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1 **Insights on catchment-wide weathering regimes from boron isotopes in riverine material**

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6 geology

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33 ABSTRACT

34 Chemical weathering contributes to the regulation of the global carbon cycle and  
35 biogeochemical cycles. Accordingly, the identification of the parameters that control weathering  
36 reactions and transport of weathering signals at the catchment scale is essential. The use of  
37 boron (B) isotopes have been shown to be a useful proxy in tracing weathering reactions due to  
38 large isotope fractionation during weathering processes. However, our knowledge of how boron  
39 isotopes record the weathering regime at the catchment scale and how that weathering signal is  
40 transported from source areas to the depositional environment remains limited. Here we  
41 characterize B isotope and major element behavior during chemical weathering and transport by  
42 analyzing the B isotopic ( $\delta^{11}\text{B}$ ) and element compositions of riverine material (riverbank sands (<  
43 63  $\mu\text{m}$ ), clay fractions (<2  $\mu\text{m}$ ) extracted from sands, and dissolved load) along the course of the  
44 Murrumbidgee River (NSW, Australia), its upstream tributaries, and monolithologic  
45 subcatchments.

46 In the Murrumbidgee, two distinct weathering regimes are present, one where mineral  
47 dissolution is associated with minimal neof ormation at higher elevations and another where  
48 mineral neof ormation dominates at lower elevations and in granitic lithologies. Significant B  
49 isotope difference between the clay fraction and the bedrock ( $\Delta^{11}\text{B}_{\text{clay-bedrock}}$ ) is observed in most  
50 monolithologic catchments at high mean elevation (excluding granites), which correlates with  
51 a large B depletion. Smaller isotope difference between the clay fraction and bedrock is observed  
52 in monolithologic catchments at lower elevations as well as in granitic catchments at all  
53 elevations and is associated with limited B removal. These results suggest that lithology and  
54 catchment topography influence B mobility during weathering and the isotopic composition of  
55 weathering products. By mass balance calculation, the B isotope and chemical composition of  
56 the clay and sand fractions in the Murrumbidgee River can be explained as a mixture of the clays  
57 and sands produced throughout the catchment delivered to the main channel by the tributaries.  
58 These results indicate that there is little or no chemical and isotopic modification of the river  
59 sediment during fluvial transport and that weathering signal produced in the sediment source  
60 areas is transferred to the depositional environment without significant modification. The boron  
61 content of the clay-sized fraction (~40 ppm) is several orders of magnitude greater than that of

62 the dissolved load while B isotope compositions of the clay-sized fraction are isotopically much  
63 lighter (up to 40 ‰). Because a maximum isotopic difference of 30 ‰ between the dissolved and  
64 solid phases is expected during adsorption processes, the observed isotope compositions in the  
65 dissolved load and the sediment clay fraction cannot be explained by pH-driven B partitioning.  
66 These observations suggest that clays are not directly precipitating from solutions  
67 compositionally similar to surface waters; deeper soil solutions are expected to play a significant  
68 role in clay formation.

69 This research highlights the potential of B isotopes in river sediments to describe the present  
70 and past weathering regimes at the catchment scale, including possible paleoenvironment  
71 reconstruction as the B isotope signature of riverine material records the conditions of its  
72 formation.

73

#### 74 **1. INTRODUCTION**

75 Chemical weathering of silicate rocks shapes Earth's surface and landscapes, supplies  
76 essential nutrients to ecosystems, and is one of the main controls that regulate global climate  
77 over millennial timescales via the consumption of atmospheric CO<sub>2</sub> and carbonate storage in the  
78 oceans (Walker et al., 1981; Berner and Berner, 1997; West et al., 2005). To better understand  
79 the climate-silicate weathering relationship on the regional or even global scales, rivers are  
80 studied as they integrate weathering conditions at the catchment scale. Many studies in the last  
81 few decades have focused on deriving quantitative estimates of modern weathering rates and  
82 identifying controls on chemical weathering through the characterization of the riverine  
83 dissolved load and estimations of elemental and/or isotopic fluxes of the water-rock system in  
84 the weathering zone using a variety of modeling techniques (e.g. Bouchez et al., 2013; Brantley  
85 and White, 2009; Millot et al., 2002; Galy and France-Lanord, 2001; Gaillardet et al., 1995). The  
86 geochemistry of river sediments can also be used to provide estimates of silicate weathering  
87 and CO<sub>2</sub> consumption (e.g. Bouchez et al., 2012; Vital and Statterger, 2000; Gaillardet et al.,  
88 1999). For instance, Gaillardet et al. (1999) reports depletions in major and trace element  
89 compositions of suspended sediments (relative to un-weathered continental crust), which were  
90 attributed to element mobility during continental weathering. In this study, low weathering

91 intensity rates of suspended sediment were found to correlate with high rates of physical  
92 denudation. Silicate weathering rates and associated CO<sub>2</sub> consumption were reported to be  
93 elevated in orogenic areas because sediment production are generally higher. However, to  
94 obtain robust information on weathering processes at the catchment scale from fluvial  
95 sediments, one needs to assess whether the weathering signal produced in the sediment source  
96 region is modified during fluvial transport. For instance, physical processes such as hydrological  
97 mineral sorting of river sediment during transport and deposition cause a bias in sediment  
98 compositions (Garzanti and Andò, 2007; Garzanti et al., 2009). In addition to physical processes  
99 which may bias the composition of river sediments, sediment re-working and weathering during  
100 transport from source to sink have also been reported to influence the original composition of  
101 river sediment obtained during formation (Bouchez et al., 2012; Lupker et al., 2012). For  
102 example, in the Amazon Basin, Bouchez et al. (2012) reported long sediment transfer times in  
103 active floodplains as a result of temporary storage and sediment reworking events; these  
104 processes ultimately lead to a significant degree of chemical weathering during transport from  
105 source areas to the final depositional environment.

106 Boron is mobile during water/rock interaction and is partitioned into the soluble and solid  
107 phases. It is released into the hydrosphere via the dissolution of primary minerals and can be  
108 incorporated into secondary phases such as clay minerals and amorphous iron oxyhydroxides.  
109 Boron has two stable isotopes, <sup>10</sup>B and <sup>11</sup>B, that undergo large isotopic fractionation during Earth  
110 surface processes, particularly during low temperature water/rock interactions (Schwarcz et al.,  
111 1969; Spivack et al., 1987; Rose et al., 2000; Lemarchand et al., 2002a; Lemarchand et al., 2012;  
112 Gaillardet and Lemarchand, 2017). The boron isotope ratio, <sup>11</sup>B/<sup>10</sup>B, is generally expressed as  
113 the δ<sup>11</sup>B notation (‰) quantifying the relative deviation from the standard NIST SRM 951  
114 isotopic composition as follows:  $\delta^{11}\text{B} = (R_{\text{sample}} / R_{\text{NIST SRM 951}} - 1) \times 10^3$ . In natural systems, δ<sup>11</sup>B  
115 values show a large range of variation from -40 ‰ in non-marine evaporitic and tourmaline  
116 minerals in the continental crust up to +60 ‰ in brines from salt lakes (Palmer and Swihart,  
117 1996). Processes responsible for B isotope fractionation include adsorption of B onto clay and  
118 detrital particles (Schwarcz et al., 1969; Spivack et al., 1987), precipitation of B during  
119 neoformation of secondary phases (Rose et al., 2000; Williams, 2001; Cividini et al., 2010;

120 Lemarchand et al., 2012), hydrothermal alteration of clays, bedrock, and oceanic crust (Spivack  
121 and Edmond, 1987; Williams, 2001; Muttik et al., 2011), evaporation and precipitation processes  
122 during B atmospheric cycle (Xiao et al., 1997; Chetelat et al., 2005; Rose-Koga et al., 2006), and  
123 cycling through vegetation (Vanderpool and Johnson, 1992; Wieser et al., 2001; Cividini et al.,  
124 2010). Significant isotope fractionation occurs during secondary phase neof ormation whereby  
125 the lighter isotope has a greater affinity for neo-formed solids becoming enriched in  $^{10}\text{B}$  leaving  
126 the residual solution enriched in the heavier isotope (Schwarcz et al., 1969; Palmer et al., 1987;  
127 Lemarchand et al., 2005). A wide range of boron isotope compositions in both the solid and  
128 dissolved phases of rivers has been reported, which was attributed to silicate weathering  
129 processes on the watershed scale. For instance, in the Himalaya, Rose et al. (2000) reported a  
130 30 ‰ range in  $\delta^{11}\text{B}$  values in the dissolved load (–6 to +24 ‰) reflecting different conditions of  
131 silicate weathering; incongruent dissolution resulting in a greater isotope fractionation than  
132 congruent dissolution. Furthermore, they showed that the extent of isotopic fractionation  
133 during incongruent dissolution is inversely correlated to the pH of reacting fluids. In the  
134 Mackenzie Basin (Canada),  $\delta^{11}\text{B}$  compositions in the dissolved load of various rivers range from  
135 –2 to +30 ‰ and were modelled to show that they reflect an increase in shale weathering rates  
136 and/or B exchange between solutions and adsorbing surfaces, since deglaciation (Lemarchand  
137 and Gaillardet, 2006). In the Changjiang basin (China),  $\delta^{11}\text{B}$  compositions were reported for both  
138 the dissolved and suspended loads of various rivers with values from –3 to +9 ‰ and –11 to –6  
139 ‰, respectively (Chetelat et al., 2009). The isotopic composition of both phases is controlled by  
140 the competition between dissolution and precipitation of secondary phases, where the former  
141 causes no apparent isotopic fractionation. In soil profiles in the Strengbach catchment (France),  
142 clay fractions have  $\delta^{11}\text{B}$  compositions ranging from –35 to –18 ‰ which were attributed to B  
143 exchange between secondary minerals and  $^{11}\text{B}$ -rich soil solutions (Lemarchand et al., 2012). Clay  
144 fractions of suevites at the Ries crater, Germany, display an average  $\delta^{11}\text{B}$  composition of  
145 approximately –25 ‰ which were significantly different from previously drilled crater suevites  
146 from the Nördlingen 1973 drill site which had an average  $\delta^{11}\text{B}$  composition of –4.1 ‰ (Muttik et  
147 al. 2011), demonstrating that temperature and pH of alteration can impart different isotopic  
148 compositions on clay fractions. These studies illustrate that B isotopes are a useful proxy for the

149 study of silicate weathering processes. However, a clear understanding of the parameters that  
150 control B isotopes during the production of secondary products and subsequent transport  
151 throughout the watershed is still lacking.

152 In this study, river bank sediments and dissolved load samples were collected along the  
153 course of the Murrumbidgee River (NSW, Australia) and from its tributaries. Bedrock and river  
154 bank sediments from monolithological catchments at different elevations within the  
155 Murrumbidgee watershed were also collected in order to determine the chemical and isotopic  
156 compositions of source material in the catchment and to investigate how lithology and elevation  
157 influence weathering and the associated B isotope signal. The composition of sediments in  
158 monolithological catchments are also used to determine how the weathering signal is  
159 transported throughout the catchment. The aim is to better understand the factors that control  
160 the B isotope composition of weathering products and how the weathering signal is transported  
161 from source areas to the depositional environment. For sediments, this study focuses on the clay  
162 fraction ( $<2 \mu\text{m}$ ) of bank sediments, because fine sediments contain a larger proportion of  
163 weathering products and are thus the most likely to carry the signature of the weathering regime  
164 (e.g. Bouchez et al., 2012; Lemarchand et al., 2012; Dellinger et al., 2014).

165

## 166 **2. STUDY AREA**

167 The Murrumbidgee River catchment covers approximately 84,000 km<sup>2</sup> in New South Wales,  
168 southeastern Australia (Green et al. 2011) and is part of the Murray-Darling Basin. The  
169 Murrumbidgee River is approximately 1,600 km long. It forms on the Monaro Plains in the Snowy  
170 Mountains northwest of Australia's highest peak, Mt. Kosciusko (2,228m), and flows north  
171 through the Southern Highlands and westward across the Riverine Plain before joining the  
172 Murray River just south of Balranald (Fig. 1 inset). Three topographic regions can be identified  
173 within the drainage basin: the mountainous Southern Highlands east of Jugiong; the valley  
174 section westward until the town of Naranderra; and the Riverine Plain west of Naranderra (Fig.  
175 1). The focus of this study is located predominately in the Southern Highlands, which itself can  
176 be subdivided into three distinct topographic units (Schumm, 1968): the highest part of the  
177 catchment, and origin of the Murrumbidgee River, on the Kosciusko Plateau upstream of Cooma

178 (average elevation: 1375 m); the section between Cooma and Canberra (average elevation: 930  
179 m) and a lower sub-region between Canberra and Jugiong (average elevation: 500 m) . The river  
180 continues into the valley section westward towards Wagga Wagga, becoming progressively wider  
181 until it reaches Narrandera (average elevation: 150 m) where the valley ends. Then, the  
182 Murrumbidgee River flows onto the Riverine Plain where it becomes highly sinuous until  
183 converging with the Murray River nearly 1,500 km from its headwaters (Schumm, 1968; Wallbrink  
184 et al., 1998). The topographic relief on the Riverine Plain is characterized by the modern river and  
185 a series of paleochannel systems with their levee systems and associated sand dunes.

186 Climate in the catchment is temperate in the Southern Highlands transitioning to semi-arid  
187 on the Riverine Plain (Murray-Darling Basin Authority, 2016). Alpine regions experience cold, wet  
188 winters (up to 1,500 mm of average annual rainfall), while the Riverine Plain is characterized by  
189 hot, dry summers (less than 300 mm of average annual rainfall). Annual rainfall increases by 250  
190 mm for every 300 m rise in elevation (Murray-Darling Basin Authority, 2015). Evapotranspiration  
191 rates increases (1,200 to 1,600 mm of potential evapotranspiration) from upper to lower  
192 elevations due to the increasing temperature gradient and decrease in precipitation, resulting in  
193 a decrease in soil moisture in lower elevations (Murray-Darling Basin Authority, 2015).

194 Upstream of Gundagai, the Murrumbidgee River drains primarily sedimentary siliciclastic  
195 rocks (sandstones, shales, and limestones), igneous intrusive rocks (predominately granite,  
196 granodiorite, and gabbro) and igneous volcanic rock compositions (Schumm, 1968). The source  
197 region of the Murrumbidgee is underlain by granite intrusives and sedimentary siliclastic rocks of  
198 Silurian and Middle Devonian ages, respectively (David and Browne, 1950). As it follows a  
199 southeastward course towards Cooma, the catchment area drains shales, sandstones, and  
200 granites of Middle Devonian age (Fig. 1). The river then flows north for 80 km over predominately  
201 volcanic and sedimentary rocks of the Silurian age, east of the Murrumbidgee batholith.  
202 Southeast of Yass, the river begins bending to the west and travels across north to south-oriented  
203 lithological units in the Southern Highlands. From east to west these lithologies include:  
204 sedimentary and volcanic formations of the Middle Devonian, granites of the Middle Devonian  
205 near Jugiong, shales, conglomerates, and volcanics of the Silurian near Gundagai, and finally a  
206 mixture of limestone and sandstone of the Ordovician period near town of Wagga Wagga



207 (Schumm, 1968). Further west, the river flows on Quaternary alluvium with small outcrops of  
208 Middle Devonian granite and clastic rocks near Narrandera.

