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## 7 Probing silicate weathering reactions in soils with B isotopes

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18

19 **Keywords**

20 Boron isotopes, Breuil-Chenué, weathering, soil minerals

21

22 **Abstract**

23 The determination of the mechanisms and extent of soil mineral weathering can be challenging, and  
24 the caveats reside in 1) difficulty identifying minerals that are actually involved in weathering  
25 reactions, 2) non-stoichiometric release of cations during weathering processes due to coupled  
26 dissolution, precipitation and transformation reactions and, 3) impact of vegetation activity on  
27 elemental cycles in upper soil horizons.

28 To better characterize mechanisms controlling mineral weathering in soils and trace the evolution of  
29 B concentration and isotope ratios during chemical weathering, quantitative mineralogical analyses  
30 were coupled to B isotopes in a group of minerals (biotite, muscovite, K-feldspar and albite). Samples  
31 were selected along an Alocrisol (Alumic Cambisol, WRB FAO) soil profile from the bedrock (at 130  
32 cm depth) up to 20 cm depth, developed on granitic bedrock in the Breuil-Chenue forest (France).  
33 The samples consist of residual primary minerals associated with weathering secondary phases  
34 (vermiculite, kaolinite...) in varying proportions.

35 The B isotopic compositions of the most pristine minerals span a very narrow range of values (around  
36  $-31\text{‰}$ ), whereas all secondary phases point to a much heavier value (around  $-16\text{‰}$ ), regardless of  
37 mineralogy. Our results also show a mineral-dependent evolution of B concentration or isotopic  
38 composition as weathering progresses: no variation is observed during dissolution of K-feldspars; B  
39 behaves like a very mobile element in micas (biotite and muscovite), whereas it concentrates in  
40 weathered products derived from albite. However, rates of B concentrations and changes in isotopic  
41 compositions appear to be much faster than those inferred from mineralogy or major element  
42 concentrations determined by XRD and bulk chemical analyses, respectively. These results indicate  
43 that B is involved in very early weathering reactions and raises the question of its actual location in  
44 the structure of the various soil minerals as well as its pathway to solution.

45

## 46 1. Introduction

47 The generation of weathered particles and dissolved elements in soils and rivers is a complex process  
48 involving a combination of physicochemical and biological mechanisms. Usually, major or trace  
49 elements are used as proxies to assess the main parameters controlling weathering. These tracers  
50 have been used to determine weathering rates from soil profiles to continental scale watersheds  
51 (Augustin et al., 2016; Bastian et al., 2017; Maffre et al., 2018; Millot et al., 2002; Rasmussen et al.,  
52 2011; Riebe et al., 2017; Turner et al., 2010; Viers et al., 2009; Viville et al., 2012; White, 2008).  
53 Determining continental weathering fluxes based on elemental mass balances from soil solutions or  
54 river chemistry may often lead to ambiguous interpretation, especially under the influence of the  
55 biota (Ganor et al., 2009; Kelly et al., 1998; Maher and Navarre-Sitchler, 2019; Wild et al., 2019). Only  
56 in rare cases, when biological and lithological processes are spatially disconnected, can the  
57 distinction between bio-related mechanisms and water/rock interaction be made (White et al.,  
58 2005).

59 Boron behaves as a very incompatible element during magmatic processes (Tonarini et al., 2003) and  
60 is incorporated into silicate minerals in either trigonal or tetrahedral crystallographic sites (Anovitz  
61 and Grew, 1996). In phyllosilicates such as biotite, muscovite, smectite and illite, B is either located in  
62 tetrahedral sites in substitution for Si (Hålenius et al., 2010; Voinot et al., 2013; Williams and Hervig,  
63 2005) or forms surface complexes on minerals and interlayer sites (Voinot et al., 2013; Williams et al.,  
64 2001). Boron can also substitute for aluminum in feldspar minerals, in trigonal sites in plagioclases  
65 (Geisinger et al., 1988; Icenhower et al., 2008; Martens et al., 2000) or tetrahedral sites in K-feldspars  
66 (Krzhizhanovskaya et al., 2012). The distribution of B isotopes between trigonal and tetrahedral sites  
67 is controlled by the crystallographic structure as well as the temperature of the fluid (Gaillardet and  
68 Lemarchand, 2018; Marschall et al., 2009; Sanchez-Valle et al., 2005; Tonarini et al., 2003).  
69 Therefore, the B isotopic composition of the various crystallographic sites within a same mineral can  
70 span a large range of values, with differences of about 40‰ observed between interlayer and

71 tetrahedral sites in illite-smectite interlayered minerals (Williams and Hervig, 2002) or up to 80%  
72 between interlayer and structural sites in biotite minerals (e.g., from the Bancroft ON, Canada  
73 pegmatite; Voinot *et al.* 2013). These intra-mineral heterogeneities give B the potential to be a  
74 suitable tracer of various weathering mechanisms such as phyllosilicate dissolution versus  
75 transformation (Voinot et al., 2013).

76 In this study, we analyzed the chemical composition as well as the B concentration and isotope ratios  
77 in a series of granite-forming minerals (biotite, muscovite, albite and K-feldspar) and their associated  
78 weathering products. Primary/secondary mineral assemblages were handpicked along a soil  
79 weathering profile. The main goal was to assess the evolution of B concentration and isotope ratios  
80 during chemical weathering of the most common granite-forming minerals, and to evaluate the  
81 potential of B as a proxy for silicate weathering reactions in soils.

## 82 2. Site and sampling

### 83 2.1. Site and soil

84 The Breuil-Chenu experimental forest site, created in 1976 by the INRA BEF team belongs to the  
85 ANAEE and SOERE F-ORE-T network. The site is located in the Morvan region (47°18' N, 4°5' E), in the  
86 northeastern part of Massif Central Mountains, on a plateau at an altitude of 638 m with a slight  
87 northwestern facing slope. The average yearly air temperature and precipitation are 9°C and 1280  
88 mm, respectively. The bedrock comprises a two-micas granite, showing small variations in the size of  
89 the mineral grains, from 0.1 to 1 mm (Mareschal et al., 2015). The main mineral phases in the  
90 bedrock granite are quartz (34 to 35%), K-feldspar (23.8 to 24.2%), albite (30.3 to 31.2%),  
91 muscovite/white mica (8.1 to 8.9%), and biotite (1.2 to 2.2%) as well as some accessory minerals such  
92 as apatite and zircon (Mareschal et al., 2010; Mareschal et al., 2012). K-feldspar and some albite  
93 crystallized as perthite (Mareschal et al., 2015), and is referred to here as simply K-Feldspar.

94 Although this granite shows very few signs of hydrothermal alteration, some scattered evidence of  
95 later hydrothermal fluid circulation has been identified through precipitation of hematite as well as  
96 the destabilization of albite and biotite into white mica and chlorite, respectively (Mareschal, 2008;  
97 Mareschal et al., 2015). Signs of hydrothermal activity are more pronounced at the boundary with  
98 the underlying unit, where aplites and pegmatites have been described with increased presence of  
99 Sn and W-rich phases (cassiterite and scheelite, respectively), some 2 km to the southwest of the  
100 study site (Carrat, 1969; Mareschal, 2008).

101 The soil is classified as an Alocrisol (AFES, 1995) or Alomic Cambisol (WRB FAO) (Mareschal et al.,  
102 2010; Mareschal et al., 2012). Two main mineral transformation reactions have been identified in this  
103 soil: 1) transformation of micas (muscovite and biotite) to 2:1 and hydroxy-interlayered  
104 phyllosilicates (vermiculite or smectite) in the upper soil horizon (20-30 cm), and 2) destabilization of  
105 biotite and albite into kaolinite and gibbsite in the deeper soil horizons (>1 m) (Figure 1, Mareschal,  
106 2008).

107 Chemical compositions of primary and associated weathering minerals have been determined in an  
108 earlier study via thin sections microprobe analysis at Lorraine University in Nancy (Mareschal, 2008).  
109 Results are reported in Table 1. The cationic exchange capacity (CEC) is very low in the lower soil  
110 horizon (2.7-5.8 cmol.kg<sup>-1</sup>), but increases in the shallower horizon (9 cmol.kg<sup>-1</sup> at 0-5 cm) due to  
111 higher organic matter content. The pH of the soil solutions range from 5.0 in the 100-140 cm soil  
112 horizon down to 3.8 in the shallowest soil horizon (Mareschal, 2008).

## 113 2.2. Mineral separation

114 About 100 to 200 mg of primary granite-forming minerals (biotite, muscovite, albite and K-feldspar,  
115 Figure 1) were handpicked under a binocular microscope from bulk soil samples and from unaltered  
116 crushed bedrock. Quartz was not considered due to its very low B concentration (usually lower than  
117 1 µg.g<sup>-1</sup>, Anovitz and Grew, 1996; Christ, 1969; Yamaoka et al., 2012).

118 Each sample consists of a mixture of residual parent mineral and secondary/replacement phases that  
119 have precipitated within parent mineral as a result of dissolution or transformation. Because of the  
120 mineral separation procedure, possible traces of accessory minerals may remain in the handpicked  
121 mineral fraction.

122 Three unaltered granite samples (noted 1, 0a and 0b) were collected at three different locations  
123 within the sampling trench (30 m long, 1.4 m deep, Figure 1). The edges of the blocks were trimmed  
124 to remove the layer of regolith, and the remaining material was crushed into millimeter-sized grains  
125 before mineral separation. The bedrock exhibits traces of very localized hydrothermal alteration,  
126 with veins of quartz and hematite. Granite block #1 was collected at a depth of 0.8 to 1m in the soil  
127 (Figure 1) and shows evidence of weathering, such as precipitation of iron oxides in veins. Granite  
128 blocks #0a and #0b were sampled at a depth of about 1.4 m, at the interface between the bedrock  
129 and the soil, from which only biotite minerals were separated and analysed (samples B0a, B0b, Figure  
130 1).

131 Samples were collected through the soil profile: 20-30 cm, as well as 110-120 cm, 120-130 cm and  
132 130-140 cm, corresponding to the soil horizons B1 and C, respectively (Figure 1, Gontier et al., 2015 ;  
133 Mareschal et al., 2010). Soil sampling intervals were selected to target specific weathering reactions  
134 described in section 2.1. As such, only biotites were collected from the shallowest soil horizon (20-30  
135 cm). Further, a distinction was made between coarse biotite grains ( $> 200 \mu\text{m}$ , separated from the  
136 0.2-2 mm sieved bulk soil) and finer grains (50-200  $\mu\text{m}$ ) to assess the influence of grain size on B  
137 isotopes and weathering reactions. Biotite minerals were handpicked from the bulk soil matrix  
138 before being processed through a magnetic sector and vibrator (AA DYNA-MITE Electric vibrator  
139 230V 50Hz, 10VA) for further separation from other mineral phases. Traces of accessory minerals  
140 were likely in the separated mineral phases, especially from those extracted from unaltered granite  
141 bedrock.



142 Of all albite samples, one sample collected between 1.3 and 1.4 m depth was showing mineralogical  
143 evidence of hydrothermal alteration (traces of hematite) and is hereafter referred to as AH.

### 144 2.3. Soil solution extraction

145 Pore and bound soil solutions were collected in soil horizons from which mineral samples were  
146 collected (20-30 cm and 120-140 cm, Figure 1). Water was extracted from the soil samples via  
147 centrifugation (Jouan KR422 centrifuge) using double-bottomed polycarbonate containers,  
148 precleaned with 0.5N HCl to minimize potential B contamination. Centrifugation was performed in  
149 two steps, starting with 20 min at 1000 rpm (acceleration of  $\approx 180$  G,  $pF = 3.25$ ) followed by 20 min at  
150 3000 rpm ( $\approx 2750$  G,  $pF = 4.2$ ) in order to extract pore and bound water, respectively (Turpault et al.,  
151 2005). A total volume of about 250 mL of water was extracted for each depth, corresponding to a  
152 mass of soil of  $\approx 11$  kg for the 20-30 cm horizon and  $\approx 25$  kg in the deepest horizon (Table 2). No pore  
153 water was extracted in the deepest soil horizon (120-140cm).

