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Differentiation analysis of boron isotopic fractionation in different forms within plant organ samples

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ABSTRACT

As a critical micronutrient, boron (B) plays an important role in plant growth and embryonic development. To further understand the effects of B uptake, transportation and isotopic fractionation, the contents and isotopic compositions of hydro-soluble B in the sap and structural B fixed in the cell within individual plant tissues were investigated. The B isotope ratio was determined by multi-collector inductively coupled plasma mass spectrometry. The $\delta^{11}B$ values in hydro-soluble and structural B in the investigated plant samples ranged from −1.57‰ to +11.30‰ and from +6.57‰ to +16.64‰, respectively. Different fractionation factors of the B isotopes, in the range of 0.9954–1.0150, were observed in these samples, indicating that in most plant tissues, the heavy isotope (^{11}B) was preferentially enriched in structural B, which was fixed into the cell. However, there was a reversal in the fractionation of B isotopic compositions in the fruit samples compared with the other plant tissue samples. It is more powerful to examine the molecular mechanisms of B transport, uptake and utilization than the use of limited plant organ samples containing a mixture of hydro-soluble and structural B within different intra-plant compartments and in inter-plant interactions. These isotopic shifts, which may be used as important isotopic indicators, contribute to the surface processes interactions in the plant–soil system and the knowledge of the molecular mechanisms of B in the uptake and absorption by different plant species in nature.

1. Introduction

Boron (B) and its isotopes (^{10}B and ^{11}B), which have relatively greater isotopic mass difference in natural samples (−70‰ and +75‰, respectively) (Xiao et al., 2013, 2014), have been used as powerful indicators to reconstruct pH values of the ancient seas (Farmer et al., 2015; He et al., 2013a; Nir et al., 2015; Xiao et al., 2012), trace water pollution (Meredith et al., 2013; Nisi et al., 2014), discriminate depositional environments (Vengosh et al., 1995; Xiao et al., 2013), and identify the provenance of agricultural products (Chang et al., 2015; Oda et al., 2001; Serra et al., 2005). The recent use of B isotopes in biological systems has focused on establishing the provenances of plants and foods (Chang et al., 2015; He et al., 2013b; Oda et al., 2001; Wieser et al., 2001), using ^{10}B as an isotopic spike for plant growth (Vanderpool and Johnson, 1992), and interpreting the mechanism of B isotopic fractionations (Rosner et al., 2011).

The $\delta^{11}B$ values in various commercial products from different regions reported by Vanderpool and Johnson (1992) range from −7.5‰ to +29.3‰, indicating that B isotopes fractionate between plant tissues and the nutrient solutions. Rosner et al. (2011) developed a method for B separation using wet chemical digestion combined with chromatography, with the observed $\delta^{11}B$ values in crops ranging from 0‰ to +34‰. This suggested regionally varying contributions from the natural background and anthropogenic activity. Xu et al. (2015) described that $\delta^{11}B$ values ranged from −19.45‰ to +28.13‰ in different plant tissues from the Qinghai–Tibetan Plateau and Shandong areas. The $\delta^{11}B$ values in various compartments of bell pepper, which ranged from −11.0‰ to +16‰, increased with the plant height, which means the young plant parts became enriched with the ^{11}B as the plant grew (Geilert et al., 2016). However, in hydroponic plant growth experiments

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with ^{10}B isotopic spikes in the artificial culture solutions, wheat and corn were preferentially enriched with ^{10}B, while varying fractionations of the B isotope occurred in broccoli (Marentes et al., 1997). This indicated that the uptake and utilization of B by different intra-plant compartments or inter-plant interactions, B isotopes were preferentially used by different plant species, which resulted in the enrichment of the heavy or light isotope in tissues having different fractionation trends. In general, during the uptake of B, featured isotope signatures are caused by different absorption mechanisms for B isotopes or the transport of B. However, these observed isotopic differences among plant tissues or inter-plant interactions include all the variations of the B isotope compositions in some tissues or the whole plant. In fact, once B, in the form of $B(OH)_3$, which was absorbed by the plant roots, was transferred to other tissues, some was fixed in the structure of the cell wall (Park and Schlesinger, 2002), which is, therefore, not transported nor does it participate in the exchange cycle within the plant (Blevins and Lukaszewski, 1998; O'Neill et al., 2004; Shaaban, 2010). The residual B unabsorbed in the sap, which was not initially utilized by the plant, is transported to other tissues by nutritional transporters for further utilization. In the foregoing reports, the mixture of the two forms of B was used for testing. Thus, the fractions of B isotopes that were utilized could not be examined within a plant. What's more, if the different forms of B were investigated separately, more details of the mechanisms of uptake, transportation could be obtained and the isotope fractionation could be interpreted in deep.

Based on the previous studies that investigated B isotope compositions in five different plant species in Qinghai-Tibet Plateau and Shandong areas (Xu et al., 2015), the objective of this study was to investigate the variation in the mass concentrations and isotopic compositions of hydro-soluble and structural B within plant samples. The B isotopic compositions were measured by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). The fractionation factors (α) of the B isotopes were investigated and discussed.