209 In this study, 18 sites along the course of the Murrumbidgee River were sampled for riverbank  
210 sediments and 12 sites for river water at the same locations. Additionally, eight major tributaries  
211 were sampled along their course and at their confluence with the Murrumbidgee. Using spatial  
212 data (see Methods below), monolithological catchments were identified in different parts of the  
213 Murrumbidgee River basin. Four catchments draining only granitic rocks were sampled for river  
214 sediments and bedrock, two of which were also sampled for river water. Four catchments  
215 draining only volcanic rocks were sampled for sediments, two of which were sampled for water  
216 and bedrock. Three catchments draining exclusively sedimentary rocks were sampled for  
217 sediments, two of which were also sampled for river water and bedrock. Bedrock, bank sediment,  
218 and dissolved load samples were also taken in a catchment draining carbonates. For sediments  
219 collected in monolithological catchments and tributaries, only the clay-sized fraction of the bank  
220 sediment was analyzed.

221

## 222 **3. METHODS**

223

### 224 **3.1. Spatial Analysis**

225 A 1-arc-second digital elevation model (DEM) (source: Geoscience Australia) was used in Esri  
226 ArcGIS™ 10.4 to determine catchment boundaries and average topographic (elevation and slope)  
227 values throughout the catchment. Monolithological catchments were identified using geological  
228 spatial data (source: Geological Survey of NSW, Australia) in combination with the DEM (location  
229 and type of lithological catchment shown in Fig. 1). Calculated catchment boundaries were also  
230 used in combination with geological spatial data (source: Geological Survey of NSW, Australia) to  
231 determine the proportions of each lithology drained at several sampling locations. Climatic data  
232 (annual mean rainfall and temperature) in each identified monolithological catchment was  
233 provided by the Australian Government, Bureau of Meteorology.

234

### 235 **3.2. Sample collection and pre-treatment**

236 Bedrock samples were collected from rock outcrops in monolithological catchments (Fig. 1).  
237 Sediments were collected by sampling an area of approximately 1 m<sup>2</sup> on the river bank or a  
238 sandbar, and amalgamated. Sediment samples were dried at 60°C and sieved at 2 mm to remove  
239 gravels and debris. The <2 mm fraction was then wet sieved at 63 µm with deionized (DI) water.  
240 Both the sand-sized (63 µm – 2 mm; termed “sand fraction” hereafter) and silt-sized (<63 µm)  
241 fractions were kept. The silt-sized fraction was further processed by centrifugation to extract the  
242 clay-sized fraction (<2 µm; termed “clay fraction” hereafter) using the protocol established by  
243 Starkey et al. (1984).

244 Preliminary experiments were performed on this protocol by repeated processing and  
245 analyses of the clay fraction and supernatant for B concentration and isotopes to verify if this  
246 procedure i) removes adsorbed B and/or ii) dissolves soluble B-bearing phases from the clay  
247 minerals. Results from these experiments indicate that the large volumes of DI and 18.2 mΩ  
248 water used in the protocol are efficient at removing adsorbed B from clay mineral surfaces and  
249 that the dissolution of B-bearing phases does not occur. After repeated processing of the same  
250 clay fraction, the B concentration in the supernatant was significantly less than that of the  
251 supernatant in the first analysis and nearly nil. This indicates that nearly all adsorbed B is  
252 exchanged with the water by using this protocol once to extract the clay fraction. Low B  
253 concentration in the supernatant of the once-processed clay fraction indicates that the adsorbed  
254 B represents approximately 1% of the total B analyzed; this is reasonable given the very high  
255 water-rock ratio and the diluted nature of B (~10 ng g<sup>-1</sup>) in rivers, which are not favorable to  
256 significant B adsorption. Boron Isotope analyses of the same clay fraction processed twice  
257 indicates the protocol does not induce a significant analytical B isotope bias ( $\delta^{11}\text{B}_{\text{clay}} = -15.3 \text{ ‰}$   
258 and  $-15.7 \text{ ‰}$ , on first and second protocol trials, respectively).

259 Bedrock samples were ground to a powder using a tungsten carbide mill while sediments  
260 samples were powdered in an agate mortar.

261 River water was collected from small streams in monolithological catchments and the  
262 Murrumbidgee River. Water samples were filtered in the field using a portable water filtration  
263 system with 0.2 µm Mixed Cellulose Ester (MCE) membrane filters. The pH and alkalinity were

264 determined on the <0.2  $\mu\text{m}$  fraction (termed “dissolved load” hereafter) following the method  
265 of Barnes (1964).

266

### 267 **3.3. Mineralogy**

268 Mineralogy of bedrock and the clay fractions from monolithological catchments was  
269 determined by X-ray diffraction (XRD) using a Phillips 1130/90 diffractometer at the University of  
270 Wollongong. The Spellman DF3 generator was set to 35 kV and 28.8 mA which produced 1 kW of  
271 power. Samples were analyzed between 4 and 70° 2-theta at 2° per minute with a step size of  
272 0.02. Following the protocol of Brindley (1980), an aliquot of the clay fraction was first mounted  
273 specifically to orient the clay minerals based on their principal reflection. Samples were then  
274 treated with ethylene glycol and processed a second time allowing better quantification of the  
275 expandable clay content. Traces were produced through a GBC 122 control system and a semi-  
276 quantitative analysis of the relative proportions of crystalline phases was performed using the  
277 Traces and SIROQUANT software. Quantification reproducibility was determined by repeated  
278 analyses of the once-prepared sample N. Booroorban and is:  $\pm 2\%$  (biotite); 0% (chlorite); 1%  
279 (quartz); 4% (muscovite); 1% (orthoclase); 2% (albite); 3% (K-feldspar); 3% (kaolinite); 4% (mixed  
280 illite/smectite layer); 4% (kaolinite); and 11% (illite) (2 SD, n = 3).

281

### 282 **3.4. Major element concentrations**

283 For sediments, 100 mg of powder were digested in a mixture of 48% HF and 65%  $\text{HNO}_3$ ,  
284 followed by aqua regia, and then refluxed in 0.3 M  $\text{HNO}_3$ . Water samples were dried down prior  
285 to analyses and also refluxed in 0.3 M  $\text{HNO}_3$ . Major and trace element concentrations were  
286 measured on a Thermo iCAP-Q quadrupole inductively coupled plasma mass spectrometer (Q  
287 ICP-MS) at the Wollongong Isotope Geochronology Laboratory (WIGL), University of Wollongong.  
288 Concentrations were quantified using a multi-element standard external calibration curve. A 1-  
289 ppb multi-element solution was measured every 10 samples and used to correct for instrumental  
290 drift, assessed to be approximately  $\pm 1\%$ . Full procedure blanks were analyzed alongside samples  
291 and yielded total blank contribution of <1% for major and trace elements. The accuracy of the  
292 entire procedure was determined by the measurement of geological reference materials: BCR-2

293 and GSP-2 (USGS; Raczek et al., 2001); JG-2 (Japanese Geological Survey; Korotev, 1996). Overall  
294 uncertainty on concentration measurements was determined by repeated analyses of  
295 individually processed aliquots of the geological reference material and was less than 10% (2 RSD,  
296 n = 5) for major and trace elements.

297

### 298 **3.5. Sample preparation for B concentration and isotope analysis**

299 Bedrock and sediment powders were digested by alkali fusion in Pt crucibles using potassium  
300 carbonate in a 5:1 flux to sample ratio. About 50 mg of powdered sample was mixed with 250  
301 mg of ground  $K_2CO_3$ , loaded into the crucible and placed into a muffle furnace at 950°C for 40  
302 min. The resulting fusion residue was cooled to room temperature. Approximately 4 mL of 1M  
303 HCl was added to the crucible causing immediate outgassing of  $CO_2$  and dissolution of carbonate  
304 phases. The sample was diluted to 35 mL with 18.2 MΩ water, ultrasonically shaken and  
305 centrifuged at 4000 rpm for 20 min. This procedure yields a solid residue; however it has been  
306 shown to not contain any boron (Lemarchand et al., 2012).

307 Boron was isolated from the supernatant by ion exchange chromatography performed under  
308 Class 100 cleanroom conditions at WIGL. This involved a two-step process following the method  
309 of Roux et al. (2015). Typically, 5 mL of solution, corresponding to approximately 300 ng B, was  
310 weighed and loaded onto a column containing 1.5 mL of BIORAD AG50W-X8 cation exchange  
311 resin. This was done primarily to remove the large amount of potassium brought by the  $K_2CO_3$   
312 flux. Boron and other elements such as silicon, are not retained on the resin and eluted in 5 mL  
313 of 0.01 M HCl. The pH of the elution was then raised to 9 using NaOH. The NaOH used was purified  
314 from B by ion exchange chromatography using Amberlite IRA 743 resin immediately before use.  
315 The sample was loaded onto a second column filled with 0.5 mL of Amberlite IRA 743 B-specific  
316 resin. Boron was eluted in 5 mL of 0.5 M HCl and ready for isotopic analysis. For dissolved load  
317 samples, a small amount of B-free NaOH was added to raise the pH to 9. This solution was then  
318 loaded onto the second column and B eluted in 5 mL of 0.5 M HCl.

319

### 320 **3.6. Boron concentration analysis**

321 Boron concentrations were determined by isotope dilution following the procedure  
322 described in Roux et al. (2015). Measurements were performed by Q ICP-MS to prevent cross-  
323 contaminating of the multi-collector ICP-MS used for isotope ratio determination. Precision and  
324 accuracy were assessed by repeated analysis of USGS W-2a diabase reference material yielding  
325 a B concentration of  $11.7 \pm 0.4$  ppm (2SD, n = 6) with a reported value of  $12.0 \pm 0.3$  ppm (2SD, n  
326 = 10) (Govindaraju, 1994). Precision on this reference material was 2% (2 RSD). The total  
327 procedural blank for sediment analysis was  $34 \pm 5$  ng (2SD, n = 6) where the majority of the B  
328 contamination originates from the  $K_2CO_3$  used as flux. The total procedural blank for water  
329 analysis was  $2.5 \pm 0.8$  ng (2SD, n = 9). For water samples with B concentrations of approximately  
330 5 ppb, 50 mL of sample (~250 ng of B) was processed. Using this protocol, the total contamination  
331 was <3 % for sediments and <1 % for waters.

332

### 333 **3.7. Boron isotope analysis**

334 Boron isotopic ratios were determined by multi-collector ICP-MS on a Thermo Neptune Plus  
335 at WIGL, using a protocol adapted from Roux et al. (2015). Sample introduction system consisted  
336 of standard sample and skimmer cones, cyclonic spray chamber, and PFA nebulizer with a  $100 \mu\text{L}$   
337  $\text{min}^{-1}$  flow rate. The instrument was tuned on mass 11 with a 50 ppb solution of NIST SRM 951.  
338 A sensitivity for  $^{11}\text{B}$  of 9 mV/ppb was typically obtained after tuning. The measured  $^{11}\text{B}/^{10}\text{B}$  ratio  
339 was corrected for instrumental mass discrimination through external normalization by standard  
340 bracketing. Mass discrimination-corrected  $^{11}\text{B}/^{10}\text{B}$  were expressed as  $\delta^{11}\text{B}$  (unit: ‰) by  
341 normalizing the ratio to that of NIST SRM 951 reference material. Between sample and standard  
342 analyses, rinsing was performed for 10 min with a 0.5 M HCl solution producing a baseline drift  
343 smaller than  $0.15 \text{ mV} \cdot \text{min}^{-1}$  which corresponds to an analytical uncertainty below 0.16‰, which  
344 is deemed acceptable for this method (Roux et al., 2015). Accuracy and precision of isotopic  
345 measurements was assessed by replicate analyses of USGS rock standard W-2a diabase and boric  
346 acid standard solution ERM AE120, which yielded  $\delta^{11}\text{B}$  values of  $12.2 \pm 0.4$  ‰ (2SD, n = 6) and –  
347  $20.5 \pm 0.4$  ‰ (2SD, n = 7), respectively. These values were in good agreement with Gangjian et  
348 al. (2013) and Vogl and Rosner, (2012) who reported  $\delta^{11}\text{B}$  values of  $12.2 \pm 0.4$  ‰ (2SD, n = 3) and  
349  $-20.2 \pm 0.6$  ‰ (2SD), respectively.

## 350 4. RESULTS

351

### 352 4.1. Spatial analysis

353 Twelve monolithological catchments were identified (Fig. 1). Catchments areas vary: <10  
354 km<sup>2</sup>, n = 4; 10 – 150 km<sup>2</sup>, n = 6; and 500 – 1000 km<sup>2</sup>, n = 2. A significant change in average  
355 landscape elevation occurs just at ~600 m above sea level (DEM and Olley and Wasson (2003)).  
356 Monolithological catchments were therefore divided in two groups: higher elevation catchments  
357 (HEC) with a mean elevation >600 m above sea level (a.s.l.), and lower elevation catchments (LEC)  
358 with a mean elevation <600 m a.s.l. The mean elevations for the HEC and LEC groups are 1270  
359 and 531 m a.s.l., respectively (Table 1). The mean annual temperature, mean annual rainfall, and  
360 mean slope for the HEC group are 9°, 1143 mm, and 13° respectively, while for the LEC group,  
361 they are 13°, 770 mm, and 7° respectively. Differences in mean annual temperature ( $p < 0.001$ ),  
362 rainfall ( $p = 0.004$ ), and slope ( $p = 0.004$ ) are significant between the HEC and LEC groups (one-  
363 way ANOVA,  $\alpha = 0.05$ ).

364 Quantification of the proportions of lithologies drained by the Murrumbidgee River was  
365 performed at nine locations along the main channel where sediments were collected (Fig. 2). The  
366 proportion of felsic volcanics, hereafter referred to as 'volcanic', decreases from 70 to 20%  
367 downstream and that of felsic intrusives, hereafter referred to as 'granitic', increases up to  
368 approximately 30% (Fig. 2). The proportion of sedimentary siliclastic rocks, hereafter referred to  
369 as 'sedimentary', is relatively constant (~ 30%), apart from one location at 350 km downstream  
370 of the source, which show proportions as low as 10% (Fig. 2). The proportions of other  
371 compositions, mainly carbonate rocks, and regolith (alluvium) are relatively low (< 10%) and  
372 constant along the Murrumbidgee River.

373

### 374 4.2. Monolithological catchments

375

#### 376 4.2.1. Bedrock

377 Bedrock samples taken from volcanic, granitic, and sedimentary monolithological catchments  
378 consist of biotite, chlorite, quartz, muscovite, orthoclase, K-feldspar, and albite; the

379 identification of secondary minerals in the bedrock was also performed and yielded traces of  
380 kaolinite (Fig. 3; Table 2). The average composition (n = 2) of sedimentary bedrock is: biotite (7%);  
381 chlorite (5%); quartz (58%); muscovite (12%); orthoclase (7%); and K-feldspar (3%). Sedimentary  
382 bedrocks contained a small portion of the secondary mineral kaolinite (10%) which is inevitable  
383 due to their formation. The average composition (n = 2) of volcanic bedrock is: biotite (5%);  
384 chlorite (3%); quartz (36%); muscovite (7%); orthoclase (5%), and albite (39%). Volcanic rocks  
385 were determined to be dacite, a common quartz-bearing volcanic rock in the Lachlan Fold Belt.  
386 The average composition (n = 3) of granitic bedrock is: biotite (14%); quartz (49%); muscovite  
387 (4%); orthoclase (6%) albite (20%); K-feldspar (5%); and trace amounts of kaolinite (3%).