## 154 3. Analytical methods

### 155 3.1. Differential thermal analyses

156 Differential thermal analyses were used to directly quantify the amount of gibbsite and kaolinite in  
157 the samples. These analyses were conducted on about 10 mg of solid sample (Caner et al., 2011)  
158 using a TA Instrument SDT Q600 at the Laboratoire Hydrasa (Université de Poitiers). During the  
159 procedure, the temperature was gradually increased at a rate of  $10^{\circ}\text{C}/\text{min}$  from 25 to  $1000^{\circ}\text{C}$ , while  
160 precisely monitoring the mass of the sample (Kissinger, 1957). The mass loss between 250 and  $285^{\circ}\text{C}$   
161 allows direct quantification of gibbsite from sample as follows:

$$162 \quad X_{gibbsite} = \frac{\Delta_{wt-spl}}{\Delta_{wt-gibbsite}} \quad (\text{eq. 1})$$

163 where  $X_{gibbsite}$  is the fraction of gibbsite in the solid sample,  $\Delta_{wt-spl}$  and  $\Delta_{wt-gibbsite}$  correspond to  
164 the relative weight loss between 250 and 285°C of the sample and the pure gibbsite, respectively  
165 ( $\Delta_{wt-gibbsite} = 31.2\%$ ) (Dejou, 1977). Similarly, the relative amount of kaolinite can be determined  
166 from the relative mass loss between 440 and 550°C ( $\Delta_{wt-kaolinite} = 13.6\%$ ) (Dejou, 1977).

### 167 3.2. X-ray diffraction

168 Identification of major mineral phases was performed by X-ray diffraction analyses on powdered  
169 samples at the Laboratoire de Biogéochimie des Ecosystèmes Forestiers (BEF, INRA, Champenoux)  
170 using a Siemens D5000 diffractometer fitted with a graphite monochromator with selected Cu-K $\alpha$   
171 radiation (30 mA/40 kV). X-ray diffraction data were collected from 1.5° to 70.2° with a 0.01°  
172 increment and 6 seconds acquisition time. In order to distinguish chlorite from vermiculite and  
173 hydroxyl-interlayered-vermiculite in biotite samples, additional X-ray diffraction analyses were  
174 performed on K-saturated oriented samples heated at 110, 330, 440, 550 and 650°C. For these  
175 analyses, diffracted rays were collected from 2° to 20° with an increment of 0.01° and 3 seconds  
176 acquisition time.

### 177 3.3. Scanning electron microscopy

178 Scanning electron microscopy (SEM) was used to confirm the presence of mineral phases identified  
179 by X-ray diffraction. A Tescan Vega II microscope equipped with an Edax Pegasus X-ray analysis  
180 device was used at the Laboratoire d'Hydrogéologie et de Géochimie de Strasbourg (LHyGeS).  
181 Samples were deposited on glass slides and carbon coated. Both secondary electron and back-  
182 scattered electron detectors were used.



203 composition of primary and secondary mineral phases (Table 1) and major element concentrations  
204 (Table 4) were used to solve the system of equations.

### 205 3.6. Boron concentrations and isotopic compositions

206 Boron was extracted from solid samples using  $K_2CO_3$  alkaline fusion (Lemarchand et al., 2012). Fifty  
207 (50) mg of sample was analysed for both B concentration and isotopic composition. A 1:5 sample/flux  
208 ratio was used, and the mixture was placed in Pt-Au crucibles before heating at 950°C for 15 min in a  
209 muffle furnace (Cividini et al., 2010). Boron was then extracted from the fusion residue by 3  
210 successive leaching steps using 1mL of ultra-pure water (Cividini et al., 2010). Boron concentrations  
211 were determined by Quadrupole ICPMS at LHyGeS on an aliquot of recovered leaching solution after  
212 a 10x dilution (Lemarchand et al., 2012). The long-term reproducibility of the method is 6% ( $\pm 2SD$ ).

213 Following a chemical purification using the B-specific resin Amberlite IRA-743 (Voinot et al., 2013), B  
214 isotopic compositions were subsequently determined by multi-collector ICP-MS (Thermo-Finnigan  
215 Neptune). The total procedural contamination is about 15 ng B and originates primarily from the  
216 muffle furnace and flux (Prigent et al., 2018). This contamination typically represents less than a few  
217 percents of the total B analysed and has a B isotopic composition (about -10 ‰) that is close to some  
218 of the samples that were measured, thus leading to limited potential isotopic shift. Boron isotopic  
219 compositions are expressed as the deviation in ‰-units from the NIST SRM 951 B isotopes standard  
220 processed though the same procedure as the samples:

$$221 \quad R = \left( \frac{{}^{11}B/{}^{10}B_{sample}}{{}^{11}B/{}^{10}B_{standard}} - 1 \right) \times 1000 \quad (\text{eq. 3})$$

222

223 The long-term reproducibility of the entire B isotope analysis procedure is 0.6 ‰ ( $\pm 2\sigma$ , n = 19)

224 (Cividini et al., 2010; Lemarchand et al., 2012). Chemical compositions (major elements) as well as B  
225 concentrations and isotopic compositions of the samples are reported in Table 4.

226

## 227 4. Results

228 The mineral phases identified by XRD and SEM in each sample are reported in Table 3. Results from  
229 the quantitative mineralogy calculations, as well as B concentrations and isotopic compositions are  
230 illustrated in Figures 2 and 3, respectively. Results for the differential thermal and X-ray diffraction  
231 analyses are provided in annex Figures A1 and A2.

### 232 4.1. K-feldspar

233 The combination of XRD, chemical and differential thermal analyses show no evidence of secondary  
234 phases in K-feldspar samples (Figures 2 and A1, Table 3). Although chemical analyses of K-feldspars  
235 show slight increase of the Na<sub>2</sub>O/K<sub>2</sub>O ratio with depth, suggesting a preferential dissolution of the  
236 albite end-member, both B concentrations and isotopic compositions in handpicked K-feldspars  
237 remain relatively constant along the soil profile, from 6.2 to 11.6 µg.g<sup>-1</sup> and -33.2 to -30.3 ‰,  
238 respectively (Figure 3a).

### 239 4.2. Muscovite

240 Chemical, XRD and SEM analyses show no evidence of weathering of the muscovite. Traces of K-  
241 Feldspar and quartz are found in muscovite samples (Figure 2) and are the result of the mineral  
242 separation procedure. In contrast to the apparent lack of alteration and secondary mineral phases of  
243 the handpicked muscovite samples, B concentrations and δ<sup>11</sup>B values cover a relatively large range of  
244 values, from 22.5 to 89.5 µg.g<sup>-1</sup> and from -30.7 to -19.4 ‰, respectively (Figure 3b). Samples M1, M2  
245 and M3 show variable δ<sup>11</sup>B values, ranging from -30.7 to -21.4‰, but have similar relatively high - B

246 concentrations between 76.1 and 89.5  $\mu\text{g}\cdot\text{g}^{-1}$ . The muscovite sample picked at the shallowest depth  
247 (M4) shows the lowest B concentration at 22.5  $\mu\text{g}\cdot\text{g}^{-1}$  and the highest  $\delta^{11}\text{B}$  value (-19.4 ‰).

#### 248 4.3. Biotite

249 Quantitative mineralogy calculations performed on biotite collected in the deeper soil horizons (B1,  
250 B2, B3 and B4) exhibit a gradual decrease of the proportion of biotite with decreasing depth, from 90  
251 to 60 %, while vermiculite and kaolinite proportions increase at shallower depths (Figure 2).

252 Overall, B concentrations in biotite samples cover a large range of values from 0.9 to 80  $\mu\text{g}\cdot\text{g}^{-1}$  and  
253 tend to decrease as the proportion of secondary phases increases. In parallel,  $\delta^{11}\text{B}$  values increase  
254 with the proportion of secondary phases, from about -30‰ in the non-weathered biotite to about -  
255 16 ‰ in the most weathered samples (Figures 2 and 3c). Biotite samples picked from unaltered  
256 granite (samples B0a and B0b) exhibit variable B concentrations (21 and 74  $\mu\text{g}\cdot\text{g}^{-1}$ , respectively) and  
257  $\delta^{11}\text{B}$  values (-31.1 ‰ and -26.8 ‰, respectively) but show small variations in their mineralogical  
258 composition (Figures 2 and 3c).

259 In the shallowest soil horizon (20-30 cm), the coarse-grained biotite (B5a, B5b, > 200  $\mu\text{m}$ ) shows  
260 mineralogical compositions that are intermediate between those from non-weathered granite (B0a  
261 and B0b) and the biotite samples picked in the deeper soil horizons (B2 and B3), with small amounts  
262 of vermiculite and kaolinite and high proportion of biotite (>60 %) (Figure 2). Samples B5a and B5b  
263 also contain small amounts of chlorite, and exhibit slightly higher isotopic compositions (-23.5 and -  
264 23‰, respectively) together with higher B concentrations (up to 80  $\mu\text{g}\cdot\text{g}^{-1}$ ) than biotite sampled in  
265 unaltered granite.

266 Finer grained samples collected from the same soil horizon (20-30cm, 50-200  $\mu\text{m}$  fraction) are more  
267 weathered and exhibit much lower amounts of residual parent biotite - between 19 % and 26 % for

268 samples B6b and B6a, respectively - associated with higher proportions of vermiculite (32-33 %) and  
269 kaolinite (around 24-25 %).

270 All samples contain approximately 10% quartz, including biotite grains sampled within the granite  
271 (samples B0a, B0b and B1), and likely result from the mineral separation process. Traces of Ti oxides  
272 (around 1 to 2 % in most samples) are also found, as well as up to 0.8% chlorite in samples B0b, B5a,  
273 B5b and B6a, with no direct correlation with B concentration or isotopic composition.

#### 274 4.4. Albite

275 Albite picked from seemingly pristine looking granite (A1) contains about 15%. In albite collected  
276 within the saprolite (samples A2, A3 and A4), the parent albite minerals have almost entirely been  
277 replaced with kaolinite. SEM analyses of sample A2 (130 - 140 cm) reveal a highly altered sponge-like  
278 structure (Figure 4) composed primarily of kaolinite, with only traces of residual albite.

279 Traces of quartz, muscovite as well as traces of gibbsite (< 2 %) are found in all albite samples.  
280 Sample AH contain a significant amount of hematite (about 3%) likely resulting from hydrothermal  
281 alteration.

282 In contrast to biotite, B concentrations increase in weathered albite when  $\delta^{11}\text{B}$  values increase from -  
283 24.7 ‰ (A1) to -15.4 ‰ (A4). Compared with other albite samples, sample AH, shows evidence of  
284 hydrothermal alteration, and is characterized by a much higher B concentration (472  $\mu\text{g}\cdot\text{g}^{-1}$ ) and a  
285 lower B isotopic composition (-27.9 ‰).

#### 286 4.5. Soil solutions

287 The extraction method used doesn't access water trapped within the phyllosilicate interlayers.  
288 Accessing this water would require a specific technique such as ion exchange, followed by neutron  
289 diffraction (OECD, 2000; Powell et al., 1997; Skipper et al., 1991). Pore waters could only be collected

290 from the uppermost soil layer (20-30 cm), as deeper soil samples from the 110 – 140 cm horizon  
291 were dry. Boron concentration and isotopic composition of shallow pore waters are 12 ng.mL<sup>-1</sup> and  
292 +30.3 ‰, respectively (Table 2). The shallow bound water shows a slightly lower B concentration (8.4  
293 ng.mL<sup>-1</sup>) and lower B isotopic composition (+22.3 ‰). The deeper bound water (110-140 cm) is  
294 characterized by a higher B concentration (12.5 ng.mL<sup>-1</sup>) and slightly lower B isotopic composition  
295 (+18.9 ‰).

## 296 5. Discussion

### 297 5.1. Influence of sorting residues

298 Most samples contain between 0 and 20 % of accessory minerals, that couldn't be separated during  
299 the mineral selection process. These include: quartz in biotite and albite, K-feldspar in muscovite and  
300 muscovite in albite (except for albite sample AH which exhibits a quartz proportion of about 35%,  
301 Figure 2). These are hereafter referred to as sorting residues.

