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Boron isotope fractionation in soils at Shale Hills CZO

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Abstract

Isotope fractionation of many elements can fingerprint the biogeochemical, weathering and erosion processes that govern the evolution of the Critical Zone (CZ). This study investigates boron isotope fractionation in two soil profiles developed on the same shale bedrock at Shale Hills Critical Zone Observatory. The first soil profile, located at the valley floor, is isotopically similar to the bedrock and appears to have lost boron mostly through the loss of fine particles matter (clays) with no isotopic fractionation. The second soil profile, located at the ridge top appears to be more depleted in boron concentration and isotopically fractionated toward lower values, as expected from mineral dissolution followed by adsorption/co-precipitation processes.

Keywords: boron isotopes; Shale Hills; critical zone; weathering

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1. Introduction

The Susquehanna Shale Hills Critical Zone Observatory (SSHCZO) is a small mono-lithological catchment where the use of multiple isotope proxies (e.g. Fe, U-series, Be, Mg and Li isotopes) aims at understanding the weathering and other geobiological and hydrological processes occurring in the Critical Zone. For this purpose, boron (B) is a promising tracer of weathering and vegetation cycling. Boron is solubilized during water-rock interaction (as indicated by its enrichment in the dissolved load of rivers) and its isotope ratio is thought to be highly fractionated upon incorporation into clay minerals. Upon reincorporation in secondary mineral, the light isotope is

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favoured, leaving a solution enriched in ^{11}B [1]. As an essential micronutrient, boron is also enriched in the vegetation and biogeochemically cycled. Although not much is known on the isotopic behaviour of boron in vegetation, recent measurements showed that the B isotope ratio of leaves and needles are usually fractionated toward heavy values [2]. In the present study, we investigated the boron concentration and isotopic ratio in two soil profiles developed on a Rose Hill formation (shale) bedrock. To understand boron behaviour during shale weathering, soil production and lateral transport along hillslopes, two soil profiles located on the ridge top and in the valley floor were investigated (reference [3] for description of the samples).

2. Samples and method

The Shale Hills CZO is a ~7.9 ha V-shaped forested catchment in central Pennsylvania. Oriented east-to-west, the catchment is bisected by a first-order ephemeral stream, and underlain by a thick unit of the Rose Hill shale formation (Clinton group). Illite, "chlorite" and quartz are the dominant minerals in the shale [3]. The term "chlorite" is used because X-ray diffraction patterns indicate that several minerals may be present, including true chlorite, as well as vermiculited chlorite [3]. Approximately 54 m in elevation separate the stream outlet from the highest ridge top point.

The two soil profiles are located along a south planar hillslope transect of the catchment with one profile from the respective ridge top (SPRT) and valley floor (SPVF) positions. All samples here, except DC1-36, were derived from the original samples of the same name described in [3]. Soil samples were collected in 10cm intervals from the surface until the depth of hand auger refusal. The zero point was defined as the interface between the mineral and organic soils. Unaltered parent material is estimated from the average composition of three bedrock samples from a 25 m-deep drill core (DC1) on the northern ridge of the catchment [3]. In the DC1 borehole, the deepest reactions observed are pyrite oxidative dissolution and ankerite dissolution, both occuring below 22 m depth. Two of the bedrock parent samples derive from above this depth while one sample, DC1-38, derives from deeper than 23 m; thus, this sample is a sample of the parent material that still contains pyrite and ankerite. Above 22 m, neither pyrite nor carbonate minerals are generally observed in the ridge top core [4].

Major elements and Zr concentrations of the bedrock samples and from the two soil profiles were previously analyzed by ICP-OES and ICP-MS (detailed description of the soils and bedrock composition can be found in [3,5]). Boron isotope ratios (δ^{11}B) and concentration in the bulk soils were measured by MC-ICP-MS using d-Dihen direct injection nebulization [6] after K_2CO_3 alkali fusion and extraction with ion-exchange chromatography. Reproducibility and accuracy were evaluated by repeated measurements on the JB-2 basalt reference material. We found δ^{11}B=7.1±0.6‰ (2 s.d.) after 12 distinct boron extractions, consistent with previous estimates for JB-2 (e.g. 6.83±0.52‰ [7]). The average boron concentration was 28±5 ppm (2s.d.), consistent with the recommended value of 30.2 ppm.

3. Results and discussion

3.1. Boron concentration and isotope ratio

Table 1. Boron isotope ratios and concentrations for soils and bedrock at Shale Hills.

