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

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Abstract

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

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soil pH fell below 3.7. It is believed that solubilisation of hydroxyl-Al in smectite interlayers enabled renewed access to K^+ or NH_4^+ ions, leading to increased collapse in *d001* spacing. However, the results show that over a diverse range of soil conditions, I/S minerals of the Batcombe series soils showed considerable resilience to major change. This is considered to be a result of competition for sorption sites by the (i) presence of competing ions added as fertiliser or liming materials, (ii) an increase in H^+ ions as soil acidity increases, (iii) the possible role of organic carbon in protecting I/S minerals and (iv) the role of the I/S minerals as K^+ reservoirs. However, the impact of decreasing soil pH should be considered when land is re-forested as this may lead to irreversible decreases in the *d(00l)* spacing of I/S minerals, thus compromising useful clay properties such as CEC.

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

1. Introduction

Clay mineral properties are fundamental to many soil functions including water and nutrient retention, contaminant (pesticides, heavy metals) attenuation, carbon storage, the maintenance of soil structure and the filtering of both ground and surface waters. However, relatively few studies have been undertaken to examine how clay mineral structure may change with (i) the inorganic chemical inputs of intensive agricultural systems and (ii) land use changes over long periods of time. Thus, soil archives from long-term experiments provide a valuable resource, allowing changes to be studied with knowledge of management practices over relatively long periods (Velde & Peck, 2002). In addition, recent advances in X-ray diffraction (XRD) techniques such as decomposition modelling have allowed greater interpretation of XRD profiles, enabling more precise identification of different soil clay mineral phases (e.g. Mathé *et al.*, 2007; Egli *et al.*, 2007). In this study we assess changes in clay mineral structure from the ‘Rothamsted Classical Experiments’ (Johnston, 1997) in relation to fertiliser additions and changing land use.

In temperate regions, attention has largely focused on 2:1 clay minerals (smectite, vermiculite, illite, chlorite and their intergrades) as they dominate the clay mineralogy of many soils (Velde, 2001). With respect to fertiliser applications, work has largely focussed on the interactions between K^+ and illite/smectite (I/S) mixed layer minerals (Singh & Goulding, 1997; Velde & Peck, 2002; Pernes-Debuyser *et al.* 2003; Mathé *et al.*, 2007; Barré *et al.* 2007a & b). These studies have shown the importance of K^+ in determining the nature of I/S minerals and the K^+ buffer capacity for plant nutrition. For example, Velde & Peck (2002) examined samples taken between 1913 and 1996 from the Morrow Plot Experiment archive at the University of Illinois. The major finding was that under continuous corn cropping and without fertilisation, the extraction of K^+ for plant nutrition led to an increase in the smectite content of I/S minerals. Pernes-Debuyser *et al.* (2003) demonstrated that in soils where plant growth was absent, the addition of K^+ fertiliser resulted in an increase in the illite (non-expandable) content of the I/S. These results, among others, led Barré *et al.* (2007a & b) to postulate that ‘illite-like layers’ can be viewed as K^+ reservoirs that can be potentially refuelled via the ‘nutrient uplift theory’ suggested by Jobbagy & Jackson (2001). Therefore, in top soils where greater K^+ is uplifted or recycled than is required by plants the system could be pushed towards the illite end of the I/S system. Changes in clay mineralogy have also been investigated in chronosequences under natural conditions where the role of K^+ has been important in determining changes in I/S mineral structure. Velde *et al.* (2003) examined changes in poldered sediments under natural pasture development. In the oldest profiles (>800 yrs), a disordered illitic I/S mineral became dominant in the upper parts of the profile whilst in the lower part of the profile a smectitic I/S mineral was predominant. Mathé *et al.* (2007) monitored soil clay minerals from recent natural polders in response to local environmental conditions and noted that with increasing age, chlorite was removed and the illite content of I/S increased. Such reactions were triggered by oxidation and in natural systems would last >1000 y but could be accelerated by artificial drainage to complete the process in a few tens of years.

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

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

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

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

2. Materials and Methods

2.1 Background and Sample Collection

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

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

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

2.2 Comparisons undertaken

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

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

Park Grass Experiment were used (i) Plot 3, the Control plot where no lime or fertiliser had been added since 1856, (ii) Plot 14 where 96 kg N ha^{-1} as $NaNO_3$ has been applied each year since 1858 and (iii) Plot 9 where 96 kg N ha^{-1} as $(NH_4)_2SO_4$ has been applied each year since 1856. Atmospheric NH_4-N deposition has been estimated as ~2.5 kg ha^{-1} a^{-1} from 1850 to 1900 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. 1999). Similarly, inputs of H^+ have varied between 0.1 and 0.4 kg ha^{-1} a^{-1}. Treatments receiving fertiliser N also receive yearly applications of 35 kg ha^{-1} P as triple superphosphate, 225 kg ha^{-1} K as K_2SO_4, 15 kg ha^{-1} Na as Na_2SO_4 and 10 kg ha^{-1} Mg as $MgSO_4$. The whole experiment received a small amount of chalk in the 1880s/1890s. Since then, plots have since been sub-divided to allow for different lime applications to produce a range of pH values from 3.5 to 7 amongst the various combinations of treatments.

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

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

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

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

2.3 Laboratory methods

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

2.3.1 Particle-size separation

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

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

2.3.2 Measurements

Samples for total organic carbon (TOC) analysis were prepared by pre-drying at 100-105°C (1.5 hours), acidifying (HCl, 50% v/v), drying at 100-105°C (1.5 hours), and analysing by combustion (1050°C) using an ‘Elementar Vario Max’ C/N analyser. CEC was determined by a compulsive displacement technique using a $BaCl_2$/triethanolamine (pH 8.1) titration method based on that proposed by Bascomb (1964). Surface-area determinations (SA) were carried out following a procedure based on the formation of a monolayer of 2-ethoxyethanol (EGME) molecules on the clay surface under vacuum (Heilman *et al.*, 1965). Churchman *et al.* (1991) discuss the assumptions necessary within the EGME method including the behaviour of clay type, and time taken to establish end points. In this study samples were expected to have similar mineralogical compositions and a standard method was used throughout. As only small amounts of material were available, 0.2 g of <0.2 μm material was covered by ~1 ml of EGME and left for 24 hours before reweighing. A conversion factor of 0.000286 g m^2 was used to calculate total surface area.