302 Given that quartz in granitic rocks is usually characterized by very low B concentrations below 1 µg.g<sup>-1</sup>  
303 (Anovitz and Grew, 1996; Christ, 1969; Yamaoka et al., 2012), the presence of quartz in the samples  
304 only affects B concentration through dilution, but is not expected to impact the δ<sup>11</sup>B value. K-feldspar  
305 samples don't show any evidence of accessory minerals and can therefore be considered as pure.  
306 Traces of K-feldspar are found in muscovite samples (< 5%), with the exception of sample M2 where  
307 the K-feldspar proportion is about 20%. Because B concentration and isotope ratios in K-feldspar  
308 span a narrow range of values (from 6.2 to 11.6 µg.g<sup>-1</sup> and -33.2 to -30.3 ‰, respectively), it's  
309 possible to correct the sample concentration and isotopic composition from the contribution of the  
310 K-feldspar sorting residue. Only the B concentration in sample M2 is affected beyond analytical  
311 errors by the presence K-feldspar, and a corrected M2 concentration of about 64 µg.g<sup>-1</sup> is therefore  
312 reported in Figure 3b (sample M2\*). All biotite samples contain about 10 to 15% quartz, thus leading



313 to a slight underestimation of their B concentrations but no impact on B isotope compositions. In  
314 albite samples, contribution of the traces of muscovite on the bulk B budget is less than  $12 \mu\text{g.g}^{-1}$ ,  
315 which represents 7.5 to 15% of the total analyzed B. Given the range of  $\delta^{11}\text{B}$  values measured in the  
316 various muscovite (from  $-30.7\text{‰}$  to  $-19.4\text{‰}$ ) and albite samples ( $-31.1\text{‰}$  to  $-16.1\text{‰}$ ), the expected  
317 maximum shift in B isotope values resulting from muscovite traces in albite samples is less than 2.2  
318 ‰. This contribution is not negligible and is greater than the analytical precision (about  $0.6\text{‰}$ ) but  
319 remains small compared to the observed range of B isotopes variation in albite samples ( $\approx 15 \text{‰}$ ).

## 320 5.2. Boron in primary non-weathered minerals

321 With the exception of albite sampled in seemingly unaltered granite (A1), which shows evidence of  
322 early weathering (presence of kaolinite), all  $\delta^{11}\text{B}$  values in non-weathered minerals span a very  
323 narrow range of values at  $-31 \pm 3\text{‰}$  (Figure 3). These values are lower than the continental crust  
324 inferred from B isotope analyses in tourmaline ( $-7 \text{‰}$ , Chaussidon and Albarède, 1992) but are  
325 consistent with published analyses of soil profiles developed on granite bedrock, like values from the  
326 Strengbach catchment (Cividini et al., 2010; Lemarchand et al., 2012) or the Guyana Shield (Spivack  
327 et al., 1987). These low values suggest cogenetic minerals in plutonic rocks have similar  $\delta^{11}\text{B}$  values.  
328 This is probably a result of the relatively small B isotopic fractionation coefficient ( $\alpha = 1.005$ )  
329 observed during crystallisation of silicate melts, as well as to the fact that B occupies similar  
330 crystallographic sites in silicate minerals, substituting for Si or Al (Marschall et al., 2009; Tonarini et  
331 al., 2003). Biotite samples that show no chemical or mineralogical evidence of alteration (B0a, B0b)  
332 exhibit a significantly larger range of B concentrations ( $21$  to  $74 \mu\text{g.g}^{-1}$ ) and  $\delta^{11}\text{B}$  values ( $-26.8\text{‰}$  to  
333  $-31.1\text{‰}$ ). Sample B0a shows a  $\delta^{11}\text{B}$  value similar to unaltered muscovite and K-feldspar samples, while  
334 sample B0b shows higher B concentration with a  $\delta^{11}\text{B}$  value similar to sample AH.  
335 Samples B0b, B5a and AH have similar  $\delta^{11}\text{B}$  values, ranging from  $-27.9$  to  $-23.5\text{‰}$  (Figures 3c and 3d).  
336 In addition, the biotite samples B0b and B5a contain traces of chlorite (about  $0.4\%$ ) and sample AH

337 contains traces of hematite. This seems to point towards a potential hydrothermal or supergene  
338 alteration fluid imprint on B isotopic composition, as chlorite and hematite have been identified as  
339 indicators of hydrothermal fluid interaction in the study site (Mareschal, 2008). High B  
340 concentrations reaching several hundreds of  $\mu\text{g}\cdot\text{mL}^{-1}$  have been observed in hydrothermal fluids, and  
341 exchange of B between host minerals and hydrothermal fluids is possible (Aggarwal and Palmer,  
342 1995; Boschi et al., 2008; Yamaoka et al., 2015; Zeng et al., 2013).

### 343 5.3. Boron in weathered minerals

344 Samples showing the highest proportions of secondary minerals (biotite B6a, B6b, B3, B4, and albite  
345 A2, A3, A4, Figures 2 and 5) have similar  $\delta^{11}\text{B}$  values around  $-18.5\text{‰} \pm 1.5\text{‰}$ . Sample M4 exhibits a  
346 similar  $\delta^{11}\text{B}$  value, yet exhibits no chemical and XRD evidence of mineralogical alteration.

347 Possible explanations for this homogeneous B isotopic composition in all weathered minerals may  
348 involve either 1) B exchange between pore waters and all phases found in the mineral habits, which  
349 has been observed in high temperature systems but not at surface conditions (Bobos and Williams,  
350 2017; Clauer et al., 2018; Tonarini et al., 2003); 2) a preferential release of B from different  
351 crystallographic sites (*i.e.*, structural or water-accessible sites), each characterized by distinct  $\delta^{11}\text{B}$   
352 signatures (Voinot et al., 2013; Williams et al., 2001) or 3) a difference in the weathering rate of at  
353 least two generations of parent minerals characterized by distinct  $\delta^{11}\text{B}$  values.

354 All weathered minerals span a very restricted range of  $\delta^{11}\text{B}$  values despite the large variety of mineral  
355 phases observed, with varying amounts of primary mineral residues associated with secondary  
356 minerals like vermiculite, kaolinite or gibbsite (Figure 5). A common  $\delta^{11}\text{B}$  signature in different  
357 minerals suggests similar mechanisms controlling the incorporation of B into mineral weathering  
358 products. The observed isotopic fractionation ( $\Delta^{11}\text{B}_{\text{solid-solution}}$ ) is therefore not mineral specific, but  
359 instead reflects similar crystallographic environment, with  $^{10}\text{B}$  enriched tetrahedral  $\text{B}(\text{OH})_4^-$  being

360 preferentially adsorbed onto the mineral surfaces (Gaillardet and Lemarchand, 2018; Lemarchand et  
361 al., 2007; Muttik et al., 2011; Spivack et al., 1987; Williams et al., 2001).

362 Considering that trapped pore water have a  $\delta^{11}\text{B}$  value around +20‰ (Table 2), and that the typical B  
363 isotopic fractionation generally observed between solids and solution at low temperature ( $\Delta_{\text{solid-}}$   
364  $\text{solution}$ ) is close to -35‰ (Gaillardet and Lemarchand, 2018; Lemarchand et al., 2012 and discussion  
365 therein; Lemarchand et al., 2007; Muttik et al., 2011; Spivack et al., 1987), minerals in isotopic  
366 equilibrium with the pore water would have  $\delta^{11}\text{B}$  values close to -15‰, consistent with minerals  
367 analyzed in this study. Similar observations were made on the evolution of B in the clay-size fractions  
368 collected from the Strengbach watershed (Lemarchand et al., 2012). However, the pore water value  
369 measured in this study only is a snapshot of the hydrogeochemical conditions at a given instant in  
370 time (July 2012), that can't be extrapolated to the several thousands of years required for the soil to  
371 develop (Moore and Singer, 1990; Stevens and Walker, 1970).

372 Interestingly, some samples show only minor changes in their mineralogical and chemical  
373 composition (muscovite samples M2, M3 and M4), yet exhibit  $\delta^{11}\text{B}$  values similar to those observed  
374 in the most weathered products ( $\delta^{11}\text{B} \approx -16$  ‰ for sample M4) (Figures 2 and 5). This observation  
375 infers a large proportion of B in the bulk mineral can potentially exchange with the surrounding  
376 environment without evidence of alteration of mineralogical or crystallographic properties. Thus, a  
377 large proportion of B in these minerals is in exchangeable sites, such as reactive surfaces like those  
378 found in the interlayers, grain boundaries or crystal defects. The transfer of B to solution appears  
379 much faster than major elements, which is in agreement with previous laboratory dissolution  
380 experiments (Voinot et al., 2013; Williams et al., 2001). In both micas, the relatively rapid transfer of  
381 B without destruction of the crystal structure, as demonstrated by XRD analyses, may likely be  
382 facilitated by interfoliar spaces. The present study cannot firmly identify the exact mechanism(s)  
383 controlling B isotopic evolution during weathering of micas (surface interactions or structural  
384 breakdown of B-bearing sites). Further investigations at the crystallographic scale should help answer

385 this question. But it's clear that B behaves like a very mobile element during the weathering of micas,  
386 similarly to what has been observed in laboratory studies (Voinot et al., 2013; Williams and Hervig,  
387 2002). While facilitated matter transport is expected in phyllosilicates where interfoliar spaces can be  
388 efficient water pathways, it challenges our understanding of water and element transport across a  
389 crystallized lattice as found in albite.

#### 390 5.4. Boron: a proxy of weathering regime?

391 The similarity in B isotopic composition between cogenetic silicate minerals can potentially be used  
392 to trace the source(s) of parent materials as well as to give information about the weathering regime,  
393 provided that 1) the signature of unaltered parent material can be recovered from samples and 2)  
394 there is an observable difference between the B isotopic composition of weathered products and  
395 parent minerals. This difference can be magnified by two conditions: 1) in systems dominated by  
396 dissolution reactions leading to a relatively small rate of B incorporation into secondary phases, and  
397 2) in systems where vegetation cover, which represents an isotopically fractionated B pool, is dense  
398 enough to control the B isotopic composition of solutions which precipitate secondary products (e.g.  
399 Cividini et al. 2010).

400 From this study, analyses of B isotopes in K-feldspar demonstrate that their dissolution in soils occurs  
401 without observable isotopic fractionation. The B isotopic composition of these minerals therefore  
402 remains unchanged during the development of the weathering profile and can be potentially used as  
403 a reference to compare against weathering products. Similarly, the homogeneity of B isotopic  
404 compositions observed in different weathering products reflects the signature of the local  
405 weathering regime, which can be described as the ratio between dissolution and precipitation rates,  
406 including a potential contribution of organic matter and atmospheric B inputs. The results of this  
407 study therefore indicate that the comparison of B isotopes between pristine primary minerals (i.e. K-  
408 feldspars) and secondary products (i.e., clay minerals) could potentially be used in various natural

409 environments to resolve processes of source mixing and secondary mineral formation or  
410 transformation of primary mineral phases, similarly to what has been shown in laboratory  
411 experiments (Voinot et al., 2013) or observed in natural systems (Ercolani et al., 2019).

412 The results herein also demonstrate that the discrepancy between the evolution of the mineral  
413 assemblage (inferred from X-ray diffraction and major element composition) and B isotopes is  
414 mineral dependent (Figures 5 and 6). This property can potentially be used to determine the extent  
415 of weathering reactions with more refinement than major element or traditional mineralogical  
416 methods, or to identify the earliest stages of weathering reactions in soils. For example, if the  $\delta^{11}\text{B}$   
417 values measured in biotite minerals are close to the ones measured in muscovites and in K-Feldspars,  
418 this would indicate a very early stage of weathering. In other cases, the progression of the  
419 weathering reactions would differentially affect each mineral assemblage (Figures 5 and 6).

420 Boron concentration variations in weathered albite crystals differ from micas. Almost all albite  
421 crystals show a near complete loss of the primary albite form by kaolinite mass (about 75%).  
422 However, contrary to what can be observed in micas, the B concentration progressively increases  
423 with the extent of weathering of the parent material, reaching up to  $185 \mu\text{g}\cdot\text{g}^{-1}$ , about twice the value  
424 of the least weathered albite sample A1. Such an increase of the B concentration together with the  
425 evolution of B isotopes may be explained by two different processes:

426 1) the presence of a low-solubility B-rich phase with a B isotopic composition close to -15‰ that  
427 progressively controls the B mass balance as the weathering reaction progresses. In order to explain  
428 B behaviour in all the samples, this accessory phase should be found in both micas and albite but not  
429 in K-feldspar. This phase should only be found at trace level in micas, as the B concentration in  
430 weathered products almost decreases to the analytical detection limit, but be in much larger  
431 proportion in albite to explain the increase in B concentration. Tourmaline might be a potential  
432 candidate for such an accessory mineral phase, but it has not been observed in our samples and so  
433 far, none of our observations can support this hypothesis.