2. Results and discussion

2.1. Variation in mass concentrations of hydro-soluble and structural B in plant samples

Several samples, including the roots, leaves and stems of *Weigela florida* cv. Red Prince (A, B, and C), roots, leaves, and stems of *Swertia mussotii* Franch. (D, E, and F), flowers and stems of *Cynomorium songaricum* Ruper. (G and H), *Pyrus pyrifolia* var. *culta* (Makino) Nakai (I), *Citrus maxima* (Burm) Merr. (J), and *Malus pumila* Mill. (K), were selected for trials to verify the variations in mass concentrations and isotopic compositions of hydro-soluble and structural B. The mass concentrations in hydro-soluble B and structural B of these samples, which are shown in Fig. 1, ranged from 13.69 to 90.91 mg kg^{-1} and from 27.21 to 67.06 mg kg^{-1} dried weight (Table 1), respectively. The plant organ samples, excluding those of the fruits, had lower amounts of hydro-soluble B than structural B (Fig. 1; left ellipse); however, in the three fruits, the amounts of hydro-soluble B were greater than those of structural B (Fig. 1; right ellipse). In plant growth, some of the hydro-soluble B was utilized by the organs to form the cell wall, which led to the accumulation of structural B in the homologous organs, which lead to the amount of hydro-soluble B being lower than of structural B in the same compartment. According to the determination, the three fruits are over 80% water. Previous reports (Blevins and Lukaszewski, 1998; Loomis and Durst, 1992) have shown that B is a chemotactic agent for propagative organ growth through reproductive tissues and that plenty of B are required for the reproductive growth. In the sap, various *cis*-polyols, such as sorbitol, fructose, glucose, and saccharose, are utilized by combining with the hydroxyls of $B(OH)_3$ and borate, which transfer B to the fruit part (Huang et al., 2014). This may be the reason for greater levels of hydro-soluble B compared with structural B in fruits.

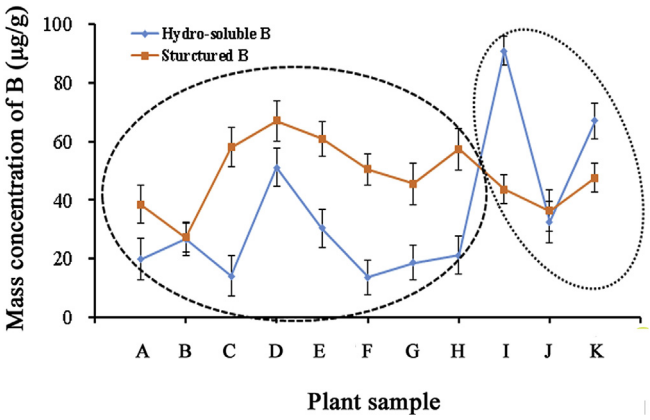

Fig. 1. Variations in mass concentrations of hydro-soluble and structural B in plant samples. A: root of *W. florida*, B: leaf of *W. florida*, C: stem of *W. florida*, D: root of *S. mussotii*, E: leaf of *S. mussotii*, F: stem of *S. mussotii*, G: flower of *C. songaricum*, H: stem of *C. songaricum*, I: *P. pyrifolia* var. *culta*, J: *C. maxima*, K: *M. pumila*.

2.2. Variation in $\delta^{11}B$ values of hydro-soluble and structural B in plant samples

The isotopic compositions of hydro-soluble and structural B in these plant organ samples were determined by MC-ICP-MS and are listed in Table 2 and shown in Fig. 2. The $\delta^{11}B$ values in hydro-soluble and structural B ranged from −1.57‰ to +11.30‰ ($\Delta\delta^{11}B$ = 12.87‰) and from 6.57‰ to 16.64‰ ($\Delta\delta^{11}B$ = 10.07‰),

Table 1
Contents of hydro-soluble B and structural B in plant organs (number of measurements, n = 3).

Plant	Organ	Mass concentration (mg/kg)	Added amount (μg)	RSD (%)	Recovery (%)
W. florida	Root	19.83[a]	0.1	4.5	98.7
		38.44[b]	0.1	3.6	103.1
	Leaf	26.73[a]	0.1	5.6	98.8
		27.21[b]	0.1	3.2	100.9
	Stem	14.05[a]	0.1	2.8	97.7
		58.07[b]	0.1	3.4	98.1
S. mussotii	Root	51.18[a]	0.1	4.1	104.7
		67.06[b]	0.1	3.7	104.3
	Leaf	30.36[a]	0.1	4.9	97.7
		60.89[b]	0.1	5.2	96.1
	Stem	13.69[a]	0.1	3.8	102.4
		50.41[b]	0.1	5.3	101.4
C. songaricum	Stem	21.08[a]	0.1	3.4	103.5
		57.32[b]	0.1	5.3	97.6
	Flower	18.69[a]	0.1	2.7	102.9
		45.54[b]	0.1	3.1	100.1
H. elliptica	Stem	26.43[a]	0.1	3.3	102.6
		52.37[b]	0.1	2.8	99.3
P. pyrifolia var. *culta*		90.91[a]	0.1	3.5	103.7
		43.58[b]	0.1	3.4	102.3
C. maxima		32.62[a]	0.1	4.3	96.5
		36.37[b]	0.1	4.0	98.4
M. pumila		67.00[a]	0.1	3.3	99.4
		47.62[b]	0.1	4.7	103.2

[a] Hydro-soluble B.
[b] Structural B.