2.3.3 X-ray diffraction analysis

In order to produce high quality diffraction traces, oriented mounts for XRD analysis were produced using ‘zero background’ silicon crystal substrates. About 15 mg of the dried <0.2 μm material was re-suspended in a minimum of deionised water, Ca-saturated using a few drops of 0.1M $CaCl_2.6H_2O$ solution, washed, pipetted onto a silicon crystal substrate and allowed to air-dry overnight. XRD analysis was carried out using a PANalytical X’Pert Pro series diffractometer fitted with a cobalt-target tube, X’Celerator detector and operated at 45kV and 40mA. The <0.2 μm oriented clay mounts were scanned from 2-35°2θ at 0.55°2θ/minute after air-drying, ethylene glycol-solvation and heating to 550°C for 2 hours. Clay mineralogy was determined by characteristic peak positions in relation to this diagnostic testing program.

In order to obtain further information about the nature of the clay minerals present in the samples, modelling of the XRD profiles was carried out using Newmod-for-Windows™ (Reynolds & Reynolds, 1996) software. The modelling process requires the input of diffractometer, scan parameters and a quartz intensity factor (instrumental conditions), and the selection of different phyllosilicate sheet compositions and chemistries. In addition, an estimate of the crystallite size distribution of the clay species may be determined by comparing peak profiles of calculated diffraction profiles with experimental data. Further information on the clay mineralogy of the samples was deduced by decomposition of the XRD profiles into their elementary component curves using the program DECOMPXR (Lanson, 1993; Lanson & Besson, 1992). Best fits were obtained using Gaussian curves following background subtraction and 7-point smoothing.

2.4 Theoretical considerations

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

Recent advances in the power of desktop computers has provided the data processing power necessary to extract further information from XRD profiles. Such processing power is required by decomposition routines whereby peak profiles are split into partially overlapping contributions due to phases with distinct but closely related crystallographic characteristics (Lanson, 1997). Decomposition therefore offers the possibility to identify the presence of different phases by monitoring parameters such as peak position, full width at half maximum intensity (FWHM), relative intensity and profile shape. Decomposition routines, such as DECOMPXR (Lanson, 1993), are iterative procedures, the quality of the fit being estimated after each iteration as well as the evolution of the adjusted parameters. The calculation is stopped when the quality of the fit is not improving and/or when adjusted parameters are stable. Due to their small crystallite-size distributions, clay minerals are often characterised by broad and overlapping XRD peaks. This is particularly so for soil clay minerals. Decomposition of soil clay mineral XRD profiles therefore offers a relatively fast identification and descriptive tool, especially suited to establishing trends when studying sample series and variations affecting their components (Lanson, 1997).

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

This 'illitization-like process' in the I/S is most likely driven by wetting and drying cycles and the subsequent reduction of structural Fe(III) in clays, sometimes mediated primarily by the enzymatically catalyzed activity of indigenous soil micro-organisms (Favre *et al.*, 2002; Kim *et al.*, 2004; Huggett & Cuadros, 2005; Kostka *et al.*, 1999; Stanjek & Marchel, 2008; Siyuan and Stucki, 1994; Stucki, 1997). The major requirement to enable this collapse in the *d(001)* spacing is a decrease in the positive charge of the octahedral sheet of the smectite. This occurs as structural Fe^{3+} is reduced to Fe^{2+}. This causes an increase in CEC and subsequently the ability to fix cations such as K^+, NH_4^+, Na^+ or H^+ in the interlayer space to balance the charge

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

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

3. Results and discussion

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

The general characteristics of soil texture and clay mineralogy in the top soils and sub soils from the Classical Experiments are summarised in Tables 2 & 3. Particle-size analyses are based on all samples examined from each experiment (Table 1). In the Park Grass Experiment there was an increase in silt content (~12 %) in the top soil compared to the sub soil. This is thought to be a result of the deposition of loess in the late Devensian about 14000-18000 years B.P. (Avery & Catt, 1995). The top soil in the Geescroft and Broadbalk experiments had similar particle size distributions. However, less silt was present than in the top soil of the Park Grass Experiment and greater sand and clay contents were found, possibly because of the Hook series, a variation of the Batcomb series, being present across some of the Park Grass Experiment (Avery & Catt, 1995). Alternatively, the period of cultivation that the Broadbalk and Geescroft sites underwent before being retuned to wilderness may have led to a slight coarsening of the soil (Lobe *et al*. 2001; Jolivet *et al*. 2003). The proportion of fine clay present is generally similar for all the top soils (2.5-5.6 %) but represents a significantly higher proportion of the Park Grass sub soils (12.5%).

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

3.2 XRD analyses

Typically, XRD analysis of the Rothamsted samples suggests that their fine clay (<0.2 µm) fractions are predominantly composed of I/S, illite and kaolinite clay minerals (Figure 1). These results are similar to previous analyses of the <0.2 µm fraction of the Broadbalk Experiment by Singh & Goulding (1997). However these authors identified the interstratified phase as a smectite/vermiculite. Decomposition of the XRD traces using DECOMPXR indicates that the 4 -11 °2θ range is composed of three different sub-species (Figure 2). NEWMOD-modelling suggests that the three peaks represent a high smectite I/S phase (~15 Å), a low smectite I/S phase (~12.5 Å), and an 'illite' phase (~11.2 Å). XRD analyses of samples prior to and following OC-removal suggest a small (~0.2 Å) increase in the *d(001)* spacing of each of the three sub-species. Velde *et al.* (2003) reported similar findings and suggested that OC was responsible for closing some of the smectite interlayers. When comparing management and land use effects on clay particles in the present study we report those obtained prior to OC-removal to ensure minimal damage to the clay minerals susceptible to decomposition from hypochlorite.

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

In previous investigations, peak decomposition modelling techniques have enabled subtle changes in the I/S *d(00l)* spacing with time to be monitored (e.g. Bain & Griffen, 2002; Mathe *et al.*, 2007, Pernes-Debuyser *et al.* 2003; Velde & Peck, 2002). In these studies changes in peak movements of less than ~0.4 Å have often been reported and discussed. However in the present study, trends have only been identified where peak movements of >0.4 Å are evident.

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

Results from the Control treatment sampled in the early years of the experiment (1870/1876) demonstrate differences in the measured CEC and SA properties of the top and sub soil (Table 3). After the removal of OC, the <0.2 µm clay particles of the top soil possessed a higher CEC and SA than the sub soil.

3.3.1 Park Grass top soil

Analyses undertaken on the <2 mm soil fraction give an indication of changes in pH and exchangeable cation status in the top soil relevant to this study (data from Rothamsted Research, Figures 3 and 4). The initial (1856) pH value of the Park Grass soil has been estimated as ~5.5 (Johnston *et al.*, 1986). Since the inception of the experiment, the soil pH of the 'control treatment' has declined slightly to ~5.1. After $NaNO_3$ treatment soil pH increased. This may have been due to a combination of Na^+ ions occupying cation exchange sites in place of H^+ ions and the increase in pH related to NO_3^- uptake by plants. Soil treated with $(NH_4)_2SO_4$ has undergone acidification to pH values of ~3.5. Values for extractable K, Ca, Mg, and Na (Figure 4) reflect fertiliser inputs and off-takes in the herbage (section 2.2.1).