434 2) the development of a very large reactive water/rock interface allowing a large amount of B to be  
435 incorporated in secondary products. Like other elements, such as U and Mo, specific chemical  
436 conditions can lead to very strong affinity with clay minerals and can show adsorbed concentrations  
437 of several hundreds of  $\mu\text{g}\cdot\text{g}^{-1}$  (Davey and Scott, 1956; Li et al., 2012; Sikalidis et al., 1989; Tournassat  
438 et al., 2018; Xu et al., 2013). It may be hypothesized that the development of a very small and dense  
439 porous network as the albite minerals are being weathered could generate such a large reactive  
440 surface. This hypothesis is supported by SEM analyses of the weathered albite samples (Figure 4) that  
441 clearly show a sponge-like porous structure. This is a well-known evolution of albite minerals for  
442 which the surface of water-rock interaction can increase by a factor of two during weathering (White  
443 et al., 2001). Similar to the B-specific resin (Amberlite IRA 743), where the spongy structure leads to  
444 apparent huge partitioning coefficient (Lemarchand et al., 2002), it can be hypothesized that the  
445 formation or activation of nano-channels may considerably increase the reactive surface of the  
446 mineral and lead to an accumulation of B in the weathered albite product. This hypothesis, which  
447 seems to best fit our data, also points to a very different description of the weathering reactions than  
448 those used in classic numerical models. Precipitation of secondary products would not be controlled  
449 by supersaturation of the bulk solution with respect to secondary phases after dissolution of the  
450 primary ones, but would be controlled by the mineralogy of the mineral parent. For biotite, the low B  
451 concentration would indicate an efficient transport of water, thus draining mobile elements. For  
452 albite, the development of a nano- to micro-porous network would drastically increase the reactive  
453 surface while slowing down the velocity of water (high porosity, but low permeability), thus leading  
454 to an enhanced incorporation of soluble elements.

## 455 6. Conclusion

456 Investigation of B concentration and isotopic composition in weathered silicate minerals (biotite,  
457 muscovite, albite and K-feldspar) with associated secondary phases (gibbsite, kaolinite, vermiculite)  
458 clearly emphasizes B sensitivity to water-rock processes. The homogenous B isotopic signature in the

459 initial primary minerals on one hand and secondary weathering products on the other can greatly  
460 help understanding weathering conditions. In particular, combining B isotope analyses in minerals  
461 with varying weathering rates could help identify the primary mineral source of B and bring  
462 quantitative information on the soil forming mechanisms.

463 Among the minerals analyzed in this study, combined analyses of K-feldspar and muscovite minerals  
464 appear to be an ideal way to investigate weathering processes in soils, as these minerals show  
465 contrasted B behaviour while still showing little to no mineralogical change with weathering, thus  
466 limiting complicated interpretations caused by presence of secondary phases. The second advance  
467 made by this study is to recognize different B behaviour during weathering, indicating distinct  
468 weathering mechanisms. B appears to behave like a very mobile element in micas from a chemical  
469 point of view but accumulates in the weathering products of albite.

470 This study points to unresolved questions that require further investigations. In particular, it remains  
471 unclear if the B isotopic composition of secondary phases reflects isotopic equilibrium with the  
472 surrounding solution or a preferential disruption of specific B-bearing sites. In addition, B shows a  
473 very high mobility B in minerals showing no evidence of crystallographic transformation.

474 Once the mechanisms controlling the B distribution in weathered silicate minerals will be better  
475 understood, combined B analyses in soil or rivers detrital mineral grains would certainly provide  
476 strong information on weathering controls and help understanding sedimentary records.

477

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679

1 Effect of a strong desire to void on walking speed in individuals with multiple  
2 sclerosis and urinary disorders

3

#### 4 **Abstract**

5 **Background.** Lower urinary tract symptoms, especially overactive bladder, are frequent and  
6 disabling in individuals with multiple sclerosis (IwMS). An association with gait disorders is  
7 common, which could aggravate continence difficulties and affect quality of life. The  
8 association between the need to void and walking has never been studied in this population.

9 **Objective.** The primary aim of this study was to assess the effect of a strong desire to void  
10 (SDV) on walking speed in IwMS and lower urinary tract symptoms. The secondary aim was  
11 to identify clinical or urodynamic factors associated with walking speed impairment at SDV  
12 in this population.

13 **Methods.** We included IwMS with urinary disorders and Expanded Disability Status Scale  
14 score  $< 7$  in this observational study. Individuals underwent 3 10-m walk tests (10MWT) and  
15 one Timed Up and Go (TUG) test at SDV and at post-void (PV).

16 **Results.** Among the 72 IwMS included (mean [SD] age 50.6 [11.6] years; 46 [64%] females),  
17 the mean (SD) speed for 10MWT was 1.00 (0.31)  $\text{m}\cdot\text{s}^{-1}$  at SDV and 1.07 (0.30)  $\text{m}\cdot\text{s}^{-1}$  at PV  
18 ( $p < 0.0001$ ). Time for TUG was also increased when individuals felt SDV: mean 11.53 (4.6)  
19 sec at SDV versus 10.77 (3.8) sec at PV ( $p = 0.004$ ). No predictors of greater impairment of  
20 walking speed at SDV were identified.

21 **Conclusion.** This study suggests a clinical impact of bladder sensation on walking speed in  
22 IwMS and urinary disorders. None of the individual characteristics could predict greater  
23 decrease in gait velocity at SDV.

24

25 Keywords: Multiple sclerosis, Walking speed, Gait, Urination, Lower urinary tract symptoms

26

## 27 **Introduction**

28 Multiple sclerosis (MS) causes demyelinating lesions and could be responsible for a number  
29 of symptoms, including motor or sensitivity disorders, cognitive impairment, visual  
30 disturbances, and urinary and bowel disorders. Gait difficulties are the most visible disability,  
31 and about 70% of patients report a psychological impact due to their walking impairment[1].  
32 Different neurological presentations can be observed in different individuals: spastic, ataxic,  
33 cerebellar, and pyramidal forms, depending on the topography of the cerebral or medullar  
34 lesions. Lower urinary tract symptoms (LUTSs) are also very common, with a prevalence of  
35 32% to 86%[2]. Overactive bladder with urgency, increased bladder frequency and urgency  
36 urinary incontinence is the most common symptoms. Obstructive symptoms are also frequent  
37 and may coexist with storage symptoms. Detrusor overactivity is the most frequent  
38 urodynamic profile, but the correlation between clinical symptoms and urodynamics data is  
39 not perfect. Other urodynamic profiles exist: bladder oversensitivity, detrusor-sphincter  
40 dyssynergia, and neurogenic detrusor underactivity, but urodynamics can be normal for 1% to  
41 34% of patients with LUTSs[2,3]. Despite a correlation between frequency and severity of  
42 LUTSs and severity of incapacity assessed by Expanded Disability Status Scale (EDSS) [4] or  
43 with number of falls[5], no strict relationship can be demonstrated between type of LUTS,  
44 urodynamics profile and type of neurological presentation (pyramidal, with or without major  
45 spasticity, cerebellar etc.)[4,6].

46 The role of bladder filling and need to void on gait has been poorly studied and only in  
47 healthy populations. Yet, some hypotheses could support a link between these 2 parameters.

48 The need to void is a sensory stimulus, integrated in different cerebral areas, including insula,  
49 periaqueductal gray, cingulate cortex, hypothalamus and prefrontal area[7,8]. A modification  
50 in gait velocity with emotions was demonstrated. Jousse et al. showed a decrease in  
51 attentional skills with a strong desire to void (SDV)[9]. These 2 studies may suggest a  
52 possible impact of the need to void on gait velocity, as a new sensory phenomenon to  
53 integrate and modulate, as a function of the locomotion task.

54 At the medullar stage, a modification of the H-reflex was demonstrated at SDV in healthy  
55 individuals[10]. The H-reflex is considered to reflect motoneuronal excitability. The impact of  
56 motoneuronal excitability on gait is not clearly established, but some studies revealed a  
57 modification of the H-reflex with gait velocity[11,12]. The H-reflex is also used as an indirect  
58 measure of spasticity, but its expression is not correlated with spasticity severity[13]. The  
59 modulation of the medullar reflex with bladder sensation, and perhaps with bladder filling or  
60 detrusor overactivity, with a possible impact on gait may explain a link between gait and the  
61 need to void.

62 The consequences of the need to void on other tasks have been little studied and only in  
63 healthy populations; however, alterations in attentional condition[9], gait velocity[14] and  
64 balance[15] performance were shown. Assessing the effect of the need to void in a neurologic  
65 population with frequent gait disorders and LUTSs could be pertinent to better understand the  
66 pathophysiological mechanisms and evaluate whether an intervention for one condition may  
67 improve the other, with the hypothesis that an appropriate management of LUTSs could lead  
68 to an improvement in some locomotor parameters.

69 The primary aim of this study was to assess the effect of an SDV on gait in individuals with  
70 multiple sclerosis (IwMS) and LUTSs. The secondary aim was to identify clinical or

71 urodynamic factors (EDSS, symptom severity, detrusor overactivity, cystometric capacity)  
72 associated with greater gait impairment.

73

## 74 **Material and methods**

### 75 Participants

76 Individuals over age 18 who were consulting for LUTSs linked with MS in the neuro-urology  
77 department of a university hospital between February 2017 and March 2017 were invited to  
78 participate in this observational study. Individuals who agreed to participate were included  
79 where they were admitted for a consultation or urodynamic assessment, and all tests were  
80 performed on the same day.

81 Inclusion criteria were MS with EDSS score 1 to 6.5 and LUTSs secondary to MS (storage or  
82 voiding symptoms). Participants had to be able to walk 50 m without human help and to hold  
83 urine for 5 min, the time required to perform the tests. They could be taking medication for  
84 MS or LUTSs. All types of MS were accepted. We excluded individuals with urinary tract  
85 infections, relapse of MS in the last 7 days, or severe cognitive impairment (Mini Mental  
86 State Examination [MMSE] score < 10).

87

### 88 Measures and procedure

89 Gait was assessed by 2 clinical tests approved for MS. The same tests were performed under 2  
90 conditions: first when the individual felt an SDV, and then immediately after micturition,  
91 spontaneously or with self-catheterization (post-void [PV]).



92 The primary outcome was gait velocity assessed by a 10-m walk test (10MWT)[16]. Three  
93 trials were recorded, as per Booth et al. [14]. Individuals were instructed to walk the 10 m at a  
94 comfortable speed. Maximum speed was not recorded to limit the impact of fatigue on test  
95 repetition, because maximal speed improves energetic cost. Only the 6 intermediate meters  
96 (meters 2 to 8) were recorded, to limit the effect of acceleration and deceleration. Tests were  
97 recorded with a manual chronometer by the same examiner for each individual, with 30 sec of  
98 rest at most between each trial.

99 Secondary outcomes were time on the Timed Up and Go Test (TUG)[17,18] and gait  
100 variability assessed by the coefficient of variation (CoV) of the 3 trials of 10MWT. The trial  
101 began with a non-recorded TUG to understand instructions and to limit the learning effect, but  
102 only one trial was recorded to limit the test duration and fatigue induced by the get up  
103 exertion.

104 Medical history, treatment, and anthropometric data were collected. An MMSE was  
105 administered to identify memory impairment. Urinary symptoms were assessed by the  
106 questionnaire Urinary Symptom Profile (USP) with 3 aspects: “stress urinary incontinence”  
107 (/9), “overactive bladder” (/21) and “low stream” (/9)[19]. Data for the last cystometry were  
108 collected (retrospectively if cystometry was not planned on the day of inclusion): detrusor  
109 overactivity, volume at first detrusor contraction, SDV during filling, and cystometric  
110 capacity. MS severity was assessed by the EDSS, a score based on measures of impairment in  
111 8 functional systems, and on walking ability[20]. Individuals with an EDSS score > 4  
112 complained of gait difficulties. Each participant was asked if they had urine leakage during  
113 the tests. PV residual volume was measured with a mobile transabdominal ultrasound  
114 apparatus (Bladder Scan®); 3 measures were taken, and the highest was recorded. Secondary  
115 analyses were planned to identify clinical or urodynamic factors associated with greater gait  
116 impairment: age, EDSS score, need for a walking device, severity of overactive bladder on

117 USP score, spontaneous void or self-catheterization, cognitive impairment assessed by the  
118 MMSE, detrusor overactivity during the last cystometry, and PV residual volume.

119

#### 120 Ethics approval

121 The study protocol and data collection were conducted in accordance with the ethical  
122 standards of the national research committee and the Declaration of Helsinki. This study was  
123 approved by the local ethics committee (registration no. 2015-A00125-44). All participants  
124 gave their consent to participate. This study was registered on ClinicalTrials.gov:  
125 NCT03204747.