388  
389 Major elements (Al, K, Mg, Na) and B concentrations were determined on 7 bedrock samples  
390 in monolithological catchments (Table 3): sedimentary (n = 2); volcanic (n = 1); and granitic (n =  
391 4); and carbonate (n = 1). In sedimentary catchments, B concentrations range from 36 to 38  $\mu\text{g}\cdot\text{g}^{-1}$ ;  
392  $\text{Mg}$  concentrations range from 7 to 12  $\text{mg}\cdot\text{g}^{-1}$ ; K concentrations range from 10 to 15  $\text{mg}\cdot\text{g}^{-1}$ ; and  
393 Al concentrations range from 29 to 30  $\text{mg}\cdot\text{g}^{-1}$ . The volcanic bedrock sample has B, Mg, K, and Al  
394 concentrations of 28  $\mu\text{g}\cdot\text{g}^{-1}$ , 7  $\text{mg}\cdot\text{g}^{-1}$ , 10  $\text{mg}\cdot\text{g}^{-1}$ , and 75  $\text{mg}\cdot\text{g}^{-1}$  respectively. Granitic bedrock  
395 samples have B, Mg, K, and Al concentrations ranging from 16 to 21  $\mu\text{g}\cdot\text{g}^{-1}$ , 4 to 14  $\text{mg}\cdot\text{g}^{-1}$ , 34 to  
396 49  $\text{mg}\cdot\text{g}^{-1}$ , and 71 to 74  $\text{mg}\cdot\text{g}^{-1}$  respectively. The carbonate bedrock sample has the lowest  
397 concentrations of B, Mg, K, and Al with values of 15  $\mu\text{g}\cdot\text{g}^{-1}$ ; 16  $\text{mg}\cdot\text{g}^{-1}$ , 10  $\text{mg}\cdot\text{g}^{-1}$ , and 14  $\text{mg}\cdot\text{g}^{-1}$ ,  
398 respectively.

399 In sedimentary catchments, bedrock  $\delta^{11}\text{B}$  range from -10.6 to -12.5 ‰ (Table 3). In the  
400 volcanic catchments, bedrock shows higher values, between -8.3 and -10.3 ‰. In granitic  
401 catchments, bedrock  $\delta^{11}\text{B}$  compositions are even higher, although overlapping with values for  
402 volcanic catchments, ranging from -5.5 to -9.0 ‰ (Table 3). Considering these values and the  
403 proportion of different lithologies derived from spatial analysis, the average  $\delta^{11}\text{B}$  of the bedrock  
404 for the Murrumbidgee River catchment at Wagga Wagga (~450 km from the source) is  $-8.9 \pm 4.4$   
405 ‰ (2SD, n = 8). In addition to having the lowest major and trace element concentrations,  
406 carbonate bedrock also has the lowest B isotope composition of -13.1 ‰.

407

408 4.2.2. Clay fraction

409 In monolithological catchments, the average mineral assemblage of the riverine clay  
410 fraction consists of kaolinite (ordered and disordered), phlogopite and lepidolite which are  
411 grouped as illites, and illite/smectite (I/S) mixed-layer clays (Table 2). The mixed-layer clays have  
412 regularly interstratified illite/smectite crystallite in a coherent stack of 2:1 layers composed of  
413 both illitic and smectitic interlayers (Veblen, 1990). Since pure smectite or montmorillonite were  
414 not detected, the proportion of mixed-layer clays is the best estimate for that of expandable clays  
415 in the sample; although illite interlayers are non-expandable. The average mineral composition  
416 of the clay fraction in each of the three types of monolithological catchments is dominated by  
417 kaolinite (56 – 60%), with lower abundances of mixed-layer clays (21 – 26%) and illite (17 – 18%).  
418 Accordingly, the average clay composition of sediments for each type of lithology is very similar  
419 to one another (Table 3). Note that small amounts (< 10 %) of primary quartz was found in some  
420 clay-sized fractions and removed prior to final quantification. Therefore, in all our samples, the B  
421 budget in the clay-size fraction is controlled in secondary clay minerals and not primary minerals.

422 Boron concentrations in the clay fraction in sedimentary catchments ranges from 33.5 to  
423 50.5  $\mu\text{g.g}^{-1}$ ; Mg, K, and Al concentrations range from 24 to 29  $\text{mg.g}^{-1}$ , 39 to 48  $\text{mg.g}^{-1}$ , and 240 to  
424 264  $\text{mg.g}^{-1}$  respectively (Table 3). In volcanic catchments, B concentrations of clay fractions range  
425 from 15.7 to 40.6  $\mu\text{g.g}^{-1}$ ; Mg, K, and Al concentrations range from 22 to 24  $\text{mg.g}^{-1}$ , 19 to 29  $\text{mg.g}^{-1}$ ,  
426 and 183 to 211  $\text{mg.g}^{-1}$  respectively. In granitic catchments, B concentrations of clay fractions  
427 show a large range of values from 34.1 to 60.6 and display the highest values. Concentration of  
428 major elements Mg, K, and Al have overlapping ranges for both sedimentary and volcanic clay  
429 fractions, with values ranging from 19 to 37  $\text{mg.g}^{-1}$ , 31 to 41  $\text{mg.g}^{-1}$ , and 226 to 255  $\text{mg.g}^{-1}$   
430 respectively. Similar to the carbonate bedrock, the carbonate clay fraction displays the lowest B  
431 concentration, with 15.7  $\mu\text{g.g}^{-1}$ . Potassium and Al concentrations of carbonate clay fractions are  
432 also lower than other lithologies with values of 10  $\text{mg.g}^{-1}$  and 192  $\text{mg.g}^{-1}$ , respectively, while Mg  
433 concentrations are among the highest (44  $\text{mg.g}^{-1}$ ). Boron isotope compositions of clay fraction in  
434 sedimentary, volcanic, and granitic lithologies range from -12.2 to -15.2 ‰, -9.7 to -13.6 ‰, and  
435 -5.6 to -9.3 ‰ respectively (Table 2). Accordingly, granitic lithologies have the heaviest B isotope  
436 composition. Conversely, carbonate clay fractions have the lowest B isotope composition of all  
437 lithologies with a value of -18.6 ‰.



438 Boron content and  $\delta^{11}\text{B}$  of the clay fraction is dependent on those of the corresponding  
439 bedrock and the extent of B leaching and isotopic fractionation between the parent material and  
440 the neoformed weathered material. Boron content in the clay fraction is typically two or three  
441 times that of the parent material and the clay fraction typically has an isotopically lighter  $\delta^{11}\text{B}$   
442 composition than the parent material (Fig. 7; Table 3). This lighter isotopic composition is  
443 explained as the clay fraction is primarily composed of weathered products which tend to  
444 incorporate  $^{10}\text{B}$  during chemical weathering (e.g. Lemarchand et al., 2012; Spivack et al., 1987;  
445 Schwarcz et al., 1969). In lower elevation catchments (LEC) and in granitic catchments, there is  
446 little difference between the B isotope composition of the clay fraction and that of the bedrock.  
447 In higher elevation catchments, the clay fraction is enriched in  $^{10}\text{B}$  (except for the granitic  
448 catchment) indicating significant isotope differences between the bedrock and clay fraction only  
449 occur in these catchments.

450

#### 451 **4.3. Murrumbidgee River and tributaries**

##### 452 4.3.1. Sand fraction

453 The sand fraction of bank sediments from the Murrumbidgee River main channel shows a  
454 narrow range of B isotopic composition, from  $-9.6\text{‰}$  to  $-11.0\text{‰}$  (Fig. 4, Table 4). The  $\delta^{11}\text{B}$   
455 composition of the sand fraction at Wagga Wagga ( $-10.4 \pm 1.0\text{‰}$ , 2SD,  $n = 6$ ) is similar to the  
456 average value calculated for this location using bedrock distribution and B isotope compositions  
457 ( $-8.9 \pm 4.4\text{‰}$ , 2SD,  $n = 8$ ). These observations suggest that (i) B isotopes are not fractionated in  
458 the sand fraction, compared to the bedrock, (ii) the B isotope composition of the sand fraction is  
459 not modified during transport and (iii) it faithfully records the average composition of the  
460 bedrock drained. These hypotheses are discussed below.

461

##### 462 4.3.2. Clay fraction

463 Boron concentrations range from 16 to 60 ppm (Table 4). B/Al, Mg/Al and K/Al ratios  
464 decrease downstream following the same trend in all the tributaries and the Murrumbidgee River  
465 samples (Fig. 5A-C). The relative decrease of B, Mg, and K concentrations with distance  
466 downstream suggests either a progressive loss of mobile elements during transport or a mixture

467 of tributary sediments formed under different weathering conditions in the Murrumbidgee River.  
468 These hypotheses are discussed below.

469 In contrast with the sand fraction, clay fractions of the Murrumbidgee River show more  
470 variable  $\delta^{11}\text{B}$  values and a systematic increase downstream (Fig. 4, Table 4). At locations with a  
471 mean elevation > 600 m (defined as the *upper catchment*), values range from  $-18.4$  to  $-11.6$  ‰.  
472 At lower mean elevation, values range from  $-12.5$  to  $-10.8$  ‰. In the eight major tributaries,  $\delta^{11}\text{B}$   
473 values range from  $-15$  to  $-9.8$  ‰. For six tributaries that were sampled along their channel, a  
474 downstream increase in  $\delta^{11}\text{B}$  values is also observed (Fig. 4, Table 4).

475

#### 476 **4.4. Dissolved load**

477 In the Murrumbidgee River, the dissolved load shows a downstream increase in B  
478 concentrations (from 1.9 to 9.2 ng/mL) (Fig. 6A; Table 4). B/Na and B/Mg ratios show a sharp  
479 decrease downstream, between approximately 50 and 100 km from the source, and little  
480 variation further downstream (Fig. 6B and 6C). Boron was compared to Na and Mg because they  
481 show a conservative behavior in the dissolved phase; downstream increase of B, Na, and Mg  
482 concentrations may indicate evaporation.

483 Boron isotope compositions range from 26 to 32 ‰ and do not show significant variations  
484 downstream (Fig. 6A; Table 4). These values are high compared to other rivers worldwide  
485 (Lemarchand et al., 2000; Rose et al., 2000; Lemarchand and Gaillardet, 2006; Chetelat et al.,  
486 2009) and to the world average value inferred from largest rivers ( $+10$  ‰; Lemarchand et al.,  
487 2002b). Such high values are also observed in the Niger River, Nigeria (35 ‰), the Maroni River,  
488 French Guyana (43 ‰) (Lemarchand et al., 2000) and in rivers of Guadeloupe, Lesser Antilles  
489 (from 39.1 to 44.8 ‰, Louvat et al. 2011).

490

491

## 492 **5. DISCUSSION**

### 493 *5.1. Lithological and climatic controls on B isotope compositions*

494 In monolithological catchments, the B isotope composition of clay fractions co-varies with  
495 that of their corresponding bedrock. The offset between the B isotope composition of bedrock  
496 and clay fraction ( $\Delta^{11}\text{B}_{\text{clay-bedrock}}$ ) is nil or close to nil in LEC and granitic HEC, and up to 5.5 ‰ in

497 the carbonate catchment (Fig. 7). Differences in B isotope compositions of clay fractions between  
498 HEC and LEC suggest that local climatic conditions and/or topography are controlling the B  
499 isotope composition of the clay fraction. The lack of isotope difference between the bedrock and  
500 clay fraction in granitic lithologies compared to other lithologies in HEC also suggests a lithological  
501 control on the B isotope composition of the clay fraction.

502 To quantitatively characterize B behavior during clay formation and investigate how this may  
503 relate to the weathering regime, the relative magnitude of the B transfer from the bedrock to  
504 the neoformed clay minerals ( $\tau_{Al,B}$ ) is calculated using samples from monolithological  
505 catchments (White et al., 2005):

506

$$507 \quad \tau_{Al,B} = \frac{[B]_{clay}}{[B]_{bedrock}} \times \frac{[Al]_{bedrock}}{[Al]_{clay}} - 1 \quad (1)$$

508 where brackets denote concentrations. Aluminum was chosen as the reference element as it is a  
509 major insoluble element during chemical weathering. Negative and positive  $\tau_{Al,B}$  values indicate  
510 respectively loss and gain of B during clay formation (a value of -1 would indicate 100% loss, for  
511 instance). It is important to note that  $\tau_{Al,B}$  values calculated here reflect the mass transfer of B  
512 from the bedrock to the clay-sized fraction only, not the bulk soil sample as reported in many  
513 other studies (e.g. White et al., 2005; White et al., 2008; Noireaux et al., 2014).

514 In monolithological catchments,  $\tau_{Al,B}$  values range from -0.27 to -0.93 (Fig. 7B). In  
515 sedimentary and carbonate catchments,  $\tau_{Al,B}$  values are < -0.80 suggesting a large (>80%) loss of  
516 B. These catchments also show the largest difference between the B isotope composition of the  
517 clay fraction and the bedrock,  $\Delta^{11}B_{clay-bedrock}$  (Fig. 7B). This suggests that the isotope difference is  
518 associated with a loss of B from the bedrock and low B re-incorporation into clays; while in  
519 granitic catchments and in LEC, the lack of isotope difference is associated with a reduced B loss  
520 from the bedrock and higher B re-incorporation into clays. Previous studies have shown that  
521 mineral/bedrock dissolution does not induce significant isotope fractionation, but instead  
522 isotope fractionation occurs during mineral neo-formation which is characterized by a  $^{10}B$   
523 enrichment in the weathering products (Lemarchand et al., 2012; Lemarchand and Gaillardet,  
524 2006; Rose et al., 2000). Isotope difference between the clay fraction and bedrock in this study  
525 is therefore assumed to be caused by precipitation of B into the clay fraction during mineral

526 neoformation. The relationship between mass transfer coefficients and B isotope difference  
527 between the bedrock and the clay fraction is best explained by a competition between  
528 dissolution and precipitation rates where greater  $\Delta^{11}\text{B}_{\text{clay-bedrock}}$  and lower  $\tau_{\text{Al,B}}$  values are  
529 observed when little B from solution is re-incorporated into the clay fraction. Conversely, lower  
530  $\Delta^{11}\text{B}_{\text{clay-bedrock}}$  and higher  $\tau_{\text{Al,B}}$  values are observed when the proportion of B involved in mineral  
531 neo-formation reactions is greater. This hypothesis assumes that (i) continual bedrock dissolution  
532 produces low  $\delta^{11}\text{B}$  soil solution values, and (ii)  $^{10}\text{B}$  is preferentially uptaken by secondary phases  
533 leading to an  $^{11}\text{B}$  enrichment in the complementary soil solution. The strength in this hypothesis  
534 lies in the fact that the B budget is mainly controlled by clay minerals and not crushed primary  
535 clay-sized minerals (Fig. 3). According to this hypothesis, as the amount of precipitation of B into  
536 secondary phases increases, the B isotopic composition of the soil solution and the clay fraction  
537 should increase. Assuming a constant isotopic difference between the soil solution and the neo-  
538 formed clay fractions of  $-30\text{‰}$  (e.g. Palmer et al., 1987; Lemarchand et al, 2015), the observed  
539  $\delta^{11}\text{B}$  bulk clay fraction values between  $-5.6$  and  $-18.6\text{‰}$  would require a soil solution with a  
540 starting  $\delta^{11}\text{B}$  composition of approximately  $+10\text{‰}$ . Such value would derive from a mixture of  
541 bedrock dissolution (average  $\delta^{11}\text{B}$  bedrock in Murrumbidgee  $\approx -9\text{‰}$ ), B cycling through  
542 vegetation (e.g.  $+35\text{‰}$ , Cividini et al., 2010), and atmospheric sources (e.g.  $+18\text{‰}$  or higher,  
543 Roux et al., 2017). In this model, the  $\delta^{11}\text{B}$  composition of clay fractions approaches that of the  
544 parent material in precipitation-dominated weathering regimes while it would be lower in  
545 dissolution-dominated weathering regimes. For example, in Shale Hills Pennsylvania Noireaux et  
546 al. (2014) reports  $\delta^{11}\text{B}$  clay fraction composition similar but slightly lighter than parent material,  
547 while Lemarchand et al. (2012) and Cividini et al. (2010) report higher than bedrock values in the  
548 Strengbach watershed, where vegetation cycling and/or atmospheric inputs are major  
549 contributors to the biogeochemical cycle of boron.

