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Boron behavior in the rivers of Réunion island, inferred from boron isotope ratios and concentrations of major and trace elements

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Abstract

A combined study of boron concentrations and isotopic ratios and of major and trace elements measured in Réunion waters, sampled up to four times between 1995 and 2012, illustrates boron behavior during water-rock interactions in tropical basaltic catchments. Boron isotope ratios measured in Réunion rivers and springs show a large range of variation between 1 and 48‰, that reflect mixed B sources and water-rock interaction processes: rain ($\delta^{11}B \approx 40‰$), hydrothermalism ($\delta^{11}B \approx 0‰$), low temperature basalt weathering in steep sided basins ($\delta^{11}B \approx 30‰$), and cycling within soil and vegetation ($\delta^{11}B > 40‰$). Réunion rivers have schematically two types of $\delta^{11}B$ signatures for low-temperature water-rock interactions: ≈30‰ for rivers with high weathering rates, and ≈45‰ for small forested catchments with relatively smoother slopes and lower weathering rates. High temperature water-rock interaction produces B enriched waters with a B isotopic signature close to that of the rocks. B behavior in the soil and vegetation cycle is more difficult to characterize but seems to result in soil solutions enriched in ^{11}B, with $\delta^{11}B \geq 45‰$.

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Keywords: boron isotopes; rivers; Réunion; weathering; hydrothermal springs;

1. Introduction

Numerous studies have now addressed boron isotope ratio variations in small and large rivers and main mechanisms for boron cycling and isotope fractionation have been identified ([1] and references therein):

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Rains have a large range of boron isotopic signatures ($\delta^{11}B$), which are however close to seawater (≈40‰) for islands. Boron is released from primary minerals and its adsorption onto secondary minerals (clays, oxides…) preferentially uptakes ^{10}B and leaves interacting waters enriched in ^{11}B. Conversely, desorption from these secondary minerals, (depending upon the hydrological state of the basins and soils, and to the waters saturation and speciation), brings ^{10}B enriched signature to the waters. Boron is an essential element in plants (B concentrations similar to those in igneous silicate rocks: a few ppm) and is actively cycled by the vegetation; precise mechanisms and isotope fractionation are poorly known, but high $\delta^{11}B$ were recorded, as in soil waters. Large rivers with low weathering rates have high $\delta^{11}B$ (soil-vegetation cycle dominates), whereas small rivers and rivers with high weathering rates have lower $\delta^{11}B$, closer to the bedrock signatures. High-temperature hydrothermal systems have $\delta^{11}B$ signatures close to those of the rocks. Boron is also widely used in human activities, and anthropogenic boron rather has low or even negative $\delta^{11}B$ signatures.

Study of small rivers draining mono-lithological basins in various conditions of temperature, rainfall and weathering regimes may add some clues to this boron cycle during water-rock interactions. Boron isotope abundance is a powerful tool for this purpose. Following our first study [2] of boron isotopes in the rivers and thermal springs of Guadeloupe (Lesser Antilles), this paper highlights the major features of boron isotopes behavior within the rivers of Réunion Island.

2. Geological and hydrological settings of Réunion Island

Réunion Island (Indian Ocean) was formed 2 Myr ago from intra-plate volcanic activity and consists of two basaltic shield volcanoes: extinct Piton des Neiges (3069m, last erupted 12 kyr ago) and still active Piton de la Fournaise (2632m). Tectonic activity and erosion has formed three deeply incised cirques (Cilaos, Mafate and Salazie) in Piton des Neiges Massif and three concentric calderas around Piton de la Fournaise, where the largest rivers of the island have developed. Rainfall can reach 7000 mm/yr on the eastern side of the island while western side is drier. Since the 1990's large works have been conducted to transfer waters from the East side of the island to the more populated West side. River discharges vary a lot during a year, from very low water stages (<10s of m^3/s, or even dry) to torrential fluxes (>2500 m^3/s). Erosion and weathering rates in Réunion deduced from river geochemistry (500 to 3500 mm/yr and 63 to 170 t/km2/yr, respectively) are among the highest reported worldwide, due to high runoffs, steep slopes, active volcanism and tectonics, and young basaltic lithology [3].