Type	Name	IGSN	Depth (cm)	δ^{11}B	2σ (‰)	[B] (ppm)
Soil	SPRT 00-10	SSH00001Q	0-10	-5.5	0.6	41
Soil	SPRT 10-20	SSH00001R	10-20	-5.2	0.6	43
Soil	SPRT 20-30	SSH00001S	20-30	-5.9	0.6	41
Soil	SPVF 0-10	SSH00001J	0-10	-4.2	0.1	59
Soil	SPVF 10-20	SSH00001K	10-20	-4.6	0.5	74
Soil	SPVF 30-40	SSH00001M	30-40	-4.6	0.8	71
Soil	SPVF 50-60	SSH000024	50-60	-4.9	1.1	73
Soil	SPVF 60-67	SSH000025	60-67	-4.4	0.1	87
Bedrock	DC1-26	SSH000SW4	6.1-6.3 m	-4.4	0.8	88
Bedrock	DC1-36	SSH000SWE	21.3-21.5 m	-4.5	0.6	89
Bedrock	DC1-38	SSH000SWG	24.4-24.5 m	-4.7	0.6	37

Boron concentrations range from 41 to 43 ppm in the ridge top soil profiles (SPRT) and from 59 to 87 ppm in the valley floor profile (SPVF). In the ridge top soils, no significant change in concentration with depth is observed while in the valley floor soil the concentration increases from top to bottom reaching a concentration similar to the shale bedrock (Table 1).

The δ^{11}B values are homogeneous in all three bedrock samples (-4.5±0.2‰) despite the lower B concentration observed in the deepest sample that contains ankerite and pyrite (DC1-38, Table 1). Due to its high carbonate content [4] this sample was discarded from the average bedrock composition, since it is known that all ankerite has been depleted in layers under the ridge above 22 m by weathering [4]. The soil isotopic ratios are homogenous with depth on both the ridge top and valley floor (Fig.1) despite the variations in concentrations. At the ridge top, the average boron isotopic ratios (-5.5±0.4‰) are significantly depleted compared to the bedrock, while at the valley floor they are similar (-4.5±0.3‰ in average) to the bedrock value.

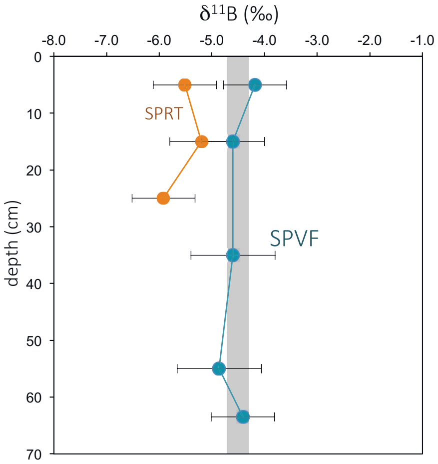

Fig. 1. δ^{11}B in the two soil profiles and bedrock (grey area).

3.2. Boron depletion profile

To correct for changes in concentration due to overall loss or gain of elements in the soils relative the parent material, the mass transfer coefficient $\tau_{Zr,X}$ is calculated (equation 1):

$$\tau_{Zr,X} = \frac{[X]_{soil}}{[X]_{bedrock}} \times \frac{[Zr]_{bedrock}}{[Zr]_{soil}} - 1 \quad (1)$$

where [X] represents the concentration of the mobile element of interest and [Zr] the known immobile element concentration. A value of -1 indicates 100% depletion of a given mobile element compared to Zr in the parent material.

Boron is depleted ($\tau_{Zr,B} < 0$) compared to the bedrock in both soil profiles (Fig. 2). In the SPVF profile, the extent of boron depletion is similar to the depletion patterns of other major elements such as Al, Fe, Mg and K (see also [3]). The correlation of the B/Zr ratios to Al/Zr, Fe/Zr, Mg/Zr and K/Zr ratio (Fig 2 and Fig. 3) is consistent with a mechanism for boron depletion that is the same as that depleting Al, Fe, Mg and K. This indicates that boron is lost concomitantly with these elements known for being representative of clay minerals. Two hypotheses have been previously proposed for loss of these elements, which may also explain B:

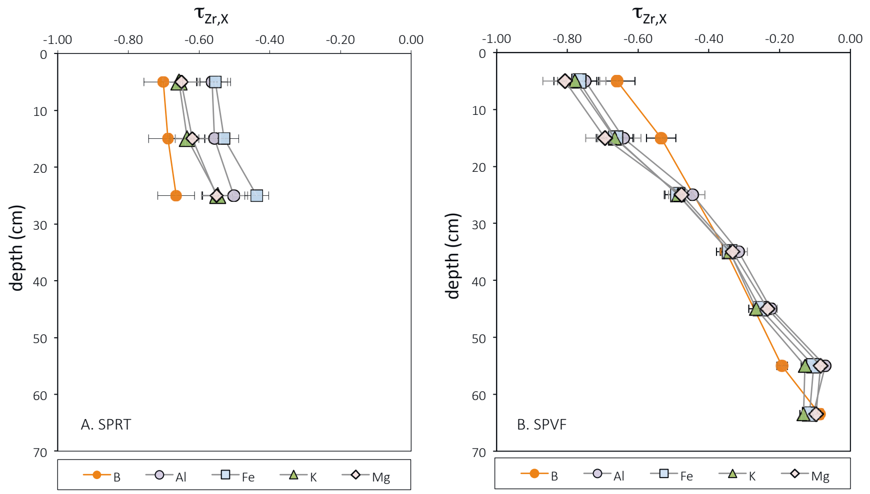

Fig. 2. Depletion factor (expressed as tau values calculated using Zr as immobile element) for major elements (data from [2,4]) and boron (this study) as a function of depth in the SPRT soil profile (A) and the SPVF soil profile (B).

- the first one is a congruent dissolution of clays minerals from the bedrock. In this case, the clays fraction would decrease from depth to the surface causing both B and Al (and Mg, Fe, K) depletion and the observed relative enrichment of Zr, an element found in the unweatherable mineral zircon [3]. As pointed out by Jin et al. [3], however, the low dissolved Al (and Fe) concentrations in the river and the high dissolved K/Al, Mg/Al ratios in the river solutes do not support this congruent dissolution mechanism as the only contributor to loss of solutes (here, B).
- the second hypothesis is a preferential loss of fine clay particles by surface erosion or subsurface particulate transport as has been previously suggested [3,5].

The higher boron depletion compared to Al in the SPRT soil profile indicates that boron was more completely mobilized compared to the valley floor soil profile (Fig.2). In addition to clay loss, this also suggests an additional loss of boron, probably by solubilisation. Boron isotopes support this idea. The 1‰ difference in isotopic composition observed between soils and bedrock in the SPRT profile can be attributed to congruent dissolution followed by partial adsorption or co-precipitation of boron in clay mineral or oxides. These two processes are indeed expected to favour immobilization of ^{10}B resulting in a solution enriched in ^{11}B by as much as 30‰ [8,9]. Assuming a fractionation factor of -30‰, a simple mass balance calculation shows that if sorption or co-precipitation occurs after congruent dissolution, then about 3% of dissolved boron is reincorporated or adsorbed in the SPRT soils.

By contrast, in the SPVF soil profile, the boron depletion profile associated with the observed similarity in δ^{11}B at depth and in the bedrock confirms that boron is predominantly lost through clay particles transport without any isotope fractionation.

Vegetation cycling is probably not a dominant control on boron here, since litter and throughfall measured in previous studies [2] were highly enriched in ^{11}B compared (δ^{11}B values of 30‰ and higher). If vegetation cycling were to be important, then it should lead to increase the measured δ^{11}B in the upper part of the soil profiles, which is not observed.

4. Conclusion

Boron concentrations and isotope ratios measured in two soil profiles at Shale Hills CZO show that, like what have been proposed for other elements, boron is mobilized by the lost of fine clay particles from the soil. Future investigation should characterize this mobile phase. However, the slight isotopic fractionation detected in the ridge top soil can be attributed to chemical weathering (dissolution followed by sorption or co-precipitation). Surprisingly, this study shows that vegetation cycling is not the dominant control on boron behavior in soil profiles at Shales Hills CZO.

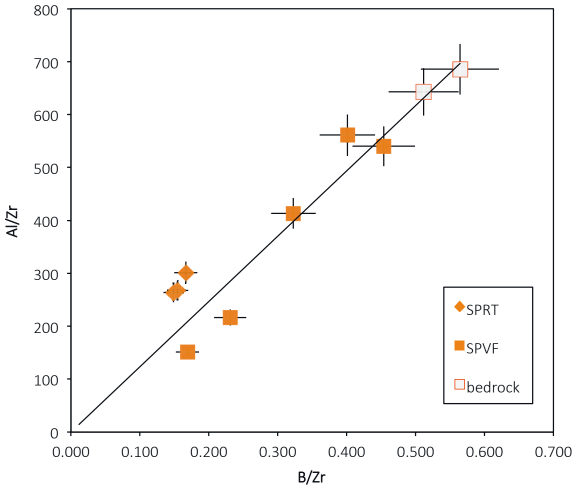

Fig.3. Correlation between Al/Zr and B/Zr in the bedrock and in the two soil profiles.

Acknowledgements

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