550 In all LEC and granitic HEC, the weathering regime appears to be precipitation-dominated as  
551 both lower  $\Delta^{11}\text{B}_{\text{clay-bedrock}}$  and higher  $\tau_{\text{Al,B}}$  values are observed. In non-granitic HECs, clay minerals  
552 form in dissolution-dominated weathering regimes (greater  $\Delta^{11}\text{B}_{\text{clay-bedrock}}$  and lower  $\tau_{\text{Al,B}}$  values).  
553 This would imply that in HEC, clay production rates are higher for granitic parent material  
554 compared to other lithologies. However, because granitic rocks show lower dissolution rates

555 compared to sedimentary, volcanic, and carbonate lithologies (e.g. Meybeck, 1986), it is unlikely  
556 higher clay production rates in granitic lithologies are driven by lithology type. Therefore, local  
557 hydrological conditions such as increased water residence time or lower water/rock ratio may  
558 possibly explain the apparent lithologic control on  $\delta^{11}\text{B}$  in granitic clays produced in HEC. The B  
559 isotope composition of clays in granitic lithologies of HEC are similar to all lithologies in LEC, both  
560 characterized by increased water residence times and lower water/rock ratios which likely  
561 increase clay production and thereby produce isotopically heavier clays. However, the granitic  
562 lithologies in the HEC also appear to be driven by local catchment topography and hydrology. In  
563 non-granitic catchments, lower B precipitation rates in HEC compared to LEC could be attributed  
564 to steeper catchment slopes (average:  $12^\circ$  in HEC, compared to  $7^\circ$  in LEC), lower annual  
565 temperatures (average:  $9^\circ\text{C}$ , compared to  $13^\circ\text{C}$  in LEC), and higher annual rainfall (average: 1,052  
566 mm, compared to 770 mm in LEC) in HEC. Prevailing conditions in HEC would therefore promote  
567 bedrock mobilization, little dissolution, and low precipitation rates because of the more active  
568 hydrologic regime. Shallower slopes and reduced rainfall in LEC could result in increased water  
569 residence time in soils (longer water-rock interactions), which coupled with increased annual  
570 temperatures, would favor more clay production and therefore a precipitation-dominated  
571 weathering regime (e.g. van Breemen and Brinkman, 1976).

572

573       5.2.    *Geochemistry and B isotope composition of Murrumbidgee River sediments – source*  
574                *mixing and fluvial transport*

575       Using the proportion of each lithology drained at each sampling locations on the  
576 Murrumbidgee and the average  $\delta^{11}\text{B}$  composition of the bedrock for each lithology, we can  
577 calculate the theoretical  $\delta^{11}\text{B}$  composition of Murrumbidgee River sand fractions at a given  
578 location along the river. This calculation assumes that (i) there is no B isotopic fractionation  
579 between bedrock and sand fraction and (ii) all lithologies contribute to the sand fraction of the  
580 Murrumbidgee proportionally to their spatial distribution for the drainage area considered.  
581 Results show that for all Murrumbidgee River sampling locations, there is generally a good  
582 agreement between calculated and observed  $\delta^{11}\text{B}$  compositions in the sand fraction (Fig. 8D).  
583 This suggests that (i) the sand fraction represents the average bedrock composition drained, (ii)

584 there is no isotopic fractionation during conversion of bedrock to sand and (iii) there is no  
585 modification of the B isotopic composition as the sand is transported downstream.

586 Murrumbidgee River clay fractions show increasing  $\delta^{11}\text{B}$  values (Fig. 4) and decreasing B/Al,  
587 Mg/Al and K/Al ratios (Fig. 5) for the first 200 km from the source, and then relatively constant  
588 values further downstream. This downstream evolution could reflect a mixing between clays  
589 from HEC with a low  $\delta^{11}\text{B}$  and high elemental ratios with clays from LEC with a high  $\delta^{11}\text{B}$  and low  
590 elemental ratios (Fig. 8A). We calculated the  $\delta^{11}\text{B}$  composition, B/Al and Mg/Al ratios of the clay  
591 fraction using the proportion of each lithology drained at each sampling locations on the  
592 Murrumbidgee (Fig. 2) and the average composition of the clay fraction for each lithology (using  
593 values from monolithological catchments shown in Fig. 7A). Results show a good agreement  
594 between calculated and measured  $\delta^{11}\text{B}$  values (Fig. 8A), as well as B/Al and Mg/Al ratios (Fig. 8C  
595 and D). This suggests that (i) the B isotope composition and Al-normalized elemental ratios of the  
596 Murrumbidgee River clay fraction faithfully represents a mixture of clays from the different  
597 catchments drained, (ii) all lithologies contribute to the Murrumbidgee clay fraction  
598 proportionally to their spatial distribution in the catchment and (ii) there is no modification of  
599 the B isotope ratio and Al-normalized elemental ratios during transport.

600 Overall, these observations suggest that the B isotope composition of the Murrumbidgee  
601 sediment load faithfully averages the composition of the different regions drained, with no  
602 modification during transport. The sand fraction records the composition of the bedrock drained,  
603 while the clay fraction reflects that of the clays across the catchment. It is interesting to note that  
604 these results also suggest that all lithologies contribute to the Murrumbidgee sediment load  
605 (both sand and clay fractions) proportionally to their spatial distribution (within the uncertainty  
606 of our calculations).

607

### 608 5.3. *The relationship between B isotopes in clays and surface waters*

609 The B isotope composition of the Murrumbidgee River dissolved load is much heavier than  
610 the world's mean value of 10 ‰ (Lemarchand et al., 2002b). Without massive production of  
611 secondary minerals removing most of the dissolved B (unlikely under southeastern Australia  
612 climate characterized as temperate to semi-arid with wet cool winters and dry hot summers,

613 Murray-Darling Basin Authority, 2016), this possibly indicates that the dissolved B is heavily  
614 impacted by vegetation recycling and/or atmospheric inputs, as these sources are characterized  
615 by isotopically heavy  $\delta^{11}\text{B}$  compositions (e.g. vegetation: 35 ‰, Cividini et al., 2010; atmosphere:  
616 18 ‰, Roux et al., 2017). Previous studies that have reported high  $\delta^{11}\text{B}$  values of the dissolved  
617 load (Lemarchand et al., 2000; Lemarchand et al., 2002b; Louvat et al., 2011) have also proposed  
618 that the B geochemical cycle be heavily impacted by biological activity and atmospheric inputs.  
619 Increasing boron concentrations of the dissolved load downstream from the source possibly  
620 reflect increased evapotranspiration on the alluvial plain (Murray-Darling Basin Authority, 2016).  
621 Our data shows higher B/Na and B/Mg values in the first 100 km from the source and then nearly  
622 constant B/Na and B/Mg ratios in the downstream portion of the river. This indicates that B  
623 behaves conservatively and similar to Na and Mg on the plain (all increasing in concentration  
624 from 100 km downstream) yet differently from Na and Mg in the headwaters. Due to high  
625 evapotranspiration on the alluvial plain, it is therefore likely that relatively constant B/Na and  
626 B/Mg ratios on the plain reflect this increase in evapotranspiration, while higher B/Na and B/Mg  
627 in the headwaters cannot be attributed to evapotranspiration as B does not behave  
628 conservatively or similar to Na and Mg.

629 For monolithological catchments, the average  $\delta^{11}\text{B}$  composition of the clay fraction is  
630 approximately -12 ‰ and that of the dissolved load is 34 ‰. Previous studies have shown that  
631 clay minerals have a  $\delta^{11}\text{B}$  composition at most about 30 ‰ lighter than that of the corresponding  
632 solution from which they precipitate (e.g. Rose et al., 2000; Palmer et al., 1987; Spivack and  
633 Edmond, 1987), and that isotopic fractionation is a function of pH. In the Murrumbidgee River,  
634 clay fractions and corresponding dissolved loads exhibit a B isotopic difference of >40 ‰. Such a  
635 difference, together with the observed relationship shown by B isotopes and B/Al ratios in clay  
636 fractions (Fig. 7B) can neither be defined as the result of B speciation between the clay fraction  
637 and dissolved load with changes in pH (as the observed relationship between pH of the river and  
638  $\delta^{11}\text{B}$  clay fraction composition do not correspond with predicted values; see Palmer et al., 1987  
639 for review) nor as a result of a Rayleigh-like evolution of surface waters as reported in Rose et al.  
640 (2000);  $\delta^{11}\text{B}$  composition of surface waters are isotopically much heavier than required to  
641 produce observed clay fraction compositions. Instead, these observations suggest that the clay

642 fraction derives its B isotopic composition from exchange with a solution characterized by an  
643 isotopic composition lighter than that of the Murrumbidgee dissolved load. Such a solution is  
644 expected deeper in the soil profile below the influence of atmospherically and biologically-cycled  
645 boron.

646 Atmospheric inputs and biological processes impart high  $\delta^{11}\text{B}$  values to soil solutions, but  
647 their influence is limited to the near surface. While the influence of atmospheric inputs decreases  
648 with increasing depth, that of biological processes reach a maximum at depth, corresponding to  
649 the depth of maximum tree root density (Cividini et al. 2010; Fig 8) and then gradually decrease  
650 downward. The depth at which atmospheric and biological process imprint a heavy isotopic  
651 signature on the soil will be very different from one location to the next. In eastern France,  
652 Cividini et al. (2010) showed that the composition of soil solutions is influenced by atmospheric  
653 inputs and biological processes down to a depth of ~2 m. At greater depths, soil solutions and  
654 sediments record only water-mineral interactions. Thus, in thin weathering profiles as found in  
655 the Murrumbidgee (Olley and Wasson, 2003), the proportion of the profile influenced by  
656 atmospheric inputs and biological processes is expected to be greater than for thick profiles such  
657 as those reported by Cividini et al., (2010) in a wetter and more dense temperate forest. It is  
658 hypothesized that this proportion would be even smaller in thicker weathering profiles formed  
659 in wetter and warmer conditions and greater in the thin profiles formed in a more arid climate.  
660 However, there are many unknown factors that could also affect this proportion such as local  
661 hydrology, residence time, and sediment and vegetation type. Consequently, clays formed in thin  
662 profiles and/or at shallow depths, are likely to preserve a record of atmospheric and biological  
663 influences, translated into high  $\delta^{11}\text{B}$  values. Conversely, clays formed at greater depths in thick  
664 profiles should be characterized by lower  $\delta^{11}\text{B}$  values since the soil solutions they interacted with  
665 show no imprint of atmospheric and biological processes. Despite thinner weathering profiles in  
666 the Murrumbidgee, the locus of clay formation appears to be deep within the profile and not  
667 influenced by atmospheric or biological processes.

668 The large difference in  $\delta^{11}\text{B}$  compositions between clay fractions and dissolved load in the  
669 Murrumbidgee can thus be explained if clays were formed at depth in thick weathering profiles  
670 while the dissolved load derived its B mostly from surface runoff and shallow waters. A deep



671 origin for clays does not imply deep erosion of weathering profiles (unlikely since mass wasting  
672 is rare in the Murrumbidgee), but rather that clay formation would take place dominantly near  
673 the base of the weathering profile. A shallow origin for the dissolved load is surprising since it  
674 was observed that solutes are generally derived from the base of the weathering profile where  
675 weathering rates are the highest (White et al., 1998; Buss et al., 2008; Pett-Ridge et al., 2009;  
676 Kurtz et al., 2011), including in southeastern Australia (Dosseto et al., 2014). This could indicate  
677 that (i) soil solutions in deeper parts of the weathering profile and (ii) groundwaters (which would  
678 also be characterized by low  $\delta^{11}\text{B}$  values) do not contribute significantly to the river dissolved  
679 load, which appears to be highly impacted by atmospheric B and vegetation cycling.

680

## 681 **6. CONCLUSIONS**

682

683 This study investigates how the B isotope composition of riverborne material records  
684 weathering regimes in the Murrumbidgee River catchment, and how this weathering “signal” is  
685 transported from source areas to the depositional environment. Two weathering regimes were  
686 identified in the catchment: (i) one where mineral dissolution is associated with minimal  
687 neoformation and (ii) another one where mineral neoformation dominates. The distribution of  
688 the two regimes is controlled by lithology, climate and topography. In low elevation catchments  
689 (mean elevation <600 m a.s.l.), the weathering regime is dominated by mineral neoformation  
690 and precipitation of B into clays, as a consequence of higher mean annual temperatures and  
691 shallower slopes allowing for longer water residence times. In high elevation catchments, granitic  
692 catchments show a similar weathering regime to lower catchments, while in non-granitic  
693 catchments, weathering is dominated by mineral dissolution, without a significant role of mineral  
694 neoformation. This difference in high elevation catchments is attributed to the role of lithology  
695 on water residence time, where water residence time could be greater in granitic environments  
696 compared to other lithologies.

697 The B isotope composition of sand fractions collected along the Murrumbidgee River shows  
698 that the sand fraction (i) can be used as a compositional proxy for the bedrock, (ii) faithfully  
699 reflects the lithologies eroded in the catchment and (iii) is not geochemically modified during

700 fluvial transport. The B isotope composition of corresponding clay fractions also shows a  
701 conservative behavior; it represents a mixture of the clays produced from the different lithologies  
702 in the Murrumbidgee catchment and it is not modified during fluvial transport. The observed  
703 monotonous changes in B isotope composition of the clay fraction and other geochemical  
704 parameters reflect the transition from one weathering regime at higher elevation to the other  
705 one at lower elevation. These results imply that the chemical and B isotopic composition of river  
706 sediment reflects the conditions of its formation and can therefore be used as a proxy catchment-  
707 wide weathering regime.

