

1 **Responses of soil clay mineralogy in the Rothamsted Classical Experiments in relation to**
2 **management practice and changing land use**

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9 **Abstract**

10 Changes in the clay mineralogy of soil samples collected from the Rothamsted Classical
11 Experiments over the past ~150 years were examined. Comparisons were undertaken to assess
12 the impact of (i) different fertiliser practices on the top soil and sub soil of the Park Grass
13 Experiment and (ii) the effects of changing land-use from agriculture to woodland where soil
14 pH either remained close to pH 7 or became acid. Analyses were undertaken on the <0.2 µm
15 clay fraction and measurements included cation exchange capacity (CEC), surface area and
16 X-ray diffraction (XRD). The fine clay fraction of all the samples is composed of
17 illite/smectite (I/S), illite and kaolinite minerals. Decomposition modelling of XRD spectra
18 identified three I/S phases including (i) a high smectite I/S phase ($d(00l) \sim 15\text{\AA}$), (ii) a low
19 smectite I/S phase ($d(00l) \sim 12.5\text{\AA}$) and (iii) an illite phase ($d(00l) \sim 11.2\text{\AA}$). The I/S phase is
20 typically made up of ~60 % of high smectite I/S, ~20 % low smectite I/S and ~20 % illite.
21 Attempts to account for changes in clay CEC and surface area with time proved to be
22 inconclusive, possibly because of the differing proportions of the three I/S phases in each
23 sample. Some temporal changes in the $d(00l)$ spacing of I/S mineral phases from the
24 decomposed XRD spectra ($>0.4\text{\AA}$) are reported in both top soil (0-23 cm) and sub soil (46-69
25 cm) and are likely related to (i) changes in soil K^+ or NH_4^+ status and/or (iii) increasing soil
26 acidity. The greatest change was found in the Park Grass Experiment $(NH_4)_2SO_4$ plot where

27 soil pH fell below 3.7. It is believed that solubilisation of hydroxyl-Al in smectite interlayers
28 enabled renewed access to K^+ or NH_4^+ ions, leading to increased collapse in $d001$ spacing.
29 However, the results show that over a diverse range of soil conditions, I/S minerals of the
30 Batcombe series soils showed considerable resilience to major change. This is considered to
31 be a result of competition for sorption sites by the (i) presence of competing ions added as
32 fertiliser or liming materials, (ii) an increase in H^+ ions as soil acidity increases, (iii) the
33 possible role of organic carbon in protecting I/S minerals and (iv) the role of the I/S minerals
34 as K^+ reservoirs. However, the impact of decreasing soil pH should be considered when land
35 is re-forested as this may lead to irreversible decreases in the $d(001)$ spacing of I/S minerals,
36 thus compromising useful clay properties such as CEC.

37

38 **Keywords: Clay minerals, Soils, Illite/Smectite, X-ray diffraction, Land management**

39

40 **1. Introduction**

41 Clay mineral properties are fundamental to many soil functions including water and nutrient
42 retention, contaminant (pesticides, heavy metals) attenuation, carbon storage, the maintenance
43 of soil structure and the filtering of both ground and surface waters. However, relatively few
44 studies have been undertaken to examine how clay mineral structure may change with (i) the
45 inorganic chemical inputs of intensive agricultural systems and (ii) land use changes over long
46 periods of time. Thus, soil archives from long-term experiments provide a valuable resource,
47 allowing changes to be studied with knowledge of management practices over relatively long
48 periods (Velde & Peck, 2002). In addition, recent advances in X-ray diffraction (XRD)
49 techniques such as decomposition modelling have allowed greater interpretation of XRD
50 profiles, enabling more precise identification of different soil clay mineral phases (e.g. Mathé
51 *et al.*, 2007; Egli *et al.*, 2007). In this study we assess changes in clay mineral structure from

52 the 'Rothamsted Classical Experiments' (Johnston, 1997) in relation to fertiliser additions and
53 changing land use.

54

55 In temperate regions, attention has largely focused on 2:1 clay minerals (smectite, vermiculite,
56 illite, chlorite and their intergrades) as they dominate the clay mineralogy of many soils (Velde,
57 2001). With respect to fertiliser applications, work has largely focussed on the interactions
58 between K^+ and illite/smectite (I/S) mixed layer minerals (Singh & Goulding, 1997; Velde &
59 Peck, 2002; Pernes-Debuyser *et al.* 2003; Mathé *et al.*, 2007; Barré *et al.* 2007a & b). These
60 studies have shown the importance of K^+ in determining the nature of I/S minerals and the K^+
61 buffer capacity for plant nutrition. For example, Velde & Peck (2002) examined samples taken
62 between 1913 and 1996 from the Morrow Plot Experiment archive at the University of Illinois.
63 The major finding was that under continuous corn cropping and without fertilisation, the
64 extraction of K^+ for plant nutrition led to an increase in the smectite content of I/S minerals.
65 Pernes-Debuyser *et al.* (2003) demonstrated that in soils where plant growth was absent, the
66 addition of K^+ fertiliser resulted in an increase in the illite (non-expandable) content of the I/S.
67 These results, among others, led Barré *et al.* (2007a & b) to postulate that 'illite-like layers' can
68 be viewed as K^+ reservoirs that can be potentially refuelled via the 'nutrient uplift theory'
69 suggested by Jobbagy & Jackson (2001). Therefore, in top soils where greater K^+ is uplifted or
70 recycled than is required by plants the system could be pushed towards the illite end of the I/S
71 system. Changes in clay mineralogy have also been investigated in chronosequences under
72 natural conditions where the role of K^+ has been important in determining changes in I/S
73 mineral structure. Velde *et al.* (2003) examined changes in poldered sediments under natural
74 pasture development. In the oldest profiles (>800 yrs), a disordered illitic I/S mineral became
75 dominant in the upper parts of the profile whilst in the lower part of the profile a smectitic I/S
76 mineral was predominant. Mathé *et al.* (2007) monitored soil clay minerals from recent natural

77 polders in response to local environmental conditions and noted that with increasing age,
78 chlorite was removed and the illite content of I/S increased. Such reactions were triggered by
79 oxidation and in natural systems would last >1000 y but could be accelerated by artificial
80 drainage to complete the process in a few tens of years.

81

82 Less work has been undertaken on the role of inorganic N fertilisers on clay mineralogy despite
83 this representing the major input of chemical elements and acidity to intensive agricultural
84 systems. The biogeochemistry of N amendments depends on the form applied. Both NO_3^- and
85 NH_4^+ applications can affect the reduction of structural Fe^{3+} to Fe^{2+} in clays, a process essential
86 to the collapse of interlayers in smectitic minerals (Stuki, 1997). For example, in waterlogged
87 soils the presence of NO_3^- has been found to inhibit the reduction of structural Fe^{3+} to Fe^{2+}
88 (Chen *et al.*, 2008; Matocha & Coyne, 2005), but its effect was found to be temporary, lasting
89 as long as sufficient NO_3^- was available. The application of ammonium fertilisers has been
90 found to increase Fe(III) reduction, probably through coupled NH_4^+ oxidation (Chen *et al.*
91 2008). The majority of this work has examined changes in the top-soil and relatively little is
92 known regarding changes in clay mineralogy in sub soils and how they react to agricultural
93 practice. However, understanding how they change with respect to time and land management
94 is important because of the role they play in the filtration and attenuation of contaminants for
95 surface and groundwater.

96

97 A second area of land management where changes in the structure of clay minerals may be
98 induced is where soils have undergone acidification either through natural or man-induced
99 processes. There has generally been a greater emphasis on using chemical, rather than
100 mineralogical measurements in these studies to demonstrate changes in clay function. The
101 effects of the addition of ammonium fertilisers has been studied by Barak *et al.* (1997) and

102 McGahan *et al.* (2003), whilst Blake *et al.* (1999) examined the effects of natural acidification
103 as agricultural land has reverted to woodland in the Geescroft Classical Experiment at
104 Rothamsted. The formation of interlayer hydroxyl-aluminium was found to be important in the
105 buffering process against acidification and can lead to a loss in clay cation exchange capacity
106 (Ulrich, 1991).

107

108 This study aims to identify changes in clay mineral structure in soils from the archive of the
109 Rothamsted Classical Experiments that extend over ~150 years. Limited analyses of clay
110 mineralogy in some of these soils, has been undertaken as part of projects where greater focus
111 was placed on chemical measurements (Blake *et al.*, 1999; Singh & Goulding, 1997). This
112 work undertakes a more systematic examination of archive samples from the Park Grass
113 Experiment and the Broadbalk and Geescroft Wildernesses using decomposition modelling of
114 XRD profiles to identify changes in clay mineralogy that have accompanied some of the
115 previously reported chemical changes (e.g. Blake *et al.*, 1999). The changes found in clay
116 structure after (i) long-term and repeated application of N and K fertilisers and (ii) natural (re-
117 forestation) and fertiliser induced acidification in the top and sub soil are reported.

118

119 **2. Materials and Methods**

120 **2.1 Background and Sample Collection**

121 Samples used in this study were taken from three of the Rothamsted Classical Experiments;
122 Park Grass, Geescroft Wilderness, and Broadbalk Wilderness. Soils from all the experiments
123 are representative of the Batcombe series or close variants. These are classified by the Soil
124 Classification for England and Wales as stagnogleyic palaeo-argillic brown earths (Avery,
125 1980) or Aquic Paleudalf (U.S.D.A, 1992). The top soil is silty clay loam forming on
126 Quaternary Clay-with-Flints deposits that can lie several metres deep over the Chalk bedrock.