126

#### 127 Statistical analysis

128 Statistical tests were performed with R for Windows (Rx64 3.2.3). In a previous study of  
129 healthy individuals, the only one assessing the effect of the need to void on gait, Booth et al.  
130 [14] showed a mean difference on gait velocity of  $0.05 \text{ m}\cdot\text{s}^{-1}$  between SDV and PV. In IwMS,  
131 we expected a slightly greater mean difference between the 2 conditions. Thus, based on this  
132 previous study, for an expected mean difference of  $0.06 \text{ m}\cdot\text{s}^{-1}$ , a standard deviation of 0.17  
133 (SD 0.18 to 0.19 in the Booth et al. study) and 80% power, we needed 65 participants. Mean  
134 gait velocity at SDV and PV were calculated for the 3 trials of 10MWT. Variability of the 3  
135 trials was assessed by the CoV (standard deviation/average). The temporal parameters of gait  
136 for 10MWT, TUG and CoV data were normally distributed. Thus, these were analyzed by  
137 Student's *t* test for paired samples. The effect size was calculated with Cohen's *d* formula.  
138 The impact of clinical and urodynamic parameters on the mean difference between TM10 at  
139 SDV and PV were analyzed by Student *t* test for qualitative variables and Spearman

140 correlation for quantitative variables. Significance was considered at  $p < 0.05$ . Missing data  
141 were not replaced.

142

### 143 **Results**

144 We included 72 individuals (mean [SD] age 50.6 [11.6] years; 46 [64%] females).  
145 Characteristics are summarized in Table 1. Three individuals performed only 2 trials of the  
146 10MWT for each condition because of physical tiredness. The mean speed for 10MWT was  
147 1.00 (0.31)  $\text{m}\cdot\text{s}^{-1}$  at SDV and 1.07 (0.30)  $\text{m}\cdot\text{s}^{-1}$  at PV ( $p < 0.0001$ ; effect size 0.79). Maximal  
148 improvement on mean 10MWT was 0.34  $\text{m}\cdot\text{s}^{-1}$  (5.03 s). Only 10 (14%) participants had a  
149 lower performance at PV than SDV. These 10 participants and the others did not differ in  
150 EDSS score, use of a walking device, existence of detrusor overactivity, or age. The  
151 distribution of gait velocity change between SDV and PV is presented in the Figure. The  
152 individual variability of the 3 trials of 10MWT, assessed by the CoV, was significant (mean  
153 [SD] 5.2% [3.9] vs 4.2% [3.6],  $p = 0.048$ ). Between the first and second try, 47% of  
154 participants showed improved gait velocity at SDV and 40% at PV. Between the second and  
155 third try, 68% of participants showed improved gait velocity at SDV and 63% at PV. Mean  
156 time for TUG was also increased when individuals felt SDV: 11.53 (4.6) sec at SDV versus  
157 10.77 (3.8) sec at PV ( $p = 0.004$ , effect size 0.35). Only one participant reported a leak during  
158 the test.

159 Secondary analysis did not identify any predictors of greater impairment of walking speed at  
160 SDV among the features explored (Tables 2 and 3).

161

## 162 **Discussion**

163 The results of this study showed an increase in gait velocity after voiding as compared with  
164 velocity during an SDV in IwMS and urinary disorders. This finding suggests a negative  
165 impact of an urgent need to void on walking speed in IwMS and urinary disorders. No clinical  
166 or urodynamic factors were found to predict greater reduction in gait performance.

167 In their study, Booth et al.[14] proposed that “the experience represents a dual task or divided  
168 attention situation” to explain the difference in the SDV and PV situation in healthy  
169 individuals. The authors introduced for the first time bladder sensation as a divided attention  
170 situation. The role of dual tasks is well established, particularly in older adults and with a risk  
171 of falling. The effect of dual tasks, in particular in gait, has been widely studied and  
172 demonstrated in IwMS. In a recent review, the presence of cognitive motor interference  
173 appeared more frequent in IwMS than in healthy individuals during gait analysis [21].  
174 Individuals with mild cognitive impairment seemed more sensitive to the influence of a  
175 cognitive task on walking speed[22]. Moreover, emotional perception of the need to void  
176 could also influence gait velocity.

177 Functional MRI shows activation of different areas during bladder filling (insula,  
178 periaqueductal gray, cingulate cortex, hypothalamus and prefrontal area, amygdala). Most of  
179 these cerebral areas are implicated in emotional control, and functional MRI studies found  
180 less activation or deactivation of some of these areas in individuals with overactive bladder as  
181 compared with healthy individuals, which suggests a lack of control of this unpleasant  
182 sensation[23]. A modification of gait velocity has been found correlated with emotion in  
183 healthy individuals[24]. In IwMS, only the fear of falling has been studied, but other emotions  
184 could also affect gait. We found no relationship between severity of symptoms and greater  
185 difference between the 2 conditions. However, the proportion of individuals with regular

186 leaks was higher (no statistical analysis) in individuals with a difference of  $> 0.1$  m/s between  
187 SDV and PV, which supports a possible distractible effect of the urge to void and the role of  
188 emotional control.

189 A second explanation is the effect of bladder sensation on motoneuronal excitability. Previous  
190 studies of individuals with spinal cord injury evoked a gait spinal central pattern  
191 generator[25,26]. Furthermore, the H-reflex, which is a spinal motoneuronal response to  
192 electrical stimulation, is considered to reflect motoneuronal excitability. Variation in H-reflex  
193 amplitude reflects modified spinal cell excitability [27]. During gait, some studies showed an  
194 increase in H-reflex amplitude, which suggests an increase in motoneuronal excitability, with  
195 variation in function of gait cycle. A proportional increase in the amplitude of the H-reflex as  
196 a function of walking speed has been demonstrated[11,12]. Thus, a role of motoneuronal  
197 excitability in gait velocity can be supposed, and a decrease in motoneuronal excitability  
198 could affect walking speed. A decrease in H-reflex in the soleus muscle occurs at SDV in  
199 healthy individuals[10]. However, no study has examined the impact of the need to void on  
200 motoneuronal excitability in IwMS, whereas in individuals with spinal cord injury, bladder  
201 filling tends to increase H-reflex amplitude[10]. Application of these findings in IwMS is  
202 difficult, as far as lesion localizations at cerebral or medullar level could affect H-reflex  
203 variability, and a specific study would be necessary.

204 Another possible explanation is that pelvic and trunk muscle activation is modified by bladder  
205 filling: the activation of pelvic floor muscles decreases when the bladder is moderately full,  
206 and the obliquus internus abdominis and rectus abdominis activation is increased. Bladder  
207 fullness also influences balance: an increase in center-of-pressure motions on a force plate  
208 was demonstrated when the bladder was full in healthy individuals[15]. These 2 parameters  
209 could participate in gait velocity decrease at SDV.

210 Our results agree with the Booth et al.[14] study of healthy individuals (continent,  
211 International Prostate Symptom Score 0-7). The authors used a GAITRite® walkway and  
212 showed an impairment of  $0.05 \text{ m}\cdot\text{s}^{-1}$  at SDV as compared with PV. Results in our study were  
213 obtained with clinical (not instrumental) tests. A potential limitation of the primary outcome  
214 is that fast speed usually has better reliability in 10MWT than comfortable speed, but  
215 energetic cost is improved at maximal speed. We chose not to record this measure to limit the  
216 impact of fatigue on the different tests.

217 Several measures were established to limit bias in recording walking tests. Participants  
218 underwent 3 trials for the 10MWT under each condition, to limit intra-individual variability  
219 and to observe whether this variability is modified by SDV, as previously described[14]. To  
220 prevent inter-judge variation, all tests were recorded by the same examiner using a  
221 standardized protocol and the same time-measuring tool. A recent study did not find a  
222 significant difference between 3 consecutive short walk tests (Timed 25-Foot Walk) [28],  
223 which suggests no spontaneous improved performance with repeated tests. Thus, to reduce the  
224 impact of tiredness on recording, we did not randomize by order of condition, and clinical  
225 tests at PV were always performed after those at SDV. This minimization of bias is also a  
226 potential limitation for highlighting a greater difference between the 2 conditions, because  
227 fatigue induced by the first tests can affect subsequent performance with a limited rest time  
228 between the 2 conditions. Individuals could also take a rest between the tests to reduce this  
229 bias. Our results did not reveal a progressive improvement in performance with the repetition  
230 of tests during the same condition. This suggests that the difference shown between SDV and  
231 PV is not related to a spontaneous improvement due to the repetition of the same exercise. For  
232 the TUG test, the learning effect was limited by a first non-recorded trial to verify  
233 comprehension of instructions. Instructions were repeated before each trial to facilitate their  
234 memorization.

235 Our study has several limitations. Clinical tests are less precise than instrumental tests, and  
236 some gait parameters such as stride length, swing time, and duration of single support could  
237 not be studied. The examiner was not blinded to condition (PV or SDV), but participants did  
238 not know the expected results and were not informed of the time performed in each test. The  
239 sequence of the test after urination can have a negative impact on performance, by the fatigue  
240 induced by the first tests and by the fatigue induced by urination, with the different stages of  
241 undressing, sitting, etc. This could influence the identification of factors associated with a  
242 greater impact of the need to void on walking speed. Moreover, because of the design of the  
243 study, the negative impact of the urgent need to void is derived from the interpretation of the  
244 increase in speed after urination. An evaluation without the need to void but away from  
245 urination could have been interesting to free oneself from possible neurological reflexes  
246 induced by micturition, especially in individuals with detrusor overactivity. In secondary  
247 analyses, an evaluation of executive functions would have allowed a more specific analysis, in  
248 the hypothesis of “dual task” impact, because the MMSE does not properly evaluate these  
249 functions.

250 The difference between SDV and PV we found is less than the minimally clinical relevant  
251 differences described in the literature, but these have been defined with small numbers of  
252 participants with high EDSS score or using a modification of EDSS score as a relevant  
253 clinical change, but the EDSS score is not sensitive to minor change[29–31]. Thus, the  
254 observed difference in our study can be difficult to interpret; we did not expect a clinical state  
255 change as a modification of the EDSS score between SDV and PV, and the comparison of our  
256 results with the mentioned thresholds is not wholly adapted (median EDSS or condition to  
257 realize the 10MWT differed from those of our study). Therefore, clinical interpretation of this  
258 PV improvement is subtle, and our data cannot lead to specific clinical recommendations.

259 There are many different perspectives from this study. First, a new study of the specific  
260 population within IwMS could improve the accuracy of results and clinical relevance. The  
261 role of detrusor overactivity was not shown, but there was likely a lack of power in secondary  
262 analysis, and owing to the study design, 27 of the 62 urodynamic data measurements available  
263 were older than 3 months. Also, all individuals did not have urodynamics data, and some  
264 measurements were prior to the inclusion date, which limits their interpretation. Further  
265 research is necessary to judge the influence on spasticity. Several conditions modify  
266 spasticity: urinary tract infections, ingrown nails, lithiasis, temperature[32]. Yet, the  
267 possibility of spasticity exacerbation during detrusor uninhibited contraction has never been  
268 considered. Moreover, considering the impact of the need to void as a dual task requires a  
269 comparison with cognitive tasks during gait evaluation, especially since an impact on  
270 attention skills has been demonstrated[9].

271 Finally, our study suggests that clinical walk tests are sensitive to changes in individual  
272 variations such as the need to void. The use of the tests in clinical practice and research must  
273 be standardized, to reduce bias in their interpretation and clinical significance.

## 274 **Conclusion**

275 This study suggests decreased walking speed at SDV in IwMS and urinary disorders, showing  
276 an increase in gait velocity after voiding with an SDV. Severity of disability and urodynamic  
277 parameters were not associated with greater difference in velocity at SDV than PV, but the  
278 heterogeneity of the MS population could suggest lack of power in our study to demonstrate  
279 the influence of a specific factor.

280



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284

285 **Conflict of interest.** No conflict of interest in relation to the study.

286 **Legend**

287 **Figure.** Walking speed change between post-void and a strong desire to void.