708 For the Murrumbidgee River and for rivers from monolithological catchments, the clay  
709 fraction has a B isotope composition much lighter than predicted by equilibrium fractionation  
710 with the dissolved load. To explain this observation, we propose that clays have formed in  
711 equilibrium with a soil solution with a lighter B isotope composition than that of the river  
712 dissolved load. The difference in B isotope composition for the soil solution that produced clays  
713 and the river dissolved load can be accounted for by a variable influence of atmospheric inputs  
714 and vegetation cycling. This influence appears greater on the dissolved load compared to clay-  
715 forming soil solutions, suggesting that the latter originates from greater depths in weathering  
716 profiles compared to the former. These results illustrate a geochemical disconnect between the  
717 origin of riverborne clays and solutes. This disconnect is not reflecting heterogeneity in  
718 catchment erosion distribution (Gaillardet et al., 1995; Gaillardet et al., 1997), different  
719 timescales of sediment and solute transport (Dosseto et al., 2006), or biased sediment sampling  
720 (resolved in Dellinger et al., 2015), but rather the locus of clay formation in weathering profiles.  
721

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731 REFERENCES

732

- 733 Barnes I. (1964) Field measurement of alkalinity and pH. *USGS Water Supply Pap.* **1535–H**.
- 734 Berner R. A. and Berner E. K. (1997) Silicate Weathering and Climate. In *Tectonic Uplift and*  
735 *Climate Change* Springer US, Boston, MA. pp. 353–365.
- 736 Bouchez J., Blanckenburg V. and Schuessler J. A. (2013) Modeling noval stable isotope ratios in  
737 the weathering zone. - *Am. J. Sci. Am. J. Sci.* **313**, 267–308.
- 738 Bouchez J., Gaillardet J., Lupker M., Louvat P., France-Lanord C., Maurice L., Armijos E. and  
739 Moquet J.-S. (2012) Floodplains of large rivers: Weathering reactors or simple silos? *Chem.*  
740 *Geol.* **332–333**, 166–184.
- 741 Brantley S. L. and White A. F. (2009) Approaches to Modeling Weathered Regolith. *Rev.*  
742 *Mineral. Geochemistry* **70**, 435–484.
- 743 Buss H. L., Sak P. B., Webb S. M. and Brantley S. L. (2008) Weathering of the Rio Blanco quartz  
744 diorite, Luquillo Mountains, Puerto Rico: Coupling oxidation, dissolution, and fracturing.  
745 *Geochim. Cosmochim. Acta* **72**, 4488–4507.
- 746 Chetelat B., Gaillardet J., Freyrier R. and Négrel P. (2005) Boron isotopes in precipitation:  
747 Experimental constraints and field evidence from French Guiana. *Earth Planet. Sci. Lett.*  
748 **235**, 16–30.
- 749 Chetelat B., Liu C.-Q., Gaillardet J., Wang Q. L., Zhao Z. Q., Liang C. S. and Xiao Y. K. (2009) Boron  
750 isotopes geochemistry of the Changjiang basin rivers. *Geochim. Cosmochim. Acta* **73**,  
751 6084–6097.
- 752 Cividini D., Lemarchand D., Chabaux F., Boutin R. and Pierret M. C. (2010) From biological to  
753 lithological control of the B geochemical cycle in a forest watershed (Strengbach, Vosges).  
754 *Geochim. Cosmochim. Acta* **74**, 3143–3163.
- 755 David T. and Browne W. (1950) The geology of the Commonwealth of Australia. *London, Arnold*  
756 **3**.
- 757 Dellinger M., Bouchez J., Gaillardet J. and Faure L. (2015) Testing the Steady State Assumption  
758 for the Earth's Surface Denudation Using Li Isotopes in the Amazon Basin. *Procedia Earth*  
759 *Planet. Sci.* **13**, 162–168.
- 760 Dellinger M., Gaillardet J., Bouchez J., Calmels D., Galy V., Hilton R. G., Louvat P. and France-  
761 Lanord C. (2014) Lithium isotopes in large rivers reveal the cannibalistic nature of modern  
762 continental weathering and erosion. *Earth Planet. Sci. Lett.* **401**, 359–372.
- 763 Dosseto A., Bourdon B., Gaillardet J., Maurice-Bourgoin L. and Allègre C. J. (2006) Weathering  
764 and transport of sediments in the Bolivian Andes: Time constraints from uranium-series

765 isotopes. *Earth Planet. Sci. Lett.* **248**, 759–771.

766 Dosseto A., Buss H. L. and Chabaux F. (2014) Age and weathering rate of sediments in small  
767 catchments: The role of hillslope erosion. *Geochim. Cosmochim. Acta* **132**, 238–258.

768 Gaillardet J., Dupré B. and Allègre C. J. (1995) A global geochemical mass budget applied to the  
769 Congo basin rivers: Erosion rates and continental crust composition. *Geochim. Cosmochim.*  
770 *Acta* **59**, 3469–3485.

771 Gaillardet J., Dupré B. and Allègre C. J. (1999) Geochemistry of large river suspended sediments:  
772 silicate weathering or recycling tracer? *Geochim. Cosmochim. Acta* **63**, 4037–4051.

773 Gaillardet J., Dupré B., Allègre C. J. and Négrel P. (1997) Chemical and physical denudation in  
774 the Amazon River Basin. *Chem. Geol.* **142**, 141–173.

775 Gaillardet J. and Lemarchand D. (2017) Boron in the Weathering Environment. In Springer,  
776 Cham. pp. 163–188.

777 Galy A. and France-Lanord C. (2001) Higher erosion rates in the Himalaya: Geochemical  
778 constraints on riverine fluxes. *Geology* **29**, 23–26.

779 Gangjian W., Jingxian W., Ying L., Ting K., Zhongyuan R., Jinlong M. and Yigang X. (2013)  
780 Measurement on high-precision boron isotope of silicate materials by a single column  
781 purification method and MC-ICP-MS. *J. Anal. At. Spectrom.* **28**, 606.

782 Garzanti E. and Andò S. (2007) Chapter 20 Heavy Mineral Concentration in Modern Sands:  
783 Implications for Provenance Interpretation. In *Developments in Sedimentology* Elsevier. pp.  
784 517–545.

785 Garzanti E., Andò S. and Vezzoli G. (2009) Grain-size dependence of sediment composition and  
786 environmental bias in provenance studies. *Earth Planet. Sci. Lett.* **277**, 422–432.

787 Govindaraju K. (1994) 1994 Compilation of working values and samples description for 383  
788 geostandards. *Geostand. Geoanalytical Res.* **18**, 1–158.

789 Green, D, Petrovic, J., Moss, P., Burrell M. (2011) Water resources and management overview:  
790 Murrumbidgee catchment. *NSW Off. Water, Sydney*.

791 Korotev R. L. (1996) A self-consistent compilation of elemental concentration data for 93  
792 geochemical reference samples. *Geostand. Newsl.* **20**, 217–245.

793 Kurtz A. C., Lugolobi F. and Salvucci G. (2011) Germanium-silicon as a flow path tracer:  
794 Application to the Rio Icacos watershed. *Water Resour. Res.* **47**.

795 Lemarchand D., Cividini D., Turpault M. P. and Chabaux F. (2012) Boron isotopes in different  
796 grain size fractions: Exploring past and present water–rock interactions from two soil  
797 profiles (Strengbach, Vosges Mountains). *Geochim. Cosmochim. Acta* **98**, 78–93.

798 Lemarchand D. and Gaillardet J. (2006) Transient features of the erosion of shales in the  
799 Mackenzie basin (Canada), evidences from boron isotopes. *Earth Planet. Sci. Lett.* **245**,  
800 174–189.

801 Lemarchand D., Gaillardet J., Göpel C. and Manhès G. (2002a) An optimized procedure for  
802 boron separation and mass spectrometry analysis for river samples. *Chem. Geol.* **182**, 323–  
803 334.

804 Lemarchand D., Gaillardet J., Lewin E. and Allegre C. J. (2002b) Boron isotope systematics in  
805 large rivers: implications for the marine boron budget and paleo-pH reconstruction over  
806 the Cenozoic. *Chem. Geol.* **190**, 123–140.

807 Lemarchand D., Gaillardet J., Lewin E. and Allegre C. J. (2000) The influence of rivers on marine  
808 boron isotopes and implications for reconstructing past ocean pH. *Nature* **408**, 951–954.

809 Lemarchand E., Schott J. and Gaillardet J. (2005) Boron isotopic fractionation related to boron  
810 sorption on humic acid and the structure of surface complexes formed. *Geochim.*  
811 *Cosmochim. Acta* **69**, 3519–3533.

812 Louvat P., Gaillardet J., Paris G. and Dessert C. (2011) Boron isotope ratios of surface waters in  
813 Guadeloupe, Lesser Antilles. *Appl. Geochemistry* **26**, S76–S79.

814 Lupker M., France-Lanord C., Galy V., Lavé J., Gaillardet J., Gajurel A. P., Guilmette C., Rahman  
815 M., Singh S. K. and Sinha R. (2012) Predominant floodplain over mountain weathering of  
816 Himalayan sediments (Ganga basin). *Geochim. Cosmochim. Acta* **84**, 410–432.

817 Meybeck M. (1986) Composition des ruisseaux non pollués de France. *Sci. Geol. Bull.* **39**, 3–77.

818 Millot R., Gaillardet J., Dupré B. and Allègre C. J. (2002) The global control of silicate weathering  
819 rates and the coupling with physical erosion: New insights from rivers of the Canadian  
820 Shield. *Earth Planet. Sci. Lett.* **196**, 83–98.

821 Murray-Darling Basin Authority (2016) Murray-Darling Basin Authority annual report 2016-  
822 2017.

823 Muttik N., Kirsimäe K., Newsom H. E. and Williams L. B. (2011) Boron isotope composition of  
824 secondary smectite in suevites at the Ries crater, Germany: Boron fractionation in  
825 weathering and hydrothermal processes. *Earth Planet. Sci. Lett.* **310**, 244–251.

826 Noireaux J., Gaillardet J., Sullivan P. L., Brantley S. L., Noireaux J, A G. J., Sullivan P L and  
827 Brantley S L (2014) Boron Isotope Fractionation in Soils at Shale Hills CZO. *Procedia Earth*  
828 *Planet. Sci.* **10**, 218–222.

829 Olley J. M. and Wasson R. J. (2003) Changes in the flux of sediment in the Upper Murrumbidgee  
830 catchment, Southeastern Australia, since European settlement. *Hydrol. Process.* **17**, 3307–  
831 3320.

832 Palmer M. R., Spivack A. J. and Edmond J. M. (1987) Temperature and pH controls over isotopic  
833 fractionation during adsorption of boron on marine clay. *Geochim. Cosmochim. Acta* **51**,  
834 2319–2323.

835 Palmer M. R. and Swihart G. H. (1996) Boron isotope geochemistry; an overview. *Rev. Mineral.*  
836 *Geochemistry* **33**.

837 Pett-Ridge J. C., Derry L. A. and Kurtz A. C. (2009) Sr isotopes as a tracer of weathering  
838 processes and dust inputs in a tropical granitoid watershed, Luquillo Mountains, Puerto  
839 Rico. *Geochim. Cosmochim. Acta* **73**, 25–43.

840 Raczek I., Stoll B., Hofmann A. W. and Jochum K. P. (2001) High-precision trace element data for  
841 the USGS reference materials BCR-1, BCR-2, BHVO-1, BHVO-2, AGV-1, AGV-2, DTS-1, DTS-2,  
842 GSP-1 and GSP-2 by ID-TIMS and MIC-SSMS. *Geostand. Newsl.* **25**, 77–86.

843 Rose-Koga E. F., Sheppard S. M. F., Chaussidon M. and Carignan J. (2006) Boron isotopic  
844 composition of atmospheric precipitations and liquid–vapour fractionations. *Geochim.*  
845 *Cosmochim. Acta* **70**, 1603–1615.

846 Rose E. F., Chaussidon M. and France-Lanord C. (2000) Fractionation of boron isotopes during  
847 erosion processes: The example of Himalayan rivers. *Geochim. Cosmochim. Acta* **64**, 397–  
848 408.

849 Roux P., Lemarchand D., Hughes H. J. and Turpault M.-P. (2015) A Rapid Method for  
850 Determining Boron Concentration (ID-ICP-MS) and  $\delta^{11}\text{B}$  (MC-ICP-MS) in Vegetation  
851 Samples after Microwave Digestion and Cation Exchange Chemical Purification. *Geostand.*  
852 *Geoanalytical Res.* **39**, 453–466.

853 Roux P., Turpault M. P., Kirchen G., Redon P. O. and Lemarchand D. (2017) Boron Dissolved and  
854 Particulate Atmospheric Inputs to a Forest Ecosystem (Northeastern France). *Environ. Sci.*  
855 *Technol.* **51**, 14038–14046.

856 Schumm S. A. (1968) River Adjustment to Altered Hydrologic Regimen- Murrumbidgee River  
857 and Paleochannels, Australia. *Geol. Surv. Professional Pap.* **598**, 1–74.

858 Schwarcz H. P., Agyei E. K. and McMullen C. C. (1969) Boron isotopic fractionation during clay  
859 adsorption from sea-water. *Earth Planet. Sci. Lett.* **6**, 1–5.

860 Slaughter M., Pevear D. R., Palkowsky D. A., Jones R. C., Reynolds R. C., Poppe L. C., Calvert C. S.,  
861 Dodd J. E., Dulong F. T., Hosterman J. W., Johnson L. R. and Davis B. L. (2015) Quantitative  
862 Mineral Analysis of Clays. *Quant. Miner. Anal. Clays* **5**, 0.

863 Spivack A. and Edmond J. (1987) Boron isotope exchange between seawater and the oceanic  
864 crust. *Geochim. Cosmochim. Acta* **51**, 1033–1043.

865 Spivack A., Palmer M. and Edmond J. (1987) The sedimentary cycle of the boron isotopes.  
866 *Geochim. Cosmochim. Acta* **51**, 1939–1949.

867 Starkey H. C., Blackmon P. D. and Pevear D. R. (1984) Sample preparation procedures for the  
868 analysis of clay minerals by X-ray diffraction. *USGS. Open-File Report* **82-934**.

869 van Breemen N. and Brinkman R. (1976) Chapter 8 Chemical Equilibria and Soil Formation. *Dev.*  
870 *Soil Sci.* **5**, 141–170.

871 Vanderpool R. A. and Johnson P. E. (1992) Boron isotope ratios in commercial produce and  
872 boron-10 foliar and hydroponic enriched plants. *J. Agric. Food Chem.* **40**, 462–466.

873 Veblen D. R. (1990) High-Resolution Transmission Electron Microscopy and Electron Diffraction  
874 of Mixed-Layer Illite/Smectite: Experimental Results. *Clays Clay Miner.* **38**, 1–13.

875 Vital H. and Stattegger K. (2000) Major and trace elements of stream sediments from the  
876 lowermost Amazon River. *Chem. Geol.* **168**, 151–168.

877 Vogl J. and Rosner M. (2012) Production and Certification of a Unique Set of Isotope and Delta  
878 Reference Materials for Boron Isotope Determination in Geochemical, Environmental and  
879 Industrial Materials. *Geostand. Geoanalytical Res.* **36**, 161–175.

880 Walker J. C. G., Hays P. B. and Kasting J. F. (1981) A negative feedback mechanism for the long-  
881 term stabilization of Earth's surface temperature. *J. Geophys. Res.* **86**, 9776.

882 Wallbrink P. J., Murray A. S., Olley J. M. and Olive L. J. (1998) Determining sources and transit  
883 times of suspended sediment in the Murrumbidgee River, New South Wales, Australia,  
884 using fallout <sup>137</sup>Cs and <sup>210</sup>Pb. *Water Resour. Res.* **34**, 879–887.

885 West A. J., Galy A. and Bickle M. (2005) Tectonic and climatic controls on silicate weathering.  
886 *Earth Planet. Sci. Lett.* **235**, 211–228.

887 White A. F., Blum A. E., Schulz M. S., Vivit D. V., Stonestrom D. A., Larsen M., Murphy S. F. and  
888 Eberl D. (1998) Chemical weathering in a tropical watershed, Luquillo Mountains, Puerto  
889 Rico: I. Long-term versus short-term weathering fluxes. *Geochim. Cosmochim. Acta* **62**,  
890 209–226.