127 Clay-with-Flints deposits were most likely derived from the Reading Formation (Lambeth
128 Group) and developed during warm periods between plateau drift and the Chalk bedrock
129 through clay particles and insoluble chalk residues infiltrating dissolution hollows in the Chalk.
130 During cold periods, cryoturbation possibly remixed this accumulation with the plateau drift
131 (Catt & Hodgson, 1976). The mineralogy of the sand fraction of the Batcombe series soils
132 found at Rothamsted is similar to that of the Reading Beds (Catt & Hodgson, 1976). Reading
133 Formation clay mineral assemblages are illite-dominated, with minor smectite, kaolin and
134 chlorite although altered ash, comprising smectite-dominated horizons are also found (Huggett
135 & Knox, 2006).

136

137 Soil samples (up to 1999) were collected with an open ended steel box (internal dimensions 15
138 x 15 x 23 cm deep). This was driven into the ground until it was flush with the surface; the soil
139 was then dug out (Poulton *et al.*, 2003). Either 3, 4 or 6 holes were taken for a composite
140 sample from each treatment. However, one of the Park Grass Experiment samples (Plot 3,
141 Unlimed, 1966) was taken as a single 15 x 15 x 23 cm sample. Samples were sieved to <2 mm,
142 air-dried and stored in sealed glass jars within the Rothamsted Sample Archive. After 1999,
143 soils were sampled by taking cores with semi-cylindrical augers. Blake *et al.* (2000) examined
144 changes in properties of the soils maintained in the soil archive and found only minor changes
145 in exchangeable K⁺ between 1959 and 1991.

146

147 **2.2 Comparisons undertaken**

148 **2.2.1 Fertiliser effects on top and sub soils using Park Grass samples**

149 The Park Grass Experiment was started in 1856 on a site which had been in permanent
150 grassland for at least 100 years. The soil was slightly acid (pH_(H₂O) 5.4-5.6) and the nutrient
151 status was considered poor (Silvertown *et al.* 2006). Soils from the following treatments of the

152 Park Grass Experiment were used (i) Plot 3, the Control plot where no lime or fertiliser had
153 been added since 1856, (ii) Plot 14 where 96 kg N ha⁻¹ as NaNO₃ has been applied each year
154 since 1858 and (iii) Plot 9 where 96 kg N ha⁻¹ as (NH₄)₂SO₄ has been applied each year since
155 1856. Atmospheric NH₄-N deposition has been estimated as ~2.5 kg ha⁻¹ a⁻¹ from 1850 to 1900
156 before rising to ~10 kg ha⁻¹ a⁻¹ in 1975 and falling to ~2.5 kg ha⁻¹ a⁻¹ in the 1990's (Blake et al.
157 1999). Similarly, inputs of H⁺ have varied between 0.1 and 0.4 kg ha⁻¹ a⁻¹. Treatments receiving
158 fertiliser N also receive yearly applications of 35 kg ha⁻¹ P as triple superphosphate, 225 kg ha⁻¹
159 K as K₂SO₄, 15 kg ha⁻¹ Na as Na₂SO₄ and 10 kg ha⁻¹ Mg as MgSO₄. The whole experiment
160 received a small amount of chalk in the 1880s/1890s. Since then, plots have since been sub-
161 divided to allow for different lime applications to produce a range of pH values from 3.5 to 7
162 amongst the various combinations of treatments.

163

164 In the present study, only soil samples from the unlimed plots or subplots collected in 1876,
165 1904, 1966/1984, and 2002 (0-23 cm) were used to give 4 points on the time-series for the top
166 soil. Changes in the sub soil (49-63 cm) clay mineralogy were monitored using samples from
167 1870/1876, 1906, 1991 and 2002. Table 1 provides a summary of the samples used.

168

169 **2.2.2 Comparison between acidic (Geescroft Wilderness) and alkaline (Broadbalk** 170 **Wilderness) woodland top soils**

171 The Geescroft Wilderness and Broadbalk Wilderness are situated ~700m apart and the soil at
172 both locations is the Batcombe series soil. Geescroft Wilderness was part of an experimental
173 field growing field beans from 1847 to 1878. After bare fallowing for 4 years, clover was
174 grown from 1883 to 1885 and it was then allowed to revert to the current wilderness area in
175 1886 (Poulton *et al.* 2003). It is dominated by mature oak, remains unlimed since the 18th
176 century and has become quite acidic (pH~4.5). Blake *et al.* (1999) studied the chemistry of soil

177 acidification in these soils and produced a conceptual model that is used as a backdrop to the
178 current XRD results.

179

180 Broadbalk Wilderness lies at the western end of the Broadbalk Wheat experiment. The area
181 that is now the wilderness was sown with wheat from 1843 to 1882 from which it was allowed
182 to revert to woodland (Poulton *et al.*, 2003). It consists of three sections, the woodland which is
183 dominated by mature oak, a section where saplings have been regularly removed (stubbed)
184 since 1900 and an area that has been grazed since 1957. Most importantly, before the
185 Broadbalk wheat experiment had started in 1843, the field had been very heavily limed (up to
186 200 t ha⁻¹); the wilderness area still has a pH of ~ 7. Therefore the comparisons between the
187 two wilderness areas will provide information on the changes of clay mineralogy (i) in top soil
188 when agricultural land is returned to forestry and (ii) caused by acidification as opposed to the
189 maintenance of pH through the liming of woodland. Only 3 sampling times were available for
190 analysis; the first of which, in 1881 or 1883, was when both sites were still under arable crops
191 or fallow (Table 1).

192

193 **2.3 Laboratory methods**

194 Changes in the clay mineralogy caused by land management practices are likely to be subtle
195 and difficult to detect and so the analytical work focussed on the fine clay fraction of the soil
196 (<0.2 µm).

197 **2.3.1 Particle-size separation**

198 Initially, organic C was not removed from the soil so as to protect the clay components from
199 potential changes caused by oxidising agents. The soils were dispersed in deionised water
200 overnight using a reciprocal shaker and 3 minutes of ultrasound treatment (Soniprep 150

201 (MSE)), before wet screening through a 63 μm sieve. The $>63 \mu\text{m}$ ('sand') fraction was dried
202 at 40°C , weighed and stored. The $<63 \mu\text{m}$ material was placed in a gas jar with 2 ml 0.1M
203 sodium hexametaphosphate ('Calgon') solution to disperse the individual clay particles and
204 prevent flocculation. After standing for a period determined using Stokes' Law (16 hours for 20
205 cm drop), a nominal $<2 \mu\text{m}$ ('clay') fraction was removed to a stock beaker. The measuring
206 cylinders were then topped up with deionised water, stirred and the particles allowed to settle
207 before extracting further $<2 \mu\text{m}$ material. This process was repeated until no clay was visibly
208 evident. The remaining 2-63 μm fraction was removed, dried at 40°C , weighed and stored. In
209 order to isolate a $<0.2 \mu\text{m}$ fraction, the $<2 \mu\text{m}$ material was centrifuged (Centaur 2 (MSE)) for
210 30 minutes at 3000 rpm before removing the supernatant ($<0.2 \mu\text{m}$) into a stock beaker. The
211 remaining material was then re-dispersed before repeating the procedure two further times. The
212 $<0.2 \mu\text{m}$ ('fine clay') material and remaining 0.2-2 μm ('coarse clay') material were then dried
213 at 40°C , weighed and stored. Organic matter was removed from the $<0.2 \mu\text{m}$ fractions by the
214 five-time application of 1M sodium hypochlorite/hydrochloric acid buffer (pH 8.0) following
215 the method of Kaiser *et al.* (2002). Siregar *et al.* (2005) suggest that this oxidising agent does
216 not attack pedogenic oxides and hydroxides and only slightly dissolves Al from the poorly
217 crystalline minerals and thus was less likely to cause alteration to the clay minerals than for
218 example, H_2O_2 .

219 **2.3.2 Measurements**

220 Samples for total organic carbon (TOC) analysis were prepared by pre-drying at $100\text{-}105^\circ\text{C}$
221 (1.5 hours), acidifying (HCl, 50% v/v), drying at $100\text{-}105^\circ\text{C}$ (1.5 hours), and analysing by
222 combustion (1050°C) using an 'Elementar Vario Max' C/N analyser. CEC was determined by
223 a compulsive displacement technique using a BaCl_2 /triethanolamine (pH 8.1) titration method
224 based on that proposed by Bascomb (1964). Surface-area determinations (SA) were carried out
225 following a procedure based on the formation of a monolayer of 2-ethoxyethanol (EGME)

226 molecules on the clay surface under vacuum (Heilman *et al.*, 1965). Churchman *et al.* (1991)
227 discuss the assumptions necessary within the EGME method including the behaviour of clay
228 type, and time taken to establish end points. In this study samples were expected to have
229 similar mineralogical compositions and a standard method was used throughout. As only small
230 amounts of material were available, 0.2 g of <0.2 μm material was covered by ~ 1 ml of EGME
231 and left for 24 hours before reweighing. A conversion factor of 0.000286 g m^2 was used to
232 calculate total surface area.

233 **2.3.3 X-ray diffraction analysis**

234 In order to produce high quality diffraction traces, oriented mounts for XRD analysis were
235 produced using 'zero background' silicon crystal substrates. About 15 mg of the dried <0.2 μm
236 material was re-suspended in a minimum of deionised water, Ca-saturated using a few drops of
237 0.1M $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ solution, washed, pipetted onto a silicon crystal substrate and allowed to air-
238 dry overnight. XRD analysis was carried out using a PANalytical X'Pert Pro series
239 diffractometer fitted with a cobalt-target tube, X'Celerator detector and operated at 45kV and
240 40mA. The <0.2 μm oriented clay mounts were scanned from $2-35^\circ 2\theta$ at $0.55^\circ 2\theta/\text{minute}$ after
241 air-drying, ethylene glycol-solvation and heating to 550°C for 2 hours. Clay mineralogy was
242 determined by characteristic peak positions in relation to this diagnostic testing program.