288

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- 375

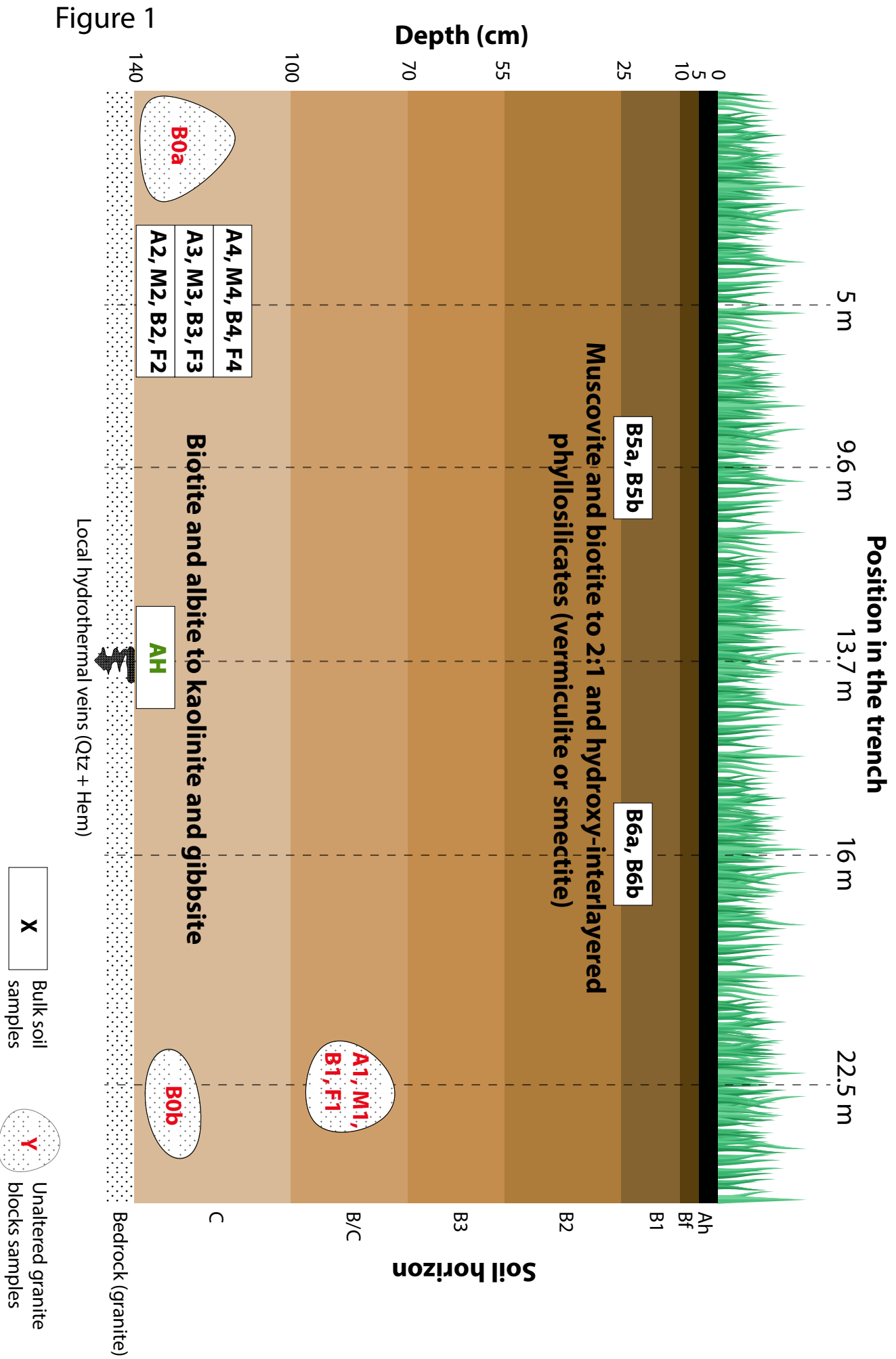
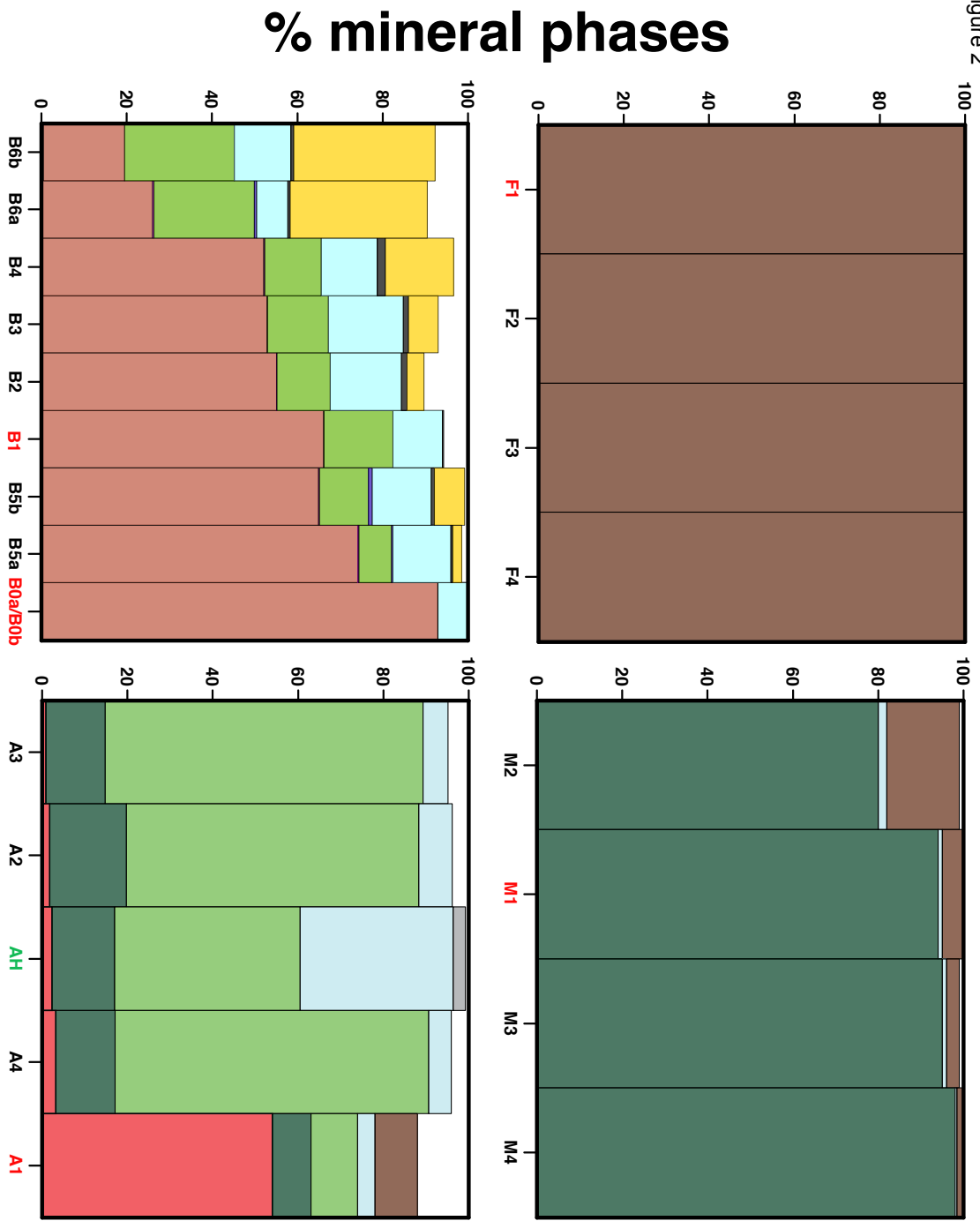


Figure 2



- Biotite
  - Chlorite
  - Vermiculite
  - Kaolinite
  - Gibbsite
  - Quartz
  - Ti-Oxides
  - Albite
  - Muscovite
  - K-Feldspar
  - Hematite
- B0/F1** Unaltered granite blocks samples
- AH** Hydrothermalized albite