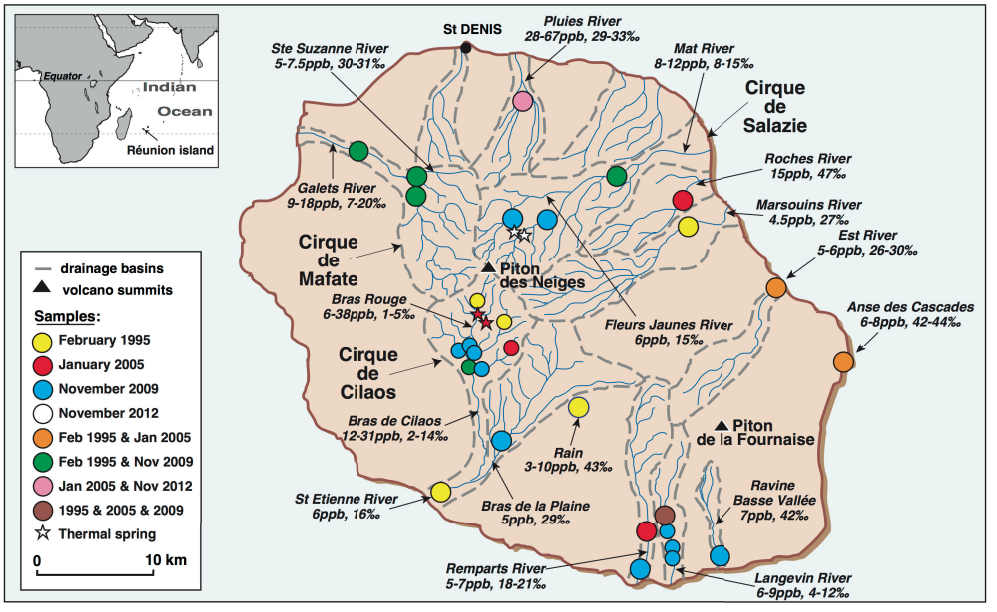


Fig. 1. Map of Reunion Island with sample locations and boron concentrations (in ppb) and isotopic ratios ($\delta^{11}B$ in ‰)

3. Sampling and analysis

Main rivers from Réunion Island, as well as some springs and drains in tunnels, were collected during four sampling sessions in January 1995, February 2005, November 2009 and November 2012 (Fig. 1). Major anions and cations concentrations were analysed by HPLC (precision ≈ 5%). Trace elements were measured by ICP-MS (precision ≈ 5%). Boron isotope ratios were determined by MC-ICP-MS with a direct injection nebulizer (d-DIHEN) [4], after boron extraction through ion chromatography (adapted from [5]), with a 2SD reproducibility between 0.1 and 2.5‰ (generally higher for thermal springs). $^{11}B/^{10}B$ ratios are expressed relative to the boric acid standard NBS 951 (NIST): $\delta^{11}B = \{(^{11}B/^{10}B)_{sample}/^{11}B/^{10}B)_{NBS951} - 1\} \times 1000$. Boron concentrations and isotopic ratios measured for Réunion water samples are given in Appendix A.

4. Spatial and temporal variability of boron concentrations and isotopic ratios in Réunion rivers and springs

Among all the samples measured from Réunion Island, boron isotopic ratios vary between -4 and 48‰, while boron concentrations range from 5 to 83ppb; one thermal spring sample (Ravine Olivette) has high [B] of 440ppb. Except for thermal springs, boron concentrations in rivers from Réunion are similar to those in Guadeloupe [2]; $\delta^{11}B$ ranges are also the same for the two volcanic islands. The highest $\delta^{11}B$ values are for a rain sample, a coastal resurgence of fast circulating water (Anse des Cascades), and two small rivers draining forested catchments (Basse Vallée and Roches). [B] measured in two rain samples were 3 and 10ppb, thus in the same range as half of the rivers. On the other hand, lowest $\delta^{11}B$ values are for thermal springs in Cilaos and Salazie Cirques (Source Bras Rouge, Source Irénée, Ravine Olivette) and for rivers with thermal spring influx (most of Cilaos rivers except Petit Bras and Calumets; Mat and Fleurs Jaunes rivers in Salazie). An exception to this is Langevin River, where $\delta^{11}B$ varies between 4 and 12‰ and no hydrothermal activity is known. Springs and groundwater tables, sampled in 2 different tunnels (Est and Mat rivers) had $\delta^{11}B$ values very low or even negatives (0 to -4‰).