243

244 In order to obtain further information about the nature of the clay minerals present in the
245 samples, modelling of the XRD profiles was carried out using Newmod-for-Windows™
246 (Reynolds & Reynolds, 1996) software. The modelling process requires the input of
247 diffractometer, scan parameters and a quartz intensity factor (instrumental conditions), and the
248 selection of different phyllosilicate sheet compositions and chemistries. In addition, an estimate
249 of the crystallite size distribution of the clay species may be determined by comparing peak
250 profiles of calculated diffraction profiles with experimental data. Further information on the

251 clay mineralogy of the samples was deduced by decomposition of the XRD profiles into their
252 elementary component curves using the program DECOMPXR (Lanson, 1993; Lanson &
253 Besson, 1992). Best fits were obtained using Gaussian curves following background
254 subtraction and 7-point smoothing.

255

256 **2.4 Theoretical considerations**

257 Theoretically, the responses of the three analyses undertaken (EGME SA, CEC and XRD)
258 should be correlated. Previous work examining a wide range of soil types has demonstrated
259 that measurements of clay SA and CEC are positively correlated (Curtin and Smillie, 1976;
260 Peterson *et al.*, 1996), particularly for the B and C horizons. Churchman *et al.*, (1991) suggest
261 that this is because EGME is a polar molecule and its uptake is related to both the charge and
262 surface area of the clay. However, for soil A horizons the presence and interactions of organic
263 matter with the clay fraction is known to complicate these relationships. In terms of inorganic
264 components, the SA and CEC of the Rothamsted soils are likely to be determined by the type
265 and quantity of I/S minerals present because of the high surface area and CEC of smectite.

266

267 Recent advances in the power of desktop computers has provided the data processing power
268 necessary to extract further information from XRD profiles. Such processing power is
269 required by decomposition routines whereby peak profiles are split into partially overlapping
270 contributions due to phases with distinct but closely related crystallographic characteristics
271 (Lanson, 1997). Decomposition therefore offers the possibility to identify the presence of
272 different phases by monitoring parameters such as peak position, full width at half maximum
273 intensity (FWHM), relative intensity and profile shape. Decomposition routines, such as
274 DECOMPXR (Lanson, 1993), are iterative procedures, the quality of the fit being estimated
275 after each iteration as well as the evolution of the adjusted parameters. The calculation is

276 stopped when the quality of the fit is not improving and/or when adjusted parameters are
277 stable. Due to their small crystallite-size distributions, clay minerals are often characterised by
278 broad and overlapping XRD peaks. This is particularly so for soil clay minerals.
279 Decomposition of soil clay mineral XRD profiles therefore offers a relatively fast
280 identification and descriptive tool, especially suited to establishing trends when studying
281 sample series and variations affecting their components (Lanson, 1997).

282

283 Characterisation of the I/S species is facilitated by precise measurements of the position of
284 their $d(00l)$ XRD peaks following decomposition (e.g. Lanson & Velde, 1992). In general
285 terms, a decrease in the $d(00l)$ of I/S species indicates a reduction in the proportion of smectite
286 interlayers present and an increase in the number of layers that act in a manner more
287 analogous to illite. In this study on the Rothamsted, such decreases are likely to result from
288 either (i) replacement of hydrated Ca^{2+} ions in the smectite interlayer space by one or a
289 combination of K^+ or NH_4^+ ions or (ii) soil acidification leading to the deposition of hydroxyl-
290 Al in the smectite interlayers. Such decreases in I/S $d(00l)$ would therefore be expected to
291 correlate with decreases in CEC and SA.

292

293 This ‘illitization-like process’ in the I/S is most likely driven by wetting and drying cycles and
294 the subsequent reduction of structural Fe(III) in clays, sometimes mediated primarily by the
295 enzymatically catalyzed activity of indigenous soil micro-organisms (Favre *et al.*, 2002; Kim
296 *et al.*, 2004; Huggett & Cuadros, 2005; Kostka *et al.*, 1999; Stanjek & Marchel, 2008; Siyuan
297 and Stucki, 1994; Stucki, 1997). The major requirement to enable this collapse in the $d(00l)$
298 spacing is a decrease in the positive charge of the octahedral sheet of the smectite. This occurs
299 as structural Fe^{3+} is reduced to Fe^{2+} . This causes an increase in CEC and subsequently the
300 ability to fix cations such as K^+ , NH_4^+ , Na^+ or H^+ in the interlayer space to balance the charge

301 (Khaled & Stucki, 1991; Kim *et al.*, 2004; Drits and Manceau, 2000; Huggett & Cuadros,
302 2005; Stanjek & Marchel, 2008; Stucki & Kostka, 2006), thus promoting a more illitic type of
303 structure.

304

305 The input of K^+ into the soil in these experiments will either be through the weathering of
306 minerals such as mica or feldspar, identified in previous XRD analyses of Rothamsted soils
307 (Singh & Goulding, 1997; Blake *et al.*, 1999), through nutrient uplift via roots or through the
308 application of inorganic fertilisers. The similar size of the dehydrated NH_4^+ cation ($K^+ = 1.33$
309 \AA ; $NH_4^+ = 1.43 \text{\AA}$), means that it is also capable of collapsing smectite interlayers in I/S (Chen
310 *et al.*, 1989; Drits *et al.*, 1997), thus fixing NH_4^+ . Soil acidification, such as that created
311 through the application of $(NH_4)_2SO_4$ fertilisers or atmospheric inputs (possibly exacerbated by
312 reforestation; Johnston *et al.*, 1986), is counteracted within the soil by a series of buffering
313 mechanisms (Ulrich, 1992; Wilson *et al.*, 1994; Blake *et al.*, 1999). Ulrich (1992) describes
314 one of the by-products of acidity buffering between pH 5 and 4.2 as the deposition of non-
315 exchangeable hydroxyl-Al into the interlayer space of clays that contribute to their collapse and
316 decreases in CEC. In addition, if H_2SO_4 is one of the acidifying agents the formation of
317 amorphous Al-hydroxy-sulphates is possible. However, as soil pH falls below 4.2 the solubility
318 of the hydroxyl-Al compounds increases, and the storage of Al-hydroxy-cations and sulphates
319 that have accumulated in the exchanger buffer range decreases.

320

321 **3. Results and discussion**

322 **3.1 General characteristics of <0.2 μm clay in top and sub soils**

323 The general characteristics of soil texture and clay mineralogy in the top soils and sub soils
324 from the Classical Experiments are summarised in Tables 2 & 3. Particle-size analyses are
325 based on all samples examined from each experiment (Table 1). In the Park Grass Experiment

326 there was an increase in silt content (~12 %) in the top soil compared to the sub soil. This is
327 thought to be a result of the deposition of loess in the late Devensian about 14000-18000 years
328 B.P. (Avery & Catt, 1995). The top soil in the Geescroft and Broadbalk experiments had
329 similar particle size distributions. However, less silt was present than in the top soil of the Park
330 Grass Experiment and greater sand and clay contents were found, possibly because of the Hook
331 series, a variation of the Batcomb series, being present across some of the Park Grass
332 Experiment (Avery & Catt, 1995). Alternatively, the period of cultivation that the Broadbalk
333 and Geescroft sites underwent before being returned to wilderness may have led to a slight
334 coarsening of the soil (Lobe *et al.* 2001; Jolivet *et al.* 2003). The proportion of fine clay present
335 is generally similar for all the top soils (2.5-5.6 %) but represents a significantly higher
336 proportion of the Park Grass sub soils (12.5%).

337

338 Table 3 reports organic carbon (OC) concentrations, CEC and surface area (SA) of the <0.2 μm
339 clay fraction at the earliest date examined from each experiment. It also demonstrates the effect
340 of OC removal on CEC and SA properties. As expected, the concentration of OC was higher in
341 top soils due to greater biological activity and particularly so for the Park Grass samples.
342 Whereas CEC decreased with OC removal from the top soil, SA increased markedly
343 suggesting its presence was helping form micro-aggregates and thus decreasing the measurable
344 SA of the clay (Mikutta *et al.*, 2004). In the sub soil the removal of OC had a minimal effect on
345 CEC and SA. Therefore to remove the effects due to OC it was removed prior to SA and CEC
346 analyses. However, the potential for incomplete removal of OC, and more importantly the
347 different quantities of I/S present made the tracking of changes in SA and CEC for the different
348 treatments over time problematic.

349

350 **3.2 XRD analyses**

351 Typically, XRD analysis of the Rothamsted samples suggests that their fine clay (<0.2 μm)

352 fractions are predominantly composed of I/S, illite and kaolinite clay minerals (Figure 1).
353 These results are similar to previous analyses of the <0.2 μm fraction of the Broadbalk
354 Experiment by Singh & Goulding (1997). However these authors identified the interstratified
355 phase as a smectite/vermiculite. Decomposition of the XRD traces using DECOMPXR
356 indicates that the 4 -11 $^{\circ}2\theta$ range is composed of three different sub-species (Figure 2).
357 NEWMOD-modelling suggests that the three peaks represent a high smectite I/S phase (~ 15
358 \AA), a low smectite I/S phase (~ 12.5 \AA), and an ‘illite’ phase (~ 11.2 \AA). XRD analyses of
359 samples prior to and following OC-removal suggest a small (~ 0.2 \AA) increase in the $d(001)$
360 spacing of each of the three sub-species. Velde *et al.* (2003) reported similar findings and
361 suggested that OC was responsible for closing some of the smectite interlayers. When
362 comparing management and land use effects on clay particles in the present study we report
363 those obtained prior to OC-removal to ensure minimal damage to the clay minerals susceptible
364 to decomposition from hypochlorite.