The first set of samples analysed in the present work were taken ~20 years after the initiation of the Park Grass Experiment. There were no identifiable trends in <0.2 µm clay CEC and SA values in the plots over the period the data covers, despite the acidification that has occurred on the $(NH_4)_2SO_4$ plots (Figure 3, Table 2). Changes in the position of the *d(001)* spacing for the three identified XRD phases for the Control, $NaNO_3$ and $(NH_4)_2SO_4$ treatments are summarised in Figure 5. There was a great deal of variability in the high smectite I/S phase (Figure 5a), presumably as it contains the highest proportion of smectite interlayers. This variability is likely a result of the high smectite I/S phase being the main reservoir and source of K^+ for plant requirements (Barré *et al.* 2007a & b). The *d(001)* spacing found in the high smectite I/S minerals from the $(NH_4)_2SO_4$ or $NaNO_3$ plots was consistently smaller than that found in the control. This difference was present at the first sampling point (1870), taken after ~20 years of repeated fertilisation and suggests that the presence of increased K^+ from the fertilisers in the first 20 years of the experiment may have already created a difference by the first analysis in this study. The maximum difference (1906) was ~0.8 Å, but was ~0.4 Å in 2001.

Only one trend was apparent in the *d(001)* spacing of the low smectite I/S phase (Figure 5b) and this was found in the $(NH_4)_2SO_4$ treatment. Relatively little variation in *d(001)* spacing was found between all treatments for much of the study period. However, in 2002, a sudden ~0.8 Å collapse in the *d(001)* spacing of the $(NH_4)_2SO_4$ sample was detected. A possible explanation for this is that as the soil pH falls to ~3.5 (Figure 3), the increasing acidity is buffered by the release of the hydroxy-Al and hydroxy-Al sulphates previously deposited in the interlayer spaces (Ulrich *et al.,* 1992). This could be considered a mild form of the acid-activation process used on bentonites; a treatment used to increase the SA of smectite-group minerals for industrial uses (e.g. Christidis *et al*., 1997). Further indications of this process were found in the SA measurement which increased from around an average of 366 $m^2\ g^{-1}$ to 591$m^2\ g^{-1}$ for this last measurement. As this process occurred interlayer space that was occupied by hydroxyl-Al may have become unoccupied, allowing K^+ or NH_4^+ to enter and to collapse it. There was little variation found in the *d(001)* spacing for the 'illite' phase (Figure 5c). The position of the peak at ~11.2 Å suggests that it contains a small number of smectite interlayers and so may show a more limited response to increased K^+ availability or acidification processes already described.

It was interesting to note that greater differences were not found between such different treatments in the Park Grass top soil, especially as soil conditions exist which have been shown to cause changes in I/S minerals (e.g. increasing soil K^+ and/or acidity). This may have been due to (i) the continued recycling of nutrients and the addition of fertilisers producing competition for interlayer spaces in the I/S layers, (ii) the differences in yearly plant requirements of K^+, balanced by the weathering of micas and uplift of K^+ and (iii) the role of organic carbon (10.7 % in the fine clay fraction; Table 3) in protecting the clay minerals by preventing access to interlayer spaces or by aggregating clay particles. In particular the protection, through restriction of access to I/S minerals by organic carbon and increased competition by H^+ ions for interlayer sites may be a reason why there was a time lag between soil pH values decreasing and the later collapse of the interlayer space in the $(NH_4)_2SO_4$ treatment.

3.3.2 Park Grass Sub soil

Changes in the clay mineralogy of the sub soil under the Park Grass Experiment were examined to determine how management practices of the top soil may have impacted on the sub soil clay mineralogy. Figure 6 shows a range of sub soil (<2 mm) characteristics for the 2002 samples; earlier sampling dates were not re-analysed. The different fertiliser treatments have caused changes in the characteristics of the <2 mm soil fraction. After the yearly application of $(NH_4)_2SO_4$ and other fertilisers, the pH has dropped to ~4.2, compared to pH ~6 of the control plot. Exchangeable K^+ has increased whilst exchangeable Ca has decreased, probably to be replaced by exchangeable $Al(OH)_x$ species, Al^{3+} and H^+. Following $NaNO_3$ and fertiliser application, pH has marginally increased to ~6.2 and both exchangeable K^+ and Na^+ have increased in concentration.

No overall treatment trend was found for either CEC or SA in the <0.2 µm clay fraction from the sub soil samples. Figure 7 shows the change in *d(001)* spacing for the three identified I/S phases. For the high smectite I/S (Figure 7a), the initial spread of data points for the different plots is greater than for the top soil, possibly reflecting a greater range and distribution of variously hydrated cations present in the smectite interlayers. Only one identifiable trend was found in the high smectite I/S; a consistent decrease in *d(001)* spacing in the control plot over the study period. Values fell from 15.5 – 14.7 Å and may have been a result of the interaction between naturally weathered K^+ with the smectite interlayers. This response contrasts with samples of the $(NH_4)_2SO_4$ and $NaNO_3$ treatments where no trends were observable despite large increases in exchangeable K^+ being found from the leaching of fertiliser (Figure 6b). In the low smectite I/S minerals a decrease from ~12.9– 12.5 Å was found in the $NaNO_3$ treatment. This is likely due to the presence of K^+ ions and their substitution with Ca^{2+} ions. No identifiable trends > 0.4 Å were found in the illite phase.

A possible explanation why greater decreases were found in the control plot than in the $NaNO_3$ and $(NH_4)_2SO_4$ treatments is competition from other ions. For example, the annual addition of $NaNO_3$ fertiliser would introduce Na^+ ions, as well as those from the other mineral fertilisers applied. Subsequently, as a result of this competition from other ions, the K^+ ions may not have been able to access sites in the smectite interlayers (Stucki & Huo, 1996) with such ease and were thus retained on the more selective frayed edge sites of the smectite component (Goulding & Talibudeen, 1978). For the $(NH_4)_2SO_4$ treatment, the increasing presence of H^+ ions as the soil acidified may have increased competition with both K^+ & Al^{3+} ions in I/S interlayers.