Rivers sampled repeatedly years apart, during low or high water stage, generally have almost the same $\delta^{11}B$ value, differences being within 1 to 4‰ (fig. 1, e.g. Anse des Cascades; Est, Remparts and Pluies rivers), while [B] concentrations can vary by a factor up to 2 (but in some rivers, like River Langevin were mostly constant during the 17 years covered by the sampling).

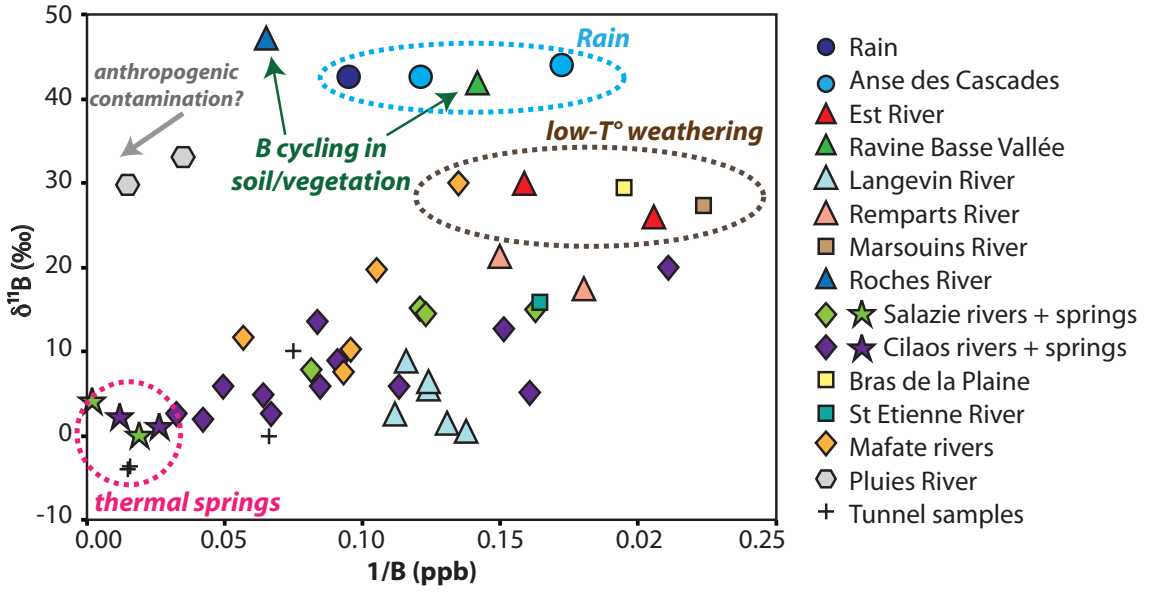


Fig. 2. Relationship between $\delta^{11}B$ and B concentrations for Réunion rivers and springs. Circles are for rain-like samples, triangles for Piton de la Fournaise rivers and springs, diamonds for Piton des Neiges's, squares for rivers in-between the two massifs, and crosses for tunnels.

Figure 2 shows an anticorrelation between $\delta^{11}B$ and B concentrations. Like in Guadeloupe, thermal springs (plus tunnel samples) seem to be the end-member for low $\delta^{11}B$ values and high [B]. Thermal springs sampled in Réunion have globally low [B] compared to Guadeloupe's (250 to 1000ppb). High temperature basalt-rock interactions likely give $\delta^{11}B$ close to the rock value, as was observed in Guadeloupe [2]. No $\delta^{11}B$ value for Réunion basalts is available, but being OIB basalts these are probably close to 0‰ or slightly lower [6]. The temperatures of the thermal springs sampled in Réunion are rather low (20 to 50°C, [3]) and they probably do not correctly reflect the high-temperature hydrothermal systems of Réunion. Their $\delta^{11}B$ values (0 to 4‰) are slightly higher than the probable range for Réunion basalts (-5 to 0‰, [6]), and may reflect boron adsorption onto secondary minerals precipitated during the transfer of these fluids toward their atmospheric bursting. In the tunnel samples, these low values (and high [B]) could reflect either congruent B dissolution from basalts (without adsorption of B onto secondary minerals) or contamination from concrete. During high temperature water-rock interaction, B is released in a much greater proportion than other soluble elements, such as Na, with enrichment factors relative to the average B/Na ratio of Réunion basalts of up to 2000. Compared to Cl, volatile during magmatic processes, B is enriched by a factor of up to 70 in thermal springs (relative to $[B/Cl]_{basalt}$), and despite a large contribution of rain to the Cl budget of Réunion rivers, B/Cl ratio of most thermal spring impacted rivers is still higher than the B/Cl average ratio of Réunion basalts. B is highly volatile and enriches in volcanic gases and steam that interact with the infiltrated water to produce hydrothermal springs. This explains that a large variability of B concentrations can be measured in thermal springs for a narrow $\delta^{11}B$ range (close to that of the rock).