365

366 General properties of the decomposed XRD peaks for each experiment are shown in Table 4,
367 including the peak position (\AA), the peak full width at half maximum (FWHM, $^{\circ}2\theta$) and the %
368 area of the total peak. The high smectite I/S presents a relatively broad XRD peak with a mean
369 FWHM of ~ 1.9 in all the samples, indicative of very small crystallite-size distributions. The
370 low smectite I/S mineral has mean FWHM values in the range 1.2 - 1.5, while smaller mean
371 FWHM values of ~ 1 were measured for the illitic phase suggesting larger crystallites than in
372 the I/S phases. The area beneath each of the decomposed peaks can be used to broadly indicate
373 the relative proportions of each phase present, particularly if the angular factor is taken into
374 account. As indicated in Table 4, the high smectite I/S (43-79 %) phase dominates both top soil
375 and sub-soil with lesser amounts of the low smectite I/S and ‘illite’ mineral phases.

376 In previous investigations, peak decomposition modelling techniques have enabled subtle

377 changes in the I/S $d(00l)$ spacing with time to be monitored (e.g. Bain & Griffen, 2002; Mathe
378 *et al.*, 2007, Pernes-Debuyser *et al.* 2003; Velde & Peck, 2002). In these studies changes in
379 peak movements of less than $\sim 0.4 \text{ \AA}$ have often been reported and discussed. However in the
380 present study, trends have only been identified where peak movements of $>0.4 \text{ \AA}$ are evident.

381

382 **3.3 Fertiliser effects on top and sub soils using Park Grass samples**

383 Results from the Control treatment sampled in the early years of the experiment (1870/1876)
384 demonstrate differences in the measured CEC and SA properties of the top and sub soil (Table
385 3). After the removal of OC, the $<0.2 \mu\text{m}$ clay particles of the top soil possessed a higher CEC
386 and SA than the sub soil.

387

388 **3.3.1 Park Grass top soil**

389 Analyses undertaken on the $<2 \text{ mm}$ soil fraction give an indication of changes in pH and
390 exchangeable cation status in the top soil relevant to this study (data from Rothamsted
391 Research, Figures 3 and 4). The initial (1856) pH value of the Park Grass soil has been
392 estimated as ~ 5.5 (Johnston *et al.*, 1986). Since the inception of the experiment, the soil pH of
393 the ‘control treatment’ has declined slightly to ~ 5.1 . After NaNO_3 treatment soil pH increased.
394 This may have been due to a combination of Na^+ ions occupying cation exchange sites in place
395 of H^+ ions and the increase in pH related to NO_3^- uptake by plants. Soil treated with $(\text{NH}_4)_2\text{SO}_4$
396 has undergone acidification to pH values of ~ 3.5 . Values for extractable K, Ca, Mg, and Na
397 (Figure 4) reflect fertiliser inputs and off-takes in the herbage (section 2.2.1).

398

399 The first set of samples analysed in the present work were taken ~ 20 years after the initiation of
400 the Park Grass Experiment. There were no identifiable trends in $<0.2 \mu\text{m}$ clay CEC and SA
401 values in the plots over the period the data covers, despite the acidification that has occurred on

402 the $(\text{NH}_4)_2\text{SO}_4$ plots (Figure 3, Table 2). Changes in the position of the $d(001)$ spacing for the
403 three identified XRD phases for the Control, NaNO_3 and $(\text{NH}_4)_2\text{SO}_4$ treatments are summarised
404 in Figure 5. There was a great deal of variability in the high smectite I/S phase (Figure 5a),
405 presumably as it contains the highest proportion of smectite interlayers. This variability is
406 likely a result of the high smectite I/S phase being the main reservoir and source of K^+ for plant
407 requirements (Barré *et al.* 2007a & b). The $d(001)$ spacing found in the high smectite I/S
408 minerals from the $(\text{NH}_4)_2\text{SO}_4$ or NaNO_3 plots was consistently smaller than that found in the
409 control. This difference was present at the first sampling point (1870), taken after ~20 years of
410 repeated fertilisation and suggests that the presence of increased K^+ from the fertilisers in the
411 first 20 years of the experiment may have already created a difference by the first analysis in
412 this study. The maximum difference (1906) was ~0.8 Å, but was ~0.4 Å in 2001.

413

414 Only one trend was apparent in the $d(001)$ spacing of the low smectite I/S phase (Figure 5b)
415 and this was found in the $(\text{NH}_4)_2\text{SO}_4$ treatment. Relatively little variation in $d(001)$ spacing was
416 found between all treatments for much of the study period. However, in 2002, a sudden ~0.8 Å
417 collapse in the $d(001)$ spacing of the $(\text{NH}_4)_2\text{SO}_4$ sample was detected. A possible explanation
418 for this is that as the soil pH falls to ~3.5 (Figure 3), the increasing acidity is buffered by the
419 release of the hydroxy-Al and hydroxy-Al sulphates previously deposited in the interlayer
420 spaces (Ulrich *et al.*, 1992). This could be considered a mild form of the acid-activation
421 process used on bentonites; a treatment used to increase the SA of smectite-group minerals for
422 industrial uses (e.g. Christidis *et al.*, 1997). Further indications of this process were found in
423 the SA measurement which increased from around an average of $366 \text{ m}^2 \text{ g}^{-1}$ to $591 \text{ m}^2 \text{ g}^{-1}$ for
424 this last measurement. As this process occurred interlayer space that was occupied by
425 hydroxyl-Al may have become unoccupied, allowing K^+ or NH_4^+ to enter and to collapse it.
426 There was little variation found in the $d(001)$ spacing for the ‘illite’ phase (Figure 5c). The

427 position of the peak at $\sim 11.2 \text{ \AA}$ suggests that it contains a small number of smectite interlayers
428 and so may show a more limited response to increased K^+ availability or acidification processes
429 already described.

430

431 It was interesting to note that greater differences were not found between such different
432 treatments in the Park Grass top soil, especially as soil conditions exist which have been shown
433 to cause changes in I/S minerals (e.g. increasing soil K^+ and/or acidity). This may have been
434 due to (i) the continued recycling of nutrients and the addition of fertilisers producing
435 competition for interlayer spaces in the I/S layers, (ii) the differences in yearly plant
436 requirements of K^+ , balanced by the weathering of micas and uplift of K^+ and (iii) the role of
437 organic carbon (10.7 % in the fine clay fraction; Table 3) in protecting the clay minerals by
438 preventing access to interlayer spaces or by aggregating clay particles. In particular the
439 protection, through restriction of access to I/S minerals by organic carbon and increased
440 competition by H^+ ions for interlayer sites may be a reason why there was a time lag between
441 soil pH values decreasing and the later collapse of the interlayer space in the $(\text{NH}_4)_2\text{SO}_4$
442 treatment.

443

444 **3.3.2 Park Grass Sub soil**

445 Changes in the clay mineralogy of the sub soil under the Park Grass Experiment were
446 examined to determine how management practices of the top soil may have impacted on the
447 sub soil clay mineralogy. Figure 6 shows a range of sub soil (<2 mm) characteristics for the
448 2002 samples; earlier sampling dates were not re-analysed. The different fertiliser treatments
449 have caused changes in the characteristics of the <2 mm soil fraction. After the yearly
450 application of $(\text{NH}_4)_2\text{SO}_4$ and other fertilisers, the pH has dropped to ~ 4.2 , compared to pH ~ 6
451 of the control plot. Exchangeable K^+ has increased whilst exchangeable Ca has decreased,

452 probably to be replaced by exchangeable $\text{Al}(\text{OH})_x$ species, Al^{3+} and H^+ . Following NaNO_3 and
453 fertiliser application, pH has marginally increased to ~ 6.2 and both exchangeable K^+ and Na^+
454 have increased in concentration.

455

456 No overall treatment trend was found for either CEC or SA in the $<0.2 \mu\text{m}$ clay fraction from
457 the sub soil samples. Figure 7 shows the change in $d(001)$ spacing for the three identified I/S
458 phases. For the high smectite I/S (Figure 7a), the initial spread of data points for the different
459 plots is greater than for the top soil, possibly reflecting a greater range and distribution of
460 variously hydrated cations present in the smectite interlayers. Only one identifiable trend was
461 found in the high smectite I/S; a consistent decrease in $d(001)$ spacing in the control plot over
462 the study period. Values fell from $15.5 - 14.7 \text{ \AA}$ and may have been a result of the interaction
463 between naturally weathered K^+ with the smectite interlayers. This response contrasts with
464 samples of the $(\text{NH}_4)_2\text{SO}_4$ and NaNO_3 treatments where no trends were observable despite
465 large increases in exchangeable K^+ being found from the leaching of fertiliser (Figure 6b). In
466 the low smectite I/S minerals a decrease from $\sim 12.9 - 12.5 \text{ \AA}$ was found in the NaNO_3
467 treatment. This is likely due to the presence of K^+ ions and their substitution with Ca^{2+} ions.
468 No identifiable trends $> 0.4 \text{ \AA}$ were found in the illite phase.

469

470 A possible explanation why greater decreases were found in the control plot than in the NaNO_3
471 and $(\text{NH}_4)_2\text{SO}_4$ treatments is competition from other ions. For example, the annual addition of
472 NaNO_3 fertiliser would introduce Na^+ ions, as well as those from the other mineral fertilisers
473 applied. Subsequently, as a result of this competition from other ions, the K^+ ions may not have
474 been able to access sites in the smectite interlayers (Stucki & Huo, 1996) with such ease and
475 were thus retained on the more selective frayed edge sites of the smectite component (Goulding
476 & Talibudeen, 1978). For the $(\text{NH}_4)_2\text{SO}_4$ treatment, the increasing presence of H^+ ions as the

477 soil acidified may have increased competition with both K^+ & Al^{3+} ions in I/S interlayers.