891 White A. F., Schulz M. S., Vivit D. V., Blum A. E., Stonestrom D. A. and Anderson S. P. (2008)  
892 Chemical weathering of a marine terrace chronosequence, Santa Cruz, California I:  
893 Interpreting rates and controls based on soil concentration-depth profiles. *Geochim.*  
894 *Cosmochim. Acta* **72**, 36–68.

895 White A. F., Schulz M. S., Vivit D. V., Blum A. E., Stonestrom D. A. and Harden J. W. (2005)  
896 Chemical weathering rates of a soil chronosequence on granitic alluvium: III.

897 Hydrochemical evolution and contemporary solute fluxes and rates. *Geochim. Cosmochim.*  
898 *Acta* **69**, 1975–1996.

899 Wieser M. E., Iyer S. S. S., Krouse H. R. R. and Cantagallo M. I. I. (2001) Variations in the boron  
900 isotope composition of *Coffea arabica* beans. *Appl. Geochemistry* **16**, 317–322.

901 Williams L. (2001) The influence of organic matter on the boron isotope geochemistry of the  
902 gulf coast sedimentary basin, USA. *Chem. Geol.* **174**, 445–461.

903 Xiao Y. K., Vocke, R. D., Swihart G. H. and Xiao Y. (1997) Boron Volatilization and Its Isotope  
904 Fractionation during Evaporation of Boron Solution. *Anal. Chem.* **69**, 5203–5207.

905

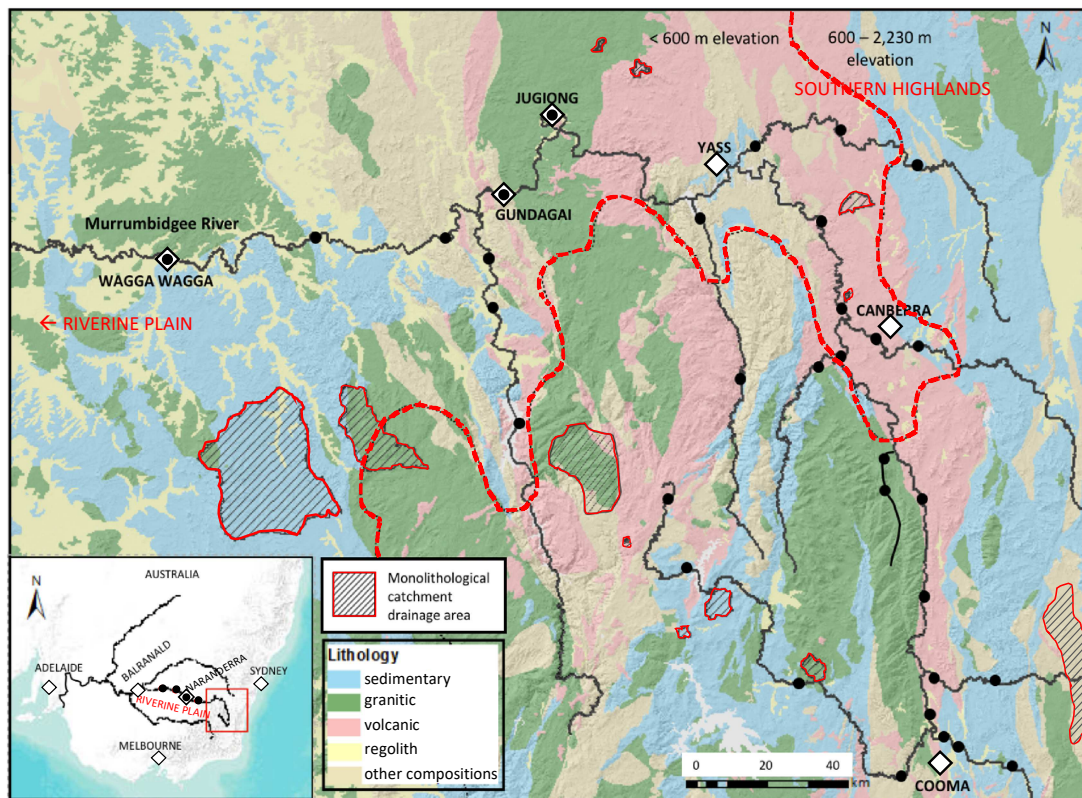


Figure 1. Lithology and digital elevation map (DEM) of the upper Murrumbidgee River and tributaries displaying sampling points for sediments and water (black dots) and sampling points for sediment, water, and bedrock in monolithological catchments with respective drainage catchment areas (hashed areas). The red dashed curve separates the upper (elevation > 600 m above sea level) and lower (< 600 m) catchments. Inset map: southeastern Australia; red rectangle shows area displayed in the main panel. Source of DEM: Geoscience Australia; source of lithology map: NSW Government; Resources and Energy; source of inset map: Esri, USGS, NOAA



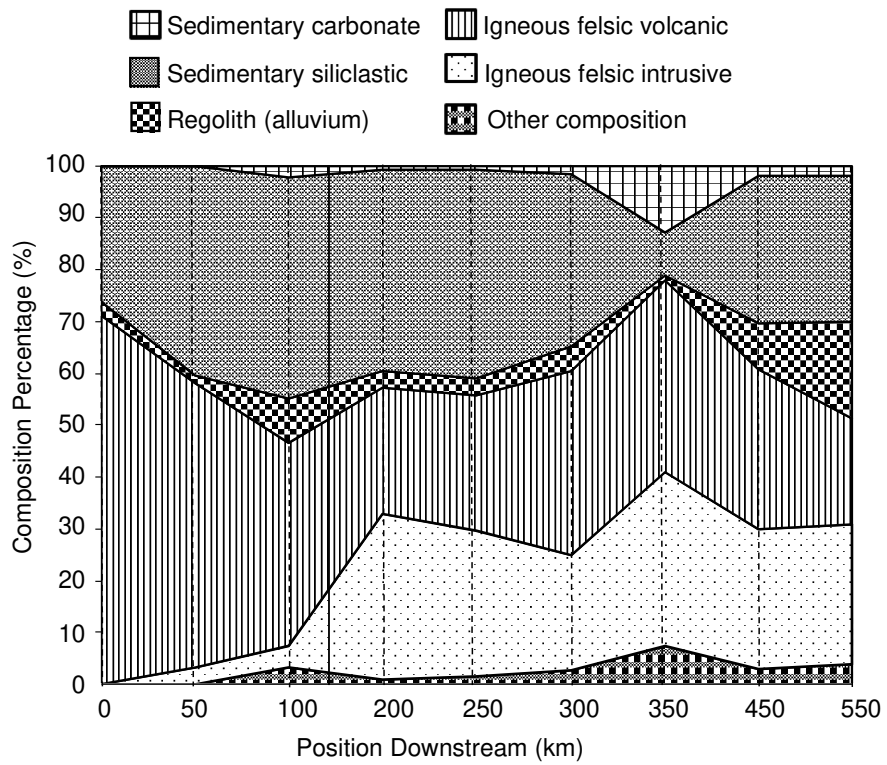


Figure 2. Proportions of the lithologies drained by the Murrumbidgee River at different locations along the main channel. The x-axis shows the distance from the source of the river. Dashed lines represent the location of sampling sites along the river at 0, 30, 111, 202, 235, 291, 354, 455, and 543 km downstream from the source. The solid line delineates the higher elevation (> 600 m) from lower elevation (< 600 m) catchments.

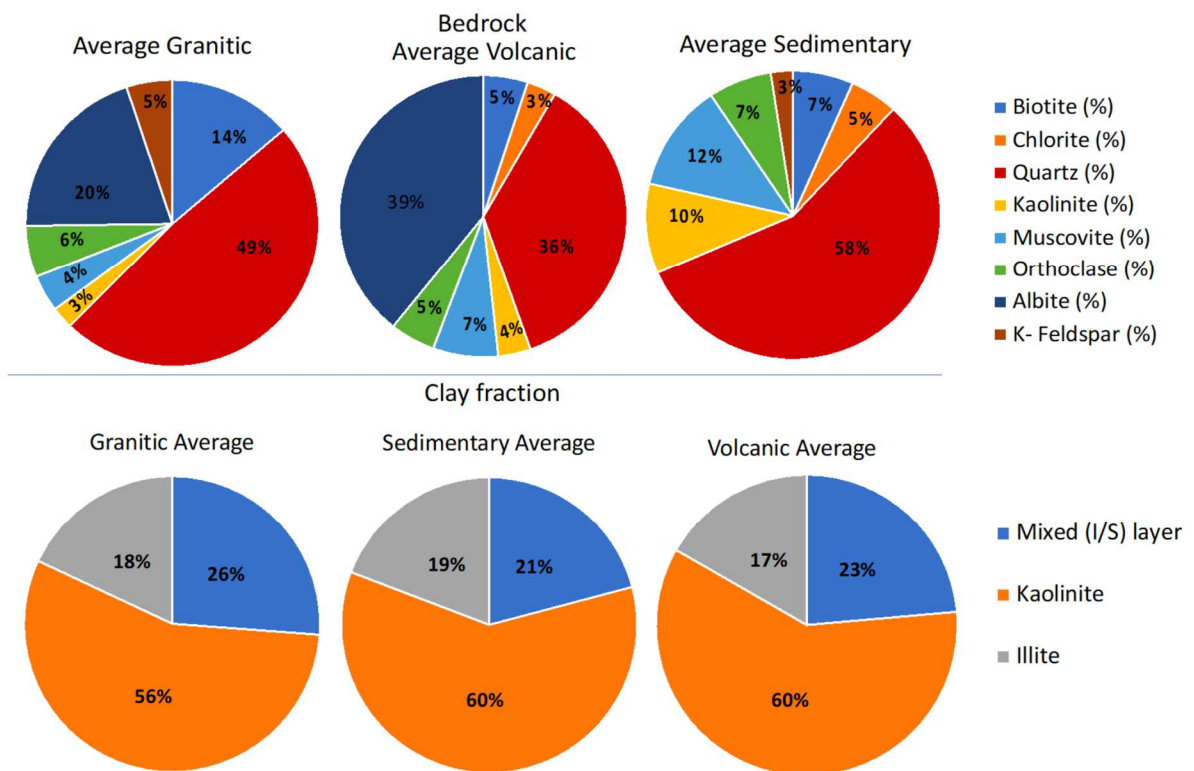


Figure 3. Mineral composition of bedrock and the clay fraction from monolithological catchments. Top panel: average mineral composition of granitic (n = 2), volcanic (n = 2), and sedimentary (n = 3) bedrock; Lower panel: average mineral composition of the clay fraction of riverine sediment taken in monolithological catchments, granitic (n = 4), sedimentary (n = 6), and volcanic (n = 4).

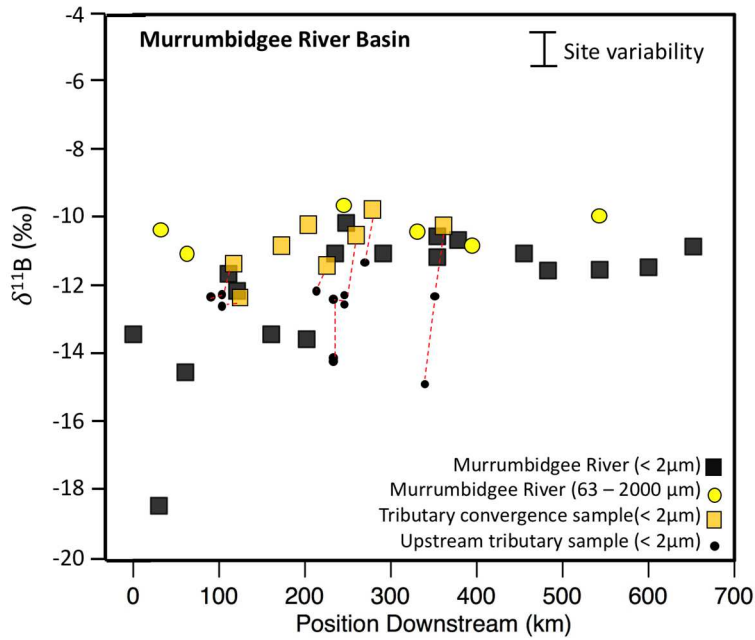


Figure 4. Boron isotope compositions in the clay (<2  $\mu\text{m}$ ) and sand fractions (63–2000  $\mu\text{m}$ ) of sediments from the Murrumbidgee River and its major tributaries. The x-axis represents the distance from the source of the Murrumbidgee River for main river samples. Tributary convergence samples are plotted at the point they converge with the main channel. Upstream tributary samples are plotted relative to the tributary convergence sample. The  $\delta^{11}\text{B}$  composition of the clay fractions from the Murrumbidgee River increases from the headwaters to the lower catchment where it levels off on the alluvial plain. The  $\delta^{11}\text{B}$  composition of the sand fractions from the Murrumbidgee River remains relatively constant downstream reflecting a mixture of unfractionated bedrock material. The  $\delta^{11}\text{B}$  composition of the clay fractions from most tributaries show a similar trend as the main river with increasing compositions further downstream. Most tributary clay fraction samples taken at the convergence with the main river appear undistinguishable from those of the main river. Site variability was assessed by collecting multiple riverbank samples several meters apart along the Yass River and determined to be approximately 1.6 ‰ (2SD,  $n = 5$ ). Analytical uncertainty of B isotope data was determined by repeated analyses of individually processed samples and is 0.4 ‰ (2SD) for all sample types.

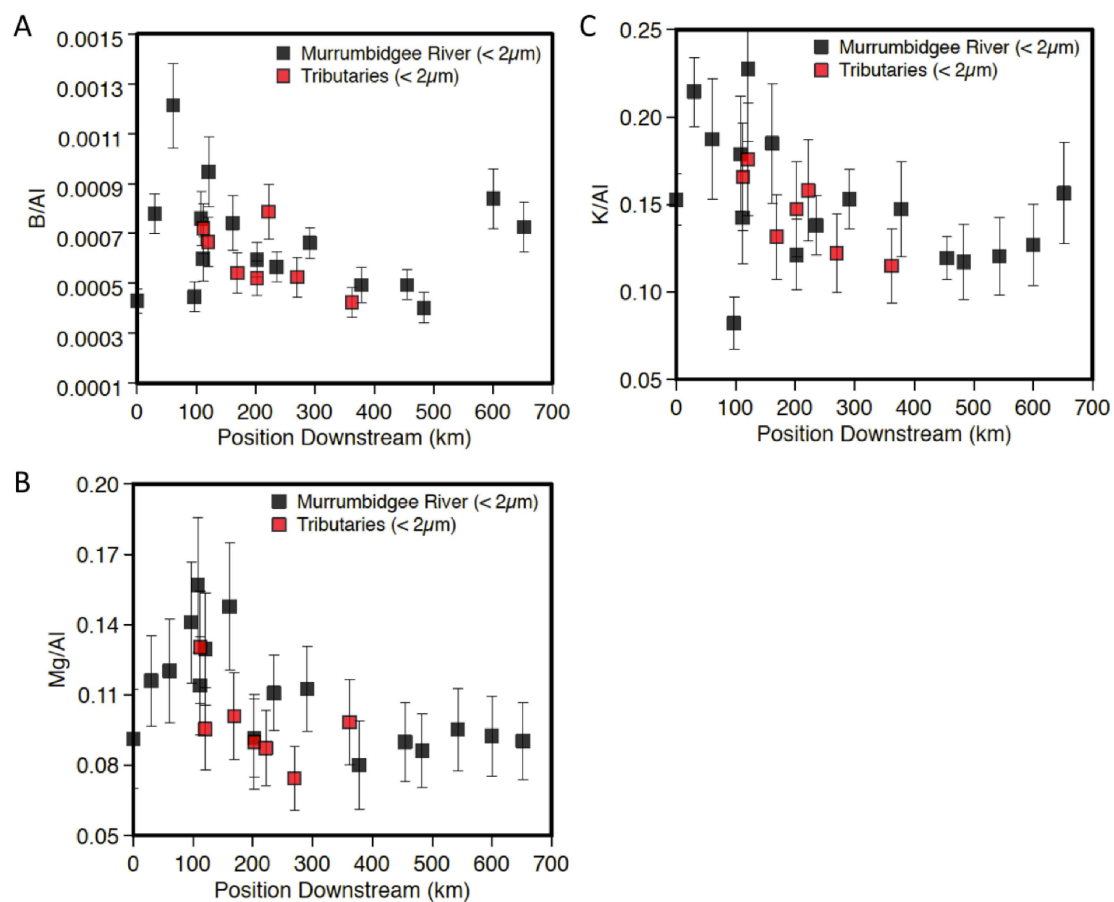


Figure 5. Major and trace elemental concentration ratios in clay fractions of the Murrumbidgee River and main tributaries. All concentrations show a relative decrease with the distance downstream from the Murrumbidgee source, suggesting a progressive loss of mobile elements such as B, Mg and K during transport or a mixture of tributary sediment delivered to the Murrumbidgee River formed under different weathering conditions in the catchment.

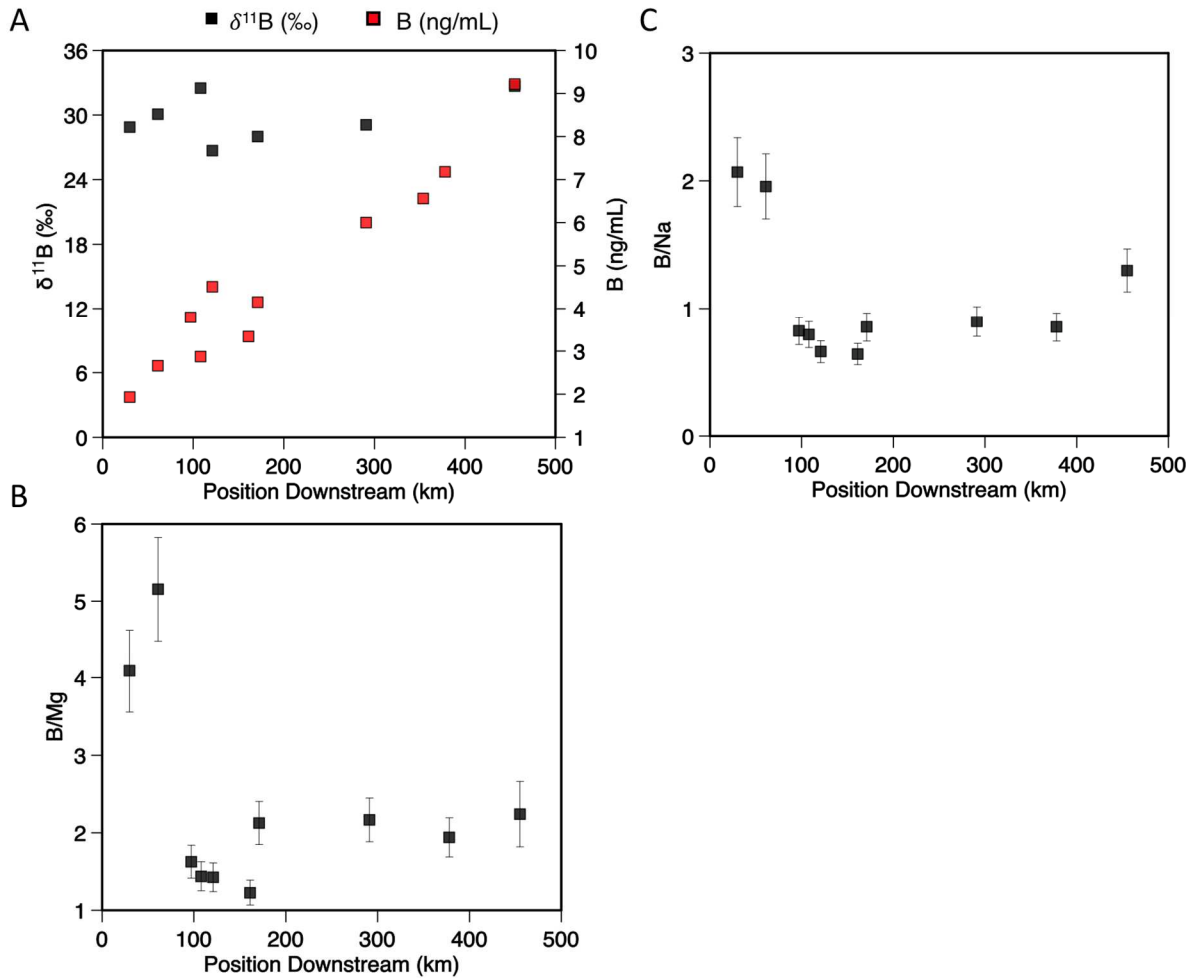


Figure 6. A) Boron concentrations and isotopic composition of the dissolved load of the Murrumbidgee River, as a function of the distance from the Murrumbidgee source. While the B concentration increases downstream, there is no significant change in isotopic composition. B) B/Mg and C) B/Na ratios of the dissolved load of the Murrumbidgee River, as a function of the distance from the Murrumbidgee source. These ratios are used as proxies to test for evaporation, as evaporation may increase both Na and Mg concentrations in the dissolved load, similar to the observed increase in B as a function of position downstream. No change in B/Mg and B/Na ratios, as observed in downstream samples, then indicates similar behavior among conservative elements in response to increasing evaporation in the lower catchment.

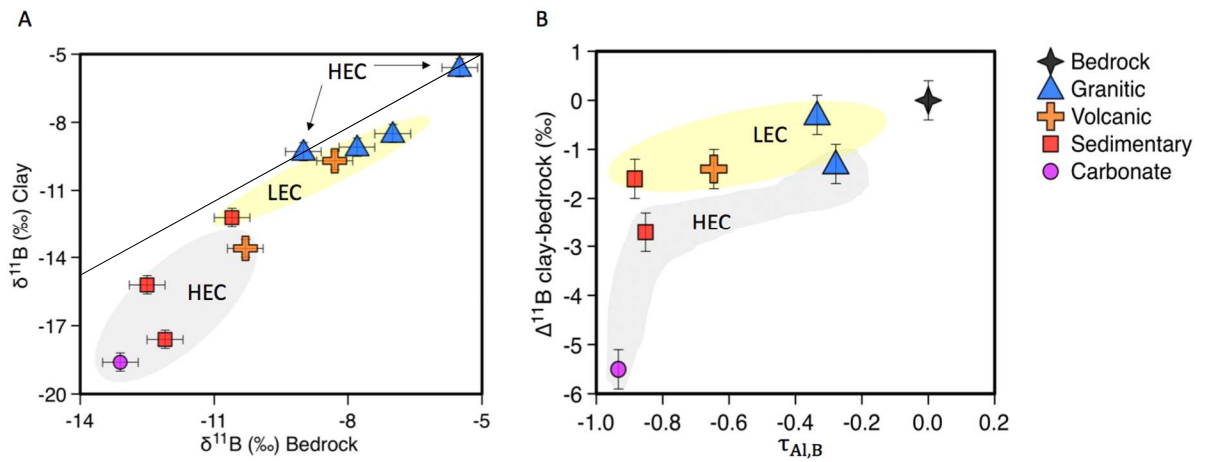


Figure 7. A)  $\delta^{11}\text{B}$  compositions of clay fractions and bedrocks for monolithological catchments. HEC: high elevation catchments (mean elevation > 600 m); LEC: low elevation catchments (mean elevation < 600 m). B) Difference between  $\delta^{11}\text{B}$  compositions of clay fractions and bedrocks,  $\Delta^{11}\text{B}_{\text{clay-bedrock}}$ , for monolithological catchments, as a function of the mass transfer coefficient for B of clay fractions ( $\tau_{\text{Al,B}}$ ; see text for details). 'Bedrock' refers to catchment bedrock; 'Granitic', 'Volcanic', 'Sedimentary', and 'Carbonate' refer to catchment lithology types.

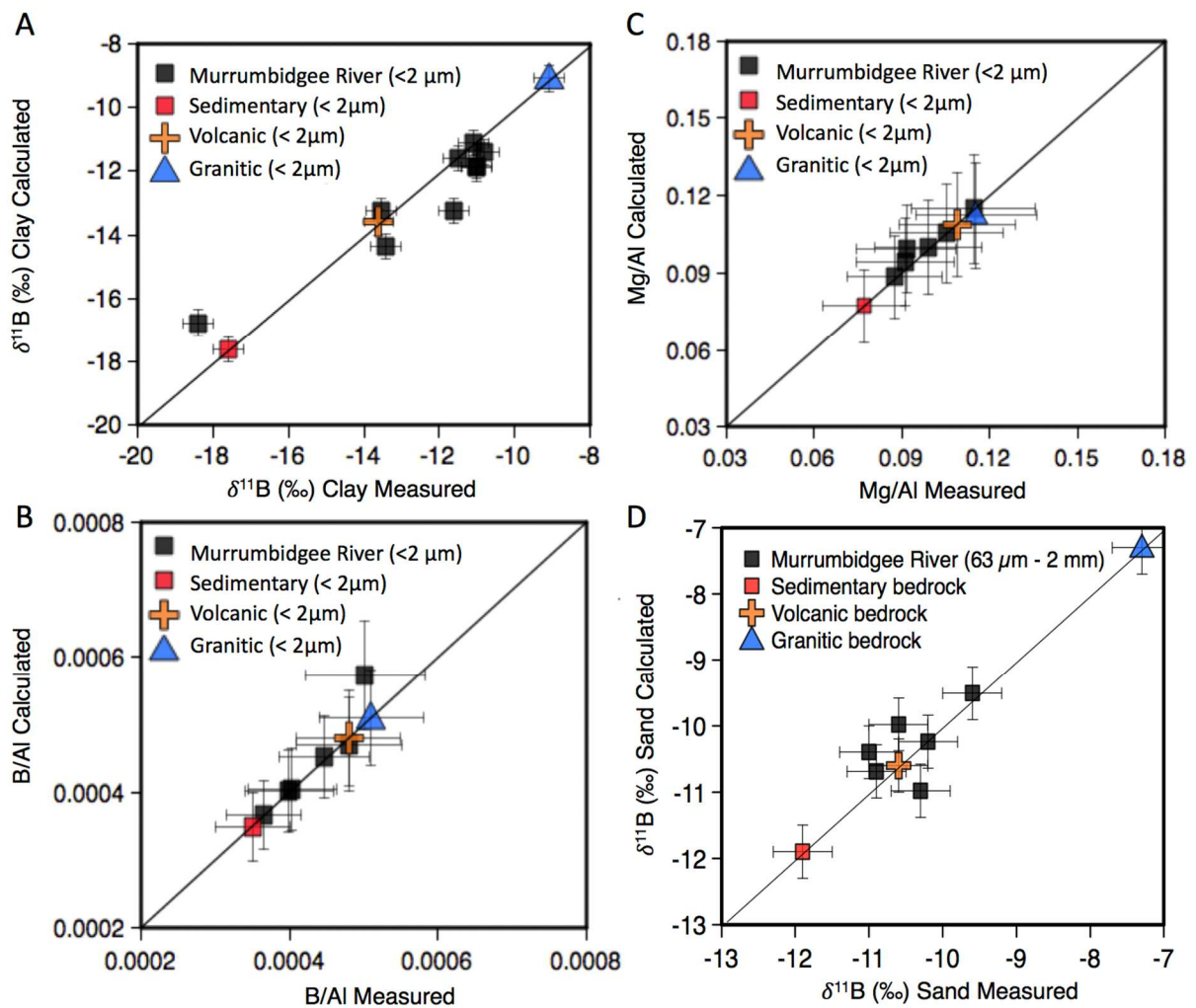


Figure 8. Calculated versus measured A)  $\delta^{11}\text{B}$  compositions, B) B/Al and C) Mg/Al for clay-sized fractions, and D)  $\delta^{11}\text{B}$  compositions for sand-sized fractions of sediments from the Murrumbidgee River. Calculated compositions are obtained by assuming that at each sample location, the clay fraction represents a mixture of clay fractions typical of each lithology. End-member compositions are derived from those measured in clay fractions of sediments from monolithological catchments (sedimentary, volcanic and granitic). These calculations illustrate the conservative behavior of these elements during fluvial transport.

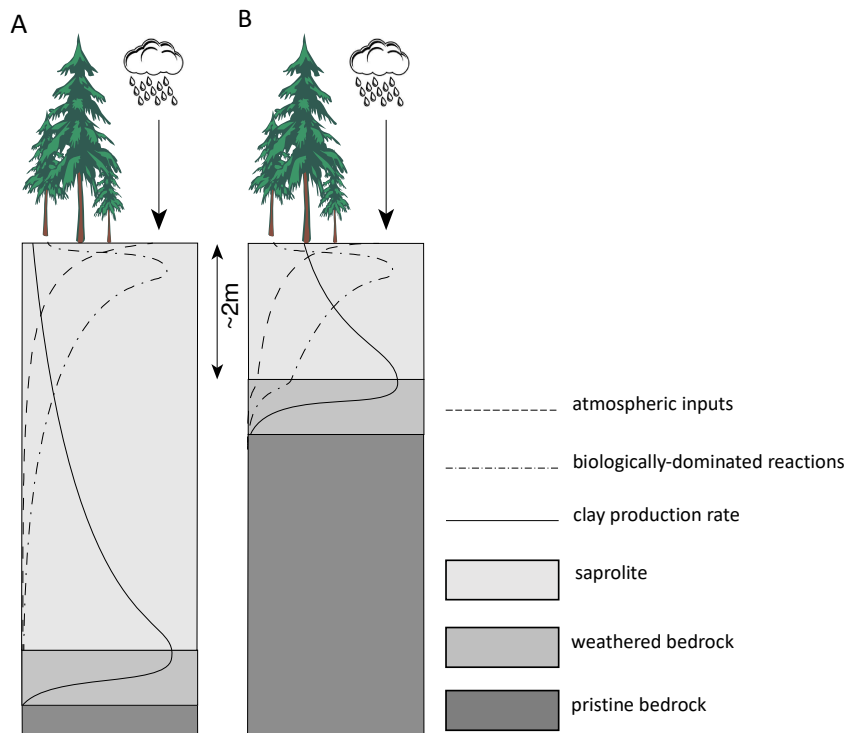


Figure 9. Schematic representation of the possible parameters controlling B isotopes in the clay fraction of soils and dissolved load. Both atmospheric and biological imprint decrease downward as solutions migrate and interact with soil minerals. In a thick weathering profile (A), the B isotope composition of clays and soil solutions would be dominated by water-rock interaction, less influenced by atmospheric inputs and biological processes since the proportion of the profile over which they exert an influence is smaller than for a thinner weathering profile (B). Cividini et al. (2010) have shown that the typical depth at which vegetation and atmospheric influence the B isotope composition of the clay fraction is approximately 2 m, however this depth is likely to be highly variable. We hypothesize that in the Murrumbidgee, the dissolved load has a shallow origin, accounting for high  $\delta^{11}\text{B}$ ; while the clay fraction is composed of clays which formed at greater depths, from a solution less influenced by atmospheric inputs and biological processes.