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

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

In the Geescroft Wilderness, the soil pH had dropped to ~pH 4.5, a pH where the main reaction products are non-exchangeable polymeric Al-hydroxy-cations (Ulrich, 1991) which can form in the interlayer space of smectite clays, thus decreasing *d001* spacings. Blake *et al*. (1999) examined the changes in soil chemistry (<2 mm) with acidification in Geescroft Wilderness and reported decreases in soil effective cation exchange capacity (ECEC), although these measurements would include the decrease in pH-dependent charge of soil organic matter found with decreasing soil pH. They suggested that the decrease in ECEC was partially a result of clay particles being covered with amphoteric Al hydroxyl cations which restricts isomorphous substitution and changes permanent charge into pH-dependent charge. An initial examination of clay mineralogy in the Geescroft experiment by Blake *et al.* (1999) was reported as a *pers. comm.* and indicated that 'with time, the interstratified swelling mineral expands less readily on solvation with ethylene glycol'. This would confirm the results reported in the present study regarding the decreasing *d(001)* spacing in the low smectite I/S phase in the Geescroft soil. The comparison between the acidic and alkaline woodlands appears to suggest that where soil pH is maintained by application of $CaCO_3$, the potential for the collapse of smectite interlayers decreases as a result of competition from weathered Ca^{2+} ions for interlayer spaces.

4. General Discussion

The results obtained, taken in conjunction with those of several other studies (Bain & Griffen, 2002; Barak et al. 1997; Velde & Peck, 2002; Velde *et al.*, 2003; Righi *et al.*, 1995; Mathé *et al.*, 2007), provide further evidence that subtle changes can occur with time in clay minerals subjected to different land management practices. However, after analysing a diverse selection of samples in terms of pH and nutrient status, it was surprising that greater differences were not seen. This was in spite of conditions of acidity and K^+ status that have been found to promote the collapse of the *d(001)* interlayer in I/S clay minerals. Despite a small number of identifiable changes being found, results generally suggest that within the context of the general use of soils in agriculture and forestry, I/S minerals of the Batcombe series soil are fairly resilient to substantial changes. This resilience appears to be derived from other soil factors. These include (i) the application of fertiliser and liming applications that increase the number of competing ions to K^+, thus decreasing access to interlayer sorption sites in the smectite (e.g. $Ca^{2+}$and Na^+), (ii) in acidifying soils, the presence of H^+ providing competition for K^+ and NH_4^+ ions, (iii) the weathering of mica and feldspar and the recycling of K^+ and (iv) the presence of organic carbon that can physically reduce the accessibility to clay minerals by creating aggregates as well as potentially entering the interlayer space (Velde *et al.*, 2003).

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

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

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

5. Conclusions

Our results demonstrate the extent to which I/S mineral phases in the top and sub soil undergo alteration in both natural and agricultural ecosystems under long term land management practices. Both K^+-plant interactions and soil acidity buffering processes can determine a change in the structure of I/S minerals. However, our results suggest that typical agronomic practices such as liming, the presence of organic carbon, and plant K^+ requirements may largely counteract the 'illitization-like process' whereby I/S minerals take on more illite-like properties in top soil and sub soil. The decrease in *d(001)* spacing observed in sub soil I/S minerals in conditions close to those of natural ecosystems warrant further investigation. Evidence suggests that K^+ released through weathering of mica and K-feldspars may decrease *d(001)* spacing and subsequently CEC therefore having potential effects on the filtration capacity of I/S minerals. The results also demonstrate the necessity to consider liming programs when afforestation of agricultural land is undertaken to avoid permanent loss of clay CEC function.

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

	Experiment initiated	Plots sampled	Years
Comparison 1			
Park Grass	1856	Top soil (0-23 cm)	
		Control	1876, 1904, 1966, 2002
		$(NH_4)_2SO_4$	1876, 1904, 1984, 2002
		$NaNO_3$	1876, 1904, 1984, 2002
Comparison 2			
Park Grass	1856	Sub soil (46-69cm)	
		Control	1876, 1906, 1966, 2002
		$(NH_4)_2SO_4$	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

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

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

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

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

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 um 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 (●), (ii) $(NH_4)_2SO_4$ (□) and (iii) $NaNO_3$ (▲) plots from the Park Grass Experiment. The point for 1856 (◊), 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) $(NH_4)_2SO_4$ 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 (●), (ii) $(NH_4)_2SO_4$ (□) and (iii) $NaNO_3$ (▲) 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) $(NH_4)_2SO_4$ 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) $(NH_4)_2SO_4$ (□) 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:

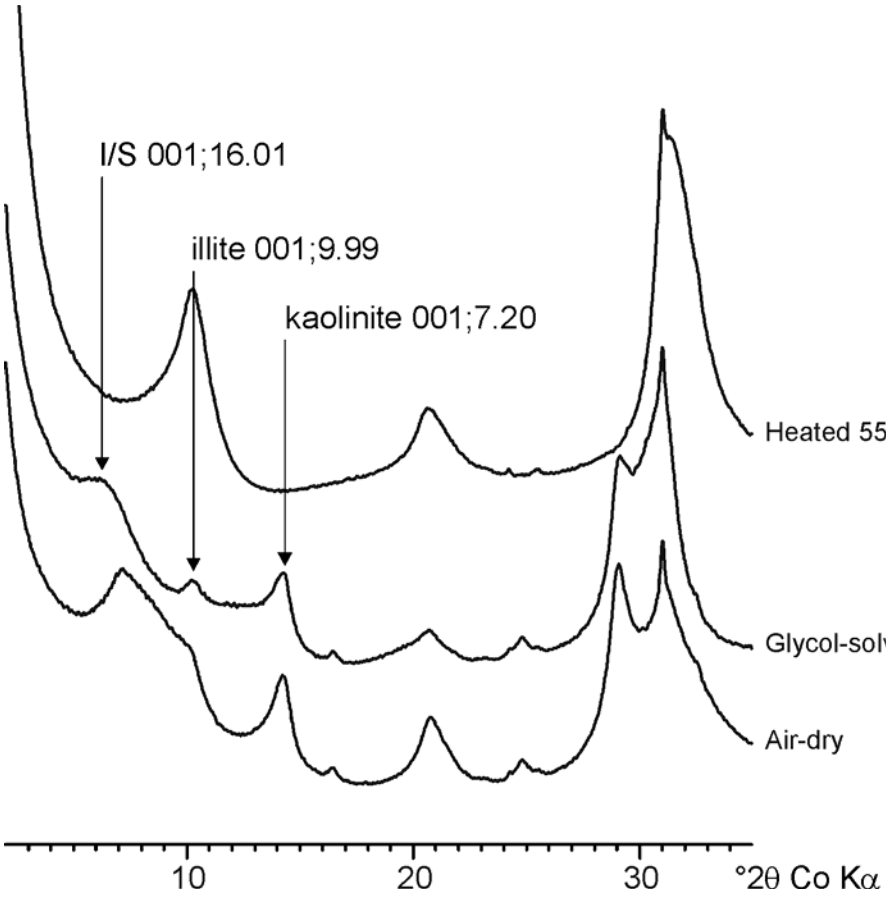

I/S 001;16.01
illite 001;9.99
kaolinite 001;7.20
Heated 550°C
Glycol-solvated
Air-dry
10
20
30
°2θ Co Kα