Rain cannot represent the second end-member for Fig. 2 trend. In rivers with [B] as low or lower as rains, boron cannot derive from rain only, as the $\delta^{11}B$ for these rivers are generally 10 to 30‰ lower than rain. This riverine boron thus has a mixed origin: rain, basalt weathering and soil/vegetation cycling. At the upper end of Fig. 2 trend, rivers with the highest $\delta^{11}B$ values (around 30‰) and lowest [B] (around 5 ppb) drain indistinctly Piton des Neiges or Piton de la Fournaise volcanoes, or both. They probably represent a "pristine" low-temperature weathering pool of river basins for Réunion Island, similar to what was observed for the rivers on Guadeloupe, that are not impacted by hydrothermalism [2] (with $\delta^{11}B$ values between 39 and 44‰, thus 10 to 15‰ higher than here).

There seems to be no general relationship between $\delta^{11}B$ values and weathering rates, which are globally higher for Piton de la Fournaise rivers, due to their higher runoffs [3]. However, hydrothermalism is more active in Salazie and Cilaos cirques than anywhere else on the island, and most of the rivers in Cilaos and Salazie are impacted by thermal springs in their chemical compositions, with a relative contribution to the total dissolved solids between 6% in Bras de St Suzanne (Salazie) and 68% in Bras Rouge (Cilaos) [3].

Some river samples plot out of the general $\delta^{11}B$ vs 1/[B] trend of Figure 2 and are examined case by case:

• Ravine Basse Vallée ($\delta^{11}B$ 42‰) is an intermittent river draining a forested small catchment, south of Piton de la Fournaise (sampled in 2009 during a tropical storm). Its major element concentrations are in the average range of Réunion rivers, but most "soluble" trace elements (e.g. Li, Rb, Sr, Ba, U, V, Mo, W) have the lowest measured concentrations of all Réunion river samples, and Fe, Al, and REE the highest. This particularity probably witnesses the leaching of weathered soils. Its high $\delta^{11}B$ value thus rather reflects a soil solution signature than the rain imprint.

• For Langevin River, no hydrothermal activity has been identified in the catchment ([Li], [B] or $[SO_4]$ not particularly high, [3]) but $\delta^{11}B$ are low and vary a lot through time (3.7 to 11.2‰) compared to the other rivers sampled many times between 1995 and 2012. We can suspect an anthropogenic contamination in this river, either from domestic effluents or from fish breeding in the basin. However, no particularly high $[NO_3]$ or [Cl] were measured for this river, their major element concentrations are in the upper average range, but they are the most enriched in V, As and W, and the most depleted in Cu, Mn and Ni. Further investigation is needed to understand these behaviors. In 2009, Langevin River was sampled four times during the same tropical storm as for Ravine Basse Vallée, and the four $\delta^{11}B$ values increased with the river discharge (from 5.6 to 11.7‰), which could reflect a dilution by rain with $\delta^{11}B \approx 40$‰. But in the same time, Fe, Al, Mn, Ni and REE concentrations also increased. The low-water chemical and isotopic signature of Langevin River was thus not diluted by rain but by a soil leachate, similar to that sampled at Ravine Basse Vallée (and which was visually observed).