478

479 **3.4 Comparison between acidic (Geescroft Wilderness) and alkaline (Broadbalk**
480 **Wilderness) woodland top soils**

481 In Broadbalk Wilderness, the soil still contains some free $CaCO_3$ following large applications
482 of chalk in the 18th and early 19th centuries; soil pH is still >7 (Section 2.1.3). In contrast, in
483 Geescroft Wilderness which had little or no chalk applied, soil acidity has developed over time
484 (Figure 8). Again there are no detectable trends in the CEC and SA measurements (results not
485 shown). Figure 9 shows the changes in the $d(001)$ spacing for each of the I/S phases in the
486 samples from the two woodland sites. The 1881-83 samples show differences in the $d(001)$
487 spacings between the two sites for each of the three phases, possibly as a result of slight
488 differences in the parent material or previous weathering processes or land-use. For the high
489 smectite I/S (Figure 9a), there is a large variation in the $d(001)$ spacing but no overall trend
490 could be identified at either site. The only readily identifiable trend was found in the
491 progressively acidifying Geescroft Wilderness soil, where a decrease in the $d(001)$ spacing of
492 ~ 13.0 to 12.5 \AA was found in the low smectite I/S phase through the period examined.
493 Although a steady decrease appeared in the illite phase in the Geescroft Wilderness, this is
494 considered too small to be definite trend. However, in the neutral Broadbalk Wilderness there
495 was minimal change in the $d(001)$ spacing measurements for both the low smectite I/S or
496 'illite' phases.

497

498 In the Geescroft Wilderness, the soil pH had dropped to \sim pH 4.5, a pH where the main reaction
499 products are non-exchangeable polymeric Al-hydroxy-cations (Ulrich, 1991) which can form
500 in the interlayer space of smectite clays, thus decreasing $d(001)$ spacings. Blake *et al.* (1999)
501 examined the changes in soil chemistry ($<2 \text{ mm}$) with acidification in Geescroft Wilderness

502 and reported decreases in soil effective cation exchange capacity (ECEC), although these
503 measurements would include the decrease in pH-dependent charge of soil organic matter found
504 with decreasing soil pH. They suggested that the decrease in ECEC was partially a result of
505 clay particles being covered with amphoteric Al hydroxyl cations which restricts isomorphous
506 substitution and changes permanent charge into pH-dependent charge. An initial examination
507 of clay mineralogy in the Geescroft experiment by Blake *et al.* (1999) was reported as a *pers.*
508 *comm.* and indicated that ‘with time, the interstratified swelling mineral expands less readily on
509 solvation with ethylene glycol’. This would confirm the results reported in the present study
510 regarding the decreasing $d(001)$ spacing in the low smectite I/S phase in the Geescroft soil.
511 The comparison between the acidic and alkaline woodlands appears to suggest that where soil
512 pH is maintained by application of CaCO_3 , the potential for the collapse of smectite interlayers
513 decreases as a result of competition from weathered Ca^{2+} ions for interlayer spaces.

514

515 **4. General Discussion**

516 The results obtained, taken in conjunction with those of several other studies (Bain & Griffen,
517 2002; Barak *et al.* 1997; Velde & Peck, 2002; Velde *et al.*, 2003; Righi *et al.*, 1995; Mathé *et*
518 *al.*, 2007), provide further evidence that subtle changes can occur with time in clay minerals
519 subjected to different land management practices. However, after analysing a diverse selection
520 of samples in terms of pH and nutrient status, it was surprising that greater differences were not
521 seen. This was in spite of conditions of acidity and K^+ status that have been found to promote
522 the collapse of the $d(001)$ interlayer in I/S clay minerals. Despite a small number of identifiable
523 changes being found, results generally suggest that within the context of the general use of
524 soils in agriculture and forestry, I/S minerals of the Batcombe series soil are fairly resilient to
525 substantial changes. This resilience appears to be derived from other soil factors. These include
526 (i) the application of fertiliser and liming applications that increase the number of competing

527 ions to K^+ , thus decreasing access to interlayer sorption sites in the smectite (e.g. Ca^{2+} and Na^+),
528 (ii) in acidifying soils, the presence of H^+ providing competition for K^+ and NH_4^+ ions, (iii) the
529 weathering of mica and feldspar and the recycling of K^+ and (iv) the presence of organic
530 carbon that can physically reduce the accessibility to clay minerals by creating aggregates as
531 well as potentially entering the interlayer space (Velde *et al.*, 2003).

532

533 With respect to the functioning of soil I/S minerals in agricultural and natural systems, where
534 decreases in $d(001)$ spacing were identified it would be expected that some of the smectite in
535 the I/S minerals will behave more like illite. Typically, this could involve a loss of CEC and
536 suppress the ability of clays to swell. The interaction of K^+ with the interlayer spaces of
537 smectite is obviously important and much of the general variation in $d001$ spacing, in all three
538 I/S phases, will be caused by the interactions of K^+ with the growth demands of the plants.
539 Barré *et al.* (2008) identified reversible changes in five different 2:1 minerals with either K^+
540 addition or by removal by plants. Decreases in $d(001)$ spacing caused by K^+ entering the
541 interlayer space of the I/S minerals is at least partially reversible. Barré *et al.* (2007a)
542 demonstrated that changes in I/S minerals as a result of K^+ removal by plants could occur
543 within 14 days and that plants could extract more K^+ than was found within the exchangeable
544 K^+ fraction. XRD analyses demonstrated a decrease in both well crystallised and poorly
545 crystallised illite after plants had been grown for 31 days. Thus Barré *et al.* (2007b) suggest
546 that ‘illite like layers’ act as a dynamic reservoir of K^+ . The decrease in $d(001)$ spacing would
547 also be reversible in the sub soil as long as it is within the rooting zone where possible uplift of
548 nutrients may occur (Jobbágy & Jackson, 2001 & 2004). Deist & Talibudeen (1967 a & b)
549 demonstrated that the exchange isotherm K^+ - Ca^{2+} in 2:1 clays is rarely completely reversible
550 and that K^+ entering the interlayer space can lead to the (i) trapping of cations as it collapses
551 the $d(001)$ spacing or (ii) the K^+ becomes fixed and thus not exchangeable leading to a loss of

552 CEC. Whilst results from this study suggest that, under typical agricultural practices of
553 fertiliser use and liming, the effect of K^+ causing collapse of the $d(001)$ spacing was minimal,
554 small losses of CEC could result in a loss of nutrients through leaching or the trapping of NH_4^+
555 ions in the interlayer space thus preventing nitrification (Chappell & Evangelou, 2000). The
556 loss of CEC and swelling capacity also has implications for reducing the soil's ability to
557 attenuate contaminants. No previous studies have reported the long-term effects of
558 management practices or natural weathering processes in the sub soil where the filtering of
559 ground and surface is a major function. This study suggests that in natural or unmanaged soils,
560 where soil pH is around neutral, K^+ released through weathering can decrease the $d(001)$
561 spacing in I/S minerals in the sub soil and over long periods, the ability of the sub soil to act as
562 a filtration system for ground and surface waters could therefore be reduced.

563

564 In terms of afforestation the use of chemical assays suggested that a permanent reduction in
565 CEC and SA of the clay could develop if soils were allowed to acidify and hydroxyl-Al
566 compounds precipitated in the interlayer space (Blake *et al.* 1999). The results presented for the
567 I/S minerals from the Geescroft Wilderness provide further evidence for such phenomena.
568 Once acidified, liming the soil to reduce acidity will not lead to the precipitated interlayer Al
569 becoming soluble. Therefore, when reforestation is undertaken, the results from this study and
570 that of Blake *et al.*, (1999) clearly demonstrate the appropriateness of a long-term liming
571 strategy for woodland to preserve clay function.

572

573 **5. Conclusions**

574 Our results demonstrate the extent to which I/S mineral phases in the top and sub soil undergo
575 alteration in both natural and agricultural ecosystems under long term land management
576 practices. Both K^+ -plant interactions and soil acidity buffering processes can determine a

577 change in the structure of I/S minerals. However, our results suggest that typical agronomic
578 practices such as liming, the presence of organic carbon, and plant K^+ requirements may largely
579 counteract the ‘illitization-like process’ whereby I/S minerals take on more illite-like properties
580 in top soil and sub soil. The decrease in $d(001)$ spacing observed in sub soil I/S minerals in
581 conditions close to those of natural ecosystems warrant further investigation. Evidence suggests
582 that K^+ released through weathering of mica and K-feldspars may decrease $d(001)$ spacing and
583 subsequently CEC therefore having potential effects on the filtration capacity of I/S minerals.
584 The results also demonstrate the necessity to consider liming programs when afforestation of
585 agricultural land is undertaken to avoid permanent loss of clay CEC function.

586

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592

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802 **Table 1:** Resume of samples from the Rothamsted Classical Experiment archive used in the
 803 current work.

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	Experiment initiated	Plots sampled	Years
Comparison 1			
Park Grass	1856	Top soil (0-23 cm)	
		Control	1876, 1904, 1966, 2002
		(NH ₄) ₂ SO ₄	1876, 1904, 1984, 2002
		NaNO ₃	1876, 1904, 1984, 2002
Comparison 2			
Park Grass	1856	Sub soil (46-69cm)	
		Control	1876, 1906, 1966, 2002
		(NH ₄) ₂ SO ₄	1870, 1906, 1984, 2002
		NaNO ₃	1876, 1906, 1984, 2002
Comparison 3			
Broadbalk Wilderness	1882	Top soil (0-23 cm)	1881, 1944, 1999
Geescroft Wilderness	1886	Top soil (0-23 cm)	1883, 1965, 1999

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837 **Table 2:** Particle size distributions for samples taken from each experiment. Averages are
 838 based on all samples analysed from each experiment.