Table 1. Climatic and geomorphic parameters for monolithological catchments

River Name	Lithology type	Latitude	Longitude	Average Catchment Elevation (m)	Catchment Area (km <sup>2</sup> )	Mean Annual Temperature (°C)	Mean Annual Rainfall (mm)	Mean Catchment Slope (°)
<b>Higher elevation catchments (HEC)</b>								
ALAC Creek	Sedimentary	35°48'0.28"S	148°40'27.27"E	1334	24	7.6	1125	9.8
Wares Creek	Sedimentary	35°52'10.61"S	148°37'36.17"E	1415	4	6.2	1259	11.1
Goodmans Creek	Volcanic	35°41'35.49"S	148°29'44.33"E	1305	1	10	1248	13.3
Journama Creek	Granitic	35°33'56.53"S	148°19'54.98"E	1145	139	9.1	1273	15.6
Back Creek	Granitic	35°58'38.12"S	148°54'4.87"E	1155	17	9.4	811	12.9
Rock Flat Creek	Carbonate	36°20'48.29"S	149°12'37.23"E	993	79	9.8	597	8.1
<b>Lower elevation catchments (LEC)</b>								
Umbango Creek	Sedimentary	35°22'50.91"S	147°46'24.17"E	433	524	13.3	843	8.3
Jugiong Creek	Volcanic	34°41'41.86"S	148°31'18.64"E	532	6	13.7	712	8.5
Big Hill Creek	Volcanic	35° 1'9.47"S	148°57'4.43"E	595	17	12.6	709	4.8
Ginninderra Creek	Volcanic	34°41'35.40"S	148°26'7.69"E	566	1	13.5	709	6.7
Yaven Yaven Creek	Granitic	35°26'2.96"S	147°55'47.58"E	595	145	12.1	986	10.5
Cunningham Creek	Granitic	34°41'35.40"S	148°26'7.69"E	470	936	14.3	660	4.7

Sources: Bureau of Meteorology, Australian Government (temperature and rainfall data); Geoscience Australia (Digital Elevation Model used for catchment area, elevation and slope)

Table 2. Mineralogical composition of bedrock and the clay fraction of bank sediments from monolithological catchments

River Name	Biotite (wt %)	Chlorite (wt %)	Quartz (wt %)	Muscovite (wt %)	Orthoclase (wt %)	Albite (wt %)	K-Feldspar (wt %)	Kaolinite (wt %)	Mixed (I/S) layer (wt %)	Kaolinite (wt %)	Illite (wt %)
	bedrock								clay fraction (< 2µm)		
<b>Granitic</b>											
Cunningham Creek	14	0	60	5	1	20	0	3	27	56	17
<i>Site Replicate</i>	-	-	-	-	-	-	-	-	36	35	29
Back Creek	9	0	41	3	7	23	15	2	34	58	8
Yaven Yaven Creek	19	0	45	5	10	17	0	5	6	76	18
<b>Average</b>	<b>14 ± 5</b>	<b>0 ± 0</b>	<b>49 ± 10</b>	<b>4 ± 1</b>	<b>6 ± 5</b>	<b>20 ± 3</b>	<b>5 ± 9</b>	<b>3 ± 2</b>	<b>26 ± 14</b>	<b>56 ± 16</b>	<b>18 ± 8</b>
<b>Sedimentary</b>											
Brooks Creek	9	0	52	8	14	0	0	12	2	49	49
<i>Site Replicate</i>	-	-	-	-	-	-	-	-	24	70	6
Jellingro Creek	-	-	-	-	-	-	-	-	22	53	25
<i>Site Replicate</i>	-	-	-	-	-	-	-	-	19	67	15
Umbango Creek	-	-	-	-	-	-	-	-	24	69	7
<i>Site Replicate</i>	-	-	-	-	-	-	-	-	36	52	13
ALAC Creek	5	5	65	17	0	0	5	9	-	-	-
<b>Average</b>	<b>7 ± 3</b>	<b>3 ± 4</b>	<b>58 ± 9</b>	<b>12 ± 6</b>	<b>7 ± 10</b>	<b>0 ± 0</b>	<b>3 ± 4</b>	<b>10 ± 2</b>	<b>21 ± 9</b>	<b>60 ± 8</b>	<b>19 ± 13</b>
<b>Volcanic</b>											
Ginninderra Creek	-	-	-	-	-	-	-	-	35	45	20
<i>Site Replicate</i>	-	-	-	-	-	-	-	-	26	62	13
Jugiong Creek	-	-	-	-	-	-	-	-	14	64	23
<i>Site Replicate</i>	-	-	-	-	-	-	-	-	20	68	12
Big Hill Creek	8	7	33	15	10	25	0	4	-	-	-
Goodmans Creek	2	0	40	0	0	54	0	4	-	-	-
<b>Average</b>	<b>5 ± 4</b>	<b>3 ± 5</b>	<b>36 ± 5</b>	<b>7 ± 11</b>	<b>5 ± 7</b>	<b>39 ± 21</b>	<b>0 ± 0</b>	<b>4 ± 0</b>	<b>23 ± 9</b>	<b>60 ± 10</b>	<b>17 ± 5</b>

Mixed layer represents a mixed illite/smectite composition; kaolinite composition includes both ordered and disordered varieties; illite composition includes phlogopite and lepidolite minerals. Error on sample average calculation is 1 SD. External reproducibility of mineral quantification in bedrock and the clay fraction was determined by repeated analyses of the once-prepared sample N. Boooroban and determined to be: ±2% (biotite); 0% (chlorite); 1% (quartz); 4% (muscovite); 1% (orthoclase); 2% (albite); 3% (K-feldspar); 3% (kaolinite); 4% (mixed illite/smectite layer); 4% (kaolinite); and 11% (2 SD, n = 3).

Table 3. Boron isotope compositions, B concentrations, and major element concentrations of clay fractions, bedrock, and the dissolved load from monolithological catchments

River Name	Elevation Group	$\delta^{11}\text{B}$ clay ‰	$\delta^{11}\text{B}$ rock ‰	$\delta^{11}\text{B}$ diss. ‰	B clay $\mu\text{g g}^{-1}$	Mg clay $\text{mg g}^{-1}$	K clay $\text{mg g}^{-1}$	Al clay $\text{mg g}^{-1}$	B rock $\mu\text{g g}^{-1}$	Mg rock $\text{mg g}^{-1}$	K rock $\text{mg g}^{-1}$	Al rock $\text{mg g}^{-1}$
<b>Sedimentary</b>												
Umbango Creek	LEC	-12.2	-10.6	30.2	33.5	29	39	240	36	12	15	30
ALAC Creek	HEC	-17.6	-12.5	31.8	50.6	-	-	-	-	-	-	-
Wares Creek	HEC	-15.2	-12.5	31.9	50.5	24	48	264	38	7	10	29
<b>Volcanic</b>												
Big Hill Creek	LEC	-9.7	-8.3	33.9	24.3	22	19	183	28	7	10	75
Deep Creek	HEC	-	-	40.7	15.7	24	29	211	-	-	-	-
Goodmans Creek	HEC	-13.6	-10.3	35.1	40.6	-	-	-	-	-	-	-
Jugiong Creek	LEC	-11.9	-	34.4	25.7	-	-	-	-	-	-	-
Ginninderra Creek	LEC	-11.2	-	33.9	36.6	-	-	-	-	-	-	-
<b>Granitic</b>												
Cunningham	LEC	-8.5	-7.0	28.7	34.9	-	-	-	21	14	36	71
Yaven Yaven	LEC	-9.1	-7.8	32.7	51.9	19	41	255	21	14	34	74
Back Creek	HEC	-9.3	-9.0	36.2	34.1	37	31	226	16	4	49	72
Journama Creek	HEC	-5.6	-5.5	27.3	60.6	-	-	-	-	-	-	-
<b>Carbonate</b>												
Rock Flat Creek	HEC	-18.6	-13.1	40.7	15.68	44	10	192	15	16	10	13

Abbreviations - HEC: high elevation catchment; LEC: lower elevation catchment; clay: clay fraction ( $<2 \mu\text{m}$ ); rock: bedrock; diss.: dissolved load. Analytical uncertainty of B isotope measurements is 0.4‰ (2 SD). Relative analytical uncertainty for major element measurements is less than 10% and for B measurements is 2% (2 RSD).

Table 4. Boron isotope, B concentration, and major element concentrations of the clay fraction, sand fraction, and dissolved load of Murrumbidgee River and tributaries

River Name	Distance from source (km)	Elevation (m)	Latitude	Longitude	$\delta^{11}\text{B}$ clay ‰	$\delta^{11}\text{B}$ sand ‰	$\delta^{11}\text{B}$ diss. ‰	B clay $\mu\text{g g}^{-1}$	B sand $\mu\text{g g}^{-1}$	Mg clay $\text{mg g}^{-1}$	K clay $\text{mg g}^{-1}$	Al clay $\text{mg g}^{-1}$	B diss. $\text{ng g}^{-1}$	Na diss. $\text{ng g}^{-1}$	Mg diss. $\text{ng g}^{-1}$
Murrumbidgee	0	1,347	35°37'38.11"S	148°34'52.23"E	-13.4	-	-	16	-	8	21	94	-	-	-
Murrumbidgee	30	1,200	35°47'58.44"S	148°40'33.30"E	-18.4	-10	28.9	35	13	10	31	113	1.9	2	1.1
Murrumbidgee	61	976	35°58'50.06"S	148°50'24.54"E	-14.5	-11	30.1	35	37	8	20	72	2.7	2.9	1.2
Murrumbidgee	97	742	36°10'13.35"S	149° 5'27.98"E	-	-	-	19	-	13	13	106	3.8	9.8	5.2
Murrumbidgee	108	712	36° 5'6.47"S	149° 8'2.63"E	-	-	32.5	29	-	13	24	94	2.9	7.7	4.5
Murrumbidgee	111	702	36° 1'25.13"S	149° 8'18.99"E	-11.6	-	-	20	-	8	17	82	-	14.2	6.3
Murrumbidgee	121	680	35°57'5.98"S	149° 7'40.90"E	-12.1	-	26.7	31	-	10	27	82	4.5	14.6	7.1
Murrumbidgee	161	521	35°34'58.59"S	149° 6'32.24"E	-13.4	-	-	28	-	13	25	95	3.3	11.1	6.1
Murrumbidgee	171	501	35°30'30.74"S	149° 4'14.73"E	-	-	28	19	-	6	16	71	4.2	10.3	4.4
Murrumbidgee	202	470	35°19'22.40"S	148°57'1.25"E	-13.5	-	-	31	-	11	23	130	-	-	-
Murrumbidgee	235	403	35° 0'15.59"S	148°50'57.16"E	-11.0	-10	-	22	17	10	20	97	-	-	-
Murrumbidgee	291	249	34°49'28.95"S	148°19'55.44"E	-11.0	-	29.1	29	-	11	24	109	6	14.3	6.2
Murrumbidgee	354	229	34°59'28.72"S	148°13'24.92"E	-11.1	-11	-	37	11	-	-	-	6.6	-	-
Murrumbidgee	378	224	35° 4'27.62"S	148° 6'19.78"E	-10.6	-	-	22	-	10	24	111	7.2	17.9	8.3
Murrumbidgee	455	183	35° 5'57.42"S	147°22'4.35"E	-11.0	-11	32.7	24	18	10	21	122	9.2	15.1	6.4
Murrumbidgee	483	176	35° 1'59.06"S	147° 6'29.70"E	-11.5	-	-	16	-	8	16	97	-	-	-
Murrumbidgee	543	145	34°45'20.53"S	146°32'53.87"E	-11.5	-	-	61	-	9	19	107	-	-	-
Murrumbidgee	600	126	34°45'20.53"S	146°32'53.87"E	-11.4	-9.6	-	33	15	8	18	99	-	-	-
Murrumbidgee	652	107	34°29'4.84"S	144°58'58.24"E	-10.8	-	-	32	-	9	25	109	-	-	-
Cotter	40	469	35°19'34.74"S	148°56'48.05"E	-10.1	-	-	20	-	10	21	97	-	-	-
Tumut	145	263	35° 7'17.87"S	148°12'21.67"E	-10.2	-	-	16	-	8	15	93	-	-	-
Tumut	110	287	35°21'53.84"S	148°15'59.46"E	-12.1	-	-	33	-	-	-	-	-	-	-
Tumut	103	298	35°23'27.09"S	148°14'52.93"E	-15.0	-	-	33	-	-	-	-	-	-	-
Molonglo	72	521	35°17'11.39"S	149° 2'21.59"E	-11.3	-	-	29	-	7	21	92	-	-	-
Molonglo	64	545	35°18'49.17"S	149° 3'45.01"E	-11.9	-	-	26	-	-	-	-	-	-	-
Goodradigbee	48	362	35° 6'38.54"S	148°40'53.59"E	-9.8	-	-	21	-	7	17	98	-	-	-

Table 4 continued

Goodradigbee	15	632	35°23'5.12"S	148°44'39.29"E	-11.5	-	-	57	-	-	-	-	-	-	-
Gudgenby	30	570	35°31'35.79"S	149° 4'22.25"E	-10.5	-	-	18	-	8	16	83	-	-	-
Gudgenby	23	635	35°34'41.61"S	149° 4'0.85"E	-11.5	-	-	19	-	-	-	-	-	-	-
Bredbo	20	699	35°57'44.41"S	149° 8'55.25"E	-12.2	-	-	25	-	8	24	94	-	-	-
Bredbo	12	708	35°59'19.01"S	149°12'32.93"E	-12.7	-	-	30	-	-	-	-	-	-	-
Numeralla	31	717	36° 4'35.84"S	149° 9'31.14"E	-11.3	-	-	27	-	11	23	94	-	-	-
Numeralla	19	716	36° 6'2.06"S	149°11'19.85"E	-12.3	-	-	22	-	-	-	-	-	-	-
Numeralla	7	740	36° 8'27.98"S	149°13'48.05"E	-12.3	-	-	23	-	-	-	-	-	-	-
Yass	102	540	34°51'45.00"S	148°48'7.16"E	-10.6	-	-	28	-	-	-	-	-	-	-
Yass	74	507	34°52'3.14"S	148°57'21.42"E	-12.2	-	-	24	-	-	-	-	-	-	-
Yass	74	507	34°52'3.14"S	148°57'21.42"E	-12.6	-	-	42	-	-	-	-	-	-	-
Yass	48	385	34°55'34.75"S	149° 6'7.13"E	-14.3	-	-	44	-	-	-	-	-	-	-
Yass	48	385	34°55'34.75"S	149° 6'7.13"E	-12.0	-	-	32	-	-	-	-	-	-	-
Yass	48	385	34°55'34.75"S	149° 6'7.13"E	-14.3	-	-	43	-	-	-	-	-	-	-

Abbreviations - clay: clay fraction (<2  $\mu m$ ); sand: sand fraction (63  $\mu m$  – 2,000  $\mu m$ ); diss.: dissolved load. Tributary samples with labels ending in A-C refer to replicate samples taken at the same site to assess site variability.