• Roches River drains a forested pristine catchment that undergoes high precipitations. Its $\delta^{11}B$ (48‰, highest measured value) and [B] (15 ppb) are close to those of Guadeloupe's rivers without hydrothermal sources [2]. The

longer Marsouins River nearby ($\delta^{11}B$=27‰, 4.5 ppb B) drains the same forested area, but with steeper slopes within the basin and an underground water flow on half of its length upstream. The role of soil-vegetation cycling for boron isotopes in river waters appears again as a key parameter to these high $\delta^{11}B$ values in tropical areas [1,2,7].

• Pluies River is close to St Denis, the largest city of Réunion Island and possible anthropogenic contaminations could explain its high [B] (28 ppb in 2005 and 67 ppb in 2012). If we suppose that this B contamination has a $\delta^{11}B$ around 0 to 5‰, then the "natural" $\delta^{11}B$ for this river would be at least 45‰, close to the value for Roches River.

For the rivers that have the highest $\delta^{11}B$ values, examination of the basin settings and weathering characteristics leads to the following observations:

• $\delta^{11}B$ are the highest (≈45‰) in small, smooth and forested basins, with lower weathering rates, but stronger water infiltration in soils, where B exchanges between water, soils and vegetation are best expressed in the river waters. The high $\delta^{11}B$ signature of these rivers arises from a complex mixing of processes: B input from oceanic rains, B release from low temperature basalt dissolution, B adsoption from solution onto secondary minerals (with preferential ^{10}B uptake), possibly B release from these secondary minerals, B uptake by plants at the soil solution - root interface and the vegetation cycle (B translocation in plant, litter – soil recycling, plant transpiration towards the atmosphere…); each of them causing possible B isotope fractionation. Boron biogeochemical studies of small basaltic catchments will probably untangle these processes.

• Interestingly, the $\delta^{11}B$ value of the low-temperature water-rock interaction end-member, that had been identified for Guadeloupe rivers is similar to those of these small forested rivers in Réunion. Thick soils and strong water infiltration characterize most of Guadeloupe river catchments.

• The rivers with low [B] and $\delta^{11}B$ around 30‰ are generally larger and drain basins with very steep flanks (like walls), extreme erosion rates characterized by catastrophic events (e.g. flank collapse), and thus low weathering / erosion ratios. Concerning boron isotope behavior, the same processes are involved in these rivers, but in different proportions as for the small forested rivers.

Altogether, these observations suggest that at least two end-members for boron arising from low-temperature weathering processes have to be define in order to caricature B behavior in Réunion rivers.

5. Conclusion

The measurements presented here show that B isotopic ratios are anticorrelated to their B concentrations in most of Réunion rivers. Hydrothermalism is one end-member of this trend with high [B] and $\delta^{11}B$ value close to basalt (0‰). Low-temperature rivers with high erosion rate define the other side of this trend ([B] ≈5ppb and $\delta^{11}B$≈30‰). Smaller rivers in forested catchments have higher $\delta^{11}B$ (≥45‰), due to B cycling in soil and vegetation, which is similar to that of the low-temperature weathering end-member defined for rivers from Guadeloupe, another volcanic tropical island characterized by thick soils.

This study confirms the large fractionation of boron isotopes in the critical zone and their potential to decipher high and low-temperature weathering processes.