Fig 2:

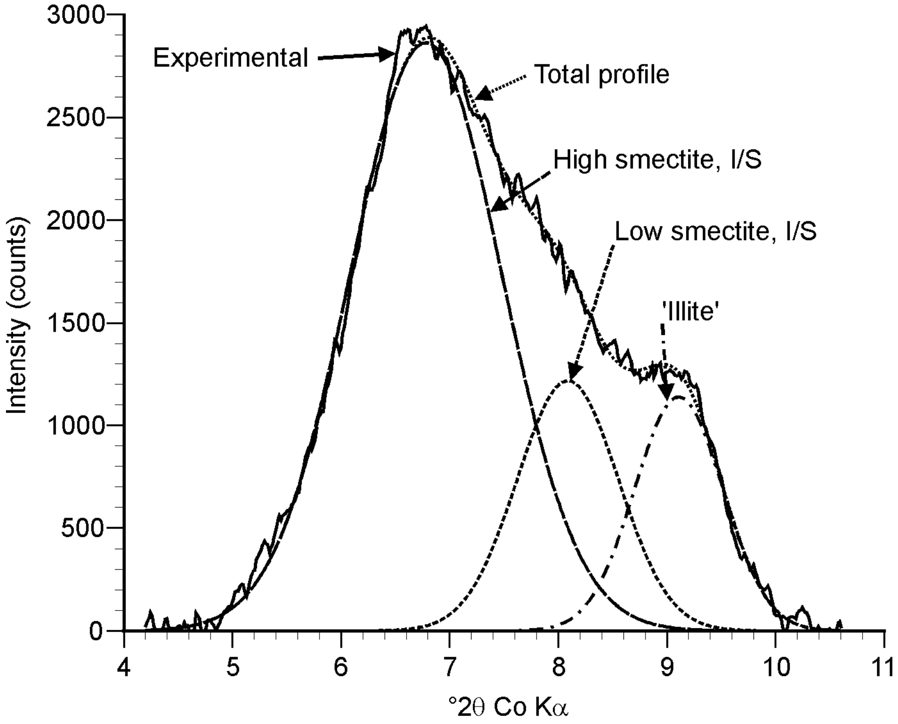

3000
2500
2000
1500
1000
500
0
Intensity (counts)
4
5
6
7
8
9
10
11
°2θ Co Kα
Experimental
Total profile
High smectite, I/S
Low smectite, I/S
'Illite'

Fig 3:

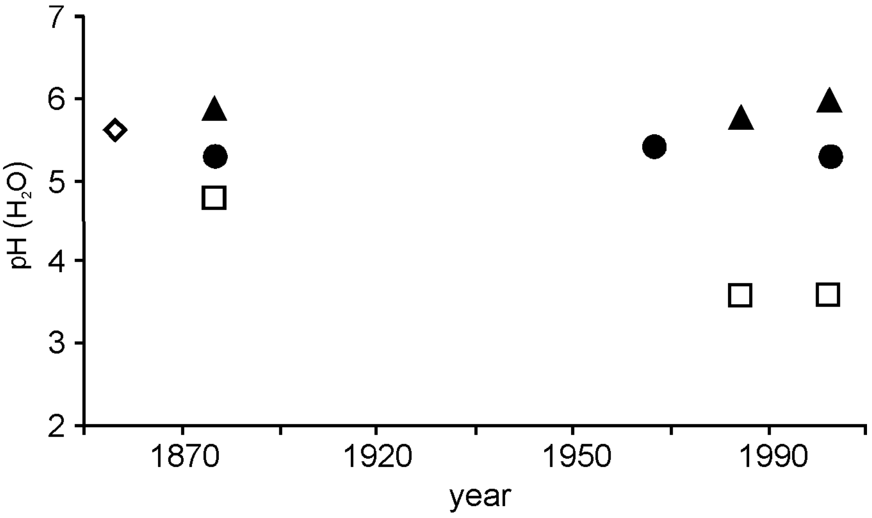


Fig 4:

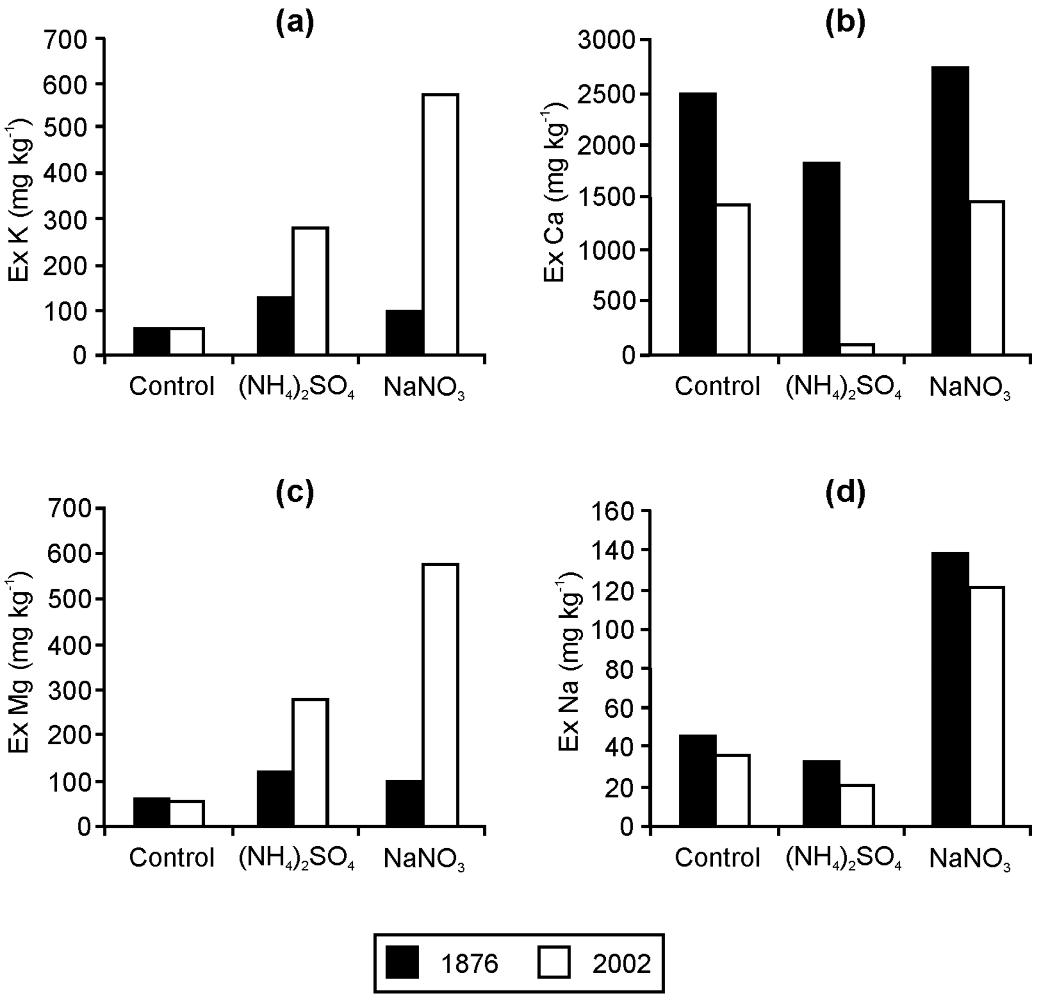

(a)
Ex K (mg kg^{-1})
0
100
200
300
400
500
600
700
Control
$(NH_4)_2SO_4$
$NaNO_3$
(b)
Ex Ca (mg kg^{-1})
0
500
1000
1500
2000
2500
3000
Control
$(NH_4)_2SO_4$
$NaNO_3$
(c)
Ex Mg (mg kg^{-1})
0
100
200
300
400
500
600
700
Control
$(NH_4)_2SO_4$
$NaNO_3$
(d)
Ex Na (mg kg^{-1})
0
20
40
60
80
100
120
140
160
Control
$(NH_4)_2SO_4$
$NaNO_3$
■ 1876
□ 2002

Fig 5:

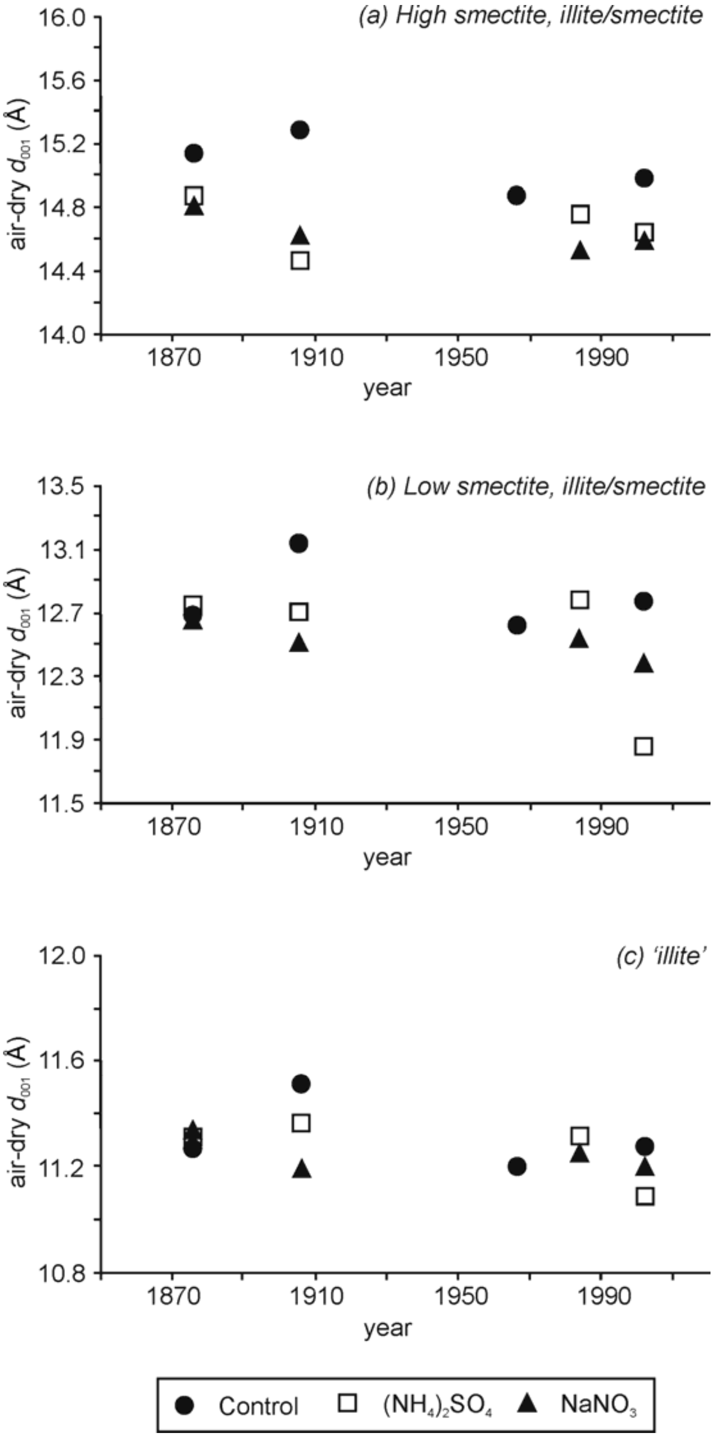

(a) High smectite, illite/smectite
air-dry d_{001} (Å)
16.0
15.6
15.2
14.8
14.4
14.0
1870
1910
1950
1990
year
(b) Low smectite, illite/smectite
air-dry d_{001} (Å)
13.5
13.1
12.7
12.3
11.9
11.5
1870
1910
1950
1990
year
(c) 'illite'
air-dry d_{001} (Å)
12.0
11.6
11.2
10.8
1870
1910
1950
1990
year
● Control
□ $(NH_4)_2SO_4$
▲ $NaNO_3$

Fig 6.

