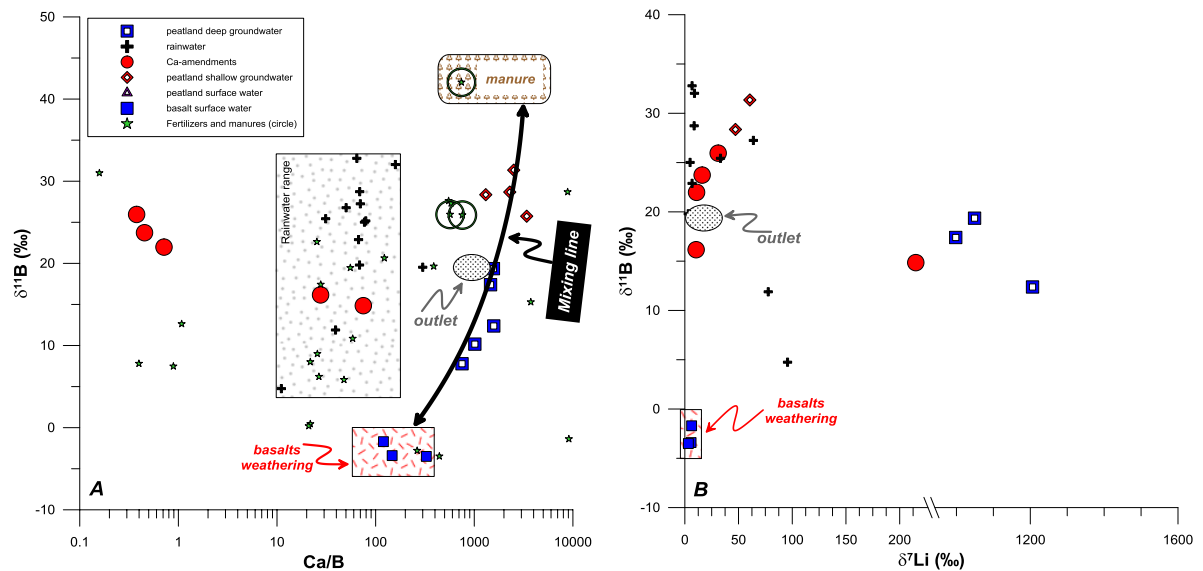


Fig. 3. (a)  $\delta^{11}\text{B}$  versus Ca/B ratios for groundwater from the peat land. Shallow groundwater and surface water at the outlet are represented; (b) Cross plot of  $\delta^{11}\text{B}$  and  $\delta^7\text{Li}^2$ , note that no  $\delta^7\text{Li}$  data are available for the manure.

### 4. Summary

The combination of the results of the present study with previous investigations (O, H, Sr, Li)<sup>2,3</sup> demonstrated a new field for B-Li isotope investigations in hydrosystems –to be further tested- and their potential utility as tracers of present-day versus past activities and concluded upon the present water status of the peat land (e.g., the water flow out of the peat land through the stream is negligible, the hydro-reservoir signatures (e.g., at least three water fluxes), and clarified the role of the human activities.

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