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Appendix A. Data table

River / Spring Name	Sampling session	Sample number	pH	$\delta^{11}B$ ‰	2SD ‰	B ppb	
Pluie 4	févr-95	Pluie 4		42.7	0.2	10.5	Piton de la Fournaise
Anse des Cascades	févr-95	DR2	8.1	42.5	0.2	8.2	
Anse des Cascade	janv-05	*Reu 05 12*	*7.93*	44.2	0.5	5.8	
Rivière de l'Est	févr-95	DR3	7.9	29.9	0.1	6.3	
Rivière de l'Est	janv-05	*Reu 05 13*	*7.89*	25.9	0.6	4.9	
Ravine Basse Vallée	nov-09	REU306	8.05	41.7	0.4	7.1	
Rivière Langevin	févr-95	DR1	8.0	4.0	0.2	7.7	
Rivière Langevin 1	nov-09	REU301	7.38	5.6	0.9	8.9	
Rivière Langevin 2	nov-09	REU302	7.75	8.7	1.8	8.1	
Rivière Langevin 3	nov-09	REU303		8.1	1.0	8.1	
Rivière Langevin 4	nov-09	REU304	7.00	11.7	0.6	8.6	
Rivière Langevin	janv-05	*Reu 05 17*	*7.83*	3.7	0.5	7.3	
Rivière des Remparts	nov-09	REU305	8.04	21.3	0.1	6.7	
Rivière des Remparts	janv-05	*Reu 05 15*	*7.43*	17.6	0.6	5.6	
Rivière des Marsouins	févr-95	DR4	8.0	27.2	1.1	4.5	
Rivière des Roches	janv-05	*Reu 05 5*	*7.58*	47.3	0.8	15.3	
Rivière du Mat aval	févr-95	DR6	8.5	15.1	0.5	8.3	Piton des Neiges
Rivière du Mat aval	nov-09	REU104	8.40	14.4	0.5	8.2	
Rivière du Mat amont	nov-09	REU101	8.40	8.0	0.2	12.3	
Rivière des Fleurs Jaunes	nov-09	REU103	8.29	15.0	0.1	6.1	
Rivière du Mat - source Fe2	nov-12	RE2012-17	6.96	0.2	0.1	54.2	
ravine Olivette 1	nov-12	RE2012-1	8.30	3.9	0.1	439	
Grand Bras de Cilaos aval	févr-95	DR7	8.5	2.8	0.2	31.2	
Petit Bras de Cilaos	nov-09	REU01	8.25	13.6	0.2	11.9	
Grand Bras de Cilaos amont	nov-09	REU03	8.43	1.8	0.2	23.9	
Grand Bras de Cilaos aval	nov-09	REU04	8.44	5.8	0.2	20.2	
Bras de Saint Paul	nov-09	REU08	8.30	9.0	0.2	11.1	
Bras de Benjouin aval	nov-09	REU06	8.25	4.7	0.7	15.7	
Bras de Benjouin amont	févr-95	DR9	8.5	5.9	0.2	11.8	
Bras des Calumets	janv-05	*Reu 05 19*	*8.48*	12.6	0.5	6.6	
Source Tête de Lion 1	nov-09	REU09-1	7.90	20.2	0.2	4.8	
Source Tête de Lion 2	nov-09	REU09-2	8.20	5.9	2.7	8.8	
Bras Rouge aval	nov-09	REU07	8.57	1.1	0.2	38.0	
Bras Rouge amont	janv-05	*Reu 05 21*	*8.35*	5.1	0.1	6.2	
Bras rouge Thermal spring	janv-05	*Reu 05 22*		2.7	0.4	15.0	
Thermal spring Irénée	janv-05	*Reu 05 20*	*6.33*	2.3	0.2	82.7	
Bras de la plaine	nov-09	REU401	6.60	29.3	0.7	5.1	
Rivière St Etienne	févr-95	DR10	8.9	15.8	0.5	6.1	
Rivière des Galets /Barage	févr-95	DR11	8.3	7.5	0.4	10.7	
Riviere des galets amont	nov-09	REU202	8.35	10.2	0.8	10.4	
Rivière des Galets /Lebot	févr-95	DR13	8.6	11.6	0.2	17.5	
Riviere des galets aval	nov-09	REU201	8.10	19.6	1.2	9.5	
Bras de Sainte Suzanne	févr-95	DR12	8.2	29.6	0.6	7.4	
Bras de Sainte Suzanne	nov-09	REU203	8.13	31.3	2.7	5.2	
Rivière des pluies	janv-05	*Reu 05 1*	*7.66*	33.1	0.5	27.9	
Rivière des Pluies	nov-12	RE2012-7	8.23	29.6	0.1	67.3	
Riv. Pluies - tunnel	nov-12	RE2012-5	9.70	-4.03	0.1	67.7	
Salazie - tunnel	nov-12	RE2012-8	10.64	-3.47	0.2	61.8	
Riv. Est - tunnel	janv-05	*Reu 05 10*		-0.01	0.7	15.0	
Riv. Est - tunnel	janv-05	*Reu 05 9*		9.94	1.9	13.3	

Table A1: $\delta^{11}B$, [B] and pH for the rivers and springs sampled in Réunion Island.

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