

1 Title: Mineral control of organic carbon storage in acid temperate forest soils in the  
2 Basque Country

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24 Abstract

25 Soil minerals are known to play a major role in soil organic carbon (SOC) stabilization.  
26 However, the exact nature of the role is still poorly understood as comparative studies  
27 are complicated by the fact that mineralogy usually varies with other important factors  
28 such as climate, land-use, texture and acidity. This study investigated naturally-  
29 occurring minerals and C storage in nine mature, second-rotation *Pinus radiata* D. Don  
30 forest plantations at a similar development stage and growing under similar climatic  
31 conditions, but established on soils derived from three different parent materials:  
32 sandstone, basalt and trachyte. We quantified the SOC stocks in the 0-20 cm soil layer,  
33 clay-size minerals and metal oxides. The distribution of SOC in labile and mineral-  
34 bound fractions and the chemical structure of the SOC were also determined, by  
35 CPMAS NMR spectroscopy. For similar tree biomass, mean SOC storage was 2 times  
36 higher in the soils derived from basalt and 2.5 times higher in the soils derived from  
37 trachyte which were relatively rich in chlorite/vermiculite mixed layers and short-range  
38 order aluminium and iron forms, than in the sandstone-derived soils dominated by illite  
39 and with no short-range order aluminium. The parent material also affected the major C  
40 components of the SOC. Thus, the proportion of aromatic-C forms in the total SOC was  
41 higher in the sandstone-derived soil than in the soils of volcanic origin. Furthermore, the  
42 proportion of SOC in the mineral-bound fraction was around 30% in the sandstone-  
43 derived soil and around 50% in the volcanic soils. We conclude that estimates of  
44 ecosystem SOC stocks in acid temperate forest soils should include proxies for clay  
45 mineralogy, such as phyllosilicate minerals, contents of Fe and Al (hydr-) oxides and  
46 non-crystalline compounds. In addition, we recommend the inclusion of soil parent  
47 material as a proxy in models aimed at estimating regional SOC stocks.

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49 Keywords: Forest soils, soil mineralogy, soil organic C, oxides, phyllosilicates

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51 Highlights:

52 • SOC differed in forest soils with similar pH/clay content but different bedrock

53 • Clay mineralogy differed in sandstone-derived and volcanic soils

54 • The amounts and quality of SOC may be related to mineralogical differences

55 • Soil parent material could be included as a proxy in SOC model development

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## 59 **1. Introduction**

60 Soil organic matter (SOM) is considered a continuum of progressively decomposing  
61 organic compounds, ranging from large plant and animal residues to more oxidized  
62 compounds of smaller molecular size, including compounds of microbial origin  
63 (Lehmann and Kleber, 2015). Stabilization of SOM depends on the multiple interactions  
64 between non-organic soil components and the continuum of progressively decomposing  
65 organic compounds. Recent research stresses the need for global, regional and local  
66 studies of SOM stabilization to take into account the nature of these soil components  
67 and also the physical-chemical characteristics of the matrix in which the components  
68 interact (Rasmussen et al., 2018; Rowley et al., 2018). In this context, information about  
69 SOM stabilization mechanisms, as affected by the composition of the soil mineral  
70 fraction, is needed to improve soil carbon management and to enable climate-related  
71 targets and the United Nations' sustainable development goals to be met.

72 Regional studies have demonstrated a relationship between the soil parent material and  
73 organic C storage in topsoil (e.g. Gray et al., 2015; Silva et al., 2016; Barré et al., 2017).  
74 The mechanisms underlying such interactions are, however, not straightforward and are  
75 probably dependent on local conditions (Barré et al., 2017). Recent research findings  
76 indicate that, among the different soil properties associated with soil genesis, the  
77 mineralogical characteristics play an important role in SOC stabilization (Singh, et al.,  
78 2018; Barré et al., 2014). Interactions between minerals and organic matter are known  
79 to be affected by the properties of the minerals, such as specific surface area and the  
80 capacity to bind to organic moieties in soil through electrostatic interactions (Six et al.  
81 2002a; Kleber et al., 2007; Feng et al. 2013). Chemical recalcitrance is not always  
82 associated with mature, stable organic matter in soils (Kleber et al., 2011; Derrien et al.,  
83 2016), and it is the interactions with soil minerals at different levels that protect organic

84 components from further degradation (Lehmann and Kleber, 2015). Thus, the ability of  
85 soil minerals to form *primary* and *secondary* organo-mineral complexes (as defined by  
86 Christensen, 1996) is a determining factor in long-term SOC stabilization.

87 The properties of soil minerals are primarily defined by the parent material, but are also  
88 affected by weathering processes. Regarding the reactive minerals present in the clay  
89 fraction, parent materials such as granite and most common sedimentary rocks favour  
90 the formation of illite-like minerals, while ferromagnesian igneous rocks favour the  
91 formation of chlorite-vermiculite mixed layer minerals (Wilson et al., 1984). In soils  
92 derived from parent materials rich in Al and Fe, the secondary minerals formed via  
93 weathering of primary minerals generally also include Fe-oxides (e.g. ferrihydrite and  
94 goethite), Al-oxyhydroxides (e.g. gibbsite), short-range order (SRO) or non-crystalline  
95 minerals (e.g. allophane and imogolite) and phyllosilicates, including halloysite and  
96 kaolinite (Lawrence et al., 2015). The SRO minerals are known to contribute to SOC  
97 stabilization in soils derived from igneous rocks (e.g. Torn et al., 1997). Coarse-textured  
98 soils have also received some attention in this regard (Grand and Lavkulich, 2011;  
99 Grand and Lavkulich, 2015). In such soils, dissolved weathering products, including Al  
100 and Fe, react with organic ligands to form organo-metal complexes (e.g., Matus et al.,  
101 2006; Sollins et al., 1996). These stable complexes determine Al/Fe solubility in soils  
102 (Berggren and Mulder, 1995; Dijkstra and Fitzhugh, 2003), and they have been shown  
103 to influence the precipitation of secondary minerals (Lawrence et al., 2014). Several  
104 studies have also demonstrated a strong significant correlation between sodium  
105 pyrophosphate-extractable Al/Fe and total soil C (e.g. Masiello et al., 2004; Wagai et  
106 al., 2011), implying a widespread association between organo-metal complexation and  
107 long-term storage and stability of SOC in soils in which these elements are abundant.

108 The nature of organic components of soil and their ability to be incorporated into  
109 organo-mineral structures at different levels are also important aspects of organo-  
110 mineral complexation. In addition to the nature of the soil organic components, and in  
111 relation to direct complexation (*primary* complexes as defined by Christensen, 1996), a  
112 number of determining factors -such as the physico-chemical characteristics of the soil  
113 solution- determine the various possible models of binding of organic molecular  
114 fragments in these complexes (Kleber et al., 2007).