figure 3

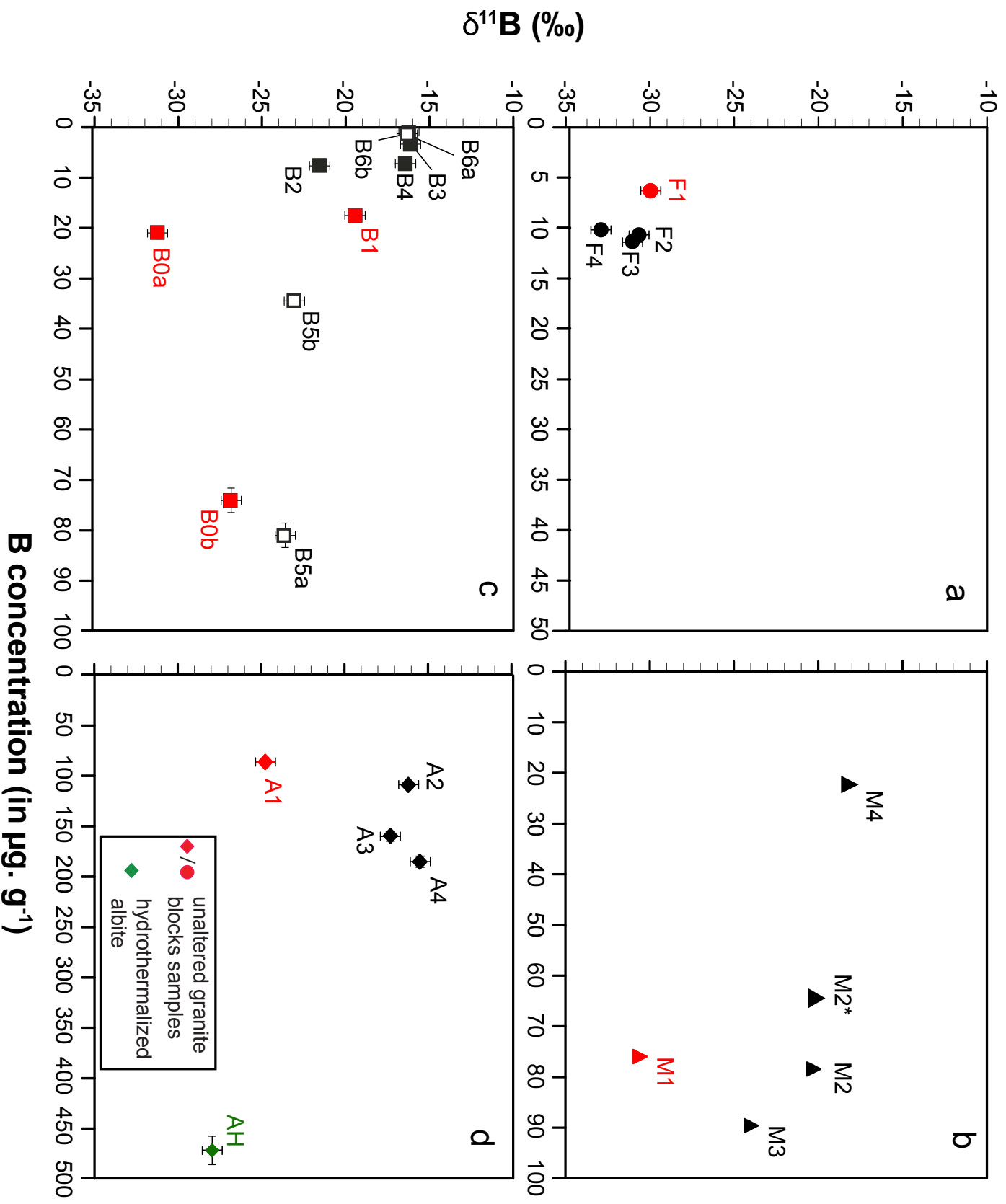


Figure 4

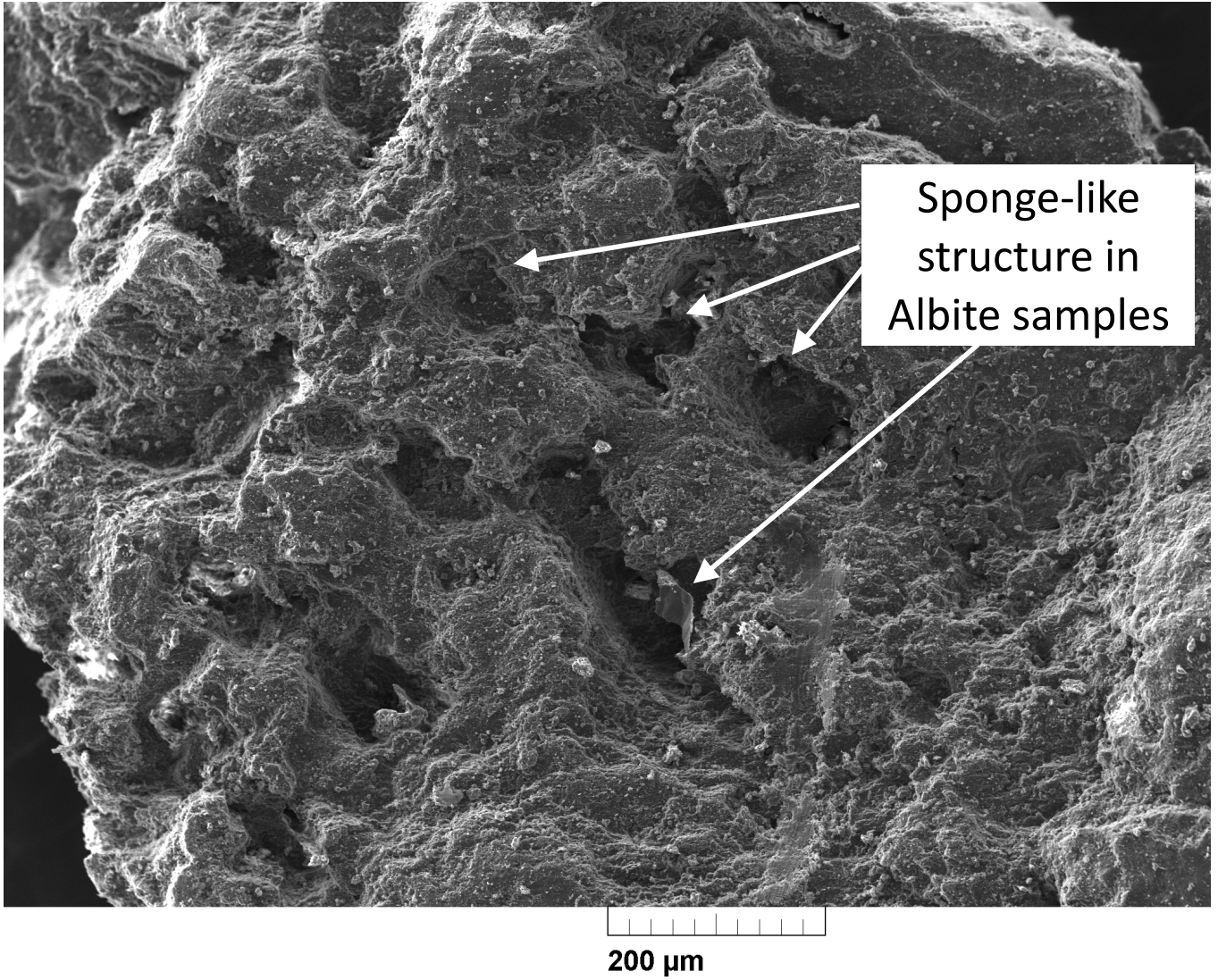


figure 5

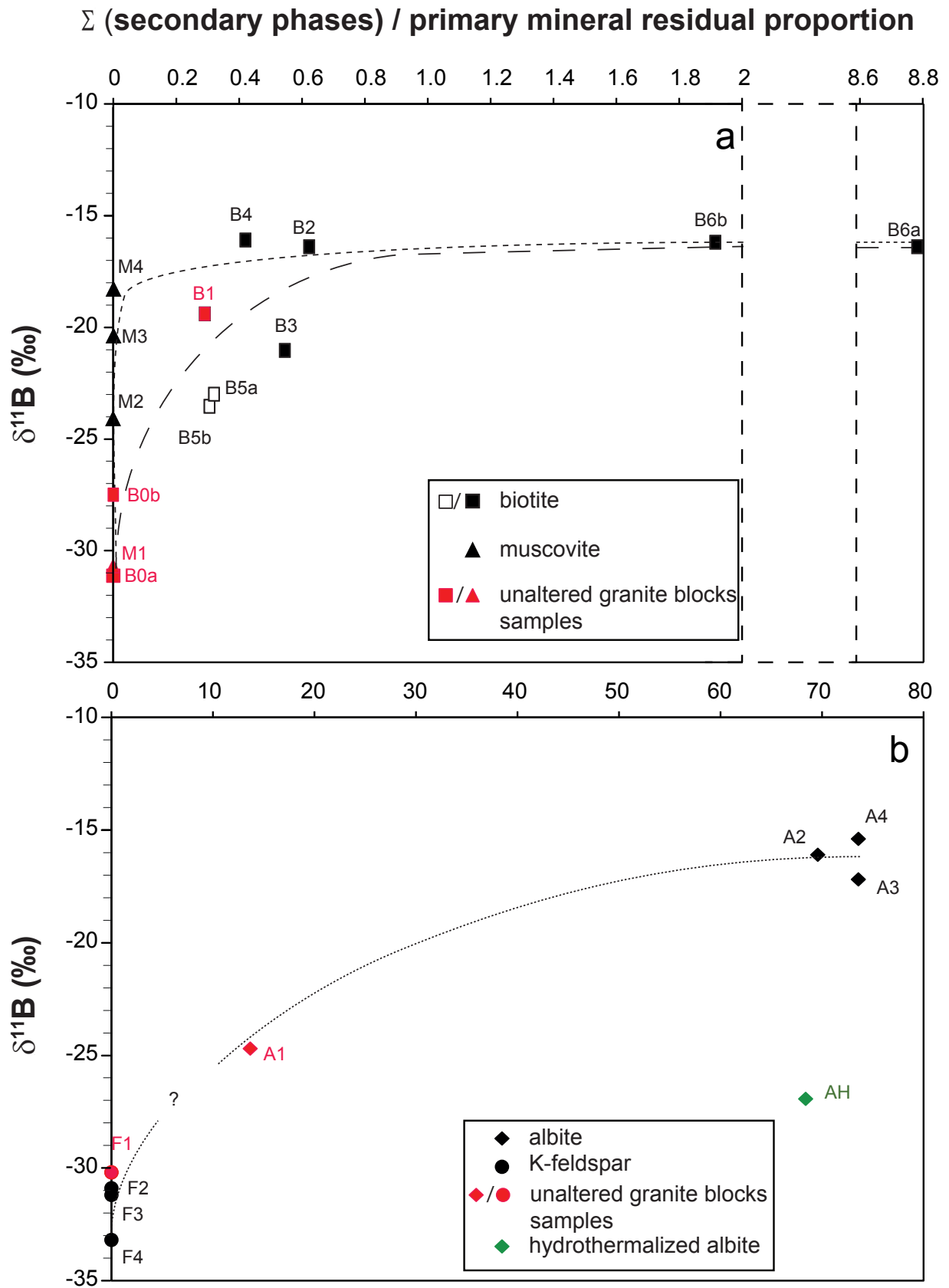




figure 6

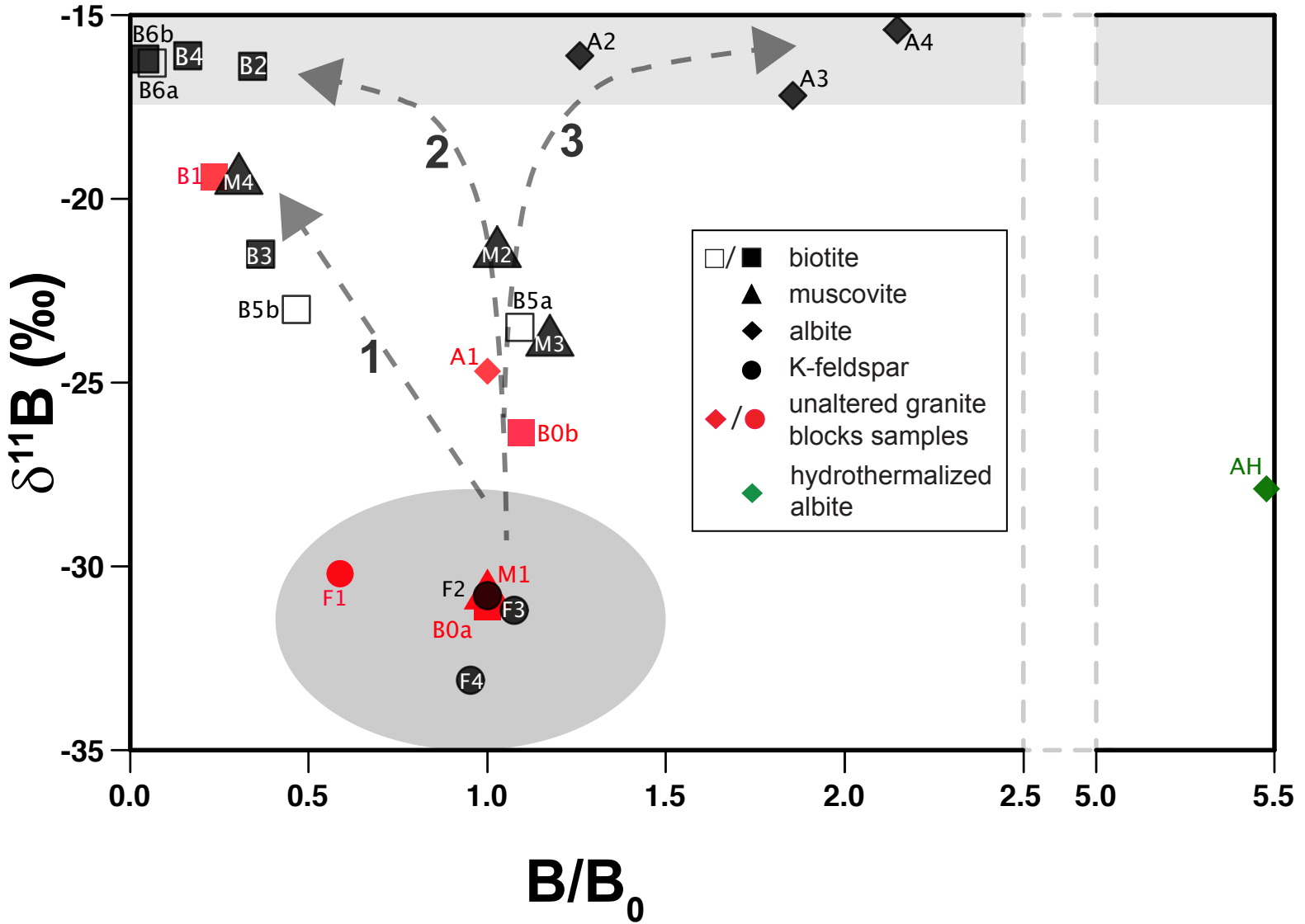


figure A1

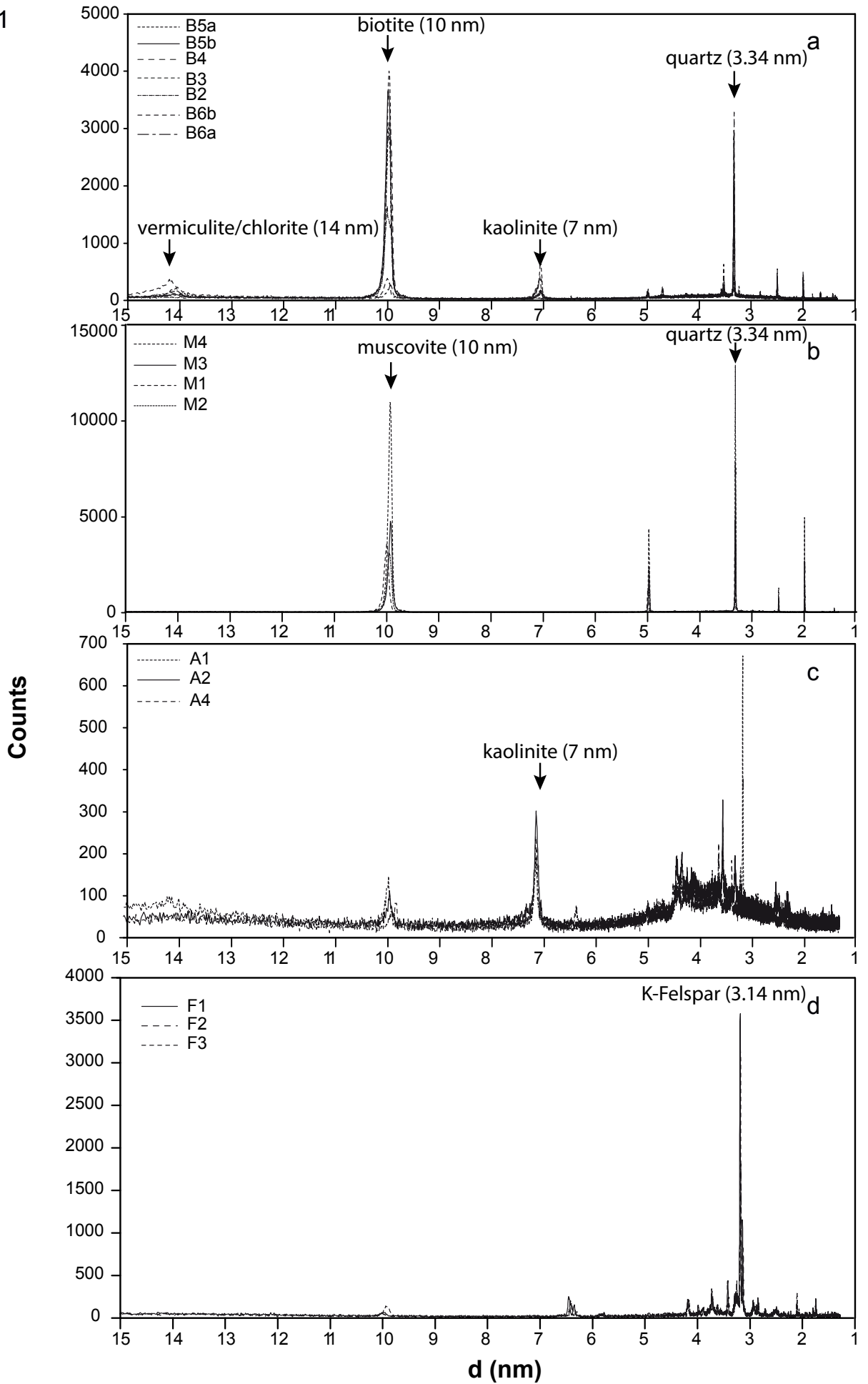


figure A2

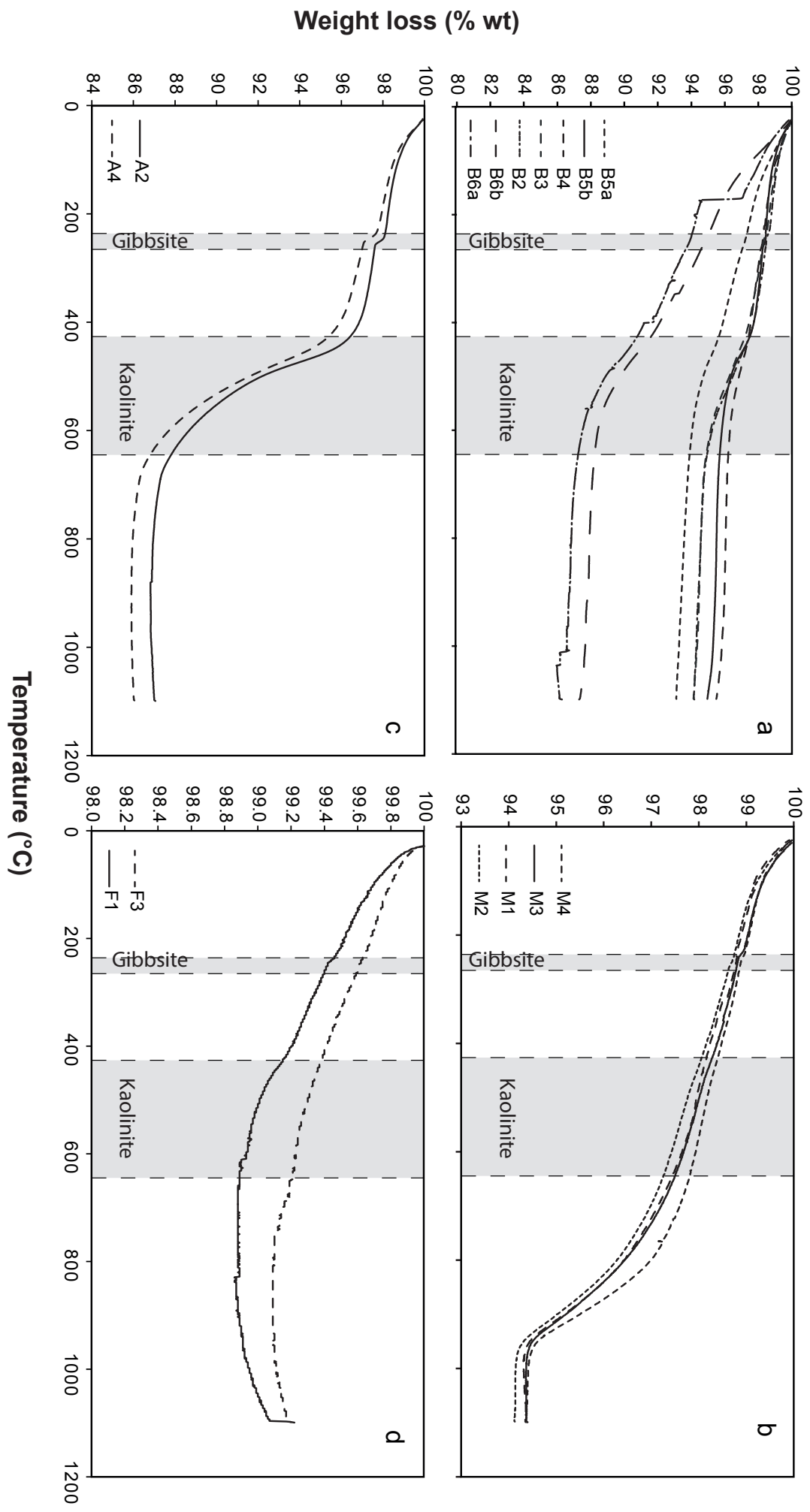


Table 1: Composition of primary and secondary minerals from well-preserved and weathered granite samples determined by microprobe analyses on granite or soil thin sections (Mareschal, 2008; Mareschal et al., 2015). Gibbsite and hematite are taken from Deer et al., 1996.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO <sup>1</sup>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	MnO	TiO <sub>2</sub>	Total
<b>Biotites</b>	34.9	18.4	22.2	<DL <sup>2</sup>	3.8	9.2	0.25	0.62	3.5	93.2
<i>STD (1 σ)</i>	0.7	1.5	0.7		0.3	0.3	0.07	0.15	1.1	-
<b>Muscovites</b>	46.0	32.2	2.45	<DL <sup>2</sup>	1.03	10.4	0.70	<DL <sup>2</sup>	0.12	93.0
<i>STD (1 σ)</i>	1.3	1.6	0.56		0.32	0.4	0.19	0.09		-
<b>K-feldspar</b>	64.3	18.1	<DL <sup>2</sup>	<DL <sup>2</sup>	<DL <sup>2</sup>	15.5	0.88	<DL <sup>2</sup>	<DL <sup>2</sup>	99.0
<i>STD (1 σ)</i>	0.4	0.4				0.96	0.59			-
<b>Albite</b>	66.4	20.7	<DL <sup>2</sup>	1.38	<DL <sup>2</sup>	0.57	10.5	<DL <sup>2</sup>	<DL <sup>2</sup>	99.6
<i>STD (1 σ)</i>	0.4	0.3		0.23		0.17	0.3			-
<b>Kaolinite</b>	45.0	39.5	1.00	<DL <sup>2</sup>	0.06	0.08	0.10	<DL <sup>2</sup>	0.20	86.6
<i>STD (1 σ)</i>	1.1	0.99	0.02		0.01	0.02	0.01	0.02		-
<b>Vermiculite</b>	49.0	33.6	1.70	<DL <sup>2</sup>	1.09	1.47	0.08	0.11	0.14	87.2
<i>STD (1 σ)</i>	1.1	0.8	0.02		0.02	0.76	0.01	0.01	0.02	-
<b>Hematite</b>	-	-	96.0	-	-	-	-	-	-	96.0
<i>STD (1 σ)</i>	-	-	-	-	-	-	-	-	-	-
<b>Gibbsite</b>	-	65.4	-	-	-	-	-	-	-	65.4
<i>STD (1 σ)</i>	-	-	-	-	-	-	-	-	-	-

<sup>1</sup>Total Fe (FeO + Fe<sub>2</sub>O<sub>3</sub>)

<sup>2</sup>Below detection microprobe limit (DL)

Table 2: Boron concentration and isotopic composition of pore and bound waters.

	[B] (ng B/ mL)	δ <sup>11</sup> B (‰)	Water/rock ratio (L/kg)
<b>20-30 cm horizon pore water</b>	12.0	30.3	0.003
<b>20-30 cm horizon bound water</b>	8.4	22.3	0.025
<b>110-140 cm horizon pore water</b>	-	-	0
<b>110-140 cm horizon bound water</b>	12.5	18.9	0.013

Table 3: Mineral phases identified in each sample using a combination of XRD, SEM and differential thermal analyses (Figure A1). These phases were then used for quantitative mineralogy calculations (Eq. 3 in text)

Samples	Identified mineral phases
<b>Biotite</b>	Biotite, kaolinite, vermiculite, titanium oxides, quartz, gibbsite, chlorite <sup>1</sup>
<b>Muscovites</b>	Muscovite, K-feldspar, quartz
<b>K-feldspar</b>	K-feldspar
<b>Albite</b>	Albite, kaolinite, gibbsite, muscovite, quartz, hematite <sup>2</sup>

<sup>1</sup>Samples B0b, B5a, B5b and B6a only

<sup>2</sup>Sample AH only

Table 4: Major elements, B concentration and B isotopic composition in all studied samples (see table 3 for abbreviations).

	Primary mineral	Depth (cm)	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	CaO	Fe <sub>2</sub> O <sub>3</sub>	MnO	TiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	δ <sup>11</sup> B (‰)	B (μg.g <sup>-1</sup> )	1
<b>DL<sup>1</sup></b>			0.009	0.002	0.0007	0.002	0.002	0.003	0.00003	0.01	0.004	+/-0.6	0.7	
<b>A1</b>	<i>Albite</i>	G.B. <sup>3</sup>	67.1	18.7	0.7	0.3	0.1	0.02	0.01	5.8	0.2	-24.7	86.2	
<b>A2</b>		130-140	48.9	33.8	0.4	<DL	0.6	<DL	<DL	0.2	2.1	-16.1	108.6	
<b>A3</b>		120-130	47.2	35	0.4	<DL	0.6	<DL	<DL	0.2	1.9	-17.2	160	
<b>A4</b>		110-120	47.8	35.1	0.5	0.1	0.6	<DL	0.1	0.1	2	-15.4	185.2	
<b>AH</b>		130-140	43.8	33.6	0.6	<DL	5.7	0.1	<DL	0.8	1.6	-27.9	471.8	
<b>B0a</b>		G.B. <sup>3</sup>	42.4	19.7	7.1	<DL	16.9	0.3	1.8	1.2	5.4	-31.1	21	
<b>B0b</b>	<i>Biotite</i>	G.B. <sup>3</sup>	43	18.9	4.2	0.1	19	0.5	2.4	0.7	7.2	-26.8	74.2	
<b>B1</b>		G.B. <sup>3</sup>	41.7	21.4	4.3	0.1	15.3	0.5	2.2	0.6	5.5	-19.4	17.5	
<b>B2</b>		130-140	42.3	20.2	4.8	<DL	15.5	0.4	2.9	0.3	4.2	-16.4	7.2	
<b>B3</b>		120-130	44.1	20.2	4.8	<DL	16.1	0.5	2.6	0.3	4.4	-21.5	7.7	

<b>B4</b>		110-120	41.1	19.9	5.5	<DL	18.7	0.5	3.3	0.3	5	-16.1	3.4
<b>B5a</b>		20-30	43.3	19.9	4.1	0.1	18.1	0.5	2.5	0.6	6.3	-23.5	81
<b>B5b</b>		20-30	43.5	20.8	4.1	0.1	17.1	0.5	2.7	0.4	5.4	-23	34.5
<b>B6a</b>		20-30	34.8	21.7	5.7	0.1	22.7	0.7	1.4	0.2	2.6	-16.3	1.3
<b>B6b</b>		20-30	39.5	20.8	3.4	0.1	19	0.8	1.3	0.5	2.4	-16.2	0.9
<b>F1</b>	<i>K-Feldspar</i>	G.B. <sup>3</sup>	64.6	18.2	<DL	0.2	0.2	<DL	<DL	3.3	11.4	-30.2	6.3
<b>F2</b>		130-140	64.7	18.2	0.1	0.1	0.2	<DL	<DL	2.7	12.1	-30.8	10.7
<b>F3</b>		120-130	64	18.3	0.1	0.1	0.3	<DL	<DL	2.6	12.2	-31.2	11.5
<b>F4</b>		110-120	62.7	18.4	0.1	0.1	0.5	<DL	<DL	2.1	12.7	-33.1	10.2
<b>M1</b>	<i>Muscovite</i>	G.B. <sup>3</sup>	44.8	31.3	1.3	0.1	3.4	0.1	0.1	0.9	9.5	-30.7	76.1
<b>M2</b>		130-140	44.3	31.2	1.4	<DL	3	0.1	0.1	1	9.5	-21.4	78.3
<b>M3</b>		120-130	45.3	31.4	1.4	<DL	3.1	0.1	0.1	0.8	9.4	-23.8	89.5
<b>M4</b>		110-120	45.7	32.1	1.3	<DL	3.1	0.1	0.1	0.7	9.7	-19.4	22.5

<sup>1</sup>Detection limit for all elements (except for boron isotopic composition where measurement external reproducibility is given).

<sup>2</sup>Loss on ignition

<sup>3</sup>Unaltered granite