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Experiment (sample)		Sand 2mm - 63µm	Silt 63 - 2µm	Coarse Clay 2 - 0.2µm	Fine Clay < 0.2µm
		%	%	%	%
Park Grass (top soil) (n=12)	Mean	16.5	72.5	8.5	2.5
	SD	4.5	3.6	1.2	0.8
Park Grass (sub soil) (n=12)	Mean	11.8	59.9	15.7	12.5
	SD	5.7	6.1	1.2	2.6
Geescroft Wilderness (top soil) (n=3)	Average	21.4	60.3	12.7	5.6
	SD	1.1	2.4	1.3	1.2
Broadbalk Wilderness (top soil) (n=3)	Average	21.1	61.1	13.5	4.3
	SD	1.7	3.2	3.1	1.5

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871 **Table 3:** Measured properties of top (0-23 cm) and sub soil (46-69 cm) fine clay fractions.
 872 CEC and surface area properties are shown before and after the removal of organic carbon.
 873 Values from the Park Grass Experiment are the mean of the 3 treatment plots from the earliest
 874 sampling point of the time series (1870/1876). Values from the Geescroft (1883) and
 875 Broadbalk (1881) Wilderness are also the earliest point of their respective time series.

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Experiment (sample)	Treatment		OC	CEC	Surface Area
			%	cmolc kg ⁻¹	m ² g ⁻¹
Park Grass (top soil)	none	Mean	10.7	78.4	68
		SD	2.8	3.5	18
Park Grass (top soil)	OC leached	Mean	Nm	70.6	366
		SD	Nm	5.2	31
Park Grass (sub soil)	none	Mean	1.1	56.0	362
		SD	0.1	2.3	36
Park Grass (sub soil)	OC leached	Mean	Nm	55.8	348
		SD	Nm	4.2	13
Geescroft Wilderness (top soil)	none		2.61	61.2	333
	OC leached		Nm	68.3	358
Broadbalk Wilderness (top soil)	None		3.19	64.2	303
	OC leached		Nm	49.0	328

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Nm = Not measured

Table 4: Properties of XRD traces obtained after peak decomposition for top and sub soil samples. The range and average values are taken from all measurements for each experiment over the period 1870 – 2002 for the Park Grass Experiment, 1883 – 1996 for the Geescroft Wilderness and 1881- 1996 for the Broadbalk Wilderness.

Experiment (sample)		High smectite I/S			Low smectite I/S			'Illite'		
		Å	FWHM	% Area	Å	FWHM	% Area	Å	FWHM	% Area
Park Grass (top soil)	Range	14.5 -15.3	1.7 -2.0	46 - 69	11.9 -13.1	1.0 -1.73	11 - 37	11.1 -11.5	0.58 -1.5	7 -29
	Mean	14.82	1.85	61	12.54	1.34	21.6	11.26	1.06	17.44
	SD	0.27	0.12	7.14	0.38	0.2	8.20	0.13	0.28	7.57
Park Grass (sub soil)	Range	14.7 – 15.4	1.5 – 2.05	50 -74	12.4 – 12.9	0.81 – 1.39	6 – 35	11.2 – 11.5	0.92 – 1.35	13 – 24
	Mean	15.0	1.88	63.22	12.65	1.19	18.89	11.27	1.09	17.9
	SD	0.25	0.16	7.85	0.17	0.2	9.27	0.1	0.13	3.7
Geescroft Wilderness (top soil)	Range	14.7 – 15.3	1.86 – 2.25	64 - 79	12.4 – 13.0	1.08 – 1.6	9 - 29	11.2 – 11.5	0.82 – 1.16	7 – 15
	Mean	14.9	2.0	71.3	12.6	1.3	17.3	11.3	1.0	11.8
	SD	0.3	0.2	0.2	0.3	0.3	8.9	0.1	0.1	0.1
Broadbalk Wilderness (top soil)	Range	14.5 – 15.1	1.62 – 2.22	43 - 73	12.0 – 12.9	1.1 – 1.9	8 - 49	11.1 – 11.4	0.8 – 1.2	8 – 21
	Mean	14.8	1.9	55.5	12.4	1.5	31.5	11.2	0.9	12.8
	SD	0.2	0.2	11.8	0.3	0.3	16.6	0.1	0.2	5.3

Figure Captions:

Figure 1: Typical air-dry, glycol-solvated and heated XRD traces for the <0.2 μm clay fraction of a sub soil taken from the Park Grass Experiment. Sample shown is from the Park Grass Experiment, 1906 Control Plot, 46-69cm.

Figure 2: Decomposition of an air-dry XRD trace for the <0.2 μm clay fraction from a Rothamsted top soil sample. Sample shown is from the Park Grass Experiment, 1876, Plot 3, 0-23 cm.

Figure 3: Changes in top soil pH (0-23cm) with time in samples taken from the (i) control (\bullet), (ii) $(\text{NH}_4)_2\text{SO}_4$ (\square) and (iii) NaNO_3 (\blacktriangle) plots from the Park Grass Experiment. The point for 1856 (\diamond), is an estimated value for the start of the experiment taken from Johnston *et al.* (1986).

Figure 4: Changes in (a) exchangeable K, (b) exchangeable Ca, (c) exchangeable Mg and (d) exchangeable Na in top soil (< 2 mm) taken from the unlimed (i) control (ii) $(\text{NH}_4)_2\text{SO}_4$ and (iii) NaNO_3 plots of the Park Grass Experiment.

Figure 5: Changes in $d(001)$ spacing with time in (a) high smectite I/S , (b) low smectite I/S and (c) 'illite' phases identified using peak decomposition for XRD traces from Park Grass (i) control (\bullet), (ii) $(\text{NH}_4)_2\text{SO}_4$ (\square) and (iii) NaNO_3 (\blacktriangle) plots analysed from the Park Grass Experiment (0-23 cm).

Figure 6: Sub soil (a) pH, (b) exchangeable K, (c) exchangeable Ca, (d) exchangeable Mg and (e) exchangeable Na in top soil (<2 mm) samples taken from the (i) control (ii) $(\text{NH}_4)_2\text{SO}_4$ and (iii) NaNO_3 plots of the Park Grass Experiment in 2002.

Figure 7: Changes in $d(001)$ spacing with time in (a) high smectite I/S , (ii) low smectite I/S and (iii) ‘illite’ phases identified using peak decomposition for XRD traces from Park Grass (i) control (●), (ii) $(\text{NH}_4)_2\text{SO}_4$ (□) and (iii) NaNO_3 (▲) plots analysed from the Park Grass Experiment (46-69 cm).

Figure 8: Changes in top soil pH with time in Broadbalk (□) and Geescroft Wildernesses (●).

Figure 9: Changes in $d001$ spacing with time in (i) high smectite I/S , (ii) low smectite I/S and (iii) ‘illite’ phases identified using XRD peak decomposition from Broadbalk and Geescroft Wildernesses.

Fig 1:

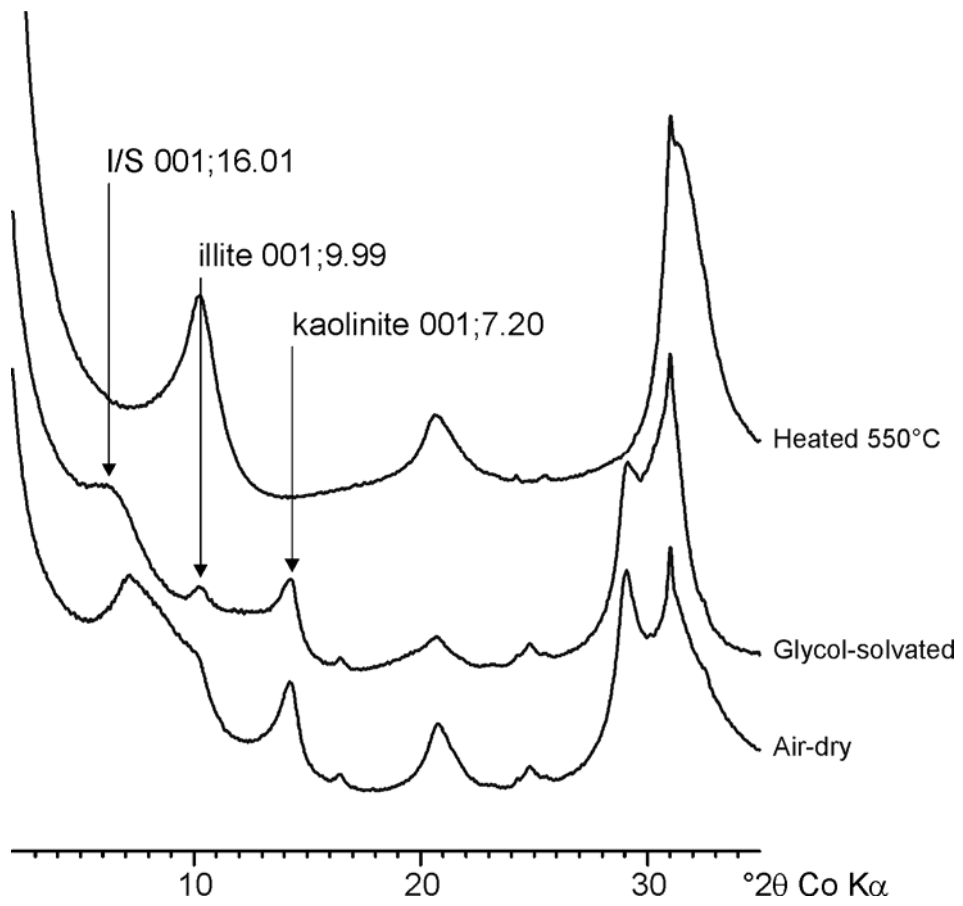


Fig 2:

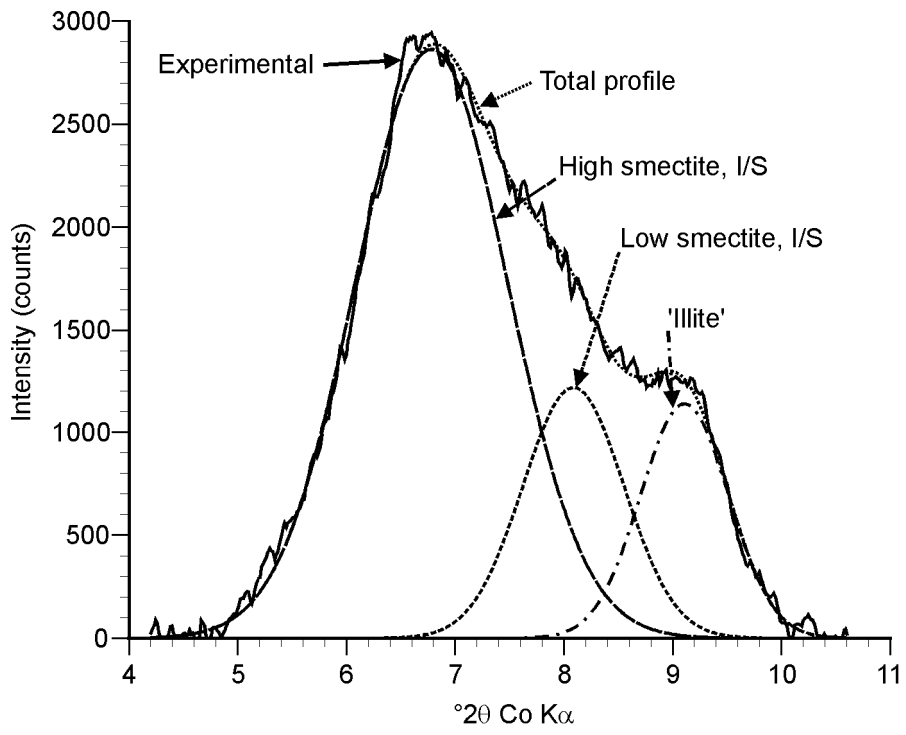


Fig 3:

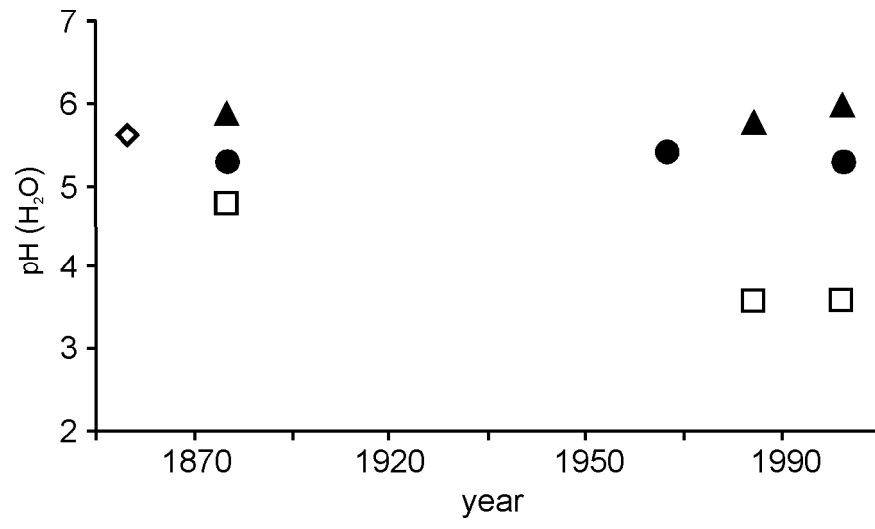


Fig 4:

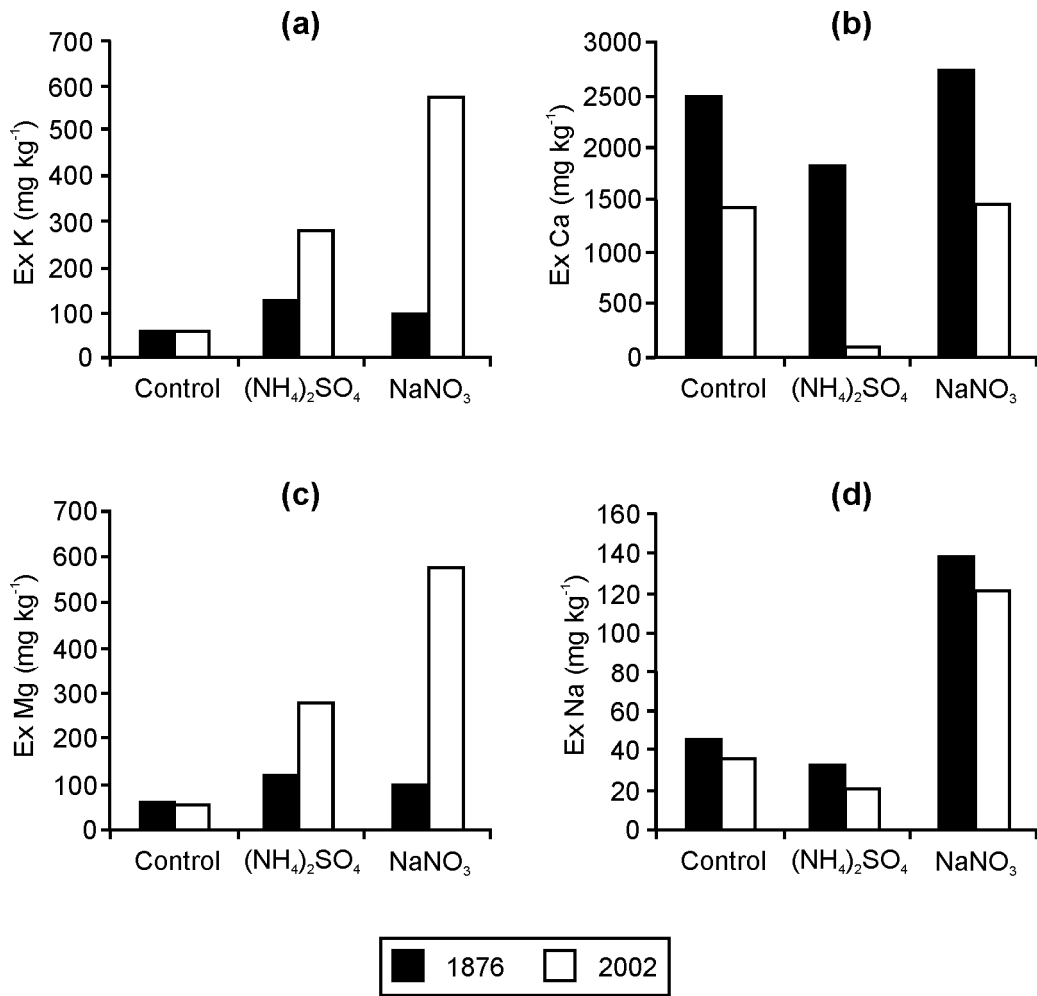


Fig 5:

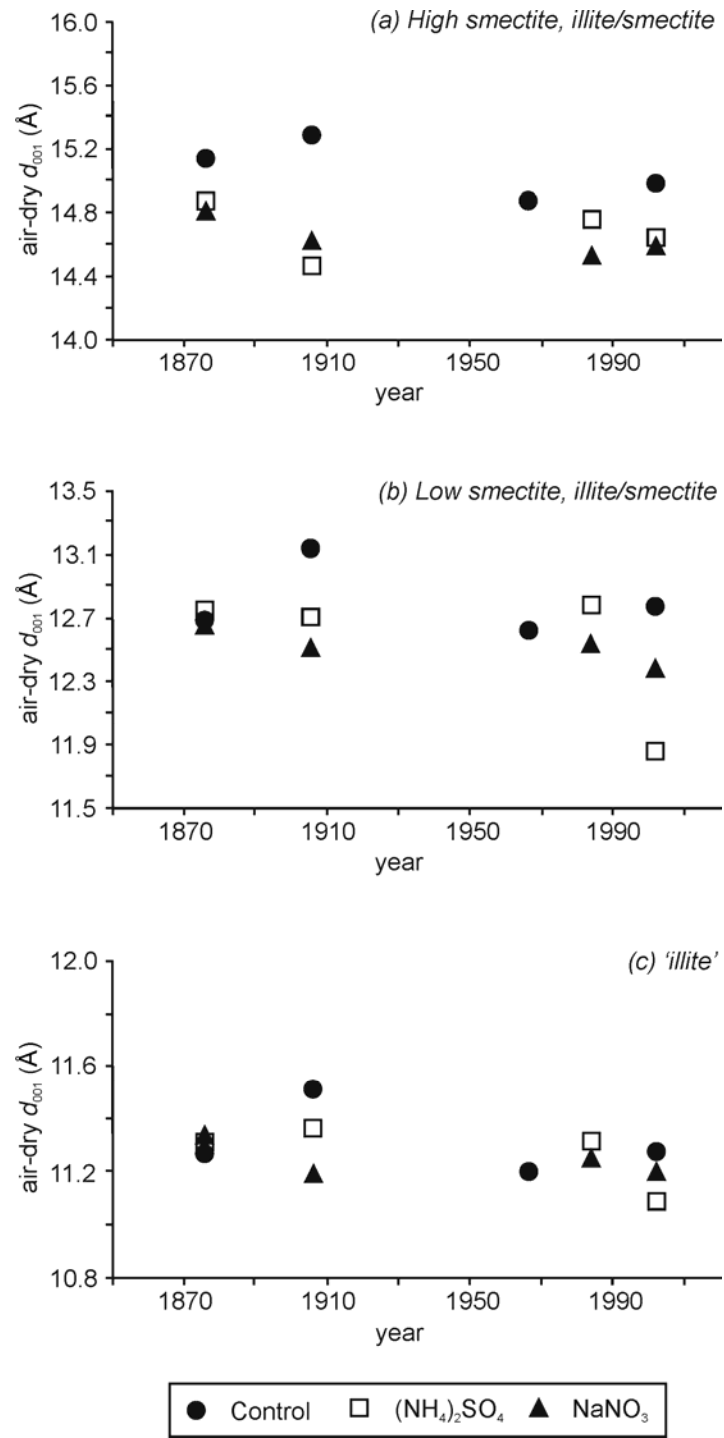


Fig 6.