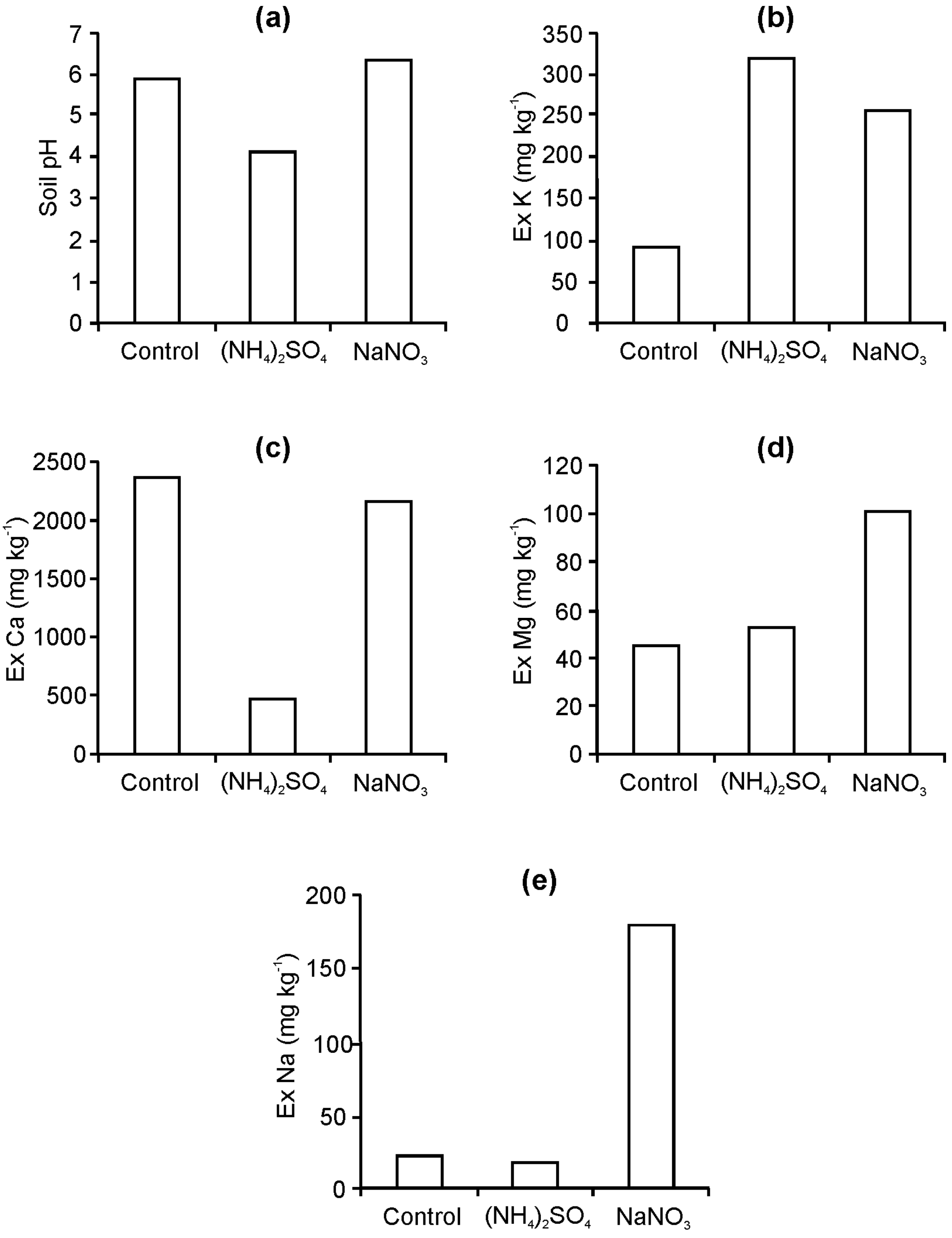

(a)
Soil pH
0
1
2
3
4
5
6
7
Control
(NH4)2SO4
NaNO3
(b)
Ex K (mg kg-1)
0
50
100
150
200
250
300
350
Control
(NH4)2SO4
NaNO3
(c)
Ex Ca (mg kg-1)
0
500
1000
1500
2000
2500
Control
(NH4)2SO4
NaNO3
(d)
Ex Mg (mg kg-1)
0
20
40
60
80
100
120
Control
(NH4)2SO4
NaNO3
(e)
Ex Na (mg kg-1)
0
50
100
150
200
Control
(NH4)2SO4
NaNO3

Fig 7:

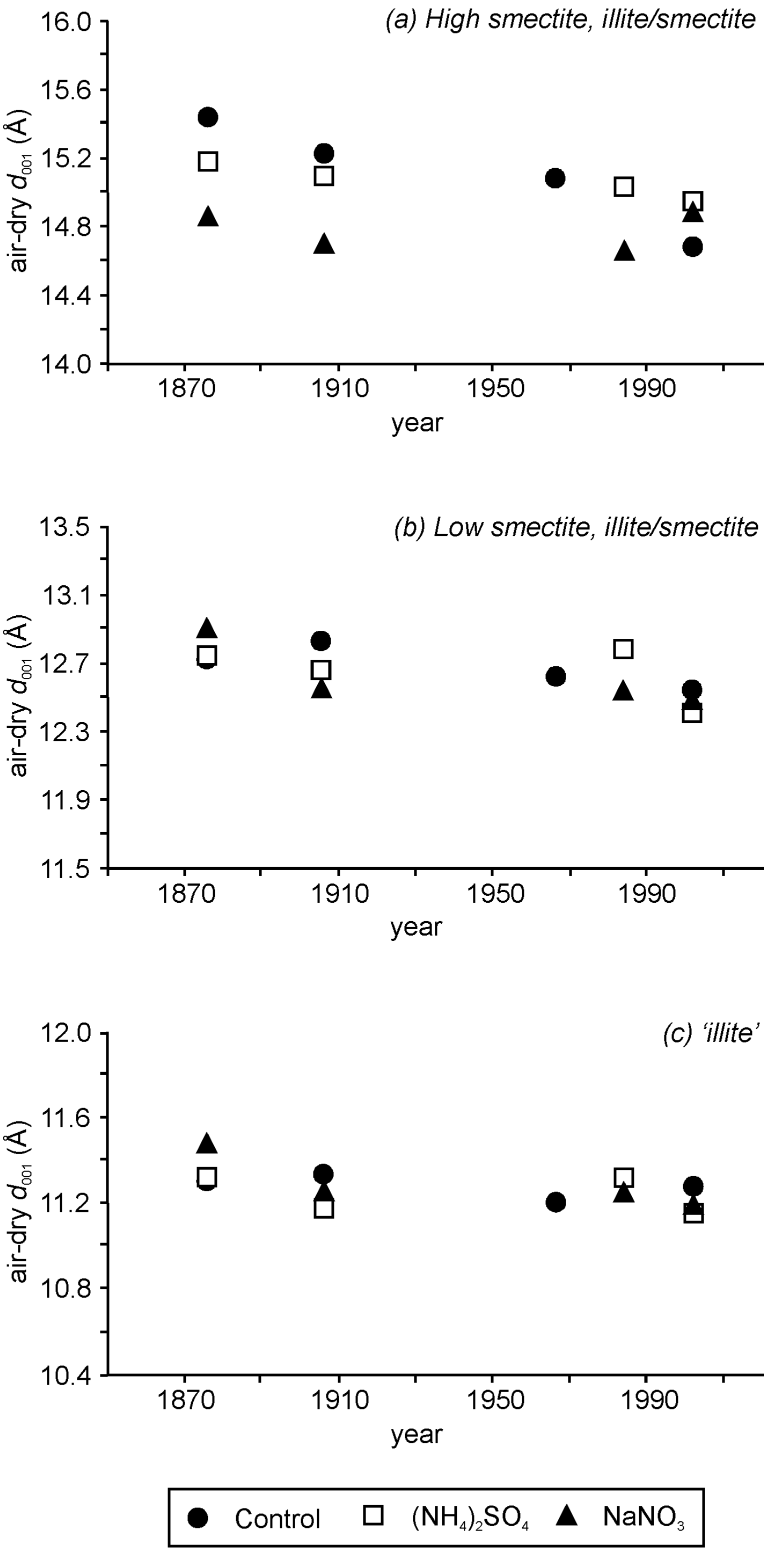

(a) High smectite, illite/smectite
air-dry d_{001} (Å)
16.0
15.6
15.2
14.8
14.4
14.0
1870
1910
1950
1990
year
(b) Low smectite, illite/smectite
air-dry d_{001} (Å)
13.5
13.1
12.7
12.3
11.9
11.5
1870
1910
1950
1990
year
(c) 'illite'
air-dry d_{001} (Å)
12.0
11.6
11.2
10.8
10.4
1870
1910
1950
1990
year
● Control
□ $(NH_4)_2SO_4$
▲ $NaNO_3$

Fig 8:

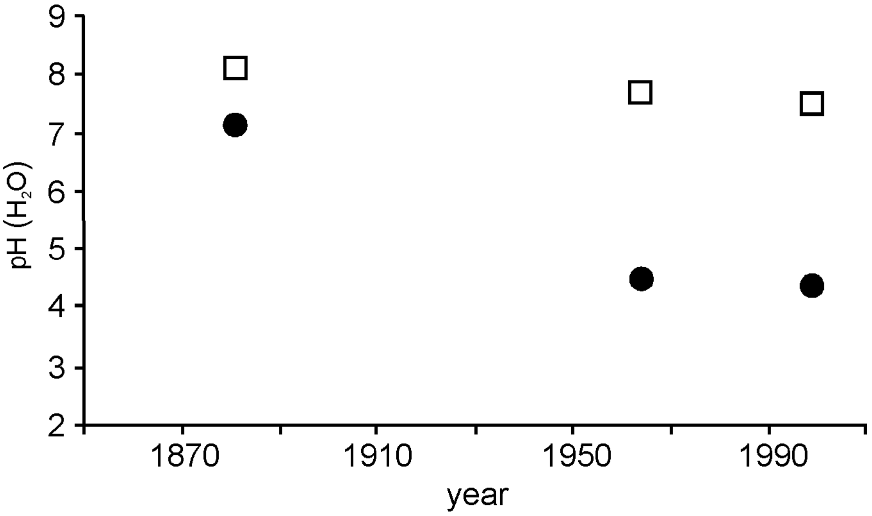
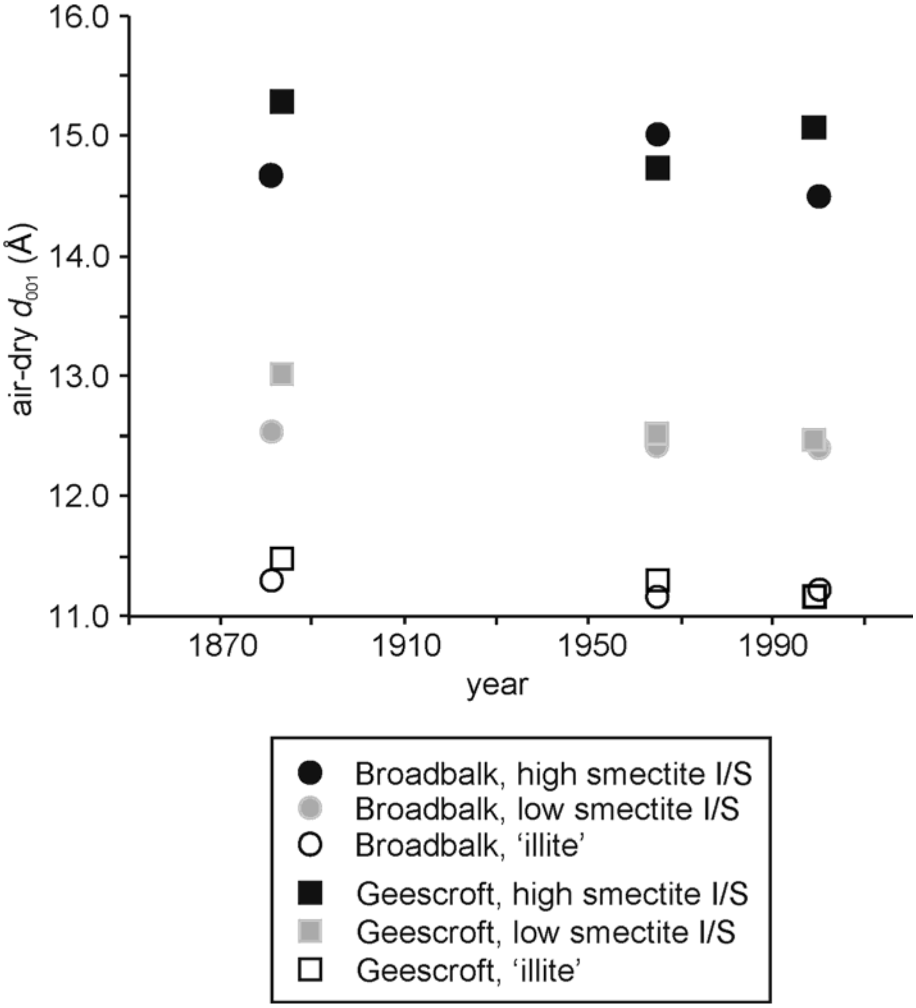


Fig 9:


16.0
15.0
14.0
13.0
12.0
11.0
air-dry d_{001} (Å)
1870
1910
1950
1990
year
● Broadbalk, high smectite I/S
● Broadbalk, low smectite I/S
○ Broadbalk, 'illite'
■ Geescroft, high smectite I/S
■ Geescroft, low smectite I/S
☐ Geescroft, 'illite'