115 Selective preservation due to the specific chemical structure of SOM compounds and  
116 fractions found in association with minerals has been proposed as a mechanism for  
117 protecting SOC (Marschner et al., 2008). Some particular types of SOM compounds are  
118 preferentially stabilized by association with soil minerals (Gu et al., 1994; Kaiser et al.,  
119 1997; Spielvogel et al., 2008). SOM functional fractions such as particulate organic  
120 matter (POM) and the chemical structure of SOM, determined by  $^{13}\text{C}$  cross polarization  
121 magic angle spinning nuclear magnetic resonance (CPMAS NMR) spectroscopy, have  
122 also been found to be involved in preferential stabilization in soils with different  
123 mineralogy (Schöning et al., 2005; Spielvogel et al., 2008). All of the above evidence  
124 indicates that studies investigating the influence of soil parent material and soil  
125 mineralogy on the preservation of soil organic matter should consider the possible bias  
126 induced by the presence of organic compounds of different origin (e.g. Plante et al.,  
127 2010). At a practical level, studies comparing different soils should consider the nature  
128 of the SOM and should ideally compare soils with similar organic inputs.

129 Studying the relationship between lithology and SOC stabilization is also of interest  
130 because geological and lithological data is generally more accessible and accurate than  
131 soil-related data (Araujo et al., 2017).

132 However, studies of the role of soil mineralogy on SOM protection under temperate  
133 climate remain scarce. This particularly applies to clay minerals, which may have  
134 different characteristics (e.g. cation exchange capacity and specific surface area) and  
135 thus different capacities to protect SOC (Barré et al., 2014; Fernández-Ugalde et al.,  
136 2016).

137 The following main difficulties in interpreting the results of these studies have been  
138 reported (Barré et al., 2014): i) data on soils rich in 1:1 clay minerals mainly correspond  
139 to tropical zones (Balbino et al., 2004), whereas data on soils dominated by 2:1 clay  
140 mainly correspond to temperate zones (thus climate, pH and oxide content covary with  
141 phyllosilicate mineralogy; Chenu et al., 2009); ii) phyllosilicate mineralogy is seldom  
142 determined in soil studies; and iii) the presence of oxides associated with phyllosilicates  
143 can also minimize or even conceal the relationship between phyllosilicate mineralogy  
144 and SOC protection (Saidy et al., 2013).

145 On the basis of existing knowledge about the role of minerals on SOC storage, we  
146 studied SOC storage in relation to mineralogy in three acidic temperate Atlantic forest  
147 soils, which were developed on volcanic rock (basalt and trachyte) and sandstone. The  
148 three soils are located in the same geographical region, under similar climatic conditions  
149 and with similar vegetation, thus ensuring valid comparisons by eliminating drawback  
150 (i) described by Barré et al. (2014). In addition, we determined the mineral composition,  
151 including the possible interactions between clay minerals, SRO and Fe and Al oxides, to  
152 address drawbacks (ii) and (iii) described by the same authors. The total amounts of  
153 organic C and of various functional OC groups were also investigated at two depths (0-  
154 5 and 5-20 cm) to elucidate how they are related to soil parent material, soil mineralogy  
155 and SOM stabilization.

156 Our study aimed to address the following: (1) the possible influence of parent material  
157 on SOC stocks and concentration in temperate forest in the Basque Country; (2) the  
158 involvement of mineralogical differences (primary and secondary organo-mineral  
159 associations) in any such relationship; (3) the possible influence of mineralogy on the  
160 chemistry of SOC in temperate forest in the Basque Country.

161 Our hypotheses were as follows: (1) soils developed on volcanic rocks are richer in  
162 minerals that favour organo-mineral interactions (swelling clays, SRO minerals,  
163 metallic oxy-hydroxides); (2) this will result in higher SOC concentrations and stocks in  
164 soils developed on volcanic rocks than in soils developed on sandstone; and (3) this will  
165 influence the chemistry of SOC in the different soils.

## 166 **2. Materials and methods**

### 167 2.1. Study area and collection of soil samples

168 An observational study was conducted in mature, second rotation *Pinus radiata* D. Don  
169 forest plantations in two areas of the Basque Country (northern Spain): (i) Mount Oiz, a  
170 sandstone massif (30T, 534075, 4783284), and (ii) Mount Karakate, a volcanic massif  
171 (with basalt and trachyte as dominant rocks) (30T, 548126, 4781437), separated by a  
172 distance of less than 25 km (Figure 1). The climate in both areas is temperate and  
173 humid, with annual mean temperature and annual mean precipitation of around 9 °C and  
174 1200 mm, respectively, and 190 rainy days. Precipitation is distributed rather evenly  
175 throughout the year, with maximum levels in autumn and spring. The sites are thus  
176 representative of Atlantic temperate conditions.

177 Three forest stands developed over each type of parent material (sandstone, basalt and  
178 trachyte) (total, 9 stands) were selected for study (Figure 1). The mean tree height  
179 (based on LIDAR data) was 26.9 m  $\pm$  0.4 standard error (SE) in the stands developed on  
180 sandstone, 24.7 m  $\pm$  2.6 SE in the stands over basaltic rock and 27.8 m  $\pm$  2.5 SE in the



181 stands on trachytic rock. Tree height was used as a proxy for forest development stage  
182 (Moreno et al., 2016) and did not differ in relation to bedrock. Five representative  
183 sampling points were selected in each stand. Soil samples were collected from the upper  
184 20 cm of the soil profile obtained by digging a 20x20x20 cm pit (after removal of forest  
185 floor material). The samples were then divided into 0-5 cm and 5-20 cm layers and  
186 combined to produce one composite sample per stand and layer. The soil samples were  
187 air-dried and sieved to < 2 mm. An additional soil core was obtained in each pit for  
188 determination of soil bulk density.

## 189 2.2. Soil chemical, physical and mineralogical data

190 Soil pH values were measured in deionised water and in 1 M KCl at a soil/ solution  
191 ratio of 1:2.5. The  $\text{pH}_{\text{NaF}}$  was measured in a suspension of 1g soil mixed with 50 ml of  
192 1M NaF solution after stirring for 2 min. The exchangeable cations and cation exchange  
193 capacity (CEC) were determined in unbuffered solutions. The exchangeable aluminium  
194 and cations were extracted with 0.1 M  $\text{BaCl}_2$  (Gillman, 1979), and the exchangeable  
195 aluminium was determined by titration with 0.1 M NaOH to pH 7.2. The exchangeable  
196  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$  in the extracts were determined by atomic absorption  
197 spectroscopy. The effective cation exchange capacity (eCEC) was calculated as the sum  
198 of base cations and Al. Air-dried soil samples were ground to pass a 250  $\mu\text{m}$  sieve for  
199 total carbon and nitrogen analysis in a LECO TruSpec autoanalyzer (LECO  
200 Corporation, MI, USA).

201 After removal of the organic matter by oxidation with  $\text{H}_2\text{O}_2$  and dispersion of the  
202 sample with Na-hexametaphosphate, the soil texture was determined by laser  
203 diffractometry (Mastersizer 2000 diffractometer, Malvern Instruments, Worcestershire,  
204 UK).

205 Mineralogical analysis of air-dried sieved soil samples (< 2 mm) (using Cu radiation  
206 from 2° to 80° 2θ) and of the clay fraction (< 2 μm) on oriented slides was conducted,  
207 by powder X-ray diffraction (XRD), to identify primary and secondary crystalline  
208 minerals in each soil sample.

209 Air-dried sieved soil samples (< 2 mm) were washed with demineralized H<sub>2</sub>O and  
210 disaggregated by attrition and ultrasound for 4 cycles each of 30 min. Clay-size particles  
211 were isolated by repeated mixing with weakly basified demineralized water until pH = 8  
212 (NH<sub>4</sub>OH) and centrifuging at 3500 rpm (in Kubota K8410 centrifuge). After each  
213 centrifugation cycle, the supernatant liquid (devoid of particles) was removed until  
214 slight turbidity was observed. The suspensions were distributed in 100 x 30 mm glass  
215 tubes and centrifuged at 1000 rpm for 100 sec. The upper 4 cm of the supernatant  
216 liquid, which only contains particles <2 microns (Stokes law), was then extracted. Clays  
217 were oriented and mounted on glass slides with the following standard treatments: Mg  
218 saturation, Mg saturation/glycerol solvation, K saturation, and heat treatment of K-  
219 saturated samples at 300°C. X-ray analysis was conducted using a diffractometer  
220 (Philips PW1710) with Bragg-Brentano geometry (θ,2θ) and Ni-filtered CuKα  
221 radiation. Diffraction data on powdered whole samples were analysed using  
222 PANalytical X'Pert Highscore Plus software, coupled to the PDF2 database of the  
223 International Centre for Diffraction Data (ICDD). Clay minerals were identified  
224 according to the position of the (00l) series of basal reflections on XRD patterns  
225 collected under indicated treatments of oriented aggregates, in the range 1 to 30° 2θ  
226 (Moore and Reynolds, 1997).

### 227 2.3 Selective extraction of soil for Fe and Al

228 The Al, Fe and Si compounds were selectively dissolved in three chemical reactants to  
229 yield the non-crystalline components. “Active” Al, Fe and Si compounds (Al<sub>ox</sub>, Fe<sub>ox</sub>,

230  $\text{Si}_{\text{ox}}$ ) were extracted in darkness after shaking the soil with an ammonium oxalate  
231 solution buffered at pH 3 (Schwertmann, 1964). For extraction of Fe and Al complexed  
232 with organic matter compounds ( $\text{Fe}_p$ ,  $\text{Al}_p$ ), the soil was shaken with a sodium  
233 pyrophosphate solution (Blakemore et al., 1987). “Free” Fe and Al compounds ( $\text{Fe}_d$ ,  
234  $\text{Al}_d$ ) were extracted using a citrate dithionite solution (Mehra and Jackson, 1960).  
235 Concentrations of Fe, Al and Si in supernatants were determined by absorption  
236 spectrophotometry (Perkin Elmer 2380, Norwalk, CT, USA). Aluminium and iron  
237 associated with inorganic short-range order (SRO) material was calculated as oxalate-  
238 extractable Al and Fe minus pyrophosphate extractable Al and Fe (Grand and  
239 Lavkulich, 2011).

#### 240 2.4. SOM fractionation

##### 241 2.4.1. Particulate organic matter (POM) and mineral-bound organic matter (MOM)

242 The C fractions in POM ( $>53 \mu\text{m}$ ) and MOM ( $<53 \mu\text{m}$ ) were determined by applying  
243 ultrasound energy to a soil-water suspension. A suspension of 5 g soil (oven-dry  
244 equivalent) and 25 mL of distilled water was held in a beaker in an ice bath and  
245 sonicated (total input  $450 \text{ J mL}^{-1}$ ) with a digital sonifier (VCX130 ultrasonic processor,  
246 max. output, 58.5W) equipped with a flat tipped probe of 13 mm diameter, operated at  
247 20 kHz.

248 The POM was retained on a  $53 \mu\text{m}$  sieve and the mixture of silt+clay fraction ( $< 53 \mu\text{m}$ )  
249 was centrifuged at  $6000 \text{ xg}$  for 30 min and filtered (cellulose acetate filter,  $0.45 \mu\text{m}$ ) in a  
250 Millipore Sterifil filtration system. Fractions were dried at  $50^\circ\text{C}$  for 48 hours and  
251 weighed to determine the recovery. The total C in both fractions was determined using  
252 the same elemental analyzer.

##### 253 2.4.2. Solid-state NMR spectroscopy

254 Cross-polarization magic-angle spinning (CPMAS)  $^{13}\text{C}$  NMR spectra of all soil samples  
255 were obtained. Samples were previously treated with HF to remove paramagnetic  
256 compounds (Gonçalves et al., 2003), as the high concentration of paramagnetic  
257 compounds in these samples does not allow acquisition of NMR spectra without prior  
258 treatment with HF.  $^{13}\text{C}$  solid state NMR spectra were acquired in a spectrometer (Bruker  
259 Avance DSX 300) equipped with a CP/MAS probe (Bruker BL 7mm). The  $^{13}\text{C}$   
260 frequency was 75.49 MHz and the  $^1\text{H}$  frequency, 300.13 MHz. CP/MAS spectra were  
261 recorded with high power decoupling. A contact time of 1 ms, a 90 degree pulse ( $^{13}\text{C}$ )  
262 of 7.5 microseconds, and a scan delay of 2 seconds proved optimal for acquisition of  
263 maximum signal and relaxed spectra. An FID of 4004 points with a spectral width of 50  
264 KHz was measured, and exponential apodization of 30 Hz was applied prior to Fourier  
265 transformation.

266 The spectra were subdivided into four regions: (i) alkyl-C (0–45 ppm); (ii) O-alkyl-C  
267 (45–110 ppm); (iii) aromatic-C (110–162 ppm), and (iv) carbonyl-C (162–190 ppm).  
268 Integration of the peaks within each of the chemical shift regions enabled estimation of  
269 the relative C contents expressed as percentages of the total area.

## 270 2.6. Data analysis

271 As this study was observational, no randomization could be carried out;  $n=1$  (including  
272 three pseudoreplicates) per parent material. Thus, mean values and 95% confidence  
273 intervals (CI) for the mean were used to reflect the degree of uncertainty in the  
274 measurements (Crawley, 2012). Depths (0–5 and 5–20 cm) were analyzed separately.  
275 Confidence intervals (95%) for the weighted (0-20 cm) means are also shown as  
276 supplementary data.

277

## 278 3. Results

279 3.1. Soil chemical, physical and mineralogical characterization

280 3.1.1. Chemical and physical properties

281 All soil samples were acidic, and the values of  $\text{pH}_{\text{H}_2\text{O}}$  ( $< 5$ ) and  $\text{pH}_{\text{KCl}}$  ( $< 4.5$ ) did not  
282 differ in relation to parent material (Table 1). However, in the 0-5 cm soil layer, the  
283  $\text{pH}_{\text{NaF}}$  was between 0.4 and 2.7 higher in soils developed on trachyte than in those  
284 developed on sandstone (Table 1). The  $\text{pH}_{\text{NaF}}$  was similar in all soils in the 5-20 cm  
285 layer (Supplementary Data 1). The three types of soil showed similar values in either  
286 the eCEC or exchangeable bases (Table 1). However, in the 0-5 cm layer the mean  
287 eCEC at pH7 was between 14.2 and 36.9  $\text{cmol}+\text{kg}^{-1}$  lower in sandstone-derived soils  
288 than trachyte-derived soils and between 9.9 and 26.0  $\text{cmol}+\text{kg}^{-1}$  lower in sandstone-  
289 derived soils than basalt-derived soils (Table 1). Soil acidity decreased with depth, as  
290 did eCEC and exchangeable bases.

291 Soil bulk density in the upper 20 cm was  $1.07 \text{ g cm}^{-3} \pm 0.04 \text{ CI}$  in the sandstone-derived  
292 soil,  $0.62 \text{ g cm}^{-3} \pm 0.03 \text{ CI}$  in basalt-derived soil and  $0.64 \text{ g cm}^{-3} \pm 0.02 \text{ CI}$  in the  
293 trachytic-derived soil. The mean soil bulk density in sandstone-derived soils was  
294 between 0.38 and 0.52  $\text{g cm}^{-3}$  higher than in basalt derived-soils and between 0.36 and  
295 0.48  $\text{g cm}^{-3}$  than in trachyte-derived soils. In the sandstone-derived soil, the sand  
296 particle content was higher and silt particles less abundant than in the soils derived from  
297 basalt and trachyte. There was no difference between the soils in the clay particle  
298 content, determined by laser diffractometry, neither in the upper 0-5 cm layer nor in the  
299 5-20 cm layer (Table 1 and Supplementary Data 1).

300 3.1.2. Mineralogy

301 Quartz was the dominant primary mineral in the sandstone-derived soil (almost 75 % of  
302 the mineral fraction) and the mean was 50-60% higher than in the soils derived from  
303 basalt and trachyte (Table 2 and Supplementary Data 1). By contrast, highly

304 weatherable minerals such as plagioclases were detected in the volcanic soils. Soils  
305 developed on basalt differed from those developed on trachyte with respect to the  
306 haematite content (Table 2 and Supplementary Data 1).

307 The proportion of phyllosilicates was 2 times lower in the sandstone-derived soil than in  
308 the soils derived from basalt and trachyte (Table 2 and Supplementary Data 1). In the  
309 sandstone-derived soil, the clay-size fraction showed a mixed mineralogy of  
310 phyllosilicates, dominated by illite, with lower proportions of hydroxyvermiculite,  
311 hydrobiotite and kaolinite, and a total absence of interstratified chlorite/vermiculite  
312 (Table 2 and Supplementary Data 2). By contrast, in the soils developed on volcanic  
313 rocks, the major crystalline mineral identified in the clay-size fraction was interstratified  
314 chlorite/vermiculite. No major differences were observed between basalt and trachyte-  
315 derived soils in the phyllosilicate mineralogy of this fraction (Table 2 and  
316 Supplementary Data 2).

317 The selective dissolution of aluminium showed that  $Al_{ox}$ ,  $Al_d$  and  $Al_p$  contents were  
318 always lower in the soil developed on sandstone than in soils developed on basalt and  
319 trachyte (Table 3 and Supplementary Data 1), but with no differences between the two  
320 soil depths (Table 3). SRO inorganic phases of aluminium ( $Al_{SRO}$ ) were not detected in  
321 the soil developed on sandstone (Table 3).

322 Selective extraction of Fe showed that the concentration of oxalate-extractable iron  
323 ( $Fe_{ox}$ ) was between 0.7 and 10.04 g kg<sup>-1</sup> lower in the sandstone-derived soil than in the  
324 volcanic soils (Supplementary Data 1); within these, the concentration was higher in the  
325 basalt-derived soil than in the trachyte-derived soil. The concentration of  $Fe_d$  was lowest  
326 in the sandstone-derived soil, and there was no difference between basalt- and trachyte-  
327 derived soils. The three types of soil were similar in pyrophosphate extractable iron  
328 ( $Fe_p$ ). The amount of oxalate-extractable silicon was higher in the basalt-derived soil

329 than in the sandstone- and trachyte-derived soils at both depths considered (Table 3 and  
330 Supplementary Data 1).

### 331 3.2 SOC and SOC fractions

#### 332 3.2.1. Total SOC storage

333 The concentrations of SOC differed between soils (Table 1 and Supplementary Data 1).

334 In the upper horizon (0-5 cm), the SOC concentration was respectively 2 and 2.7 times  
335 higher in the soils developed on basalt and from trachyte than in the soil developed on  
336 sandstone. In the subsoil horizon (5-20 cm), the SOC was 4 times and 5 times higher in  
337 the basalt and trachyte-derived soils than in the sandstone-derived soil. SOC

338 concentrations in the basalt- and trachyte-derived soils were similar (Table 1 and  
339 Supplementary Data 1). As a consequence, and despite the differences in bulk density,

340 the SOC stocks were lower in the sandstone-derived soil than in the trachyte- derived  
341 soils (Table 1 and Supplementary Data 1). The SOC stocks in the upper 20 cm  
342 amounted to  $61.5 \text{ Mg C ha}^{-1} \pm 4.2 \text{ CI}$  in the sandstone-derived soil,  $119.5 \text{ Mg C ha}^{-1} \pm$   
343  $34.7 \text{ CI}$  in the basalt-derived soil and  $152.8 \text{ Mg C ha}^{-1} \pm 54.8 \text{ CI}$  in the trachyte-derived  
344 soil, and the differences in SOC stocks were greatest in the deeper soil layers (5-20 cm).

#### 345 3.2.2. Particulate organic matter (POM) and mineral-bound organic matter (MOM)

346 The mean concentrations of POM-associated C were  $29.9 \pm 3.9 \text{ CI}$  ( $\text{mg C-POM g}^{-1} \text{ soil}$ )

347 in the sandstone-derived soil, and  $53.6 \pm 19.3 \text{ CI}$  and  $92.0 \pm 30.4 \text{ CI}$  ( $\text{mg C-POM g}^{-1}$

348 soil) in respectively the basalt- and trachyte-derived soils, in the upper 0-5 cm of the

349 soil profile (Table 1). The proportion of SOC in the POM fraction was similar in all

350 soils in the upper layer; however, in the lower layer (5-20 cm), the proportion of SOC in

351 the POM fraction was higher in the sandstone-derived soil than in either of the volcanic

352 soils.

353 Conversely, in the upper 0-5 cm of the soil profile, the concentration of MOM-  
354 associated C was  $19.5 \pm 3.1$  CI (mg C-MOM g<sup>-1</sup> soil) in the sandstone-derived soil and  
355  $55.8 \pm 21.4$  CI and  $49.4 \pm 5.6$  CI (mg C-MOM g<sup>-1</sup> soil) in respectively the basalt- and  
356 trachyte-derived soils (Table 1) The proportion of SOC in the MOM fraction for the  
357 soils developed on basalt was higher compared to the soils developed on sandstone or  
358 trachyte in the 0-5 cm layer. In the lower part of the studied layer (5-20 cm), both  
359 volcanic soils contained higher proportions of SOC bound to minerals: around 50% of  
360 the SOC was present in the MOM fraction in the volcanic soils, while 30% of SOC was  
361 present in MOM in soils derived from sandstone.

### 362 3.2.3. Chemical structure of organic matter

363 Integration of the major regions of <sup>13</sup>C NMR spectra indicated that the major C  
364 components in all soils were dominated by O-alkyl C (37.6-40.3 % of total intensity)  
365 and alkyl C (34.3-42.3 % of total intensity) (Fig 2a). This indicates high proportions of  
366 lipids, amino acids and polysaccharides as well as cellulose and hemicellulose. The  
367 proportion of alkyl-C in the total C increased with depth, but no differences were  
368 observed in the proportion of O-alkyl C in the total C. The trachyte-derived soil  
369 contained lower proportions of aromatic-C in total C than the sandstone-derived soil,  
370 while the values were intermediate in the basalt-derived soil (Fig 2a and Supplementary  
371 Data 1). The proportion of aromatic-C in total C decreased with depth (Fig 2b and 2c).

## 372 4. Discussion

### 373 4.1. Influence of parent material on soil characteristics and SOC in temperate 374 forest in the Basque Country

375 In this study, we hypothesized that parent material would determine to some extent the  
376 amount and type of organic matter stored in the upper layer of forest soils in the Basque  
377 Country. We based this hypothesis on previous observations that organo-mineral



378 interactions are dependent on soil mineralogy (Six et al., 2002b; Kleber et al., 2007;  
379 Rasmussen et al., 2018), which in turn was expected to be different in the soils derived  
380 from volcanic rocks or a clastic sedimentary rock such as sandstone.

381 Our observations confirmed that the underlying parent material strongly influenced the  
382 soil matrix in the upper soil layer, which differed in texture and mineralogy at the three  
383 study sites (Tables 1, 2 and 3).

384 Establishing an interaction between parent material, soil mineralogy and organic matter  
385 stabilisation is, however, not straightforward (Wiesmeier et al., 2019). In fact, most  
386 temperate soils contain a mixture of layer silicates, crystalline oxides and poorly  
387 crystalline materials, and there is evidence showing that all of these materials play direct  
388 or indirect roles in stabilizing organic matter (Sollins et al. 2009). However, although  
389 soil clay mineralogy is known to influence the composition, turnover and amount of soil  
390 organic matter (Barré et al., 2014; Singh et al., 2018; Wiesmeier et al., 2019), it is  
391 difficult to attribute differences in SOM in different soil types to phyllosilicate  
392 mineralogy alone, as many parameters can co-vary with clay mineralogy. In addition,  
393 stabilization mechanisms are also influenced by land management, climate and  
394 vegetation (Matus et al., 2014; Wiesmeier et al., 2019).

395 In our study, the nine stands considered were located in the same geographical area, and  
396 were thus affected by similar climatic conditions, and on soils with similar pH  
397 conditions and exchangeable cations. All were radiata pine stands established at least 50  
398 years ago and they were at a similar stage of forest development, thus enabling us to  
399 assume similarities in the amount and type of OM inputs (litter, exudates...). Site-  
400 related differences in SOC were therefore assumed to be the result of the interactions  
401 between SOC and the soil matrix. In this context, total SOC concentration was greater  
402 in the soils developed from volcanic materials (basalt and trachyte) than in the soil

403 developed on sandstone, although the values were intermediate in the soil derived from  
404 basalt. Total C stocks in the upper 20 cm of the soil profile were also higher in the  
405 volcanic soils, despite the lower bulk densities. In another recent study on forest soils,  
406 Barré et al. (2017) also observed that parent material affected SOM stocks, which were  
407 much lower in soils developed on loess deposits than in soils developed on chalk,  
408 mudstone or grainstone. However, the parent material only marginally explained the  
409 observed effect on topsoil organic C stocks due to the effect on soil clay abundance. In  
410 the present study, the clay content of the soils was similar, and the observed differences  
411 are probably explained by the nature of the minerals.

412 As summarized in the recent review by Wiesmeier et al. (2019), current knowledge of  
413 the impact of clay mineralogy on SOC stabilization is based on limited and conflicting  
414 data; however, it is usually accepted that the SOC stabilizing capacity is higher in soils  
415 dominated by 2:1 clay minerals (mainly smectite) than in soils dominated by 1:1 clay  
416 minerals (kaolinite) (Bruun et al., 2010). This is due to the higher reactivity of 2:1 clay  
417 minerals, which would promote organo-mineral complexation (Kaiser and  
418 Guggenberger, 2003; Kahle et al., 2004; Kleber et al., 2007; Feng et al., 2013), and/or to  
419 the capacity of these minerals to promote aggregation (Fernández-Ugalde et al., 2013).

420 Clay mineralogy in the soils under study was dominated by 2:1 clay minerals (Table 2).  
421 However, the soils showed contrasting clay mineral composition and concentrations of  
422 Al and Fe forms (Table 3). Within the 2:1 clay minerals, those with a high cation  
423 exchange capacity (CEC) and larger specific surface, such as montmorillonite and  
424 vermiculite, have a higher SOM binding potential than clay minerals with a lower CEC  
425 and smaller specific surface area, such as illite (Greenland, 1965). Mixed layer chlorite-  
426 vermiculite minerals, considered an intermediate step in the vermiculitization process,  
427 are formed in weathered rock microsystems (Velde and Meunier, 2008), such as the

428 basalts and trachytes considered here. Illite can be formed during weathering cycles  
429 (water/rock interactions) in temperate to cold climates on rocks containing abundant  
430 aluminium and potassium. The most common sedimentary rocks (e.g. sandstone) favour  
431 the formation of illite (Velde and Meunier, 2008). These phyllosilicate clay minerals  
432 occur in association with oxides and organic matter forming microaggregates, which  
433 ultimately contribute to stabilising SOC (Chenu and Plante, 2006); however, further  
434 research is required in order to clarify the associations between phyllosilicates, oxides  
435 and organic matter within microaggregates (Churchman, 2018).

436 Regarding Al and Fe forms, previous studies (Kaiser et al., 2002; Eusterhues et al.,  
437 2005) have suggested that iron oxides and SRO Al and Fe phases are the most important  
438 surfaces for the formation of organo-mineral associations in acid forest Podzols. Grand  
439 and Lakuvlich (2015) also reported that organically-bound Fe and Al were the major  
440 factors determining the SOC in podzols of forests in coastal British Columbia. Without  
441 considering clay mineralogy, Garrido and Matus (2012) observed that the  $Al_p$ , soil pH  
442 and allophane content explained most of the variation in SOC. Bruun et al. (2010) also  
443 concluded that the content of active Fe (hydr-) oxides determined SOC stabilization in  
444 kaolinitic soils under moist semi-deciduous primary or secondary forests located in  
445 lowland humid tropical areas. More recently, Rowley et al. (2018) reviewed the relative  
446 role of polyvalent cations in SOC stabilization. These authors proposed a conceptual  
447 model in which, in acidic environments, complexation of organic ligands by free  $Al^{3+}$   
448 and  $Fe^{3+}$ , as well as their mineral forms and the cementation of aggregates by Fe oxides  
449 are probably determining factors in SOC stabilization. This model provides a good  
450 explanation for the observed results, in which within three acid environments with  
451 similar amounts and types of organic inputs, the amount and nature of organic matter

452 differed clearly in the two soils containing the highest concentrations of Fe and Al  
453 (Table 3).  
454 Overall, our results (a difference between 32 and 150 Mg C ha<sup>-1</sup> between trachyte- and  
455 sandstone-derived soils, and a difference between 19 and 97 Mg C ha<sup>-1</sup> between basalt-  
456 and sandstone-derived soils) are generally consistent with those reported by Peña  
457 Ramirez et al. (2009), who observed a strong relationship between Al content in  
458 organo–mineral complexes (extractable with pyrophosphate) and the accumulation of  
459 organic C in volcanic soils less than 8000 years old. However, as phyllosilicate  
460 mineralogy covaried with metallic oxy-hydroxides, the influence of these factors was  
461 not able to be determined in the present study.

#### 462 **4.2. SOC chemistry differed slightly in the three soils under study**

463 The second hypothesis of this study was that the soil parent material would also  
464 influence the SOC chemistry in the different soils, as a result of the various interactions  
465 of the soil matrix and organic C inputs from the vegetation.

466 The first factor regulating such interactions would be the nature of these inputs. In this  
467 respect, differences in the nature of SOC between the two depths considered in the three  
468 soil types were slight, as alkyl-C and O-alkyl-C were the dominant forms of C in topsoil  
469 (0-5 cm) and subsoil (5-20 cm) in the three soils, followed by aromatic-C and carbonyl-  
470 C. This can be attributed to the type of vegetation in the study stands, dominated by  
471 *Pinus radiata*. The forest floor of mature pine plantation of radiata pine in the same  
472 climatic area showed a major signal in the O-alkyl region of carbons, which is  
473 characteristic of the carbons in cellulose and hemicellulose (Gartzia-Bengoetxea et al.,  
474 2009).

475 However, comparison of SOC composition between sites revealed an important  
476 difference in the proportional contribution of aromatic-C forms to total SOC, which was

477 higher in the sandstone-derived soil than in both soils of volcanic origin. Organic matter  
478 in direct contact with mineral surfaces is often depleted in aromatic structures, such as  
479 lignin and phenolic components (Guggenberger et al., 1994; Kiem and Koegel-Knabner,  
480 2003), and enriched in carboxyl and O-alkyl carbon, which are considered highly labile  
481 structures (Mahieu et al., 1999; Spielvogel et al., 2008). This has been confirmed by e.g.  
482 Kinyangi et al. (2006), who found that aromatic-C decreased significantly when organic  
483 matter was bound to minerals, suggesting a transformation that oxidized C=C to COOH  
484 forms. These results are consistent with the higher proportion of POM over SOC in the  
485 sandstone-derived soil in the 5-20 cm layer, and they therefore support our hypothesis  
486 of the soil matrix exerting an influence on the typology of organic forms in the studied  
487 soils, in line with Kleber et al. (2010), who also observed the absence of highly  
488 aromatic humic-like organic compounds from mineral-associated soil organic matter  
489 pools.

490 In summary, the fact that the concentration of phyllosilicates was lower in the  
491 sandstone-derived soil, together with a lower concentration of Fe and Al forms  
492 potentially contributing to aggregate stabilization (Rasmussen et al., 2005), may explain  
493 why SOM in this soil was richer in relatively fresh and only slightly decomposed plant  
494 material than the SOM in the trachyte-derived soil (Schoning et al., 2005).

495

## 496 **5. Conclusions**

497 Although it seems that the consistency of the importance of parent material to SOC may  
498 be weak at the global scale (Wiesmeier et al., 2019), the present findings support the  
499 observation reported in a recent review study (Rasmussen et al., 2018). Thus, the  
500 mineralogy of the air dried (<2mm) soil and clay fraction may be good predictors of  
501 SOC content in acid temperate forest soils in the Basque Country, as there were no

502 differences in the commonly used proxies for SOC (i.e. pH and clay content) between  
503 the three soils under study, even though SOC storage differed. Soils derived from basalt  
504 and from trachyte, which were relatively rich in chlorite/vermiculite mixed layers and  
505 short-range order aluminium and iron forms, contained between 35-102 g C kg<sup>-1</sup> and  
506 between 42-140 g C kg<sup>-1</sup> more SOC than the sandstone-derived soils dominated by illite  
507 and with no short-range order aluminium.

508 Dynamic models of SOC turnover in acid temperate forest soils could therefore be  
509 improved by including proxies for clay mineralogy and Fe and Al (hydr-) oxide  
510 contents. However, further research is required to determine the particular influence of  
511 phyllosilicate mineralogy and metallic oxy-hydroxides.

512

513 At a larger scale, our findings support the view that soil parent material could be  
514 included as a proxy in models aimed at estimating regional SOC stocks, as geological  
515 maps are more widely available and often more accurate than soil maps.

516

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526

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727 Figure caption

728 Figure 1: Location of the 9 forest stands under study and details from the lithological

729 map of the Basque Country (EVE, 1984) for mount Oiz (left) and mount Karakate

730 (right).

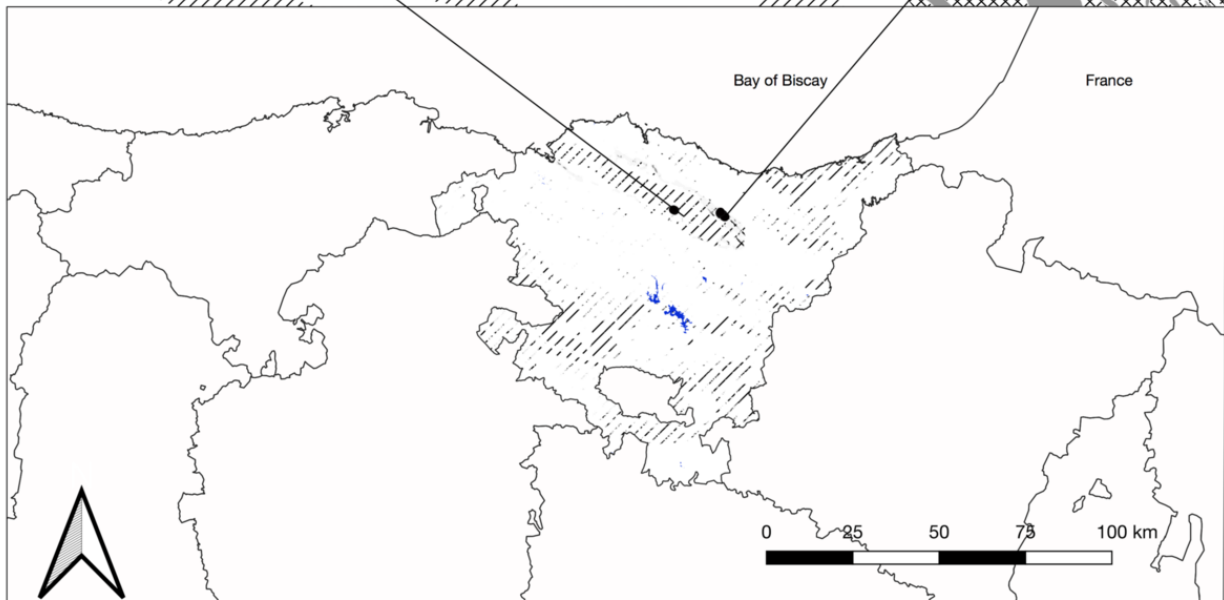
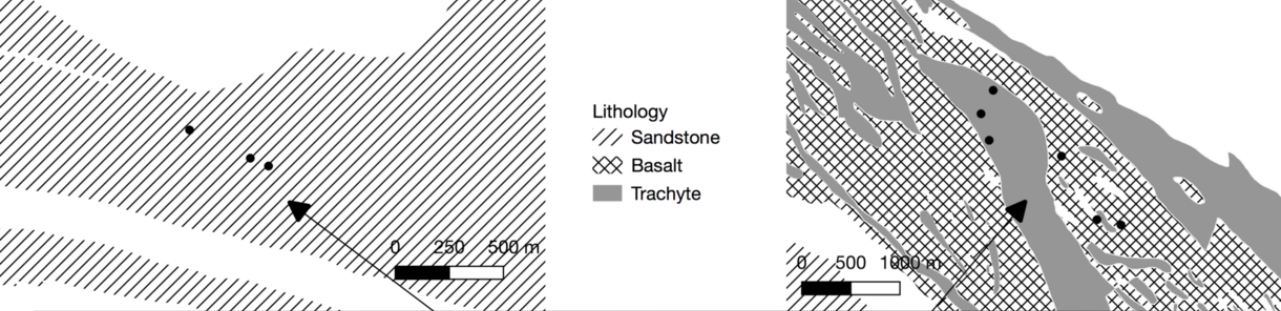
731 Figure 2: (a) Composition of C functional groups (% of the total signal intensity) in

732 soils (0-20 cm; weighed means) developed on different parent materials, as

733 characterized by CPMAS <sup>13</sup>C NMR spectra: composition of C functional groups

734 in (b) 0-5 cm and (c) 5-20 cm layers.





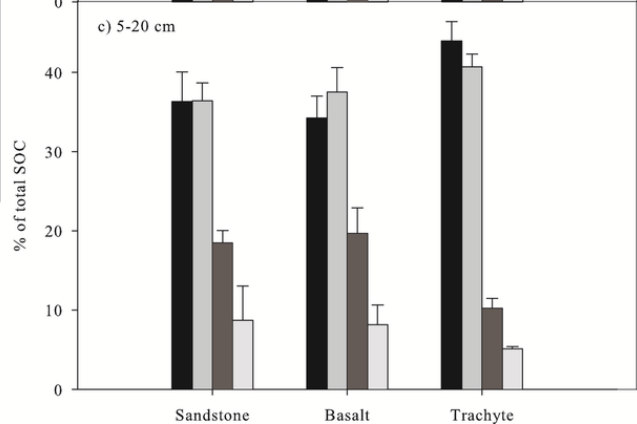
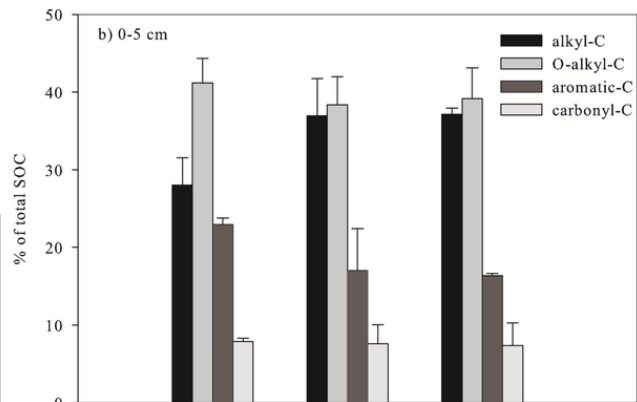
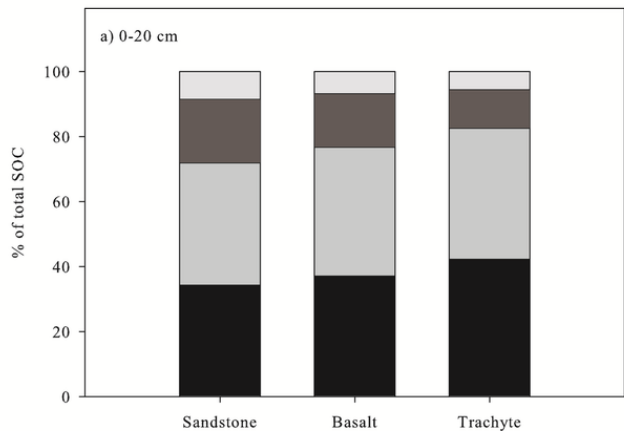


Table 1: Main chemical and physical properties of the soil samples. SOC stock ( $\text{Mg C ha}^{-1}$ ), SOC, soil organic carbon ( $\text{g C kg}^{-1}$ ), POM, particulate organic matter ( $\text{g C kg}^{-1}$ ), MOM, mineral-bound organic matter ( $\text{g C kg}^{-1}$ ), texture (%), eCEC, effective cation exchange capacity ( $\text{cmol+ kg}^{-1}$ ), CEC pH7, cation exchange capacity at pH =7 ( $\text{cmol+ kg}^{-1}$ ) and exchangeable calcium, magnesium, sodium and potassium ( $\text{cmol+ kg}^{-1}$ ). Mean values are shown with 95% confidence interval.

	Sandstone		Basalt		Trachyte	
	0-5 cm	5-20cm	0-5 cm	5-20cm	0-5 cm	5-20cm
Organic matter						
SOC stock	29.2 ± 1.0	32.4 ± 3.4	36.7 ± 9.7	82.8 ± 25.3	48.3 ± 12.8	104.6 ± 42.8
SOC	54.8 ± 2.7	20.3 ± 1.7	120 ± 29.1	90.4 ± 25.6	151.0 ± 38.0	109.2 ± 40.6
POM	29.9 ± 3.8	11.2 ± 6.4	53.6 ± 19.3	41.4 ± 10.8	92.0 ± 27.6	59.1 ± 30.3
MOM	19.5 ± 3.0	10.8 ± 2.7	55.8 ± 21.4	50.4 ± 29.3	49.4 ± 7.4	46.3 ± 5.6
Texture						
Clay	23 ± 3.9	27 ± 4.3	23 ± 1.3	24 ± 1.3	19 ± 0.3	20 ± 1.8
Silt	37 ± 6.0	34 ± 4.4	50 ± 4.0	53 ± 1.9	53 ± 2.3	55 ± 2.2
Sand	41 ± 10.3	40 ± 8.6	27 ± 4.7	23 ± 3.0	28 ± 2.6	25 ± 1.8

Chemical properties						
pH (H2O)	4.5 ± 0.4	4.8 ± 0.3	4.6 ± 0.2	4.7 ± 0.1	4.5 ± 0.0	4.6 ± 0.1
pH (KCl)	3.4 ± 0.2	3.7 ± 0.2	3.9 ± 0.1	3.9 ± 0.1	4.3 ± 0.7	3.8 ± 0.3
pH (NaF)	8.1 ± 0.5	9.3 ± 0.3	8.9 ± 0.2	9.6 ± 0.2	9.3 ± 1.1	9.7 ± 0.9
eCEC	10.2 ± 0.7	7.8 ± 0.3	14.8 ± 2.1	11.7 ± 1.8	16.1 ± 4.1	12.3 ± 3.7
CEC pH7	19.4 ± 2.4	13.0 ± 1.1	37.3 ± 5.6	33.1 ± 5.7	44.9 ± 8.9	36.5 ± 7.4
Ca	3.3 ± 1.4	1.7 ± 0.8	4.5 ± 1.5	2.3 ± 0.9	5.8 ± 2.1	2.6 ± 1.3
Mg	0.7 ± 0.2	0.3 ± 0.1	1.1 ± 0.4	0.7 ± 0.3	1.3 ± 0.7	0.7 ± 0.4
K	0.02 ± 0.01	0.01 ± 0.0	0.02 ± 0.0	0.01 ± 0.0	0.02 ± 0.01	0.01 ± 0.0
Na	0.26 ± 0.1	0.14 ± 0.05	0.19 ± 0.01	0.17 ± 0.02	0.23 ± 0.07	0.18 ± 0.05

Table 2: Mineralogical analysis (XRD) of the soil samples and clay fraction in %. Mean values are shown with 95% confidence interval.

	Sandstone		Basalt		Trachyte	
	0-5 cm	5-20cm	0-5 cm	5-20cm	0-5 cm	5-20cm
<b>Air dried soil &lt; 2 mm</b>						
Quartz	72.0 ± 8.5	75.3 ± 2.4	9.3 ± 0.7	19.0 ± 7.4	22.0 ± 9.3	19.3 ± 2.8
Phyllosilicates	28.0 ± 8.5	24.7 ± 2.4	59.3 ± 5.2	48.0 ± 5.2	57.7 ± 13.5	48.7 ± 9.2
Potassium feldspar	0.0	0.0	2.3 ± 4.6	6.4 ± 19	5.7 ± 5.6	13.3 ± 4.6
Plagioclase	0.0	0.0	16.0 ± 4.9	19.0 ± 2.0	14.7 ± 1.7	18.7 ± 6.9
Haematite	0.0	0.0	13.0 ± 4.1	7.7 ± 2.4	0.0	0.0
<b>Phyllosilicates in the clay-size fraction (&lt; 2 μm)</b>						
Illite	60.7 ± 7.3	52.3 ± 1.7	21.0 ± 41.2	15.7 ± 30.7	12.7 ± 24.8	9.7 ± 18.9
Hydrobiotite	8.3 ± 4.7	10.7 ± 3.3	0.0	0.0	0.0	0.0
Hydroxyvermiculite	19.0 ± 3.0	24.7 ± 2.4	0.0	0.0	0.0	0.0
Kaolinite	12.0 ± 2.0	12.7 ± 2.4	0.0	0.0	0.0	0.0

Chlorite/vermiculite	0.0	0.0	$79.0 \pm 41.2$	$84.3 \pm 30.7$	$87.3 \pm 24.8$	$90.3 \pm 18.9$
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Table 3: Chemical selective dissolution of Al, Fe and Si in g kg<sup>-1</sup>. Al<sub>SRO</sub> and Fe<sub>SRO</sub> were calculated as oxalate-extractable Al and Fe minus pyrophosphate Al and Fe. Mean values are shown with 95% confidence interval.

	Sandstone		Basalt		Trachyte	
	0-5 cm	5-20cm	0-5 cm	5-20cm	0-5 cm	5-20cm
Al <sub>ox</sub>	1.39 ± 0.42	1.53 ± 0.42	9.24 ± 1.15	7.49 ± 2.2	8.07 ± 1.21	6.14 ± 2.8
Al <sub>d</sub>	2.55 ± 0.31	2.33 ± 0.45	8.33 ± 0.25	7.48 ± 2.18	7.37 ± 0.69	5.44 ± 2.93
Al <sub>p</sub>	1.45 ± 0.39	1.65 ± 0.40	7.55 ± 0.46	6.39 ± 2.81	7.05 ± 1.41	4.01 ± 3.75
Al <sub>SRO</sub>	nd	nd	1.69 ± 0.72	1.09 ± 0.61	1.01 ± 0.28	2.13 ± 1.05
Fe <sub>ox</sub>	3.47 ± 1.61	3.66 ± 1.57	11.79 ± 3.01	11.06 ± 2.03	7.31 ± 2.21	8.48 ± 3.56
Fe <sub>d</sub>	10.7 ± 3.68	13.9 ± 6.87	25.8 ± 1.66	27.0 ± 3.17	19.0 ± 2.12	24.4 ± 1.15
Fe <sub>p</sub>	3.85 ± 1.24	4.64 ± 1.72	8.12 ± 0.87	5.86 ± 2.22	5.78 ± 1.39	4.25 ± 4.68
Fe <sub>SRO</sub>	nd	nd	3.67 ± 2.15	5.19 ± 3.94	1.53 ± 0.82	4.23 ± 1.20
Si <sub>ox</sub>	0.46 ± 0.08	0.53 ± 0.07	1.10 ± 0.29	1.02 ± 0.13	0.54 ± 0.11	0.85 ± 0.07