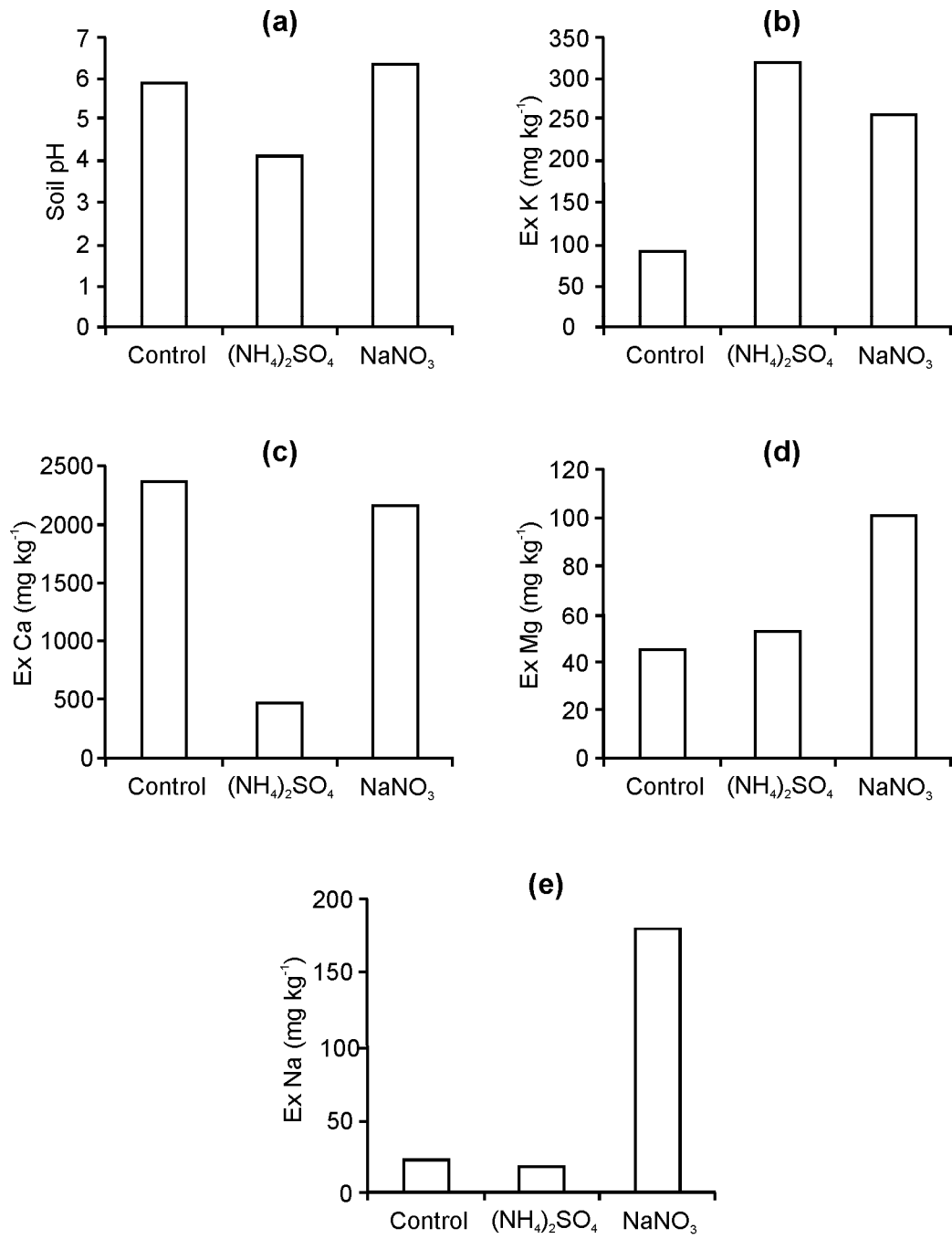


Fig 7:

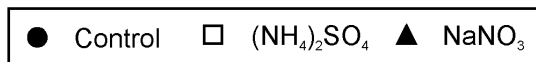
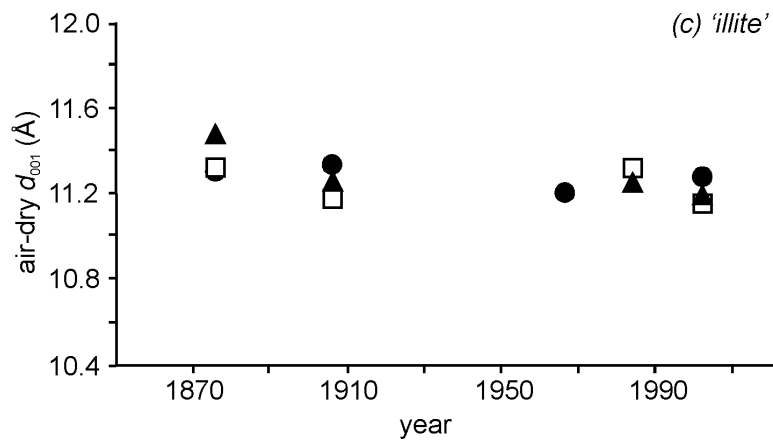
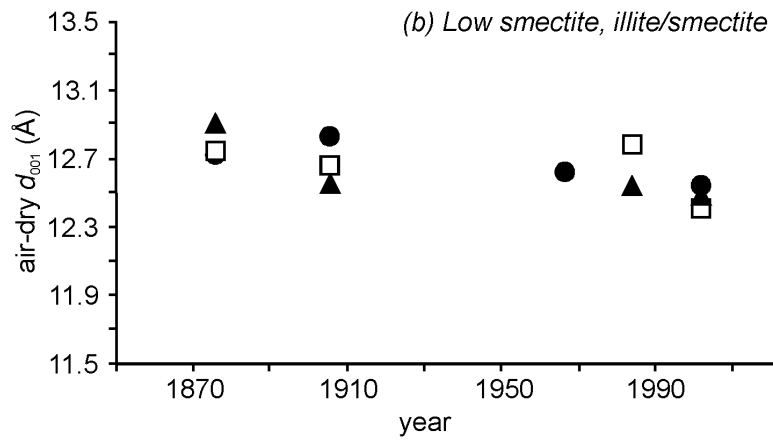
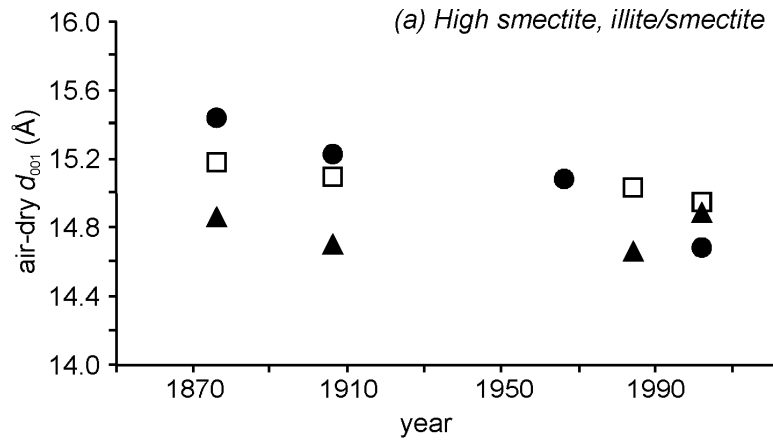


Fig 8:

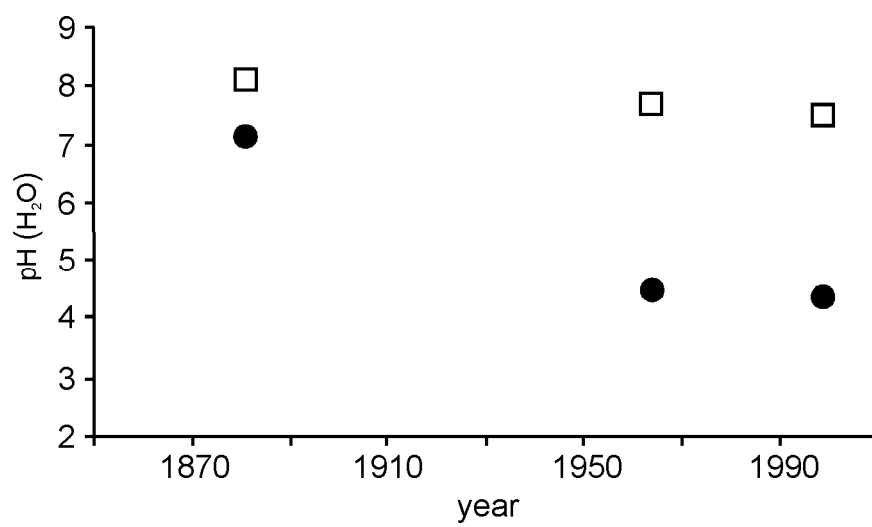


Fig 9:

