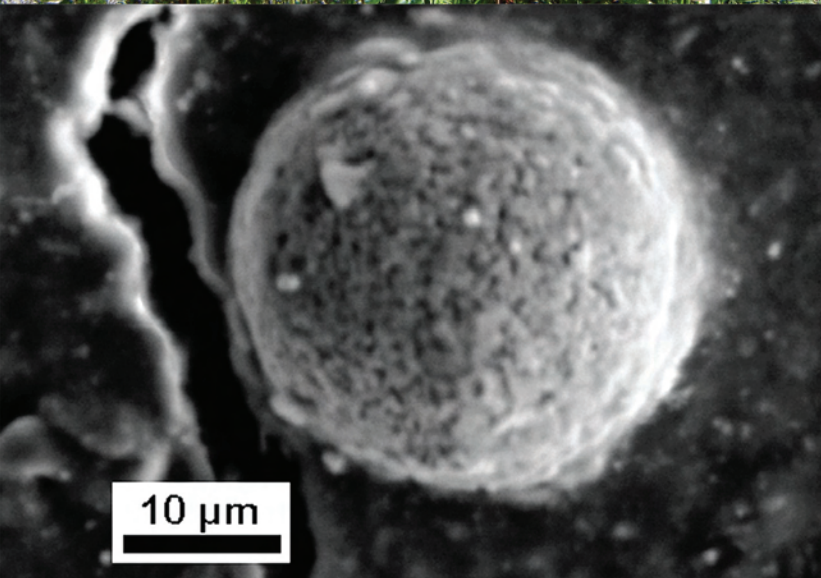


# Mineralogy and chemistry of sandy acid sulfate soils in the Perth metropolitan area of the Swan Coastal Plain



Department of  
Environment and Conservation



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Mineralogy and chemistry of sandy acid sulfate  
soils in the Perth metropolitan area of  
the Swan Coastal Plain

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## **Executive Summary, Finding and Recommendations**

Acid sulfate soils (ASS) are a major issue for urban development on the Swan Coastal Plain. Soils on Swan Coastal Plain have the potential to become actual acid sulfate soils unless the watertable is maintained at a suitable level to prevent the oxidation of acid generating sulfide minerals. Up until recently, the management of acid sulfate soils in Western Australia has been based on methodologies and conceptual models developed in Queensland and New South Wales. However, the acidity issue in the Bassendean Dunes is different from most other areas in Australia where sulfide minerals are predominantly associated with silty- or clayey-textured soils. The acid sulfate soil management criteria developed on the eastern seaboard are not appropriate for the Bassendean Dunes. As a consequence of this, the Department of Environment and Conservation (DEC) has carried out a survey of ASS occurrence in the Perth metropolitan area. The purpose of the study reported here was to support the survey by providing detailed characterisation of the identified soil materials. A particular aim was also to characterise sulfidic materials in soils that show ASS field indicators but have sulfur content lower than the current action criteria for ASS management.

All samples and associated field data were provided by DEC for geochemical and mineralogical analysis. Field data and bulk sulfur analysis of the representative samples was interpreted in conjunction with detailed physico-chemical and mineralogical properties measured using a range of modern chemical, X-ray diffraction and electron optical techniques. Physico-chemical measurements included total chemical composition, extractable cations, cation exchange capacity, batch titrations and incubations studies. Synchrotron x-ray diffraction and electron microscopy (SEM and TEM) were used to detect and characterise the nature of sulfidic materials in soils which have bulk sulfur content lower than the current action criteria.

These investigations indicated that sandy soils in the Perth metropolitan area are dominated by quartz, which has no capacity to buffer soil pH. The limited pH buffering capacity present is provided by organic matter, allophane  $(Al, Fe)_2O_3(SiO_2)_{1.3-2}(H_2O)_{2.5-3}$ , kaolin, gibbsite and Fe-oxides which have high surface area with exposed hydroxyl. Primary minerals (feldspar, ilmenite etc) are minor constituents of these soils and are sand-size and essentially insoluble so they do not provide any effective buffering capacity. The poor pH buffering capacity of these sandy soils is also demonstrated by batch titrations and cation exchange capacity measurements. No carbonates were

detected in soils developed on the highly leached Bassendean Dune System. Therefore, any acid generating event, such as the oxidation of sulfide minerals, is expected to have a strong impact on lowering the soil pH.

Synchrotron X-ray diffraction (SXR) investigations of the soil fine concentrates revealed that acidifying sulfur minerals are commonly present in the permanently water-logged soil horizons below the groundwater table. Pyrite is the main acid-generating mineral while elemental sulfur and marcasites also occur as minor constituents in some horizons with high organic matter content. Pyrite occurs in all horizons (including E, B and coffee rock, mud, peat and C horizons) that are water-logged and show low  $pH_{FOX}$ . No pyrite was detected by SXR technique in soil horizons above the water table but very small amounts of pyrite were detected by TEM in some of these materials.

Abundant jarosite was found in soil fines of unsaturated zones of soil profiles (mainly the A horizon). Where present, its occurrence was consistent with field observations of low soil pH (~4.0) and yellow brown mottles.

Scanning and transmission electron microscope investigations of the fine fractions were consistent with SXR investigations. Pyrite is commonly present as particles of various sizes and shapes in water-logged section of the soil profiles. The two most common morphologies present are framboids of 1-10  $\mu m$  diameter and sub-micron sized single crystals. Both framboids and single crystals appeared to have growth related pores/cavities, suggesting high surface area and thus potentially high reactivity of these pyrites. A combination of high reactivity of pyrite and extremely low pH buffering capacity of these soils makes them prone to acidification during even a short exposure (less than a week) to air during temporary excavation or dewatering.

A subset of samples represented soil profiles with low sulfur content (<0.03%S) while their  $pH_{FOX}$  was in the range of 1.8 to 2.5. Based on the experience in other parts of country, soils with such low  $pH_{FOX}$  are expected to have sulfur content greater than ASS action criteria (0.03% $S_{CR}$ ). In the Perth metropolitan area, however, such sandy soils often have sulfur content less than the current action criterion (0.03% $S_{CR}$ ) which allows these to be disturbed without the requirement of a management plan. Analytical electron microscopy has demonstrated the presence of microcrystalline pyrite in these soils. Low  $pH_{FOX}$  is therefore attributed to a combination highly reactive nature of microcrystalline pyrite and extremely poor buffering capacity of the Bassendean sands. Such minor amounts of acid-generation potential would not normally be of concern but

the extremely small acid buffering capacity of some Bassendean Dune materials results in significant reductions in pH on oxidation. The  $\text{pH}_F$  and  $\text{pH}_{\text{FOX}}$  tests are considered helpful in identifying the type of ASS. The  $\text{pH}_{\text{FOX}}$  test provides useful information on the potential acidity of poorly buffered soil samples where Cr-S is not often detected using normal laboratory techniques.

## Findings

1. Based on the SXRD patterns, acidifying sulfur minerals are commonly present in soil horizons below the groundwater level. The fine fraction samples above groundwater level (mainly A horizon) contain jarosite whereas the fine fraction of samples below groundwater level (including E, B and coffee rock, mud, peat and C horizons) contain pyrite as the main acid-generating mineral. Elemental sulfur and marcasite occur as minor constituents in some horizons which have a high organic matter content.
2. Scanning electron microscope and transmission electron microscope results for the fine fractions show that iron sulfide is present in all water logged soil horizons that recorded  $\text{pH}_{\text{FOX}} < 3$ . It occurs as particles of various sizes and shapes including 1-10  $\mu\text{m}$  framboids and single crystal pyrite ( $\leq 1 \mu\text{m}$ ) which have high surface area and are thus potentially very reactive. Some materials directly above the groundwater level can contain very small amounts of pyrite and can become acidic when oxidized.
3. Some acidifying samples have very low  $S_{\text{CR}}$  (lower than detection limit  $< 0.005\%$ ) and sulfur minerals could not be detected synchrotron x-ray diffraction, we have demonstrated their presence using analytical electron microscopy.
4. Such minor amounts of acid-generation potential would not normally be of concern but the extremely small acid buffering capacity of some Bassendean Dune materials results in significant reductions in pH on oxidation.  $\text{pH}_F$  and  $\text{pH}_{\text{FOX}}$  tests are helpful in identifying the type of acid sulfate soil. The  $\text{pH}_{\text{FOX}}$  test provides excellent information on the potential acidification of poorly buffered soil samples where Cr-S is not detected.
5. Buffering of acidity is provided by organic matter, allophane ( $(\text{Al}, \text{Fe})_2\text{O}_3(\text{SiO}_2)1.3-2(\text{H}_2\text{O})_{2.5-3}$ ), kaolin, gibbsite and Fe-oxides which have high surface area with exposed hydroxyl. Primary minerals (feldspar, ilmenite etc) are

minor constituents of these soils and are sand-size and essentially insoluble so they do not provide effective buffering capacity.

## Recommendations

The key recommendations for managing pyritic very sandy; quartz-rich soils are as follow:

1. Acid sulfate soils on the Bassendean Dunes system should be managed appropriately, including undertaking chemical analysis before disturbance or drainage. We have established that even when the Cr reducible S content of these soils is at or below the current sandy-textured soil action criterion ( $0.03\%S_{CR}$ ), sufficient S compounds are generally present in these soils to trigger acidification on oxidation. These S compounds are responsible for observed low  $pH_{FOX}$  and would also cause low soil pH on natural oxidation if these soils are disturbed.
2. An inexpensive and easy method for identifying ASS occurrence is to use the field peroxide ( $pH_{FOX}$ ) test to assess the potential acidity risk. By selecting the soils that record low  $pH_{FOX}$  values, further laboratory confirmatory analysis at a detection limit of  $0.005\%S_{CR}$  can be undertaken to confirm that these soils contain low levels of sulfide minerals.
3. Based on this investigation, we recommend that a combination of  $pH_{FOX} < 3$  and an analytical value of  $0.01\%S_{CR}$  or greater are excellent indicators of ASS and can be used as a basis for managing of potential ASS in the Bassendean Dune System.

Summary of  $S_{CR}(\%)$  analyses of some pyrite containing materials and the evaluation of these samples by direct mineralogical methods to determine if the  $S_{CR}(\%)$  value is a reliable indicator of the presence of pyrite.

Sample No	Site	Horizon	Depth (cm)	$pH_F$	$pH_{FOX}$	$S_{CR}(\%)$	SXRD	SEM	TEM
N_01	616-01-05	B horizon	620-630	5.5	2.7	0.014	✘	✓ <sup>d</sup>	✓ <sup>d</sup>
N_02	616-02-68	B horizon	450	7.2	1.8	0.027	✓ <sup>e</sup>	✓ <sup>e</sup>	✓ <sup>e</sup>
N_04	616-02-179	B horizon	375-400	6.1	1.6	0.013	✓ <sup>e</sup>	✓ <sup>e</sup>	✓ <sup>e</sup>
N_06	616-02-78	B horizon	400-500	4.8	1.5	0.014	✓ <sup>e</sup>	✓ <sup>e</sup>	✓ <sup>e</sup>
N_07	616-02-81	B horizon	400-800	6.2	1.4	0.052	✓ <sup>e</sup>	✓ <sup>e</sup>	✓ <sup>e</sup>
N_08	616-02-110	B horizon	200-500	6.3	1.8	0.036	✓ <sup>e</sup>	✓ <sup>e</sup>	✓ <sup>e</sup>
N_09	616-02-174	B horizon	250-550	5.5	2.5	<0.005	✘	✓ <sup>d</sup>	✓ <sup>d</sup>
N_10	616-02-65	B horizon	200	5.7	3.0	0.005	✘	✘	✓ <sup>d</sup>

✘ = non detectable pyrite; ✓ = detectable pyrite, d = difficult to detect pyrite, e = easy to detect pyrite

SXRD = synchrotron XRD, SEM = scanning electron microscopy with EDS, TEM = transmission electron microscopy with EDS.

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## 1. Objectives and Aims

The main objectives are to:

1. Characterise and quantify sulfur forms in Bassendean Dune soils that are not detected by the current standard laboratory methods and
2. Understand forms of acidity in the topographic sequence of the Bassendean Dune system in the Perth region, including the Gnangara and Jandakot Mounds

The specific aims of this project as defined by DEC are to:

1. Determine the amounts and forms of acidity and pH buffering of Bassendean soils at non-wetland locations;
2. Characterise forms of sulfur in landscapes with low potential sulfidic acidity ( $S_{CR}$ ) content;
3. Evaluate the adequacy of the current acidity trigger value of 0.03%S for assessing stored acidity in the Bassendean Dune System using a combination of physical and chemical methods for mineral analysis; and
4. Determine the latent acidity in waterlogged horizons of other soil types on the SCP and adjacent Darling Range

## 2. Introduction

Perth, Western Australia, relies heavily on the aquifers in the Bassendean Sand on the Swan Coastal Plain for potable and irrigation water. The two main sources of potable water are the Gnangara Mound to the north of Perth and the Jandakot mound, to the south. These supply about 40 to 45% of metropolitan drinking water. The soils of swales in these mounds are the subject of this report. The various descriptions and discussions below are based on the following literature (Salama *et al.*, 2005; McArthur, 2004).

In the Perth region, the Swan Coastal Plain is on the eastern onshore edge of the Perth Basin, extending between Geraldton in the north and Dunsborough in the south. It is bounded to the west by the Indian Ocean and by the Gingin, Darling and Whicher Scarps to the east. The surficial materials of the Swan Coastal Plain are predominately alluvium and three major sand dunes deposits. The youngest and most western dune system is the calcareous Quindalup Dune System. Next in sequence, inland is the Spearwood Dune System with orange earthy sand overlying calcarenite. Finally and most easterly are the purely siliceous Bassendean dunes. The dunes are all from the Quaternary period and all have been deposited adjacent to beaches by aeolian processes



(McArthur, 2004). Between and within the dune systems, inlets, lakes and swamps occur. The swales may be occupied by swamps and lakes so rich in organic matter, that they frequently contain peats (Salama *et al.*, 2005).

The Bassendean Dunes have low relief with minor variations in topography, which translate to a variable depth to the water table. Low hills of siliceous sand are interspersed with poorly drained swale areas including both seasonal and permanent swamps. The depth to ground-water varies from close to the surface to at most 10 m below the surface. The water is suitable for irrigation. This dune system originated along a coastline, and probably consisted of calcareous sand, but leaching has continued for so long (about 800,000 years old) that all carbonate has been lost and the steep relief characteristic of beach dunes has been modified. The highly leached soils are infertile and acidic. Three types of Bassendean sand soil profiles have been identified reflecting depth to watertable: the Jandakot, Gavin and Joel sands (McArthur, 2004).

Acid sulfate soils (ASS) are a major issue for urban developments on Swan Coastal Plain regions. Soils on Swan Coastal Plain have the potential to become actual acid sulfate soils unless the watertable is maintained at a suitable level to prevent the oxidation of acid generating minerals. Management of acid sulfate soils has been based on Queensland and New South Wales models; however, the acidity issue in the Bassendean Dunes are different from other areas with clayey soils. To manage poorly buffered, pyritic quartz-rich soils special criteria that are suitable for Bassendean Dunes system soil types need to be developed.

During the past ten years it has been recognised that the cause of acidification in drying Bassendean Dune podosols is the oxidation of pyrite and possibly other reduced minerals present in these soils. Unfortunately the nature and distribution of these minerals is poorly understood and is the focus of the present investigation. The very low acid buffering capacity of Bassendean Dune soils is unable to neutralise the acidity produced by oxidation so the nature of the buffering capacity also requires investigation.

The extent to which pyrite containing soil materials may occur in wet horizons under other landscape elements of the Bassendean Dunes, and particularly “downstream” of organic-rich wetlands is unknown.

During recent years it has become evident that drying of humic podosols in Bassendean Dune soils in and adjacent to swale positions due to lowered water table levels has caused acidification of groundwater. This is of concern because:

- (i) acidification degrades metals, concrete and other infrastructure and the acid impact of dewatering and excavation can extend to considerable distances from the site of operations
- (ii) acid groundwater kills vegetation and irrigation with acid water containing dissolved Al, As and possibly other toxic elements is undesirable.
- (iii) Bassendean Dune aquifers provides a considerable proportion of Perth's drinking water and must not be contaminated by acid water from oxidised podosols.
- (iv) the ecologically unique lakes within and adjacent to the Bassendean Dunes become acid and inhospitable as they dry and the organic sediments and adjacent soils are aerated resulting in catastrophic damage to the ecology of the lakes.
- (v) the standard chemical methods for assessing the amounts of pyrite in soils are unsuitable for detecting the low concentrations of pyrite present in humus podosols. It is important to critically evaluate the validity of the chemical methods and to develop more appropriate criteria for use by developers and regulators.

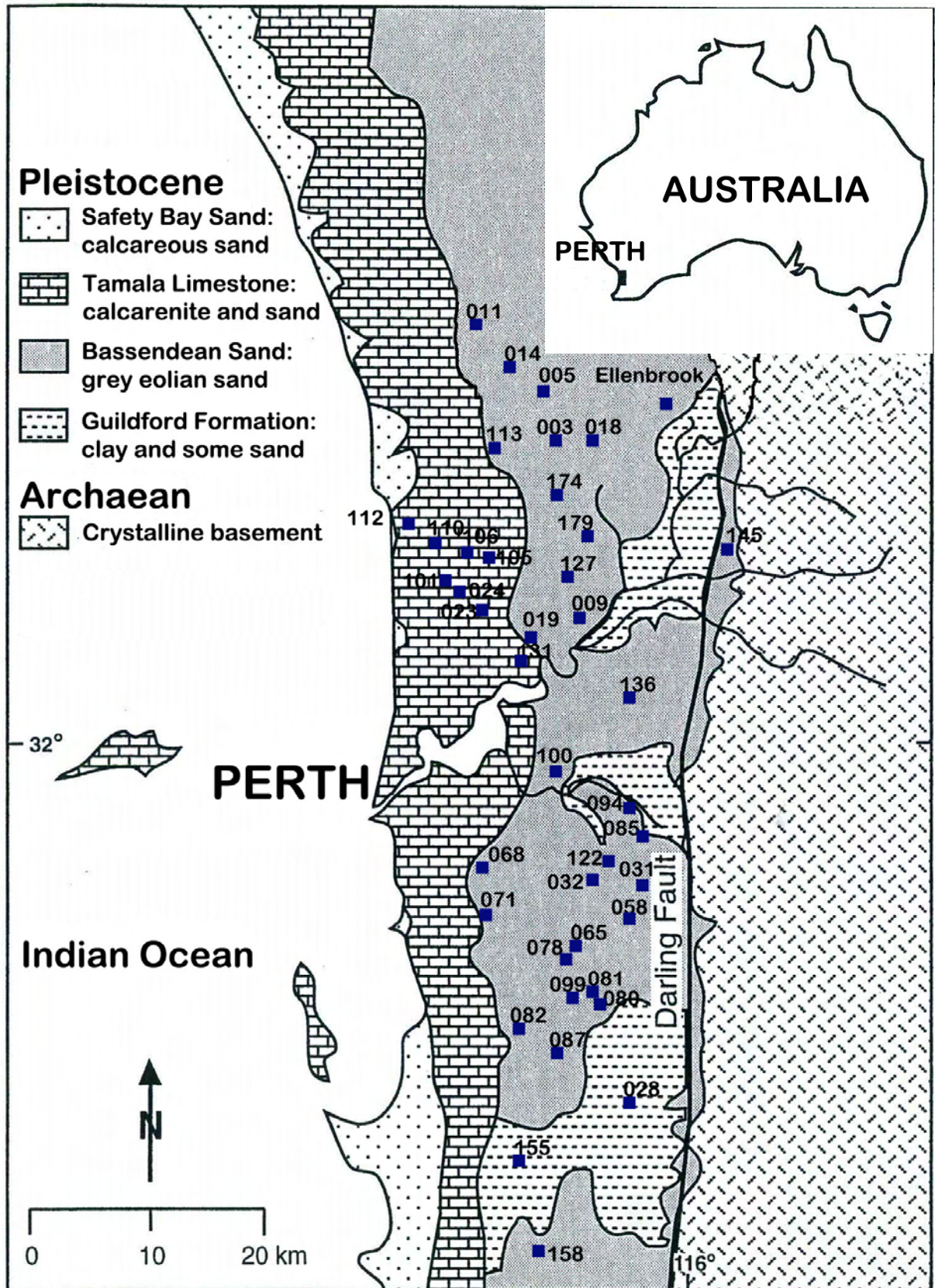
### 3. Materials and methods

#### 3.1 Soil selection

Sites for investigation were selected and sampled by Department of Environment and Conservation staff. The main geological formations of the superficial units are the Tamala Limestone, Bassendean Sand, Guildford Formation and Safety Bay Sand. All soil samples were selected and sampled soils in swales and were mostly below ground water level. The total samples represent 41 profiles, with 186 samples including A horizon (25 samples), E horizon (64 samples), B horizon (39 samples), coffee rock (31 samples), mud (6 samples), peat (10 samples) and C horizon (11 samples). All studied sites are shown in Appendix Table 1 and Figure 1. Soil samples from sites 003, 005, 009, 011, 014, 018, 019, 031, 032, 058, 065, 068, 071, 078, 080, 081, 082, 085, 087, 094, 099, 100, 113, 122, 127, 136, 145, 158 174, 179 and Ellenbrook were collected from the Bassendean Sand, soil samples from sites 023, 024, 101, 105, 106, 110, 112, 131 were from acidic sandy swales in the Tamala Limestone mapping unit. Soil profiles at sites 028, 155 were from Guildford Formation (Figure 1) (Thierrin *et al.*, 1991).

#### 3.2 Soil reaction (pH), electrical conductivity (EC) and H<sub>2</sub>O<sub>2</sub> oxidation

After collection all soils were kept in a cool room and enclosed so as to exclude air and remain wet. However in many instances this did not prevent partial oxidation during extraction, transport and storage of cores. Soil pH and EC were determined in water for a soil: solution ratio of 1: 5 and soil pH CaCl<sub>2</sub> was measured in 0.01N CaCl<sub>2</sub> at a 1: 5 solid to solution ratio. Sodium fluoride solution (1N NaF) was adjusted to pH 8.5, and used to measure soil pH at a solid to solution ratio of 1: 5. The pH H<sub>2</sub>O<sub>2</sub> reaction with soil was done with 4 mL of peroxide solution and 2 g of soil samples (1: 2 soil to solution). The pH of the 30% hydrogen peroxide solution was adjusted to 5.5 with 0.1M NaOH. The contents were stirred with a glass rod for 30 minutes before measuring the pH with a standardized pH meter (National Soil Survey Centre, 1996).



**Figure 1** Sampling locations for podosols on the Bassendean Dune System on the Swan Coastal Plain, WA. Note that several locations investigated in this research are acidic sandy swales in the Tamala mapping unit or alluvium belonging to the Guildford Formation.

### **3.3 Total C and N**

Ground oven dried soil weighing 300 mg was placed on tin foil and total carbon and nitrogen determined using a Vario Macro elemental analyzer.

### **3.4 Cation exchange capacity (CEC)**

One to two grams of whole wet soil (<2 mm) depending on texture was placed in a 50 mL screw-top centrifuge container and least two blank samples were prepared. Forty mL of 0.01M silver thiourea (AgTU)<sup>+</sup> was added, stoppered securely and mechanically shaken end-over-end at approximately 25°C for 16h. The extract was centrifuged until a clear supernatant was obtained. The supernatant was diluted depending on the CEC value. An aliquot (0.100 mL) of original supernatant soil extract was pipetted into a 10 mL polypropylene screwtop tube, and 9.9 mL of MQ water added from a calibrated dispenser. The same procedure was followed with the (AgTU)<sup>+</sup> standard. Ag absorbance at 338.3 nm was measured by AAS. CEC-AgTU values are reported on a 105°C oven-dry basis.

### **3.5 Extractable Fe, Al, Mn, Si**

#### **3.5.1 Dithionite-Citrate-Bicarbonate (DCB) extractable Fe, Al, Mn, Si**

The amounts of Fe, Al, Mn, Si extracted from soils by various dissolution methods (so called specific reagents) are commonly taken to indicate particular solid state forms of these elements in soil. The results are useful in studies of soil classification, soil genesis and soil behaviour. The DCB extractant removes virtually no Fe, Al or Mn from most crystalline silicate minerals, and thus provides an estimate of “free oxide” (e.g. non layer silicate mineral Fe, Al, Mn, Si) in soils.

One gram of whole wet soil (< 2 mm) was weighed into a 50 mL centrifuge tube to which 45 mL of buffer solution (0.3 M Na-citrate + 0.1 M Na bicarbonate) were added. The tube was then placed in a water bath at 70°C. One gram of Na-dithionite powder was added to the tube, the mixture was stirred constantly for 1 minute and occasionally during next 15 minutes. The tube contents were centrifuged for 15 minutes at 2000 rpm. Clear supernatant was decanted into a 250 mL volumetric flask. This extraction procedure was repeated twice, then the volume was made up to 250 mL with deionized water and the solution was kept for further analysis. For determination of Fe, Al, Mn, Si by atomic

absorption spectrophotometry (AAS), standard solutions of these elements were prepared in a matrix of extracting solution.

### **3.5.2 Oxalate extractable Fe, Al, Mn, Si**

A sample of one gram of whole wet soil (<2 mm) was weighed into a 25 mL centrifuge tube, 10 mL of 0.2 M ammonium oxalate solution at pH 3.0 were added to the tube, the tube was shaken for 4 h in darkness. Next five drops of 0.4% Superfloc were added to the tube, which was swirled and then centrifuged, clear supernatant was kept for further analysis by AAS. Predicted allophane content was calculated from  $Si_o (g\ kg^{-1}) \times 100)/13.3$ .

### **3.5.3 Pyrophosphate extractable Fe, Al, Mn, Si**

Various organic complexes of Fe, Al, Mn, Si occur in soils. Pyrophosphate solution has been used to extract these organic complexes. A subsample of 1 g of whole wet soil (<2 mm) was weighed into a 50 mL shaking tube and 30 mL of 0.1M sodium pyrophosphate solution was added before shaking overnight.

The tube contents were centrifuged for 15 minutes at 2000 rpm and the clear supernatant was kept for measurement of Fe, Al, Mn, Si by AAS.

### **3.6 Extractable sulfate (Turbidimetric method)**

A sample of five grams of whole wet soil (<2 mm) was weighed into a 50 mL centrifuge tube, 20 mL of extraction solution (0.5N ammonium chloride + 0.06 g  $Ca(OH)_2$ ) was added to the tube. The tube was shaken for 15 minutes at high speed (250 oscillations per minute). The extract was filtered using Whatman 42 filter paper. A 5 mL aliquot of supernatant soil extract was pipetted into a 10 mL polypropylene screwtop tube, 1 mL of seed solution (210 mL of 100 ppm  $SO_4$  stock solution + 2 mL conc. HCl + 13.87 g  $NH_4Cl$  in 500 mL) was added and 1 mL of precipitation solution (225 g barium acetate + 100 mL acetic acid in 1 L), contents were mixed by slow inversion. The extracts were poured into polystyrene cuvetts and allowed to stand for 10 minutes. The extract was analysed on a spectrophotometer at 550 nm.

### **3.7 Chromium-reducible sulfur method ( $S_{CR}$ )**

The standard chromium-reducible sulfur method of (QASSIT *et al.*, 2004) was used for  $S_{CR}$  determinations (detection limit = 0.005%).

### **3.8 Total element analysis (X-ray fluorescence)**

The element composition (total analysis) of Si, Al, Ti, Fe, Mn, Ca, K, Mg, Na, P, S, V, Ni, Cu, Zn, Rb, Sr, Ba, Zr, Co, As, La and Pb was determined for some samples using a Philips P1400 XRF spectrometer fitted with a rhodium tube. Soil samples were finely ground and heated at 105°C overnight then 0.700 g of sample was fused with 7.000 g of lithium meta/tetraborate flux at 1050°C in a platinum crucible and cast into a disc for analysis.

### **3.9 Mineralogical properties**

A sample of twenty grams of whole wet soil was weighed into a 50 mL centrifuge tube, 20 mL of DI water and a few drop of chloroform was added to the tube to suppress microbial activity. The fine fraction was dispersed by ultrasonic treatment and separated by sedimentation.

#### **3.9.1 Synchrotron XRD**

Powder samples of the fine fraction of soils were mounted into glass capillaries, and analysed over an angular range of 4 - 60° 2Theta. The wavelength was set at ~1.0Å to provide for adequate dispersion/resolution and provided a high peak/background for identifying minor constituents.

#### **3.9.2 Conventional XRD**

Minerals were determined by X-ray diffraction (XRD) analysis using a Philips PW- 3020 diffractometer with a graphite diffracted beam monochromator (CuK $\alpha$ , 50 kV, 20 mA). The fine fraction of soils was scanned from 4 to 65° 2 $\theta$ , using a step size of 0.02° 2 $\theta$  and a scan speed of 0.04° 2 $\theta$  sec<sup>-1</sup>.

#### **3.9.3 Differential X-ray powder diffraction (DXRD)**

X-ray powder diffraction (XRD) patterns of the fine fraction of samples before and after oxalate treatment were obtained with a Philips PW 3020 diffractometer using monochromated CuK $\alpha$  radiation. Differential XRD patterns (DXRD) were obtained using the Traces program.

### **3.10 Inductively coupled plasma optical emission spectrometry**

The chemical composition of strong acid extracts of whole oven dried soil samples was determined using inductively coupled plasma optical emission spectrometry (ICP-OES). For this aqua regia digestion, 0.25 g of fine ground whole dried soil was dissolved in 2 mL of conc. HNO<sub>3</sub> and 5 mL of conc. HCl at 130°C for 1 h. The volume was made to 20 mL mark with MQ water. Supernatant was transferred into suitable clean and marked vials and analysed by ICP-OES. Data were assessed for accuracy and precision using a rigorous control system including reagent blanks and a certified international reference material (STSD-1). The aqua regia digestion only dissolves a small part of the resistant sand size minerals (particularly quartz), thus the results represents amounts of trace elements present in the fine fraction. For fusion acid digestion method, 0.1 g of fine ground whole dried soils was fused with 1 g of lithium meta/tetraborate flux at 1050°C in a platinum crucible and then dissolved in 100 mL 10% HCl. The solution was transferred into suitable clean vials and analysed by ICP-OES.

### **3.11 Transmission electron microscopy (TEM)**

For analytical transmission electron microscopy (TEM), specimens were prepared from dispersed samples. A highly diluted suspension of the fine fraction was prepared in distilled water and dispersed by ultrasonic treatment. A drop of the suspension was deposited onto a carbon-coated Cu grid and examined using a JEOL 3000 electron microscope operated at 300 kV.

For elemental analysis, electron diffraction and morphology of particles single crystals on carbon film were investigated using a JEOL 3000 transmission electron microscope operated at 300 kV. Energy dispersive spectra (EDS) for well separated single crystals were collect at 500-1500 counts per second for 100 live seconds.

### **3.12 Scanning electron microscopy (SEM)**

#### **3.12.1 Thin section preparation**

This was done by putting the soil sample in an aluminium tray and impregnating with a polyester resin. When the resin polymerized, it hardened to produce a compact block that encompasses the soil sample, conserving its natural structure with no alteration.



To ensure that the resin penetrates well; impregnation of the samples was carried out under vacuum. After the sample had been impregnated and hardened, cutting and polishing was done with oil as a lubricant to avoid dissolving soluble minerals (e.g. gypsum). Firstly, the impregnated soil was cut with a diamond cut-off saw to obtain a flat surface. The cut surface was polished to eliminate traces of cutting and to obtain a flat surface that is as smooth as possible. The polished surface was stuck onto a glass microscope slide with a colourless, isotropic cementing agent, and then cut to obtain a thin slice. The slice was trimmed and polished until it had a thickness of about 30 microns and so was suitable for both optical and SEM examination.

### **3.12.2 Fine fraction deposited on a stub**

A sample of ten grams of whole wet soil was weighed into a 50 mL centrifuge tube, 20 mL of DI water and a few drop of chloroform was added to the tube to suppress microbial activity. The fine fraction was dispersed by ultrasonic treatment and separated by sedimentation. A drop of the suspension was deposited on a carbon tape which adhered to an aluminium stub and was examined using a JEOL 6400 SEM.

### **3.12.3 Analysis of thin sections**

Samples were coated with carbon prior to examination using a backscattered electron image and elemental mapping on a JEOL 6400 SEM operated at a 15 kV electron beam accelerating voltage. Electron microprobe analysis (EMPA) and energy dispersive spectroscopy (EDS) provided quantitative microanalysis to determine the chemical composition of distinct micromorphological features (matrix, grains).

## **3.13 Incubation**

Three laboratory incubation methods including standard method (USA/ Australian standard methods) (Isbell, 2002; Soil Survey Staff, 2006), nearly saturated soil and moist soil methods were used for this study. For standard and nearly saturated soil methods, all soil materials had at uniform thickness of 10 mm. The 20 mm thickness of soil samples were used for the moist soil method. All incubation soil materials were incubated for 12 months, the pH measured every day for 8 days, after that pH was measured every week for 8 weeks, and measured every month until 12 months. Water contents were maintained throughout the observation period.

### 3.14 Batch titration

The present investigation is a part of a comprehensive study by DEC in which changes in soil and solution chemistry are being monitored to evaluate progressive acidification. An important component of this work is the assessment of the acid buffering capacity of acidifying materials. The acid buffering capacity of soil materials was investigated in a laboratory titration experiment. Briefly, in the batch titration experiment, 50 ml of water or a  $\text{H}_2\text{SO}_4$  solution (0.0012, 0.0036, 0.0060, 0.0072, 0.0144 and 0.0288M for coffee rock and B horizon corresponding to acid loads of 24-576  $\text{mmol H}^+ \text{kg}^{-1}$  and 0.000005, 0.000010, 0.000025, 0.000050, 0.000075 and 0.00010M for other soil horizons corresponding to acid loads of 0.1-2.0  $\text{mmol H}^+ \text{kg}^{-1}$ ) was added to a set of 5-g whole wet soil samples in centrifuge tubes, shaken and pH was measured immediately. The pH values after  $\text{H}_2\text{O}_2$  oxidation were then used in conjunction with the titration curves for establishing the amount of  $\text{H}^+$  required to reach this pH. For the batch titration against alkali experiment, the studied soils were oxidised by  $\text{H}_2\text{O}_2$  before the measurements were made. 50 ml of water or a NaOH solution (0.00001, 0.0012, 0.0024, 0.0048, 0.0072, 0.0120, 0.0144 and 0.0288M for coffee rock and B horizon corresponding to alkali loads of 0.1-288  $\text{mmol OH}^- \text{kg}^{-1}$  and 0.00001, 0.00002, 0.00005, 0.00010, 0.00015, 0.00020, 0.00030M for other soil horizons corresponding to base loads of 0.1-3.0  $\text{mmol OH}^- \text{kg}^{-1}$ ) was added to a set of 5-g whole wet soil samples (after  $\text{H}_2\text{O}_2$  treatment) in centrifuge tubes and pH was measured immediately. The initial pH  $\text{H}_2\text{O}$  of the soil was used for the end point to calculate from the titration curve the amount of  $\text{OH}^-$  required to neutralise the acidity released by  $\text{H}_2\text{O}_2$  addition.

#### 4. Macromorphology and soil classification

Soil morphology properties such as texture and colour can be related to potential acidification. For example, sandy soils have poorly buffering capacity whereas clayey soils have the ability to neutralise acidity. The soil horizons vary in morphology in response to drainage status and in particular depth to groundwater. However, most soil horizons have sand texture (quartz rich soils), except for B and coffee rock horizons which may be loaming sand. Most soil horizons have little buffering capacity due to their sand texture.

Where the relief is very low and where the water table is within 2 m of the surface an iron-humus podosol forms often with the B horizon being partly cemented. In the lowest topographic sites, which are subject to seasonal flooding, the soil is a humus podosol (Isbell, 2002) often with a strong cemented dark brown B horizon (coffee rock) which is a spodic horizon. The soils examined in this project are all located in these low-lying sites. Dr. Balbir Singh selected and sampled all representative podosol materials for the detailed examination of materials described in this report. All studied sites are shown in Appendix Table 1 and Figure 1. The podosols occur in swale sites in Tamala Limestone, Bassendean Sand and Guildford Formation mapping units (Thierrin *et al.*, 1991).

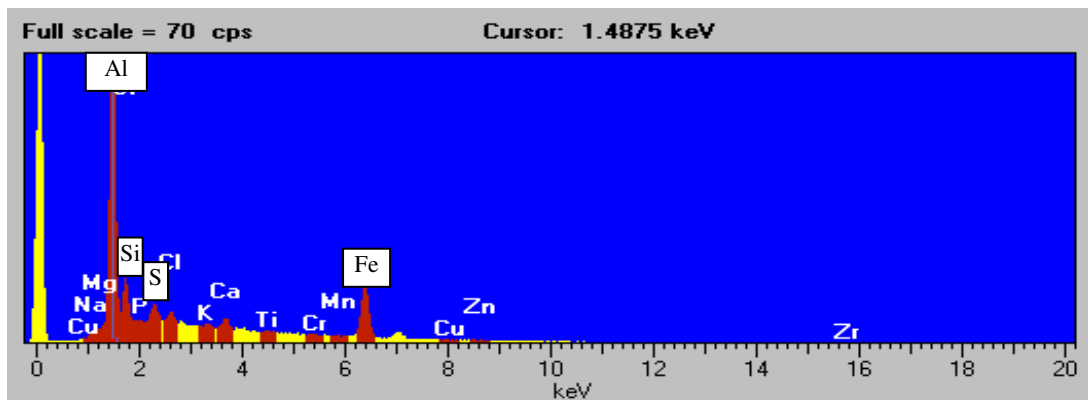
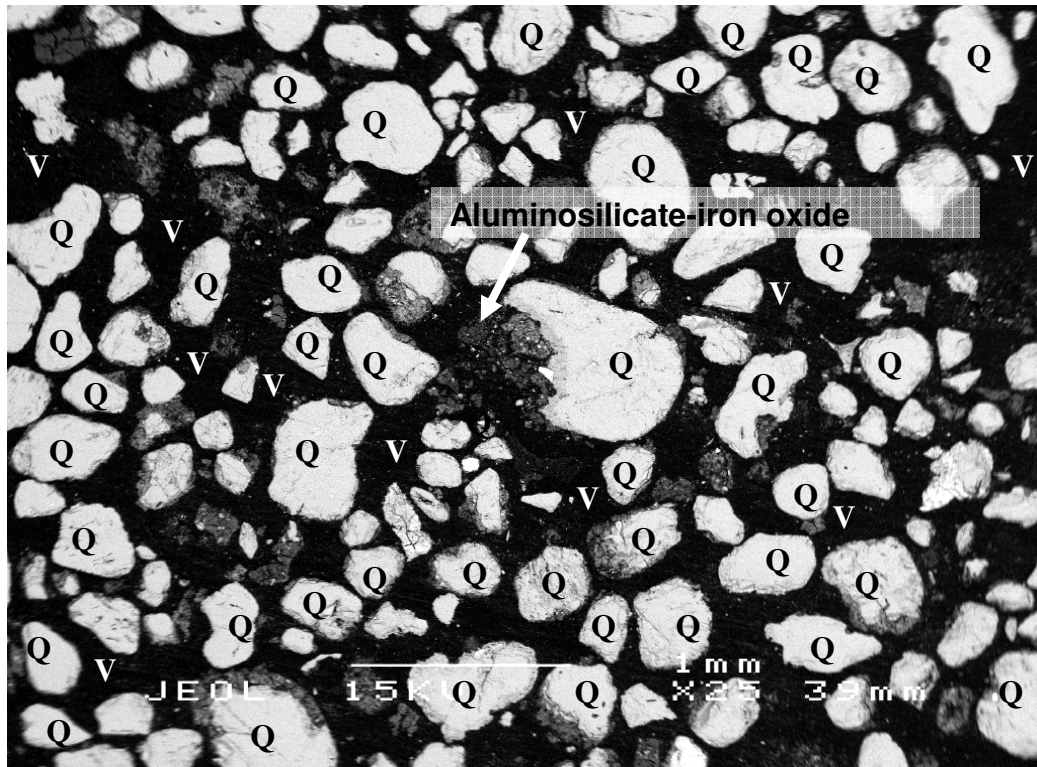
Most studied soils are Podosols<sup>1/</sup>. Present models of podzolisation emphasize the mobilization and precipitation of dissolved organic matter, together with Al(-silicates) and Fe. All the soil profiles are deep (Appendix Figure 1). The moisture condition of all soils is aquic<sup>2/</sup> (Isbell, 2002; Soil Survey Staff, 2006). Most studied soils are poorly drained, exhibiting a 2.5YR to 10YR hue with low chroma colour ( $\leq 2$ ) resulting from the reduction/ oxidation cycles imposed over many years (Appendix Figure 1). The distribution of redoximorphic features indicates that many of these soils are permanently saturated with water in all layers.

These profiles represent an extreme stage of leaching reflecting their age, the substantial annual rainfall (about 800 mm at present) and the very high sand content (>95%) of the parent material.

<sup>1/</sup> Soil with B horizons dominated by the accumulation of compounds of organic matter, aluminium and/or iron. These soils are recognised world-wide, and Australia is particularly noted for its 'giant' forms (Isbell, 2002).

<sup>2/</sup> Soils with long-term saturation in the B horizon. The saturation may be caused as in the semiaquic soils but the duration is of the order of months. The period of saturation is sufficient to reduce most iron compounds and move them out of the B horizon, hence Bh horizons are usually prominent (Isbell, 2002).

Soil texture is sand except for some B, coffee rock, alluvial mud and peat horizons. B horizon and coffee rock have a loamy sand texture due to the high organic matter and allophane contents. The sand grains of the Bassendean Dune System are characteristically well rounded and are well sorted which indicates that the sand came ashore after transport and sorting by water and was then further sorted by wind (Figure 2).



**Figure 2** SEM backscattered electron image and x-ray spectrum of matrix material a thin section from coffee rock (1.8-2.0 m) site 616-01 -03 (Q = quartz, V = void). The matrix material is a complex of amorphous aluminosilicate, iron oxides and organic matter cementing together rounded and well sorted quartz grains.

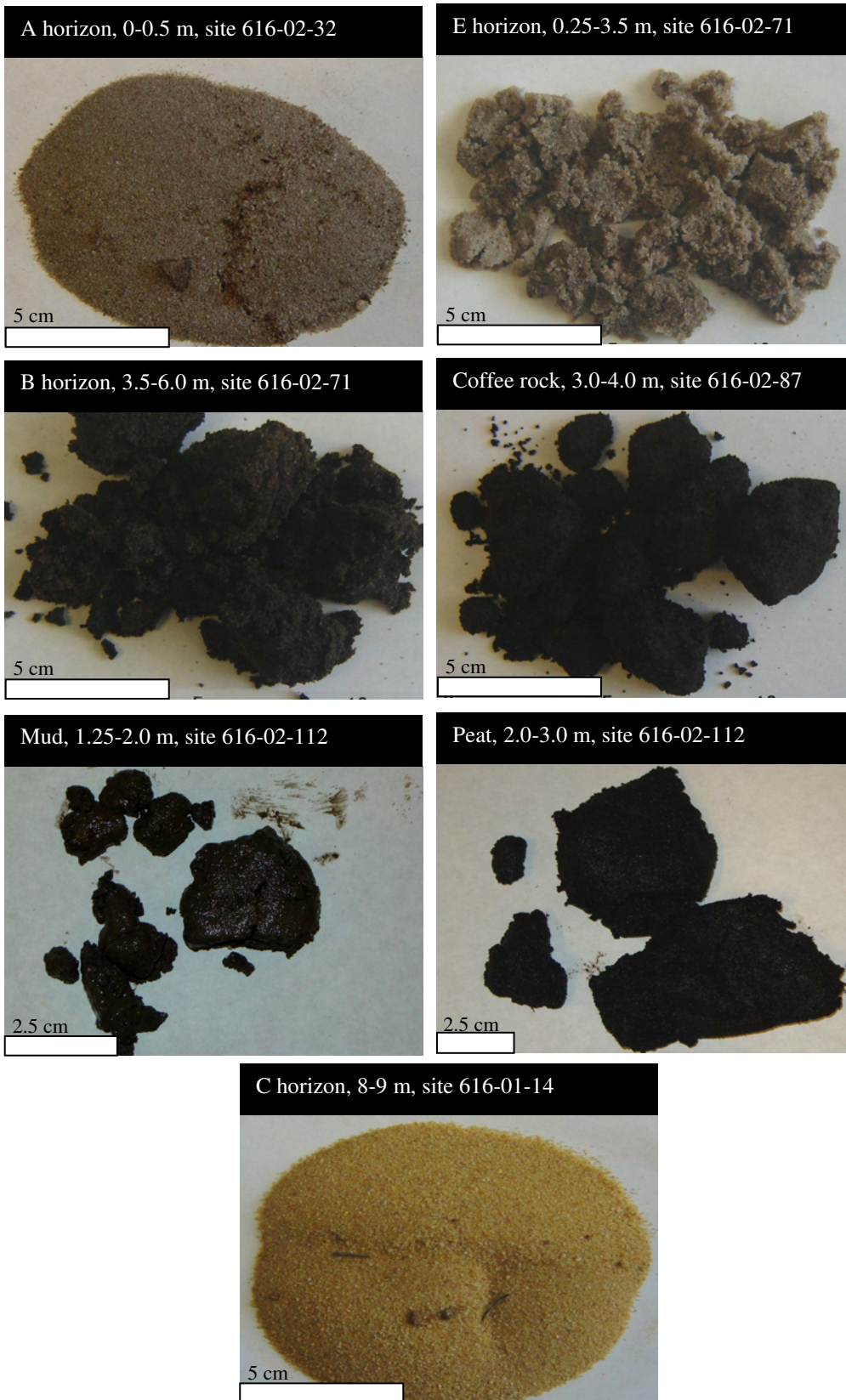
Some soil profiles (Site 616-01-05, 616-01-18 and 616-02-31) show distinct deep sub-soil horizons (2E horizon and 2coffee rock) which indicates that these soil profiles are buried palaeopodosols. The summary of soil classification (Soil orders) for this study is shown in Appendix Figure 1. Soil profiles have a high diversity in macromorphological properties, descriptions of each soil profile are shown in Appendix Figure 1.

Hand specimens of A horizon, bleached E horizon, brown B horizon, strong dark cemented B horizon (coffee rock), mud, peat and C horizon are shown in Figure 3. This figure is a useful guide to the recognition of podosol materials.

- A horizon: the A horizon of all soils is relatively rich in organic matter.
- E horizon: A horizon is underlain by grey quartz sand which becomes increasingly bleached with depth.
- B1 horizon: below the bleached sand is the illuvial B horizon which is highly porous sand coloured brownish gray to brownish black but which does not contain cemented material.
- B2, coffee rock: the coffee rock is sand which has a dark colour (yellowish brown to black), high organic matter and is strongly cemented. There appears to be a reduced porosity within the coffee rock due to the precipitation of iron oxyhydroxide, organic matter and aluminosilicate-organic complexes. The formation of coffee rock is related to the zone of watertable fluctuation.
- Mud: mud is a wet clayey (dark gray to black) which is soft and adhesive (sometime shelly). It is of rare occurrence and represents Recent alluvium.
- Peat: An unconsolidated deposit of partially decomposed plant matter, in a water-saturated environment. Peat is spongy and has a very dark black colour
- C horizon: the parent material consisting of dune sand (light brownish gray to yellowish brown).

The morphological properties of soil materials are very important for management because the occurrence and oxidation rate of acid generating minerals and acid buffering capacity depend on soil composition. Moreover, soil morphology has a strong relationship with the position of groundwater in the soil profile. For example, coffee rock is formed mainly in the zone of watertable fluctuation.

(NB at some locations buried podosols (palaeosols) are present and contain several horizons)



**Figure 3** Hand specimens of representative A, E, B, coffee rock, mud, peat and C horizons.

## 5. Results

### 5.1 Chemical properties

Table 1 shows the chemical properties of these soils. Soil pH in 1: 5 H<sub>2</sub>O varies between pH 4.2 - pH 8.8 for the A horizon, pH 2.6 - pH 8.6 for E horizon, pH 2.5 - pH 8.7 for the B horizon, pH 3.6 - pH 6.6 for coffee rock, pH 2.9 - pH 8.9 for mud, pH 2.4 - pH 7.6 for peat and pH 4.7 - pH 8.2 for the C horizon (Table 1 and Appendix Figure 2).

Most values of pH (1: 5) CaCl<sub>2</sub> are substantially lower than pH (1: 5) H<sub>2</sub>O with an average difference of 0.56. Soil pH in 1: 5 CaCl<sub>2</sub> varies between pH 3.2 - pH 7.8 for the A horizon, pH 2.6 - pH 7.5 for E horizon, pH 2.5 - pH 7.9 for the B horizon, pH 3.0 - pH 5.7 for coffee rock, pH 2.6 - pH 8.4 for mud, pH 2.1 - pH 7.6 for peat and pH 4.1 - pH 8.0 for the C horizon (Table 1 and Appendix Figure 3).

The pH of the H<sub>2</sub>O<sub>2</sub> solution used to extract the soils is pH 5.5. The range of pH (H<sub>2</sub>O<sub>2</sub>) is pH 1.5 - pH 8.1 with the rare high values being for calcareous alluvium. Soil pH H<sub>2</sub>O<sub>2</sub> varies between pH 2.1 - pH 6.4 for the A horizon, pH 1.9 - pH 7.8 for E horizon, pH 1.8 - pH 8.1 for the B horizon, pH 1.9 - pH 5.3 for coffee rock, pH 1.7 - pH 7.7 for mud, pH 1.5 - pH 6.4 for peat and pH 3.3 - pH 7.6 for the C horizon (Table 1 and Appendix Figure 4). Delta pH (pH H<sub>2</sub>O - pH H<sub>2</sub>O<sub>2</sub>) ranges from 0.010-4.4 unit, high values being indicative of the presence of sulfide (Soil Survey Staff, 2006).

The pH in sodium fluoride solution ranges upward from pH 8.2 and provides an estimate of the content of exposed hydroxyl on organic matter, sesquioxides and poorly ordered alumino-silicate minerals. It thus provides an indication of acid buffering capacity. Mostly pHNaF of soil samples is higher than pHH<sub>2</sub>O except for an A horizon sample (site 616-01-23) where the pHH<sub>2</sub>O is higher than pHNaF 0.15 unit. The pHNaF values range from 1.2 - 7.9 unit higher than pHH<sub>2</sub>O.

Soil pHNaF varies between pH 7.5 - pH 11.5 for the A horizon, pH 7.5 - pH 11.7 for E horizon, pH 6.8 - pH 12 for the B horizon, pH 6.8 - pH 12 for coffee rock, pH 9.2 - pH 11.5 for mud, pH 6.4 - pH 11.5 for peat and pH 8.3 - pH 11.5 for the C horizon (Table 1 and Appendix Figure 5). The pH NaF values range from 1.3 - 5.4 unit (mean = 3.1 unit) higher than pH H<sub>2</sub>O for A horizon, 1.2 - 7.3 unit (mean = 4.4 unit) for E horizon, 1.7 - 7.9 unit (mean = 5.3 unit) for B horizon, 2.8 - 7.8 unit (mean = 6.0 unit) for coffee rock, 2.6 - 6.3 unit (mean = 3.9 unit) for mud, 1.2 - 7.3 unit (mean = 4.3 unit) for peat and 2.0 - 5.0 unit (mean = 3.9 unit) for C horizon.

Clearly, coffee rock and B horizon materials have high amounts of surface OH<sup>-</sup> which will provide substantial anion and cation exchange sites (buffering capacity).

The organic carbon content is mostly low in E and C horizons ranging between 0.016 - 1.2%. The organic carbon content of A, B, and coffee rock horizons is higher (ranging from 0.05 - 3.6%) (Table 1 and Appendix Figure 6). The organic carbon of the supposed peat samples ranges from 0.41 - 51%, the lower values clearly indicate that some of these materials are not strictly peats (Isbell, 2002) so we have used the term (peat E horizon transition zone; PETZ). The high carbon content in mud and a few C horizon samples may reflect the presence of carbonate. The nitrogen content is mostly low in all samples (0.00046 - 0.85%) except for peat (0.025 - 1.73 %) (Table 1 and Appendix Figure 7). Cation exchange capacity values for A, B, coffee rock, mud and peat horizon are quite high (median between 1.4 - 8.0 meq/ 100 g soil) except for E and C horizons (median 0.60-0.69 meq/ 100 g soil) (Table 1 and Appendix Figure 8). There are close positive statistical relationships between C% and N% (Figure 4) and between C% and CEC (meq/ 100 g soil) (Figure 5) as is usual for soils (McArthur, 2004). Most soil samples have a low soluble sulfate content (less than 200 mg kg<sup>-1</sup>) (Table 1 and Appendix Figure 9).

Electrical conductivity (EC 1: 5) values are mostly low (less than 4100 μS/ cm) but some higher values occur including the alluvial mud samples representing slightly to moderately saline materials (Table 1 and Appendix Figure 10). There is no close relationship between soluble sulfate and EC (Table 1).



**Table 1** Chemical properties of soil samples.

Site	Horizon	Depth (cm)	pH H <sub>2</sub> O	pH CaCl <sub>2</sub>	pH H <sub>2</sub> O <sub>2</sub> *	ΔpH**	pH NaF***	C	N	CEC	SO <sub>4</sub> <sup>2-</sup> ****	EC
								(-----%------)	meq/100g	mg kg <sup>-1</sup>	(μS/cm)	
616-01-003	A horizon	0-25	6.3	5.5	4.9	1.4	8.6	0.92	0.03	3.60	11	62
616-01-003	Coffee rock	175-200	4.6	4.0	2.8	1.9	11.7	2.58	0.07	1.93	41	41
616-01-003	C1 horizon	200-300	5.1	4.3	5.0	0.1	10.1	0.28	0.01	1.05	47	18
616-01-003	C2 horizon	300-400	5.7	4.7	5.2	0.5	9.6	0.07	0.00	1.47	39	18
616-01-003	C3 horizon	400-600	6.3	5.7	4.7	1.6	8.3	0.02	0.00	0.96	30	27
616-01-005	B horizon	620-630	5.0	4.5	2.8	2.2	10.4	0.30	0.03	0.34	127	19
616-01-005	A horizon	0-20	5.7	4.8	4.1	1.6	7.8	2.94	0.07	5.21	11	44
616-01-005	E horizon	20-180	5.4	4.0	5.2	0.3	8.2	0.11	0.01	0.57	30	16
616-01-005	Coffee rock	180-200	5.0	3.9	4.3	0.6	11.5	1.77	0.05	1.52	23	23
616-01-005	B horizon	200-250	4.9	3.7	4.3	0.6	8.8	0.48	0.01	1.39	14	17
616-01-005	2E1 horizon	250-260	4.4	3.3	4.0	0.4	8.1	1.18	0.03	2.79	40	24
616-01-005	2E2 horizon	260-400	4.2	3.1	3.8	0.4	7.7	1.11	0.03	2.34	46	27
616-01-005	2E3 horizon	400-500	5.1	3.5	3.4	1.6	7.8	0.08	0.00	0.61	42	14
616-01-005	2E4 horizon	500-830	4.6	3.8	2.6	2.0	8.1	0.18	0.00	0.49	19	29
616-01-005	2Coffee rock1	830-900	5.3	4.1	4.8	0.4	10.6	0.53	0.01	0.92	24	36
616-01-005	2Coffee rock2	900-1000	5.5	4.2	4.9	0.6	11.2	0.62	0.01	1.04	19	31
616-02-009	E1 horizon	225-250	3.8	3.8	3.0	0.8	10.4	0.06	0.01	0.35	79	80
616-02-009	E2 horizon	325-350	2.9	2.9	2.5	0.4	9.3	0.05	0.01			792
616-01-011	A horizon	0-75	5.7	4.7	4.0	1.7	7.8	1.32	0.05	2.94	11	36
616-01-011	E1 horizon	75-500	6.0	4.4	5.2	0.8	8.0	0.04	0.00	0.07	20	16
616-01-011	E2 horizon	500-600	6.1	4.5	4.4	1.6	8.0	0.04	0.00	0.73	16	16
616-01-011	E3 horizon	600-700	4.0	3.8	2.6	1.4	8.0	0.05	0.00	0.35	85	90
616-01-014	A horizon	0-50	6.4	5.7	4.8	1.7	8.3	0.41	0.01	1.23	11	37
616-01-014	E1 horizon	50-300	6.1	5.2	5.2	0.9	8.0	0.09	0.00	0.39	48	23
616-01-014	E2 horizon	300-650	6.4	5.6	5.5	0.9	10.3	0.07	0.01	1.01	18	19
616-01-014	Coffee rock	650-800	6.3	5.7	5.3	1.0	10.4	0.10	0.01	1.00	28	61
616-01-014	C1 horizon	800-900	6.3	5.4	5.4	0.9	10.3	0.07	0.00	1.33	18	17
616-01-014	C2 horizon	900-1000	6.4	5.5	5.4	1.0	10.8	0.13	0.01	0.41	25	20
616-01-014	C3 horizon	1000-1200	6.3	5.2	5.4	0.9	9.1	0.02	0.00	0.30	32	16
616-01-014	C4 horizon	1200-1300	5.0	4.1	4.9	0.2	9.3	0.02	0.00	0.69	32	23
616-01-018	A horizon	0-25	7.4	6.6	5.3	2.1	8.7	0.31	0.01	2.14	11	40
616-01-018	E1 horizon	25-200	4.4	3.6	3.7	0.6	7.9	0.55	0.01	2.02	32	39
616-01-018	E2 horizon	200-300	4.4	3.7	4.4	0.0	8.2	0.65	0.01	1.18	44	32
616-01-018	E3 horizon	300-400	4.8	3.9	4.6	0.2	8.1	0.22	0.01	0.83	44	27
616-01-018	Coffee rock	400-450	4.2	4.0	3.8	0.3	11.5	1.40	0.03	1.15	44	56
616-01-018	2E horizon	450-600	4.6	4.2	4.0	0.6	10.1	0.21	0.01	0.31	29	39
616-01-018	2Coffee rock1	600-700	5.3	4.5	3.0	2.3	10.7	0.30	0.01	0.76	22	42
616-01-018	2Coffee rock2	700-800	5.0	4.5	3.9	1.1	11.7	0.67	0.01	0.70	46	49
616-01-019	A horizon	0-50	4.7	3.2	3.1	1.7	7.6	0.58	0.02	0.79	43	26
616-01-019	E1 horizon	50-200	5.4	3.7	4.1	1.3	8.1	0.09	0.01	0.62	11	20
616-01-019	E2 horizon	200-250	6.1	4.5	2.8	3.3	8.4	0.14	0.01	1.11	13	23
616-01-019	B horizon	250-300	4.2	4.0	3.5	0.7	12.1	2.19	0.06	1.13	74	74

\*pH H<sub>2</sub>O<sub>2</sub> adjusted to 5.5, \*\* Δ pH = pH H<sub>2</sub>O-pH H<sub>2</sub>O<sub>2</sub>, \*\*\* pH NaF adjusted to 8.2, \*\*\*\* Turbidimetric method (0.5 N ammonium chloride extraction)

**Table 1** (Cont.) chemical properties of soil samples.

Site	Horizon	Depth (cm)	pH H <sub>2</sub> O	pH CaCl <sub>2</sub>	pH H <sub>2</sub> O <sub>2</sub> *	ΔpH**	pH NaF***	C	N	CEC	SO <sub>4</sub> <sup>2-****</sup>	EC
								(-----%-----)	meq/100g	mg kg <sup>-1</sup>	(μS/cm)	
616-01-023	A horizon	0-25	8.8	7.8	5.9	2.9	8.7	0.13	0.02	2.30	10	81
616-01-023	E horizon	25-100	6.6	5.0	4.4	2.2	8.4	0.05	0.01	0.51	46	35
616-01-023	B horizon	100-200	5.1	4.2	4.4	0.8	9.5	0.06	0.01	0.34	18	22
616-01-023	C1 horizon	200-300	5.8	4.5	4.2	1.6	10.4	0.13	0.02	0.30	15	20
616-01-023	C2 horizon	300-500	4.7	4.3	3.8	0.9	8.8	0.02	0.01	0.07	23	37
616-01-023	C3 horizon	500-1000	4.9	4.2	3.3	1.5	8.9	0.03	0.01	0.64	34	43
616-01-024	A horizon	0-25	6.0	4.4	3.8	2.2	7.5	1.01	0.03	3.12	10	35
616-01-024	E horizon	25-150	5.4	3.8	3.8	1.7	7.9	0.20	0.01	0.78	15	43
616-01-024	B horizon	150-200	4.8	3.8	3.8	1.1	9.1	0.35	0.02	1.59	13	25
616-01-024	2E horizon	200-400	6.0	4.7	4.5	1.4	8.6	0.03	0.01	0.10	18	23
616-01-024	2B horizon	400-500	5.5	4.4	3.3	2.2	11.7	0.83	0.02	1.34	19	39
616-01-024	3E horizon	500-800	5.9	4.7	4.3	1.6	8.7	0.04	0.01	0.89	19	124
616-02-028	B horizon	30-100	3.5	3.5	2.6	0.9	9.1	0.17	0.03	0.84	146	383
616-02-028	Mud1	100-200	2.9	2.6	1.7	1.2	9.2	2.65	0.15	6.15	376	5540
616-02-028	Mud2	200-250	7.3	7.3	6.1	1.2	11.2	4.53	0.16			4420
616-02-028	Mud3	250-400	7.4	7.2	6.2	1.2	11.0	5.46	0.22			5800
616-02-028	Mud4	400-600	7.4	7.2	3.5	3.9	10.8	3.02	0.17			5190
616-02-031	A horizon	0-75	5.3	3.9	3.9	1.4	7.5	2.29	0.08	5.26	5	23
616-02-031	E horizon	75-200	5.5	4.0	5.1	0.4	7.9	0.08	0.00	0.48	0.48	18
616-02-031	Coffee rock1	200-300	5.5	4.5	3.6	1.9	11.3	2.04	0.06	5.78	51	647
616-02-031	Coffee rock2	200-300	5.7	4.5	3.9	1.8	11.3	1.65	0.04	3.93	96	466
616-02-031	2E horizon	300-400	4.1	4.1	1.9	2.3	9.0	0.08	0.00	0.16	225	168
616-02-031	2Coffee rock1	400-500	5.5	4.7	2.1	3.5	10.9	0.49	0.01	1.83	367	206
616-02-031	2Coffee rock2	500-600	6.1	4.8	3.1	2.9	10.9	0.56	0.01	1.74	262	135
616-02-032	A horizon	0-50	8.4	7.3	6.0	2.4	10.0	0.72	0.02	3.02	11	120
616-02-032	E horizon	50-200	4.2	3.6	4.2	0.1	7.8	0.28	0.00	0.41	45	65
616-02-032	Coffee rock1	160	4.0	3.0	3.0	1.0	6.8	2.99	0.05	5.46	44	61
616-02-032	Coffee rock2	200-300	4.1	3.6	3.0	1.1	10.5	2.62	0.05	2.38	48	60
616-02-032	2E1 horizon	300-350	4.1	3.2	3.1	1.0	7.5	0.84	0.02	1.66	62	82
616-02-032	2E2 horizon	350-400	4.6	3.4	3.1	1.5	7.6	1.03	0.02	2.01	40	55
616-02-058	B horizon	300-500	5.1	3.5	2.5	2.6	6.8	3.27	0.07	4.65	30	61
616-02-065	B horizon	200	5.4	4.9	3.6	1.8	10.9	2.16	0.13	5.72	115	128
616-02-065	Peat/ E horizon (PETZ)	0-20	5.6	4.9	3.9	1.8	11.5	2.60	0.13	7.29	61	267
616-02-065	Peat/ E horizon (PETZ)	20-180	5.1	4.5	3.9	1.2	11.1	1.63	0.05			87
616-02-065	B1 horizon	180-350	3.2	3.5	2.2	1.0	9.5	0.19	0.02			167
616-02-065	B2 horizon	350-480	3.4	3.6	2.3	1.2	9.5	0.44	0.02			171
616-02-065	Coffee rock1	480-560	4.5	4.2	3.0	1.5	11.5	1.91	0.04	4.75	85	263
616-02-065	Coffee rock2	560-650	4.8	4.4	3.3	1.5	11.7	0.92	0.02			136
616-02-065	Coffee rock3	650-700	4.5	4.2	2.8	1.7	11.0	0.42	0.02	1.00	120	136
616-02-065	Coffee rock4	700-800	4.2	4.1	2.5	1.7	10.8	0.64	0.02			185

\*pH H<sub>2</sub>O<sub>2</sub> adjusted to 5.5, \*\* Δ pH = pH H<sub>2</sub>O-pH H<sub>2</sub>O<sub>2</sub>, \*\*\* pH NaF adjusted to 8.2, \*\*\*\* Turbidimetric method (0.5 N ammonium chloride extraction)

**Table 1 (Cont.)** chemical properties of soil samples.

Site	Horizon	Depth (cm)	pH H <sub>2</sub> O	pH CaCl <sub>2</sub>	pH H <sub>2</sub> O <sub>2</sub> *	ΔpH**	pH NaF***	C	N	CEC	SO <sub>4</sub> <sup>2-****</sup>	EC
								(-----%-----)	meq/100g	mg kg <sup>-1</sup>	(μS/cm)	
616-02-068	B horizon	450	3.2	3.5	2.2	0.9	10.0	0.09	0.02	0.21	62	173
616-02-068	A horizon	0-75	6.0	4.5	3.8	2.2	8.0	0.24	0.02	0.82	48	45
616-02-068	E1 horizon	75-300	6.4	5.2	5.1	1.3	8.0	0.03	0.01	0.08	18	35
616-02-068	E2 horizon	300-375	6.4	5.4	2.1	4.4	8.8	0.09	0.01	0.59	74	54
616-02-068	E3 horizon	375-600	6.3	5.1	2.2	4.1	8.4	0.04	0.01	0.53	76	58
616-02-068	A horizon	0-25	5.1	4.2	3.9	1.2	9.3	0.31	0.02	0.17	77	18
616-02-068	E horizon	25-200	5.8	5.1	4.1	1.6	10.3	0.02	0.01	1.07	39	14
616-02-068	coffee rock	200-300	3.9	3.7	2.4	1.5	9.9	0.64	0.02	0.00	147	280
616-02-068	B1 horizon	300-400	3.4	3.4	2.5	0.9	10.0	0.09	0.01		157	340
616-02-068	B2 horizon	400-500	3.1	3.4	2.2	0.9	9.9	0.07	0.01			355
616-02-068	B3 horizon	500-600	3.0	3.4	2.3	0.7	9.2	0.04	0.01	0.37	188	468
616-02-068	B4 horizon	600-700	2.7	2.9	2.1	0.5	9.0	0.05	0.01			812
616-02-068	B5 horizon	700-800	2.6	2.9	2.1	0.5	9.0	0.04	0.01			865
616-02-071	E horizon	25-350	6.9	6.1	5.3	1.6	8.1	0.06	0.01	0.44	15	50
616-02-071	B horizon	350-600	5.8	4.4	1.8	4.0	8.1	0.58	0.03	1.50	75	52
616-02-078	B horizon	400-500	3.2	3.6	2.2	1.0	9.7	0.14	0.02	0.21	122	142
616-02-080	Coffee rock	200-400	6.6	5.3	4.2	2.3	10.5	1.92	0.05	6.50	60	84
616-02-081	B horizon	400-800	3.0	3.4	2.0	1.0	9.1	0.22	0.03	0.40	66	341
616-02-082	A horizon	0-75	6.1	4.5	3.7	2.4	8.4	0.05	0.01	0.95	42	29
616-02-082	E1 horizon	75-200	5.4	4.2	3.1	2.3	8.4	0.06	0.01	0.43	46	31
616-02-082	E2 horizon	200-300	4.4	4.2	1.9	2.5	8.5	0.08	0.01	0.76	368	91
616-02-082	B horizon	300-400	4.5	4.2	2.1	2.4	8.6	0.08	0.01	0.50	327	121
616-02-082	2E horizon	400-500	4.1	4.0	2.0	2.2	8.6	0.07	0.01	0.68	303	152
616-02-082	Coffee rock	500-600	4.1	4.1	1.9	2.2	8.8	0.10	0.01	1.00	617	183
616-02-085	A horizon	0-70	6.3	6.1	5.6	0.7	10.6	2.97	0.26	11.30	71	75
616-02-085	B1 horizon	100-300	4.6	4.2	3.0	1.6	10.0	0.16	0.03	2.53	73	99
616-02-085	B2 horizon	300-400	2.7	2.9	2.3	0.4	9.4	0.04	0.01	0.05	181	1320
616-02-085	Mud	400-600	6.5	6.1	3.1	3.5	10.4	2.55	0.14	10.15	134	2290
616-02-087	Coffee rock1	200-300	6.1	5.1	3.9	2.2	12.0	2.31	0.05	2.56	43	77
616-02-087	Coffee rock2	300-400	6.1	4.7	4.3	1.8	11.9	3.57	0.08	6.88	28	71
616-02-087	B horizon	500-600	6.0	4.8	2.2	3.8	8.3	0.25	0.01	0.78	76	48
616-02-094	A1 horizon	0-100	4.8	4.0	2.7	2.1	9.4	0.73	0.08	4.32	67	91
616-02-094	A2 horizon	100-175	4.6	3.8	3.0	1.6	9.9	0.14	0.02	2.24	61	72
616-02-094	E horizon	175-600	3.6	3.6	2.5	1.1	10.0	0.07	0.02	0.33	165	432
616-02-099	E horizon	25-200	6.2	5.4	4.9	1.3	10.2	0.53	0.06	2.08	109	86
616-02-099	B1 horizon	200-300	5.9	5.5	2.8	3.1	10.1	0.20	0.02	1.60	188	141
616-02-099	B2 horizon	300-400	2.7	2.5	2.0	0.7	9.0	0.37	0.02	0.00	389	1988
616-02-099	2E horizon	400-600	3.3	3.0	2.5	0.7	9.0	0.02	0.00			456
616-02-100	A horizon	0-80	7.6	7.4	6.4	1.2	11.2	0.66	0.04	0.00	128	271
616-02-100	Peat	80-110	6.0	5.7	2.9	3.1	9.7	6.90	0.36	8.61	634	661
616-02-100	Peat/ E horizon (PETZ)	110-200	3.2	3.2	2.3	0.9	10.5	0.41	0.03	0.46	351	1189
616-02-100	E horizon	200-600	3.5	3.4	3.1	0.4	10.3	0.03	0.01	0.23	76	138

\*pH H<sub>2</sub>O<sub>2</sub> adjusted to 5.5, \*\* Δ pH = pH H<sub>2</sub>O-pH H<sub>2</sub>O<sub>2</sub>, \*\*\* pH NaF adjusted to 8.2, \*\*\*\* Turbidimetric method (0.5 N ammonium chloride extraction)

**Table 1 (Cont.)** chemical properties of soil samples.

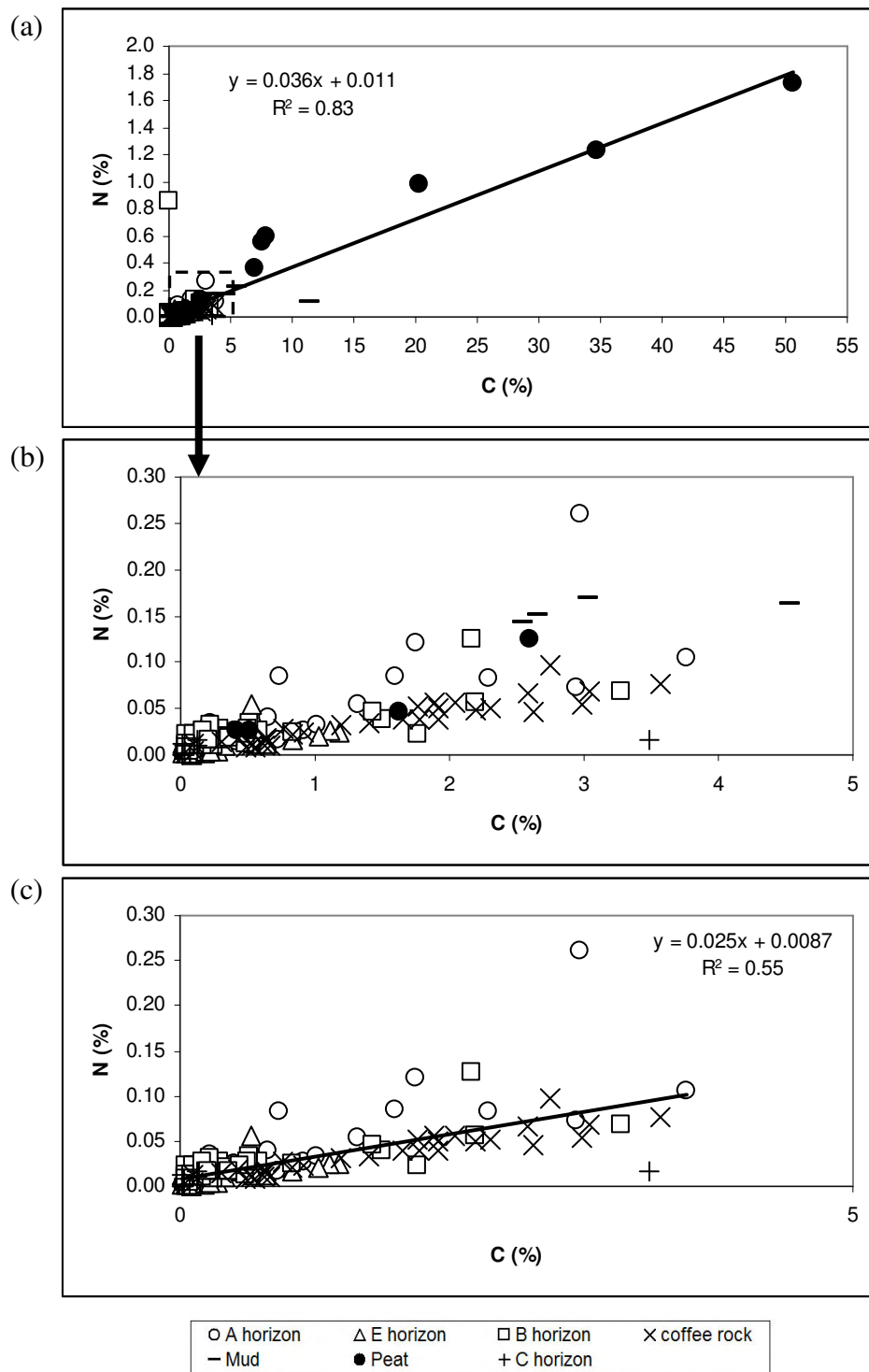
Site	Horizon	Depth (cm)	pH H <sub>2</sub> O	pH CaCl <sub>2</sub>	pH H <sub>2</sub> O <sub>2</sub> *	ΔpH**	pH NaF***	C	N	CEC	SO <sub>4</sub> <sup>2-****</sup>	EC
								(-----%-----)	meq/100g	mg kg <sup>-1</sup>	(μS/cm)	
616-02-101	A horizon	0-75	8.0	7.0	5.9	2.1	10.5	0.40	0.03	2.79	310	92
616-02-101	Peat1	150-200	7.6	7.7	6.4	1.2	10.9	20.29	0.98	11.92	217	858
616-02-101	Peat/ E horizon (PETZ)	200-350	6.5	6.1	4.0	2.5	8.7	7.88	0.60			389
616-02-101	E horizon	350-600	3.0	3.0	2.5	0.6	9.0	0.05	0.01	0.41	192	720
616-02-105	A horizon	0-160	7.4	7.0	5.4	2.0	11.0	1.59	0.08	7.49	99	101
616-02-105	Peat	250-360	2.4	2.1	1.5	0.9	6.4	34.69	1.22	8.00	667	11
616-02-105	Peat/ E horizon (PETZ)	360-480	2.9	2.7	1.8	1.0	8.9	0.51	0.03	1.24	362	11
616-02-105	E horizon	480-700	5.9	6.1	5.0	0.9	10.4	0.03	0.01	0.28	47	1494
616-02-106	A horizon	0-50	4.2	3.7	2.1	2.2	8.6	3.76	0.11	3.52	137	29
616-02-106	E horizon	50-700	3.3	3.0	2.5	0.8	9.2	0.04	0.01	0.00	196	547
616-02-110	B horizon	200-500	7.2	7.2	6.5	0.7	11.4	1.76	0.02	2.94	89	601
616-02-112	B horizon	25-80	8.6	7.9	8.1	0.5	11.5	0.00	0.86	4.96	115	901
616-02-112	Mud	125-200	8.9	8.4	7.7	1.2	11.5	11.44	0.11	5.57	135	1691
616-02-112	Peat	200-300	6.7	7.1	3.9	2.8	7.8	50.65	1.73	11.51	239	4
616-02-112	Bb horizon	300-400	8.0	7.7	6.8	1.2	11.1	1.51	0.04	6.83	155	669
616-02-112	C horizon	400-600	8.2	8.0	7.6	0.6	11.5	3.49	0.02	3.17	102	173
616-02-113	A horizon	0-50	6.1	6.6	3.6	2.5	9.4	1.75	0.12	4.83	213	118
616-02-113	E1 horizon	50-250	3.6	3.9	3.1	0.5	10.3	0.04	0.01			125
616-02-113	E2 horizon	250-300	2.8	2.7	2.2	0.6	9.3	0.07	0.02	0.00	294	1251
616-02-113	E3 horizon	300-600	2.8	2.6	2.2	0.6	9.0	0.04	0.01			1814
616-02-122	E horizon	20-235	5.7	5.0	4.3	1.4	10.1	0.19	0.02	0.73	136	49
616-02-122	B horizon	235-315	6.6	5.8	5.6	1.1	11.7	0.51	0.03	2.30	107	20
616-02-122	2E1 horizon	315-375	5.0	4.7	3.4	1.6	10.5	0.06	0.01			40
616-02-122	2E2 horizon	375-500	2.8	2.9	2.5	0.3	10.0	0.03	0.01	0.00	91	430
616-02-122	2E3 horizon	500-700	3.4	3.5	2.8	0.6	10.3	0.02	0.01			395
616-02-122	B/E horizon	700-900	3.5	3.9	2.9	0.7	10.9	0.11	0.01	0.08	67	119
616-02-122	3E horizon	900-1000	2.6	2.8	2.5	0.1	9.9	0.02	0.01			638
616-02-127	E horizon	40-100	5.1	4.6	4.5	0.6	11.7	0.20	0.02			50
616-02-127	Coffee rock	100-235	4.9	4.4	4.1	0.8	11.9	2.75	0.10	1.73	108	78
616-02-127	2E1 horizon	235-300	4.1	4.4	3.2	0.8	10.9	0.07	0.01	0.21	77	50
616-02-127	2E2 horizon	300-600	4.0	4.2	3.2	0.8	11.3	0.09	0.01			104
616-02-131	A horizon	0-50	6.3	5.8	4.8	1.5	11.5	0.22	0.03	1.21	47	22
616-02-131	E horizon	50-325	6.4	6.3	5.0	1.4	10.6	0.03	0.01	0.07	35	20
616-02-131	B horizon	325-425	5.2	4.4	3.7	1.4	10.5	0.22	0.03	6.15	69	72
616-02-131	2E horizon	425-600	5.1	4.6	4.1	1.0	10.5	0.03	0.01	1.36	57	33
616-02-136	A horizon	0-25	5.8	5.0	4.8	1.0	9.0	0.40	0.02	1.35	167	68
616-02-136	Coffee rock	200-260	6.3	5.1	4.9	1.4	11.8	1.88	0.06	4.93	81	92
616-02-136	E horizon	260-600	3.0	2.8	2.4	0.6	9.6	0.08	0.02	0.99		691
616-02-145	E1 horizon	50-300	6.2	6.3	4.9	1.3	10.5	0.02	0.02	0.00	27	16
616-02-145	E2 horizon	300-450	3.4	3.7	2.7	0.7	10.1	0.02	0.01	0.00	110	163
616-02-145	B horizon	450-475	4.9	4.8	3.6	1.3	11.1	0.50	0.03	2.10	85	150
616-02-145	2E horizon	475-600	3.3	3.4	2.5	0.9	10.3	0.08	0.01	0.35	158	387

\*pH H<sub>2</sub>O<sub>2</sub> adjusted to 5.5, \*\* Δ pH = pH H<sub>2</sub>O-pH H<sub>2</sub>O<sub>2</sub>, \*\*\* pH NaF adjusted to 8.2, \*\*\*\* Turbidimetric method (0.5 N ammonium chloride extraction)

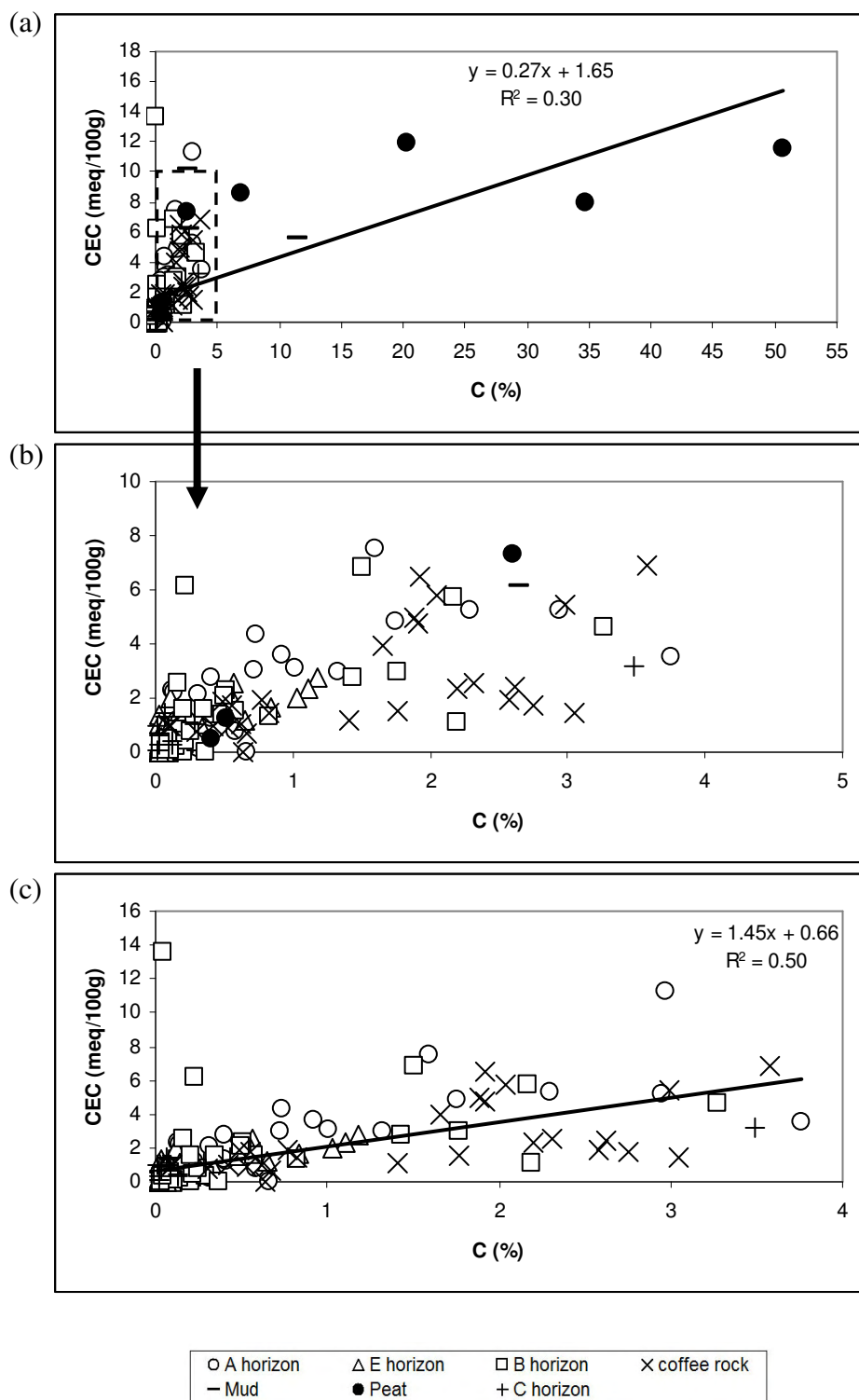
**Table 1 (Cont.)** chemical properties of soil samples.

Site	Horizon	Depth (cm)	pH H <sub>2</sub> O	pH CaCl <sub>2</sub>	pH H <sub>2</sub> O <sub>2</sub> *	ΔpH**	pH NaF***	C	N	CEC	SO <sub>4</sub> <sup>2-</sup> ****	EC
								(-----%-----)	meq/100g	mg kg <sup>-1</sup>	(μS/cm)	
616-02-155	E horizon	50-150	8.6	7.5	7.8	0.8	11.1	0.57	0.02	2.52	45	52
616-02-155	2E horizon	200-500	3.2	3.1	2.2	1.0	9.5	0.11	0.01	2.03	229	699
616-02-155	B horizon	500-600	8.7	7.4	7.4	1.4	10.7	0.04	0.02	13.60	36	198
616-02-158	E horizon	25-225	4.8	4.0	4.1	0.7	10.1	0.09	0.01	0.00	41	8
616-02-158	Coffee rock1	225-300	4.7	4.3	3.9	0.8	11.9	3.05	0.07	1.46	55	26
616-02-158	Coffee rock2	300-400	3.6	3.8	2.5	1.1	10.7	2.20	0.05	2.36	125	299
616-02-174	B horizon	250-550	5.6	4.8	2.2	3.4	10.0	1.44	0.05	2.77	57	58
616-02-179	B horizon	375-400	3.9	4.3	2.8	1.1	10.7	0.09	0.02	0.46	84	64
Ellenbrook	E horizon	0-150	4.5	4.4	4.5	0.0	10.4	0.03	0.01	0.00	56	11
Ellenbrook	Coffee rock	150-200	4.0	4.3	3.1	0.9	11.9	0.77	0.03	1.92	118	163
Ellenbrook	B horizon	200-500	2.6	2.6	1.9	0.7	8.9	0.16	0.01			1069
Ellenbrook	Coffee rock	200	4.3	4.2	3.0	1.4	11.8	1.20	0.03			163
Ellenbrook	2B1 horizon	500-550	2.5	2.5	1.9	0.6	8.6	0.20	0.02	0.00	406	1842
Ellenbrook	2B2 horizon	500-600	2.7	2.6	1.9	0.8	8.8	0.19	0.01			1252
Ellenbrook	Coffee rock	150-200	4.6	4.1	2.9	1.7	11.8	1.78	0.04			62
LOC50A	A horizon	10-20	5.2	4.6	4.4	0.9	10.6	0.16	0.02	0.23	15	38
LOC50A	A horizon	0-100	5.4	4.3	3.7	1.8	8.9	0.16	0.01	1.19	29	28
LOC50A	E horizon	300-400	4.8	3.9	4.2	0.6	9.4	0.34	0.01	0.88	21	34
LOC50A	Coffee rock	400-500	3.7	3.4	3.3	0.4	7.8	0.83	0.02	1.45	53	136

\*pH H<sub>2</sub>O<sub>2</sub> adjusted to 5.5, \*\* Δ pH = pH H<sub>2</sub>O-pH H<sub>2</sub>O<sub>2</sub>, \*\*\* pH NaF adjusted to 8.2, \*\*\*\* Turbidimetric method (0.5 N ammonium chloride extraction)



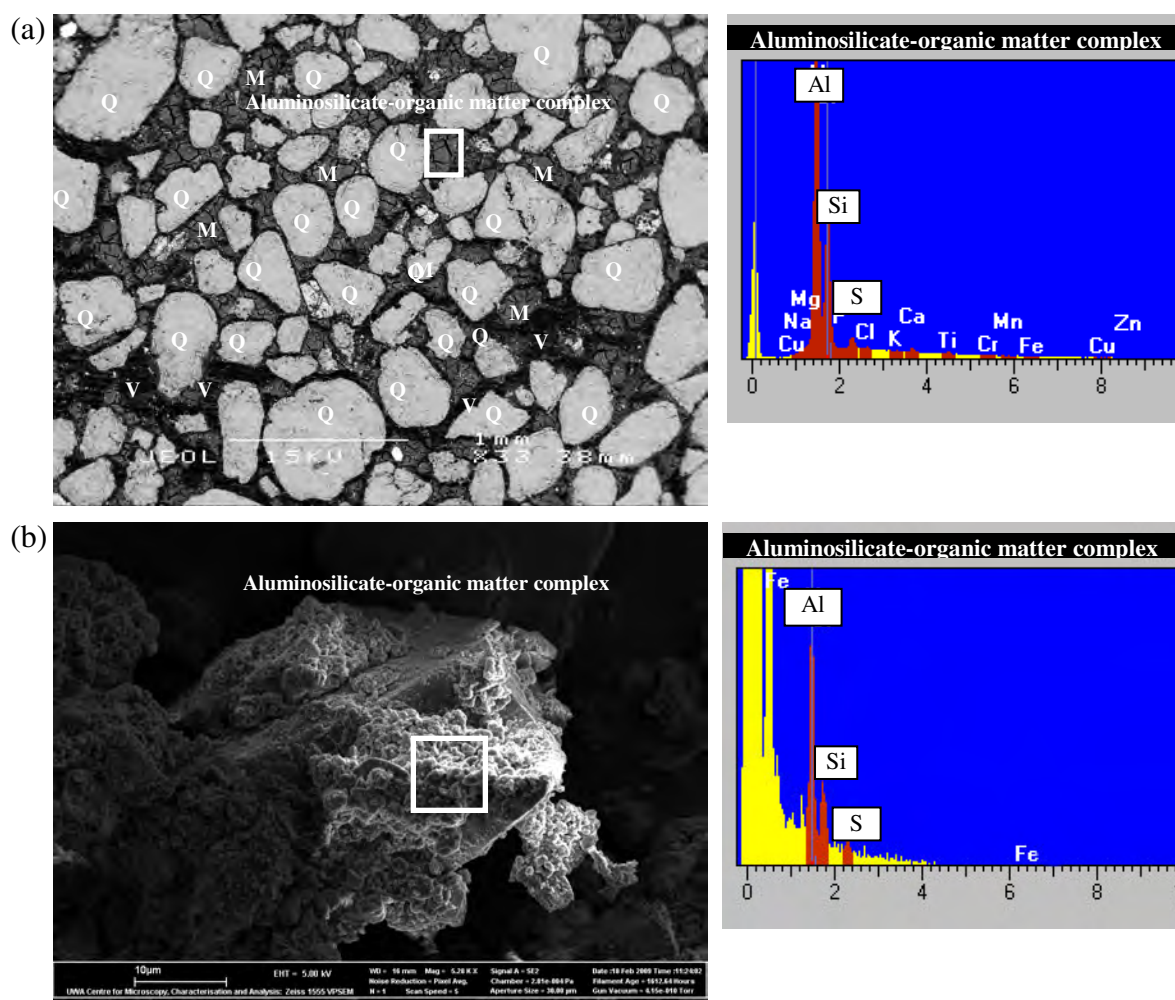
**Figure 4** Bivariate relationships between carbon and nitrogen for (a) all soil samples, (b) soil samples with carbon ranging from 0.0-5.0% and nitrogen ranging from 0.0-0.3% and (c) A, E, B, coffee rock and C horizons.



**Figure 5** Bivariate relationships between carbon and cation exchange capacity for (a) all soil samples, (b) some soil samples with carbon ranging from 0.0-5.0% and cation exchange capacity ranging from 0.0-10.0 meq/100g and (c) A, E, B, coffee rock and C horizons.

## 5.2 Micromorphological and mineralogical properties

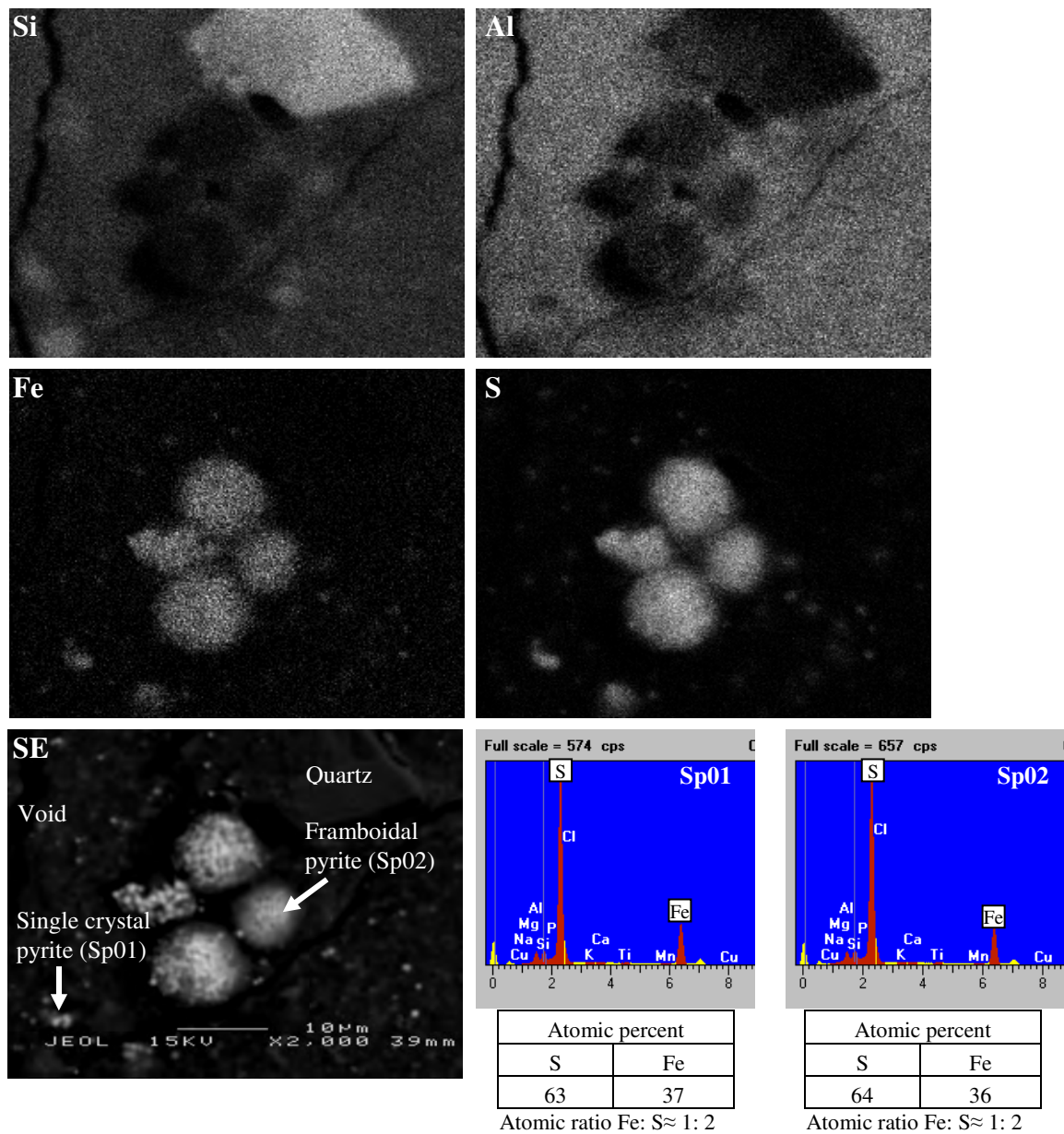
Scanning electron microscopy showed that all soil horizons consist mainly of rounded quartz grains with some horizons containing various amounts of aluminosilicate organic matter complex which contains small amounts of sulfur (Figure 6). The X-ray spectra of particles indicate that this sulfur is probably mostly present as pyrite; some of the iron content is also in iron oxides and probably iron is also in the structure of the aluminosilicate. Some coffee rock does not contain ferruginous cemented material (Figure 6) as the cemented material consists only of aluminosilicate and organic matter. In some cases coffee rock samples have a matrix mainly consisting of aluminosilicate mixed with organic matter and ferruginous cemented material (Figure 2).



**Figure 6** (a) SEM backscattered electron image and x-ray spectrum of a thin section from coffee rock (9.0-1.0 m) site 616-01-05 (N.B. this is a palaeopodosol-coffee rock horizon) ( $\text{pH}_F = 6.2$ ,  $\text{pH}_{\text{FOX}} = 4.5$ ,  $S_{\text{CR}} = <0.02\%$ ). (b) SEM secondary electron image and x-ray spectrum of fine fraction from coffee rock (3.0-4.0 m) site 616-02-087 ( $\text{pH}_F = 6.1$ ,  $\text{pH}_{\text{FOX}} = 4.1$ , No  $S_{\text{CR}}$  data) (Q = quartz, M = matrix, V = void).



Iron sulfide is present in E, B, coffee rock, mud, peat horizons as various size and shape particles including 1-10  $\mu\text{m}$  framboids (Bush and Sullivan, 1999) and single crystal pyrite ( $\leq 1 \mu\text{m}$ ) (Figure 7). Framboidal pyrite is present in this example of coffee rock (5.0-6.0 m, site 616-02-82) together with single crystals of pyrite, which are very small ( $\leq 1 \mu\text{m}$ ), have high surface area and are thus potentially very reactive. Pyrite occurs in all E, B and coffee rock horizons examined. The iron to sulfur ratio of these particles is consistent with pyrite (Fe: S  $\approx$  1: 2) (Figures 7-10) (Shamshuddin *et al.*, 2004).



**Figure 7** SEM secondary electron image, element mapping and x-ray spectra of the fine fraction from coffee rock (5.0-6.0 m, site 616-02-82) deposited on a stub ( $\text{pH}_F = 6.9$ ,  $\text{pH}_{\text{FOX}} = 1.3$ ,  $S_{\text{CR}} = 0.26\%$ ).

Transmission electron microscope results for the fine fraction of these soils shows the crystal morphology of pyrite crystals from E, B and coffee rock horizons and x-ray spectra confirm the atomic ratio of Fe: S  $\approx$  1: 2 indicative of pyrite (Figures 8-10). Elemental sulfur is a minor constituent of some B horizon and coffee rock samples (Figure 11) with an atomic ratio of Fe: S  $\approx$  0: 1 (Boman *et al.*, 2008). The X-ray spectra of single crystals of pyrite obtained by SEM and TEM contain peaks from silicon and aluminium from the soil matrix surrounding the pyrite particles. However, the iron to sulfur ratio is consistently that of pyrite (Fe: S  $\approx$  1: 2). Electron diffraction patterns obtained for single crystals in the TEM can be indexed by reference to the pyrite unit cell which confirms the identify of pyrite (Figure 12a). Jarosite is present in some A horizon samples (Figures 12b and 13).

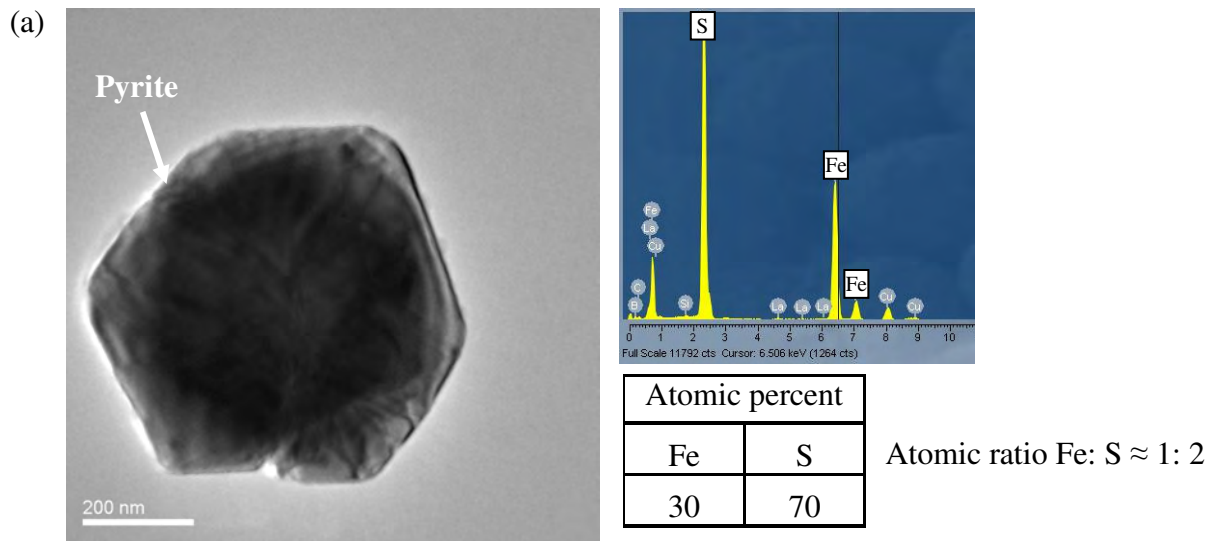
Microcrystalline kaolin crystals occur in E, B and coffee rock horizons (Figures 8-11). A representative TEM micrograph of kaolin crystals from coffee rock (5.25-5.75 m, site 616-02-82) is shown in Figure 10b together with the corresponding EDX spectrum. In this micrograph many platy kaolin crystals are viewed perpendicular to their cleavage. The chemical composition of the indicated crystal is provided by the EDX spectrum and is consistent with kaolin (Al: Si = 1: 1).

Scanning electron microscope and transmission electron microscope results for the fine fractions show that iron sulfide is present in all water logged soil horizons that recorded  $\text{pH}_{\text{FOX}} < 3$ . It occurs as particles of various sizes and shapes including 1-10  $\mu\text{m}$  framboids and single crystal pyrite ( $\leq 1 \mu\text{m}$ ) which have high surface area and are thus potentially very reactive. Some materials directly above the groundwater level can contain small amount of pyrite and can become acidic when oxidized (Figure 14).

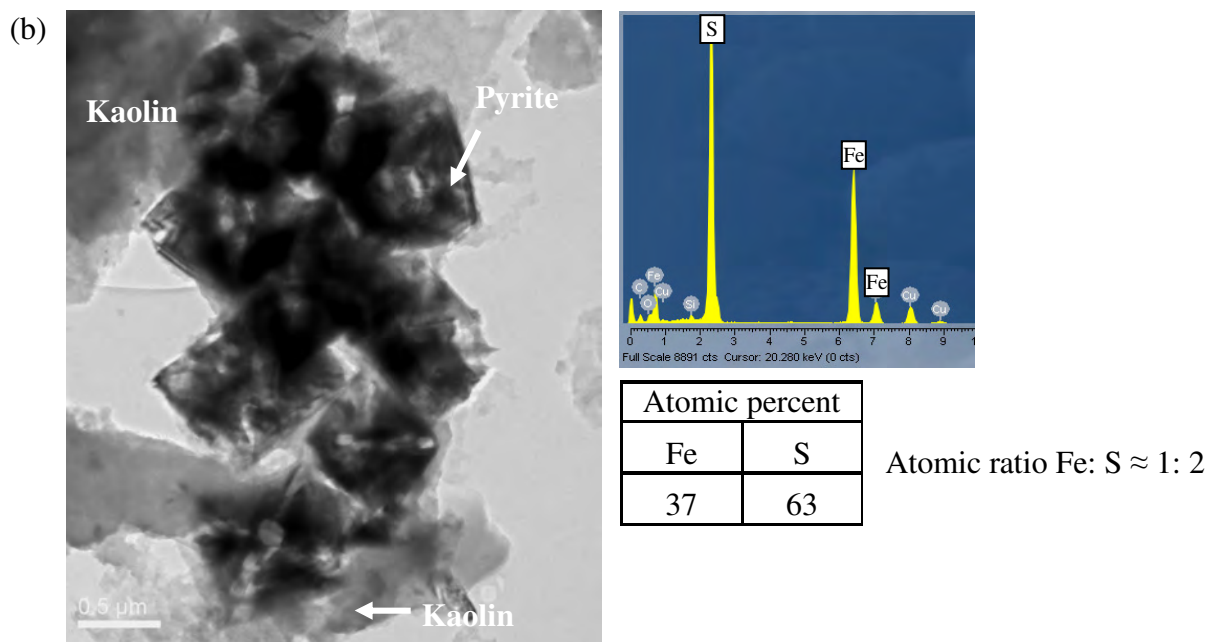
Framboidal pyrite may occur as a result of the activity of bacteria and in association with organic substrate, whereas single crystals (euhedral and anhedral pyrite) may be formed solely by chemical reaction. Therefore, soil horizons with a high organic matter content (including B and coffee rock horizon) contain framboidal pyrite and single crystal pyrite but soil horizons with a low organic matter content (E horizon) contain euhedral and anhedral single crystals of pyrite. All low  $\text{pH}_{\text{FOX}}$  samples investigated in this study contained pyrite while no pyrite was detected in surface horizons where  $\text{pH}_{\text{FOX}}$  was above 3. Pyrite occurred across all horizons where  $\text{pH}_{\text{FOX}}$  was low suggesting pyrite formation is not related to recent pedogenetic processes. Understanding pyrite

micromorphology and consequent pyrite oxidation behaviour in acid sulfate soils are very important for management.

E horizon

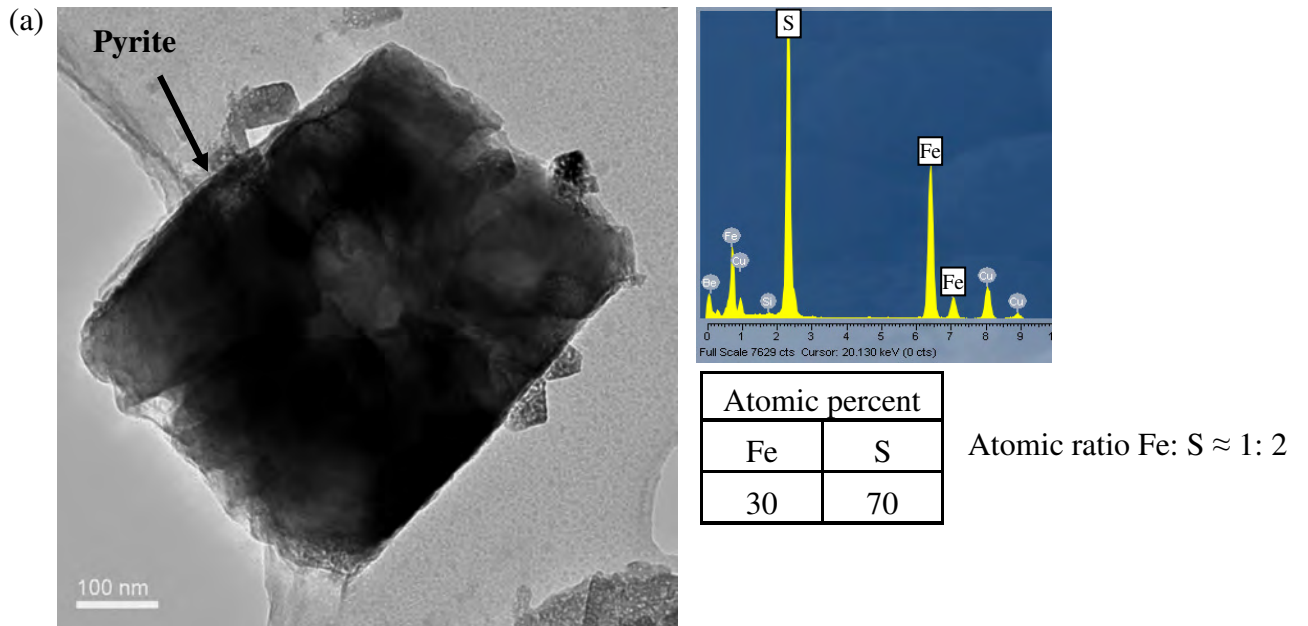


E horizon

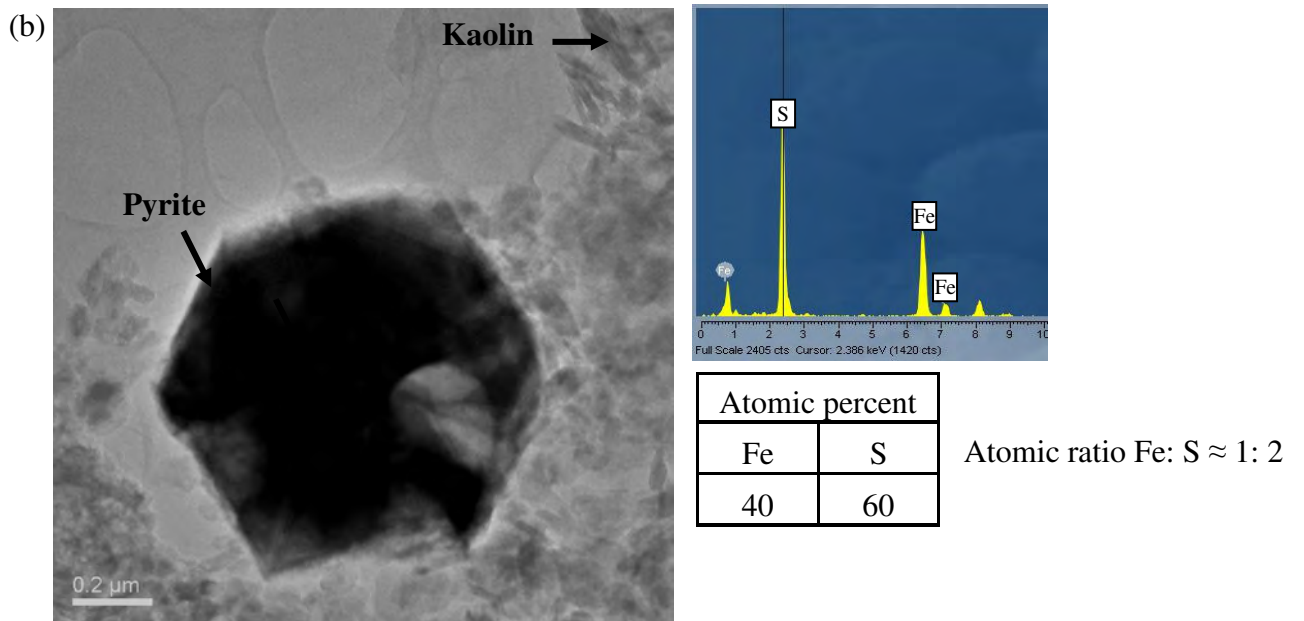


**Figure 8** TEM transmission electron micrograph and x-ray spectrum of pyrite crystals from the fine fraction from (a) E horizon 1.75-3.5 m, site 616-02-71) ( $pH_F = 6.5$ ,  $pH_{FOX} = 4.2$ , No  $S_{CR}$  data) and (b) E horizon (3.0-3.75 m, site 616-02-68) ( $pH_F = 6.6$ ,  $pH_{FOX} = 1.7$ ,  $S_{CR} = <0.02\%$ ).

B horizon

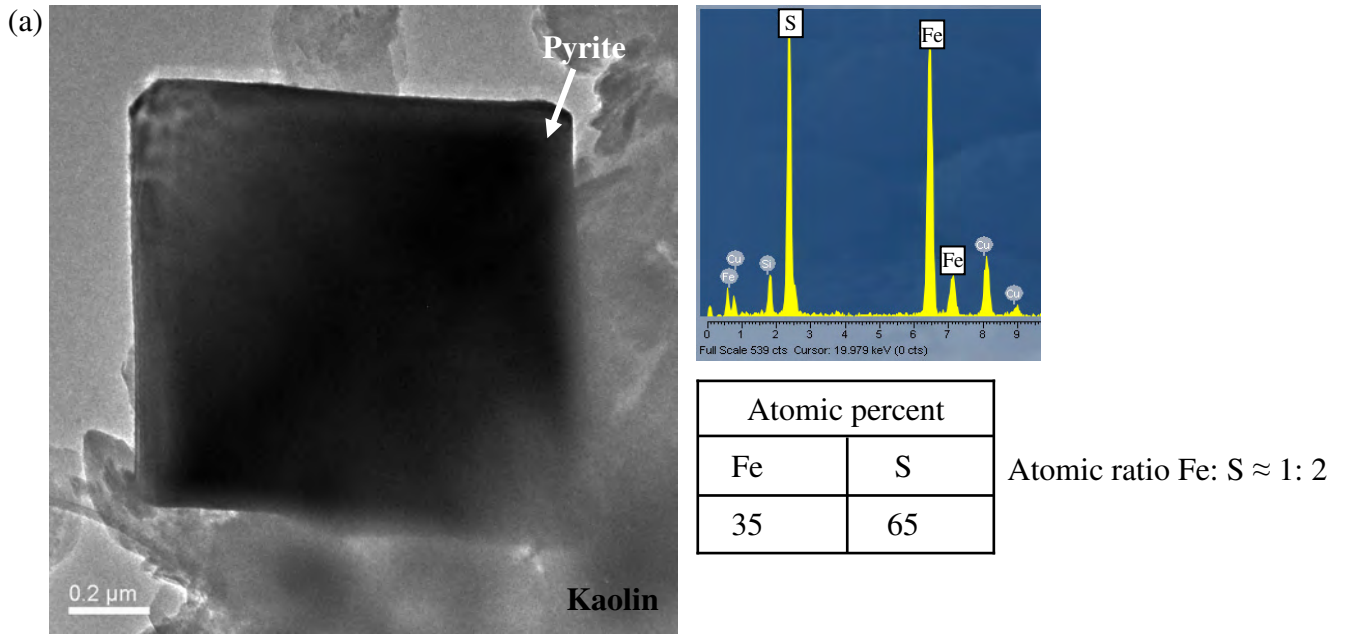


Coffee rock

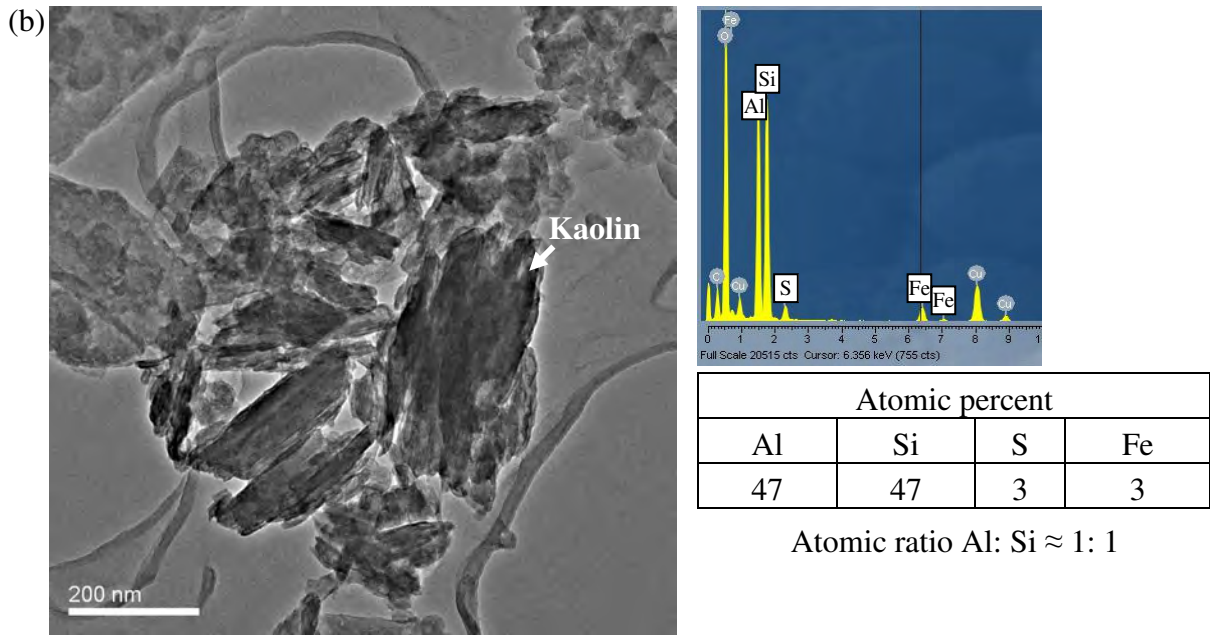


**Figure 9** TEM transmission electron micrograph and x-ray spectrum of pyrite crystals of the fine fraction from (a) B horizon (3.5-6.5 m, site 616-02-71) ( $pH_F = 5.9$ ,  $pH_{FOX} = 2.8$ ,  $S_{CR} = < 0.10\%$ ) and (b) coffee rock (5.0-6.0 m, site 616-02-82) ( $pH_F = 6.9$ ,  $pH_{FOX} = 1.3$ ,  $S_{CR} = 0.26\%$ ).

Coffee rock

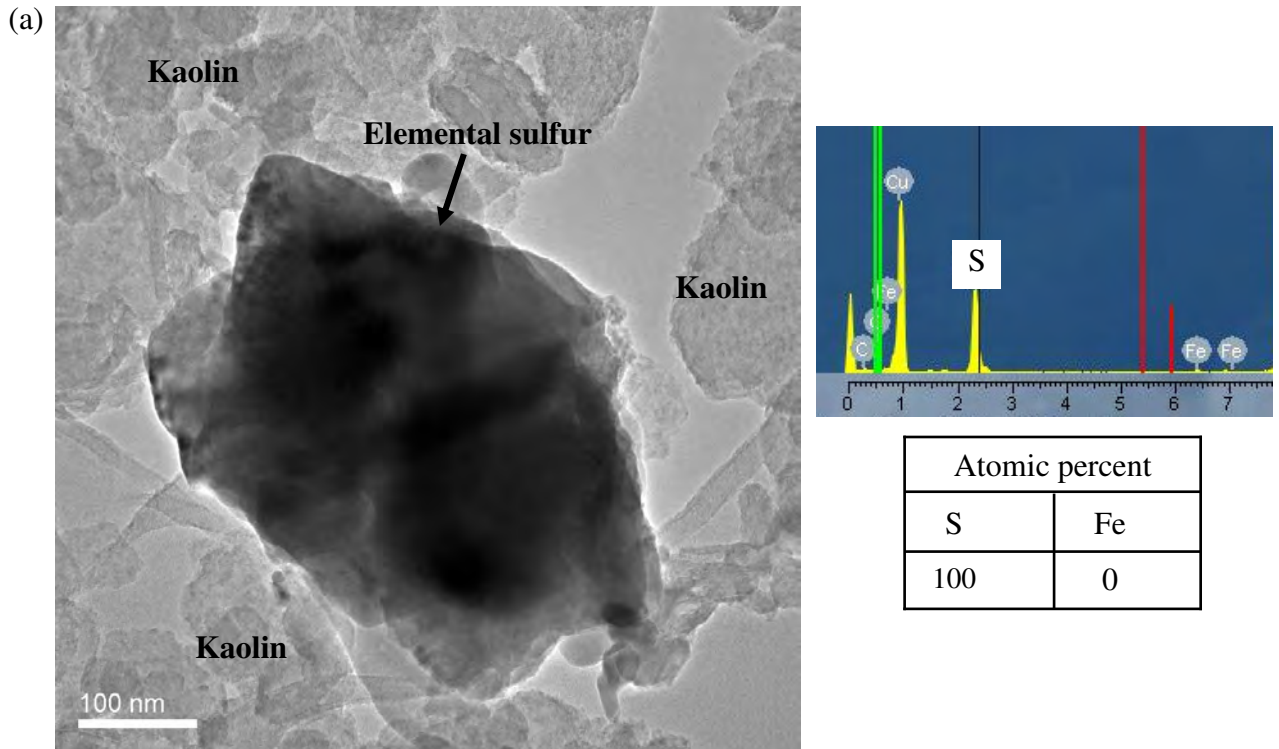


Coffee rock

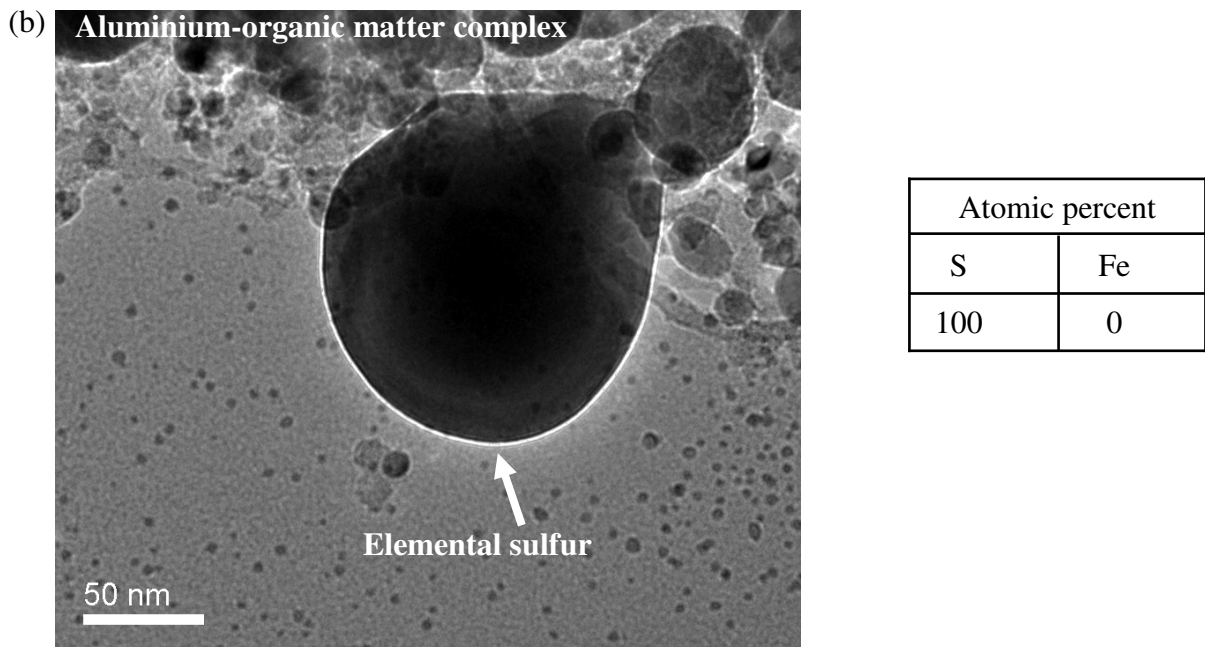


**Figure 10** TEM transmission electron micrograph and x-ray spectrum of (a) an octahedral pyrite crystal from the fine fraction from coffee rock (2.25-4.0 m, site 616-02-80) ( $pH_F = 3.9$ ,  $pH_{FOX} = 2.1$ ,  $S_{CR} = < 0.02\%$ ) and (b) a platy kaolin crystal from coffee rock viewed perpendicular to its cleavage (5.0-6.0 m, site 616-02-82) in an aggregate of kaolin crystals ( $pH_F = 6.9$ ,  $pH_{FOX} = 1.3$ ,  $S_{CR} = 0.26\%$ ).

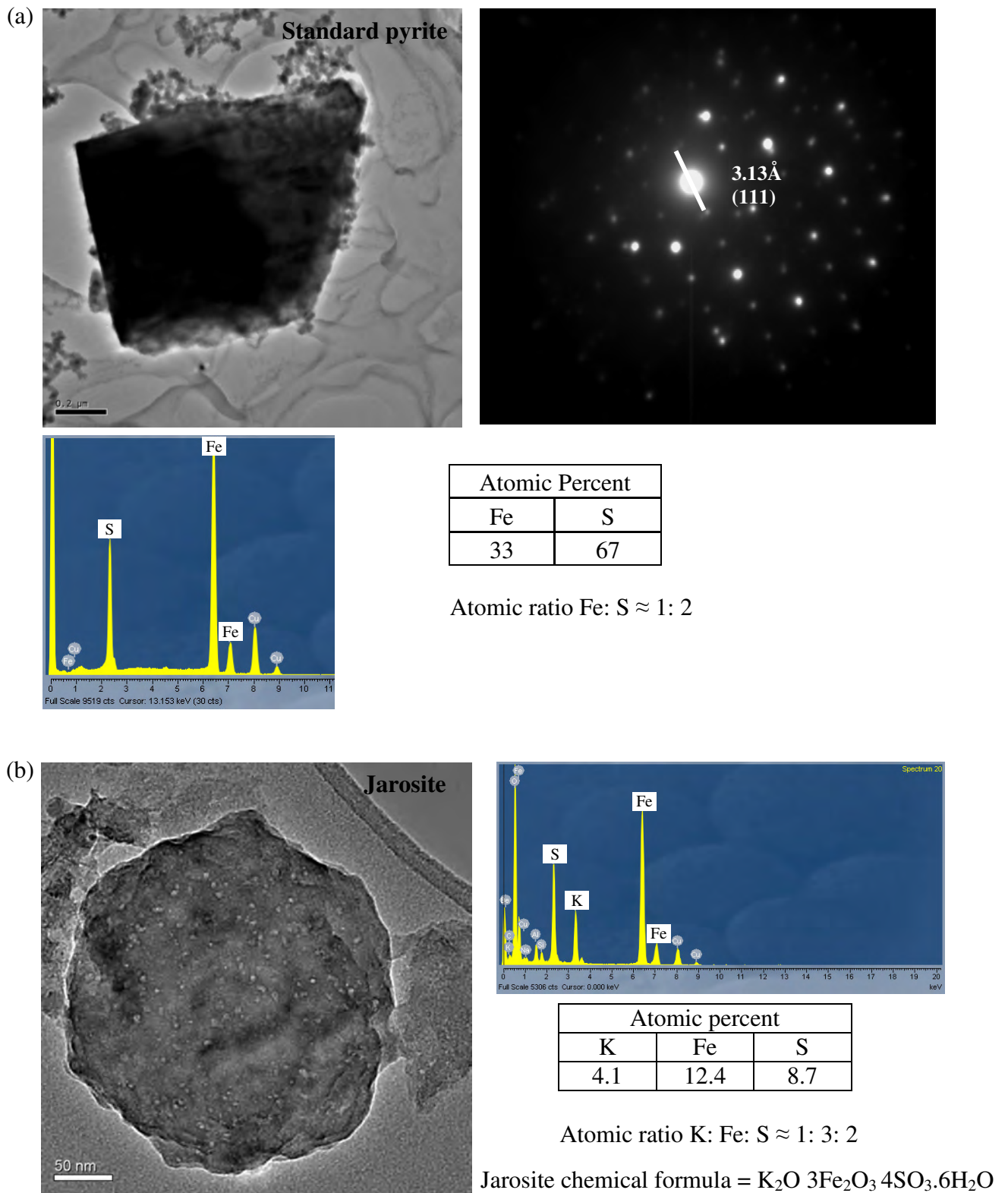
Coffee rock



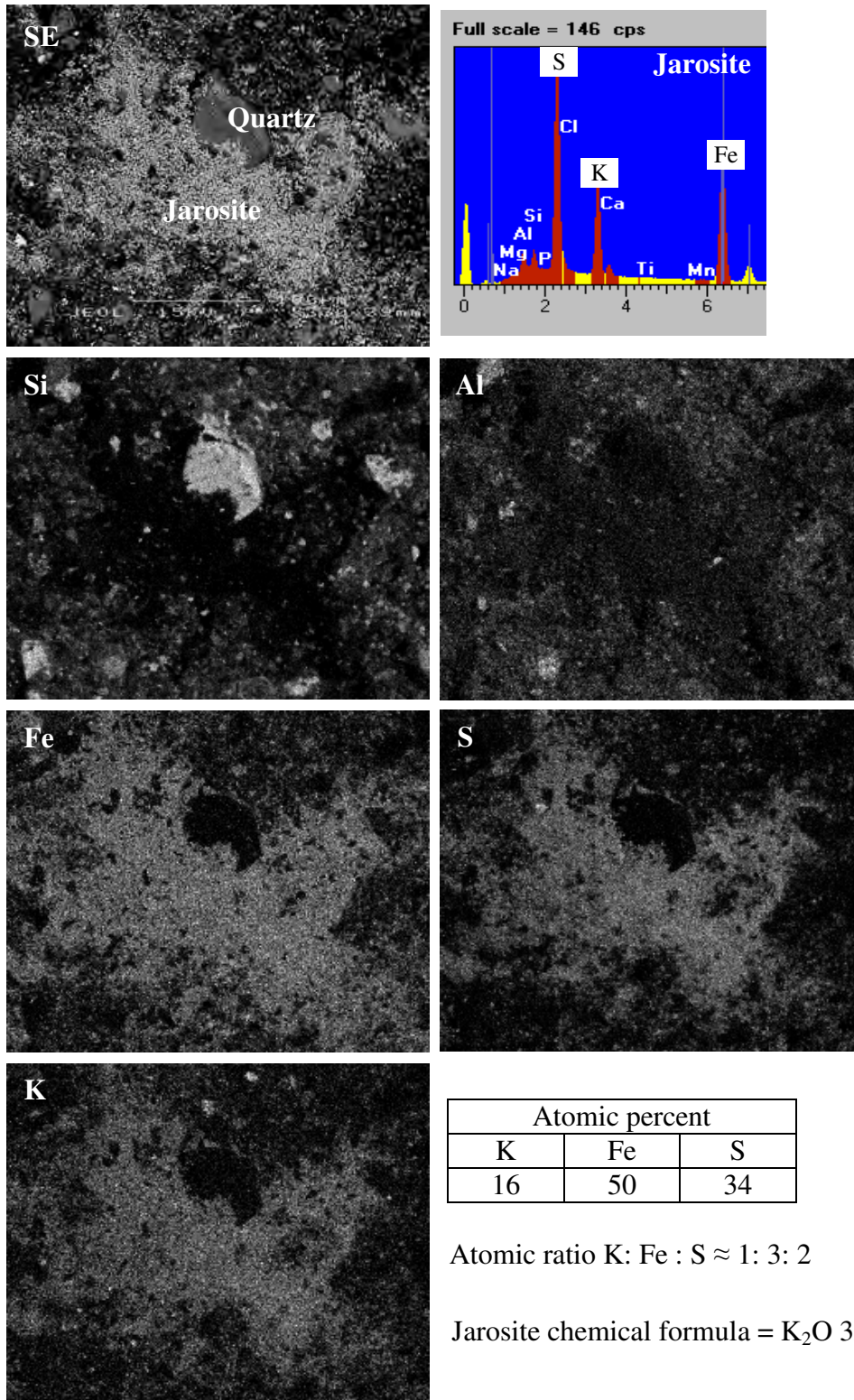
B horizon



**Figure 11** TEM transmission electron micrograph and x-ray spectrum of elemental sulfur particles from (a) coffee rock (5.0-6.0 m, site 616-02-82) ( $pH_F = 6.9$ ,  $pH_{FOX} = 1.3$ ,  $S_{CR} = 0.26\%$ ), (b) B horizon (3.0-5.0 m, site 616-02-58) ( $pH_F = 4.9$ ,  $pH_{FOX} = 1.9$ ,  $S_{CR} = <0.02\%$ ). (Cu radiation is from the supporting grid).

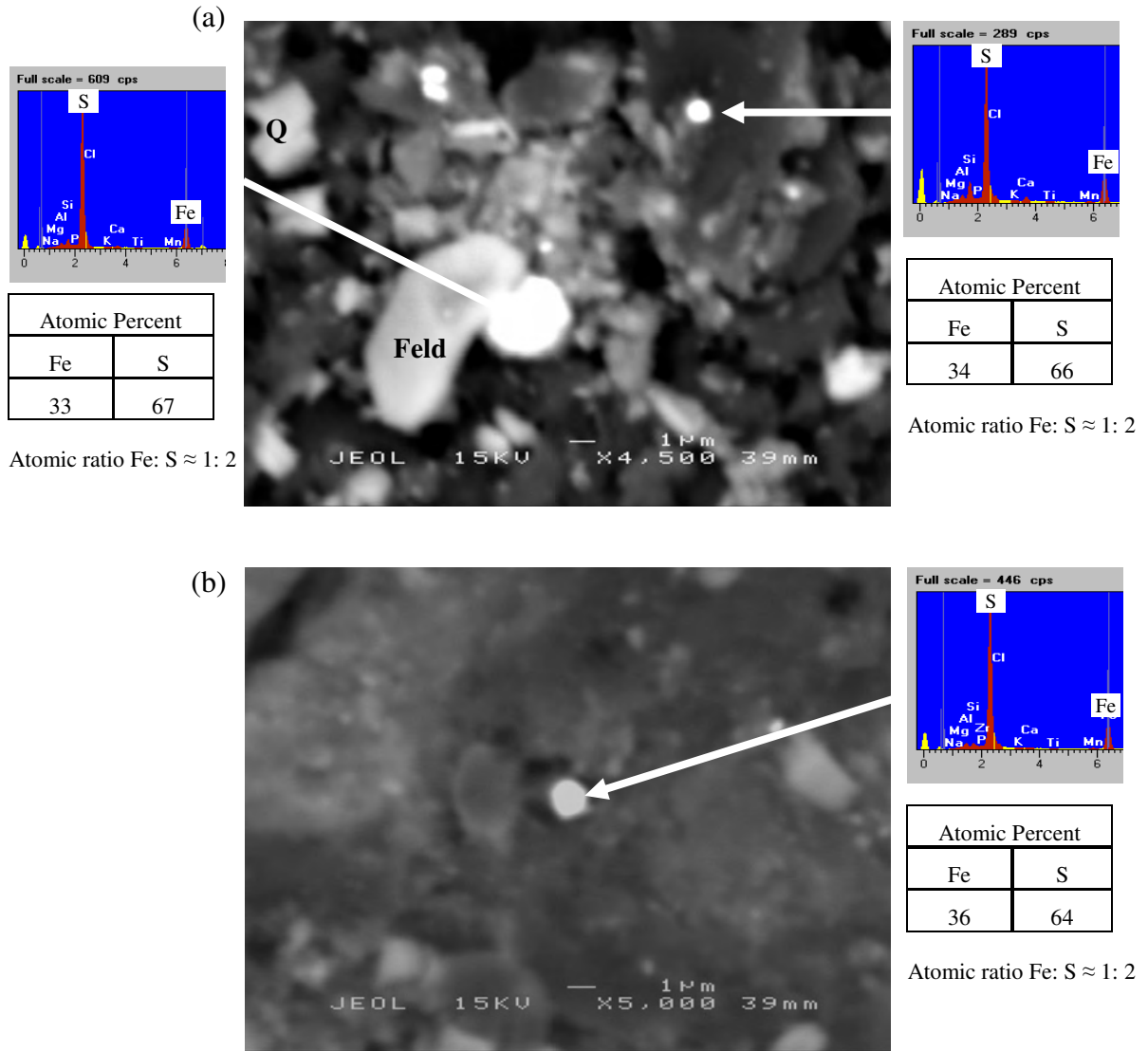


**Figure 12** (a) TEM transmission electron micrograph, x-ray spectrum and electron diffraction pattern of a pyrite crystal from a standard pyrite specimen. Pyrite crystals from the podosols gave the same electron diffraction pattern; (b) TEM transmission electron micrograph, x-ray spectrum of a jarosite crystal from the A horizon (0-100 cm, site 616-02-94) ( $\text{pH}_F = 4.0$ ,  $\text{pH}_{\text{FOX}} = 1.9$ ,  $S_{\text{CR}} = 0.09\%$ ).



**Figure 13** SEM secondary electron image, x-ray spectrum and element mapping of jarosite from the fine fraction from A horizon (0-100 cm, site 616-02-94) ( $pH_F = 4.0$ ,  $pH_{FOX} = 1.9$ ,  $S_{CR} = 0.09\%$ ).





**Figure 14** (a) SEM backscattered electron image and x-ray spectra of a thin section from E horizon (0-150 cm) Ellenbrook site (Q = quartz, Feld = feldspar, laboratory  $\text{pHH}_2\text{O}$  = 4.47,  $\text{pHH}_2\text{O}_2$  = 4.45, SCR no data); (b) SEM backscattered electron image and x-ray spectrum of a thin section from coffee rock (150-200 cm) Ellenbrook site. These horizons were above the watertable at the time of sampling (laboratory  $\text{pHH}_2\text{O}$  = 4.00,  $\text{pHH}_2\text{O}_2$  = 3.10, SCR no data) (Groundwater table level = 7 m).

### 5.3 X-ray diffraction

All studied soils have a very high quartz sand content and small amounts of other minerals that provide acidity and buffering; therefore the fine fraction which contains most of these minor minerals was dispersed by ultrasonic treatment, separated from sand size quartz by sedimentation and used for XRD analysis.

The highly intense monochrome synchrotron X-ray beam provides the sensitivity required for detecting minor quantities of pyrite, sulfur and other crystalline constituents in soil and extracted fine fraction. Conventional XRD of the fine fraction of some podosol fine fraction materials was sensitive enough to provide information on the nature and amounts of sulfides but is inadequate for samples where little sulfide or sulfur is present. It is these materials that are of great concern to DEC as conventional chemical methods to determine S are insensitive. In this case conventional XRD does not recognize low concentrations of some minerals of particular interest such as pyrite, sulfur and jarosite, so synchrotron XRD must be used.

The fine fraction of 93 samples was analysed by synchrotron XRD, 36 samples contain pyrite. The synchrotron XRD patterns of fine fractions extracted from all horizons show that quartz is the dominant mineral of the fine fraction for all horizons with a minor amount of microcline, kaolin and in some samples gibbsite. Halite is present in some subsoils with a high EC level. Resistant minerals, including anatase and ilmenite are present in some samples (Table 2, Appendix Tables 11-25).

The synchrotron XRD patterns of fine fractions extracted from podosol horizons show that jarosite occur in the A horizon (above groundwater level) and in mud and rarely in the B horizon. Pyrite is present in most E, B and coffee rock, mud, peat and C horizons, especially where the samples are located below groundwater level (Table 3). Elemental sulfur occurs as a minor constituent in some horizons which have a high organic matter content. The A horizon samples studied to date do not contain pyrite. Marcasite is present in a few samples. The distribution of pyrite content (semi quantitative %) of the fine fraction of soil samples are shown in Figure 15 (based on synchrotron XRD). Based on data and the origins of these soil samples, pyrite occurs in areas which have the water table at less than 40 metres above mean sea level and there is more pyrite at lower altitudes.

The relationships between sulfur minerals and  $S_{CR}$  are shown in Figure 16. Mud sample (site 616-02-028, 200-250 cm) and peat sample (site 616-02-112) have quite high  $pH_{FOX}$  (>4) because these samples have high calcite and organic matter contents respectively.

Bivariate relationship between sulfur minerals and  $S_{CR}$  for A, E, B, coffee rock, mud and peat horizons and sulfur minerals and  $S_{CR}$  of A, E, B and coffee rock horizons are shown in the Figure 16a, b). The Figure 16b plot omits data for the mud and peat samples which makes the relationship nonsignificant showing that the apparently significant relationships in Figure 16a is spurious due to the bimodal distribution of these data. One reason for the absence of a relationship is because the sulfur minerals were determined on the fine fraction whereas whole soil samples were used for  $S_{CR}$  analysis.

Synchrotron XRD is an excellent technique for identification of minor constituent minerals. However, synchrotron XRD was unable to detect very small amounts of sulfide minerals in some A, E, B, coffee rock, mud, peat samples with very low  $S_{CR}$  contents (less than 0.005%) (Appendix Figures 18, 24 and 25). TEM and SEM enabled the identification very small amount of pyrite in these samples where pyrite was not detected by SXRD (Figures 17-24) indicating that acidification (low  $pH_{FOX}$ ) is generally due to the presence of pyrite (and very low buffering). [The samples shown in Figures 17-24 were also used for the Murdoch University soil column experiment.]

**Table 2** Mineralogical composition (semi quantitative %) of the fine fraction of soil samples (based on synchrotron XRD)\*.

No	Site	Horizon	Depth (cm)	pH <sub>F</sub>	pH <sub>FOX</sub>	S <sub>CR</sub> (%)	GW (cm)	Ill	Kao	Pyr	S	Jar	Mar	Mac	Micro	Na Ca Feld	Alb	Am	Gib	Goe	Qua	Zir	Ilm	Hal	Cal	Ara
003	616-01-005	Coffee rock	180-200	6.3	4.7	no data	640	-	0.8	-	-	-	-	-	0.6	-	-	-	2.0	-	96.6	-	-	-	-	-
022	616-02-031	Coffee rock1	200-300	5.3	3.2	< 0.02	75	-	0.1	-	-	-	-	-	0.2	-	-	-	0.3	-	99.4	-	-	-	-	-
023	616-02-031	Coffee rock2	200-300	5.3	3.2	< 0.02	75	-	0.5	-	-	-	-	-	1.8	-	-	-	1.9	-	95.8	-	-	-	-	-
034	616-01-003	Coffee rock	175-200	5.0	3.6	no data	490	-	0.5	-	-	-	-	-	0.8	-	-	-	0.5	-	98.2	-	-	-	-	-
040	616-01-014	C1 horizon	800-900	6.3	5.3	no data	1350	-	0.4	-	-	-	-	-	1.3	-	-	-	3.2	-	95.1	-	-	-	-	-
052	616-02-068	E3 horizon	375-600	7.2	1.8	<0.02	200	0.3	2.8	8.7	0.7	-	-	-	14.3	-	-	-	1.8	-	71.4	-	-	-	-	-
055	616-02-080	Coffee rock	200-400	5.3	3.2	<0.02	200	-	3.6	0.4	-	-	-	-	-	-	-	-	1.7	-	94.4	-	-	-	-	-
058	616-02-082	E2 horizon	200-300	5.0	1.8	0.02	50	-	1.0	2.3	-	-	-	-	10.8	-	-	-	0.6	-	85.3	-	-	-	-	-
059	616-02-082	B horizon	300-400	5.8	1.6	0.11	50	-	33.2	3.2	0.3	-	-	-	4.1	-	-	-	0.3	-	59.0	-	-	-	-	-
060	616-02-082	2E horizon	400-500	6.2	1.6	0.26	50	-	0.7	8.3	-	-	0.2	-	10.8	-	-	-	0.7	-	79.3	-	-	-	-	-
061	616-02-082	Coffee rock	500-600	6.7	1.5	no data	50	-	1.6	6.7	0.5	-	-	-	8.6	-	-	-	1.6	-	77.7	-	-	3.3	-	-
062	616-02-087	Coffee rock1	200-300	6.1	3.9	no data	150	-	-	-	-	-	-	-	1.2	-	-	-	0.9	-	97.9	-	-	-	-	-
063	616-02-087	Coffee rock2	300-400	6.0	4.1	no data	150	-	-	-	-	-	-	-	-	-	-	-	11.7	-	88.3	-	-	-	-	-
069	616-01-019	B horizon	250-300	4.4	3.9	no data	400	-	0.9	-	-	-	-	-	2.0	-	-	-	0.5	-	96.6	-	-	-	-	-
086	616-02-085	A horizon	0-70	6.1	3.9	no data	150	-	52.7	-	-	-	-	-	47.3	-	-	-	-	-	-	-	-	-	-	-
087	616-02-085	B1 horizon	100-300	6.7	2.0	0.28	150	-	4.9	-	1.5	-	-	3.8	3.6	3.8	-	-	-	-	82.4	-	-	-	-	-
088	616-02-085	B2 horizon	300-400	7.1	2.0	0.80	150	1.8	3.5	9.0	-	-	-	-	9.0	-	9.4	-	2.5	-	64.8	-	-	-	-	-
089	616-02-085	Mud	400-600	7.4	2.6	0.40	150	-	0.7	-	0.2	3.1	-	-	0.7	1.7	-	-	-	-	91.9	1.9	-	-	-	-
090	616-02-028	B horizon	30-100	4.3	2.3	0.27	150	-	0.6	-	-	0.6	0.8	-	0.8	-	1.8	-	-	-	95.5	-	-	-	-	-
091	616-02-028	Mud1	100-200	6.6	3.0	0.89	150	-	-	1.5	-	-	-	-	4.5	3.0	-	-	-	-	91.0	-	-	-	-	-
092	616-02-028	Mud2	200-250	7.4	6.0	no data	150	0.8	1.9	16.0	-	-	-	-	2.9	1.8	-	1.4	-	-	64.6	-	1.4	-	9.2	-
095	616-02-094	A1 horizon	0-100	4.0	1.9	0.09	350	-	1.3	-	-	5.2	-	-	2.0	-	-	-	-	-	91.5	-	-	-	-	-
096	616-02-094	A2 horizon	100-175	4.3	2.8	<0.02	350	-	0.2	-	-	2.0	-	-	2.6	-	-	-	-	-	95.2	-	-	-	-	-
097	616-02-094	E horizon	175-600	5.9	3.6	0.03	350	0.1	0.2	0.2	-	-	-	-	0.9	-	-	-	-	-	98.6	-	-	-	-	-
098	616-02-100	A horizon	0-80	8.0	5.5	no data	200	-	1.6	-	1.5	-	-	-	4.7	-	-	-	1.8	-	77.5	-	-	-	12.9	-
099	616-02-100	Peat	80-110	7.8	4.2	no data	200	-	-	-	-	-	-	-	-	-	-	-	-	-	100.0	-	-	-	-	-
100	616-02-100	Peat/Ehorizon	110-200	7.1	3.3	0.08	200	-	0.7	2.6	-	-	0.9	-	3.2	-	-	-	-	-	92.6	-	-	-	-	-
101	616-02-100	E horizon	200-600	6.4	2.1	0.02	200	-	1.0	1.0	-	-	-	-	8.9	-	-	-	-	-	89.1	-	-	-	-	-

Ill = Illite, Kao = Kaolinite, Pyr = Pyrite, S = Elemental S, Jar = Jarosite, Mar = Marcasite, Mac = Mackinawite, Micro = Microcline, Na Ca Feldspar, Alb = Albite, Am = Amphibole, Gib = Gibbsite, Goe = Goethite, Qua = Quartz, Zir = Zircon, Ilm = Ilmenite, Hal = Halite, Cal = Calcite, Ara = Aragonite, - = not detected.

\* allophane is present in most coffee rock and some other samples but could not be detected by synchrotron XRD due to its diffuse reflections and the nature of background scattering from the glass capillary sample holder.

**Table 2 (Cont.)** Mineralogical composition (semi quantitative %) of the fine fraction of soil samples (based on synchrotron XRD)\*.

No	Site	Horizon	Depth (cm)	pH <sub>F</sub>	pH <sub>FOX</sub>	S <sub>CR</sub> (%)	GW (cm)	Ill	Kao	Pyr	S	Jar	Mar	Mac	Micro	Na Ca Feld	Alb	Am	Gib	Goe	Qua	Zir	Ilm	Hal	Cal	Ara
102	616-02-099	E horizon	25-200	7.2	3.5	< 0.02	50	-	-	-	-	-	-	-	-	-	-	-	-	-	100.0	-	-	-	-	-
103	616-02-099	B1 horizon	200-300	7.1	2.5	0.10	50	-	5.1	3.8	-	-	-	-	4.3	-	-	-	-	-	86.8	-	-	-	-	-
104	616-02-099	B2 horizon	300-400	7.2	1.8	0.12	50	-	0.3	3.8	-	-	-	-	1.5	-	-	-	-	-	94.4	-	-	-	-	-
105	616-02-099	2E horizon	400-600	6.8	2.1	0.05	50	-	0.4	7.6	-	-	-	-	1.8	-	-	-	-	-	90.2	-	-	-	-	-
106	616-02-101	A horizon	0-75	7.4	3.8	< 0.02	150	-	1.2	-	0.4	-	-	-	6.2	-	-	-	1.1	-	91.2	-	-	-	-	-
107	616-02-101	Peat1	150-200	7.4	5.4	no data	150	-	-	4.7	-	-	-	-	6.0	-	-	-	-	-	89.3	-	-	-	-	-
108	616-02-101	Peat2	200-350	7.1	1.6	0.74	150	-	-	4.3	-	-	-	-	5.5	-	-	-	-	-	82.3	-	-	-	7.9	-
109	616-02-101	E horizon	350-600	8.5	2.0	0.05	150	-	0.2	1.8	-	-	-	-	10.0	-	-	-	-	-	88.1	-	-	-	-	-
110	616-02-009	E1 horizon	225-250	5.8	4.9	no data	180	-	0.3	-	-	-	-	-	7.4	-	-	-	-	-	92.3	-	-	-	-	-
112	616-02-105	A horizon	0-160	7.8	4.7	no data	170	-	3.3	-	-	-	-	-	6.2	-	-	-	-	-	90.5	-	-	-	-	-
113	616-02-105	Peat	250-360	6.3	1.4	1.97	170	-	-	61.9	-	-	-	-	-	-	-	-	-	-	38.1	-	-	-	-	-
114	616-02-105	Peat/Ehorizon	360-480	6.7	2.0	0.08	170	-	0.2	1.6	0.1	-	-	-	3.2	0.2	-	-	-	-	94.6	-	-	-	-	-
115	616-02-105	E horizon	480-700	7.1	3.9	0.05	170	-	0.2	0.1	-	-	-	-	5.5	-	-	-	-	-	93.9	-	-	0.4	-	-
116	616-02-106	A horizon	0-50	4.3	2.2	< 0.02	180	-	1.1	-	-	3.7	-	-	3.4	-	-	-	-	-	90.7	-	-	1.1	-	-
117	616-02-106	E horizon	50-700	4.9	2.1	0.04	180	-	0.3	1.2	0.4	-	-	-	8.2	1.3	-	-	-	-	88.7	-	-	-	-	-
119	616-02-112	Mud	125-200	7.7	6.4	no data	100	-	-	-	-	-	-	-	4.1	-	-	-	-	-	3.1	-	-	11.3	81.5	-
120	616-02-112	Peat	200-300	7.6	4.3	0.60	100	-	-	27.5	-	-	-	-	8.6	-	-	-	-	-	-	-	-	63.9	-	-
121	616-02-112	B horizon	300-400	7.5	3.9	no data	100	-	0.4	1.3	-	-	-	-	1.9	-	-	-	-	-	59.0	-	-	-	37.3	-
122	616-02-112	C horizon	400-600	7.9	6.5	no data	100	-	-	0.4	-	-	-	-	0.9	-	-	-	-	-	7.9	-	-	-	90.9	-
123	616-02-113	A horizon	0-50	6.5	3.9	no data	50	-	0.8	-	-	-	-	-	6.9	-	-	-	-	-	92.3	-	-	-	-	-
124	616-02-113	E1 horizon	50-250	7.6	3.7	< 0.02	50	-	0.3	-	-	-	-	-	7.1	-	0.7	-	-	-	92.0	-	-	-	-	-
125	616-02-113	E2 horizon	250-300	7.6	1.6	0.10	50	-	0.3	1.9	-	-	-	-	5.7	-	5.9	-	-	-	86.2	-	-	-	-	-
127	616-02-122	E horizon	20-235	6.3	3.6	<0.02	240	-	0.2	-	-	-	-	-	2.6	-	-	-	-	-	97.1	-	-	-	-	-
128	616-02-122	B horizon	235-315	6.9	4.4	no data	240	-	1.0	-	-	-	-	-	5.4	-	-	-	0.8	-	92.7	-	-	-	-	-
130	616-02-122	2E3 horizon	500-700	6.5	1.9	< 0.02	240	0.2	0.3	-	-	-	-	-	17.5	-	-	-	0.2	-	81.8	-	-	-	-	-
131	616-02-127	E horizon	40-100	5.9	4.1	no data	200	-	0.2	-	-	-	-	-	0.5	-	-	-	-	-	99.3	-	-	-	-	-
132	616-02-127	Coffee rock	100-235	5.2	3.1	< 0.02	200	-	-	-	-	-	-	-	2.7	-	-	-	-	-	97.3	-	-	-	-	-
133	616-02-127	2E1 horizon	235-300	5.0	3.2	< 0.02	200	-	0.4	-	-	-	-	-	1.8	-	-	-	-	-	97.8	-	-	-	-	-
134	616-02-127	2E2 horizon	300-600	6.1	2.3	< 0.02	200	-	0.4	-	-	-	-	-	-	-	-	-	-	-	99.6	-	-	-	-	-

Ill = Illite, Kao = Kaolinite, Pyr = Pyrite, S = Elemental S, Jar = Jarosite, Mar = Marcasite, Mac = Mackinawite, Micro = Microcline, Na Ca Feldspar, Alb = Albite, Am = Amphibole, Gib = Gibbsite, Goe = Goethite, Qua = Quartz, Zir = Zircon, Ilm = Ilmenite, Hal = Halite, Cal = Calcite, Ara = Aragonite, - = not detected.

\* allophane is present in most coffee rock and some other samples but could not be detected by synchrotron XRD due to its diffuse reflections and the nature of background scattering from the glass capillary sample holder.

**Table 2 (Cont.)** Mineralogical composition (semi quantitative %) of the fine fraction of soil samples (based on synchrotron XRD)\*.

No	Site	Horizon	Depth (cm)	pH <sub>F</sub>	pH <sub>Fox</sub>	S <sub>CR</sub> (%)	GW (cm)	Ill	Kao	Pyr	S	Jar	Mar	Mac	Micro	Na Ca Feld	Alb	Am	Gib	Goe	Qua	Zir	Ilm	Hal	Cal	Ara
135	616-02-131	A horizon	0-50	7.4	4.9	no data	200	-	1.4	-	-	-	-	-	2.4	-	-	1.7	0.8	-	93.7	-	-	-	-	-
136	616-02-131	E horizon	50-325	7.3	4.2	<0.02	200	-	0.9	-	-	-	-	-	3.1	-	-	-	0.4	-	95.6	-	-	-	-	-
137	616-02-131	B horizon	325-425	6.4	3.6	<0.02	200	0.2	0.9	-	-	-	-	-	0.8	-	-	-	-	0.2	97.8	-	-	-	-	-
138	616-02-131	2E horizon	425-600	6.3	4.2	<0.02	200	0.1	0.1	-	-	-	-	-	0.8	0.8	-	-	-	-	98.2	-	-	-	-	-
139	616-02-136	A horizon	0-25	7.0	4.4	no data	180	-	-	-	-	-	-	-	2.2	-	-	-	-	-	97.8	-	-	-	-	-
140	616-02-136	Coffee rock	200-260	6.6	3.6	no data	180	-	9.6	-	-	-	-	-	8.5	-	-	-	-	-	81.9	-	-	-	-	-
141	616-02-136	E horizon	260-600	6.3	2.0	0.02	180	0.2	1.2	0.6	0.8	-	2.5	-	16.4	-	-	-	-	-	78.3	-	-	-	-	-
142	616-02-068	A horizon	0-25	5.9	4.8	no data	200	-	-	-	-	-	-	-	2.1	-	-	-	-	-	97.9	-	-	-	-	-
143	616-02-068	E horizon	25-200	6.1	4.7	<0.02	200	-	-	-	-	-	-	-	19.1	-	-	-	-	-	77.6	-	-	-	3.3	-
144	616-02-068	Coffee rock	200-300	5.6	2.7	0.04	200	-	0.5	-	-	-	-	-	5.0	-	-	-	0.2	-	94.3	-	-	-	-	-
145	616-02-068	B1 horizon	300-400	6.3	1.2	<0.02	200	-	0.9	0.4	0.4	-	-	-	6.3	-	-	-	0.8	-	91.2	-	-	-	-	-
146	616-02-068	B2 horizon	400-500	6.7	1.4	<0.02	200	-	1.3	0.8	-	-	-	-	7.1	-	-	-	1.3	-	89.5	-	-	-	-	-
147	616-02-068	B3 horizon	500-600	7.3	1.4	<0.02	200	-	1.4	2.6	0.8	-	-	-	12.1	-	-	-	1.2	-	81.9	-	-	-	-	-
150	616-02-065	Peat1	0-20	6.5	3.7	<0.02	150	-	2.6	-	-	-	-	-	2.6	-	-	-	-	-	94.8	-	-	-	-	-
154	616-02-065	Coffee rock1	480-560	6.0	1.6	<0.02	150	-	2.9	1.9	-	-	-	-	1.4	-	-	-	4.8	-	88.9	-	-	-	-	-
156	616-02-065	Coffee rock3	650-700	5.9	1.6	<0.02	150	-	0.5	-	-	-	-	-	2.8	-	-	-	1.3	-	95.4	-	-	-	-	-
158	616-02-122	B/E horizon	700-900	6.2	2.2	no data	240	-	0.3	-	-	-	-	-	4.5	-	-	-	0.6	-	94.6	-	-	-	-	-
159	616-02-122	2E2 horizon	375-500	6.2	1.9	no data	240	-	1.1	-	-	-	-	-	12.6	-	-	-	0.6	-	85.7	-	-	-	-	-
161	Ellenbrook	E horizon	0-150	4.5	4.5	no data	700	-	0.1	-	-	-	-	-	0.1	-	-	-	-	-	99.8	-	-	-	-	-
162	Ellenbrook	Coffee rock	150-200	4.0	3.1	no data	700	-	5.7	-	-	-	-	-	-	-	-	-	-	-	94.3	-	-	-	-	-
163	Ellenbrook	B horizon	200-500	2.6	1.9	no data	700	-	0.8	-	-	-	-	-	7.1	-	-	-	-	-	92.1	-	-	-	-	-
164	Ellenbrook	Coffee rock	200	4.3	3.00	no data	700	-	7.1	-	-	-	-	-	33.9	-	-	-	2.1	-	56.9	-	-	-	-	-
167	Ellenbrook	Coffee rock	150-200	4.6	1.9	no data	700	-	1.0	-	-	-	-	-	1.2	-	-	-	1.0	-	96.8	-	-	-	-	-
169	616-02-155	E horizon	50-150	9.1	5.5	no data	250	-	-	-	-	-	-	-	2.8	-	-	-	-	-	77.3	-	-	-	18.8	1.1
171	616-02-155	B horizon	500-600	8.3	7.1	no data	250	-	1.6	-	-	-	-	-	-	-	-	-	0.4	-	98.1	-	-	-	-	-
174	616-02-145	B horizon	450-475	7.1	2.6	no data	220	-	12.9	-	-	-	-	-	2.7	-	-	-	4.5	2.9	77.0	-	-	-	-	-
178	616-02-158	Coffee rock2	300-400	5.6	2.1	no data	290	-	0.7	-	-	-	-	-	3.4	-	-	-	1.8	-	94.1	-	-	-	-	-

Ill = Illite, Kao = Kaolinite, Pyr = Pyrite, S = Elemental S, Jar = Jarosite, Mar = Marcasite, Mac = Mackinawite, Micro = Microcline, Na Ca Feldspar, Alb = Albite, Am = Amphibole, Gib = Gibbsite, Goe = Goethite, Qua = Quartz, Zir = Zircon, Ilm = Ilmenite, Hal = Halite, Cal = Calcite, Ara = Aragonite, - = not detected.

\* allophane is present in most coffee rock and some other samples but could not be detected by synchrotron XRD due to its diffuse reflections and the nature of background scattering from the glass capillary sample holder.

**Table 2 (Cont.)** Mineralogical composition (semi quantitative %) of the fine fraction of soil samples (based on synchrotron XRD)\*.

No	Site	Horizon	Depth (cm)	pH <sub>F</sub>	pH <sub>Fox</sub>	S <sub>CR</sub> (%)	GW (cm)	Ill	Kao	Pyr	S	Jar	Mar	Mac	Micro	Na Ca Feld	Alb	Am	Gib	Geo	Qua	Zir	Ilm	Hal	Cal	Ara
N1	616-01-005	B horizon	620-630	5.5	2.7	0.014	640	-	0.6	-	-	-	-	-	0.6	-	-	-	0.8	-	98.0	-	-	-	-	-
N2	616-02-068	B horizon	450	7.2	1.8	0.027	200	-	0.9	1.8	-	-	-	-	5.3	-	-	-	1.1	-	90.9	-	-	-	-	-
N4	616-02-179	B horizon	375-400	6.1	1.6	0.013	320	-	1.0	0.5	-	-	0.6	-	1.2	-	-	-	0.7	-	96.1	-	-	-	-	-
N6	616-02-078	B horizon	400-500	4.8	1.5	0.014	200	-	0.2	1.6	-	-	-	-	0.3	-	-	-	-	-	97.6	-	-	0.3	-	-
N7	616-02-081	B horizon	400-800	6.2	1.4	0.052	300	-	0.3	1.7	-	-	0.7	-	3.9	-	-	-	-	-	93.4	-	-	-	-	-
N8	616-02-110	B horizon	200-500	6.3	1.8	0.036	180	-	1.0	12.3	-	-	-	-	2.8	-	-	-	-	-	26.2	-	-	-	57.7	-
N9	616-02-174	B horizon	250-550	5.5	2.5	<0.005	310	-	0.2	-	-	-	-	-	0.2	-	-	-	-	-	99.6	-	-	-	-	-
N10	616-02-065	B horizon	200	5.7	3.0	0.005	150	-	1.2	-	-	-	-	-	2.5	-	-	-	-	-	96.3	-	-	-	-	-

Ill = Illite, Kao = Kaolinite, Pyr = Pyrite, S = Elemental S, Jar = Jarosite, Mar = Marcasite, Mac = Mackinawite, Micro = Microcline, Na Ca Feldspar, Alb = Albite, Am = Amphibole, Gib = Gibbsite, Goe = Goethite, Qua = Quartz, Zir = Zircon, Ilm = Ilmenite, Hal = Halite, Cal = Calcite, Ara = Aragonite, - = not detected.

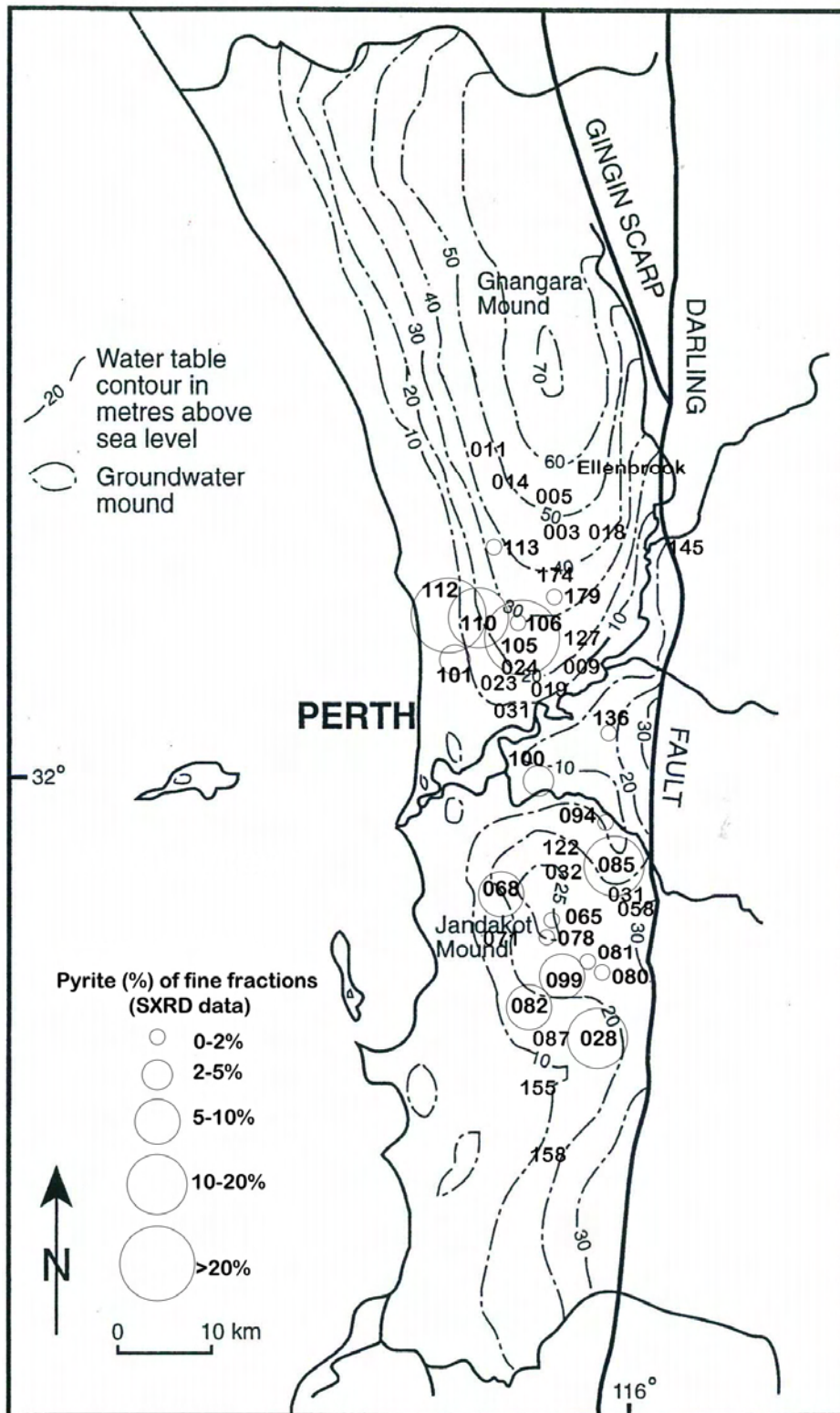
\* allophane is present in most coffee rock and some other samples but could not be detected by synchrotron XRD due to its diffuse reflections and the nature of background scattering from the glass capillary sample holder.

**Table 3** Semi quantitative SXRD analyses for sulfur minerals in the fine fraction and some soil properties.

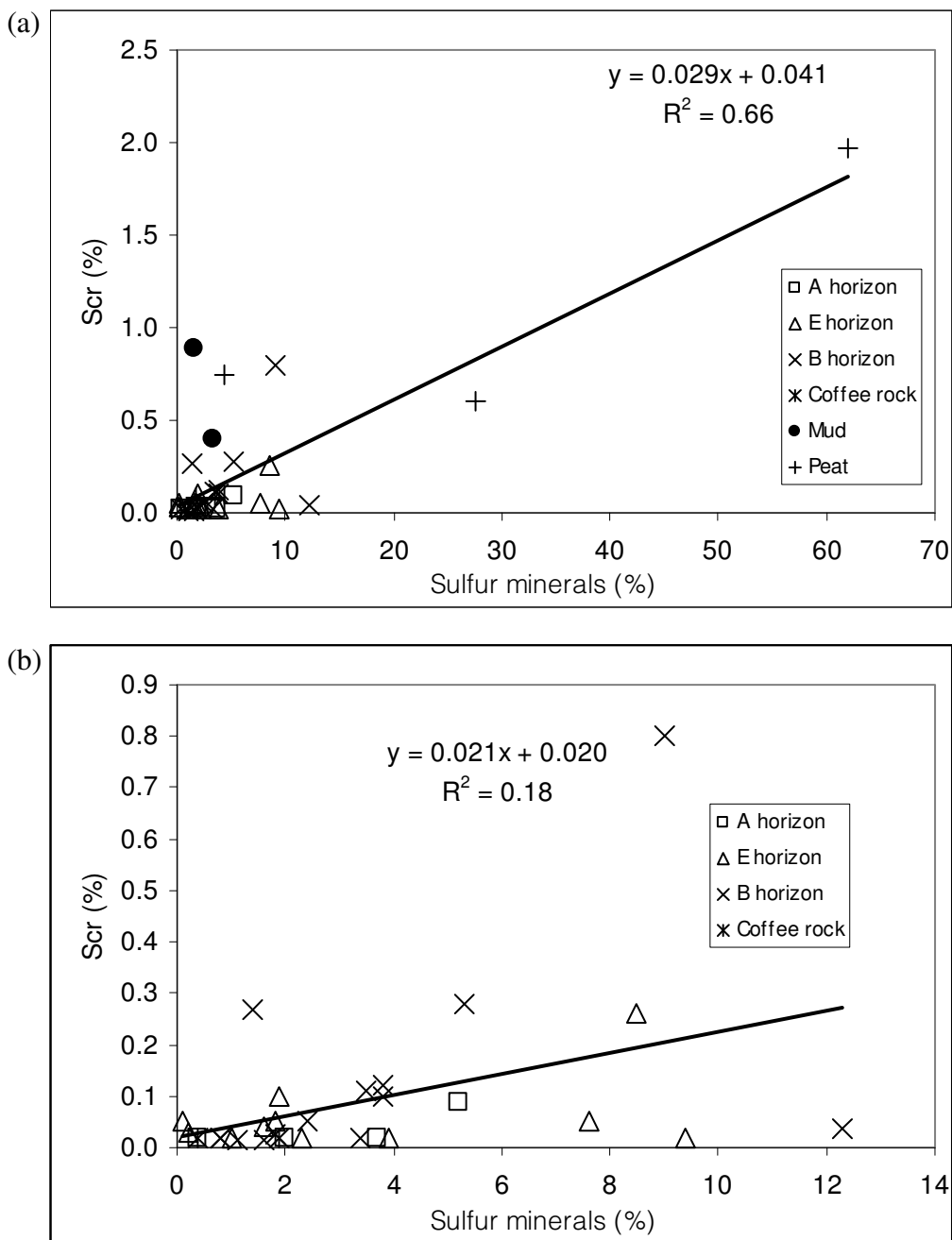
Sample No.	Site	Horizon	Depth (cm)	pH <sub>F</sub>	pH <sub>FOX</sub>	S <sub>CR</sub> (%)	GW (cm)	-----%-----				
								Pyr	S	Jar	Mar	Mac
095	616-02-094	A horizon	0-100	4.50	2.13	0.09	350	-	-	5.2	-	-
096	616-02-094	A horizon	100-175	4.27	2.77	<0.02	350	-	-	2.0	-	-
098	616-02-100	A horizon	0-80	8.00	5.53	no data	200	-	1.5	-	-	-
106	616-02-101	A horizon	0-75	7.43	3.77	<0.02	150	-	0.4	-	-	-
116	616-02-106	A horizon	0-50	4.25	2.20	<0.02	180	-	-	3.7	-	-
052	616-02-068	E horizon	375-600	7.21	1.76	<0.02	200	8.7	0.7	-	-	-
058	616-02-082	E horizon	200-300	5.04	1.84	0.02	50	2.3	-	-	-	-
060	616-02-082	E horizon	400-500	6.18	1.60	0.26	50	8.3	-	-	0.2	-
097	616-02-094	E horizon	175-600	5.88	3.56	0.03	350	0.2	-	-	-	-
101	616-02-100	E horizon	200-600	6.43	2.07	0.02	200	1.0	-	-	-	-
105	616-02-099	E horizon	400-600	6.76	2.06	0.05	50	7.6	-	-	-	-
109	616-02-101	E horizon	350-600	8.52	1.99	0.05	150	1.8	-	-	-	-
115	616-02-105	E horizon	480-700	7.11	3.90	0.05	170	0.1	-	-	-	-
117	616-02-106	E horizon	50-700	4.90	2.13	0.04	180	1.2	0.4	-	-	-
125	616-02-113	E horizon	250-300	7.60	1.57	0.10	50	1.9	-	-	-	-
141	616-02-136	E horizon	260-600	6.32	1.97	0.02	180	0.6	0.8	-	2.5	-
059	616-02-082	B horizon	300-400	5.78	1.55	0.11	50	3.2	0.3	-	-	-
087	616-02-085	B horizon	100-300	6.69	2.02	0.28	150	-	1.5	-	-	3.8
088	616-02-085	B horizon	300-400	7.10	1.95	0.80	150	9.0	-	-	-	-
090	616-02-028	B horizon	30-100	4.33	2.25	0.27	150	-	-	0.6	0.8	-
103	616-02-099	B horizon	200-300	7.08	2.54	0.10	50	3.8	-	-	-	-
104	616-02-099	B horizon	300-400	7.20	1.83	0.12	50	3.8	-	-	-	-
121	616-02-112	B horizon	300-400	7.45	3.93	no data	100	1.3	-	-	-	-
145	616-02-068	B horizon	300-400	6.30	1.18	<0.02	200	0.4	0.4	-	-	-
146	616-02-068	B horizon	400-500	6.73	1.40	<0.02	200	0.8	-	-	-	-
147	616-02-068	B horizon	500-600	7.28	1.35	<0.02	200	2.6	0.8	-	-	-
N2	616-02-068	B horizon	450	7.20	1.80	0.027	200	1.8	-	-	-	-
N4	616-02-179	B horizon	375-400	6.10	1.60	0.013	320	0.5	-	-	0.6	-
N6	616-02-078	B horizon	400-500	4.80	1.50	0.014	200	1.6	-	-	-	-
N7	616-02-081	B horizon	400-800	6.20	1.40	0.052	300	1.7	-	-	0.7	-
N8	616-02-110	B horizon	200-500	6.30	1.80	0.036	180	12.3	-	-	-	-
055	616-02-080	Coffee rock	200-400	5.30	3.17	<0.02	200	0.4	-	-	-	-
061	616-02-082	Coffee rock	500-600	6.73	1.50	no data	50	6.7	0.5	-	-	-
154	616-02-065	Coffee rock	480-560	6.00	1.57	<0.02	150	1.9	-	-	-	-
089	616-02-085	Mud	400-600	7.43	2.56	0.40	150	-	0.2	3.1	-	-
091	616-02-028	Mud	100-200	6.63	2.98	0.89	150	1.5	-	-	-	-
092	616-02-028	Mud	200-250	7.35	5.98	no data	150	16.0	-	-	-	-
100	616-02-100	Peat	110-200	7.06	3.24	0.08	200	2.6	-	-	0.9	-
107	616-02-101	Peat	150-200	7.37	5.37	no data	150	4.7	-	-	-	-
108	616-02-101	Peat	200-350	7.13	1.60	0.74	150	4.3	-	-	-	-
113	616-02-105	Peat	250-360	6.25	1.43	1.97	170	61.9	-	-	-	-
114	616-02-105	Peat	360-480	6.65	1.98	0.08	170	1.6	0.1	-	-	-
120	616-02-112	Peat	200-300	7.62	4.30	0.60	100	27.5	-	-	-	-
122	616-02-112	C horizon	400-600	7.86	6.46	no data	100	0.4	-	-	-	-

- = not detected, Pyr = Pyrite; S = Elemental S; Jar = Jarosite; Mar = Marcasite; Mac = Mackinawite, S<sub>CR</sub> = Chromium reducible sulfur; GW = Groundwater level



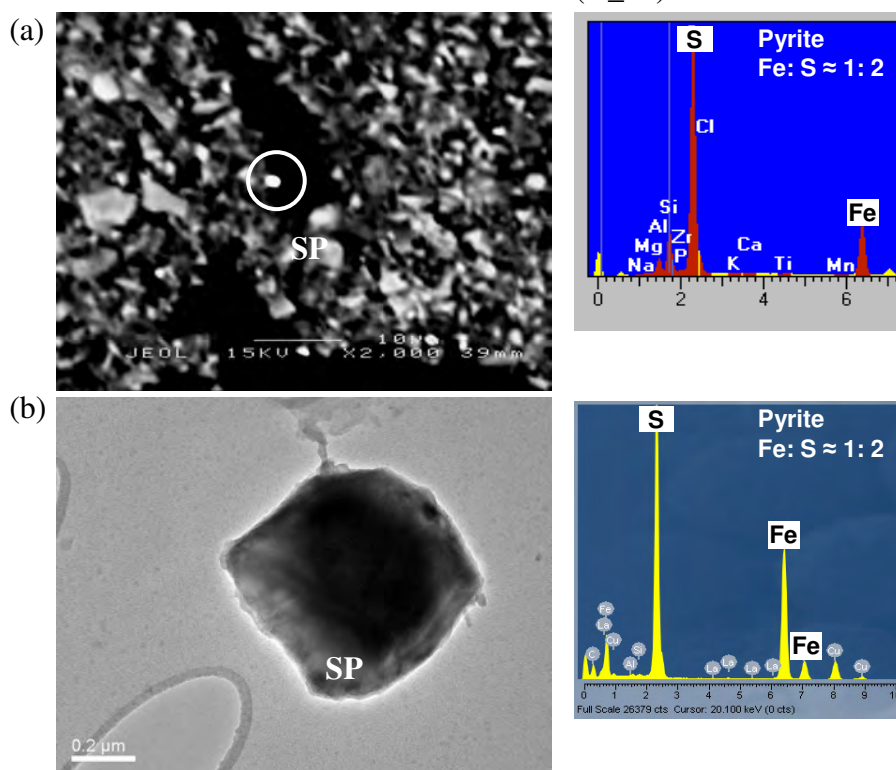


**Figure 15** The spatial distribution of pyrite content (semi quantitative %) of the fine fraction of soil samples (based on synchrotron XRD) related to water table contours for the Perth region.



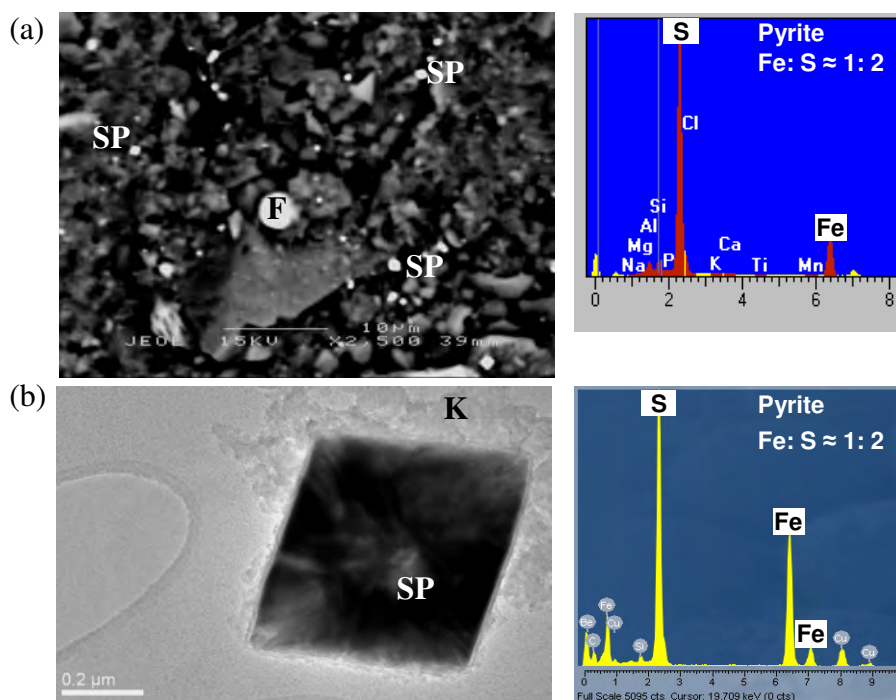
**Figure 16** Bivariate relationship between (a) sulfur minerals (%) and  $S_{CR}$  of A, E, B, coffee rock, mud and peat horizons (%), (b) sulfur minerals (%) and  $S_{CR}$  of A, E, B and coffee rock horizons. RHS plots omit the mud and peat samples which make the relationship nonsignificant showing that the LHS relationships are spurious due to the bimodal distribution of these data.

B horizon (N\_01)



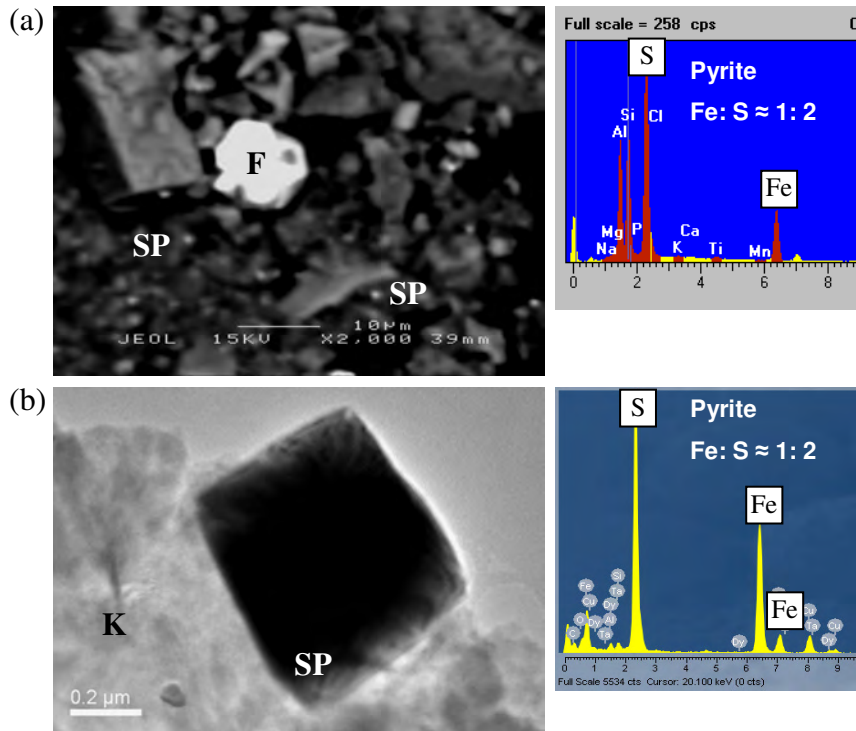
**Figure 17** (a) SEM backscattered electron image (b) TEM transmission electron micrograph and x-ray spectrum of fine fraction pyrite from the B horizon (620-630 cm, site 616-01-005) ( $pH_F = 5.5$ ,  $pH_{FOX} = 2.7$ ,  $S_{CR} = 0.014\%$ ), pyrite was not detected by SXR but at high magnification rare pyrite crystals can be seen (SP = Single crystal pyrite).

B horizon (N\_02)



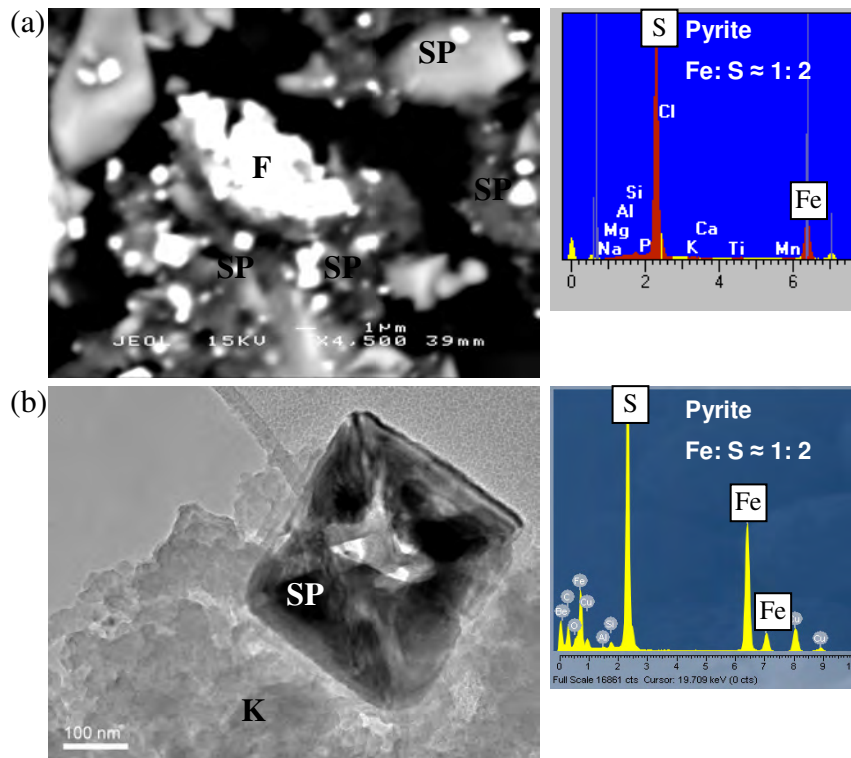
**Figure 18** (a) SEM secondary electron image (b) TEM transmission electron micrograph and x-ray spectrum of fine fraction pyrite from the B horizon (450 cm, site 616-02-068) ( $pH_F = 7.2$ ,  $pH_{FOX} = 1.8$ ,  $S_{CR} = 0.027\%$ ) (F = Framboidal pyrite, SP = Single crystal pyrite, K = Kaolin).

B horizon (N\_04)



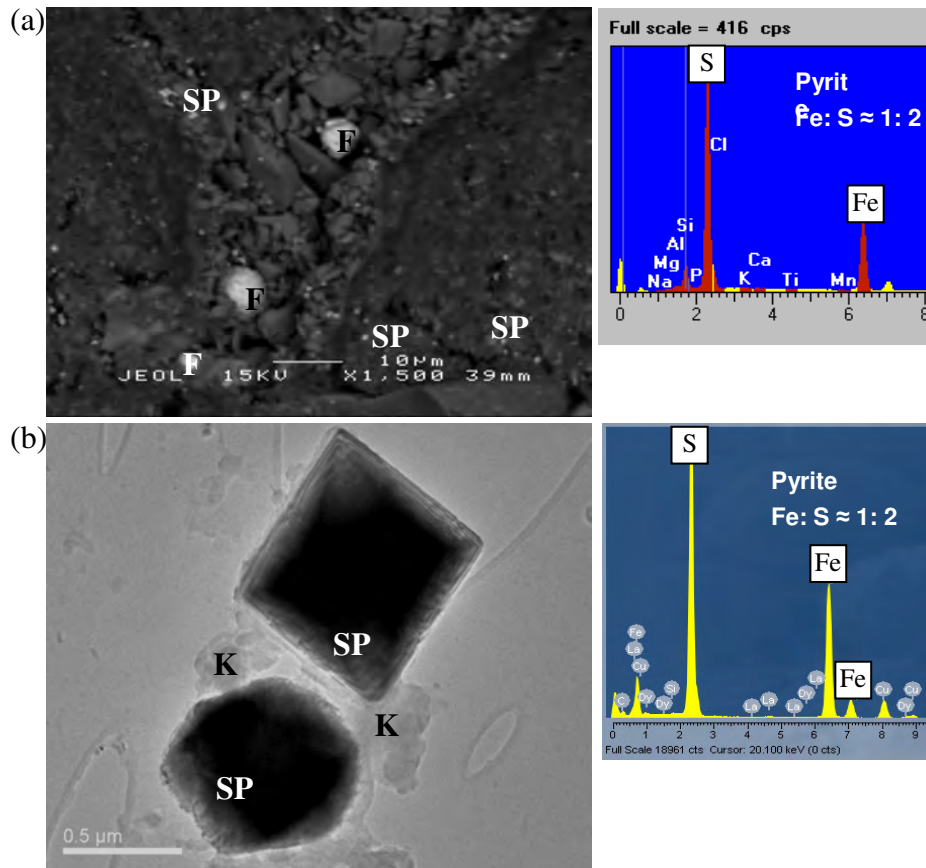
**Figure 19** (a) SEM backscattered electron image (b) TEM transmission electron micrograph and x-ray spectrum of fine fraction pyrite from the B horizon 375-400 cm, site 616-02-179) ( $\text{pH}_F = 6.1$ ,  $\text{pH}_{\text{FOX}} = 1.6$ ,  $S_{\text{CR}} = 0.013\%$ ) (F = Framboidal pyrite, SP = Single crystal pyrite, K = Kaolin).

B horizon (N\_06)



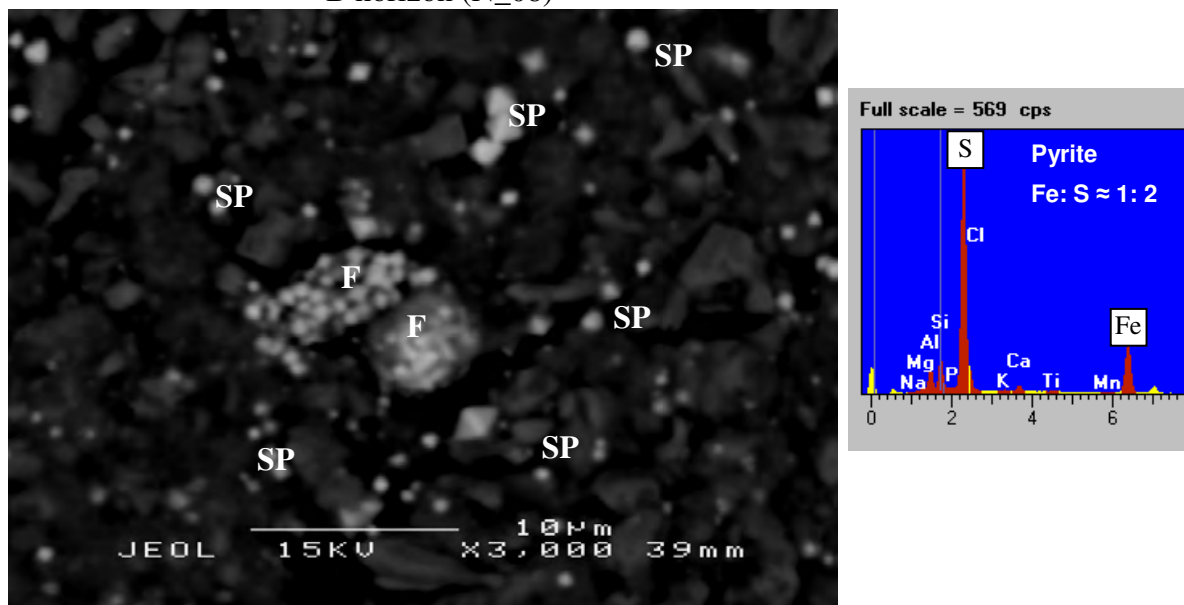
**Figure 20** (a) SEM backscattered electron image (b) TEM transmission electron micrograph and x-ray spectrum of fine fraction pyrite from the B horizon (400-500 cm, site 616-02-078) ( $\text{pH}_F = 4.8$ ,  $\text{pH}_{\text{FOX}} = 1.5$ ,  $S_{\text{CR}} = 0.014\%$ ) (F = Framboidal pyrite, SP = Single crystal pyrite, K = Kaolin).

B horizon (N\_07)



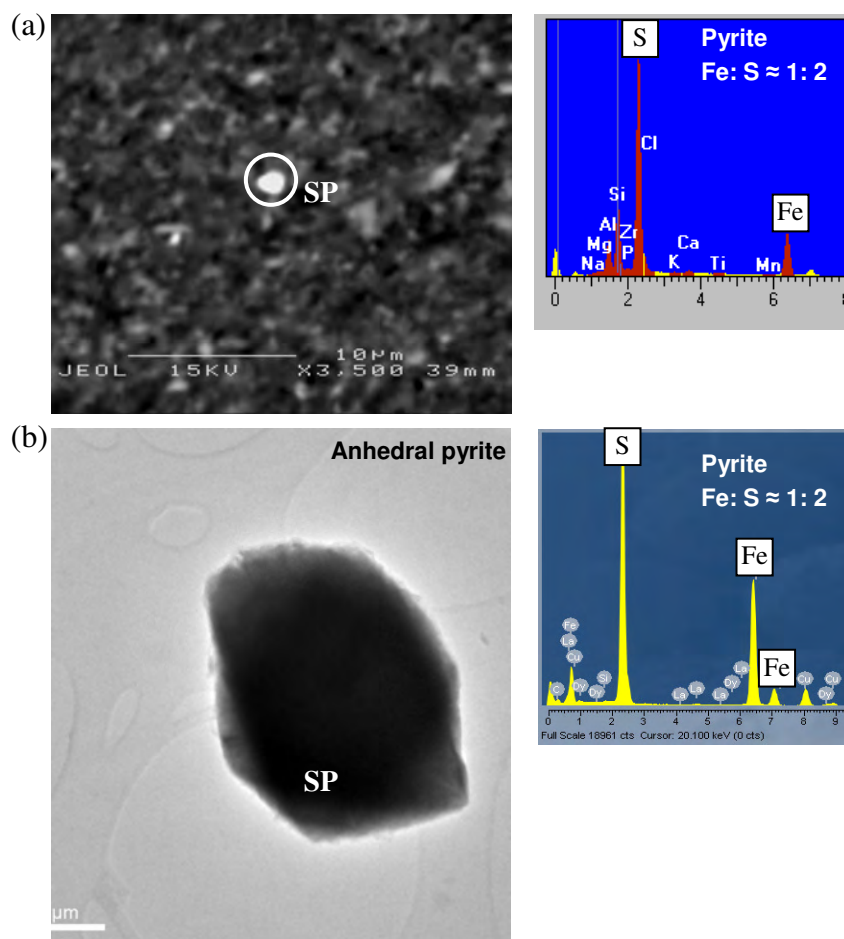
**Figure 21** (a) SEM secondary electron image (b) TEM transmission electron micrograph and x-ray spectrum of fine fraction pyrite from the B horizon (400-800 cm, site 616-02-081) ( $pH_F = 6.2$ ,  $pH_{FOX} = 1.4$ ,  $S_{CR} = 0.052\%$ ) (F = Framboidal pyrite, SP = Single crystal pyrite, K = Kaolin).

B horizon (N\_08)



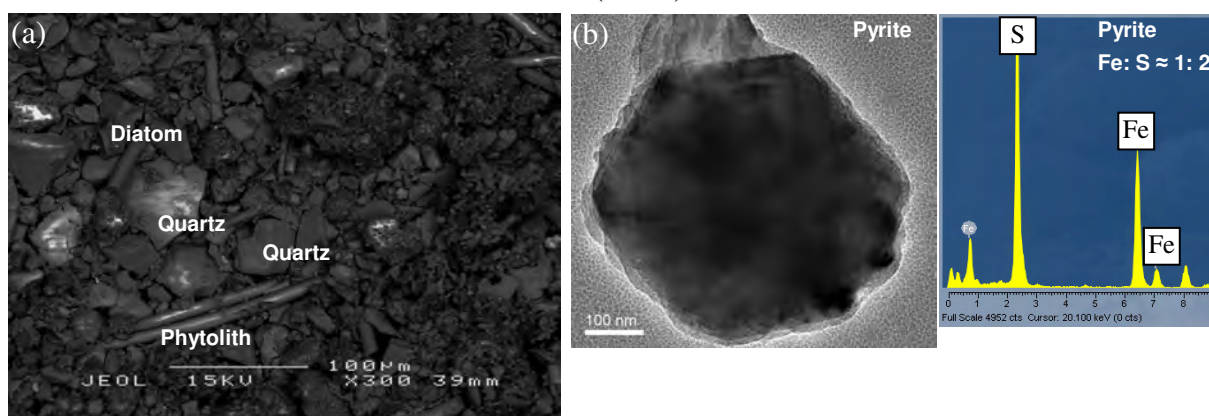
**Figure 22** SEM secondary electron image and x-ray spectrum of fine fraction pyrite from the B horizon (200-500 cm, site 616-02-110) ( $pH_F = 6.3$ ,  $pH_{FOX} = 1.8$ ,  $S_{CR} = 0.036\%$ ) (F = Framboidal pyrite, SP = Single crystal pyrite).

B horizon (N\_09)



**Figure 23** (a) SEM backscattered electron image (b) TEM transmission electron micrograph and x-ray spectrum of fine fraction pyrite from the B horizon (250-550 cm, site 616-02-174) ( $\text{pH}_F = 5.5$ ,  $\text{pH}_{\text{FOX}} = 2.5$ ,  $S_{\text{CR}} = <0.005\%$ ). Pyrite was not detected by SXRD however at high magnification rare pyrite crystals can be seen (SP = Single crystal pyrite).

B horizon (N\_10)



**Figure 24** (a) SEM backscattered electron image with no evident pyrite (b) TEM transmission electron micrograph and x-ray spectrum of fine fraction pyrite from the B horizon (200 cm, site 616-02-065) ( $\text{pH}_F = 5.7$ ,  $\text{pH}_{\text{FOX}} = 3.0$ ,  $S_{\text{CR}} = 0.005\%$ ). Pyrite was not detected by SXRD and SEM however at high magnification rare pyrite crystals can be seen.

#### 5.4 Total chemical composition (ICP and XRF data)

The complete chemical analyses of the whole soils (XRF analysis) are shown in Appendix Table 2. The median and range of minor element concentrations in A, E, B, coffee rock, mud, peat and C horizons (ICP-OES analysis) are given in Appendix Figures 26-59. All soil profiles have quite similar compositions except for a buried soil profile (site 616-02-112) and alluvium

XRF analysis shows that silica dominates in most soil horizons (70-100%) except for mud (8-66%) and peat samples (1-25%). The alumina content of coffee rock is higher than for other horizon (Appendix Table 2). Calcium content is high in mud, peat and C horizons. Sulfur is a very minor constituent of the studied soils. The concentration of iron is highly variable in coffee rock (Appendix Table 2) which is consistent with SEM/EDS data that indicated that iron is not always present at elevated concentrations in coffee rock and that some cemented materials contain little iron (Figures 2 and 6). The Bassendean soil samples have a very high quartz sand content, so that XRF analysis unable to detect some elements in some samples.

For ICP-OES analysis, a combined procedure, involving an aqua regia partial digest and acid digestion of a fusion of whole soil, provides total element compositions. These data enable identification of associations of elements in the fine materials and resistant minerals (Appendix Tables 3 and 4).

Aluminium is relatively abundant in coffee rock (Appendix Figure 27). The Al: Si ratio is always high in coffee rock. Aqua regia dissolves allophane but the Al: Si ratio for this digest is too high for allophane (2: 1) alone and some aluminium comes from kaolin (1: 1), gibbsite (1: 0) and aluminium-organic (1: 0) complex. Iron is relatively abundant in some coffee rock samples; sulfur concentrations are highest in coffee rock and E horizons. Lead and other heavy metals are not present at hazardous concentrations. Arsenic is present in one peat sample at a hazardous concentration (418 mg kg<sup>-1</sup>) (accepted limit 20-50 mg kg<sup>-1</sup>) (Appendix Figure 39). Peat has relatively high sodium content as it is salty (Appendix Figure 30). The sulfur content of E, B, coffee rock and peat horizons is higher than for normal surface soils worldwide (Appendix Figure 38).

The relationships between element concentrations and EC are shown in Table 4. There are very close positive relationships for sulfur, arsenic, iron, C and N (Table 4) however, there are a bimodal distributions of data for the relationships between carbon

and arsenic, carbon and sulfur and nitrogen and sulfur (Figure 25) reducing the statistical validity of these relationships. Some elements and soil properties have positive relationships with a more normal distributions of data (Figure 26).

Factor analysis and principal component analysis was carried out on chemical analyses of whole soil using only data for Bassendean sand dune samples (not include alluvium samples). These results show that only 46% of the variation in chemical data for the soils is explained by the first two factors which is a consequence of the diverse nature of these soil materials (Figure 27a). Three affinity groups of elements are recognized. The first group consists of Si ( $\text{SiO}_2$ ) which simply relates to the sand fraction of the soils and is not positively related to any other elements. The second group is strongly negatively related to Si, it consists of As, S, C and N which are associated with organic matter. The third group which is also negatively related to Si consists of all remaining elements samples (Al, Ba, Be, Ca, Ce, Co, Cu, Cr, Fe, Ga, Gd, Ge, Hf, K, La, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Sc, Sr, Th, Ti, V, Y, Zn, Zr) and represents the diverse minerals and adsorbed species in the fine fraction of these soils.

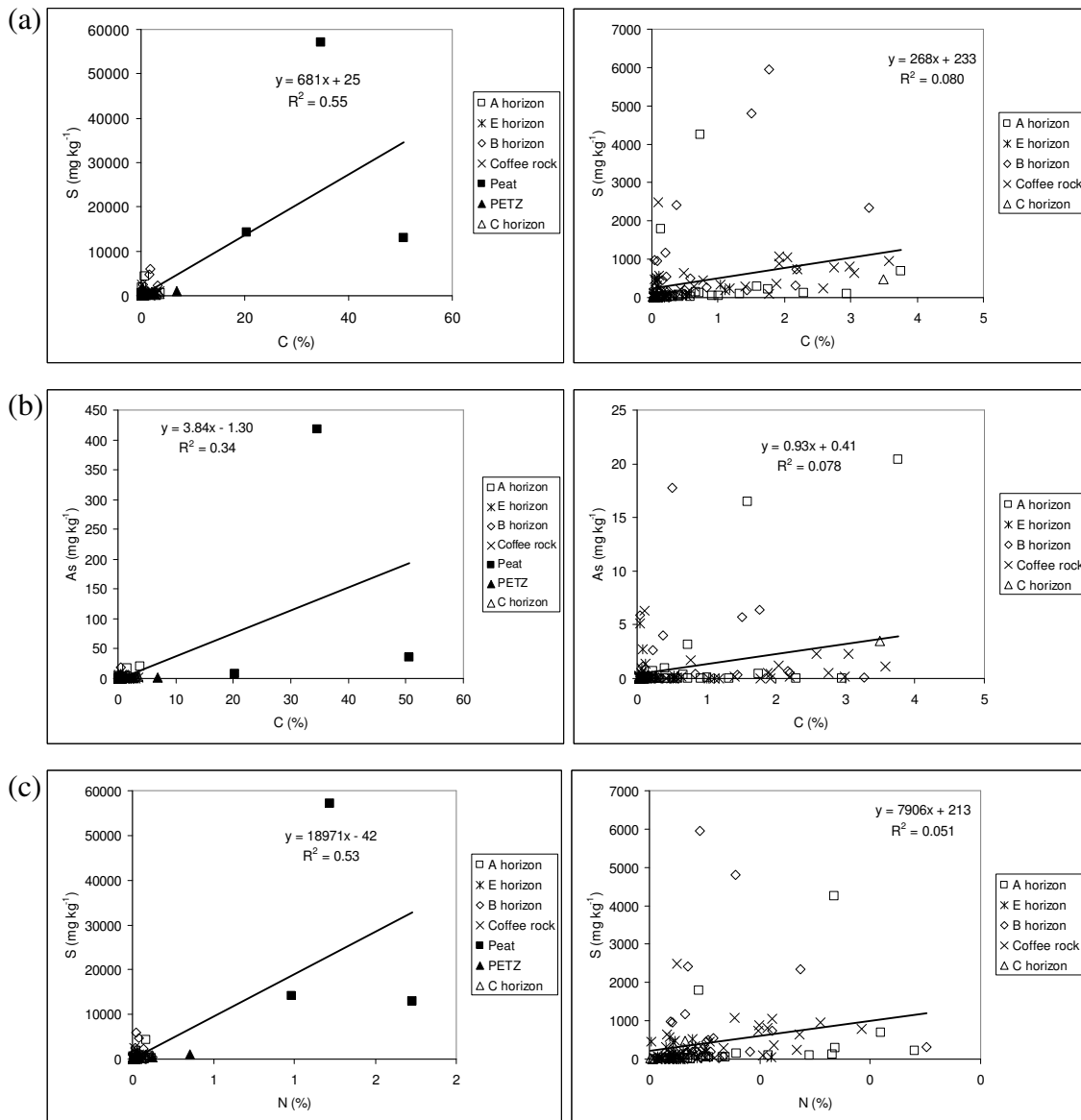
For the cases factor plot, most soil samples are quite similar (group 1) (Figure 26b). All peat samples have relatively high sulfur, arsenic carbon and nitrogen concentrations (group 2) The B horizons are diverse because some B horizons contain relatively high Al and Fe concentrations (group 3).



**Table 4** Correlation matrix (r) showing significant relationships between concentrations of elements for whole soil samples (ICP-OES analysis) (p<0.05)

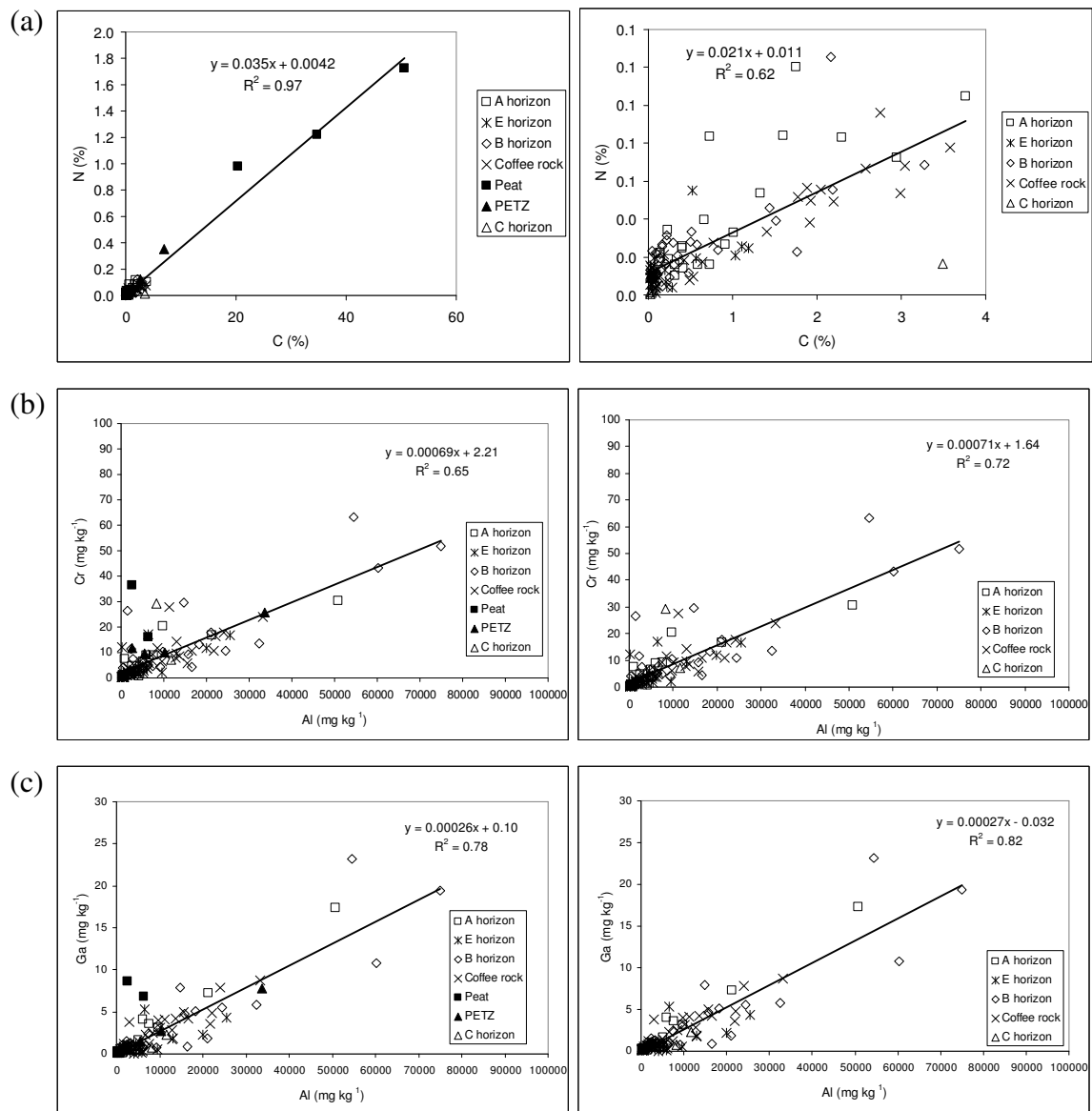
(N = 124).

	C	N	EC	Si	Al	Na	K	Ca	Mg	Fe	Mn	Ti	Zn	Zr	P	S	As	Cu	Cr	Pb	Ni	Ba	Be	Ce	Co	Ga	Gd	Ge	Hf	La	Mo	Nd	Sc	Sr	Th	V	Y		
C	1.00																																						
N	0.99	1.00																																					
EC			1.00																																				
Si	-0.86	-0.87		1.00																																			
Al				-0.30	1.00																																		
Na	0.60	0.59		-0.53	0.27	1.00																																	
K			0.29	-0.19	0.62	0.43	1.00																																
Ca	0.22	0.22		-0.43				1.00																															
Mg	0.79	0.81		-0.83	0.28	0.66	0.22	0.44	1.00																														
Fe	0.37	0.40		-0.63	0.59	0.24	0.31		0.38	1.00																													
Mn	0.31	0.37	0.25	-0.40	0.19	0.24	0.26	0.42	0.52	0.40	1.00																												
Ti					0.49		0.34			0.26		1.00																											
Zn													1.00																										
Zr											0.76			1.00																									
P	0.33	0.35		-0.46	0.34			0.32	0.44	0.37	0.41				1.00																								
S	0.73	0.73		-0.72		0.20		0.19	0.41	0.60	0.29				0.24	1.00																							
As	0.59	0.57		-0.58					0.22	0.58						0.96	1.00																						
Cu				-0.26	0.47	0.33	0.29		0.23	0.47	0.21	0.29	0.37		0.28		1.00																						
Cr				-0.49	0.81		0.41	0.26	0.38	0.75	0.35	0.42		0.22	0.47	0.29	0.28	0.39	1.00																				
Pb					0.35					0.39			0.64		0.27		0.60	0.38	1.00																				
Ni	0.45	0.49	0.27	-0.56	0.24	0.34			0.46	0.48	0.34				0.34	0.39	0.33		0.39		1.00																		
Ba	0.35	0.42		-0.58	0.47	0.35	0.35	0.46	0.58	0.59	0.69	0.21			0.69	0.33	0.52	0.57	0.32	0.37	1.00																		
Be	0.41	0.41		-0.53	0.25				0.18	0.77					0.31	0.75	0.82		0.57	0.21	0.42	0.30	1.00																
Ce			0.20	-0.33	0.62	0.24	0.61	0.25	0.30	0.44	0.25	0.53		0.40	0.40		0.42	0.63	0.33		0.54	0.22	1.00																
Co				-0.30	0.64	0.22	0.41		0.35	0.57	0.22	0.45		0.35	0.28		0.32	0.70	0.32	0.26	0.41	0.45	0.49	1.00															
Ga				-0.42	0.88	0.21	0.38		0.31	0.81	0.36	0.49		0.23	0.45	0.21	0.19	0.53	0.87	0.48	0.35	0.60	0.51	0.59	0.64	1.00													
Gd							0.29	0.42				0.21		0.29	0.39				0.33			0.27		0.72			1.00												
Ge																																							
Hf					0.26							0.20							0.18		-					0.20	0.34	0.83	1.00										
La			0.19	-0.36	0.70	0.22	0.57	0.30	0.35	0.43	0.25	0.57		0.38	0.44		0.39	0.72	0.33	0.19	0.55	0.23	0.94	0.53	0.63	0.73		0.19	1.00										
Mo			0.34	-0.29	0.36	0.30	0.24		0.20	0.48	0.20	0.34			0.24	0.22		0.48	0.34	0.28	0.21	0.45	0.25	0.42	0.30	0.46			0.38	1.00									
Nd			0.19	-0.39	0.63	0.22	0.58	0.33	0.32	0.47	0.24	0.50		0.37	0.46	0.21		0.39	0.68	0.31	0.19	0.55	0.31	0.98	0.49	0.61	0.77		0.95	0.41	1.00								
Sc				-0.32	0.89	0.27	0.53		0.35	0.66	0.21	0.55		0.27	0.24			0.54	0.78	0.37	0.24	0.48	0.28	0.63	0.75	0.84		0.69	0.45	0.61	1.00								
Sr				-0.30				0.86	0.39		0.47				0.29			0.28				0.42					0.37			0.28	0.25		1.00						
Th				-0.28	0.88	0.23	0.53		0.29	0.64	0.20	0.68		0.43	0.22			0.43	0.80	0.42	0.21	0.43	0.31	0.66	0.77	0.85	0.21		0.18	0.73	0.44	0.65	0.94		1.00				
V				-0.19	0.49					0.62					0.31			0.60	0.44	0.31	0.30	0.56	0.26	0.53	0.66			0.27	0.30	0.27	0.52		0.59	1.00					
Y	0.39	0.38		-0.53				0.36	0.25	0.54					0.31	0.74	0.76		0.45			0.33	0.73	0.45	0.33	0.27	0.41		0.41	0.19	0.54	0.18	0.27	0.18	0.27		1.00		

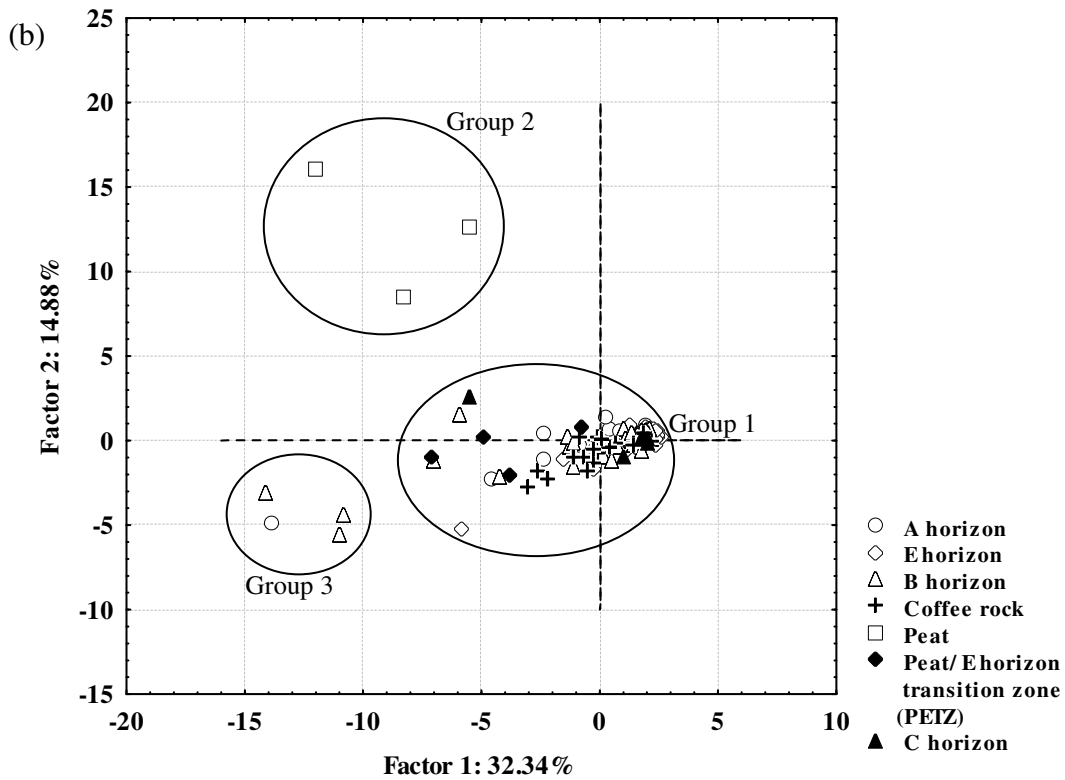
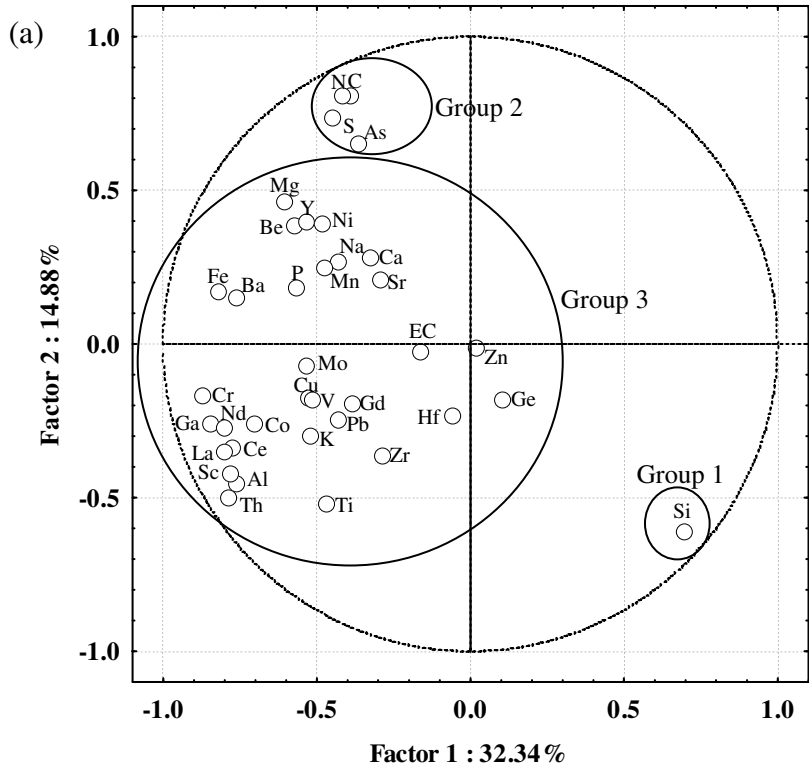


**Figure 25** Some significant bivariate relationships between (a) carbon and sulfur (b) carbon and arsenic and (c) nitrogen and sulfur. RHS plots omit the PETZ and peat samples which make the relationships non significant showing that the LHS relationships are spurious due to the bimodal distribution of these data.

NB all data for whole soil samples.



**Figure 26** Some highly significant bivariate relationships (for a more normal distribution of data) between (a) carbon and nitrogen (b) aluminium and chromium and (c) aluminium and gallium. RHS plots omit the PETZ and peat samples but the relationship continue to be highly significant showing that the LHS relationships are not spurious due to the abnormal distribution of these data.



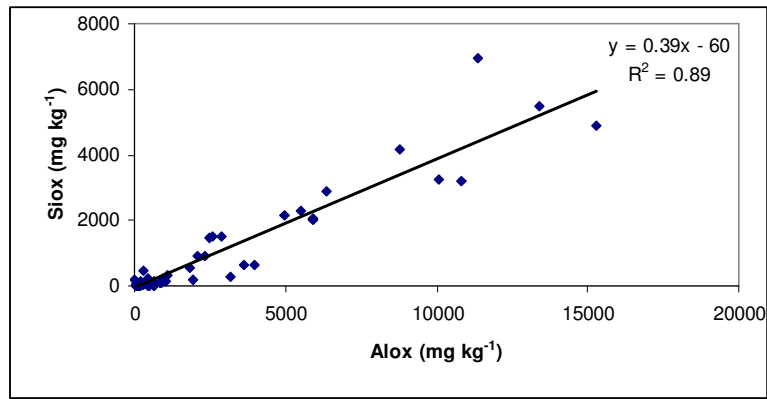
**Figure 27** Factor analysis for chemical analyses by aqua regia digests and fusion acid digestion methods of whole soil samples and some soil properties of whole soil materials (N = 124) (a) distribution of elements and some soil properties (variables) (b) distribution of soil samples (cases).

## 5.5 Extractable silicon, aluminium, iron, manganese

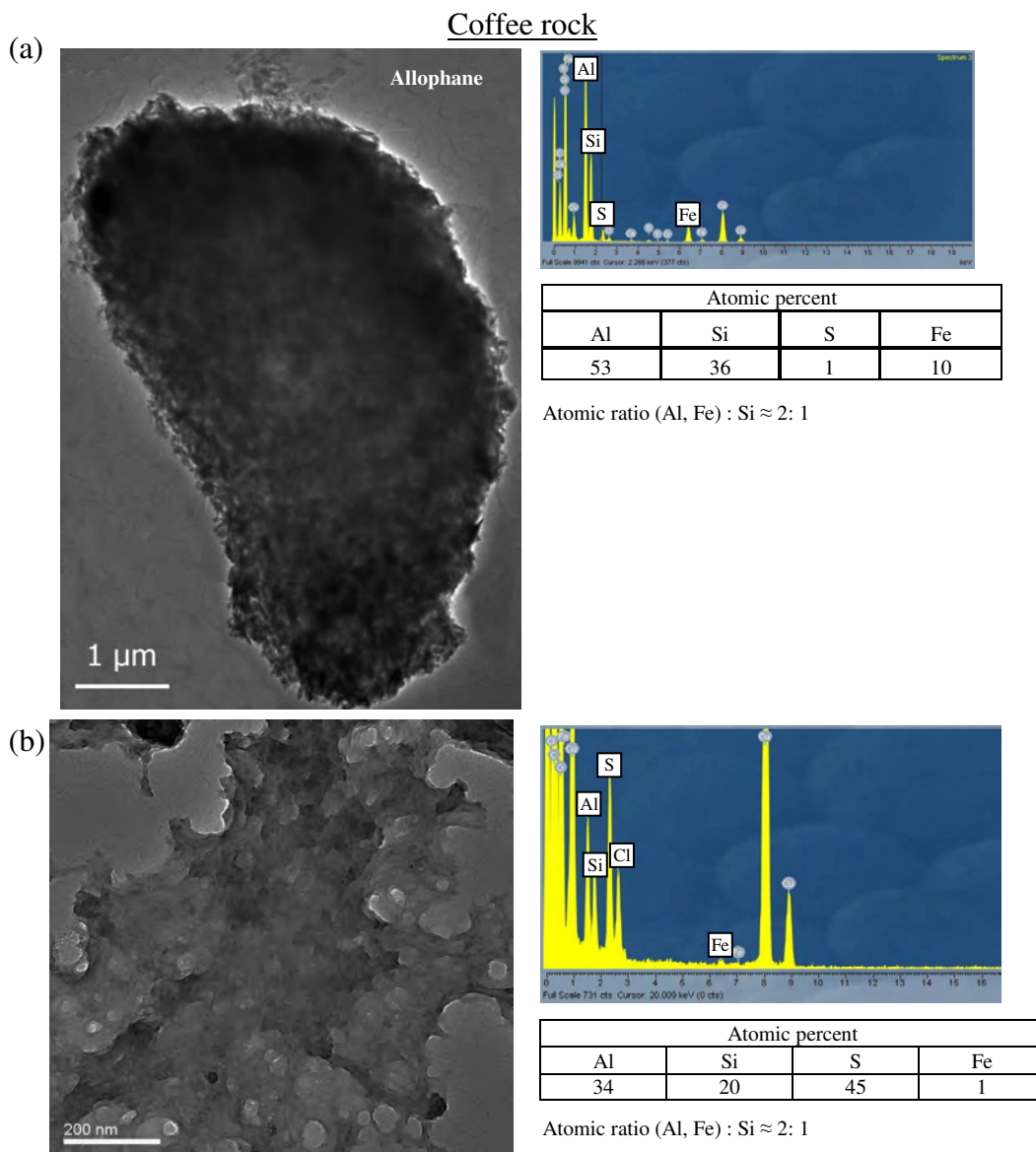
Si, Al, Fe and Mn concentrations of extractable by dithionite-citrate-bicarbonate (d), ammonium oxalate (ox) and pyrophosphate (p) are also given in Appendix Table 5. These extractions estimate the various “reactive” constituents of soils: respectively crystalline oxides, amorphous oxides and OM complexes (García-Rodeja, *et al.*, 2004). Maximum, minimum and median values of extractable Si, Al, Fe, Mn are presented in Appendix Figures 60-71. Si contents of all extractions of coffee rock are higher than for other soil horizons, especially the concentration of silicon extracted by ammonium oxalate which has a close relationship with amorphous minerals, particularly allophane in this instance.

Aluminium (Ald, Alox and Alp) are high in coffee rock and B horizon because of the amorphous alumino-silicate cementing agent between sand grains. The ratio Alox/ Siox of coffee rock and B horizon may indicate the composition of the allophane present in these soils. Figure 28 is a bivariate plot of Siox and Alox which has a slope of 0.4 which is similar to that expected for allophane (García-Rodeja, *et al.*, 2004). A TEM of allophane is shown in Figure 29.

Extractable iron analysis uses three separate techniques to determine the types of ferric minerals present in soil samples. Crystalline iron oxides as estimated by DCB extraction (Fed), whereas the concentration of amorphous iron compounds (active iron) in soils is estimated by oxalate extraction. Organically bound iron and aluminium are extracted with a Na-pyrophosphate solution. The pyrophosphate-soluble iron concentration of B horizon, coffee rock and peat is higher than for other soil horizons, probably because of Fe complexing with the more abundant organic matter. Manganese concentrations for all extractions are very low.



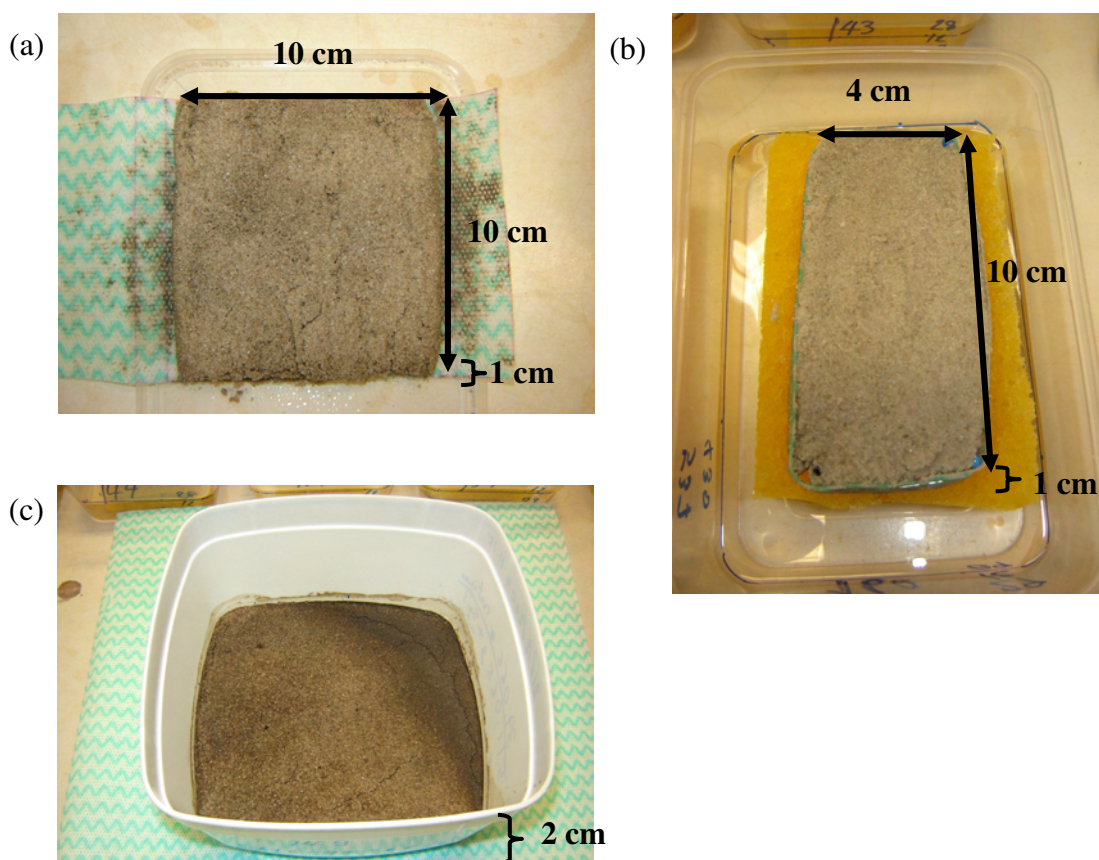
**Figure 28** Bivariate relationship between Alox and Siox of coffee rock and B horizons.



**Figure 29** Transmission electron micrograph and X-ray spectrum of an allophane ( $\text{Al, Fe}_2\text{O}_3 \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ ) particle from (a) coffee rock (5.0-6.0 m, site 616-02-82), (b) coffee rock (3.0-5.0 m, site 616-02-58), this allophanic material contains much elemental or incorporated S.

## 5.6 Incubation

Potential acid sulfate soils can be identified by incubation of soil samples in an open tray. This procedure simulates oxidation under natural conditions. Three incubation methods at different soil moisture contents were used to identify sulfidic materials in this research (Figure 30). Summary details of the incubation study are shown in Table 5. Three soil profiles (17 soil samples), including site 616-02-65, 616-02-68 and 616-02-122, were studied by the incubation method to determine the pH trend as natural (not  $H_2O_2$ ) oxidation takes place. Only sample No 149 (site 616-02-68 B horizon; depth 7.0-8.0 m) was used for all three incubation methods. Some samples from the soil column experiment (site 616-02-05, 616-02-68 and 616-02-179) were also used for the standard incubation method.



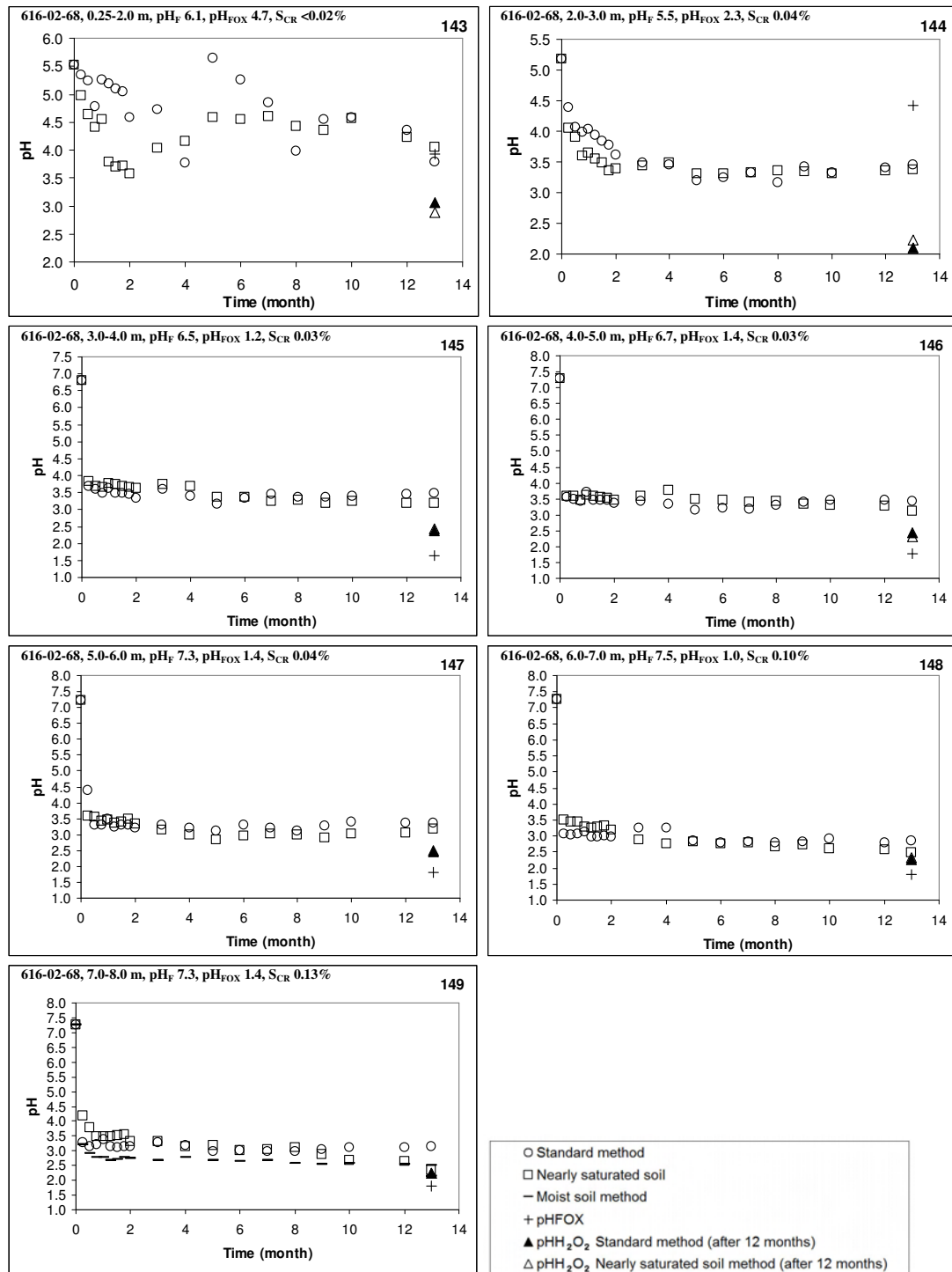
**Figure 30** (a) standard method prescribed by the USDA/ Australian soil classifications (1 cm soil thick); (b) modified standard method for nearly saturated soil (1 cm soil thick) and (c) modified method for moist soil (2 cm soil thick).

All soil pH values decreased by more than 0.5 units therefore all soils are sulfidic material, an accelerated oxidation of sulfide occurred when the pH decreased below pH 4.0 (Soil Survey Staff, 2006) (Figures 31-34). The pH of many samples decreased to low or very low values (Figures 31-34). The pH values for many soil samples appears to have reached a steady state but these steady state values are much higher than those obtained with H<sub>2</sub>O<sub>2</sub>.

For many samples, the starting pH was already lower than field pH measured in water because some oxidation had occurred during sampling and storage consequently incubation commenced with samples that were considerably more acid than their original field condition. For Figure 34 (site 616-02-05, 616-02-68 and 616-02-179), the field pH (water) indicated in this figure is the starting pH (0 day). The pH decreased very quickly but after 2 months, the pH was quite stable and pH(H<sub>2</sub>O) did not decrease to pH(H<sub>2</sub>O<sub>2</sub>). pH(H<sub>2</sub>O<sub>2</sub>) for the standard and nearly saturated soil methods is higher than field pH(H<sub>2</sub>O<sub>2</sub>) (pH<sub>FOX</sub>) possibly because some acid buffering reactions take place during the incubations but did not during the rapid field H<sub>2</sub>O<sub>2</sub> (pH<sub>FOX</sub>) oxidation (Figures 31-34). Figure 34 compares the pH values produced by incubation and peroxide treatment (pH<sub>FOX</sub>) for B horizon samples.

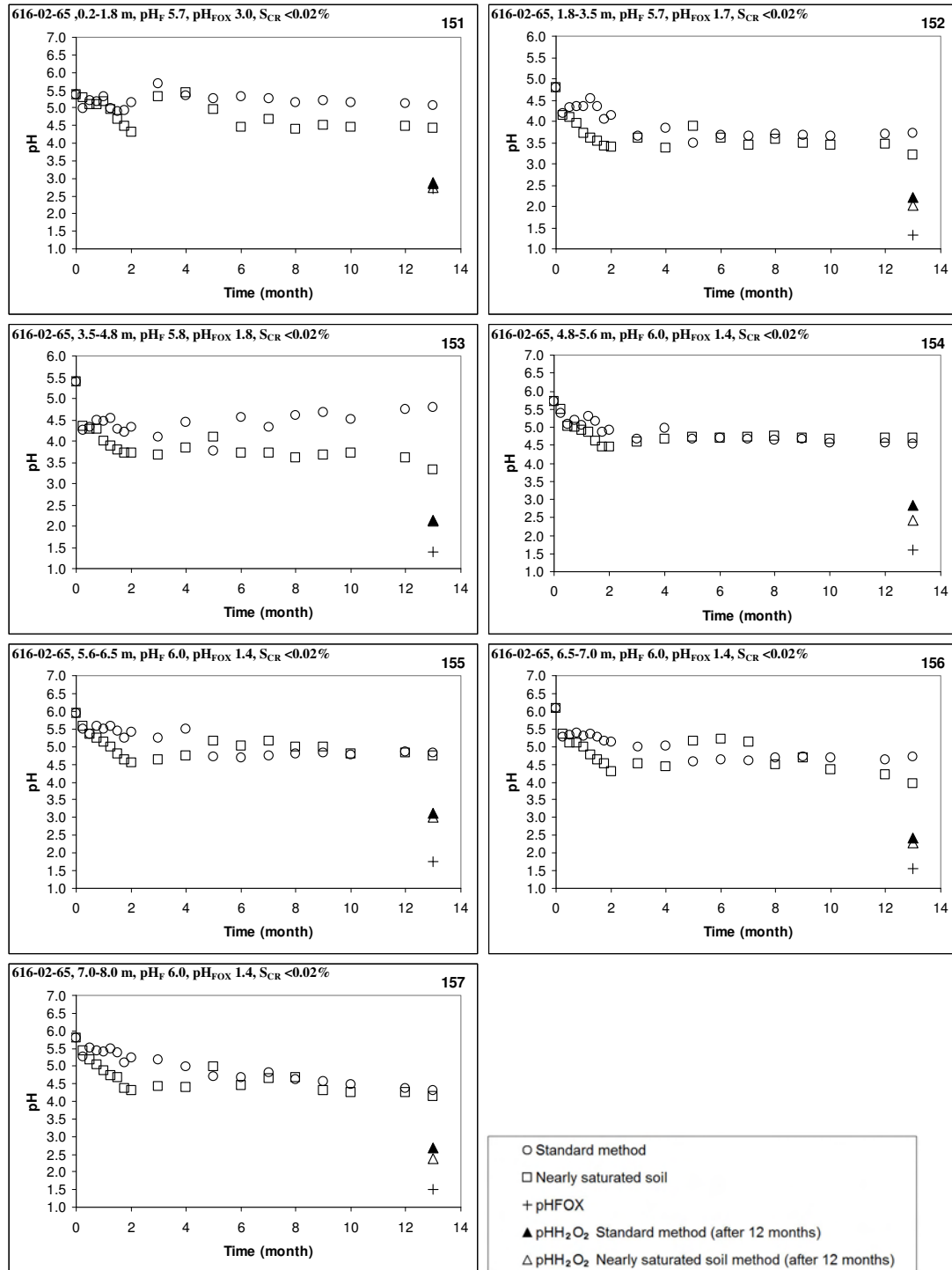
The actual acidity released from these soils is related to the rate of acidification. Oxidation of organic matter and amorphous iron-aluminosilicate minerals may affect acidification. Comparing soil sample 616-02-65 (mainly coffee rock) and 616-02-122 (mainly E horizon), both materials have a low S<sub>CR</sub> content (<0.02%), the standard method of assessment shows that pH(H<sub>2</sub>O) of the coffee rock incubated for 13 months was above 4 (Figure 32) whereas, pH(H<sub>2</sub>O) of the E horizon material dropped to less than 4 within 1 day (Figure 33). It is clear that the neutralising behaviours of coffee rock and E horizon are different with the coffee rock having a higher acid neutralising capacity than E horizon material. Thus the morphology of soil profile materials especially depth and thickness of coffee rock and E horizons may be directly related to the potential environmental hazard of acid sulfate soils when they are exposed to air. Some potential acid sulfate materials may be not become a hazard to the environment if the acidity is released at a slow rate and buffering processes are available to neutralise the acidity.





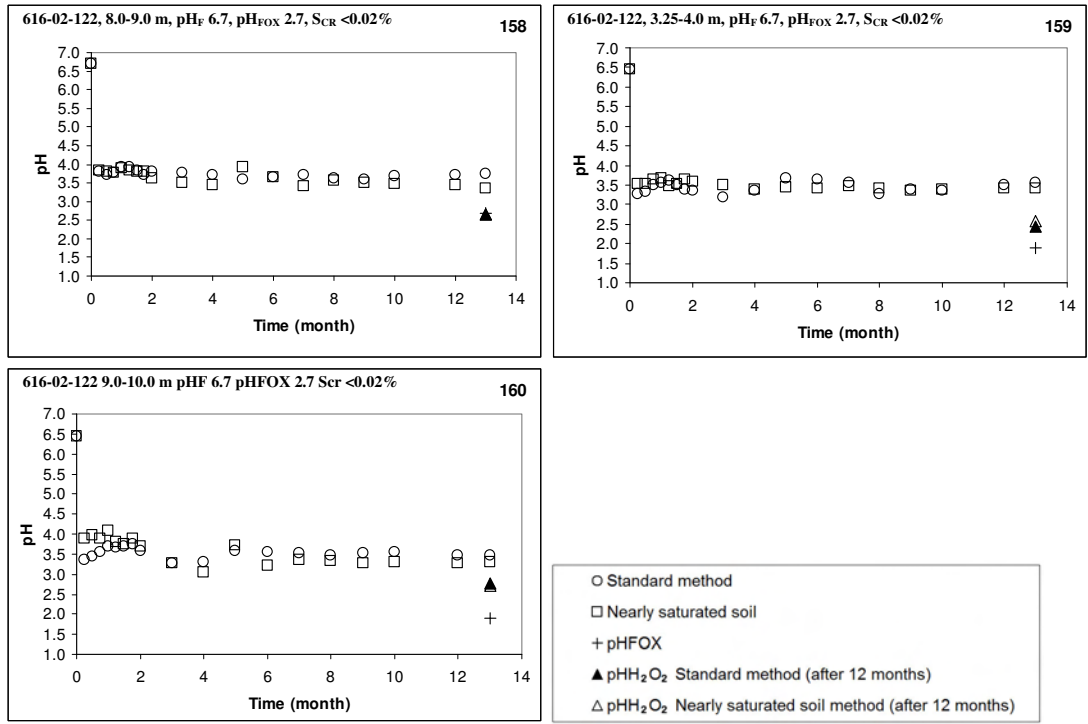
**Figure 31** Changes in pH of soil samples from site 616-02-68 during the 12 month incubation period (the USA/Australian standard methods requires 8 weeks incubation).

N.B. Start pH was already lower than pH<sub>F</sub> because some oxidation had occurred during sampling and storage so that incubation commenced with samples that were considerably more acid than their original field condition.



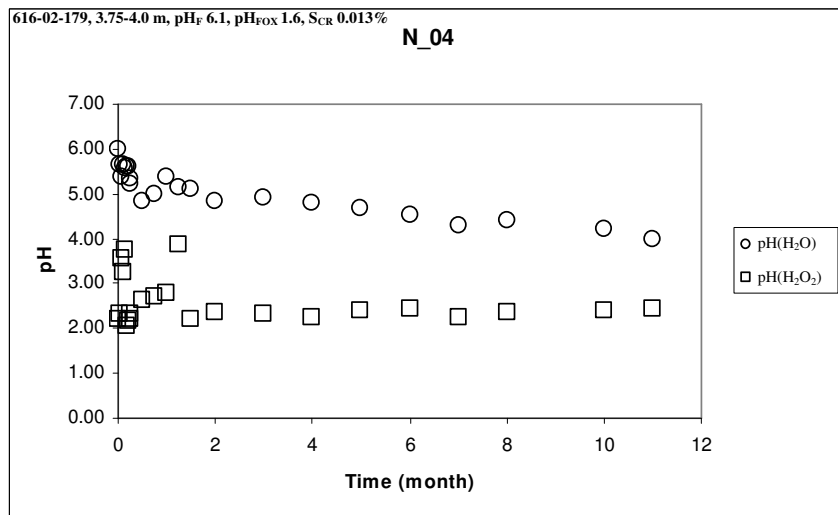
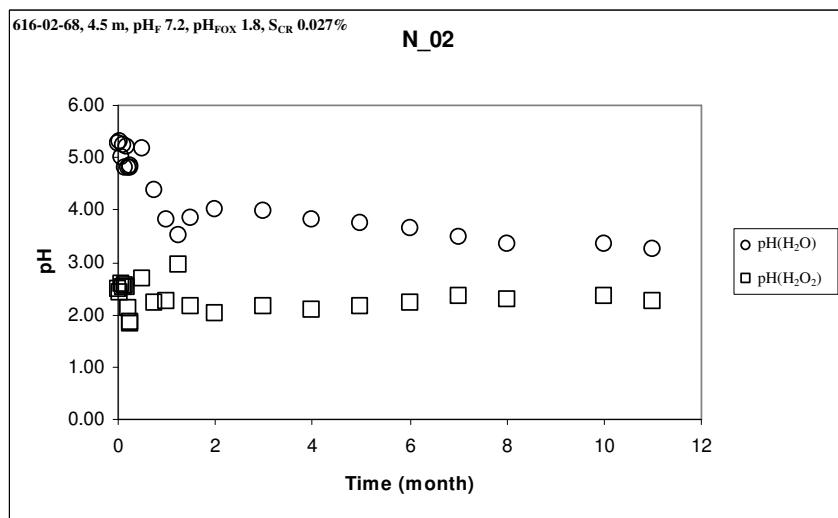
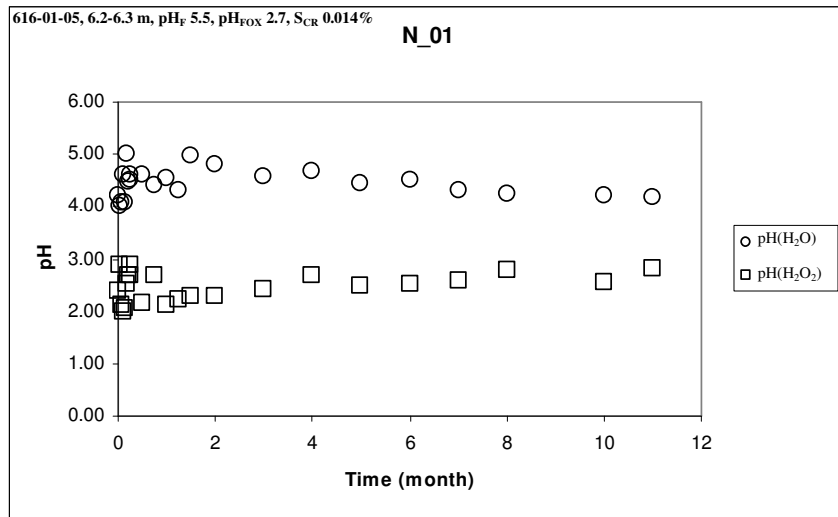
**Figure 32** Changes in pH of soil samples from site 616-02-65 during the 12 month incubation period (the USA/Australian standard methods requires 8 weeks incubation).

N.B. Start pH was already lower than  $pH_F$  because some oxidation had occurred during sampling and storage so that incubation commenced with samples that were considerably more acid than their original field condition.



**Figure 33** Changes in pH of soil samples from site 616-02-122 during the 12 month incubation period (the USA/Australian standard methods requires 8 weeks incubation).

N.B. Start pH was already lower than pH<sub>F</sub> because some oxidation had occurred during sampling and storage so that incubation commenced with samples that were considerably more acid than their original field condition.



**Figure 34** Changes in pH of B horizon from site 616-02-05 (N\_01), 616-02-68 (N\_02) and 616-02-179 (N\_04) the during 11 month incubation period (the USA/Australian standard methods requires 8 weeks incubation).

**Table 5** Summary of incubation results for some representative soil samples and several incubation procedures.

No	Site	Horizon	Depth (m)	pH <sub>F</sub>	pH <sub>FOX</sub>	S <sub>CR</sub> (%)	Standard method	Nearly saturated soil method	Moist soil method	Standard method	Nearly saturated soil method	Moist soil method
							pHH <sub>2</sub> O	pHH <sub>2</sub> O	pHH <sub>2</sub> O	pHH <sub>2</sub> O <sub>2</sub>	pHH <sub>2</sub> O <sub>2</sub>	pHH <sub>2</sub> O <sub>2</sub>
							-----after 12 months-----					
143	616-02-68	E horizon	0.25-2.0	6.1	4.7	<0.02	3.8	4.1	-	3.1	2.9	-
144	616-02-68	coffee rock	2.0-3.0	5.5	2.3	0.04	3.5	3.4	-	2.1	2.2	-
145	616-02-68	B1 horizon	3.0-4.0	6.5	1.2	0.03	3.5	3.2	-	2.4	2.4	-
146	616-02-68	B2 horizon	4.0-5.0	6.7	1.4	0.03	3.4	3.1	-	2.4	2.3	-
147	616-02-68	B3 horizon	5.0-6.0	7.3	1.4	0.04	3.4	3.2	-	2.5	2.5	-
148	616-02-68	B4 horizon	6.0-7.0	7.5	1.0	0.10	2.9	2.5	-	2.3	2.3	-
149	616-02-68	B5 horizon	7.0-8.0	7.3	1.4	0.13	3.2	2.4	2.5	2.2	2.2	2.1
151	616-02-65	Peat2	0.2-1.8	5.7	3.0	<0.02	5.1	4.4	-	2.9	2.7	-
152	616-02-65	B1 horizon	1.8-3.5	5.7	1.7	<0.02	3.7	3.2	-	2.2	2.0	-
153	616-02-65	B2 horizon	3.5-4.8	5.8	1.8	<0.02	4.8	3.3	-	2.2	2.1	-
154	616-02-65	coffee rock1	4.8-5.6	6.0	1.4	<0.02	4.5	4.7	-	2.8	2.4	-
155	616-02-65	coffee rock2	5.6-6.5	6.0	1.4	<0.02	4.8	4.7	-	3.1	3.0	-
156	616-02-65	coffee rock3	6.5-7.0	6.0	1.4	<0.02	4.7	4.0	-	2.4	2.3	-
157	616-02-65	coffee rock4	7.0-8.0	6.0	1.4	<0.02	4.3	4.1	-	2.7	2.4	-
158	616-02-122	B/E horizon	8.0-9.0	6.7	2.7	<0.02	3.7	3.4	-	2.7	2.7	-
159	616-02-122	2E2 horizon	3.25-4.0	6.7	2.7	<0.02	3.6	3.4	-	2.4	2.6	-
160	616-02-122	3E horizon	9.0-10.0	6.7	2.7	<0.02	3.5	3.3	-	2.8	2.7	-
N_01	616-01-05	B horizon	6.2-6.3	5.5	2.7	0.014	4.2	-	-	2.8	-	-
N_02	616-02-68	B horizon	4.5	7.2	1.8	0.027	3.2	-	-	2.3	-	-
N_04	616-02-179	B horizon	3.75-4.0	6.1	1.6	0.013	4.0	-	-	2.5	-	-

## 5.7 Buffering capacity

Acid buffering capacity of the A, E, B, coffee rock and C horizon materials was determined by acid batch titration against  $\text{H}_2\text{SO}_4$  (0.0012, 0.0036, 0.0060, 0.0072, 0.0144 and 0.0288M for coffee rock and B horizon corresponding to acid loads of 24-576  $\text{mmol H}^+ \text{kg}^{-1}$  and 0.000005, 0.000010, 0.000025, 0.000050, 0.000075 and 0.00010M for other soil horizons corresponding to acid loads of 0.1-2.0  $\text{mmol H}^+ \text{kg}^{-1}$ ). The buffering curves were used to estimate the acid required to reach the pH  $\text{H}_2\text{O}_2$  value and these provide an estimate of acid generated on oxidation of pyrite and sulfur (also dissolution of jarosite) (Table 6, Figures 35-36). However, some pyrite was probably oxidised during the titration resulting in an underestimation of acid production.

Total acid production, including oxidation pyrite and sulfur and digestion of organic matter, on oxidation was also determined by base (NaOH) batch titration (0.00001, 0.0012, 0.0024, 0.0048, 0.0072, 0.0120, 0.0144 and 0.0288M for coffee rock and B horizon corresponding to base loads of 0.1-288  $\text{mmol OH}^- \text{kg}^{-1}$  and 0.00001, 0.00002, 0.00005, 0.00010, 0.00015, 0.00020, 0.00030M for other soil horizon corresponding to base loads of 0.1-3.0  $\text{mmol OH}^- \text{kg}^{-1}$ ). The initial pH  $\text{H}_2\text{O}$  of the soil was used in conjunction with the  $\text{OH}^-$  buffering curve to calculate the amount of  $\text{OH}^-$  required to neutralise the acidity released by  $\text{H}_2\text{O}_2$  addition (Table 7, Figures 37-38).

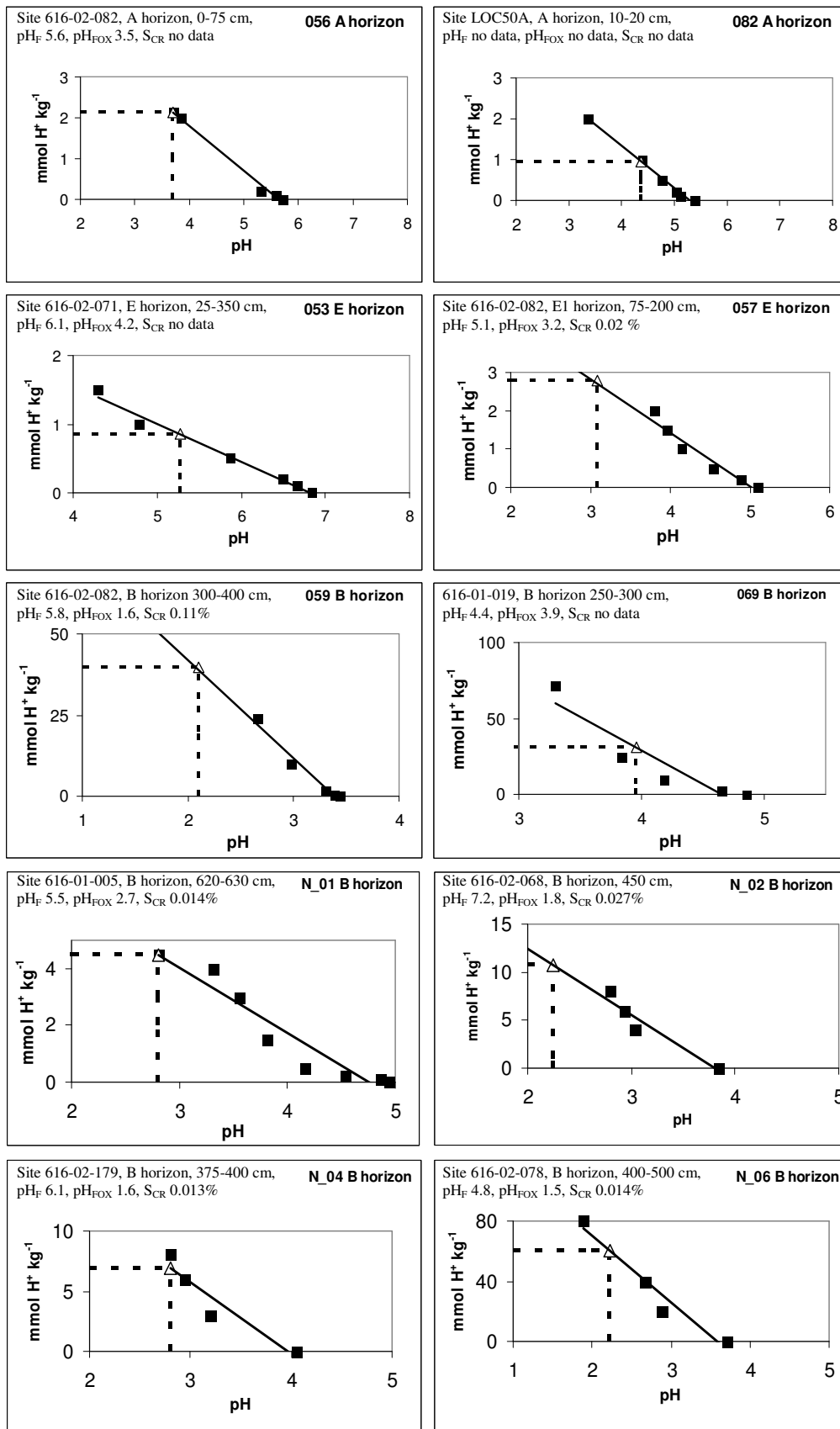
The oxidation of pyrite and marcasite ( $\text{FeS}_2$ ) and elemental sulfur produces  $\text{H}^+$ , oxidation of humus organic-Al complex releases Al which hydrolyses causing acidity and dissolution of jarosite releases acidity. Buffering of acidity is provided by organic matter, allophane ( $(\text{Al, Fe})_2\text{O}_3(\text{SiO}_2)_{1.3-2}(\text{H}_2\text{O})_{2.5-3}$ ), kaolin, gibbsite and Fe-oxides which have high surface area with exposed hydroxyl. Primary minerals (feldspar, ilmenite etc) are minor constituents of these soils and are sand-size and are essentially insoluble so they do not provide a rapid buffering capacity.

On the basis of both acid and alkali batch titrations, it is evident that coffee rock and B horizon have a much greater acid buffering and acidity production than the other horizons.

[NB These are both imprecise measures of the acidity produced by oxidation of pyrite, marcasite and sulfur and dissolution of jarosite. Acidity is also produced *inter alia* by oxidation of organic matter and hydrolysis of aluminium from the aluminium-organic matter complex.]

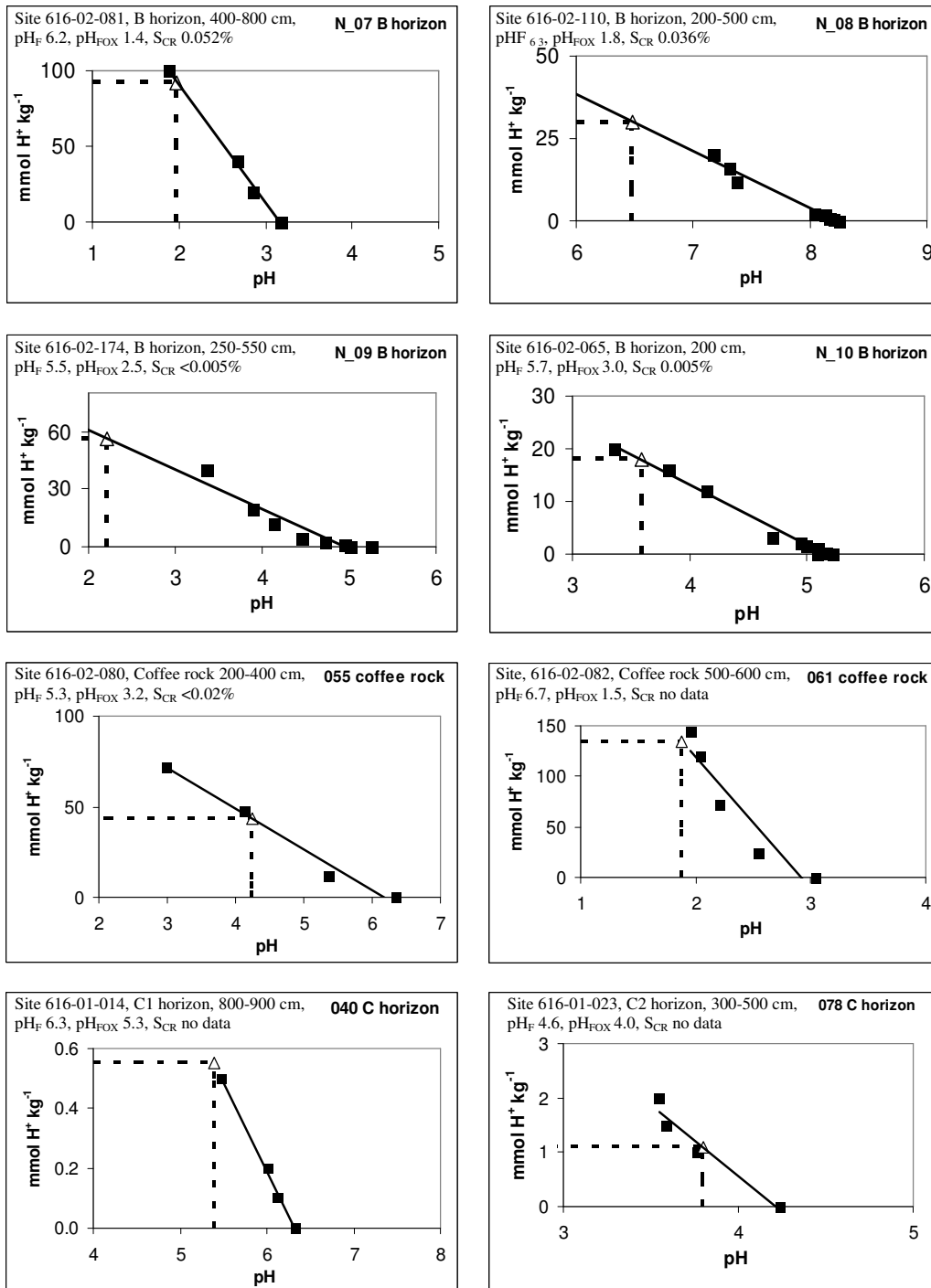
The relationships between buffering capacity and some soil properties are shown in Table 8 and Figures 39-40. The buffering capacity of coffee rock and B horizons has positive relationships with iron extracted by Na-pyrophosphate and  $\text{NH}_4$  oxalate (Figure 40). Finally, the summary of  $S_{\text{CR}}$  (%) analyses of some pyrite B horizon materials and the evaluation of these samples by direct mineralogical methods is shown in Table 9. Evidently analytical values of 0.01%  $S_{\text{CR}}$  correctly identify the presence of pyrite. A result of <0.005%  $S_{\text{CR}}$  might be interpreted as the sample not containing pyrite but in this example (N09) pyrite was present. Clearly the useful LLD for  $S_{\text{CR}}$  % should be 0.005%  $S_{\text{CR}}$  or better.

$\text{pH}_{\text{FOX}}$  is an excellent indicator to predict acidification minerals in very sandy soils. Table 9 shows that when  $\text{pH}_{\text{FOX}}$  is more than 2.5, SXRD is unable to detect pyrite. Treatment of a small samples with hydrogen peroxide offers a quicker method of prediction of potential acid sulfate soils, especially very sandy (quartz rich) soils. The criterion for the  $\text{pH}_{\text{FOX}}$  of potential acid sulfate soils should be a value of  $\text{pH} < 2.5$ . Brinkman and Pons (1973) also suggested a tentative limit for dangerous acid sulfate soils of  $\text{pH} 2.5$  after peroxide treatment.



**Figure 35** Acid batch titration results for A, E and B horizons. Dashed lines correspond to the pH of H<sub>2</sub>O<sub>2</sub> oxidised samples ( $\Delta$  = predicted mmol H<sup>+</sup> kg<sup>-1</sup> value from linear equation).





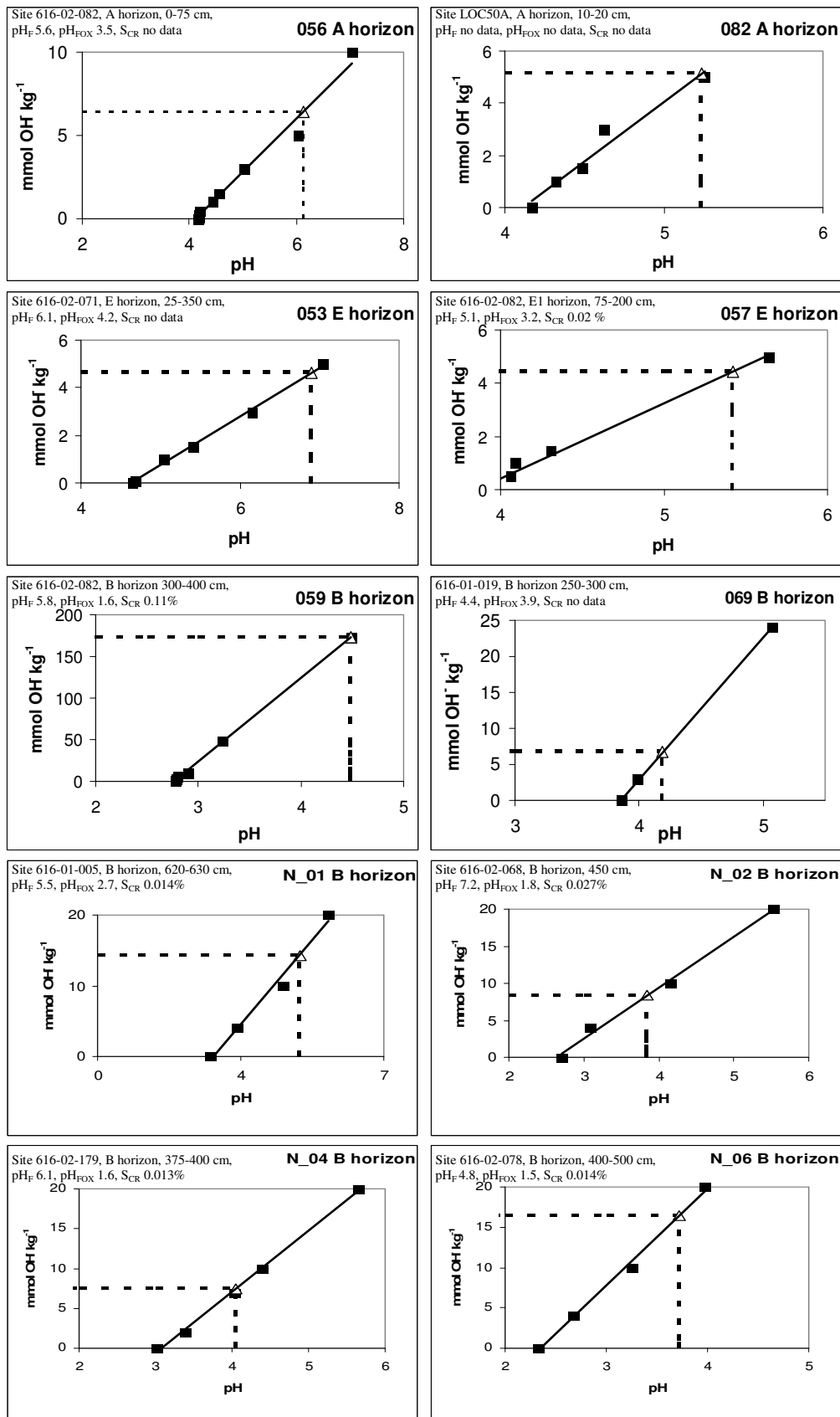
**Figure 36** Acid batch titration results for B, coffee rock and C horizon. Dashed lines correspond to the  $\text{pH}$  of  $\text{H}_2\text{O}_2$  oxidised samples ( $\Delta$  = predicted  $\text{mmol H}^+ \text{kg}^{-1}$  value from linear equation).

**Table 6** Buffering capacity (buffer<sup>a</sup>) of representative horizons of soil samples calculated from linear equations for acid batch titration.

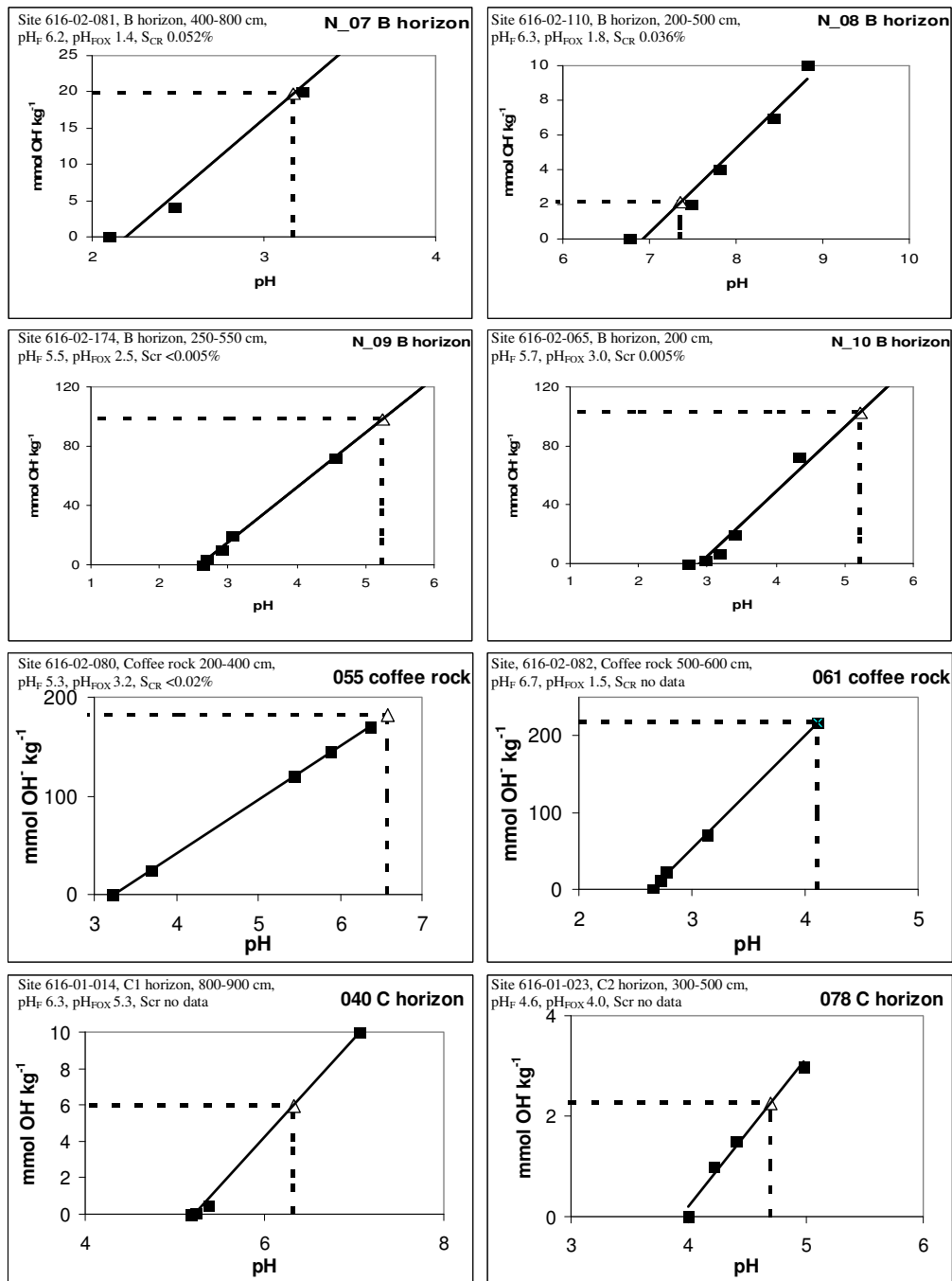
No	Horizon	R <sup>2</sup>	Linear equation*	Buffering capacity (mmol H <sup>+</sup> kg <sup>-1</sup> / pH)	mmol H <sup>+</sup> kg <sup>-1</sup> **
056	A horizon	0.99	y = -1.11x + 6.24	1.1	2.1
082	A horizon	0.99	y = -1.04x + 5.48	1.0	1.0
053	E horizon	0.98	y = -0.55x + 3.77	0.6	0.9
057	E horizon	0.94	y = -1.45x + 7.24	1.4	2.8
059	B horizon	0.97	y = -30.8x + 104	31	40
069	B horizon	0.86	y = -44.0x + 183	44	31
N_01	B horizon	0.91	y = -2.30x + 10.9	2.3	4
N_02	B horizon	0.92	y = -6.89x + 26.2	6.9	11
N_04	B horizon	0.90	y = -5.94x + 23.5	5.9	7
N_06	B horizon	0.95	y = -44.2x + 158	44	60
N_07	B horizon	0.98	y = -78.5x + 248	79	92
N_08	B horizon	0.97	y = -17.3x + 142	17	30
N_09	B horizon	0.88	y = -20.5x + 102	21	56
N_10	B horizon	0.99	y = -11.5x + 59.0	12	18
055	coffee rock	0.98	y = -22.5x + 139	23	43
061	coffee rock	0.89	y = -129x + 376	129	134
040	C horizon	0.99	y = -0.59x + 3.75	0.6	0.55
078	C horizon	0.94	y = -2.62x + 11.0	2.6	1.1

\* y = mmol H<sup>+</sup> kg<sup>-1</sup>; x = pH

\*\* interpreted from the graph as the amount of H<sup>+</sup> required to achieve the pH value obtained after H<sub>2</sub>O<sub>2</sub> oxidation (values indicated in corresponding Figures 35-36).



**Figure 37** Base batch titration results for  $H_2O_2$  treated samples of A, E and B horizons. Dashed lines correspond to the initial pH  $H_2O$  value ( $\Delta$  = predicted mmol  $OH^-$   $kg^{-1}$  value from linear equation).



**Figure 38** Base batch titration results for  $H_2O_2$  treated samples of B, coffee rock and C horizons. Dashed lines correspond to the initial pH  $H_2O$  value ( $\Delta$  = predicted  $mmol\ OH^- \ kg^{-1}$  value from linear equation).

**Table 7** Buffering capacity (buffer<sup>b</sup>) of representative horizons of soil samples calculated from linear equation for base batch titration.

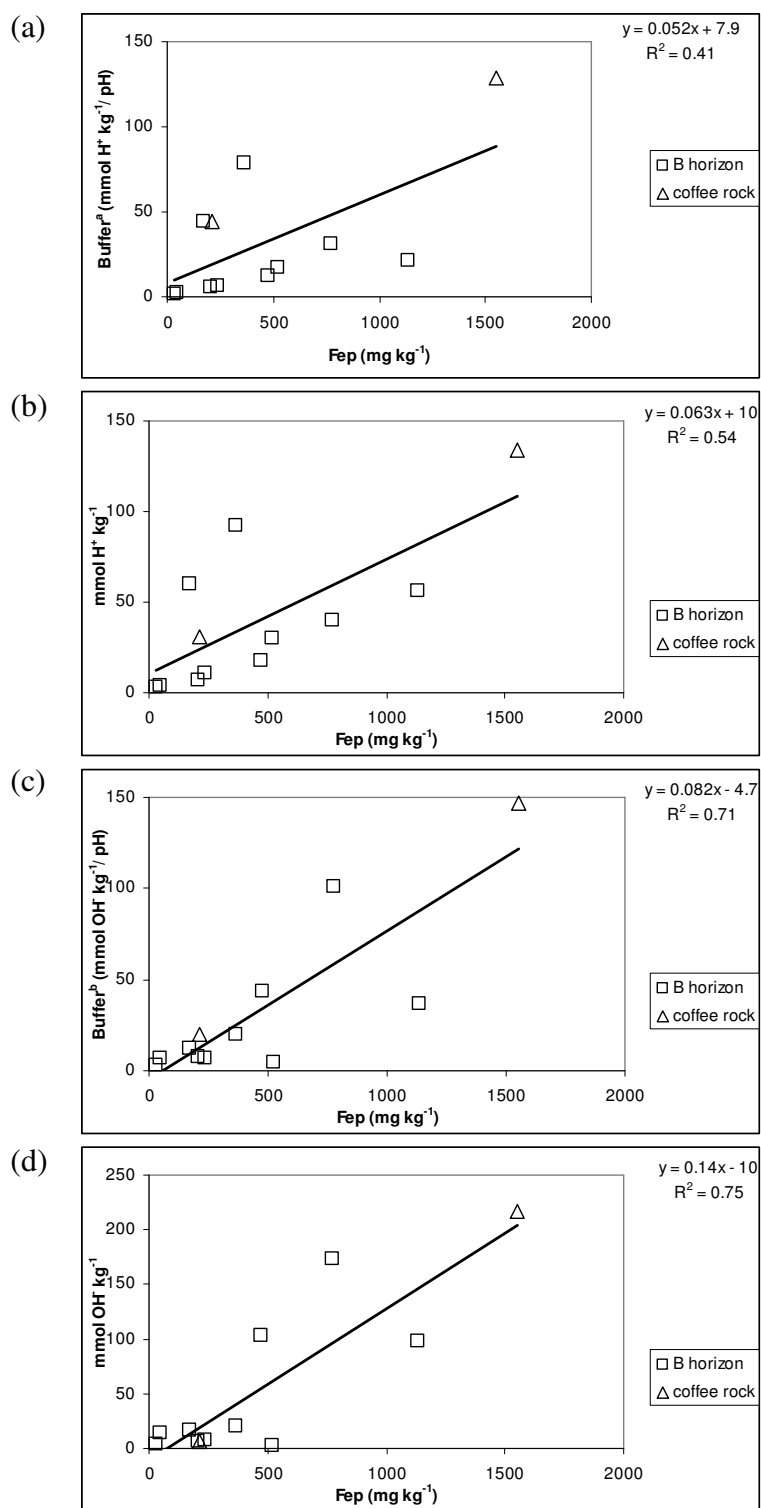
No	Horizon	R <sup>2</sup>	Linear equation*	Buffering capacity (mmol OH <sup>-</sup> kg <sup>-1</sup> /pH)	mmol OH <sup>-</sup> kg <sup>-1</sup> **
056	A horizon	0.98	y = 3.23x - 13.4	3.2	6.4
082	A horizon	0.96	y = 4.54x - 18.6	4.5	5.1
053	E horizon	1.00	y = 2.05x - 9.49	2.1	4.6
057	E horizon	0.99	y = 2.82x - 10.8	2.8	4.4
059	B horizon	0.99	y = 101.3x - 281	101	173
069	B horizon	1.00	y = 19.7x - 75.8	20	6.7
N_01	B horizon	0.99	y = 6.78x - 19.2	7	14
N_02	B horizon	0.99	y = 6.85x - 18.0	7	8
N_04	B horizon	1.00	y = 7.71x - 23.8	8	7
N_06	B horizon	1.00	y = 12.0x - 28.2	12	16
N_07	B horizon	1.00	y = 20.3x - 44.6	20	20
N_08	B horizon	0.97	y = 4.87x - 33.7	4.9	2.1
N_09	B horizon	1.00	y = 37.0x - 96.0	37	98
N_10	B horizon	0.99	y = 43.7x - 125	44	103
055	coffee rock	1.00	y = 54.3x - 176	54	182
061	coffee rock	0.99	y = 147x - 387	147	217
040	C horizon	1.00	y = 5.42x - 28.3	5.4	6.0
078	C horizon	0.98	y = 2.94x - 11.6	2.9	2.3

\* y = mmol OH<sup>-</sup> kg<sup>-1</sup>; x = pH

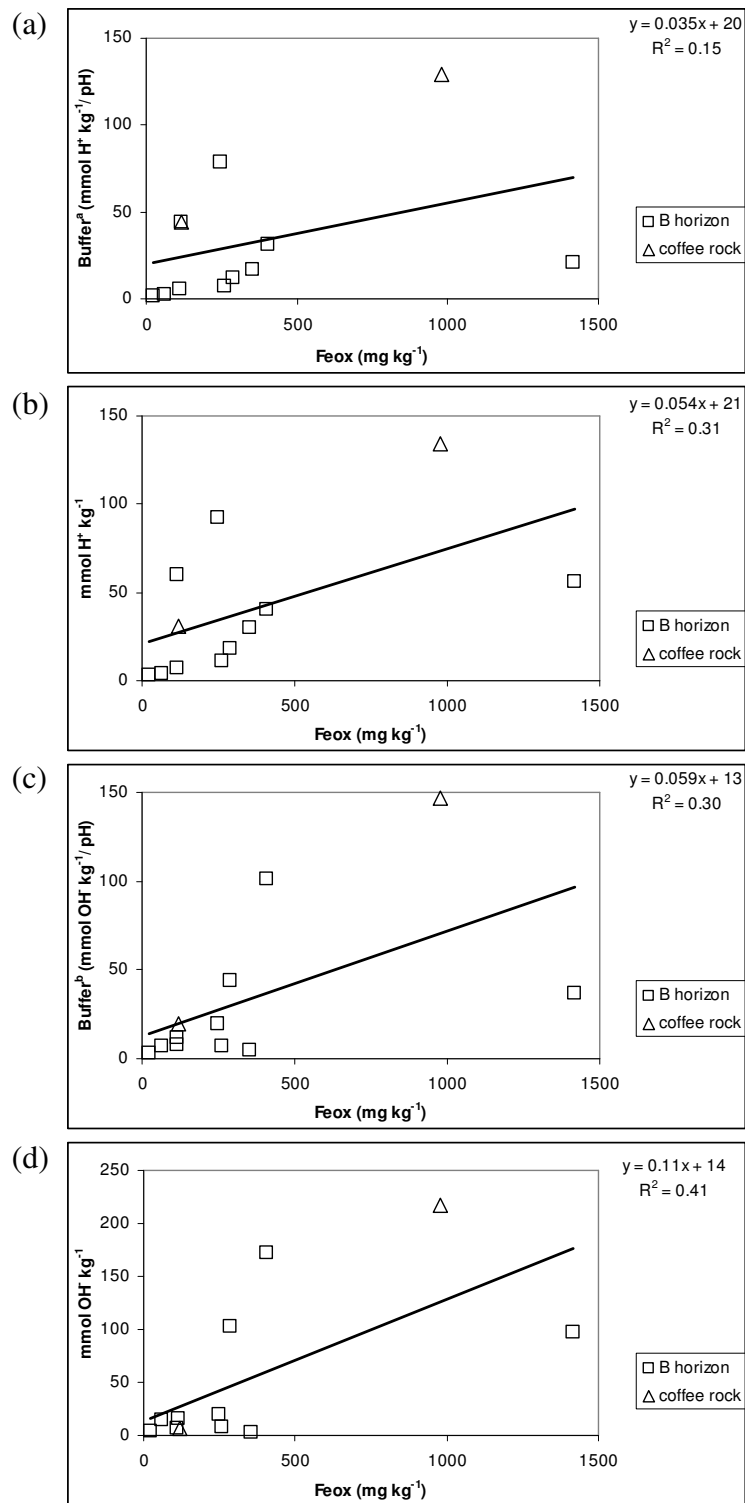
\*\* interpreted from the graph for a sample oxidised with H<sub>2</sub>O<sub>2</sub> as the OH<sup>-</sup> required to achieve the initial pH H<sub>2</sub>O value (values indicated in corresponding Figures 37-38).

**Table 8** Correlation matrix (r) for relationships between buffering capacity (buffer<sup>a</sup> and buffer<sup>b</sup>), mmmol H<sup>+</sup> kg<sup>-1</sup>, mmolOH<sup>-</sup> kg<sup>-1</sup>, Al, Fe, Si and Mn extracted by dithionite citrate bicarbonate (d); NH<sub>4</sub> oxalate (ox) and Na-pyrophosphate (p) and some soil properties for whole soil samples (p<0.05) (N = 18).

	Buffer <sup>a</sup>	H <sup>+</sup>	Buffer <sup>b</sup>	OH <sup>-</sup>	pH H <sub>2</sub> O	pH CaCl <sub>2</sub>	pH H <sub>2</sub> O <sub>2</sub>	pH NaF	C	N	CEC	SO <sub>4</sub> <sup>2-</sup>	EC	Sid	Ald	Fed	Mnd	Sip	Alp	Fep	Mnp	Siox	Alox	Feox	Mnox	
Buffer <sup>a</sup>																										
H <sup>+</sup>	0.96																									
Buffer <sup>b</sup>	0.73	0.73																								
OH <sup>-</sup>	0.56	0.63	0.93																							
pH H <sub>2</sub> O																										
pH CaCl <sub>2</sub>					0.89																					
pH H <sub>2</sub> O <sub>2</sub>	-0.48	-0.50			0.81	0.87																				
pH NaF																										
C								0.70																		
N								0.52	0.78																	
CEC				0.50	0.47				0.80	0.72																
SO <sub>4</sub> <sup>2-</sup>	0.77	0.71	0.93	0.75																						
EC																										
Sid								0.59	0.84	0.57	0.72															
Ald								0.65	0.75	0.51				0.66												
Fed														0.51												
Mnd																										
Sip				0.67					0.50	0.51	0.83															
Alp				0.69					0.50	0.53	0.84							0.99								
Fep	0.68	0.77	0.85	0.82								0.75				0.69										
Mnp		-0.49							-0.48								0.79									
Siox								0.56	0.64						0.92											
Alox								0.58	0.62						0.93							1.00				
Feox	0.47	0.61	0.58	0.55								0.48		0.56		0.83				0.86						
Mnox									0.47	0.58				0.72		0.55								0.71		



**Figure 39** Bivariate relationships between (a) buffering capacity (acid; buffer<sup>a</sup>) and iron extracted by Na-pyrophosphate (Fep), (b) mmol H<sup>+</sup> kg<sup>-1</sup> and Fep, (c) buffering capacity (base; buffer<sup>b</sup>) and Fep and (d) mmol OH<sup>-</sup> kg<sup>-1</sup> and Fep.



**Figure 40** Weak bivariate relationships between (a) buffering capacity (acid;  $\text{buffer}^a$ ) and iron extracted by oxalic acid (Feox), (b)  $\text{mmol H}^+ \text{kg}^{-1}$  and Feox, (c) buffering capacity (base;  $\text{buffer}^b$ ) and Feox and (d)  $\text{mmol OH}^- \text{kg}^{-1}$  and Feox.



**Table 9** Summary of  $S_{CR}$  (%) analyses of some pyrite containing podosol materials and the evaluation of these samples by direct mineralogical methods to determine if the  $S_{CR}$  (%) values are a reliable indicator of the presence of pyrite.

Sample No	Site	Horizon	Depth (cm)	pH <sub>F</sub>	pH <sub>FOX</sub>	$S_{CR}$ (%)	SXRD	SEM	TEM
N_01	616-01-05	B horizon	620-630	5.5	2.7	0.014	✘	✓ <sup>d</sup>	✓ <sup>d</sup>
N_02	616-02-68	B horizon	450	7.2	1.8	0.027	✓ <sup>e</sup>	✓ <sup>e</sup>	✓ <sup>e</sup>
N_04	616-02-179	B horizon	375-400	6.1	1.6	0.013	✓ <sup>e</sup>	✓ <sup>e</sup>	✓ <sup>e</sup>
N_06	616-02-78	B horizon	400-500	4.8	1.5	0.014	✓ <sup>e</sup>	✓ <sup>e</sup>	✓ <sup>e</sup>
N_07	616-02-81	B horizon	400-800	6.2	1.4	0.052	✓ <sup>e</sup>	✓ <sup>e</sup>	✓ <sup>e</sup>
N_08	616-02-110	B horizon	200-500	6.3	1.8	0.036	✓ <sup>e</sup>	✓ <sup>e</sup>	✓ <sup>e</sup>
N_09	616-02-174	B horizon	250-550	5.5	2.5	<0.005	✘	✓ <sup>d</sup>	✓ <sup>d</sup>
N_10	616-02-65	B horizon	200	5.7	3.0	0.005	✘	✘	✓ <sup>d</sup>

✘ = no detectable pyrite; ✓ = detectable pyrite, d = difficult to detect pyrite, e = easy to detect pyrite

SXRD = synchrotron XRD, SEM = scanning electron microscopy with EDS, TEM = transmission electron microscopy with EDS.

## 6. Overview and Recommendations

Perth metropolitan area of the Swan Coastal Plain is covered by sandy aeolian sediments primarily of the Bassendean Dune System (BDS). These sandy soils developed on dune sands are classified as podosols in recognition of their highly leached near surface horizons (A and E horizons) and subsurface horizon (B horizon) enriched by compounds of organic matter, Al and Fe. Aeric podosols occur on well drained dunes where groundwater table is 2.0 metres below ground and aquic podosols are common in poorly drained low-lying areas of the BDS.

These podosols are dominated by quartz sand. Their clay content is generally <1% so that these soils are extremely sandy with a small buffering capacity provided by organic matter, allophane ( $\text{Al, Fe}_2\text{O}_3(\text{SiO}_2)_{1.3-2}(\text{H}_2\text{O})_{2.5-3}$ ), kaolin, gibbsite and Fe-oxides which have high surface area with exposed hydroxyl. Primary minerals (feldspar, ilmenite etc) are minor constituents of these soils and are sand-size and essentially insoluble so they do not provide any effective buffering capacity. Poor pH buffering capacity of these sandy soils is also demonstrated by batch titrations and cation exchange capacity measurements carried out in this study.

No carbonates or considerable amounts of clay were detected in soils developed on the highly leached Bassendean Due System. Therefore, any acid generating event, such as oxidation of sulfidic material, is expected to have a strong impact on lowering the soil pH.

The investigation has firmly established that horizons of podosols that are at or below the water table commonly and variously contain small amounts of pyrite, marcasite, elemental sulfur and jarosite. SXRDR investigations of the soil fine concentrates revealed that acidifying sulfur minerals are commonly present in the permanently water-logged soil horizons. Pyrite is the main acid-generating mineral while elemental sulfur and marcasites also occur as minor constituents in some horizons with high organic matter content. Pyrite occurs in all horizons (including E, B and coffee rock, mud, peat and C horizons) that are water-logged and show low  $\text{pH}_{\text{FOX}}$ .

No pyrite was detected by SXRDR technique in soil horizons above the water table where it probably oxidised, if present, when exposed to air in past. Abundant jarosite was found in soil fines of unsaturated zones of soil profiles (mainly A

horizon). Where present, its occurrence was consistent with field observations of low soil pH (~4.0) and yellow brown mottles.

Electron microscopic investigations of the fine fractions have demonstrated the occurrence of pyrite in form of particles of various sizes and shapes in field capacity and water-logged section of the soil profiles. The two most common morphologies present are framboids of 1-10  $\mu\text{m}$  diameter and sub-micron sized single crystals. Both framboids and singles appeared to have growth related pores/cavities, suggesting high surface area and thus potentially high reactivity of these pyrites. A combination of high reactivity of pyrite, extremely low pH buffering capacity and high porosity of these sandy soils makes them prone to acidification during even a short exposure (less than a week) to air during temporary excavation or dewatering.

Western Australia adopts a texture based action criteria for managing ASS based on Queensland and New South Wales model. Accordingly sandy soils with sulfur content  $<0.03\%S$  require no ASS management. In the Perth metropolitan area, however, such sandy soils often record low  $\text{pH}_{\text{FOX}}$  values less than 3 which indicates that these sandy soils are likely to become acidic on exposure to air. These soils with low sulfur content have been a particular focus of this investigation.

Analytical electron microscopy and synchrotron X-ray diffraction carried out in the present study have demonstrated the presence of pyrite in these low sulfur sandy soils. Table 9 shows that pyrite is readily detected by SXRDR in soils with  $>0.01\%S$  while soils with  $<0.01\%S$  pyrite can only be detected by SEM and TEM. Table 9 shows that when  $\text{pH}_{\text{FOX}}$  is more than 2.5, SXRDR is unable to detect pyrite. Treatment of a small sample with hydrogen peroxide offers a quick method of prediction potential soil acidity, especially for sandy (quartz rich) soils. Brinkman and Pons (1973) also suggested a tentative limit for dangerous acid sulfate soils of pH 2.5 after peroxide treatment.

The minor amounts of acid-generation potential would not normally be of concern but the extremely small acid buffering capacity of some Bassendean Dune materials results in significant reductions in pH on oxidation. This interpretation has been substantiated by the incubation studies where soils with  $<0.03\% S_{\text{CR}}$  resulted in soil pH to less than 3. It must be noted that sandy soils as defined in the texture based criteria may contain up to 5% clay which is far greater than the clay

content of Bassendean sands. Typically, Bassendean sands contain <1% clay content so that texture based criteria developed in Ahern *et al.* (1998) may not be directly applicable.

Thus these soils are acid sulfate soils and should be managed appropriately including chemical analysis before disturbance or drainage. We have established that even when the Cr reducible S content is at or below the detection limit of 0.005% there may be minor amounts of these S compounds in the soils.

This minor amount of reduced S in the soil may still constitute a hazard in view of the very weak acid buffering capacity of some soil horizons (particularly E horizon) but the newly adopted more sensitive chemical analysis procedure is clearly much more appropriate than the procedures developed for coastal clayey acid sulfate soils.

Chemical analysis has demonstrated that apart from the acidifying potential of the S minerals in soils and the elevated As concentration in some peaty soils the concentration of heavy metals is well below hazardous levels.

A clear priority for future work is to identify the extent of sulfidic soil materials in the Bassendean Dune landscape and in particular to identify if these hazardous materials exist in wet horizons beneath other landscape elements of the Bassendean Dunes (slope, crest position) and if they occur in deep horizons.

## **Recommendations**

The key recommendations for managing pyrite very sandy soil samples; quartz-rich soils are as follow:

1. Acid sulfate soils on Bassendean Dunes System should be managed appropriately including chemical analysis before disturbance or drainage. We have established that even when the  $S_{CR}$  content is at or below the current action criteria (~0.03%), oxidation S compounds are present in the soils. These S compounds are responsible for observed low  $pH_{FOX}$  values and low soil pH under natural oxidation if these soils are disturbed.
2. The least expensive, easy and quick method to identify acid sulfate soils is using a combination of field water and hydrogen peroxide pH ( $pH_F$  and

pH<sub>FOX</sub>) to predict the extreme soil acidity. However laboratory analysis is still required to determine the appropriate liming rate.

3. Based on this investigation, we recommend that pH<sub>FOX</sub>, soil morphology and analytical value of 0.01% S<sub>CR</sub> or greater are excellent indicators of acid sulfate soil and can be used as a basis for managing potential acid sulfate soils in the Bassendean Dunes System. The action criteria need to be re-evaluated as the data indicate that more appropriate criterion is required for soils of sandy texture.

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## Appendix



**Appendix Table 1** Latitude and longitude of soil sample sites.

Site	Latitude	Longitude
616-01-003	-31.8135	115.9156
616-01-005	-31.7777	115.9075
616-01-011	-31.7224	115.8356
616-01-014	-31.7408	115.8781
616-01-018	-31.8134	115.9446
616-01-019	-31.9386	115.8735
616-01-023	-31.9237	115.8150
616-01-024	-31.9098	115.8009
616-02-009	-31.9245	115.9433
616-02-028	-32.2779	115.9373
616-02-031	-32.0909	115.9593
616-02-032	-32.0921	115.9125
616-02-058	-32.1436	115.9515
616-02-065	-32.1673	115.8817
616-02-068	-32.0818	115.8354
616-02-071	-32.1319	115.8347
616-02-078	-32.1770	115.8768
616-02-080	-32.1982	115.9056
616-02-081	-32.1984	115.8855
616-02-082	-32.2117	115.8419
616-02-085	-32.0422	115.9562
616-02-087	-32.2326	115.8625
616-02-094	-32.0336	115.9432
616-02-099	-32.1966	115.9023
616-02-100	-32.0202	115.8762
616-02-101	-31.9059	115.7933
616-02-105	-31.8802	115.8234
616-02-106	-31.8798	115.8136
616-02-110	-31.8741	115.7900
616-02-112	-31.8548	115.7584
616-02-113	-31.8169	115.8150
616-02-122	-31.9117	115.8871
616-02-127	-31.9026	115.9243
616-02-131	-31.9543	115.8724
616-02-136	-31.9710	115.9452
616-02-145	-31.9212	115.9793
616-02-155	-32.3050	115.8263
616-02-158	-32.3542	115.8303
616-02-174	-31.8434	115.9129
616-02-179	-31.8744	115.9383
Ellenbrook	-31.7910	115.9741
LOC50A	-	-

**Appendix Table 2** Total chemical composition (XRF analyses) of oven dried whole soil samples.

Site	Horizon	Depth (cm)	Al <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub> TiO <sub>2</sub> Fe <sub>2</sub> O <sub>3</sub> MnO CaO K <sub>2</sub> O MgO Na <sub>2</sub> O P <sub>2</sub> O <sub>5</sub> SO <sub>3</sub> V Cr Ni Cu Zn Rb Sr Ba Zr Co As La Pb											(------%-----) (------mg kg <sup>-1</sup> -----)												
			(------%-----)											(------mg kg <sup>-1</sup> -----)												
616-01-003	A horizon	0-25	0.15	94	0.18	0.07	0.002	0.154	0.110	0.015	nd	0.009	nd	11	nd	65	34	nd	17	17	26	154	nd	8	15	12
616-01-003	Coffee rock	175-200	3.14	86	0.12	1.51	0.002	0.013	0.096	0.022	0.010	0.012	0.04	18	nd	62	29	nd	1	31	59	51	4	9	15	13
616-01-003	C1 horizon	200-300	0.88	96	0.15	0.04	0.003	nd	0.219	nd	0.000	0.005	nd	nd	nd	44	43	2	20	9	66	110	13	1	19	17
616-01-003	C2 horizon	300-400	0.59	97	0.16	0.04	0.001	nd	0.160	0.011	0.005	0.008	nd	4	nd	56	40	1	13	18	nd	88	11	4	17	20
616-01-003	C3 horizon	400-600	0.48	99	0.21	0.11	0.002	nd	0.148	nd	nd	0.006	nd	7	nd	50	31	9	26	17	129	161	9	13	34	12
616-01-005	B horizon	620-630	0.32	98	0.10	nd	0.010	0.063	0.035	nd	0.140	nd	0.00	nd	nd	nd	3	nd	13	4	105	66	nd	nd	14	13
616-01-005	A horizon	0-20	0.19	92	0.10	0.57	0.003	0.195	0.007	0.018	0.005	0.014	nd	1	522	61	30	6	12	26	nd	74	16	3	20	14
616-01-005	E horizon	20-180	0.07	99	0.12	0.44	0.004	nd	0.008	nd	nd	0.005	nd	nd	389	73	44	nd	15	15	49	63	10	4	nd	11
616-01-005	Coffee rock	180-200	2.03	93	0.23	0.41	0.006	0.008	0.034	0.033	0.005	0.015	0.00	12	370	72	24	1	11	18	106	164	nd	0	11	18
616-01-005	B horizon	200-250	0.60	97	0.14	0.45	0.005	nd	0.023	0.147	0.030	0.007	0.00	14	369	68	33	11	20	16	111	109	12	1	nd	8
616-01-005	2E1 horizon	250-260	0.45	96	0.12	0.37	0.001	nd	nd	0.021	nd	0.005	0.06	1	352	62	39	19	9	16	17	69	13	2	18	12
616-01-005	2E2 horizon	260-400	0.19	95	0.11	0.48	0.003	nd	nd	nd	nd	0.006	0.04	nd	426	62	39	6	12	36	69	49	16	5	nd	31
616-01-005	2E3 horizon	400-500	nd	99	0.08	nd	0.000	nd	nd	nd	nd	0.005	nd	7	nd	49	50	nd	5	16	12	14	17	3	14	12
616-01-005	2E4 horizon	500-830	nd	92	0.09	0.00	0.000	nd	nd	nd	nd	0.005	nd	nd	nd	62	38	nd	20	14	56	42	20	1	nd	nd
616-01-005	2Coffee rock1	830-900	0.23	97	0.13	nd	0.000	nd	nd	0.010	0.000	0.005	0.02	nd	nd	50	47	7	21	22	47	58	13	8	33	28
616-01-005	2Coffee rock2	900-1000	0.89	96	0.38	0.13	0.005	nd	0.221	0.001	nd	0.009	0.02	4	nd	57	38	nd	23	21	152	221	5	7	14	5
616-02-009	E1 horizon	225-250	0.99	97	0.21	0.05	0.014	0.086	0.438	nd	0.090	nd	0.00	nd	20	nd	20	10	31	3	151	80	nd	5	nd	6
616-01-011	A horizon	0-75	nd	97	0.12	0.02	0.001	0.102	nd	0.004	0.000	0.010	0.00	nd	nd	54	39	9	7	42	54	44	13	1	5	2
616-01-011	E1 horizon	75-500	nd	98	0.14	0.01	0.001	nd	nd	0.003	0.000	0.006	nd	25	nd	61	30	6	2	32	88	80	9	0	41	nd
616-01-011	E2 horizon	500-600	nd	100	0.21	0.08	0.003	nd	nd	0.014	0.005	0.006	nd	nd	nd	54	39	nd	nd	13	52	174	4	11	32	nd
616-01-011	E3 horizon	600-700	1.46	99	0.60	0.26	0.011	nd	0.902	0.013	0.015	0.012	0.00	17	nd	45	40	6	31	37	233	346	18	7	17	19
616-01-014	A horizon	0-50	nd	100	0.05	0.02	nd	0.041	nd	0.011	nd	0.008	nd	19	nd	47	40	3	0	24	32	28	3	0	47	10
616-01-014	E1 horizon	50-300	nd	97	0.07	nd	0.001	nd	nd	nd	nd	0.007	nd	21	nd	63	51	3	nd	7	42	36	nd	nd	57	20
616-01-014	E2 horizon	300-650	0.57	98	0.10	0.20	0.000	0.000	0.016	0.006	0.000	0.006	nd	nd	nd	62	39	2	7	23	5	48	22	nd	34	4
616-01-014	Coffee rock	650-800	0.97	99	0.11	0.24	0.001	nd	0.008	nd	0.000	0.007	nd	16	nd	49	26	2	13	23	nd	65	13	10	26	14
616-01-014	C1 horizon	800-900	0.94	97	0.11	0.64	0.004	0.007	nd	0.005	0.000	0.008	nd	nd	253	67	40	2	12	16	32	53	9	7	32	17
616-01-014	C2 horizon	900-1000	0.91	97	0.11	0.64	0.003	0.008	nd	nd	nd	0.008	nd	3	269	54	44	nd	12	21	67	38	3	6	nd	17
616-01-014	C3 horizon	1000-1200	0.66	97	0.16	0.37	0.002	nd	0.073	0.003	0.000	0.007	nd	nd	264	62	39	9	nd	27	93	101	19	10	nd	7
616-01-014	C4 horizon	1200-1300	2.53	94	0.44	0.18	0.006	nd	0.409	0.010	0.005	0.010	nd	10	nd	58	36	2	13	19	131	328	11	8	nd	2

**Appendix Table 2 (Cont.) total chemical composition (XRF analyses) of oven dried whole soil samples.**

Site	Horizon	Depth (cm)	-----%-----											-----mg kg <sup>-1</sup> -----												
			Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	CaO	K <sub>2</sub> O	MgO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	V	Cr	Ni	Cu	Zn	Rb	Sr	Ba	Zr	Co	As	La	Pb
616-01-018	A horizon	0-25	0.01	99	0.06	0.28	0.004	0.069	nd	0.022	0.010	0.004	nd	6	234	53	45	nd	6	16	84	35	15	2	nd	8
616-01-018	E1 horizon	25-200	nd	97	0.05	0.35	0.003	0.005	nd	0.008	0.005	0.007	0.02	nd	348	49	44	8	4	39	51	25	16	0	nd	9
616-01-018	E2 horizon	200-300	0.04	97	0.08	0.44	0.003	0.005	nd	0.011	nd	0.007	0.02	3	421	63	46	nd	5	10	63	37	16	nd	51	3
616-01-018	E3 horizon	300-400	nd	98	0.06	0.43	0.002	nd	nd	nd	nd	0.005	nd	nd	389	70	47	3	13	16	6	25	9	12	14	8
616-01-018	Coffee rock	400-450	1.28	93	0.13	0.01	0.001	nd	0.011	nd	0.000	0.010	0.06	32	nd	62	40	6	10	15	57	43	20	6	10	2
616-01-018	2E horizon	450-600	0.10	98	0.11	nd	0.001	nd	nd	nd	nd	0.004	0.00	7	nd	66	22	nd	19	17	91	63	12	5	26	1
616-01-018	2Coffee rock1	600-700	0.14	97	0.07	0.50	0.005	0.002	nd	0.008	0.005	0.007	nd	20	415	61	48	11	14	18	5	55	7	nd	17	18
616-01-018	2Coffee rock2	700-800	2.65	93	0.15	0.44	0.003	0.000	0.056	0.004	0.010	0.010	0.06	9	322	71	36	nd	5	19	27	77	7	nd	26	7
616-01-019	A horizon	0-50	0.05	97	0.12	nd	0.010	0.059	0.038	nd	0.050	nd	nd	nd	nd	nd	14	2	6	19	nd	65	nd	nd	18	4
616-01-019	E1 horizon	50-200	0.03	95	0.15	nd	0.011	0.056	0.025	nd	0.030	nd	nd	1	10	nd	20	11	22	1	13	107	nd	10	25	4
616-01-019	B horizon	250-300	4.78	83	0.34	0.06	0.010	0.059	0.280	nd	0.030	nd	0.12	36	18	1	nd	4	13	12	88	135	nd	2	39	12
616-01-023	A horizon	0-25	0.11	100	0.13	nd	0.011	0.098	0.060	nd	0.040	nd	nd	2	nd	nd	18	5	7	13	57	66	nd	nd	nd	5
616-01-023	E horizon	25-100	0.14	100	0.18	nd	0.012	0.059	0.076	nd	0.120	nd	0.00	nd	4	nd	9	nd	15	13	70	122	nd	5	nd	nd
616-01-023	B horizon	100-200	1.39	97	0.19	0.01	0.013	0.059	0.143	nd	0.110	nd	0.00	11	nd	nd	19	nd	17	11	87	128	nd	10	35	14
616-01-023	C3 horizon	500-1000	1.04	98	0.12	nd	0.009	0.060	0.320	nd	0.120	nd	0.02	2	5	1	14	nd	39	6	112	77	nd	2	1	15
616-01-024	A horizon	0-25	0.04	92	0.09	nd	0.010	0.088	0.026	nd	0.100	nd	0.00	1	0	1	11	4	15	14	124	69	nd	nd	33	nd
616-01-024	E horizon	25-150	0.04	92	0.12	nd	0.011	0.058	0.020	nd	0.110	nd	nd	nd	nd	nd	7	nd	16	6	4	127	nd	2	11	6
616-01-024	B horizon	150-200	0.47	99	0.11	nd	0.010	0.058	0.065	nd	0.000	nd	0.01	8	nd	nd	14	nd	12	20	132	46	nd	3	12	nd
616-01-024	2B horizon	400-500	1.82	91	0.17	0.00	0.010	0.074	0.165	nd	nd	nd	0.06	15	9	nd	19	nd	31	18	108	77	nd	6	nd	3
616-01-024	3E horizon	500-800	0.56	97	0.09	nd	0.010	0.060	0.137	nd	0.030	nd	nd	nd	5	0	13	nd	33	24	95	41	nd	1	nd	2
616-02-028	B horizon	30-100	2.78	92	0.27	1.47	0.016	0.148	1.112	nd	0.350	nd	0.26	20	28	7	17	2	56	20	331	179	nd	10	29	1
616-02-028	Mud1	100-200	9.74	66	0.97	6.39	0.064	0.445	1.093	0.227	0.840	0.020	2.42	91	56	32	28	15	44	37	187	351	27	14	31	22
616-02-031	A horizon	0-75	nd	96	0.30	0.02	0.001	0.105	nd	0.045	0.000	0.010	0.00	26	nd	57	35	nd	7	21	20	198	8	8	32	3
616-02-031	E horizon	75-200	nd	89	0.54	0.03	0.001	nd	nd	nd	nd	0.006	nd	4	nd	53	38	nd	3	11	51	673	5	3	13	nd
616-02-031	Coffee rock1	200-300	4.81	86	0.77	0.44	0.002	0.003	0.056	0.079	0.070	0.019	0.21	14	8	57	41	3	1	23	83	678	7	8	nd	21
616-02-031	Coffee rock2	200-300	5.14	85	0.78	0.37	0.004	0.001	0.057	0.074	0.055	0.020	0.28	8	5	64	36	nd	5	25	106	638	9	11	13	26
616-02-031	2E horizon	300-400	0.28	100	0.30	0.14	0.004	nd	0.156	0.003	0.010	0.009	0.14	nd	nd	60	44	nd	17	8	55	257	2	nd	30	12
616-02-031	2Coffee rock1	400-500	3.93	92	0.27	0.17	0.004	0.006	0.467	0.037	0.020	0.037	0.19	8	3	77	28	nd	7	27	174	100	0	13	37	12
616-02-031	2Coffee rock2	500-600	2.26	93	0.22	0.11	0.005	0.008	0.506	0.035	0.020	0.029	0.10	15	nd	47	34	nd	20	43	191	99	10	10	nd	14

**Appendix Table 2 (Cont.)** total chemical composition (XRF analyses) of oven dried whole soil samples.

Site	Horizon	Depth (cm)	-----%-----													-----mg kg <sup>-1</sup> -----												
			Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	CaO	K <sub>2</sub> O	MgO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	V	Cr	Ni	Cu	Zn	Rb	Sr	Ba	Zr	Co	As	La	Pb		
616-02-032	A horizon	0-50	0.03	96	0.37	0.12	0.005	1.161	nd	0.021	nd	0.008	0.00	2	nd	61	45	11	16	45	nd	308	8	2	34	16		
616-02-032	E horizon	50-200	nd	99	0.33	0.06	0.004	nd	nd	nd	nd	0.009	0.00	nd	nd	60	43	5	2	24	17	252	19	0	6	0		
616-02-032	Coffee rock1	160	0.39	91	1.48	0.21	0.011	0.001	0.013	0.035	0.005	0.013	0.14	40	5	56	35	7	nd	16	56	473	nd	2	19	11		
616-02-032	Coffee rock2	200-300	2.92	89	0.34	0.15	0.004	nd	0.100	0.018	0.000	0.010	0.09	12	36	65	31	5	8	20	64	230	21	2	42	30		
616-02-032	2E1 horizon	300-350	0.49	95	0.96	0.41	0.017	nd	0.300	0.013	0.005	0.011	0.05	nd	2	58	42	6	12	22	141	542	13	nd	56	22		
616-02-032	2E2 horizon	350-400	0.77	94	0.75	0.33	0.013	nd	0.442	0.021	0.005	0.010	0.08	7	11	50	41	1	21	26	130	448	19	nd	31	23		
616-02-058	B horizon	300-500	0.24	86	0.29	0.06	0.014	0.076	0.049	nd	0.000	nd	0.19	19	16	4	6	7	21	12	29	107	nd	3	15	7		
616-02-065	B horizon	200	3.79	88	0.30	0.15	0.013	0.143	0.173	0.012	0.120	0.011	0.07	19	19	nd	10	5	11	15	28	141	nd	0	23	1		
616-02-065	PETZ	0-20	6.74	84	0.30	0.37	0.011	0.231	0.185	0.105	0.170	0.085	0.11	23	15	7	nd	nd	18	34	101	83	nd	8	26	17		
616-02-065	Coffee rock1	480-560	2.05	93	0.38	0.15	0.013	0.096	0.115	0.007	0.000	nd	0.27	14	40	41	8	nd	5	9	62	236	nd	4	27	1		
616-02-065	Coffee rock3	650-700	0.50	98	0.14	nd	0.011	0.068	0.116	nd	0.100	nd	0.06	1	6	8	4	nd	15	6	7	88	nd	1	44	11		
616-02-068	B horizon	450	1.59	97	0.37	0.17	0.016	0.073	0.551	nd	0.080	nd	0.07	20	24	nd	14	nd	21	19	127	205	nd	2	20	8		
616-02-068	A horizon	0-25	0.09	100	0.07	nd	0.011	0.073	0.047	nd	0.070	nd	nd	nd	nd	11	11	12	11	nd	43	nd	1	22	nd			
616-02-068	E horizon	25-200	0.12	100	0.14	nd	0.012	0.059	0.064	nd	0.130	nd	nd	15	9	6	7	nd	4	2	24	67	nd	6	7	6		
616-02-068	Coffee rock	200-300	1.72	96	0.22	0.08	0.012	0.084	0.354	nd	0.020	nd	0.08	19	9	nd	6	5	25	17	32	113	nd	8	4	23		
616-02-068	B1 horizon	300-400	1.14	93	0.27	0.10	0.015	0.067	0.420	nd	0.140	nd	0.04	17	20	6	2	13	20	5	104	172	nd	8	14	3		
616-02-068	B3 horizon	500-600	1.26	98	0.38	0.17	0.017	0.071	0.571	nd	0.110	nd	0.08	7	32	3	2	0	34	26	234	171	nd	3	8	6		
616-02-068	A horizon	0-75	0.12	97	0.09	0.00	0.010	0.070	0.072	nd	0.110	nd	nd	0	nd	nd	17	4	16	7	51	56	nd	nd	nd	14		
616-02-068	E1 horizon	75-300	0.12	92	0.12	nd	0.010	0.058	0.064	nd	0.020	nd	0.00	13	nd	37	21	9	23	nd	nd	94	nd	4	nd	8		
616-02-071	E horizon	25-350	0.06	100	0.10	nd	0.011	0.062	0.020	nd	0.060	nd	nd	6	nd	6	4	nd	14	11	49	78	nd	7	nd	5		
616-02-071	B horizon	350-600	0.75	96	0.25	0.10	0.013	0.072	0.307	nd	0.050	nd	0.14	3	13	1	nd	7	14	9	142	98	nd	5	8	8		
616-02-078	B horizon	400-500	0.03	98	0.20	nd	0.009	0.063	0.019	nd	0.080	nd	0.05	12	6	nd	1	nd	25	nd	44	85	nd	nd	nd	6		
616-02-080	Coffee rock	200-400	2.81	85	0.31	0.15	0.010	0.105	0.206	0.026	0.130	nd	0.21	20	17	5	13	nd	17	10	80	115	nd	4	5	3		
616-02-081	B horizon	400-800	0.49	92	0.22	0.08	0.012	0.077	0.292	nd	0.090	nd	0.17	7	4	nd	nd	nd	33	18	125	113	nd	nd	44	21		
616-02-082	A horizon	0-75	0.80	94	0.28	0.04	0.013	0.061	0.524	nd	0.090	nd	0.00	11	5	20	16	5	29	13	84	193	nd	2	nd	17		
616-02-082	E1 horizon	75-200	1.04	97	0.29	0.05	0.013	0.063	0.607	nd	0.150	nd	nd	8	24	nd	13	1	17	20	110	188	nd	2	12	1		
616-02-082	B horizon	300-400	1.72	91	0.40	0.34	0.017	0.075	0.909	nd	0.080	nd	0.31	31	18	nd	14	nd	45	23	175	236	nd	nd	12	14		
616-02-082	Coffee rock	500-600	2.51	93	0.40	0.57	0.016	0.085	0.959	nd	nd	nd	0.65	28	27	nd	18	6	48	18	263	249	nd	9	12	23		
616-02-085	A horizon	0-70	14.47	60	0.93	9.04	0.149	0.785	0.851	0.372	0.530	0.419	0.08	133	75	38	69	73	56	59	359	251	31	47	55	73		
616-02-085	B1 horizon	100-300	5.97	88	0.45	0.65	0.016	0.254	1.555	0.004	0.710	nd	0.03	31	37	11	25	10	50	42	391	183	nd	3	nd	8		
616-02-085	B2 horizon	300-400	3.00	92	0.14	0.28	0.012	0.200	1.198	nd	0.480	nd	0.35	20	14	5	21	1	53	37	423	74	nd	7	14	nd		
616-02-085	Mud	400-600	11.67	63	1.19	7.01	0.106	2.911	1.582	0.492	0.910	0.031	2.83	129	51	11	32	25	80	207	533	364	23	9	26	21		

**Appendix Table 2 (Cont.) total chemical composition (XRF analyses) of oven dried whole soil samples.**

Site	Horizon	Depth (cm)	(------%-----)											(------mg kg <sup>-1</sup> -----)												
			Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	CaO	K <sub>2</sub> O	MgO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	V	Cr	Ni	Cu	Zn	Rb	Sr	Ba	Zr	Co	As	La	Pb
616-02-087	Coffee rock2	300-400	6.52	78	0.39	0.11	0.012	0.129	0.650	0.015	0.140	nd	0.11	9	31	6	10	nd	34	14	179	116	nd	8	23	7
616-02-087	B horizon	500-600	0.81	97	0.65	0.27	0.018	0.060	0.425	nd	0.050	nd	0.07	54	19	nd	15	nd	19	21	179	318	nd	7	15	14
616-02-094	A1 horizon	0-100	9.53	71	1.43	7.59	0.026	0.219	1.469	0.130	0.780	0.012	1.39	141	53	6	38	12	40	29	361	487	18	20	10	37
616-02-094	A2 horizon	100-175	3.93	90	0.98	2.45	0.017	0.144	0.714	0.046	0.400	nd	0.64	79	49	nd	29	6	50	26	203	474	7	8	nd	14
616-02-094	E horizon	175-600	1.52	92	2.37	1.14	0.039	0.083	0.225	nd	0.180	nd	0.07	145	45	2	23	4	18	9	151	3244	1	11	nd	19
616-02-099	E horizon	25-200	0.28	98	0.13	0.03	0.012	0.090	0.062	nd	0.020	nd	0.01	6	19	nd	19	nd	21	16	38	71	nd	6	nd	9
616-02-099	B1 horizon	200-300	0.35	97	0.18	0.06	0.011	0.090	0.054	nd	0.160	nd	0.04	nd	16	nd	26	nd	16	0	104	97	nd	6	50	4
616-02-099	B2 horizon	300-400	0.55	97	0.31	0.43	0.016	0.101	0.094	nd	0.070	nd	0.67	15	17	nd	27	11	24	9	96	165	nd	9	nd	12
616-02-100	A horizon	0-80	1.28	93	0.32	1.28	0.016	1.347	0.240	0.022	0.150	0.006	0.04	33	35	43	30	41	21	53	54	113	nd	29	31	28
616-02-100	PETZ	80-110	1.17	83	0.23	0.62	0.013	0.509	0.208	0.108	0.230	0.018	0.09	24	41	24	14	3	15	41	101	95	nd	2	9	10
616-02-100	PETZ	110-200	1.72	89	0.73	0.78	0.023	0.083	0.349	nd	0.280	0.010	0.57	59	39	3	24	nd	27	19	92	384	nd	7	37	10
616-02-100	E horizon	200-600	0.30	96	0.05	nd	0.011	0.060	0.141	nd	0.130	nd	0.01	nd	11	31	17	1	6	5	46	28	nd	1	44	0
616-02-101	A horizon	0-75	1.22	95	0.11	0.68	0.010	0.201	0.206	nd	0.120	nd	0.00	19	21	nd	17	15	22	5	15	56	nd	4	nd	11
616-02-101	Peat1	150-200	1.22	25	0.08	5.44	0.071	14.879	0.474	0.479	0.290	0.051	5.14	19	30	1	16	13	40	138	331	52	5	18	18	11
616-02-101	E horizon	350-600	1.87	94	0.11	0.06	0.012	0.090	1.199	nd	0.170	nd	0.13	6	nd	nd	11	nd	53	36	241	65	nd	4	41	17
616-02-105	A horizon	0-160	2.17	92	0.16	0.96	0.009	0.407	0.350	nd	0.160	0.017	0.09	46	18	9	14	3	21	19	89	80	0	17	17	20
616-02-105	Peat	250-360	0.58	5	0.03	12.16	0.011	1.480	0.047	0.239	0.090	0.003	2.88	nd	49	nd	9	11	20	16	75	20	28	369	17	532
616-02-105	PETZ	360-480	0.60	98	0.07	0.11	0.010	0.099	0.247	nd	0.170	nd	0.27	2	nd	nd	14	2	25	10	45	34	nd	11	nd	3
616-02-105	E horizon	480-700	0.76	99	0.12	nd	0.011	0.074	0.450	nd	0.150	nd	nd	11	25	nd	26	nd	27	nd	199	79	nd	18	9	7
616-02-106	A horizon	0-50	0.51	96	0.10	0.40	0.010	0.104	0.192	nd	0.040	0.020	0.13	nd	18	6	2	2	12	30	179	73	nd	17	nd	20
616-02-106	E horizon	50-700	1.18	97	0.20	0.16	0.013	0.095	0.631	nd	0.090	nd	0.16	10	22	10	5	11	29	23	202	71	nd	9	6	15
616-02-110	B horizon	200-500	4.01	73	0.16	1.31	0.012	9.685	2.304	0.057	0.290	0.011	1.95	nd	10	5	6	5	74	79	527	89	nd	13	46	12
616-02-112	B horizon	25-80	0.04	3	0.03	nd	0.026	49.751	0.045	3.781	0.650	0.031	0.47	15	47	15	25	5	2	1324	265	102	nd	nd	nd	10
616-02-112	Mud	125-200	0.03	8	0.02	nd	0.024	35.130	0.051	2.009	0.670	0.007	1.00	nd	9	2	15	nd	3	1063	325	87	nd	4	44	5
616-02-112	Peat	200-300	0.08	1	0.02	0.59	0.014	0.937	0.155	0.737	3.210	0.001	2.29	nd	12	nd	11	nd	28	62	113	12	nd	31	nd	45
616-02-112	Bb horizon	300-400	2.94	85	0.20	1.59	0.053	3.714	0.760	0.101	0.360	0.022	1.44	23	58	11	16	nd	50	271	245	130	nd	9	52	24
616-02-112	C horizon	400-600	1.70	59	0.23	0.35	0.017	22.811	0.575	0.168	0.270	0.012	0.14	4	102	106	17	19	23	499	198	169	nd	8	39	21
616-02-113	A horizon	0-50	1.10	93	0.13	0.14	0.010	0.226	0.497	nd	0.150	0.006	0.06	6	14	3	nd	39	30	24	184	81	nd	2	19	10
616-02-113	E2 horizon	250-300	1.33	98	0.21	0.16	0.015	0.091	0.719	nd	0.140	nd	0.20	5	25	nd	10	17	26	21	239	128	nd	4	11	5
616-02-122	E horizon	20-235	0.11	100	0.09	nd	0.010	0.078	0.059	nd	0.030	nd	nd	8	10	2	20	6	13	23	nd	64	nd	nd	8	7
616-02-122	B horizon	235-315	0.98	92	0.20	0.04	0.013	0.100	0.163	nd	0.040	nd	0.01	nd	6	nd	13	nd	13	19	131	149	nd	4	9	2
616-02-122	2E2 horizon	375-500	0.99	97	0.76	0.42	0.026	0.063	0.500	nd	0.090	nd	0.02	29	26	nd	nd	nd	25	11	162	353	nd	7	36	10
616-02-122	B/E horizon	700-900	0.70	99	0.15	nd	0.010	0.061	0.113	nd	0.040	nd	0.02	nd	18	3	6	1	15	10	111	91	nd	4	45	5

**Appendix Table 2 (Cont.)** total chemical composition (XRF analyses) of oven dried whole soil samples.

Site	Horizon	Depth (cm)	-----%-----											-----mg kg <sup>-1</sup> -----												
			Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	CaO	K <sub>2</sub> O	MgO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	V	Cr	Ni	Cu	Zn	Rb	Sr	Ba	Zr	Co	As	La	Pb
616-02-127	Coffee rock	100-235	1.57	94	0.13	nd	0.009	0.090	0.074	nd	0.110	nd	0.13	nd	14	2	13	17	10	16	13	77	nd	8	nd	4
616-02-127	2E1 horizon	235-300	0.31	92	0.23	0.05	0.013	0.059	0.061	nd	0.060	nd	0.00	8	nd	nd	5	nd	21	9	53	192	5	3	36	5
616-02-131	A horizon	0-50	1.54	96	0.21	0.55	0.013	0.166	0.219	0.004	0.090	nd	0.00	8	25	11	19	13	23	9	141	74	nd	8	31	12
616-02-131	E horizon	50-325	0.62	98	0.18	0.01	0.010	0.064	0.275	nd	0.140	nd	nd	9	4	2	10	14	25	12	155	74	nd	1	37	9
616-02-131	B horizon	325-425	15.22	70	1.00	7.90	0.022	0.129	1.158	0.226	0.360	nd	0.00	111	96	11	27	9	53	24	348	431	18	14	14	18
616-02-131	2E horizon	425-600	4.05	92	0.13	0.24	0.009	0.090	1.094	nd	0.420	nd	nd	14	6	nd	13	11	44	10	306	76	nd	12	29	1
616-02-136	A horizon	0-25	0.09	99	0.39	0.03	0.012	0.076	0.053	nd	0.080	nd	0.00	14	14	14	10	12	20	12	15	229	nd	nd	18	1
616-02-136	Coffee rock	200-260	2.35	93	0.76	0.26	0.016	0.136	0.212	nd	0.200	nd	0.09	31	42	17	10	6	31	24	105	458	nd	5	28	14
616-02-145	E1 horizon	50-300	0.17	92	0.30	nd	0.010	0.060	0.087	0.002	0.120	nd	nd	3	3	nd	3	nd	21	4	10	181	nd	2	6	5
616-02-145	E2 horizon	300-450	0.30	94	0.23	nd	0.011	0.058	0.081	nd	0.070	nd	0.02	5	40	102	11	nd	21	5	41	143	2	5	nd	nd
616-02-145	B horizon	450-475	11.18	70	0.44	10.62	0.013	0.090	0.276	0.088	0.120	0.036	0.07	392	98	17	4	18	33	10	112	189	23	33	nd	40
616-02-145	2E horizon	475-600	5.86	87	0.21	0.27	0.009	0.068	0.720	nd	0.060	nd	0.10	2	15	4	3	4	42	18	175	89	nd	9	6	8
616-02-155	E horizon	50-150	0.66	90	0.19	0.02	0.011	2.334	0.404	0.017	0.050	nd	nd	9	nd	6	6	5	28	76	138	75	nd	nd	27	11
616-02-155	2E horizon	200-500	2.63	94	0.32	0.30	0.014	0.100	0.953	nd	0.150	nd	0.19	12	11	7	1	nd	35	30	228	148	nd	3	11	11
616-02-155	B horizon	500-600	11.27	74	1.18	4.12	0.028	0.326	1.548	0.411	0.280	nd	nd	123	76	11	14	0	50	29	403	453	7	24	67	26
616-02-158	E horizon	25-225	0.07	100	0.19	nd	0.012	0.059	0.036	nd	0.180	nd	nd	14	3	nd	14	1	5	nd	nd	70	nd	6	41	4
616-02-158	Coffee rock1	225-300	3.26	88	0.52	0.46	0.015	0.067	0.241	nd	0.040	0.043	0.14	28	16	6	7	3	10	14	117	236	nd	6	24	2
616-02-158	Coffee rock2	300-400	2.29	84	0.81	0.41	0.022	0.072	0.454	nd	0.110	nd	0.17	47	18	5	5	6	34	19	253	387	nd	4	22	4
616-02-174	B horizon	250-550	0.52	93	0.13	0.13	0.011	0.107	0.055	nd	0.020	nd	0.05	17	nd	nd	nd	9	19	3	10	43	nd	0	nd	nd
616-02-179	B horizon	375-400	0.73	97	0.11	nd	0.010	0.062	0.101	nd	0.090	nd	0.03	7	14	1	10	4	24	14	nd	35	nd	nd	36	7
Ellenbrook	E horizon	0-150	0.04	97	0.22	nd	0.011	0.058	0.018	nd	0.020	nd	nd	8	nd	nd	0	3	4	0	73	254	nd	2	12	15
Ellenbrook	Coffee rock	150-200	4.17	91	0.21	0.15	0.011	0.092	0.070	nd	0.070	0.003	0.15	15	25	nd	15	7	7	20	178	194	nd	8	26	4
Ellenbrook	2B1 horizon	500-550	0.35	96	0.09	0.09	0.010	0.064	0.192	nd	0.060	nd	0.28	nd	7	nd	nd	nd	23	14	92	46	nd	0	19	1

**Appendix Table 3** Element analyses by ICP-OES of aqua regia method (in mg kg<sup>-1</sup> unit).

Site	Horizon	Depth (cm)	Ca	Mg	Fe	Mn	P	Zn	S	As	Cu	Pb	Ba	Be	Ce	Co	Cr	Ga	Gd	Ge	Hf	La	Mo	Nd	Sc	Sr	Th	V	Y
616-01-03	A horizon	0-25	1170	71	559	12	10	0.90	51	nd	0.85	0.14	5.83	0.009	1.82	0.19	0.95	0.13	0.10	0.07	0.07	1.16	0.15	0.65	0.02	10.64	0.56	0.82	2.70
616-01-03	coffee rock	180-200	150	44	10415	3	25	1.08	230	2.33	1.77	2.91	2.45	0.051	3.48	0.57	10.81	4.24	0.44	0.15	0.10	2.59	0.30	1.37	0.31	2.46	3.89	13.89	1.14
616-01-03	E horizon	250-300	28	14	277	6	8	0.67	74	nd	1.08	0.47	2.09	0.019	1.46	0.29	3.00	0.92	0.09	0.05	0.04	0.74	0.04	0.53	0.07	0.61	0.80	1.23	1.35
616-01-03	E horizon	400	29	10	254	7	5	0.58	19	nd	0.67	0.29	2.32	0.012	1.14	0.20	2.53	0.61	0.05	0.05	0.03	0.61	0.06	0.45	0.04	0.50	0.74	1.17	1.73
616-01-03	E horizon	600	18	12	244	9	3	0.12	36	nd	0.16	1.58	2.50	0.012	2.55	0.18	1.57	0.69	0.14	0.04	0.03	1.45	0.01	0.99	0.06	0.34	1.10	1.05	1.63
616-01-05	B horizon	620-630	49	16	315	5	3	1.82	49	0.05	0.32	0.55	1.31	nd	0.91	0.05	2.29	1.09	0.07	nd	nd	0.63	0.12	0.41	0.05	1.07	0.32	0.86	0.13
616-01-05	A horizon	0-20	1266	108	464	7	26	4.29	86	nd	1.23	1.62	4.29	0.008	1.13	0.19	1.17	0.32	0.08	0.07	0.05	0.77	0.15	0.47	0.03	5.52	0.39	0.74	0.91
616-01-05	E horizon	130-150	22	8	128	4	5	1.18	29	nd	0.36	nd	1.18	0.005	0.98	0.12	0.52	0.49	0.05	nd	0.04	0.57	0.09	0.37	0.03	0.38	0.41	0.67	4.14
616-01-05	coffee rock	180-200	88	40	520	6	18	1.04	98	nd	0.55	0.57	2.26	0.028	1.58	0.25	6.26	4.01	0.09	0.08	0.05	1.12	0.22	0.63	0.14	1.64	0.64	3.37	1.02
616-01-05	B horizon	220-250	11	10	239	5	4	1.58	99	nd	0.85	nd	0.82	0.007	1.19	0.14	2.86	0.92	0.07	0.02	0.03	0.74	0.10	0.49	0.06	0.28	0.56	1.18	1.70
616-01-05	E horizon	250-260	10	10	130	3	3	2.25	245	nd	2.78	nd	0.94	0.007	0.89	0.35	2.86	1.08	0.04	0.05	0.03	0.76	0.10	0.38	0.07	0.27	0.41	1.08	1.30
616-01-05	E horizon	260-300	14	8	87	2	3	0.92	194	nd	0.96	nd	0.66	0.007	0.86	0.15	1.76	0.71	0.05	0.03	0.01	0.46	0.08	0.37	0.06	0.27	0.40	0.95	1.93
616-01-05	E horizon	440-470	9	6	113	2	2	0.07	30	1.34	0.40	nd	0.46	0.004	0.61	0.05	0.41	0.11	0.01	0.02	0.02	0.29	0.01	0.21	0.02	0.09	0.23	0.38	1.73
616-01-05	E horizon	710-730	7	5	251	4	4	0.55	50	nd	0.89	0.26	1.54	0.010	0.52	0.25	1.47	0.27	0.02	0.02	0.33	0.14	0.19	0.04	0.28	0.22	0.71	1.17	
616-01-05	coffee rock	840-860	32	42	67	2	5	nd	127	nd	0.27	4.02	1.61	0.015	1.29	0.14	4.08	1.22	0.10	0.05	0.04	0.77	0.08	0.49	0.26	0.80	0.92	1.58	0.19
616-01-05	coffee rock	940-960	54	31	230	10	11	0.09	136	0.08	0.36	3.22	2.16	0.023	2.25	0.17	5.89	2.11	0.15	0.05	0.08	1.26	0.14	0.84	0.32	0.86	1.74	2.60	0.39
616-02-09	E horizon	225-250	45	23	366	11	7	nd	39	0.44	0.08	1.33	7.41	0.002	2.66	nd	3.00	0.85	0.12	0.00	nd	1.63	0.04	0.96	0.07	0.61	0.69	0.62	0.19
616-01-11	A horizon	0-50	924	82	320	7	21	3.19	100	0.02	1.32	1.61	6.75	0.010	1.45	0.22	0.83	0.31	0.08	0.06	0.01	0.75	0.11	0.57	0.04	5.48	0.49	0.59	1.14
616-01-11	E horizon	230-250	32	4	198	5	3	0.16	12	nd	0.56	nd	1.33	0.004	0.87	0.14	0.37	0.22	0.05	0.01	0.01	0.56	0.10	0.37	0.01	0.20	0.29	0.42	1.83
616-01-11	E horizon	520-540	22	4	300	9	2	0.15	11	nd	0.27	nd	1.39	0.007	1.30	0.26	0.65	0.22	0.07	0.03	0.02	0.66	0.06	0.51	0.04	0.22	0.39	0.82	2.89
616-01-11	E horizon	640-660	47	25	560	24	7	0.28	76	nd	0.19	1.64	8.39	0.016	5.07	0.34	1.83	1.13	0.23	0.03	0.02	2.70	0.10	1.94	0.11	1.31	1.75	1.69	0.09
616-01-14	A horizon	0-50	361	18	307	3	6	0.95	25	nd	1.05	nd	2.12	0.003	0.87	0.21	0.97	0.18	0.05	0.04	0.03	0.52	0.16	0.35	0.03	1.42	0.32	0.45	1.88
616-01-14	E horizon	250-270	43	5	161	3	2	0.23	9	nd	0.50	nd	1.39	0.002	0.70	0.13	0.34	0.10	0.03	0.00	0.05	0.31	0.08	0.26	nd	0.39	0.24	0.55	2.98
616-01-14	E horizon	600	41	12	1222	3	7	0.31	8	0.26	0.20	nd	1.30	0.012	1.54	0.15	3.87	1.19	0.07	0.01	0.61	0.16	0.38	0.07	0.49	0.80	2.55	1.28	
616-01-14	coffee rock	700	48	22	1859	2	9	0.43	21	nd	0.30	0.10	1.26	0.017	1.60	0.19	4.64	1.45	0.08	0.07	0.02	0.87	0.16	0.44	0.08	0.54	0.86	3.70	0.92
616-01-14	E horizon	800	41	14	1536	4	7	0.60	9	nd	0.22	0.04	1.27	0.015	1.66	0.20	4.21	1.55	0.09	0.05	0.07	0.83	0.11	0.43	0.10	0.51	0.88	3.18	1.70
616-01-14	E horizon	900	107	15	1853	2	10	0.56	12	nd	0.15	0.02	1.57	0.020	1.71	0.16	3.28	1.50	0.10	0.07	0.00	0.95	0.17	0.47	0.07	0.69	0.83	3.72	1.74
616-01-14	C horizon	1000	30	10	408	7	7	4.95	4	nd	0.31	1.13	2.97	0.010	1.57	0.24	2.85	1.02	0.07	0.05	0.08	0.96	0.08	0.54	0.05	0.56	1.20	1.52	1.75
616-01-14	C horizon	1250-1270	24	14	364	10	6	0.34	16	nd	0.24	5.11	8.19	0.017	3.17	0.38	7.18	2.28	0.10	0.12	0.08	2.06	0.31	1.00	0.17	1.08	3.01	1.77	nd
616-01-18	A horizon	0-25	363	11	143	2	4	1.01	17	nd	0.40	nd	2.36	0.003	1.00	0.24	0.66	0.17	0.05	0.03	0.00	0.59	0.01	0.35	0.00	1.36	0.39	0.56	2.81
616-01-18	E horizon	180-200	75	4	50	1	4	2.57	128	nd	0.49	nd	0.70	0.003	0.89	0.07	0.70	0.56	0.04	0.02	0.05	0.51	0.19	0.33	nd	0.26	0.45	0.84	2.22
616-01-18	E horizon	280-300	44	3	48	1	3	0.68	98	nd	0.35	0.34	0.70	0.000	0.83	0.09	0.51	0.32	0.05	0.01	nd	0.59	nd	0.31	0.01	0.20	0.33	0.47	1.86
616-01-18	E horizon	380-400	23	3	43	1	3	0.74	37	0.16	0.41	0.02	0.65	0.000	0.79	0.07	0.32	0.21	0.04	0.02	0.03	0.38	0.11	0.31	nd	0.19	0.23	0.97	2.53
616-01-18	coffee rock	420-440	21	13	233	2	15	1.16	297	0.21	2.15	1.36	1.06	0.028	2.51	0.25	5.57	2.28	0.18	0.07	0.04	1.38	0.12	0.99	0.37	0.38	1.13	2.77	0.73
616-01-18	E horizon	520-540	16	9	158	4	5	0.24	79	0.25	0.34	0.02	1.02	0.008	1.12	0.20	1.00	0.66	0.05	0.03	0.58	0.23	0.43	0.07	0.25	0.41	0.98	1.56	
616-01-18	coffee rock	600-625	59	7	576	7	6	2.96	62	nd	3.03	0.10	0.85	0.005	1.36	1.13	3.01	0.49	0.08	0.02	0.90	0.29	0.54	0.06	0.41	0.60	0.66	1.88	
616-01-18	coffee rock	700-725	41	25	727	4	21	2.22	323	nd	2.38	1.66	1.77	0.042	3.19	0.58	6.66	3.40	0.29	0.11	0.16	2.02	0.31	1.41	0.40	0.59	2.95	6.55	1.14
616-01-19	A horizon	25-50	43	34	106	3	8	1.07	19	0.00	0.14	0.44	3.00	0.002	1.68	0.02	0.42	0.06	0.08	0.07	0.03	0.86	0.19	0.62	0.05	0.92	0.47	0.98	2.51
616-01-19	E horizon	125-150	15	5	162	6	5	0.67	9	nd	0.17	0.46	2.03	0.002	1.82	0.04	0.40	0.27	0.08	0.03	0.03	1.07	0.25	0.68	0.03	0.27	0.51	1.61	4.96
616-01-19	E horizon	225-250	25	8	1635	12	6	0.94	15	nd	1.64	0.35	1.75	0.001	2.26	0.15	9.16	0.13	0.11	0.02	0.00	1.32	2.09	0.84	0.03	0.32	0.78	1.47	2.67
616-01-19	B horizon	275-300	31	57	605	6	37	0.54	737	0.51	0.76	6.63	10.42	0.069	8.45	0.23	10.82	5.53	0.57	0.12	0.19	4.93	0.42	3.28	0.92	1.61	4		

**Appendix Table 3 (Cont.)** Element analyses by ICP-OES of aqua regia method (in mg kg<sup>-1</sup> unit).

Site	Horizon	Depth (cm)	Ca	Mg	Fe	Mn	P	Zn	S	As	Cu	Pb	Ba	Be	Ce	Co	Cr	Ga	Gd	Ge	Hf	La	Mo	Nd	Sc	Sr	Th	V	Y
616-01-23	A horizon	0-25	406	25	188	5	5	0.46	15	0.04	0.14	0.66	2.90	0.004	1.38	0.09	0.29	0.14	0.08	0.03	0.01	0.97	0.03	0.50	0.05	3.17	0.46	1.00	2.93
616-01-23	E horizon	25-50	16	5	187	7	4	0.14	5	nd	0.12	0.68	2.53	0.001	1.56	0.04	0.27	0.24	0.07	0.03	0.03	0.95	0.02	0.60	0.05	0.25	0.48	1.16	4.79
616-01-23	B horizon	150-175	14	30	437	8	6	0.32	28	0.15	0.18	0.99	2.97	0.024	1.81	0.20	4.68	2.37	0.11	0.03	0.03	1.15	0.58	0.66	0.19	0.93	0.86	2.29	1.54
616-01-23	E horizon	250-275	37	33	451	9	8	0.03	41	0.01	0.18	5.47	3.44	0.023	1.90	0.21	7.36	2.25	0.12	0.04	0.04	1.15	0.10	0.70	0.22	0.67	1.13	2.00	1.72
616-01-23	E horizon	550	16	10	223	5	3	nd	44	0.04	0.18	0.91	2.32	0.005	1.26	0.12	2.66	0.49	0.06	0.04	0.03	0.61	0.02	0.47	0.07	0.30	0.61	0.94	2.25
616-01-23	E horizon	825	23	20	300	6	4	nd	48	nd	0.27	2.33	6.60	0.009	1.67	0.13	4.52	0.52	0.08	0.03	0.04	1.13	0.07	0.60	0.13	0.59	0.82	1.30	2.01
616-01-24	A horizon	0-25	337	57	116	3	8	4.61	42	0.09	0.11	0.27	2.71	0.003	0.96	0.07	0.23	0.13	0.06	0.05	0.01	0.68	0.10	0.37	0.06	2.13	0.43	0.31	2.21
616-01-24	E horizon	100-125	25	9	153	6	4	0.58	9	nd	0.13	0.30	1.01	0.002	0.70	0.03	0.31	0.20	0.03	0.04	0.03	0.24	0.28	0.26	0.04	0.25	0.18	1.10	4.01
616-01-24	B horizon	150-175	21	12	198	3	4	nd	79	nd	0.18	0.62	1.28	0.009	1.20	0.07	2.53	1.12	0.08	0.03	0.00	0.77	0.29	0.48	0.09	0.40	0.47	1.27	2.16
616-01-24	E horizon	350-375	20	4	156	6	4	0.56	7	0.03	0.12	1.11	1.44	0.001	1.58	0.06	0.54	0.10	0.07	0.02	0.02	0.95	0.08	0.62	0.06	0.20	0.47	0.91	4.85
616-01-24	B horizon	450-475	164	65	434	6	20	0.63	264	0.39	0.40	3.63	7.10	0.077	8.02	0.21	10.38	3.05	0.56	0.08	0.12	4.26	0.08	3.48	0.87	1.48	2.17	5.52	2.89
616-01-24	E horizon	550-575	22	14	173	4	3	0.73	16	0.12	0.17	1.02	3.61	0.012	1.11	0.09	3.27	0.21	0.06	0.02	0.02	0.72	0.05	0.47	0.08	0.33	0.48	0.82	2.22
616-02-28	B horizon	25-50	132	271	13994	33	21	nd	452	0.29	1.31	2.40	11.61	0.041	3.76	1.36	9.13	4.71	nd	nd	nd	1.92	0.84	1.30	0.85	1.97	3.47	12.72	0.47
616-02-28	B horizon	125-150	1819	1510	32526	368	79	8.91	28940	6.91	9.95	12.08	16.91	0.597	37.12	36.99	26.34	14.87	0.58	nd	0.05	15.35	7.64	12.59	5.81	16.51	10.97	50.65	9.73
616-02-31	A horizon	0-20	878	140	315	5	14	0.45	108	nd	0.32	0.95	4.70	0.007	1.25	0.12	0.36	0.22	0.06	0.04	0.05	0.74	0.11	0.47	0.05	7.32	0.38	0.48	1.45
616-02-31	E horizon	150-170	10	3	142	4	1	0.01	5	nd	0.06	nd	0.66	0.006	1.27	0.11	0.38	0.19	0.05	0.04	0.05	0.69	0.09	0.49	0.05	0.14	0.43	0.62	0.85
616-02-31	coffee rock	200-300	83	366	2693	11	40	nd	1052	1.15	0.49	9.60	8.46	0.182	9.83	0.80	17.69	7.87	0.72	0.20	0.26	5.28	0.63	3.96	0.65	5.24	4.40	10.45	1.90
616-02-31	coffee rock	200-300	57	279	1949	7	32	nd	1064	0.75	0.07	7.89	6.86	0.141	7.61	0.60	14.98	7.03	0.53	0.20	0.19	4.10	0.34	3.02	0.50	4.09	3.63	9.08	1.22
616-02-31	E horizon	380-400	12	20	734	9	2	nd	446	0.27	0.11	1.30	6.75	0.010	1.74	0.31	1.02	0.69	0.06	0.00	0.07	1.00	0.05	0.62	0.03	0.84	0.78	1.11	1.51
616-02-31	coffee rock	430-450	99	225	1044	7	95	nd	644	nd	0.15	6.87	16.45	0.065	7.04	0.48	10.82	3.55	0.32	0.12	0.10	4.91	0.15	2.42	0.27	5.54	2.51	4.53	2.33
616-02-31	coffee rock	530-550	106	213	651	10	85	0.10	390	nd	0.15	2.83	12.30	0.053	5.52	0.36	8.67	2.07	0.30	0.08	0.09	3.15	0.10	2.02	0.29	3.44	2.28	3.42	1.88
616-02-32	A horizon	0-20	8155	137	315	12	14	0.27	128	nd	0.61	nd	1.89	0.009	0.90	0.24	7.61	0.27	0.06	0.06	0.03	1.09	0.11	0.37	0.01	28.75	0.52	0.72	1.58
616-02-32	E horizon	150-160	44	19	275	11	2	0.77	83	0.07	0.51	0.09	0.67	0.006	2.14	0.26	12.32	0.35	0.09	0.02	0.02	1.31	0.20	0.90	0.04	0.33	0.59	0.86	2.45
616-02-32	coffee rock	160	64	134	467	24	10	0.81	805	0.16	0.18	5.77	3.63	0.023	10.35	0.44	4.95	3.76	0.45	0.06	0.10	6.59	0.18	3.84	0.26	3.57	3.53	3.84	0.41
616-02-32	coffee rock	220-240	47	35	602	12	17	0.02	706	nd	0.91	13.55	3.71	0.031	6.57	0.40	58.37	4.13	0.39	0.15	0.14	4.07	0.53	2.39	0.44	1.23	3.84	5.25	1.70
616-02-32	E horizon	320-340	54	80	757	36	9	0.81	252	nd	0.29	8.20	5.17	0.025	12.73	0.57	5.91	1.59	0.46	0.05	0.04	7.10	0.29	4.70	0.19	2.20	4.46	3.82	0.37
616-02-32	E horizon	380-400	27	97	777	38	8	0.46	340	nd	0.25	6.37	4.95	0.031	11.01	0.55	6.29	1.19	0.43	0.08	0.04	6.25	0.12	3.90	0.19	1.87	4.14	3.18	0.62
616-02-58	B horizon	400-500	242	423	540	12	7	nd	2352	0.08	0.96	5.69	7.03	0.023	3.39	0.29	26.45	0.74	0.20	0.18	0.11	2.31	0.34	1.21	0.23	4.22	0.77	3.48	0.55
616-02-65	B horizon	200	755	615	1135	13	67	4.34	321	0.67	1.04	5.14	26.86	0.116	6.98	0.95	13.28	5.09	0.38	nd	0.00	3.99	0.34	2.74	0.64	9.94	1.08	5.15	1.67
616-02-65	B horizon	0-20	1335	1133	2441	15	258	1.84	444	2.29	3.17	7.83	47.43	0.408	22.65	2.61	25.88	7.82	1.58	nd	0.06	12.15	0.35	9.50	2.14	23.08	3.20	13.70	6.55
616-02-65	coffee rock	480-560	365	547	824	7	35	1.57	1076	0.42	0.17	6.08	9.63	0.037	2.87	0.41	9.21	3.17	0.17	0.01	0.06	1.67	0.18	1.15	0.63	5.00	2.06	4.61	0.64
616-02-65	coffee rock	650-700	87	115	304	5	4	1.91	221	0.01	0.25	1.76	2.32	0.005	1.47	0.04	2.58	0.93	0.10	nd	0.02	0.90	0.12	0.59	0.16	1.19	0.67	1.25	0.19
616-02-68	A horizon	50	101	19	216	4	7	0.23	12	nd	0.20	nd	3.67	0.003	2.17	0.09	0.32	0.17	0.10	0.01	0.02	1.21	0.14	0.81	0.01	1.43	0.63	1.67	0.05
616-02-68	E horizon	140-150	9	5	118	4	4	0.24	1	nd	0.21	nd	1.42	0.002	2.00	0.12	0.23	0.10	0.09	0.03	0.01	1.05	0.15	0.77	nd	0.25	0.58	1.50	nd
616-02-68	E horizon	340-350	39	51	663	16	8	0.14	188	nd	0.21	1.94	3.63	0.018	5.15	0.26	4.93	0.79	0.24	0.06	0.01	2.76	0.22	1.91	0.05	0.49	1.88	1.93	nd
616-02-68	E horizon	540-550	49	9	681	13	5	0.11	360	nd	0.07	0.26	2.73	0.015	4.41	0.29	2.54	0.56	0.22	0.04	0.03	2.29	0.08	1.66	0.07	0.43	1.69	2.43	nd
616-02-68	A horizon	0-25	147	21	118	2	6	2.30	14	nd	0.14	0.71	7.49	0.000	1.56	0.01	0.56	0.25	0.10	nd	0.01	0.89	0.03	0.58	0.02	1.85	0.43	0.01	0.15
616-02-68	E horizon	25-200	21	6	190	4	2	2.50	3	0.13	0.07	0.22	1.90	nd	1.77	nd	0.89	0.10	0.11	nd	nd	1.00	0.11	0.71	0.02	0.16	0.43	0.24	0.14
616-02-68	coffee rock	200-300	224	162	615	11	14	2.07	285	0.20	0.30	4.21	4.53	0.012	3.89	0.13	11.73	2.53	0.19	nd	0.01	2.29	0.59	1.39	0.10	1.15	0.92	1.64	0.25
616-02-68	B horizon	300-400	47	61	610	14	5	2.26	182	nd	0.10	1.78	5.00	nd	3.28	0.01	4.77	0.79	0.13	nd	0.02	1.92	0.06	1.29	0.08	0.44	1.29	0.93	0.24
616-02-68	B horizon	450	64	58	669	19	4	2.04	188	nd	0.18	1.92	6.46	nd	2.75	0.03	7.96	1.00	0.12	nd	0.01	1.62	0.11	1.07	0.09	0.86	1.04	1.02	0.27
616-02-68	B horizon	500-600	82	18	743	19	4	1.95	243	nd	0.13	1.60	5.06	nd	4.91	nd	5.08	0.79	0.22	nd	nd	2.79	0.03	1.90	0.13	0.55	1.75	1.25	0.46
616-02-71	E horizon	350-370	18	11	145	3	3	0.17	21	nd	0.09	nd	0.82	0.002	1.09	0.06	0.32	0.11	0.07	0.01	0.02	0.62	0.14	0.42	nd	0.23	0.32	1.30	nd
616-02-71	B horizon	550-570	87	83	624	10	5	0.31	498	nd	0.31	1.33	3.69	0.024	4.19	0.30	2.81	0.82	0.22	0.03	0.04	2.38	0.13	1.47	0.22	1.28	1.36	1.94	0.11



**Appendix Table 3 (Cont.)** Element analyses by ICP-OES of aqua regia method (in mg kg<sup>-1</sup> unit).

Site	Horizon	Depth (cm)	Ca	Mg	Fe	Mn	P	Zn	S	As	Cu	Pb	Ba	Be	Ce	Co	Cr	Ga	Gd	Ge	Hf	La	Mo	Nd	Sc	Sr	Th	V	Y
616-02-78	B horizon	450	50	14	385	4	5	1.55	189	nd	0.17	0.51	2.16	nd	0.39	0.06	4.06	0.20	nd	0.01	0.01	0.23	0.11	0.15	0.03	0.44	0.10	0.33	0.10
616-02-80	coffee rock	350-400	342	603	720	6	12	0.04	885	nd	0.18	4.63	8.92	0.057	3.03	0.90	5.68	5.00	0.18	0.08	0.08	1.97	0.26	1.11	0.28	5.54	1.26	4.50	0.02
616-02-81	B horizon	500	144	32	1003	15	3	2.06	548	nd	0.10	1.21	4.73	nd	2.18	0.11	1.92	0.41	0.09	nd	0.01	1.29	0.10	0.90	0.09	0.90	0.61	1.72	0.40
616-02-82	A horizon	25-75	nd	4	221	8	7	0.36	10	nd	0.30	nd	2.94	0.008	3.75	0.15	0.66	0.40	0.14	0.03	0.04	2.05	0.04	1.39	0.01	0.29	1.19	1.11	nd
616-02-82	E horizon	125-175	nd	6	272	12	5	0.13	18	0.05	0.24	1.04	3.66	0.010	4.21	0.18	1.63	0.37	0.16	0.01	nd	2.27	0.03	1.54	0.04	0.42	1.12	1.69	nd
616-02-82	E horizon	225-275	17	15	2147	15	8	1.87	1586	nd	0.36	0.58	5.72	0.031	4.02	0.35	4.17	0.65	0.22	0.07	0.02	2.45	0.21	1.47	0.09	0.63	1.73	2.86	nd
616-02-82	E horizon	325-375	46	27	1433	14	8	0.17	958	1.08	0.18	1.67	5.05	0.029	7.29	0.36	4.20	0.73	0.35	0.05	0.04	4.07	0.14	2.68	0.12	0.88	2.62	2.71	0.06
616-02-82	E horizon	425-475	67	33	2332	32	11	0.68	1385	2.40	0.11	2.29	6.98	0.040	7.56	0.56	7.22	1.08	0.41	0.10	0.02	4.17	0.16	2.82	0.22	1.34	3.85	4.11	nd
616-02-82	coffee rock	525-575	128	39	3500	21	17	0.57	2482	6.36	0.24	4.11	5.26	0.080	5.60	0.90	14.33	1.71	0.40	0.10	0.11	3.65	0.12	2.15	0.44	1.50	2.86	4.74	1.19
616-02-85	A horizon	0-25	4157	1879	43557	961	1094	43.22	241	19.70	53.51	90.24	194.28	2.553	120.71	35.41	46.41	19.99	4.99	nd	nd	54.34	5.39	37.19	10.11	26.25	15.46	92.19	38.03
616-02-85	B horizon	125-150	433	270	2923	30	13	nd	73	0.28	2.74	4.94	20.26	0.108	12.73	1.55	13.70	5.80	0.52	nd	0.02	7.02	1.14	4.50	2.99	4.23	7.36	9.83	1.57
616-02-85	E horizon	350-400	237	120	2279	39	14	nd	984	0.21	0.61	1.41	8.10	0.136	6.39	3.05	4.37	0.90	0.30	nd	0.02	3.16	0.96	2.20	0.40	2.49	1.41	3.62	1.79
616-02-85	B horizon	450-475	19702	2840	35378	694	109	5.47	30601	5.50	14.13	16.17	46.55	1.310	64.68	19.21	34.90	17.15	2.03	nd	0.08	28.95	6.61	20.87	6.88	178.73	13.75	75.63	19.64
616-02-87	coffee rock	200-300	221	128	2128	16	53	nd	579	1.64	2.77	3.45	5.28	0.113	13.81	0.40	35.13	5.28	1.63	0.25	0.34	6.76	2.69	6.25	2.47	2.17	7.53	8.62	4.44
616-02-87	coffee rock	300-400	536	348	538	8	37	nd	964	1.14	0.18	2.28	10.07	0.200	11.99	0.41	23.81	8.69	1.18	0.28	0.27	6.17	0.58	5.48	1.85	5.90	6.72	9.12	3.16
616-02-87	B horizon	500-600	19	21	339	3	5	nd	171	0.07	0.24	0.65	2.93	0.009	1.89	0.16	3.30	0.29	0.10	0.05	0.01	1.15	0.25	0.70	0.09	0.39	0.69	1.77	0.17
616-02-94	B horizon	50-75	345	546	37195	71	50	nd	4256	3.19	11.20	35.70	77.34	0.293	33.28	3.53	30.48	17.33	nd	nd	nd	11.36	8.48	10.37	6.87	13.20	13.56	63.30	5.47
616-02-94	B horizon	150-175	225	582	14223	37	13	nd	1782	nd	2.08	27.67	22.30	0.193	14.90	3.06	16.65	7.26	nd	nd	0.02	6.49	1.12	4.86	2.21	8.11	6.92	19.27	2.39
616-02-94	E horizon	400-425	127	409	3250	38	7	nd	194	nd	1.40	12.74	8.19	0.282	26.12	4.96	17.17	5.32	1.35	nd	0.05	9.54	0.41	8.37	1.90	1.94	9.70	11.72	3.68
616-02-99	E horizon	25-50	260	61	530	8	35	nd	49	0.21	0.34	1.74	1.84	0.005	1.00	0.18	1.83	0.56	0.05	nd	nd	0.51	0.27	0.37	0.04	1.60	0.24	1.02	0.14
616-02-99	B horizon	250-275	325	32	481	8	6	nd	165	0.20	0.51	0.97	4.61	0.005	1.17	0.19	2.02	0.49	0.04	nd	nd	0.69	3.70	0.42	0.16	1.31	0.72	1.85	0.14
616-02-99	E horizon	350-375	382	103	3417	23	7	nd	2424	3.99	1.12	1.73	3.73	0.021	3.06	0.88	2.91	1.29	0.01	nd	0.00	1.51	6.43	1.19	0.33	1.70	1.02	3.18	0.49
616-02-100	E horizon	25-50	10380	407	7677	26	55	26.98	133	0.37	6.90	99.20	11.11	0.023	7.16	0.75	8.90	4.07	nd	nd	nd	3.79	0.40	2.35	0.42	42.18	1.84	22.18	1.08
616-02-100	Peat soil	80-100	2968	1212	2699	16	66	nd	1102	1.68	1.39	5.50	27.76	0.194	28.47	0.56	9.69	1.49	1.67	nd	0.02	14.15	1.93	8.97	2.27	19.90	2.59	14.62	6.82
616-02-100	B horizon	175-200	167	135	3674	39	67	nd	1610	1.33	0.37	5.98	8.81	0.032	19.62	0.60	10.12	2.73	0.90	nd	0.02	10.20	5.87	7.34	0.77	1.87	6.20	10.39	3.38
616-02-100	E horizon	425-450	19	16	92	1	4	nd	36	0.07	0.05	0.51	1.89	0.005	1.22	0.12	1.97	0.37	0.10	nd	0.01	0.87	0.09	0.49	0.06	0.41	0.51	0.14	1.17
616-02-101	A horizon	50-75	1662	205	2906	13	34	2.84	61	0.94	1.82	6.09	10.63	0.033	3.93	0.47	6.40	1.65	0.03	nd	0.01	1.73	0.17	1.16	0.36	4.26	1.23	5.96	0.55
616-02-101	B horizon	170-190	78369	3054	25928	335	157	2.41	14208	7.31	1.39	2.06	83.02	0.126	6.11	1.75	15.90	6.84	nd	nd	nd	2.61	0.95	1.82	0.51	96.49	1.84	24.46	1.83
616-02-101	E horizon	440-450	114	31	937	8	4	nd	424	0.49	0.05	0.48	6.17	0.004	3.37	0.09	2.02	0.50	0.12	nd	0.00	1.78	0.04	1.20	0.05	0.62	0.95	1.63	0.30
616-02-105	A2 horizon	75-100	2947	229	5605	11	86	nd	293	16.48	2.20	3.10	17.71	0.537	6.75	5.49	20.51	3.15	0.47	nd	0.01	2.67	0.29	2.31	0.50	9.20	1.37	33.64	7.37
616-02-105	Peat soil	300-325	10479	1216	54503	50	72	0.03	57117	417.92	1.34	1.33	25.90	4.050	8.23	1.90	36.50	8.68	nd	nd	nd	4.30	2.17	5.41	0.38	13.66	1.09	4.16	30.20
616-02-105	B horizon	425-450	478	51	1585	4	5	nd	1053	8.01	0.19	1.02	10.64	1.024	4.62	5.28	11.91	0.51	0.71	nd	0.01	2.57	0.07	2.41	0.24	1.66	0.90	1.17	10.85
616-02-105	E horizon	575-600	47	9	207	6	4	nd	11	0.27	0.05	0.85	5.10	0.060	2.54	0.17	1.71	0.02	0.14	nd	0.01	1.38	0.01	0.90	0.04	0.30	0.65	1.08	1.54
616-02-106	A2 horizon	25-50	391	129	4377	7	132	nd	693	20.39	1.12	4.46	28.26	0.010	2.40	0.09	4.72	0.77	nd	nd	0.00	1.26	0.19	0.88	0.17	5.59	0.72	2.52	0.49
616-02-106	E horizon	425-450	37	15	968	12	4	nd	488	5.08	0.04	1.32	2.90	nd	4.30	0.41	3.61	0.36	0.13	nd	0.01	2.55	0.02	1.57	0.09	0.39	1.41	0.57	0.38
616-02-110	B horizon	420	51235	657	6985	13	58	nd	5941	6.40	0.34	1.92	11.16	0.070	48.28	1.17	17.69	1.83	2.05	nd	nd	13.71	0.27	15.66	0.86	24.07	2.88	2.91	15.57
616-02-112	B horizon	25-50	249900	11338	203	76	111	nd	1276	1.93	0.43	nd	291.63	0.030	0.49	0.25	0.70	nd	0.05	nd	nd	0.52	0.34	nd	nd	1548.52	0.01	nd	0.13
616-02-112	B horizon	125-150	241411	9636	234	116	91	nd	1364	1.36	0.44	nd	447.80	0.032	0.54	0.39	0.95	nd	0.02	nd	nd	0.51	0.45	0.03	nd	1633.83	0.04	nd	0.14
616-02-112	Peat soil	250-275	7622	4950	4198	58	67	nd	12948	34.89	1.45	nd	20.38	0.011	0.41	0.29	1.21	nd	nd	0.03	0.28	1.58	0.05	0.05	56.69	0.10	0.41	0.17	
616-02-112	B horizon	350-375	29271	1104	9625	353	102	nd	4812	5.71	1.32	3.21	48.71	0.185	14.17	1.28	29.63	7.91	0.51	nd	0.00	7.08	0.64	4.88	1.11	292.06	2.50	13.63	4.66

**Appendix Table 3 (Cont.)** Element analyses by ICP-OES of aqua regia method (in mg kg<sup>-1</sup> unit).

Site	Horizon	Depth (cm)	Ca	Mg	Fe	Mn	P	Zn	S	As	Cu	Pb	Ba	Be	Ce	Co	Cr	Ga	Gd	Ge	Hf	La	Mo	Nd	Sc	Sr	Th	V	Y
616-02-122	E horizon	50-75	111	22	206	7	7	nd	18	0.01	0.57	0.68	4.15	nd	1.51	nd	0.44	0.15	0.04	0.00	nd	0.89	0.12	0.58	0.04	0.73	0.38	0.61	0.13
616-02-122	B horizon	275-300	354	72	298	8	8	nd	68	nd	0.20	1.20	3.51	0.001	1.67	0.02	6.55	0.97	0.08	nd	0.01	1.04	0.37	0.64	0.15	2.08	0.75	0.83	0.17
616-02-122	B horizon	800-900	37	17	260	5	3	1.71	109	0.03	0.18	1.92	4.00	0.003	1.15	0.04	7.58	1.02	0.06	nd	0.00	0.67	0.17	0.42	0.10	0.47	0.51	2.18	0.13
616-02-122	E horizon	325-400	38	16	740	27	1	2.35	118	nd	0.06	2.66	3.96	nd	2.31	nd	3.55	0.60	0.10	nd	0.01	1.43	0.08	0.94	0.20	0.42	1.54	2.46	0.24
616-02-127	coffee rock	125	271	94	296	4	25	nd	796	0.49	0.35	1.70	10.39	0.112	7.91	0.22	9.28	1.21	0.66	nd	0.00	4.38	0.13	3.39	0.90	1.99	2.33	2.50	1.25
616-02-127	E horizon	275	15	11	396	15	14	nd	39	nd	0.04	0.71	3.69	nd	0.90	nd	2.14	0.85	0.08	nd	0.01	0.59	0.11	0.42	0.08	0.50	0.46	1.00	0.10
616-02-131	E horizon	50	565	253	5652	24	59	10.78	38	0.72	5.81	23.77	11.52	0.056	4.61	0.67	9.09	3.60	nd	nd	nd	2.46	0.59	1.60	0.56	3.31	1.72	14.26	0.57
616-02-131	E horizon	250	35	15	208	5	2	nd	11	0.05	0.15	0.49	2.30	nd	1.04	nd	1.09	0.45	0.08	nd	nd	0.66	0.02	0.43	0.04	0.39	0.34	0.38	0.11
616-02-131	B horizon	375	325	888	36170	60	13	nd	32	2.65	5.72	8.32	13.20	0.151	20.56	2.55	51.71	19.39	nd	nd	0.04	11.79	0.84	7.30	7.38	3.11	14.10	39.01	1.75
616-02-131	E horizon	450	72	181	1349	7	4	nd	22	0.13	1.32	1.85	6.23	0.027	4.57	0.36	11.76	2.22	0.19	nd	0.02	2.81	0.09	1.56	1.08	0.74	2.67	2.75	0.45
616-02-136	E horizon	50	240	67	192	6	7	2.87	37	nd	0.15	1.39	4.41	nd	3.76	nd	0.63	0.31	0.13	nd	nd	2.12	0.10	1.38	0.05	1.30	0.97	0.55	0.18
616-02-136	coffee rock	250	777	255	668	12	25	1.58	364	0.49	0.71	14.75	14.98	0.096	16.53	0.32	27.70	4.09	0.74	0.00	0.03	9.81	0.27	5.54	0.53	6.45	4.81	4.15	1.05
616-02-145	E horizon	50	16	6	201	2	1	1.05	3	0.14	0.02	0.44	1.47	nd	0.67	0.05	0.78	0.33	nd	nd	nd	0.40	0.13	0.27	0.02	0.16	0.20	0.23	0.06
616-02-145	E horizon	350	19	25	332	3	2	1.37	106	0.20	0.07	2.42	3.09	0.019	3.32	0.03	1.51	0.67	0.12	nd	nd	2.29	0.09	1.21	0.08	0.33	0.91	0.70	0.38
616-02-145	B horizon	450	249	435	51808	36	126	nd	185	17.78	0.38	46.18	32.13	2.813	16.46	7.37	63.13	23.20	nd	nd	nd	7.64	3.01	6.24	6.09	2.63	17.36	456.05	4.80
616-02-145	B horizon	550	82	192	1623	4	13	1.05	308	2.76	0.19	7.85	14.25	0.259	7.78	2.25	16.62	4.36	0.28	nd	0.06	5.76	0.27	2.24	1.08	4.33	4.55	9.13	1.04
616-02-155	E horizon	50	17689	716	490	11	6	1.09	102	0.12	0.05	0.53	5.59	0.003	2.05	0.13	2.37	0.40	0.17	nd	0.01	1.26	0.07	0.87	0.13	70.49	0.59	0.97	0.69
616-02-155	E horizon	325	297	251	1727	16	4	2.94	579	1.39	0.16	4.37	6.07	0.066	4.83	0.63	9.64	1.81	0.15	nd	0.02	2.52	1.10	1.66	0.81	1.76	2.99	7.88	0.56
616-02-155	B horizon	550	1984	2408	18457	48	11	2.20	17	5.90	1.85	8.36	16.23	0.180	18.20	10.77	43.33	10.77	nd	nd	0.03	11.84	1.25	6.13	9.04	9.75	19.77	42.23	3.63
616-02-158	E horizon	75	13	4	73	2	1	1.72	3	0.08	0.02	0.30	0.70	nd	0.27	0.01	0.22	0.11	0.04	nd	0.01	0.18	0.10	0.11	0.01	0.11	0.07	0.14	0.04
616-02-158	coffee rock	250	75	73	2272	12	172	1.16	635	2.32	0.33	6.07	5.92	0.092	4.21	0.22	8.43	4.24	0.23	0.00	0.02	2.35	1.64	1.69	0.40	1.39	1.43	14.97	0.67
616-02-158	coffee rock	400	125	208	1042	24	41	2.84	738	0.14	0.24	7.88	11.73	0.001	2.86	0.30	7.76	2.80	0.13	0.01	0.02	1.82	1.50	1.09	0.24	2.50	1.24	3.36	0.29
616-02-174	B horizon	400	380	68	1304	13	42	3.21	191	0.31	1.55	0.93	2.27	0.007	1.11	1.23	11.41	1.53	0.02	nd	0.00	0.71	1.08	0.44	0.09	1.75	0.49	0.95	0.20
616-02-179	B horizon	375-400	37	23	315	3	4	1.70	121	0.26	0.09	0.44	3.13	0.008	1.18	0.05	3.31	0.99	0.06	0.01	0.01	0.75	0.11	0.50	0.09	0.57	0.38	1.54	0.17
Ellenbrook	E horizon	0-150	16	5	80	2	1	1.45	5	nd	0.02	0.32	1.34	nd	0.42	nd	0.30	0.24	0.02	0.00	nd	0.24	0.04	0.16	0.02	0.12	0.19	0.08	0.12
Ellenbrook	coffee rock	150-200	295	57	1222	2	42	0.54	447	1.68	nd	5.84	11.26	0.111	7.60	0.50	16.54	4.81	0.67	0.01	0.09	4.09	0.18	3.18	1.37	1.43	3.66	7.99	1.88
Ellenbrook	B horizon	500-550	117	32	1498	2	3	1.49	1164	0.15	0.07	1.79	5.40	0.009	1.46	0.34	1.21	0.35	nd	nd	nd	0.95	0.05	0.53	0.09	0.86	0.36	0.57	0.27
LOC50A	A horizon	10-20	22	26	1802	6	11	1.54	16	0.08	0.17	0.89	2.08	0.015	1.72	0.14	2.63	1.30	0.09	0.04	0.03	0.89	0.22	0.58	0.09	0.65	0.56	3.39	1.62
LOC50A	A horizon	0-100	31	21	919	5	7	0.18	9	0.01	0.13	0.46	1.98	0.006	1.43	0.09	1.45	0.83	0.07	0.03	0.00	0.89	0.21	0.52	0.08	0.64	0.42	2.38	2.35
LOC50A	E horizon	300-400	15	24	598	15	9	0.53	56	nd	0.18	1.59	2.23	0.011	2.77	0.20	7.65	3.78	0.14	0.06	nd	1.73	0.07	0.99	0.13	0.71	0.95	2.45	1.21
LOC50A	coffee rock	400-500	12	19	336	11	5	nd	217	nd	1.20	1.14	1.25	0.007	1.87	0.08	7.31	1.67	0.08	0.06	0.02	1.24	0.12	0.69	0.10	0.43	0.81	3.91	0.88

**Appendix Table 4** Element analyses by ICP-OES of fusion acid digestion method (in mg kg<sup>-1</sup> unit).

Site	Horizon	Depth (cm)	Si	Al	Na	K	Ti	Zr	Ni
616-01-003	A horizon	0-25	574151	1393	nd	1199	1162	126	9
616-01-003	coffee rock	175-200	525701	16618	nd	1039	706	72	6
616-01-003	C2 horizon	300-400	580656	3590	nd	1666	831	95	18
616-01-005	A horizon	0-20	589662	949	290	271	392	39	9
616-01-005	E horizon	20-180	620853	743	270	244	437	86	8
616-01-005	coffee rock	180-200	567058	9667	310	474	1178	92	7
616-01-005	B horizon	200-250	609737	2879	311	385	589	69	8
616-01-005	2E1 horizon	250-260	586392	2757	272	235	615	63	11
616-01-005	2E2 horizon	260-400	581294	1604	180	157	487	67	7
616-01-005	B horizon	620-630	562310	1554	233	269	482	78	41
616-01-005	2coffee rock1	830-900	612839	1702	234	188	616	34	10
616-02-009	E1 horizon	225-250	574749	5257	875	3685	915	69	39
616-01-011	A horizon	0-75	598427	717	334	294	656	64	7
616-01-011	E1 horizon	75-500	614726	171	222	118	949	104	7
616-01-014	A horizon	0-50	604248	474	312	223	285	34	10
616-01-014	E1 horizon	50-300	612585	290	216	181	343	58	8
616-01-014	coffee rock	650-800	593181	5195	nd	314	716	62	5
616-01-014	C3 horizon	1000-1200	581823	3542	nd	926	871	71	4
616-01-014	C4 horizon	1200-1300	589859	11603	300	2927	1730	154	13
616-01-018	A horizon	0-25	587482	614	nd	342	179	15	6
616-01-018	E3 horizon	300-400	529774	298	nd	28	212	17	6
616-01-018	coffee rock	400-450	580955	6636	161	383	648	50	7
616-01-018	2E horizon	450-600	604485	1176	252	200	525	52	8
616-01-018	2coffee rock1	600-700	590684	1201	nd	203	248	24	5
616-01-019	A horizon	0-50	552451	276	nd	181	561	58	8
616-01-019	E1 horizon	50-200	622488	191	nd	106	833	60	11
616-01-019	B horizon	250-300	514023	24396	nd	2227	2019	137	13
616-01-023	A horizon	0-25	625790	580	nd	378	640	65	10
616-01-023	E horizon	25-100	585393	600	nd	419	802	107	6
616-01-023	B horizon	100-200	607163	7367	nd	1081	1177	207	11
616-01-023	C3 horizon	500-1000	564159	5193	nd	2457	772	51	9
616-01-024	A horizon	0-25	609782	325	nd	nd	403	42	8
616-01-024	E horizon	25-150	596073	243	nd	32	769	139	10
616-01-024	B horizon	150-200	553318	2276	nd	360	599	45	16
616-01-024	2B horizon	400-500	587107	9803	nd	1333	914	83	11
616-01-024	3E horizon	500-800	609088	3084	nd	1041	558	33	9
616-02-028	B horizon	30-100	586730	15698	7731	10697	1757	161	26
616-02-028	Mud1	100-200	410234	55930	12943	10806	6439	432	29
616-02-031	A horizon	0-75	549139	444	113	134	1500	142	5
616-02-031	E horizon	75-200	595116	325	210	110	2481	439	5
616-02-031	coffee rock1	200-300	522554	24079	1120	797	4709	539	13
616-02-031	2E horizon	300-400	594130	1555	131	1165	1409	118	6
616-02-031	2coffee rock1	400-500	567072	21767	635	4364	1684	84	12
616-02-032	A horizon	0-50	585966	957	255	308	2238	267	10
616-02-032	E horizon	50-200	607288	271	nd	61	2008	203	15
616-02-032	coffee rock1	160	560815	2946	nd	425	8773	473	6
616-02-032	2E2 horizon	350-400	580096	4443	108	3882	5129	571	6
616-02-058	B horizon	300-500	559439	1480	nd	304	1777	120	9
616-02-065	Peat1	0-20	492354	33645	1332	1394	1791	98	45
616-02-065	coffee rock1	480-560	533329	10181	389	932	2563	370	45
616-02-065	coffee rock3	650-700	572934	2471	137	866	889	109	40
616-02-065	B horizon	200	557836	6677	537	3973	1499	279	49
616-02-068	B horizon	450	561620	3836	258	758	461	91	47
616-02-068	A horizon	0-75	592681	743	nd	486	588	84	6
616-02-068	E1 horizon	75-300	604555	593	nd	498	803	77	12
616-02-068	A horizon	0-25	587653	476	39	281	245	30	79
616-02-068	E horizon	25-200	592108	497	230	504	794	122	44
616-02-068	coffee rock	200-300	567239	8489	393	2985	1594	311	42
616-02-068	B1 horizon	300-400	583146	6149	378	3598	1524	142	36
616-02-068	B3 horizon	500-600	564463	6365	394	4904	2471	467	42
616-02-071	E horizon	25-350	610669	162	nd	69	532	79	7
616-02-071	B horizon	350-600	573637	3610	nd	2558	1497	140	7
616-02-078	B horizon	400-500	568948	3204	280	2818	1372	218	41
616-02-080	coffee rock	200-400	555971	15617	70	1812	2172	141	13

**Appendix Table 4** (Cont.) Element analyses by ICP-OES of fusion acid digestion method (in mg kg<sup>-1</sup> unit)..

Site	Horizon	Depth (cm)	Si	Al	Na	K	Ti	Zr	Ni
616-02-081	B horizon	400-800	454142	21062	2949	20288	754	108	29
616-02-082	A horizon	0-75	588106	4205	118	4622	1950	197	8
616-02-082	E1 horizon	75-200	581750	5371	72	5127	1898	250	8
616-02-082	B horizon	300-400	585625	9206	202	8049	2774	219	3
616-02-082	coffee rock	500-600	575373	12918	283	8566	2434	329	8
616-02-085	A horizon	0-70	372001	80116	9982	8753	6362	279	nd
616-02-085	B1 horizon	100-300	559100	32431	11413	15326	2961	188	39
616-02-085	B2 horizon	300-400	598857	16502	9357	11731	715	60	49
616-02-085	Mud	400-600	391766	64337	13070	15305	7694	412	12
616-02-087	coffee rock2	300-400	488632	33192	130	5466	2368	131	9
616-02-087	B horizon	500-600	598393	4453	nd	3602	3964	389	7
616-02-094	A1 horizon	0-100	429471	50787	7652	13286	7929	623	7
616-02-094	A2 horizon	100-175	532807	21176	4457	6632	6210	800	29
616-02-094	E horizon	175-600	570227	6488	1757	2033	11621	4600	46
616-02-099	E horizon	25-200	586418	1432	867	540	424	31	38
616-02-099	B1 horizon	200-300	599191	2284	707	478	1147	135	50
616-02-099	B2 horizon	300-400	587888	3257	907	871	1580	271	48
616-02-100	A horizon	0-80	564245	6042	1533	1937	2013	151	41
616-02-100	Peat	80-110	443875	5547	1488	1678	1058	177	36
616-02-100	Peat/ E horizon	110-200	535717	10239	1031	3663	5180	869	38
616-02-100	E horizon	200-600	602621	1421	879	978	126	23	59
616-02-101	A horizon	0-75	453164	5055	754	1226	369	44	34
616-02-101	Peat1	150-200	158163	6363	2141	3861	283	36	nd
616-02-101	E horizon	350-600	542576	9548	1398	10510	524	50	42
616-02-105	A horizon	0-160	526831	9789	1254	2766	722	72	39
616-02-105	Peat	250-360	36140	2478	1002	339	68	8	nd
616-02-105	Peat/ E horizon	360-480	563278	2656	802	1896	327	38	46
616-02-105	E horizon	480-700	573359	3962	1155	3866	706	58	44
616-02-106	A horizon	0-50	574812	2547	1317	1668	414	132	36
616-02-106	E horizon	50-700	591803	6159	1464	5312	961	117	41
616-02-110	B horizon	200-500	551345	2322	30	268	506	46	51
616-02-112	B horizon	0-80	21030	433	6868	322	13	2	2
616-02-112	Mud	125-200	56771	303	8137	471	5	2	13
616-02-112	Peat	200-300	6914	363	22932	842	17	2	nd
616-02-112	B horizon	300-400	589392	14759	2430	7221	1091	105	42
616-02-112	C horizon	400-600	342593	8304	1666	4873	1098	104	26
616-02-113	A horizon	0-50	559730	5065	846	4019	778	116	39
616-02-113	E1 horizon	50-250	578347	5874	869	5719	1363	110	50
616-02-122	E horizon	20-235	580536	549	97	336	562	82	47
616-02-122	B horizon	235-315	555068	4768	169	1221	1100	121	40
616-02-122	2E2 horizon	375-500	580031	4319	330	3610	5239	690	35
616-02-122	B/E horizon	700-900	572739	2794	54	445	510	42	42
616-02-127	coffee rock	100-235	537675	7535	595	569	627	80	43
616-02-127	2E1 horizon	235-300	572083	1630	192	492	1485	451	42
616-02-131	A horizon	0-50	557731	7600	496	1928	1187	79	42
616-02-131	E horizon	50-325	576149	2942	531	2206	930	184	44
616-02-131	B horizon	325-425	396098	74968	3559	10200	6192	582	nd
616-02-131	2E horizon	425-600	512696	19930	2408	9428	612	91	34
616-02-136	A horizon	0-25	578463	515	118	381	2485	358	45
616-02-136	coffee rock	200-260	541960	11209	417	1739	5149	768	46
616-02-145	E1 horizon	50-300	578018	668	114	341	975	143	52
616-02-145	E2 horizon	300-450	597136	1736	144	611	1288	207	41
616-02-145	B horizon	450-475	428666	54443	695	2164	2507	204	nd
616-02-145	2E horizon	475-600	547193	25455	406	4717	1060	95	46
616-02-155	E horizon	50-150	580116	2608	367	2555	676	39	41
616-02-155	2E horizon	200-500	560552	12952	877	8236	1887	93	44
616-02-155	B horizon	500-600	427061	60220	2313	14845	8681	855	22
616-02-158	E horizon	25-225	606162	306	314	204	1349	37	44
616-02-158	coffee rock1	225-300	518566	13644	398	1814	2897	317	39
616-02-158	coffee rock2	300-400	521450	12752	407	4163	6140	513	33
616-02-174	B horizon	250-550	540075	18346	529	1180	1685	129	47
616-02-179	B horizon	375-400	575878	381	184	99	2365	399	51
Ellenbrook	E horizon	0-150	589071	201	70	69	1445	316	40
Ellenbrook	coffee rock	150-200	532665	22078	119	532	1182	354	38
Ellenbrook	2B1 horizon	500-550	572214	1720	136	1456	407	41	38

**Appendix Table 5** Aluminium, Fe, Si and Mn extracted by dithionite citrate bicarbonate (d); oxalic acid (ox) and Na-pyrophosphate (p) for whole wet soil samples\* (in mg kg<sup>-1</sup> unit).

Site	Horizon	Depth (cm)	Al <sub>d</sub>	Al <sub>ox</sub>	Al <sub>p</sub>	Fe <sub>d</sub>	Fe <sub>ox</sub>	Fe <sub>p</sub>	Si <sub>d</sub>	Si <sub>ox</sub>	Si <sub>p</sub>	Mn <sub>d</sub>	Mn <sub>ox</sub>	Mn <sub>p</sub>
616-01-003	A horizon	0-25	40	36	60	237	188	51	61	6	97	nd	1.5	1.1
616-01-003	Coffee rock	175-200	7285	10094	4895	7874	5196	3643	1400	3224	486	nd	0.16	nd
616-01-003	C1 horizon	200-300	267	482	1059	63	50	55	55	88	495	nd	0.40	nd
616-01-003	C2 horizon	300-400	86	196	476	79	43	39	38	62	325	nd	0.16	nd
616-01-003	C3 horizon	400-600	8	43	345	25	11	20	12	19	288	nd	0.02	nd
616-01-005	B horizon	620-630	168	147	214	82	62	44	22	18	44	2.6	0.68	0.46
616-01-005	A horizon	0-20	154	166	237	307	251	72	32	11	111	2.6	2.3	2.5
616-01-005	E horizon	20-180	53	30	190	35	14	20	24	3	154	nd	0.10	0.03
616-01-005	Coffee rock	180-200	3650	3189	6796	239	142	349	319	294	2261	nd	0.03	0.13
616-01-005	B horizon	200-250	721	505	1732	184	143	96	52	19	598	nd	1.3	0.56
616-01-005	2E1 horizon	250-260	980	862	1968	41	42	63	65	5	432	nd	0.33	0.09
616-01-005	2E2 horizon	260-400	889	855	1434	31	36	44	72	6	323	nd	0.27	nd
616-01-005	2E3 horizon	400-500	14	8	17	71	39	33	23	2	36	nd	0.34	0.25
616-01-005	2E4 horizon	500-830	92	90	311	230	196	153	47	6	227	nd	1.9	1.55
616-01-005	2Coffee rock1	830-900	1161	1056	864	50	9	27	184	129	89	nd	nd	0.01
616-01-005	2Coffee rock2	900-1000	1235	1828	1163	58	9	17	198	551	99	nd	0.06	0.04
616-02-009	E1 horizon	225-250	78	51	92	40	30	72	58	10	93	0.78	0.30	nd
616-01-011	A horizon	0-75	99	68	105	193	93	89	52	4	140	2.25	1.7	3.4
616-01-011	E1 horizon	75-500	nd	2	2	96	49	32	27	3	102	nd	0.43	0.34
616-01-011	E2 horizon	500-600	nd	4	2	114	130	47	30	7	127	nd	1.2	0.47
616-01-011	E3 horizon	600-700	16	29	174	80	52	66	12	3	217	nd	0.07	nd
616-01-014	A horizon	0-50	33	31	44	228	110	66	29	7	70	nd	0.77	0.46
616-01-014	E1 horizon	50-300	15	11	25	94	45	37	17	4	72	nd	0.29	nd
616-01-014	E2 horizon	300-650	245	303	711	874	84	296	43	90	285	nd	0.14	nd
616-01-014	Coffee rock	650-800	317	441	883	1104	97	411	59	132	321	nd	0.09	nd
616-01-014	C1 horizon	800-900	247	441	900	870	104	393	44	131	329	nd	0.10	nd
616-01-014	C2 horizon	900-1000	445	965	858	1121	221	421	54	296	250	nd	0.21	nd
616-01-014	C3 horizon	1000-1200	23	87	479	196	50	66	30	41	440	nd	0.19	nd
616-01-014	C4 horizon	1200-1300	36	162	1670	59	40	35	23	44	1787	nd	0.17	nd
616-01-018	A horizon	0-25	24	47	35	136	77	30	23	13	87	nd	1.2	0.36
616-01-018	E1 horizon	25-200	590	345	444	117	47	32	95	2	109	nd	0.33	0.04
616-01-018	E2 horizon	200-300	455	428	407	71	18	12	53	3	71	nd	0.15	nd
616-01-018	E3 horizon	300-400	157	138	206	40	8	9	41	2	57	nd	0.07	nd
616-01-018	Coffee rock	400-450	3768	3948	2830	128	32	72	716	639	138	nd	0.03	nd
616-01-018	2E horizon	450-600	497	324	645	80	20	43	135	49	293	nd	0.07	nd
616-01-018	2Coffee rock1	600-700	639	949	591	596	658	336	189	240	129	2.43	5.4	3.7
616-01-018	2Coffee rock2	700-800	1008	5525	1387	148	128	83	161	2298	102	nd	0.46	0.14
616-01-019	A horizon	0-50	12	15	19	22	14	6	19	4	114	nd	0.05	nd
616-01-019	E1 horizon	50-200	3	5	7	9	3	1	8	19	51	nd	0.03	nd
616-01-019	E2 horizon	200-250	13	17	258	1407	1326	237	45	38	166	4.38	5.6	0.22
616-01-019	B horizon	250-300	2853	13406	17	102	118	213	138	5476	156	nd	0.25	2.4
616-01-023	A horizon	0-25	10	16	34	58	47	5	16	20	41	nd	0.06	nd
616-01-023	E horizon	25-100	6	13	23	30	17	30	4	28	143	nd	0.02	nd
616-01-023	B horizon	100-200	127	624	16	20	17	11	12	150	66	nd	0.02	nd
616-01-023	C1 horizon	200-300	177	670	3164	50	38	130	25	251	2688	nd	0.08	nd
616-01-023	C2 horizon	300-500	23	69	1496	17	15	63	14	28	1214	nd	0.01	nd
616-01-023	C3 horizon	500-1000	22	80	187	50	31	16	12	43	186	nd	0.04	nd

\* drying soils before analysis may affect the relative amounts extracted by the 3 extractions

**Appendix Table 5** (Cont.) Aluminium, Fe, Si and Mn extracted by dithionite citrate bicarbonate (d); oxalic acid (ox) and Na-pyrophosphate (p) for whole wet soil samples\* (in mg kg<sup>-1</sup> unit).

Site	Horizon	Depth (cm)	Al <sub>d</sub>	Al <sub>ox</sub>	Al <sub>p</sub>	Fe <sub>d</sub>	Fe <sub>ox</sub>	Fe <sub>p</sub>	Si <sub>d</sub>	Si <sub>ox</sub>	Si <sub>p</sub>	Mn <sub>d</sub>	Mn <sub>ox</sub>	Mn <sub>p</sub>
616-01-024	A horizon	0-25	35	33	2799	71	36	59	11	8	164	nd	0.08	0.07
616-01-024	E horizon	25-150	4	5	44	14	4	31	5	26	108	nd	0.03	nd
616-01-024	B horizon	150-200	288	445	5	48	39	4	15	166	68	nd	0.19	nd
616-01-024	2E horizon	200-400	22	45	1151	20	8	65	8	37	759	nd	0.04	nd
616-01-024	2B horizon	400-500	1219	4985	783	102	93	61	81	2164	867	nd	nd	nd
616-01-024	3E horizon	500-800	9	50	1303	8	7	75	8	23	216	nd	0.05	nd
616-02-028	B horizon	30-100	53	50	557	3414	1864	1395	68	32	911	6.5	6.3	2.0
616-02-028	Mud1	100-200	719	1154	3394	4268	5441	8985	261	154	4127	79	57	151
616-02-031	A horizon	0-75	62	64	68	249	141	61	43	3	71	1.49	1.7	1.7
616-02-031	E horizon	75-200	nd	3	1	56	44	6	16	1	56	nd	0.35	nd
616-02-031	Coffee rock1	200-300	2400	8786	2668	1155	799	650	329	4166	350	0.79	2.7	2.9
616-02-031	Coffee rock2	200-300	2694	6351	2142	604	457	303	440	2886	226	nd	0.93	0.65
616-02-031	2E horizon	300-400	34	31	101	121	47	289	18	13	72	nd	0.04	nd
616-02-031	2Coffee rock1	400-500	339	2572	927	206	307	274	72	1509	469	nd	0.16	nd
616-02-031	2Coffee rock2	500-600	466	2465	1056	96	176	136	89	1475	546	nd	0.20	nd
616-02-032	A horizon	0-50	28	54	45	66	44	28	20	15	31	0.19	2.3	0.57
616-02-032	E horizon	50-200	2	4	8	15	7	14	21	2	37	nd	0.08	nd
616-02-032	Coffee rock1	160	677	652	806	52	18	45	69	3	152	nd	0.07	0.25
616-02-032	Coffee rock2	200-300	3519	3603	5585	107	125	158	648	621	2519	nd	0.30	0.35
616-02-032	2E1 horizon	300-350	143	166	178	19	19	15	43	14	57	nd	0.15	nd
616-02-032	2E2 horizon	350-400	370	296	471	33	20	29	38	3	142	nd	0.12	nd
616-02-058	B horizon	300-500	632	627	782	83	67	76	23	nd	87	nd	0.31	0.08
616-02-065	B horizon	200	709	2099	5558	291	287	475	135	928	5185	9.3	8.3	11
616-02-065	PETZ	0-20	1308	8265	3617	871	1631	800	354	4658	2404	5.9	9.5	3.7
616-02-065	Coffee rock1	480-560	1333	2317	3226	183	262	225	408	933	1808	0.54	0.55	0.3
616-02-065	Coffee rock3	650-700	926	1104	1857	303	415	919	256	309	654	1.8	1.9	1.7
616-02-068	B horizon	450	19	34	258	221	260	237	11	11	166	0.20	0.47	0.22
616-02-068	A horizon	0-75	10	13	20	128	68	29	24	6	79	1.3	0.93	0.66
616-02-068	E1 horizon	75-300	1	3	4	77	37	10	4	9	52	0.20	0.31	nd
616-02-068	E2 horizon	300-375	36	140	341	127	120	140	15	93	266	nd	0.09	nd
616-02-068	E3 horizon	375-600	4	48	110	148	133	209	16	37	118	nd	0.11	nd
616-02-068	A horizon	0-25	20	21	39	74	50	33	22	2	115	1.5	1.2	0.80
616-02-068	E horizon	25-200	4	6	7	36	39	16	7	4	42	0.39	0.58	0.03
616-02-068	Coffee rock	200-300	493	215	1250	236	191	303	244	17	885	0.45	0.30	0.03
616-02-068	B1 horizon	300-400	40	49	398	173	189	236	19	14	275	0.27	0.29	0.11
616-02-068	B3 horizon	500-600	52	37	358	285	295	381	36	17	279	0.30	0.48	0.09
616-02-071	E horizon	25-350	5	12	6	67	44	6	6	17	17	nd	0.44	nd
616-02-071	B horizon	350-600	266	317	941	166	160	239	64	61	901	nd	0.17	nd
616-02-078	B horizon	400-500	28	27	31	121	117	171	1	1	14	0.08	0.17	0.24
616-02-080	Coffee rock	200-400	1180	2881	9651	91	109	569	168	1496	9739	0.16	0.39	0.59
616-02-081	B horizon	400-800	51	40	135	304	247	365	11	4	114	0.18	0.29	0.15
616-02-082	A horizon	0-75	30	48	82	107	80	36	13	32	75	0.01	0.51	0.03
616-02-082	E1 horizon	75-200	31	53	385	28	21	32	13	19	360	nd	0.07	nd
616-02-082	E2 horizon	200-300	63	141	374	843	820	760	31	102	337	nd	0.07	nd
616-02-082	B horizon	300-400	24	61	555	467	406	775	16	38	500	nd	0.06	nd
616-02-082	2E horizon	400-500	24	90	996	497	379	1033	24	71	881	nd	0.19	nd
616-02-082	Coffee rock	500-600	51	186	3606	1152	978	1553	35	116	3195	nd	0.23	0.18

\* drying soils before analysis may affect the relative amounts extracted by the 3 extractions

**Appendix Table 5** (Cont.) Aluminium, Fe, Si and Mn extracted by dithionite citrate bicarbonate (d); oxalic acid (ox) and Na-pyrophosphate (p) for whole wet soil samples\* (in mg kg<sup>-1</sup> unit).

Site	Horizon	Depth (cm)	Al <sub>d</sub>	Al <sub>ox</sub>	Al <sub>p</sub>	Fe <sub>d</sub>	Fe <sub>ox</sub>	Fe <sub>p</sub>	Si <sub>d</sub>	Si <sub>ox</sub>	Si <sub>p</sub>	Mn <sub>d</sub>	Mn <sub>ox</sub>	Mn <sub>p</sub>
616-02-085	A horizon	0-70	1786	4208	1139	11031	11546	1954	283	1066	552	551	555	108
616-02-085	B1 horizon	100-300	245	95	2933	482	457	1069	356	56	4721	4.0	1.5	2.5
616-02-085	B2 horizon	300-400	219	314	341	1328	1761	1271	128	57	359	22	29	25
616-02-085	Mud	400-600	64	618	487	3437	6039	1491	158	374	869	126	113	126
616-02-087	Coffee rock1	200-300	3048	15421	2879	535	1356	376	136	697	130	3.4	7.6	5.7
616-02-087	Coffee rock2	300-400	4444	15265	5067	75	70	59	352	4870	162	nd	0.22	nd
616-02-087	B horizon	500-600	26	90	431	133	112	264	17	91	528	nd	0.10	nd
616-02-094	A1 horizon	0-100	341	310	4648	7619	2400	2445	310	116	7227	2.0	1.37	2.4
616-02-094	A2 horizon	100-175	346	144	2036	5717	597	1603	320	41	3639	1.8	0.65	1.4
616-02-094	E horizon	175-600	242	79	1091	286	173	600	270	16	1604	0.75	0.46	0.32
616-02-099	E horizon	25-200	119	219	172	435	133	148	25	64	174	7.8	9.96	6.7
616-02-099	B1 horizon	200-300	128	99	130	273	254	316	98	28	106	3.4	3.07	4.7
616-02-099	B2 horizon	300-400	207	187	471	1486	1697	1586	112	36	491	11	13	10
616-02-100	A horizon	0-80	69	190	116	530	355	218	23	77	118	3.7	4.1	2.3
616-02-100	Peat	80-110	424	637	649	1468	2121	2471	74	74	365	1.9	2.9	2.3
616-02-100	PETZ	110-200	678	1073	826	1300	1312	929	192	370	343	3.2	3.7	3.0
616-02-100	E horizon	200-600	nd	11	30	42	46	64	3	3	53	0.62	0.30	nd
616-02-101	A horizon	0-75	160	116	110	1000	526	322	89	56	137	5.2	6.4	2.2
616-02-101	Peat	150-200	17	130	84	971	2576	860	158	251	547	34	53	42
616-02-101	E horizon	350-600	5	19	38	473	728	661	27	18	102	2.5	2.4	1.7
616-02-105	A horizon	0-160	540	655	315	4219	4509	846	305	392	182	4.6	7.5	2.1
616-02-105	Peat	250-360	303	475	538	14657	23449	23486	21	35	69	6.8	22	22
616-02-105	PETZ	360-480	72	97	142	1200	1748	1485	40	29	138	0.81	1.4	0.64
616-02-105	E horizon	480-700	nd	11	7	33	56	25	2	5	34	0.49	0.27	nd
616-02-106	A horizon	0-50	95	69	453	3945	3959	2314	168	23	928	0.84	2.5	1.0
616-02-106	E horizon	50-700	102	175	220	494	917	750	34	28	165	0.60	0.75	0.11
616-02-110	B horizon	200-500	154	68	101	699	355	522	161	19	115	0.63	0.67	0.74
616-02-112	B horizon	25-80	nd	4	nd	10	3	38	185	166	118	2.9	2.1	2.1
616-02-112	Mud	125-200	nd	3	5	29	2	54	27	26	111	5.0	1.1	4.8
616-02-112	Peat	200-300	nd	22	8	281	569	137	3	8	27	6.3	9.1	11
616-02-112	Bb horizon	300-400	90	669	2882	1145	2365	2015	42	72	3524	106	133	97
616-02-112	C horizon	400-600	39	168	6	273	166	51	12	82	82	1.6	1.31	4.6
616-02-113	A horizon	0-50	144	180	258	557	485	427	28	27	192	2.6	2.7	2.3
616-02-113	E2 horizon	250-300	10	28	135	643	914	749	16	17	178	0.75	0.90	0.31
616-02-122	E horizon	20-235	32	48	73	52	50	54	12	4	108	0.66	0.44	nd
616-02-122	B horizon	235-315	782	891	1240	32	25	48	140	85	392	0.62	0.36	0.26
616-02-122	2E2 horizon	375-500	21	25	104	139	151	152	9	8	99	0.13	0.26	nd
616-02-122	B/E horizon	700-900	168	236	257	77	98	103	29	31	58	0.19	0.24	0.13
616-02-127	Coffee rock	100-235	2469	5907	2654	73	84	62	347	1997	238	0.80	0.25	nd
616-02-127	2E1 horizon	235-300	83	164	128	46	41	49	32	47	66	0.52	0.30	nd
616-02-131	A horizon	0-50	408	487	193	1936	314	342	41	108	56	4.3	5.0	0.79
616-02-131	E horizon	50-325	47	33	88	63	4	45	25	5	69	0.28	0.24	nd
616-02-131	B horizon	325-425	415	432	232	9917	1597	243	175	247	288	0.89	1.4	0.50
616-02-131	2E horizon	425-600	253	108	91	220	118	49	265	25	115	0.61	0.36	nd
616-02-136	A horizon	0-25	12	17	24	21	13	17	9	5	42	0.34	0.27	nd
616-02-136	Coffee rock	200-260	2505	5930	2342	81	83	76	301	2053	247	0.48	0.26	0.02

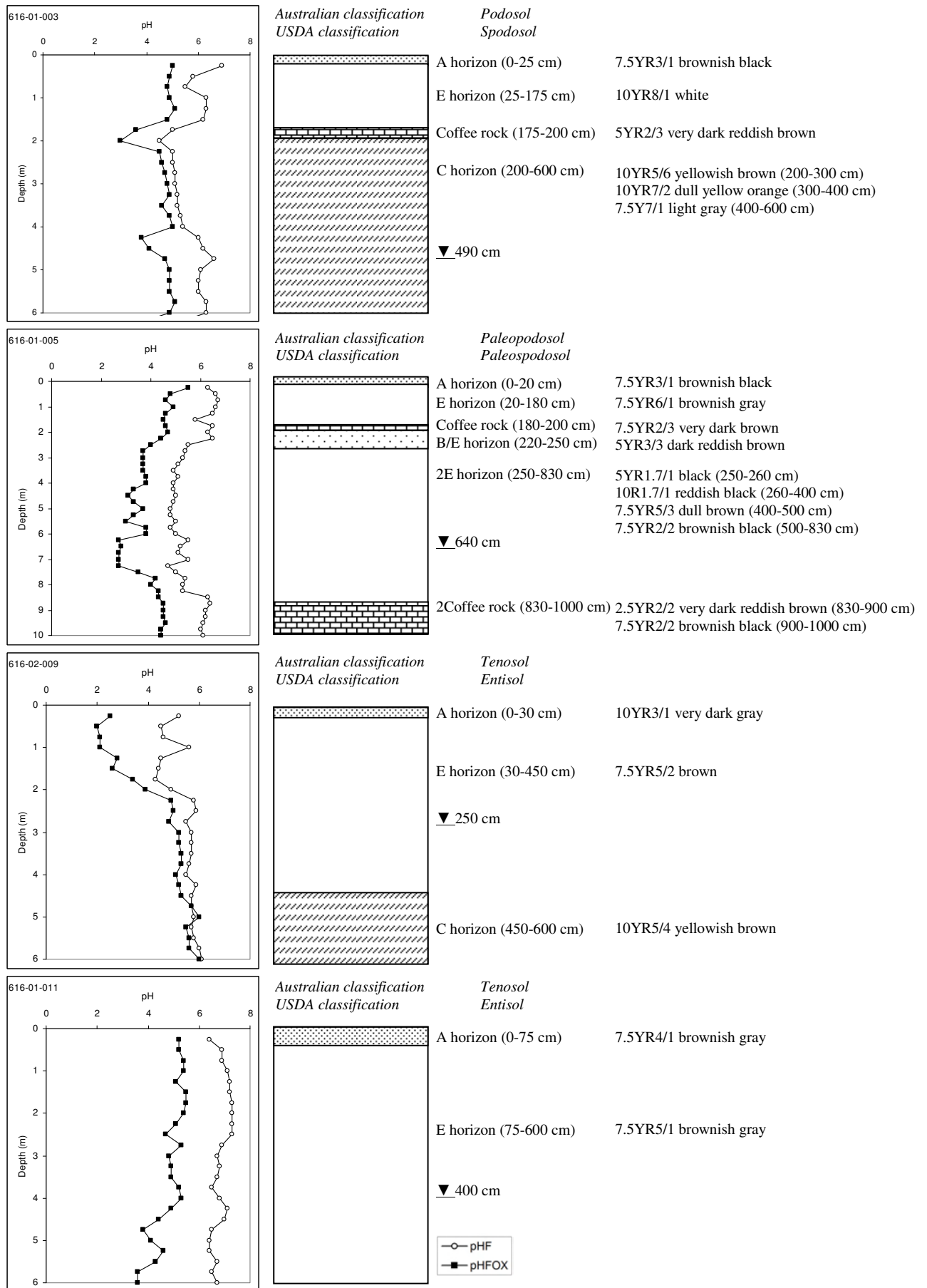
\* drying soils before analysis may affect the relative amounts extracted by the 3 extractions

**Appendix Table 5** (Cont.) Aluminium, Fe, Si and Mn extracted by dithionite citrate bicarbonate (d); oxalic acid (ox) and Na-pyrophosphate (p) for whole wet soil samples\* (in mg kg<sup>-1</sup> unit).

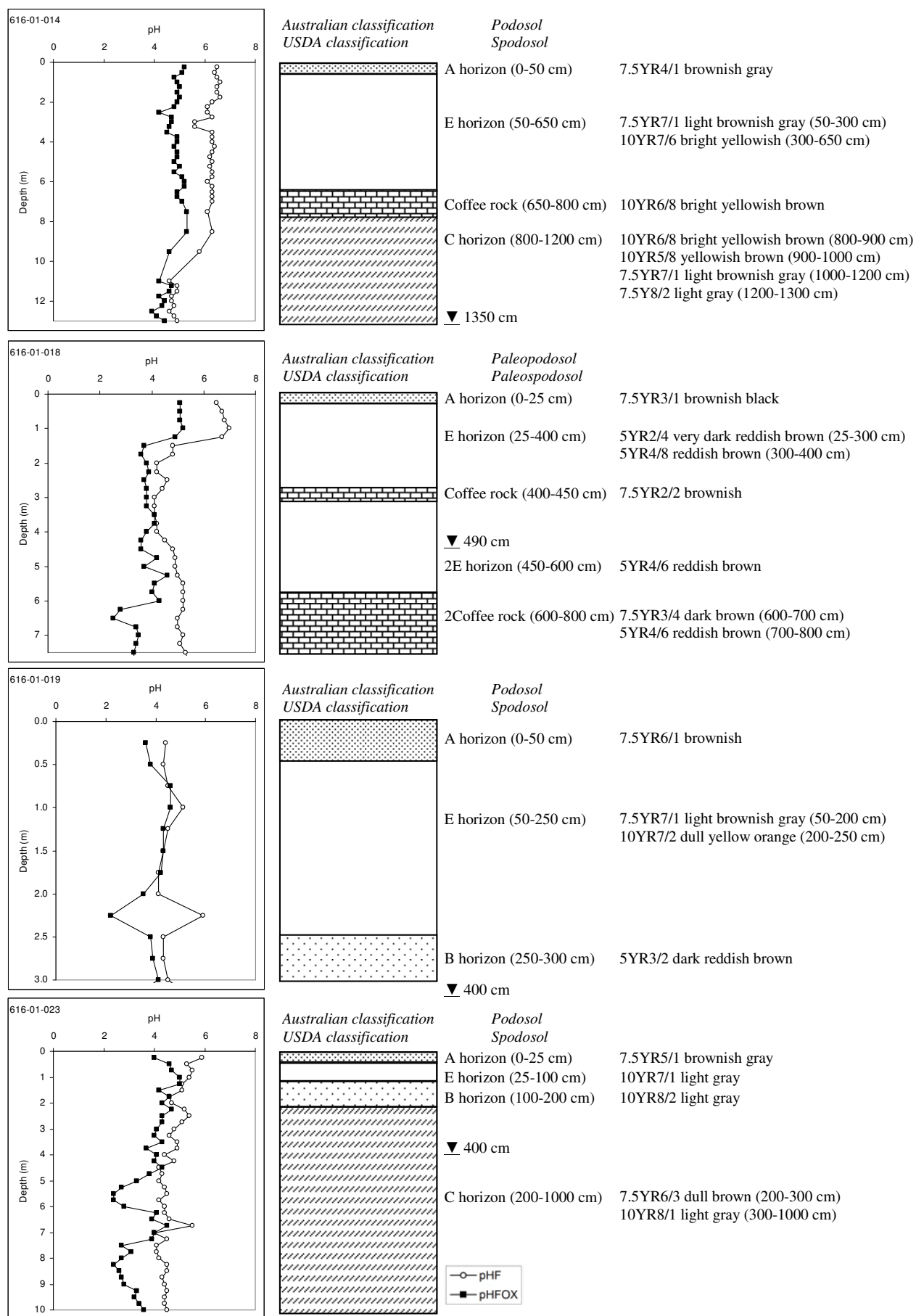
Site	Horizon	Depth (cm)	Al <sub>d</sub>	Al <sub>ox</sub>	Al <sub>p</sub>	Fe <sub>d</sub>	Fe <sub>ox</sub>	Fe <sub>p</sub>	Si <sub>d</sub>	Si <sub>ox</sub>	Si <sub>p</sub>	Mn <sub>d</sub>	Mn <sub>ox</sub>	Mn <sub>p</sub>
616-02-145	E1 horizon	50-300	3	17	50	59	39	24	4	6	85	0.14	0.17	0.08
616-02-145	E2 horizon	300-450	26	41	177	145	133	152	12	18	225	0.60	0.34	5.1
616-02-145	B horizon	450-475	937	425	1121	7611	366	3524	62	101	523	0.53	0.29	2.4
616-02-145	2E horizon	475-600	46	167	236	413	370	345	18	51	142	0.31	0.56	0.51
616-02-155	E horizon	50-150	27	31	19	148	66	17	63	31	97	3.9	4.0	1.3
616-02-155	2E horizon	200-500	90	178	1174	474	641	792	66	61	1351	0.34	0.59	0.63
616-02-155	B horizon	500-600	239	313	7351	9224	496	3196	327	471	12491	3.2	0.81	3.6
616-02-158	E horizon	25-225	nd	14	5	8	4	3	nd	4	31	nd	0.03	nd
616-02-158	Coffee rock1	225-300	5384	10814	5148	1112	1045	666	452	3183	154	0.55	0.79	0.37
616-02-158	Coffee rock2	300-400	2973	1911	2574	386	345	386	875	194	579	0.60	0.62	0.73
616-02-174	B horizon	250-550	1223	826	1098	1711	1417	1133	267	72	227	18	14	13
616-02-179	B horizon	375-400	190	173	327	128	113	208	47	16	76	nd	0.10	nd
Ellenbrook	E horizon	0-150	nd	2	nd	5	2	5	1	3	15	nd	0.03	nd
Ellenbrook	Coffee rock	150-200	1378	11366	1736	832	910	645	162	6947	244	0.02	0.04	nd
Ellenbrook	2B1 horizon	500-550	106	115	190	1205	1366	1425	17	13	99	0.08	0.83	0.55
LOC50A	A horizon	10-20	612	1069	292	1074	178	12	58	225	311	nd	0.09	nd
LOC50A	A horizon	0-100	137	165	2117	551	104	664	11	39	974	nd	0.08	nd
LOC50A	E horizon	300-400	352	785	710	6	13	266	11	100	556	nd	0.03	nd
LOC50A	Coffee rock	400-500	1562	429	4930	60	8	136	53	21	1702	nd	0.02	nd

\* drying soils before analysis may affect the relative amounts extracted by the 3 extractions.

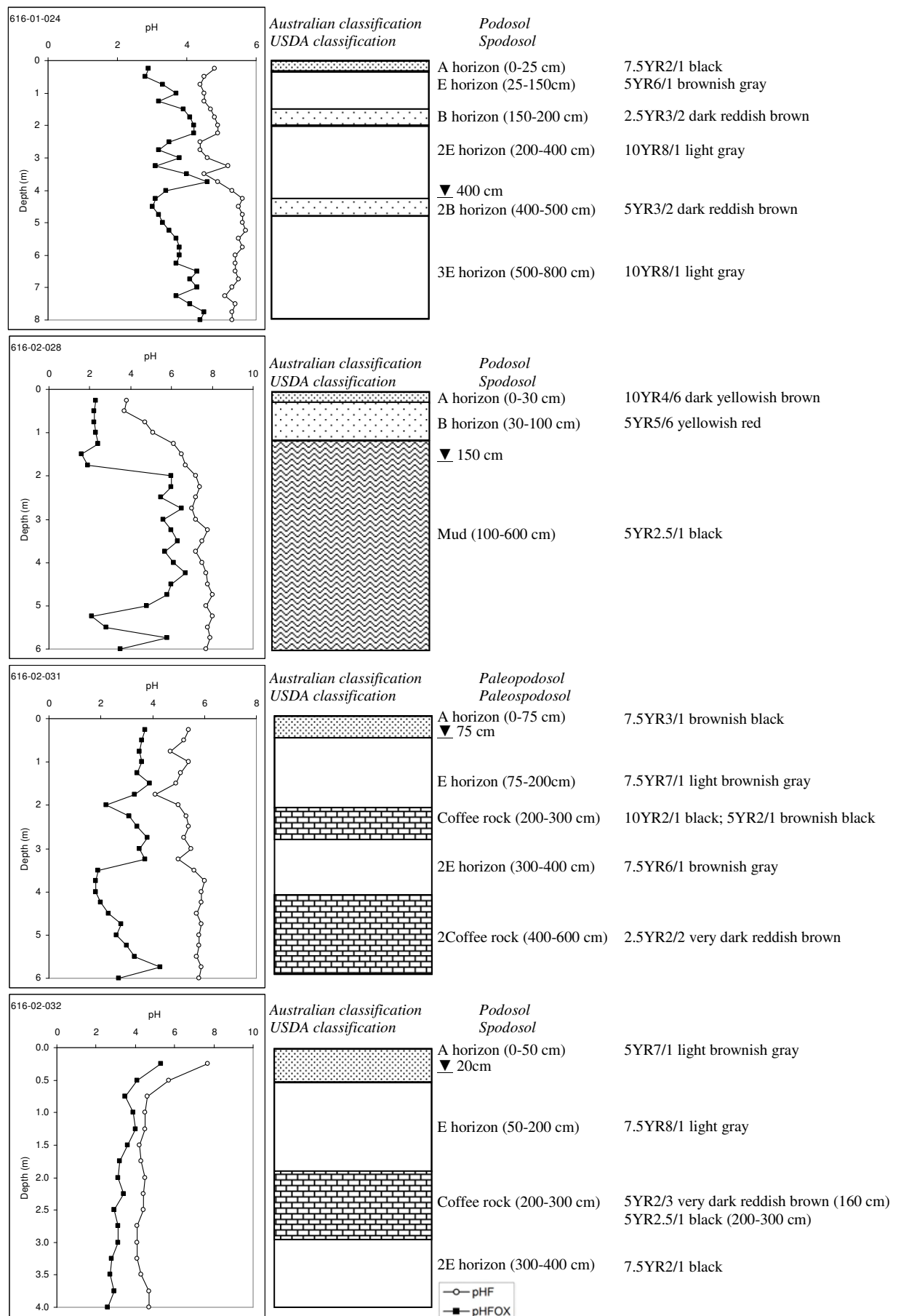




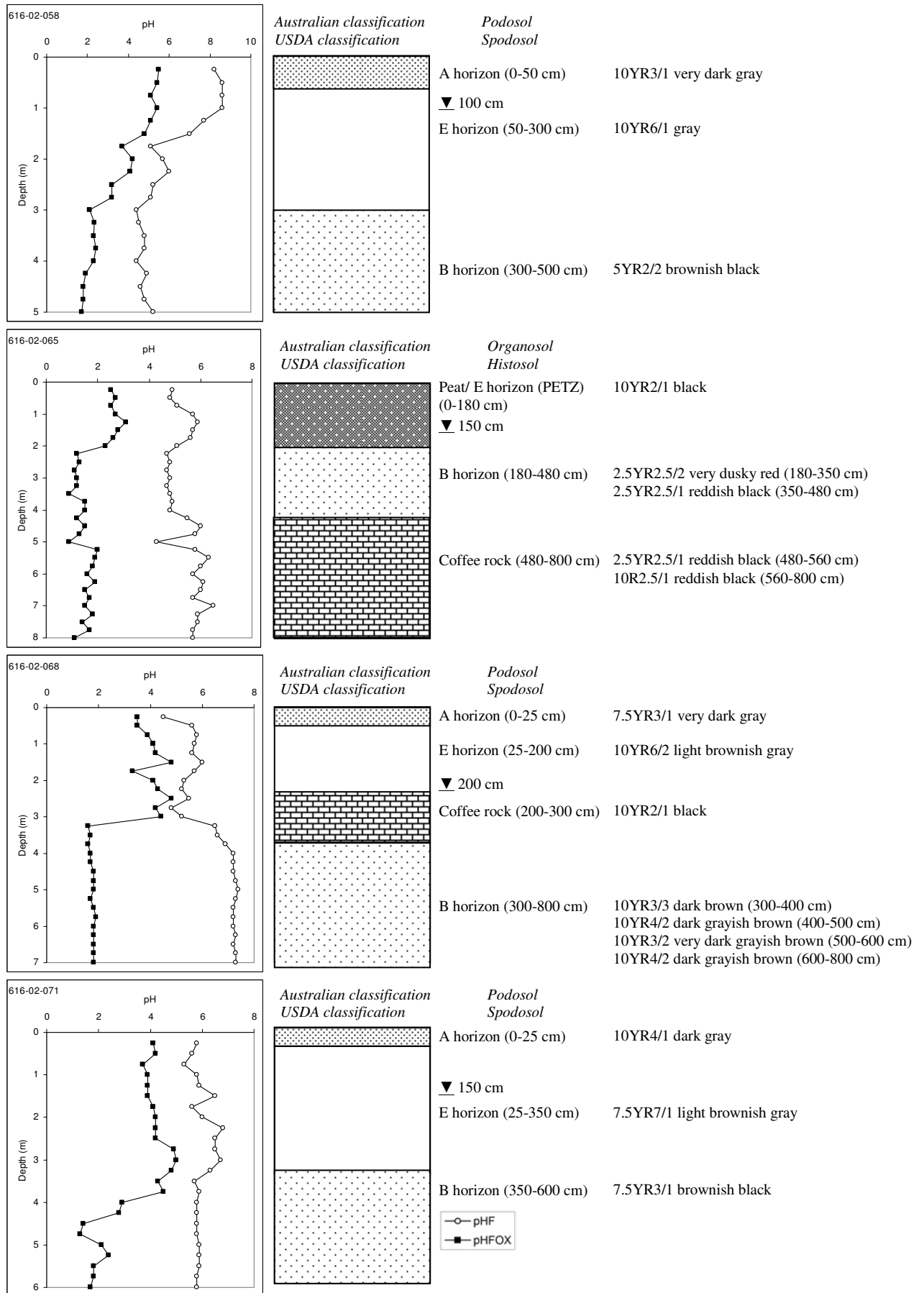
**Appendix Figure 1** Field  $\text{pH}_{\text{H}_2\text{O}}$ ,  $\text{pH}_{\text{H}_2\text{O}_2}$ , soil colour with depth, an illustration of soil profiles and soil classification (▼ = groundwater level).



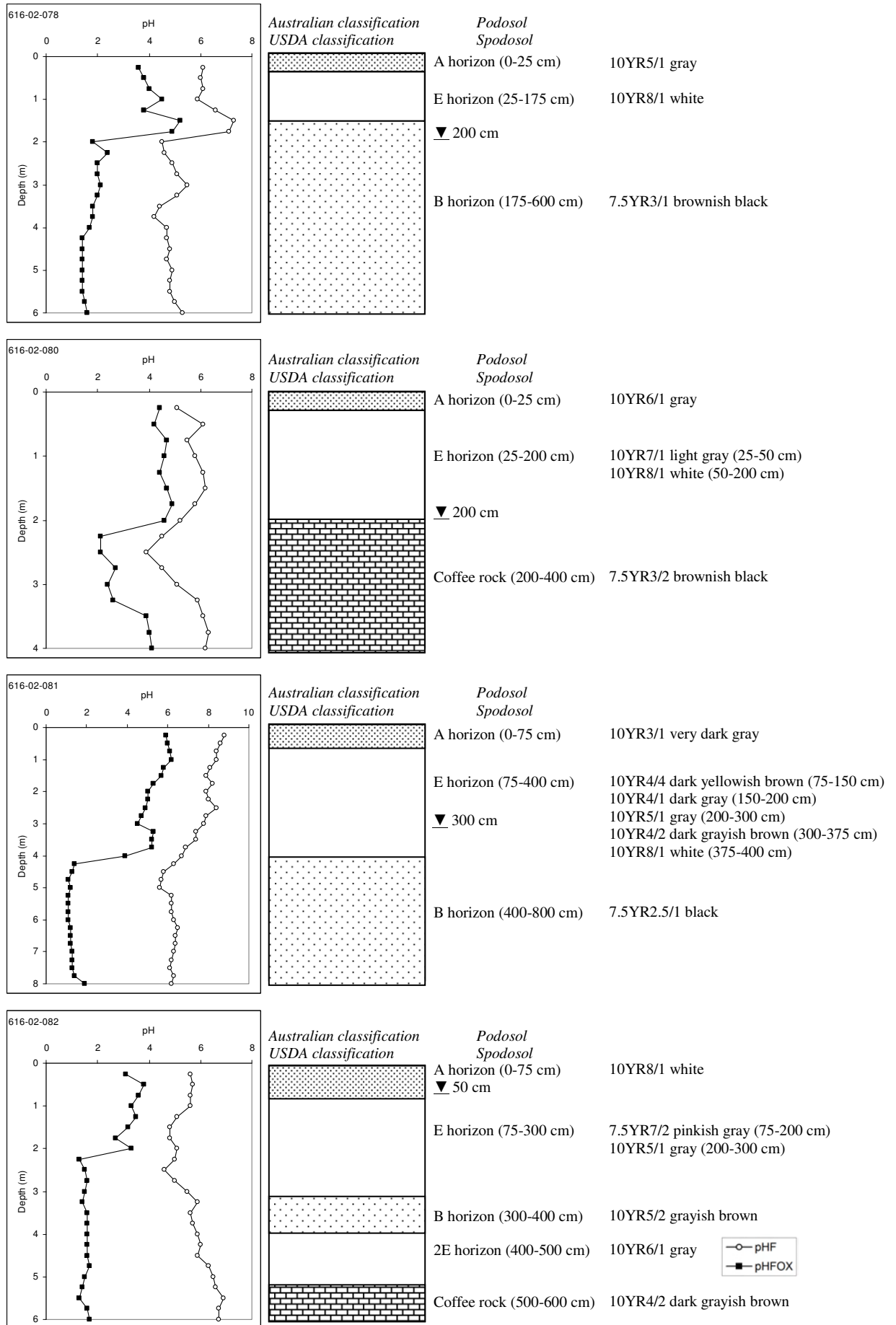
**Appendix Figure 1 (Cont.)** Field  $pH_{H_2O}$ ,  $pH_{H_2O_2}$ , soil colour with depth, an illustration of soil profiles and soil classification (▼ = groundwater level).



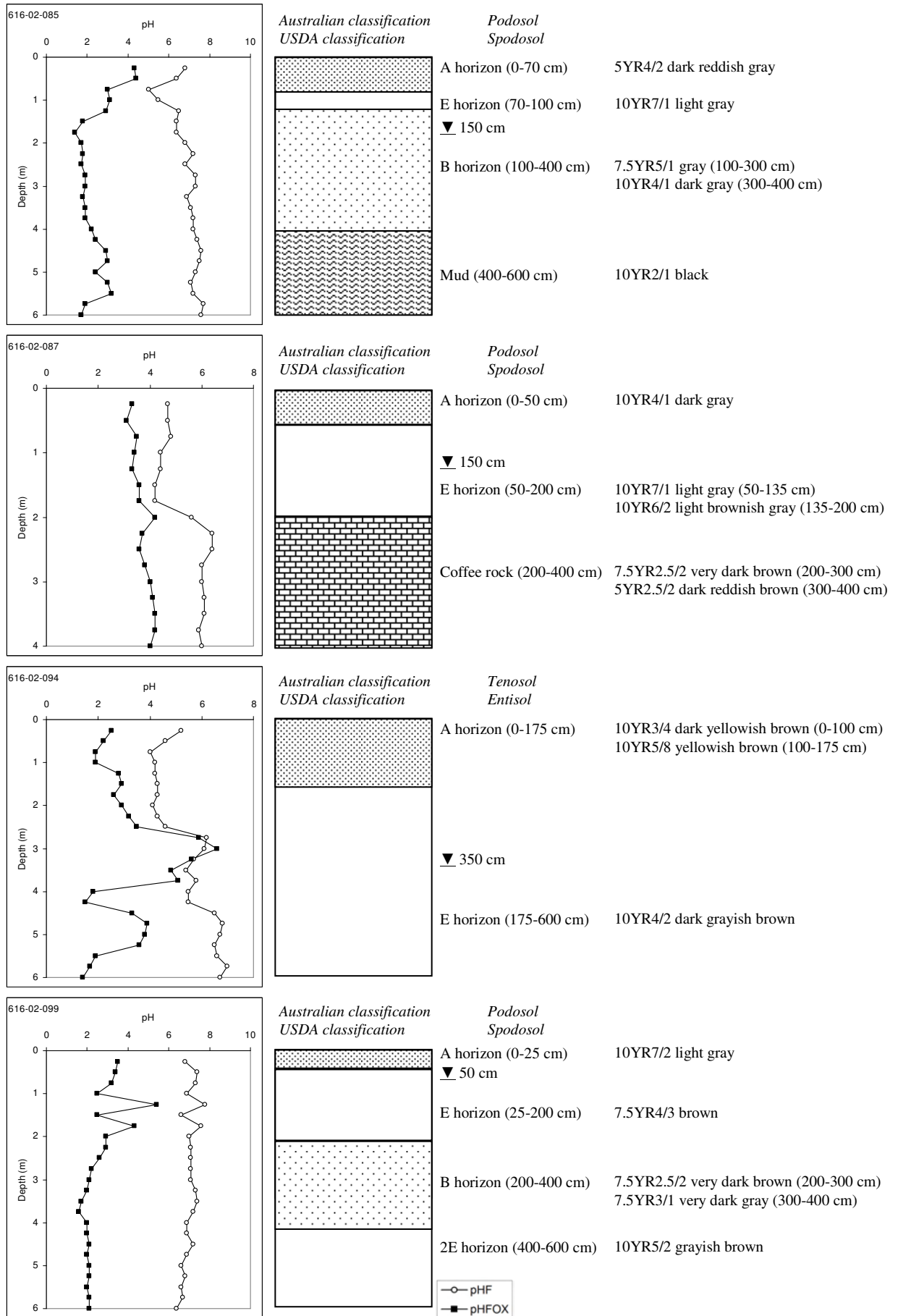
**Appendix Figure 1 (Cont.)** Field  $\text{pHH}_2\text{O}$ ,  $\text{pHH}_2\text{O}_2$ , soil colour with depth, an illustration of soil profiles and soil classification (▼ = groundwater level).



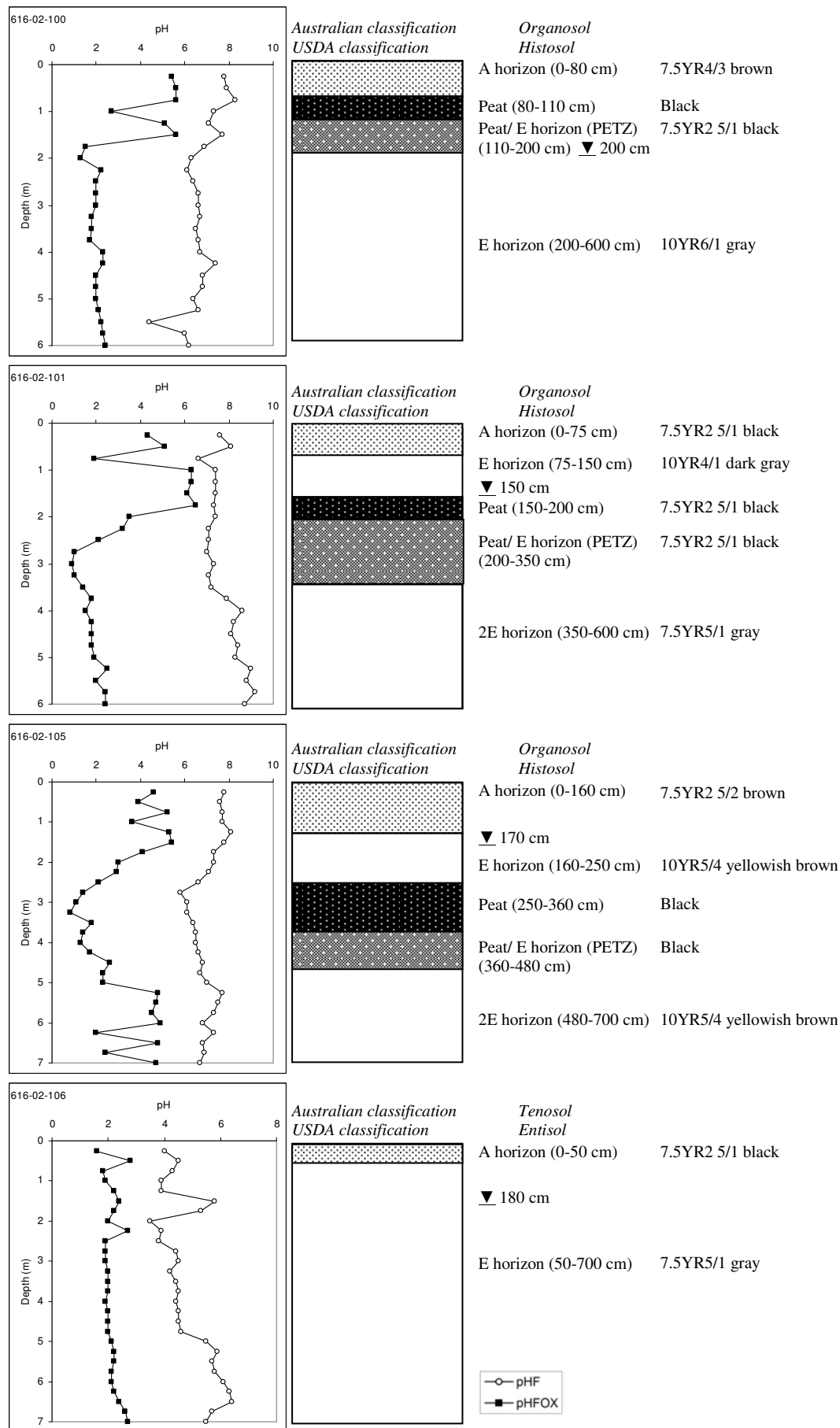
**Appendix Figure 1 (Cont.)** Field  $\text{pHH}_2\text{O}$ ,  $\text{pHH}_2\text{O}_2$ , soil colour with depth, an illustration of soil profiles and soil classification (▼ = groundwater level).



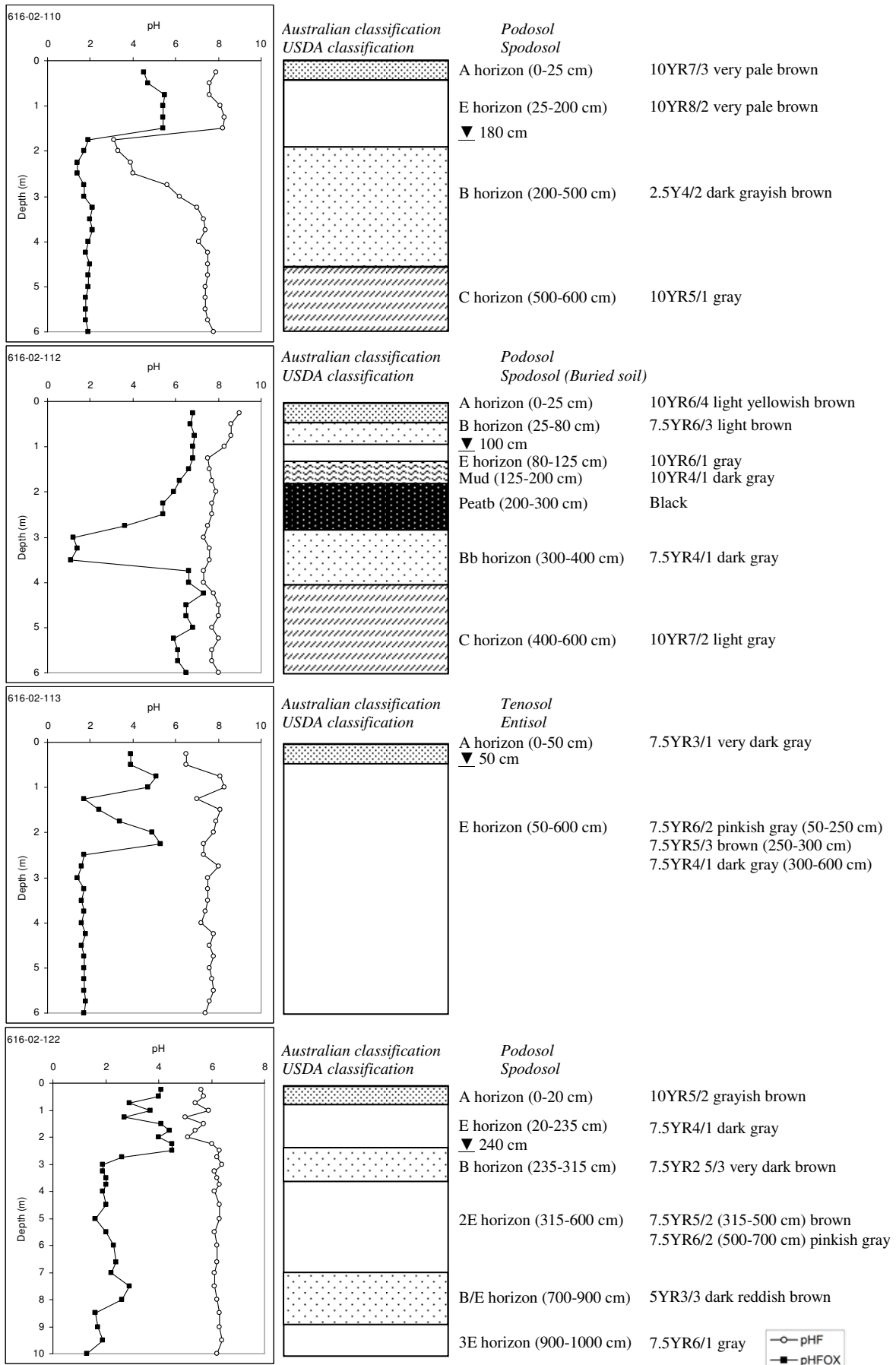
**Appendix Figure 1 (Cont.)** Field  $pH_{H_2O}$ ,  $pH_{H_2O_2}$ , soil colour with depth, an illustration of soil profiles and soil classification (▼ = groundwater level).



**Appendix Figure 1 (Cont.)** Field  $\text{pH}_{\text{H}_2\text{O}}$ ,  $\text{pH}_{\text{H}_2\text{O}_2}$ , soil colour with depth, an illustration of soil profiles and soil classification (▼ = groundwater level).

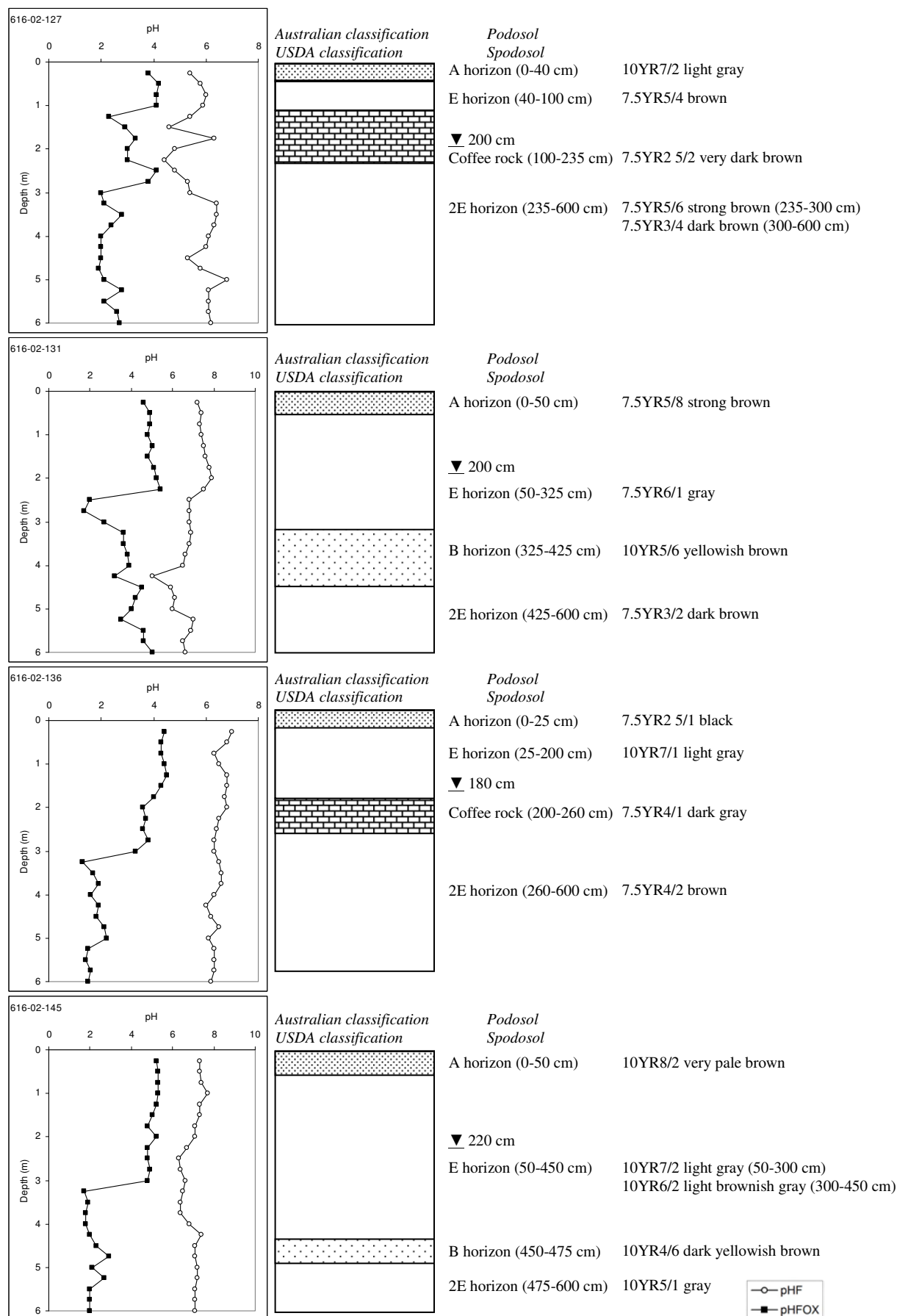


**Appendix Figure 1 (Cont.)** Field  $\text{pH}_{\text{H}_2\text{O}}$ ,  $\text{pH}_{\text{H}_2\text{O}_2}$ , soil colour with depth, an illustration of soil profiles and soil classification (▼ = groundwater level).

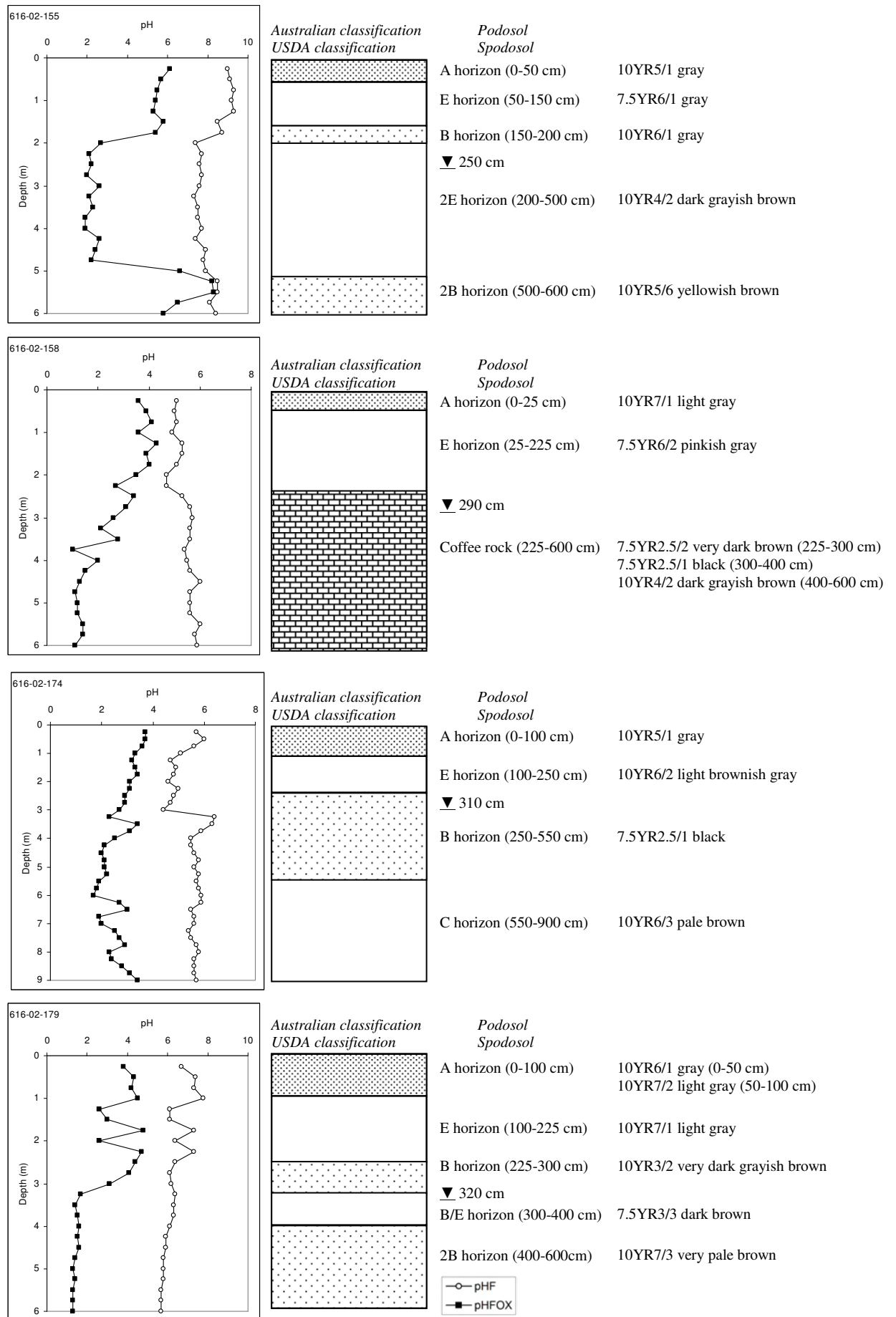


**Appendix Figure 1 (Cont.)** Field  $\text{pH}_{\text{H}_2\text{O}}$ ,  $\text{pH}_{\text{H}_2\text{O}_2}$ , soil colour with depth, an illustration of soil profiles and soil classification (▼ = groundwater level; b = buried soil).



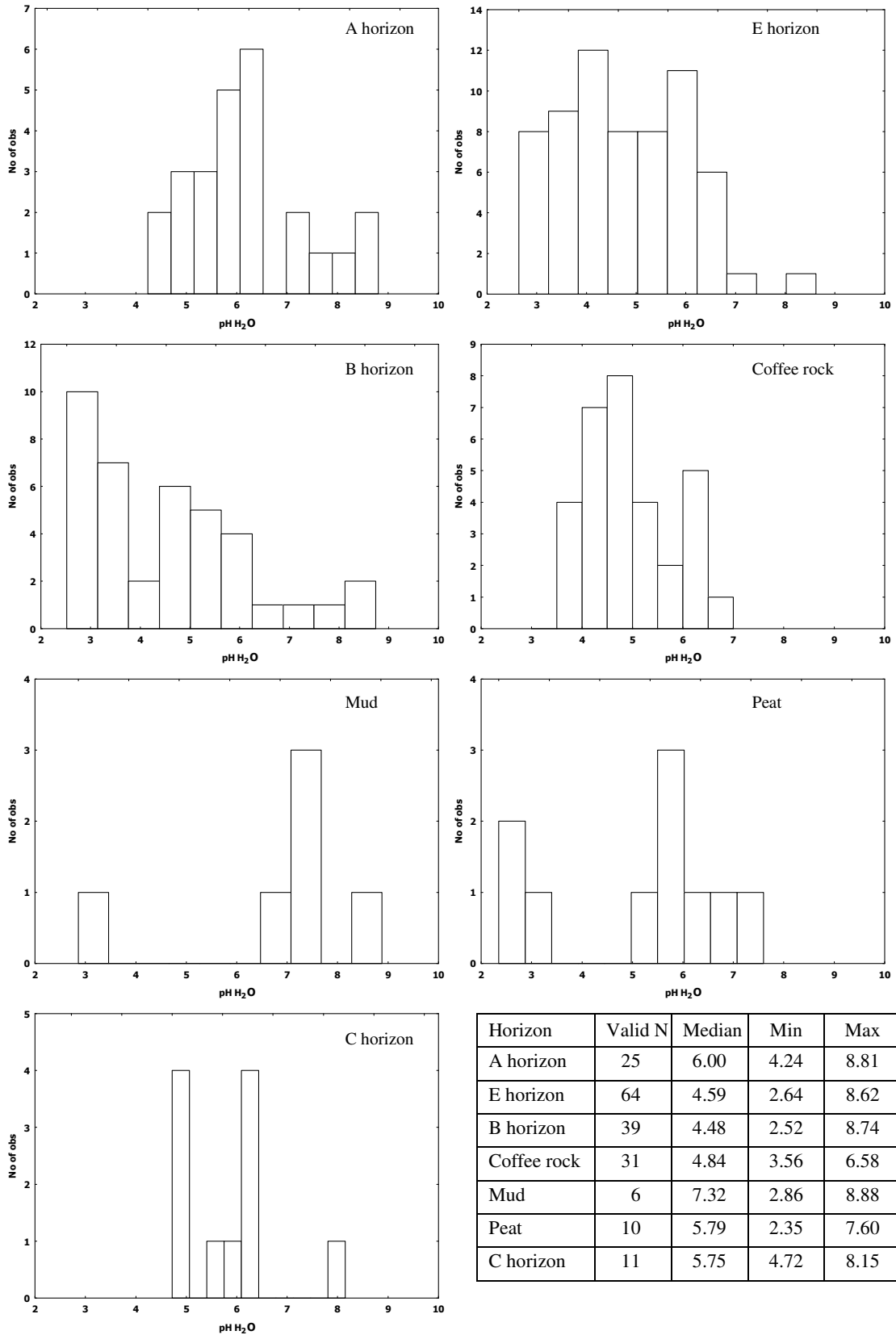


**Appendix Figure 1 (Cont.)** Field  $\text{pHH}_2\text{O}$ ,  $\text{pHH}_2\text{O}_2$ , soil colour with depth, an illustration of soil profiles and soil classification (▼ = groundwater level).



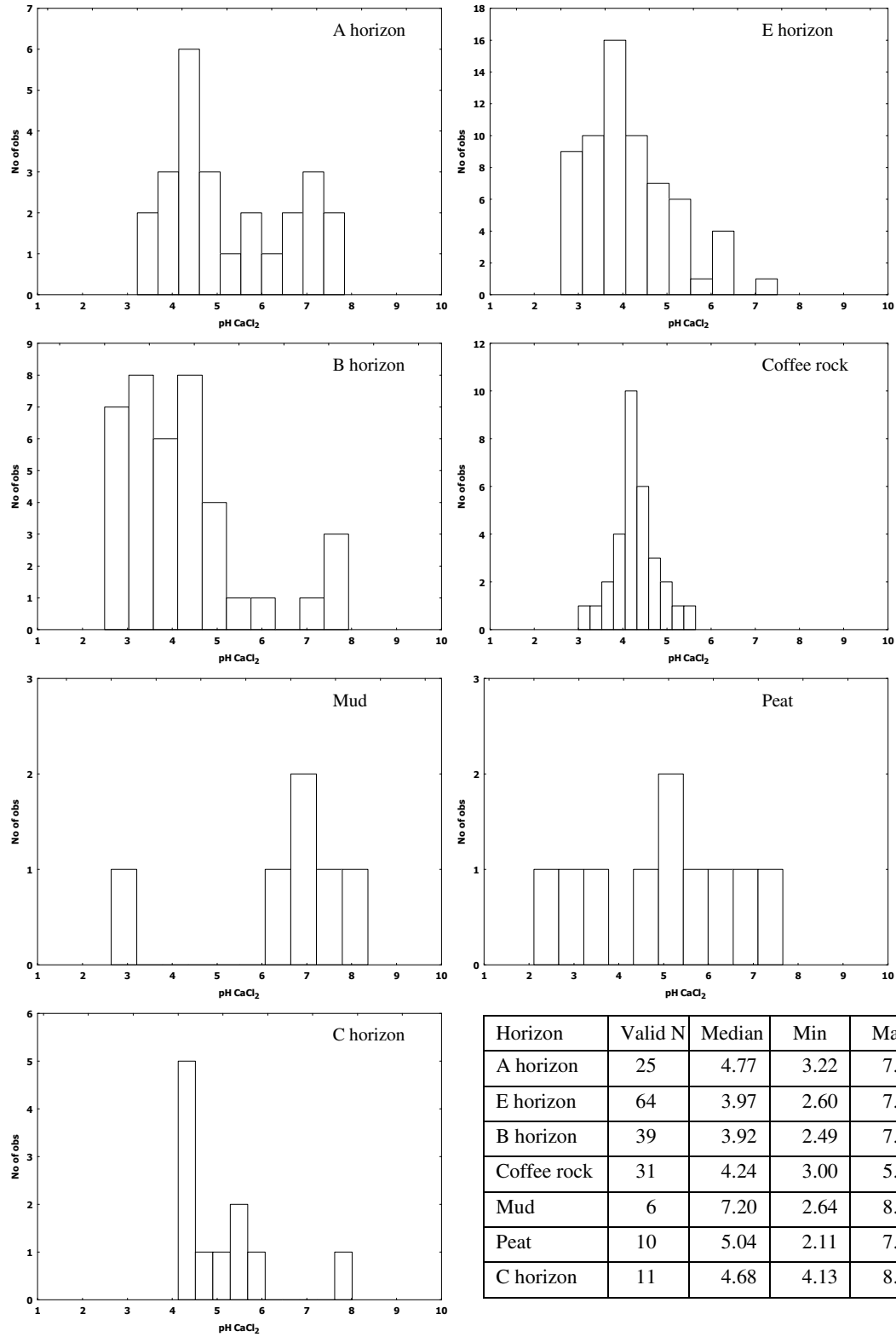
**Appendix Figure 1 (Cont.)** Field  $\text{pH}_{\text{H}_2\text{O}}$ ,  $\text{pH}_{\text{H}_2\text{O}_2}$ , soil colour with depth, an illustration of soil profiles and soil classification (▼ = groundwater level).

pH H<sub>2</sub>O

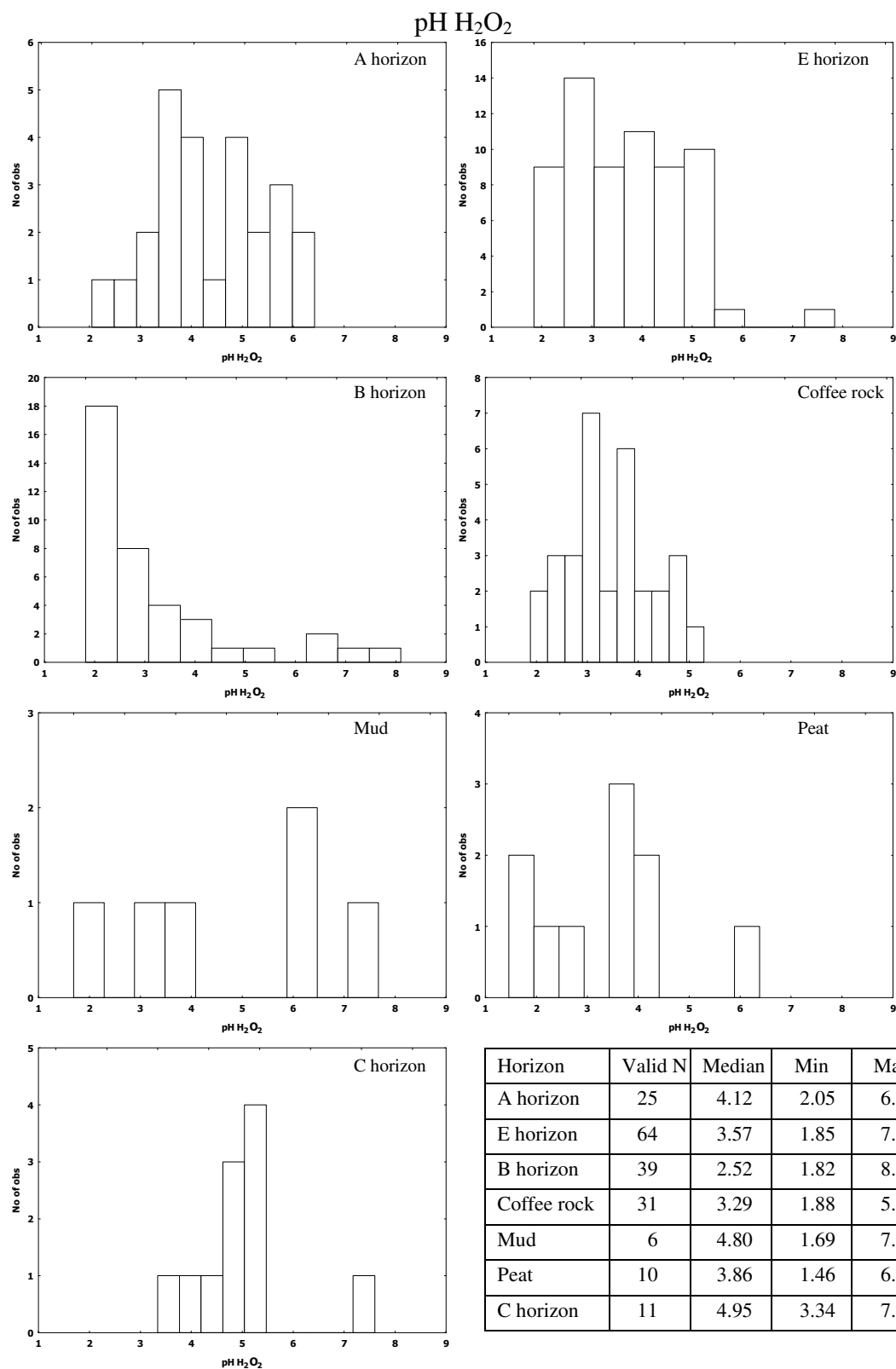


**Appendix Figure 2** Histograms of the frequency of pH<sub>H<sub>2</sub>O</sub> values for A, E, B, coffee rock, mud, peat and C horizons.

pH CaCl<sub>2</sub>

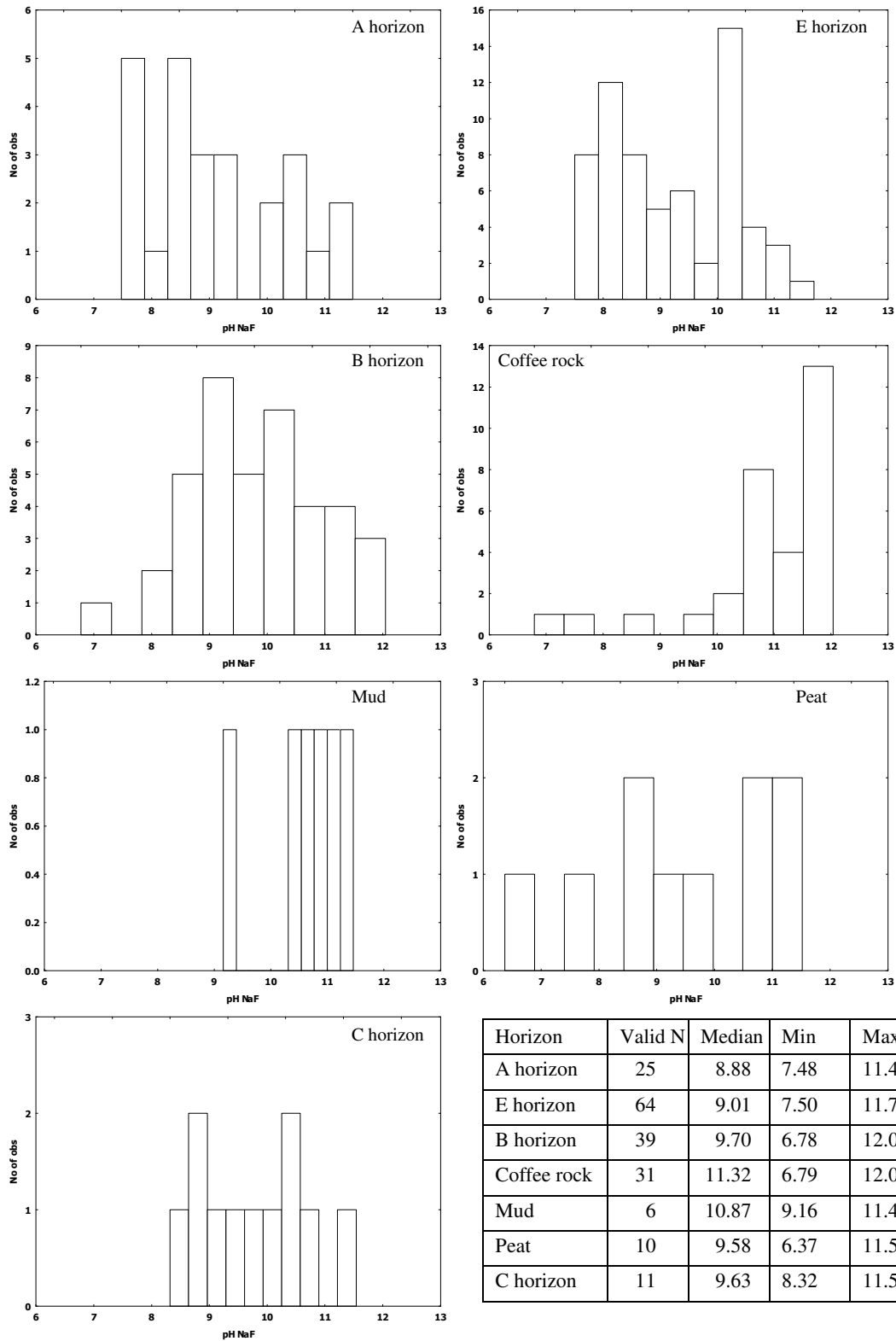


**Appendix Figure 3** Histograms of the frequency of pHCaCl<sub>2</sub> values for A, E, B, coffee rock, mud, peat and C horizons.



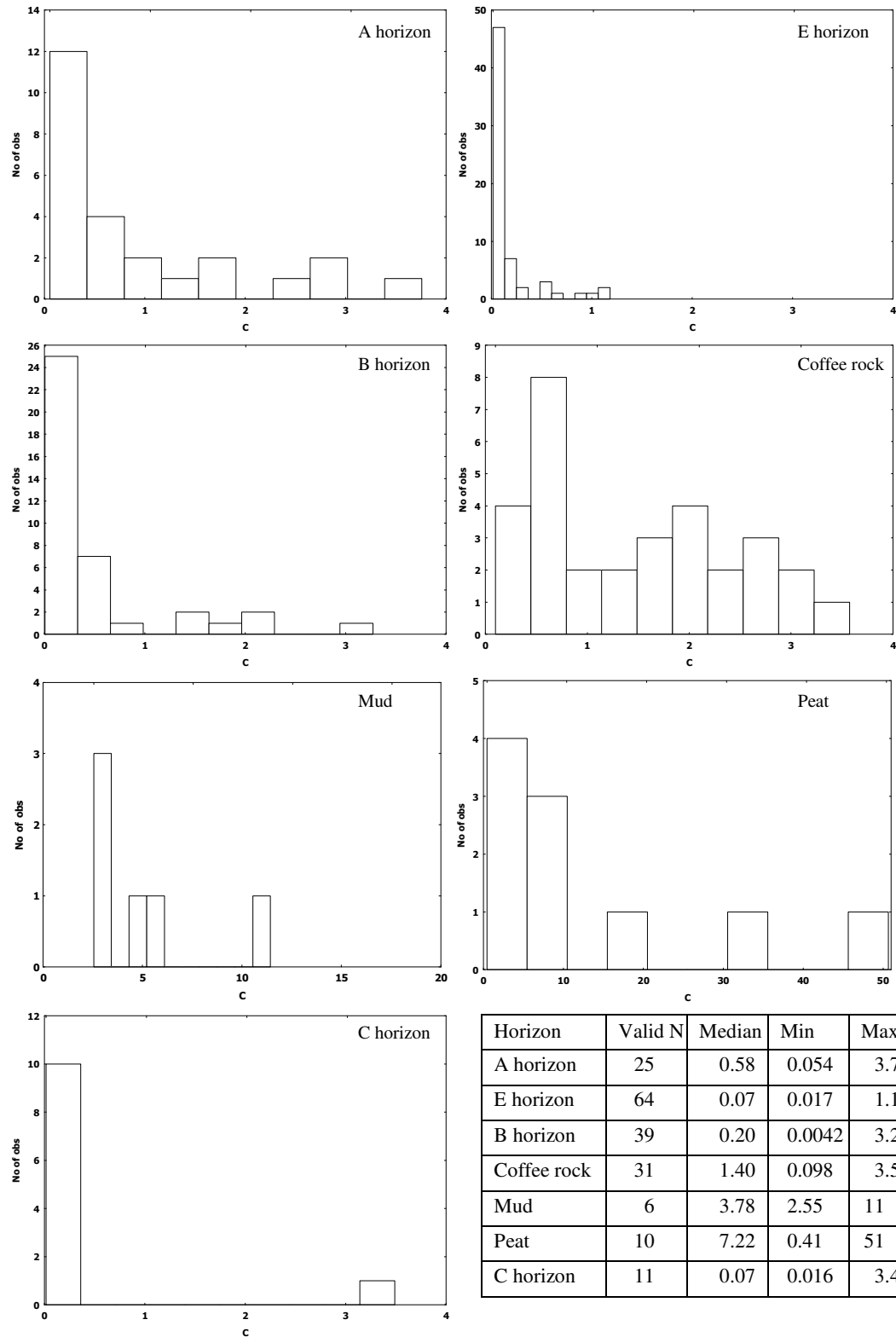
**Appendix Figure 4** Histograms of the frequency of pH<sub>H<sub>2</sub>O<sub>2</sub></sub> values for A, E, B, coffee rock, mud, peat and C horizons.

pH NaF



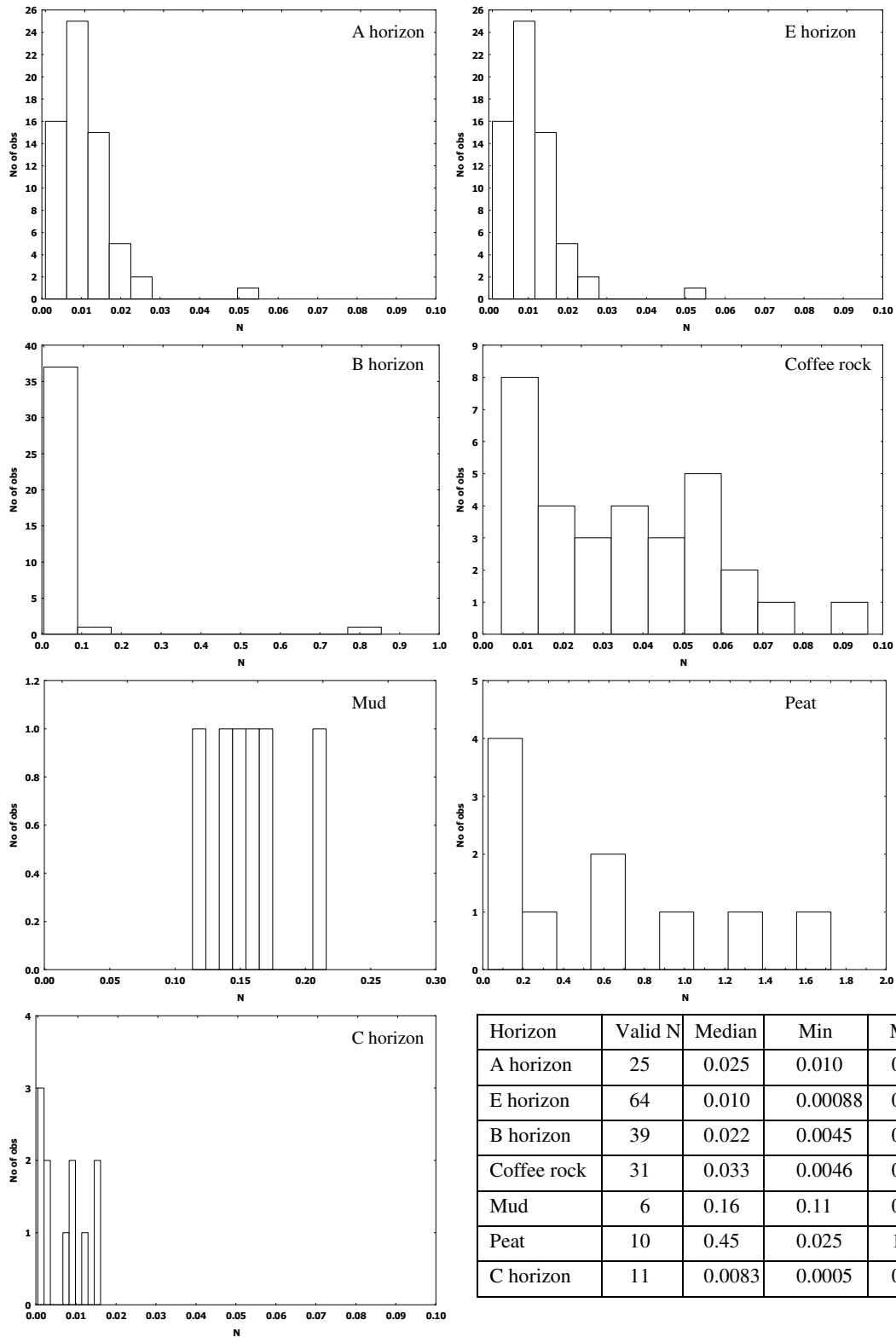
**Appendix Figure 5** Histograms of the frequency of pHNaF values for A, E, B, coffee rock, mud, peat and C horizons.

## Carbon



**Appendix Figure 6** Histograms of the frequency of carbon values for A, E, B, coffee rock, mud, peat and C horizons (in percentage unit).

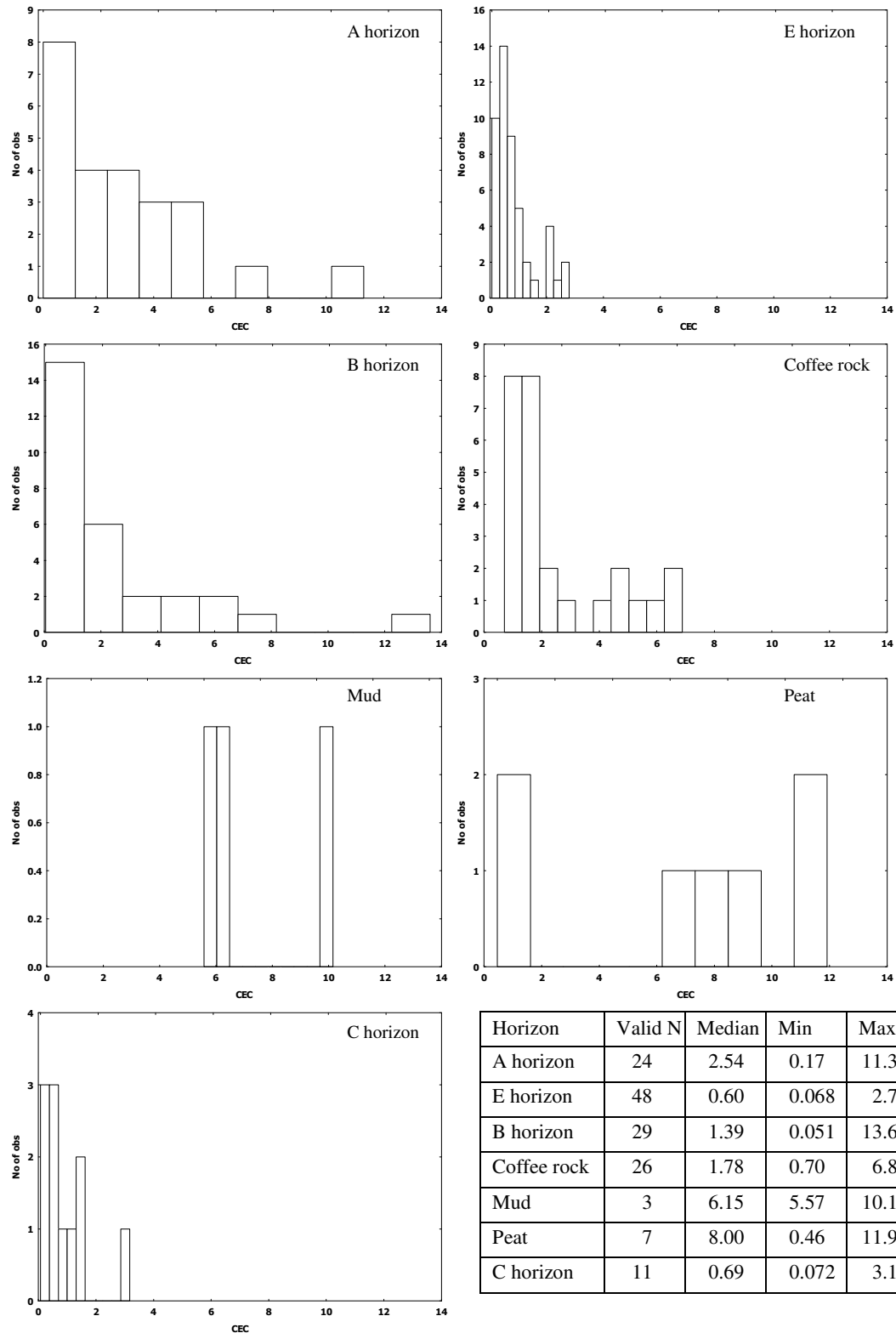
## Nitrogen



**Appendix Figure 7** Histograms of the frequency of nitrogen values for A, E, B, coffee rock, mud, peat and C horizons (in percentage unit).

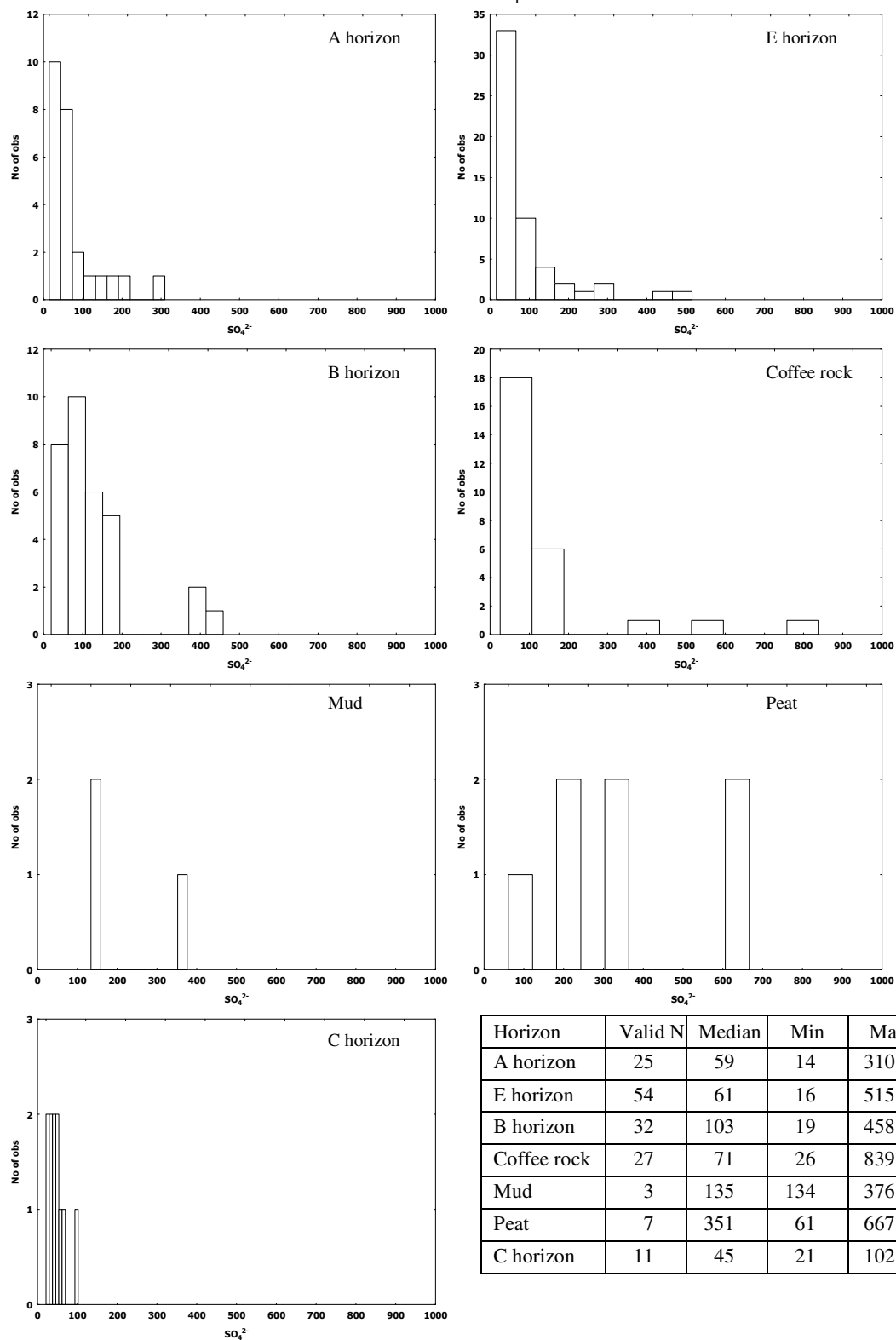


## Cation exchange capacity



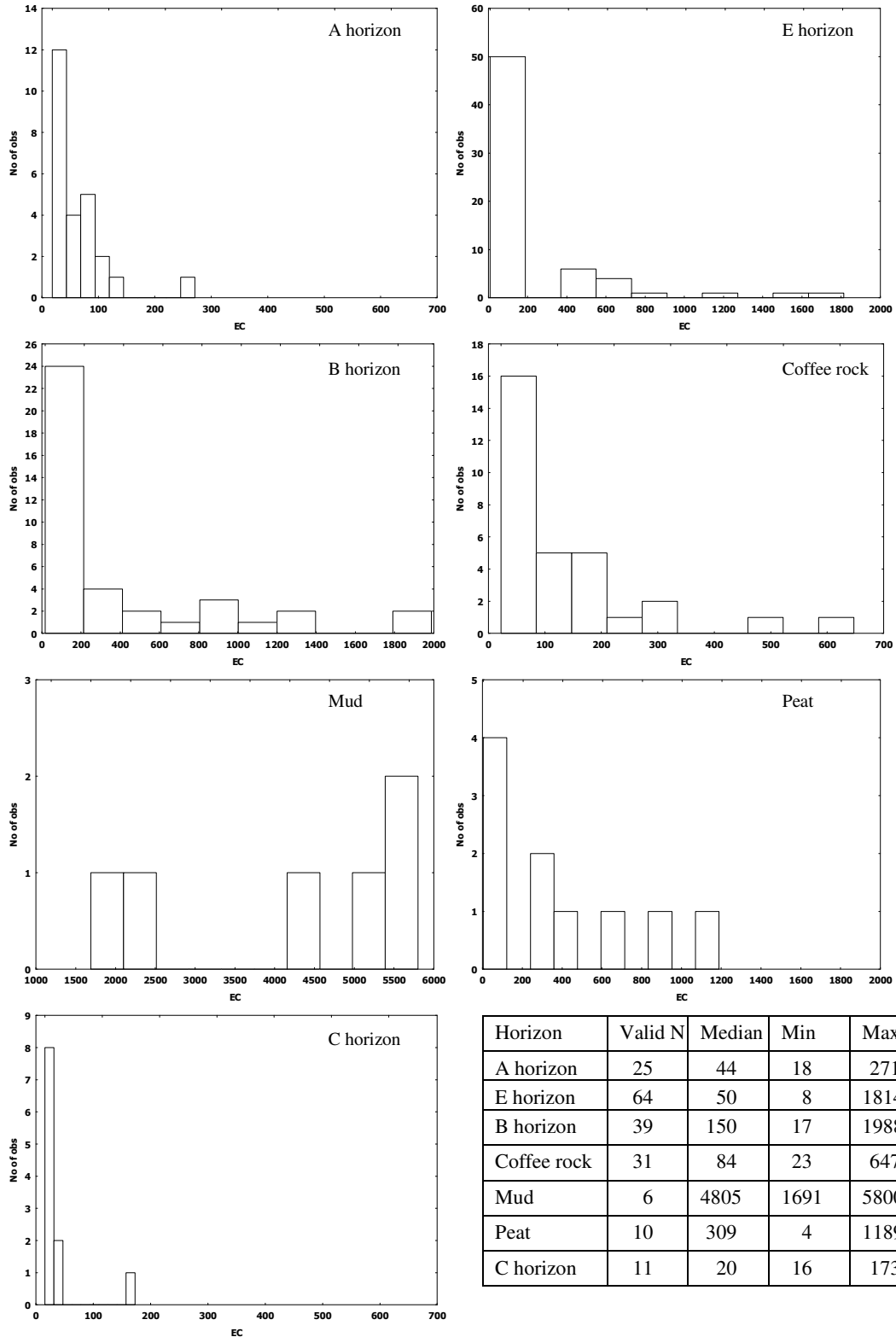
**Appendix Figure 8** Histograms of the frequency of cation exchange capacity values for A, E, B, coffee rock, mud, peat and C horizons (in meq/100g unit).

### Soluble $\text{SO}_4^{2-}$



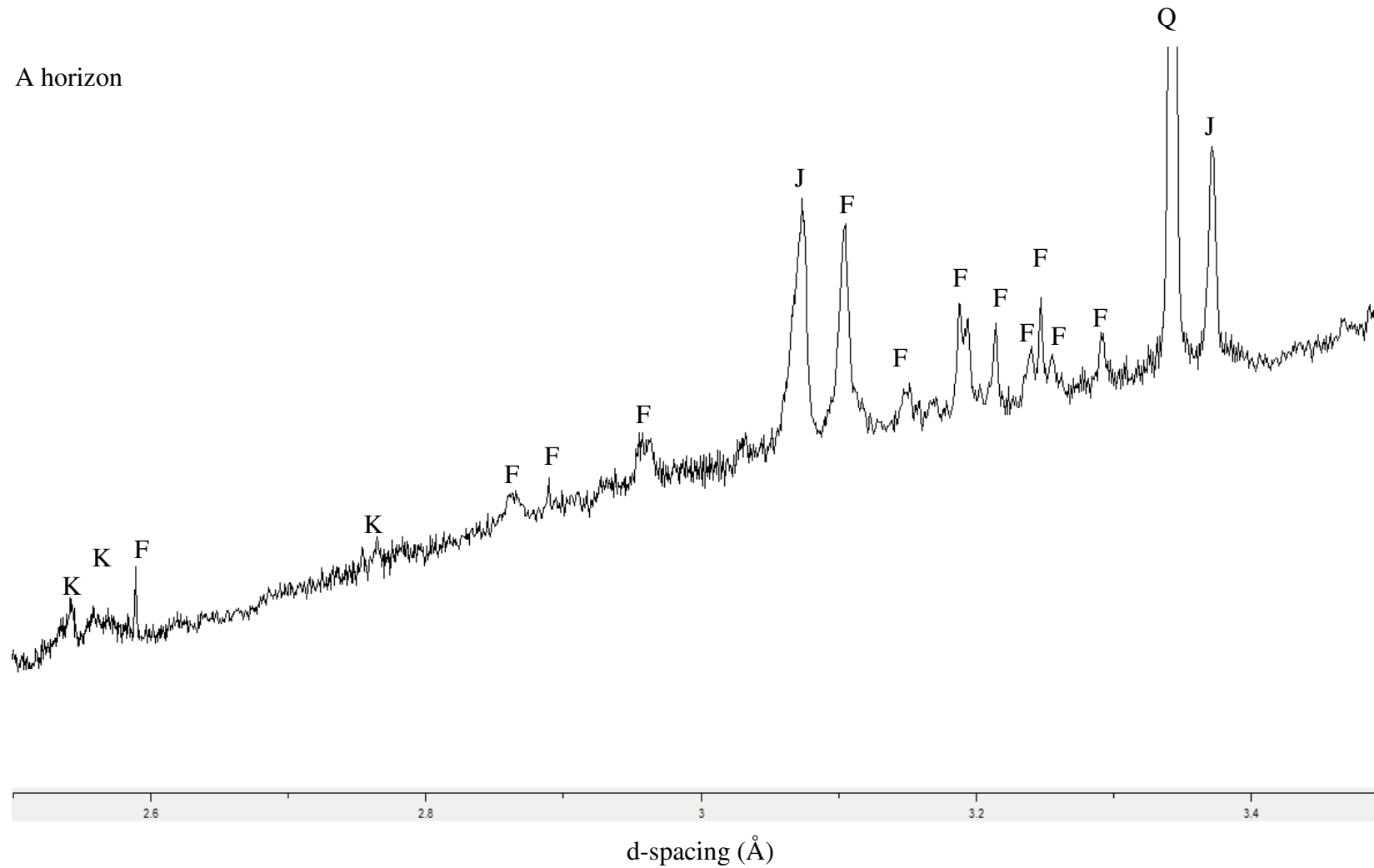
**Appendix Figure 9** Histograms of the frequency of soluble  $\text{SO}_4^{2-}$  concentrations for A, E, B, coffee rock, mud, peat and C horizons (in  $\text{mg kg}^{-1}$  unit).

## Electrical conductivity

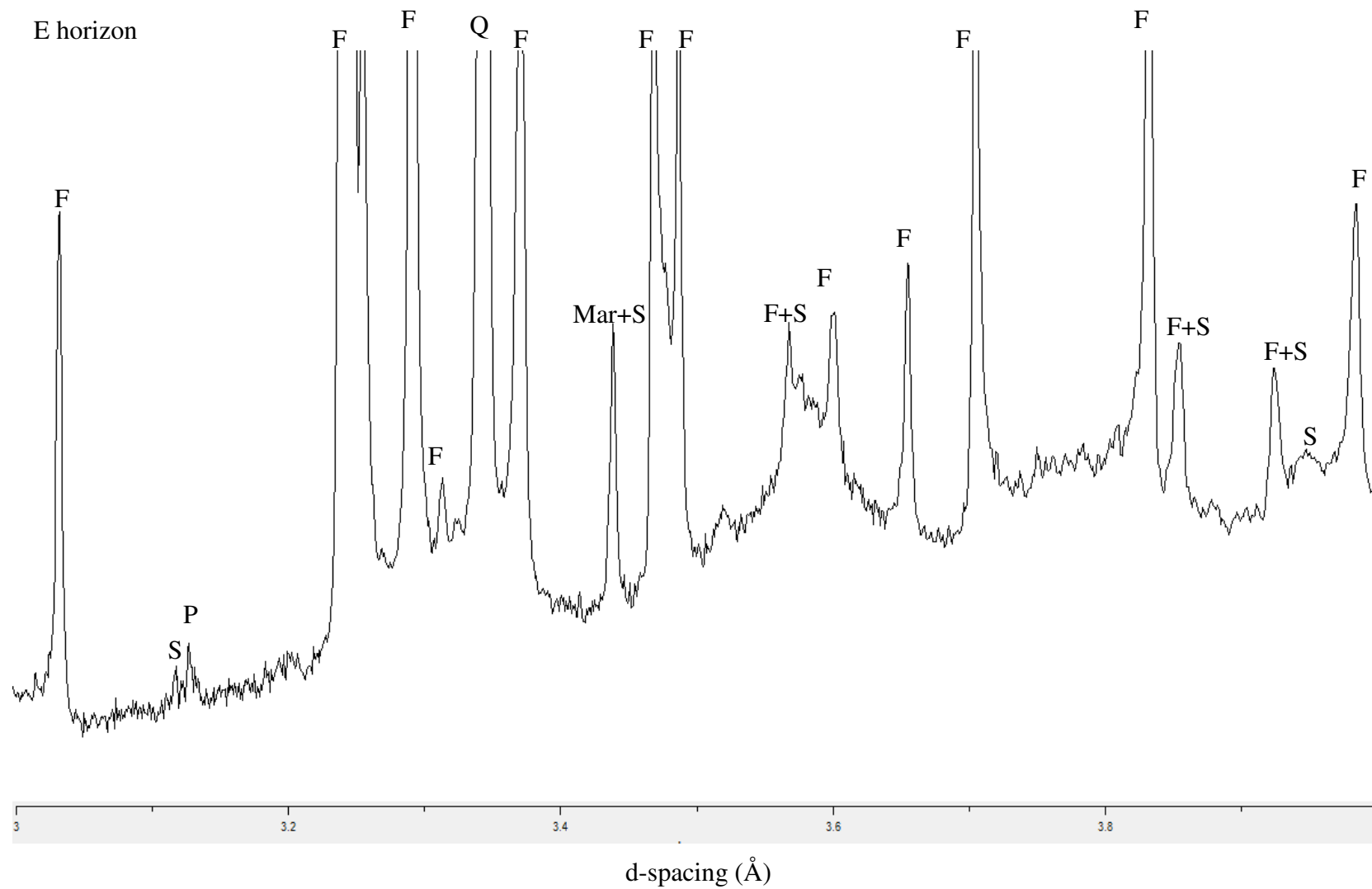


**Appendix Figure 10** Histograms of the frequency of electrical conductivity values for A, E, B, coffee rock, mud, peat and C horizons (in  $\mu\text{S}/\text{cm}$  unit).

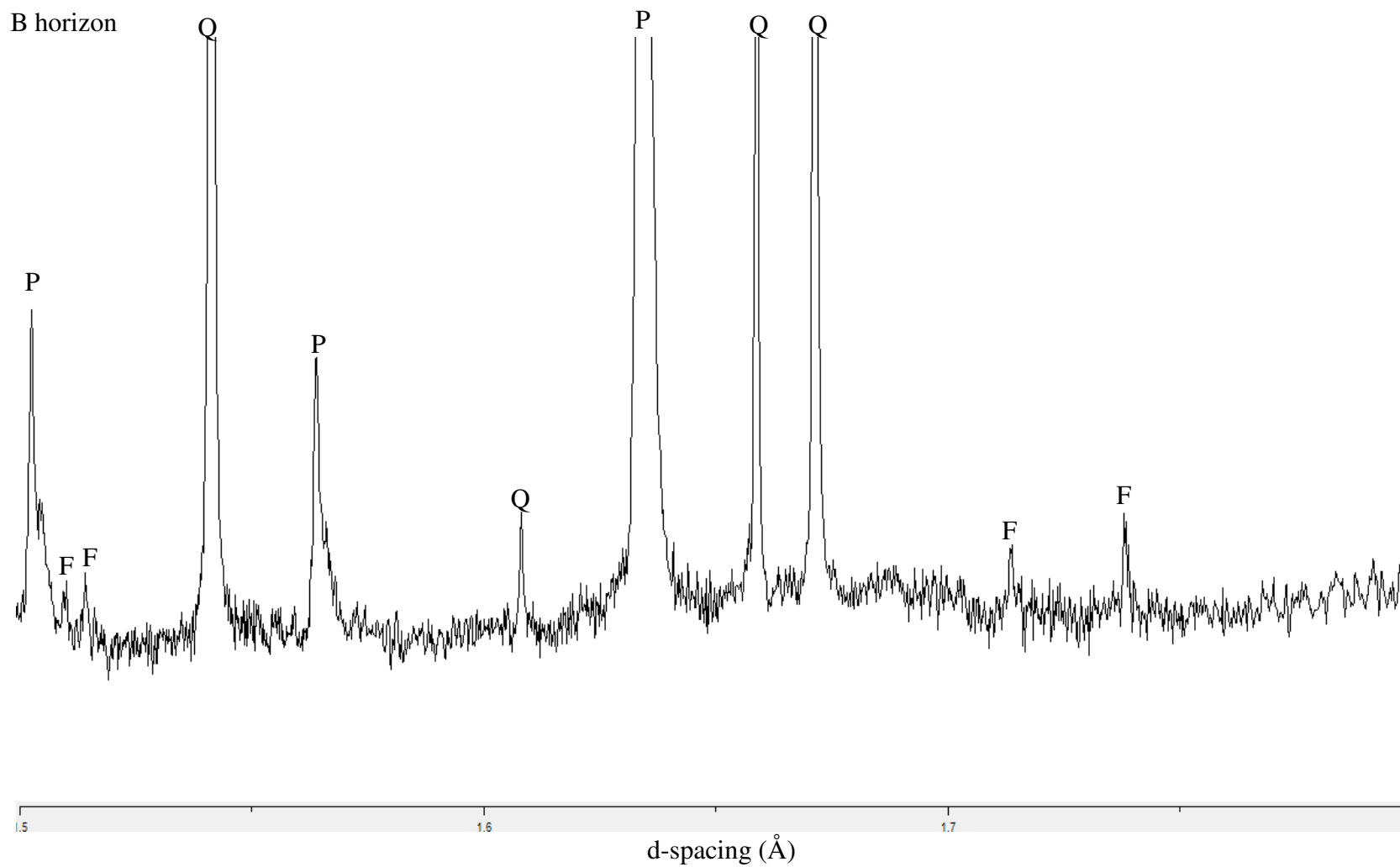
A horizon



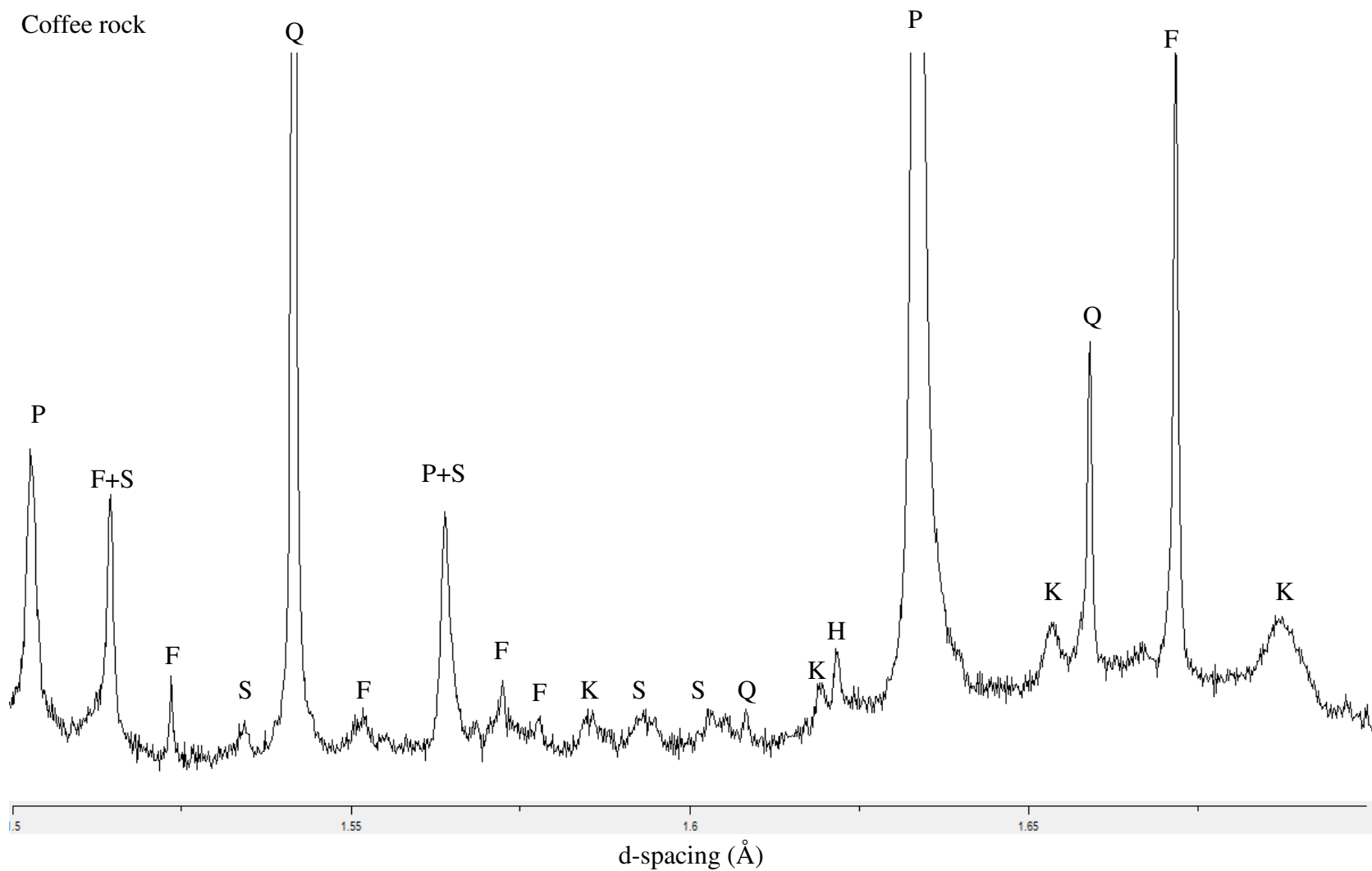
**Appendix Figure 11** Synchrotron XRD pattern of the fine fraction from the A horizon (0-100 cm, site 616-02-094) (pHF = 4.5, pHFOX = 2.1, Scr = 0.09%) (Q = Quartz, F = Feldspar, K = Kaolin, J = Jarosite).



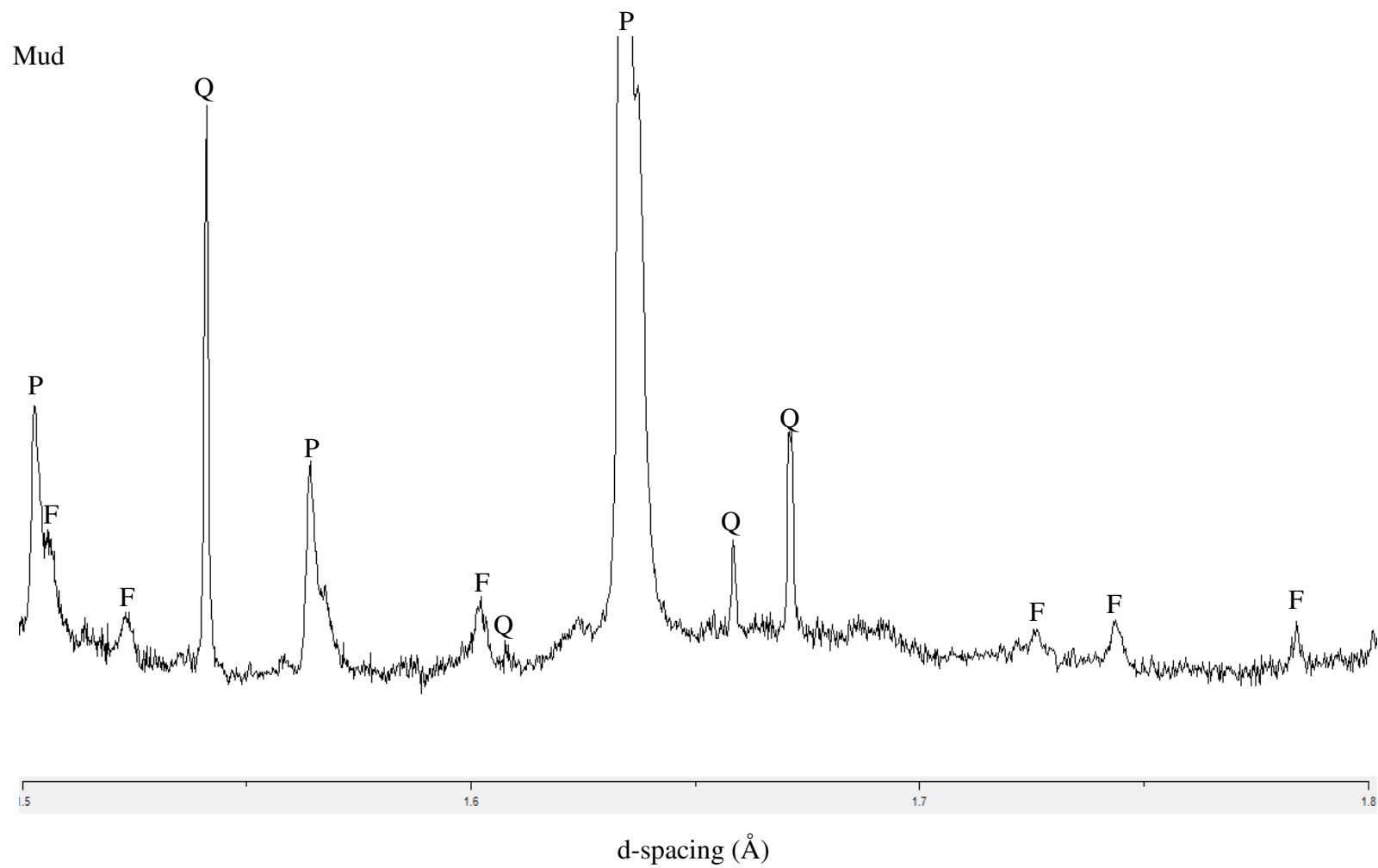
**Appendix Figure 12** Synchrotron XRD pattern of the fine fraction from the E horizon (260-600 cm, site 616-02-136) (pHF = 6.3, pHFOX = 2.0, Scr = 0.02%) (Q = Quartz, F = Feldspar, K = Kaolin, P = Pyrite, S = Elemental S, Mar = Marcasite).



**Appendix Figure 13** Synchrotron XRD pattern of the fine fraction from the B horizon (300-400 cm, site 616-02-099) (pHF = 7.2, pHFOX = 1.8, Scr = 0.12%) (Q = Quartz, F = Feldspar, K = Kaolin, P = Pyrite).

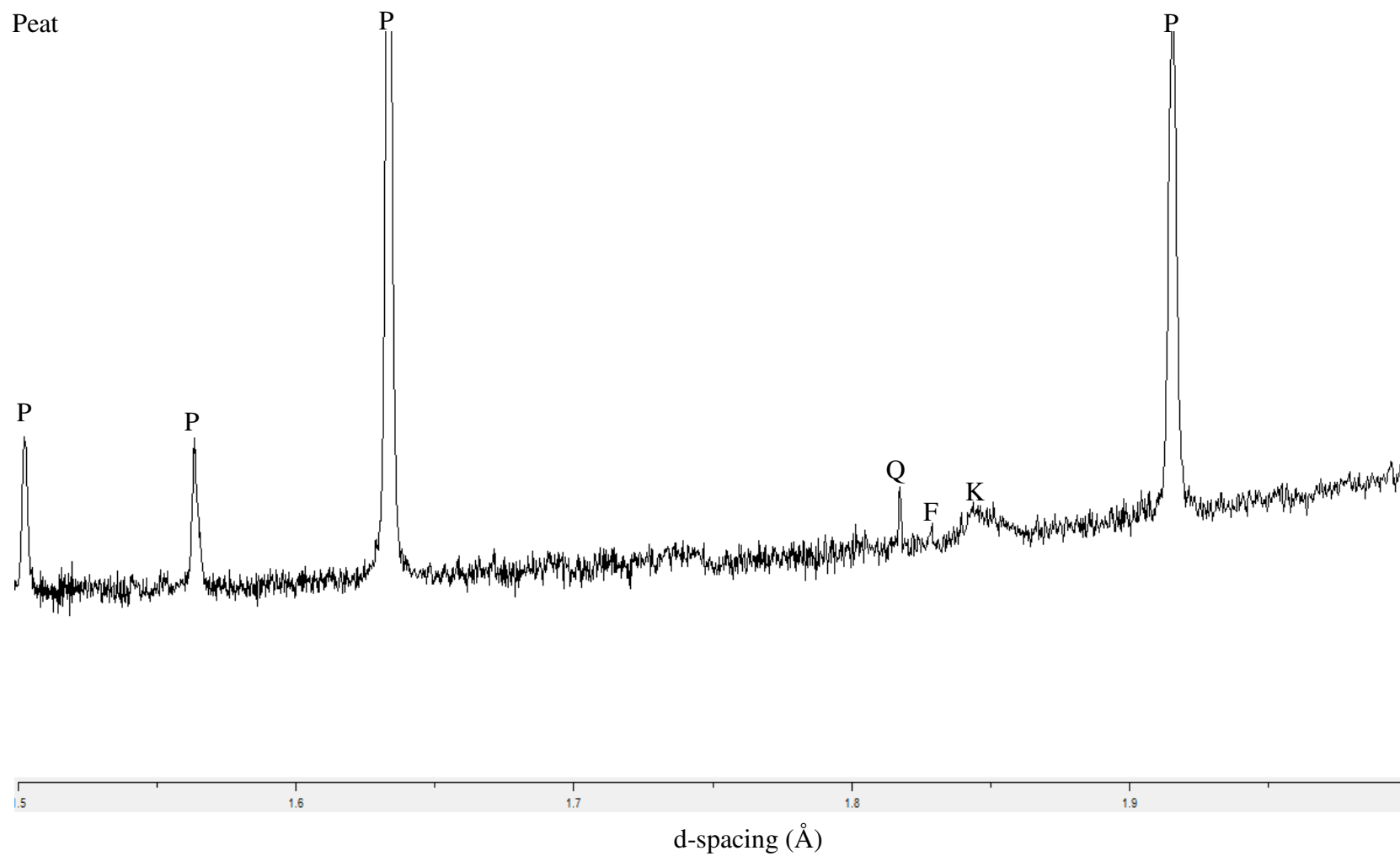


**Appendix Figure 14** Synchrotron XRD pattern of the fine fraction from the coffee rock (500-600 cm, site 616-02-082) (pHF = 6.7, pHFOX = 1.5, No Scr data) (Q = Quartz, F = Feldspar, K = Kaolin, P = Pyrite, S = Elemental S, H = Halite).

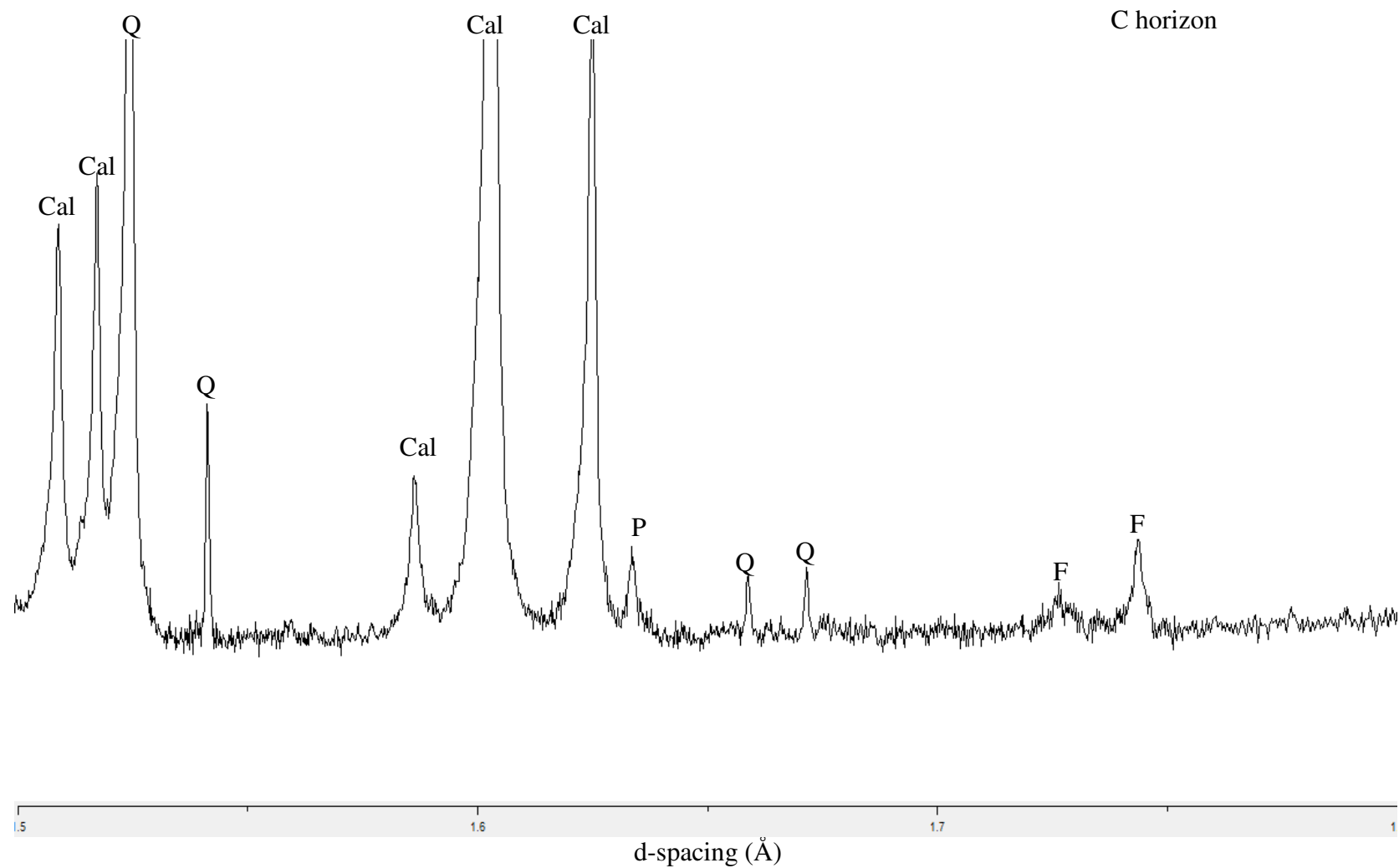


**Appendix Figure 15** Synchrotron XRD pattern of the fine fraction from the mud of (200-250 m, site 616-02-028) (pHF = 7.4, pHFOX = 6.0, No Scr data) (Q = Quartz, F = Feldspar, P = Pyrite).



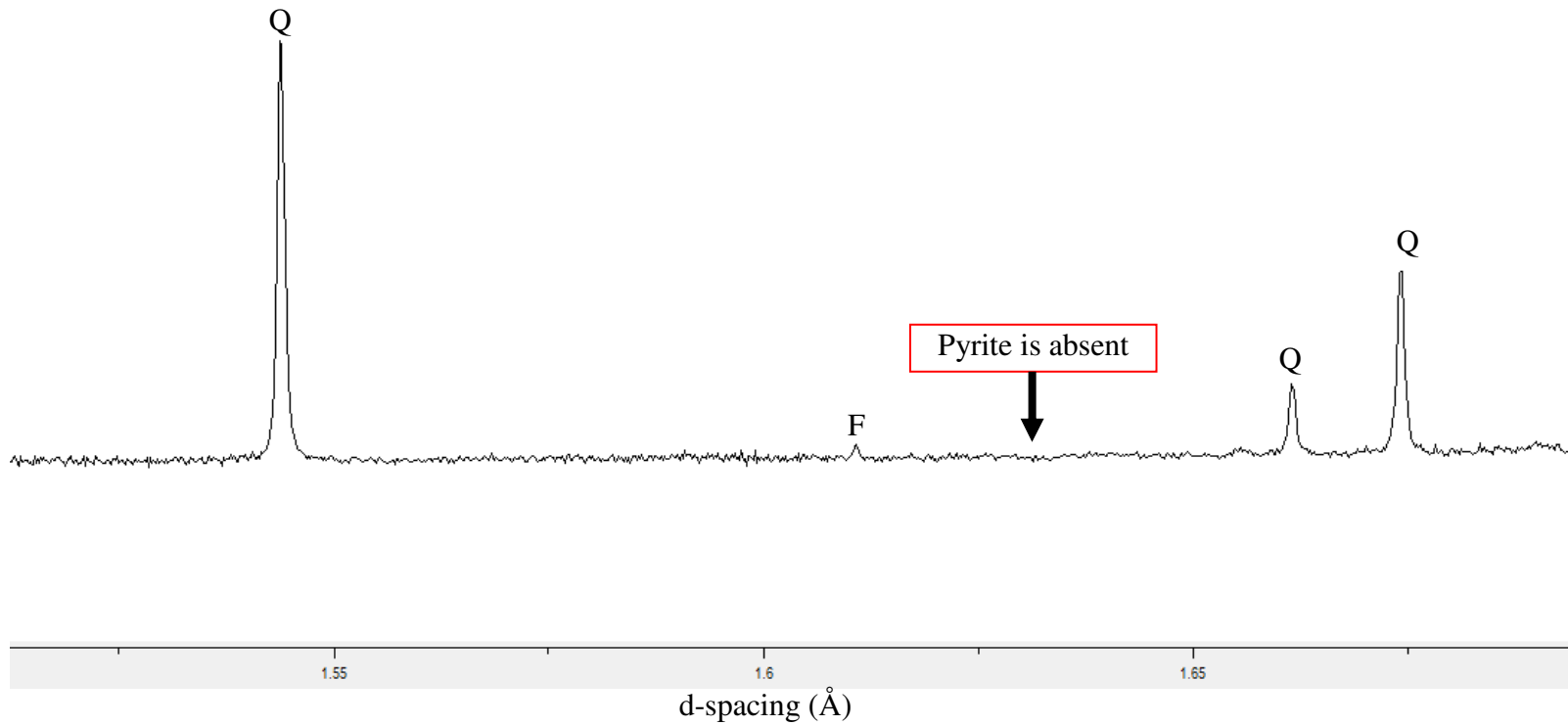


**Appendix Figure 16** Synchrotron XRD pattern of the fine fraction from the peat (250-360 cm, site 616-02-105) (pHF = 6.3, pHFOX = 1.4, Scr = 1.97%) (Q = Quartz, F = Feldspar, K = Kaolin, P = Pyrite).



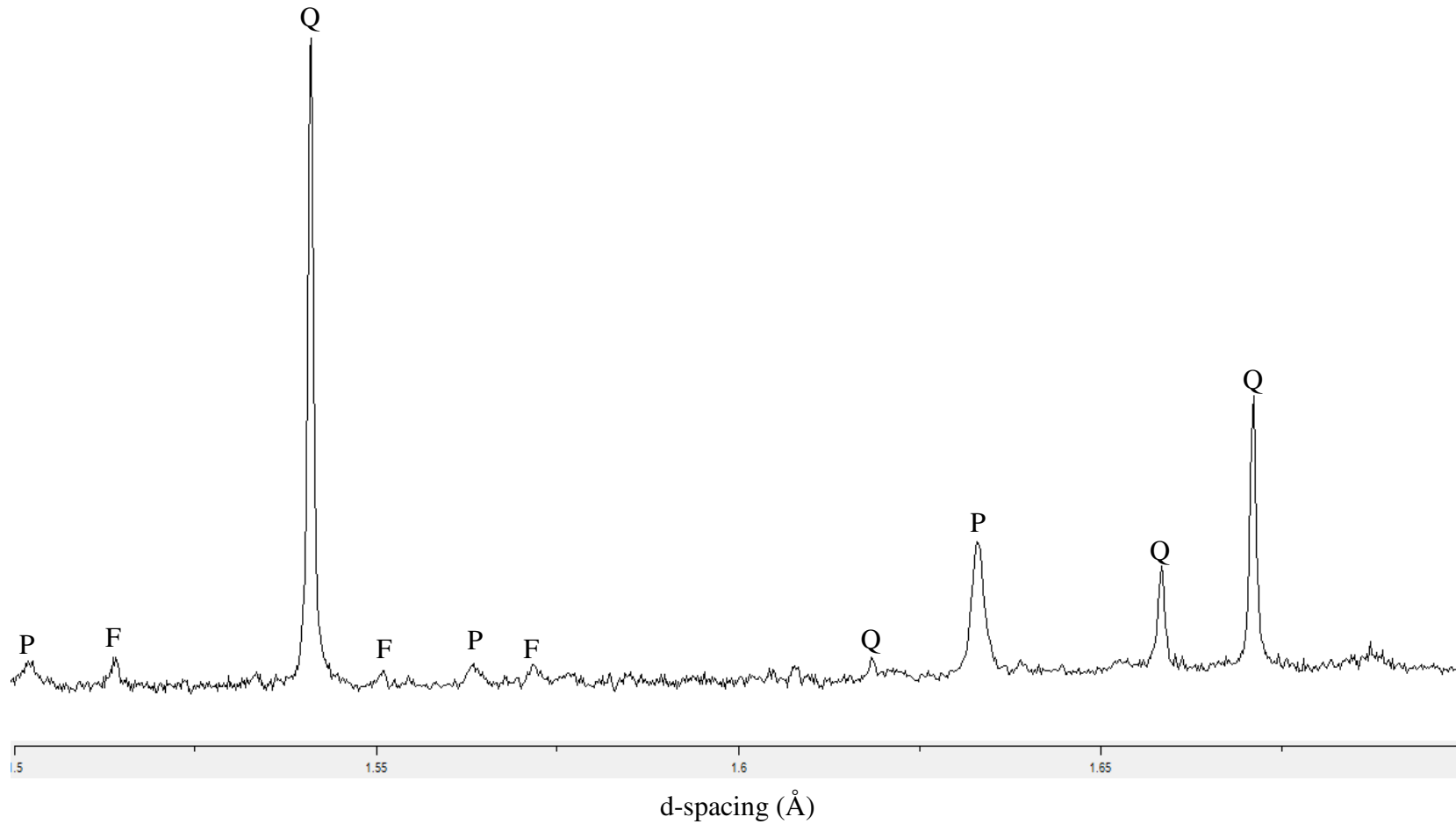
**Appendix Figure 17** Synchrotron XRD pattern of the fine fraction from the C horizon (400-600 cm, site 616-02-112) (pHF = 7.9, pHFOX = 6.5, No Scr data) (Q = Quartz, F = Feldspar, P = Pyrite, Cal = Calcite).

B horizon (N\_01)



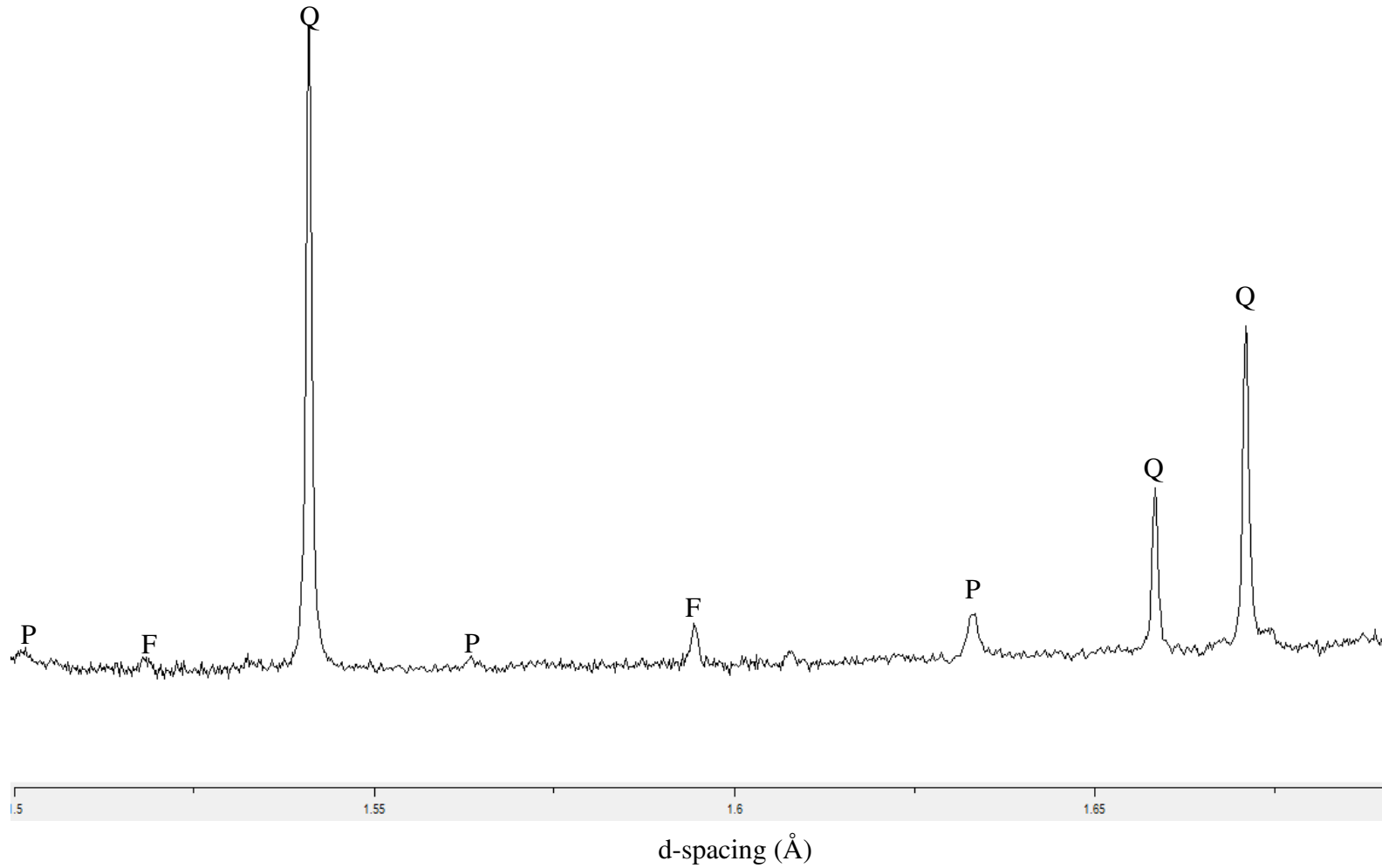
**Appendix Figure 18** Synchrotron XRD pattern of the fine fraction from the B horizon (620-630 cm, site 616-01-005) (pHF = 5.5, pHFOX = 2.7, Scr = 0.014%) (Q = Quartz; F = Feldspar).

B horizon (N\_02)

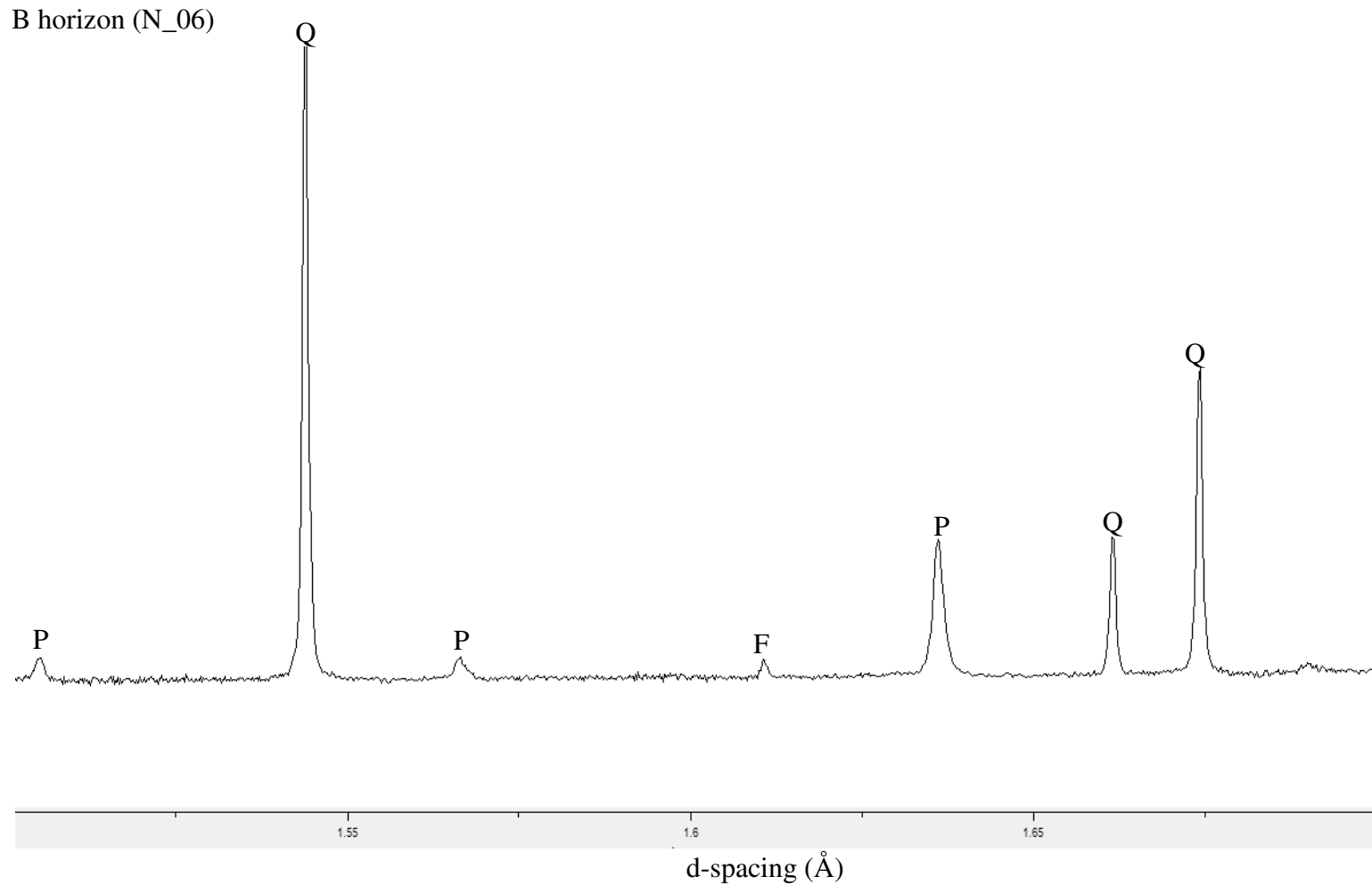


**Appendix Figure 19** Synchrotron XRD pattern of the fine fraction from the B horizon (450 cm, site 616-02-068) (pHF = 7.2, pHFOX = 1.8, Scr = 0.027%) (Q = Quartz, F = Feldspar, P = Pyrite).

B horizon (N\_04)

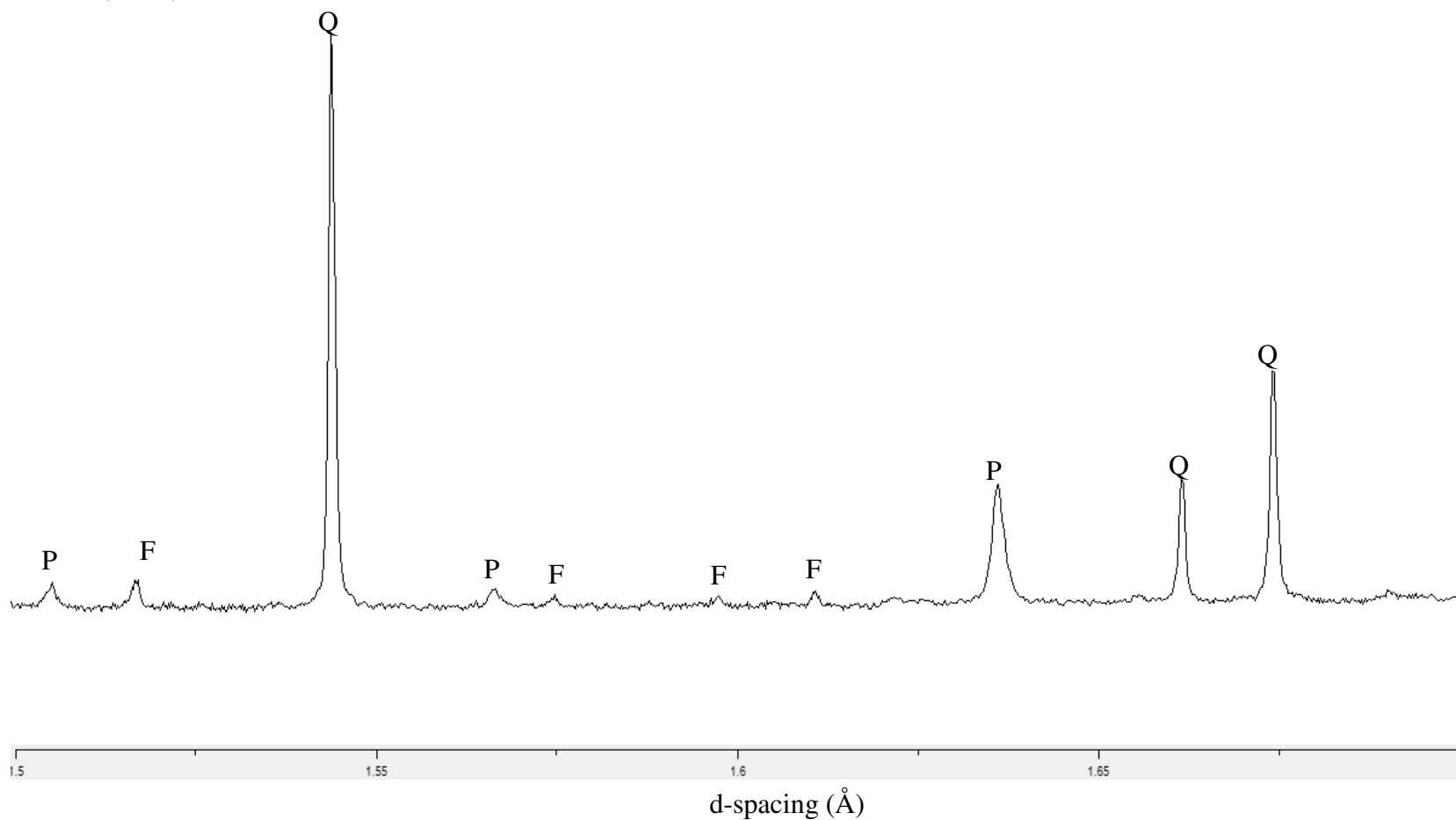


**Appendix Figure 20** Synchrotron XRD pattern of the fine fraction from the B horizon (375-400 cm, site 616-02-179) (pHF = 6.1, pHFOX = 1.6, Scr = 0.013%) (Q = Quartz, F = Feldspar, P = Pyrite).



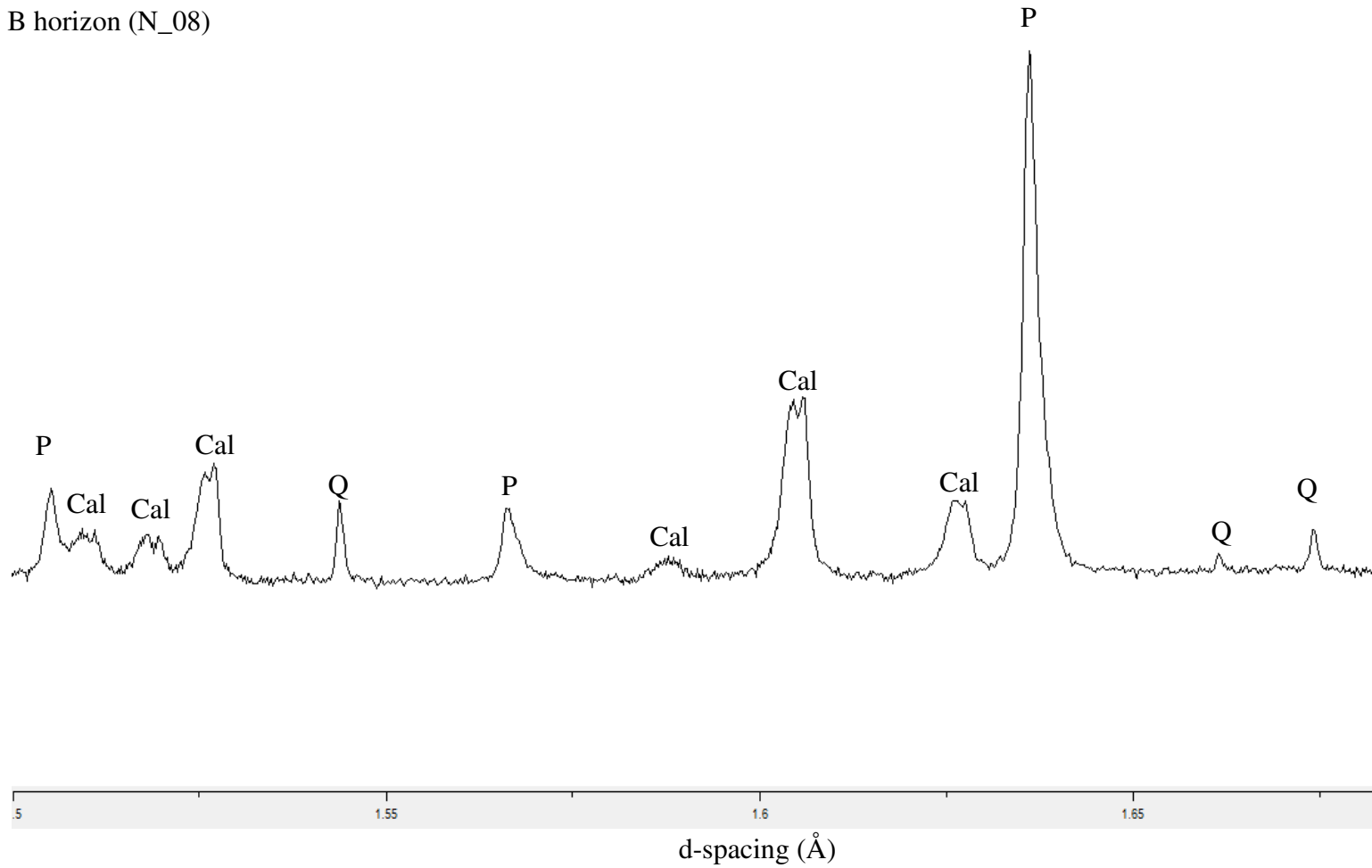
**Appendix Figure 21** Synchrotron XRD pattern of the fine fraction from the B horizon (400-500 cm, site 616-02-078) (pHF = 4.8, pHFOX = 1.5, Scr = 0.014%) (Q = Quartz, F = Feldspar, P = Pyrite).

B horizon (N\_07)



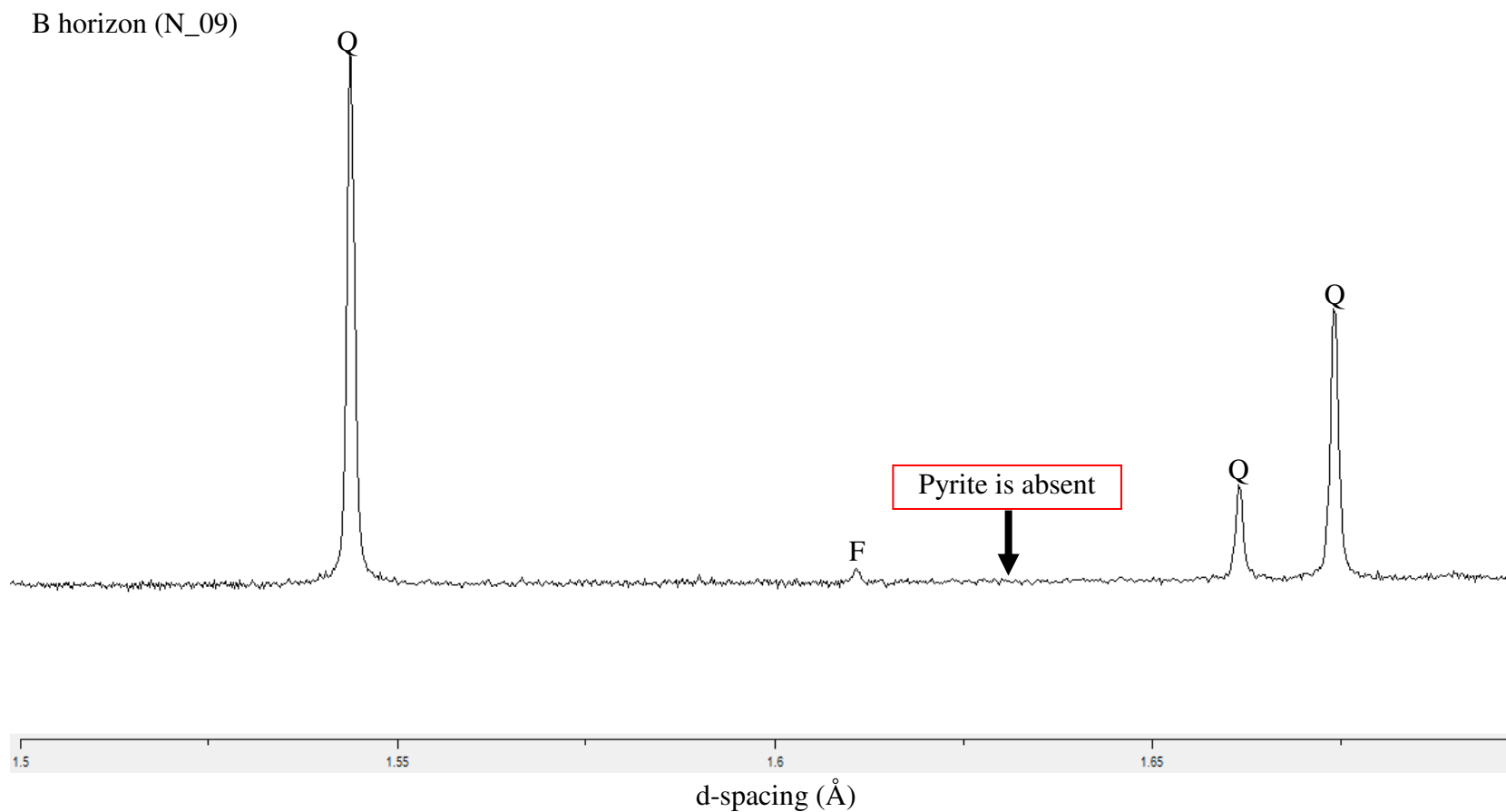
**Appendix Figure 22** Synchrotron XRD pattern of the fine fraction from the B horizon (400-800 cm, site 616-02-081) (pHF = 6.2, pHFOX = 1.4, Scr = 0.052%) (Q = Quartz, F = Feldspar, P = Pyrite).

B horizon (N\_08)

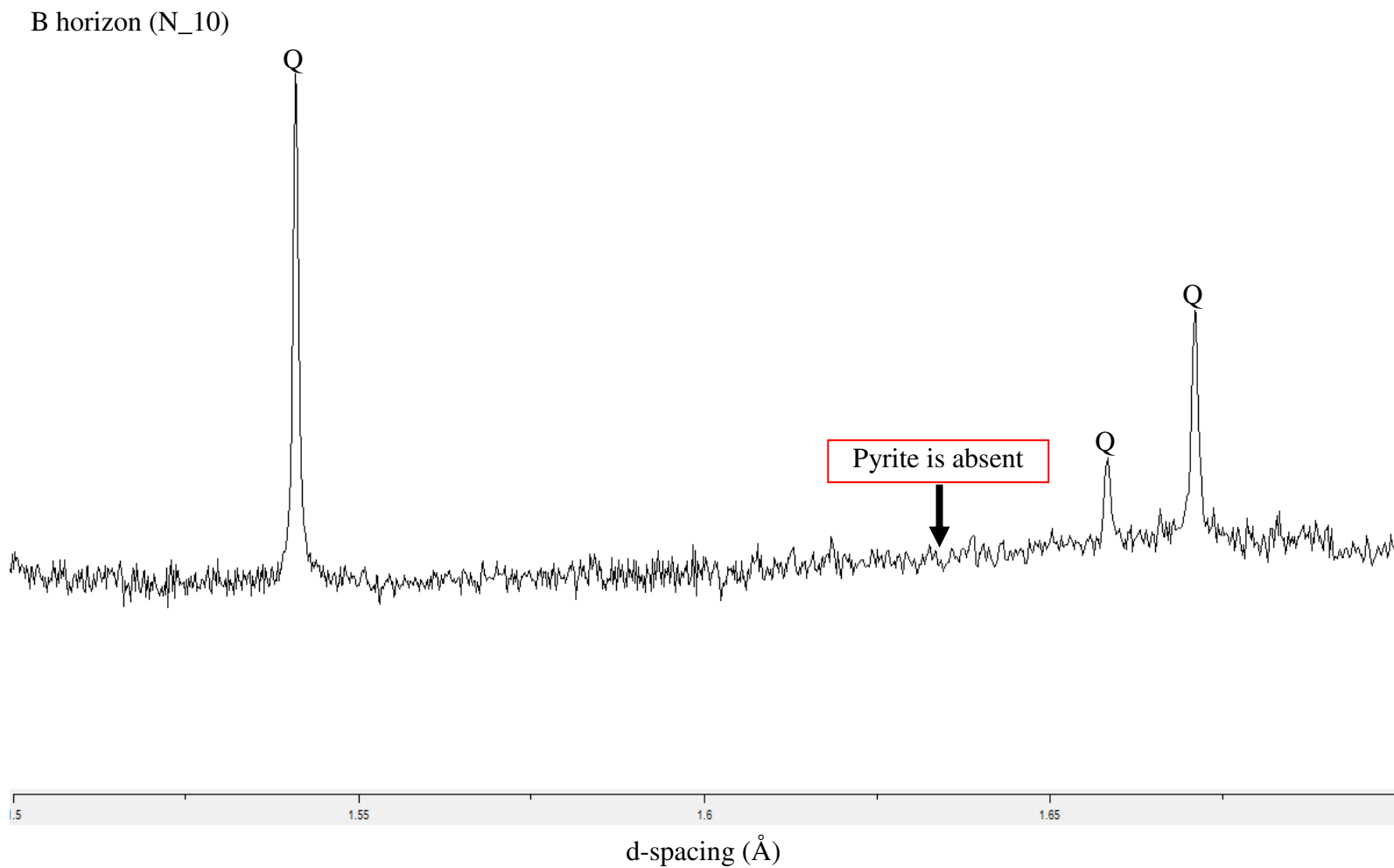


**Appendix Figure 23** Synchrotron XRD pattern of the fine fraction from the B horizon (200-500 cm, site 616-02-110) (pHF = 6.3, pHFOX = 1.8, Scr = 0.036%) (Q = Quartz, Cal = Calcite, P = Pyrite).



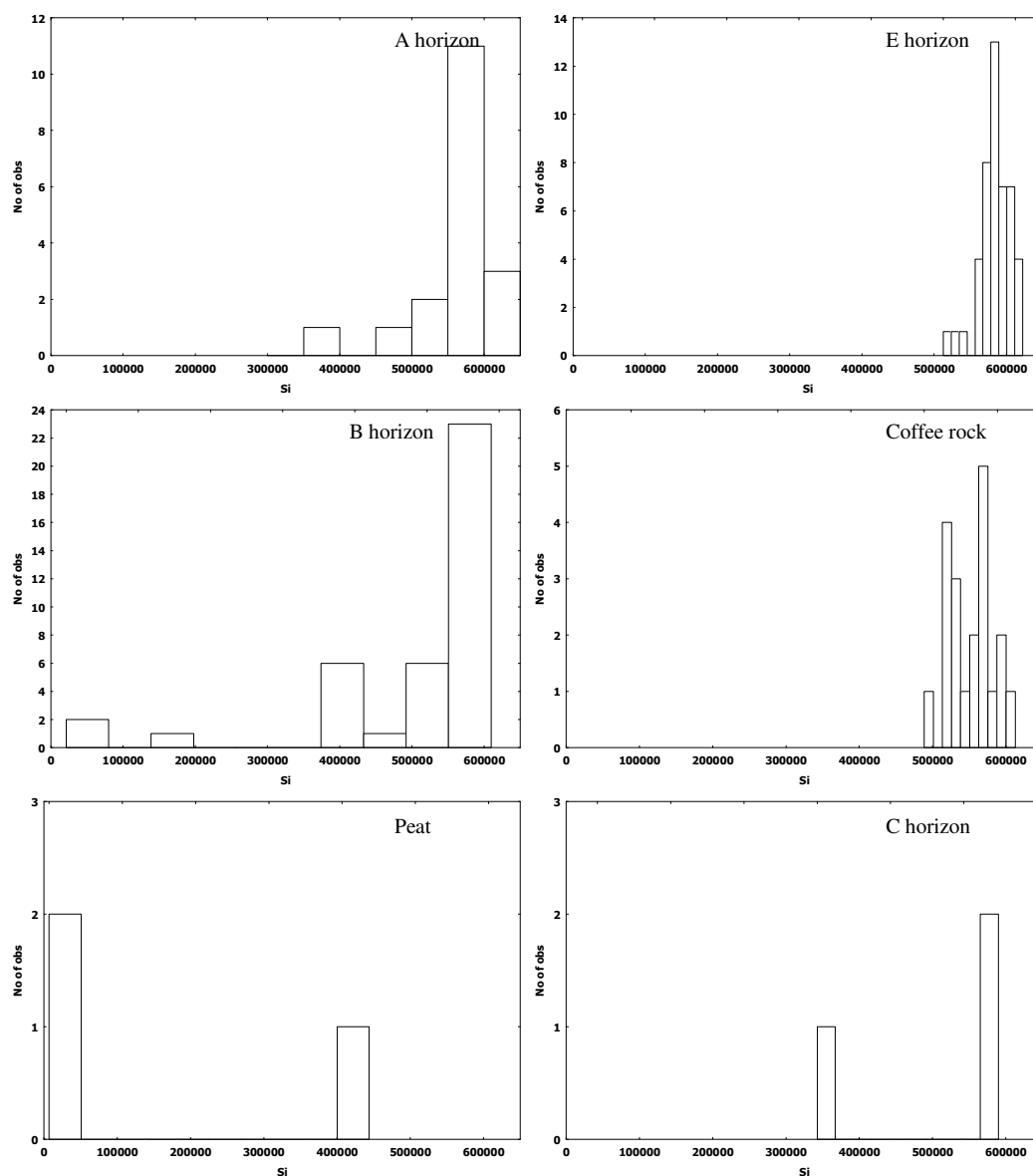


**Appendix Figure 24** Synchrotron XRD pattern of the fine fraction from the B horizon (250-550 cm, site 616-02-174) (pHF = 5.5, pHFOX = 2.5, Scr = <0.005%) (Q = Quartz, F = Feldspar).



**Appendix Figure 25** Synchrotron XRD pattern of the fine fraction from the B horizon (200 cm, site 616-02-065) (pHF = 5.7, pHFOX = 3.0, Scr = 0.005%) (Q = Quartz)

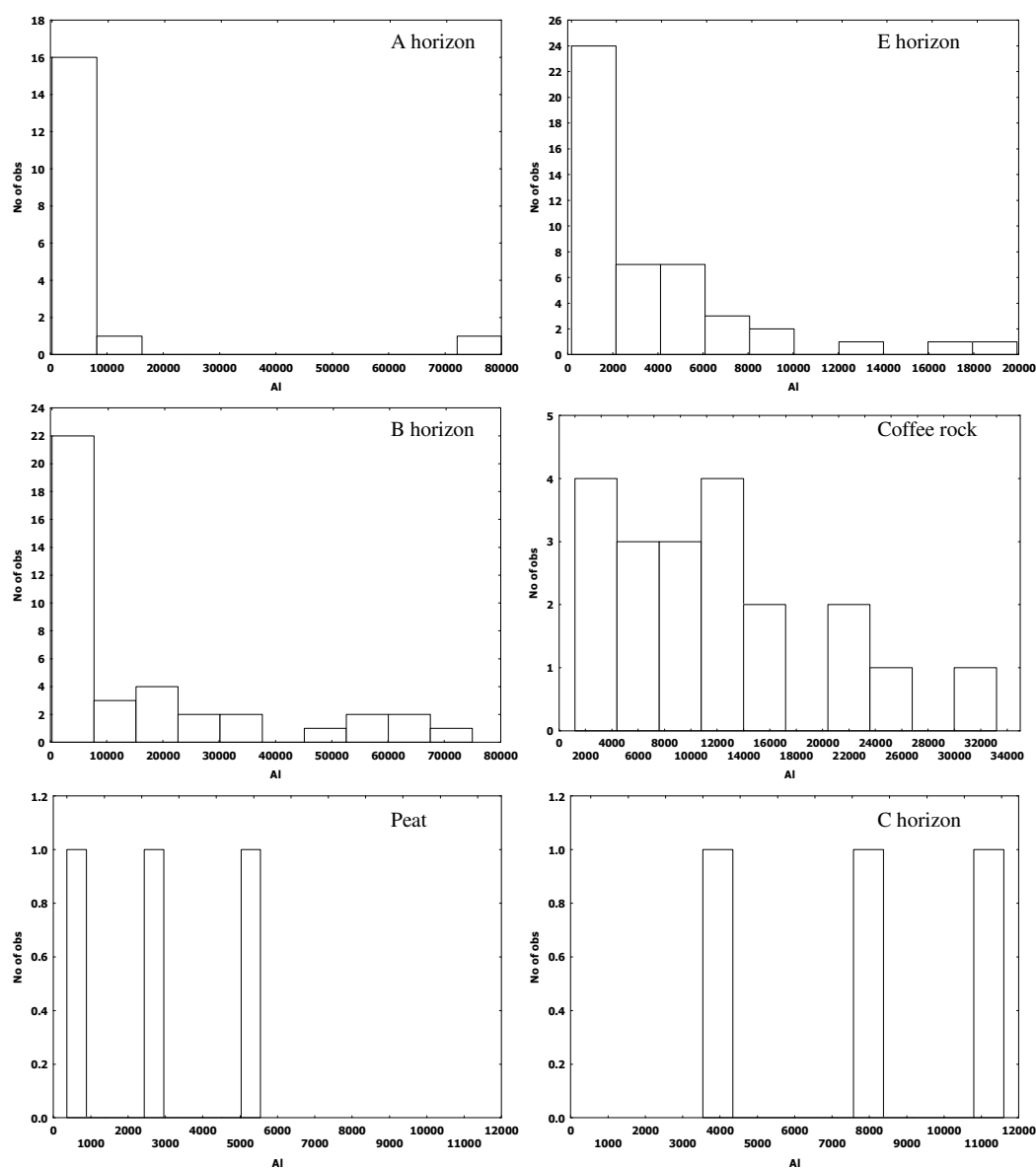
## Si



Horizon	Valid N	Median	Min	Max	Std. Dev.
A horizon	18	586724	372001	625790	61105
E horizon	46	585509	512696	622488	21920
B horizon	39	557836	21030	609737	138732
Coffee rock	20	558393	488632	612839	30877
Peat	3	36140	6914	443875	244280
C horizon	3	581823	342593	589859	140497
Mean values for normal surface soils worldwide 250000-410000 mg kg <sup>-1</sup> *					

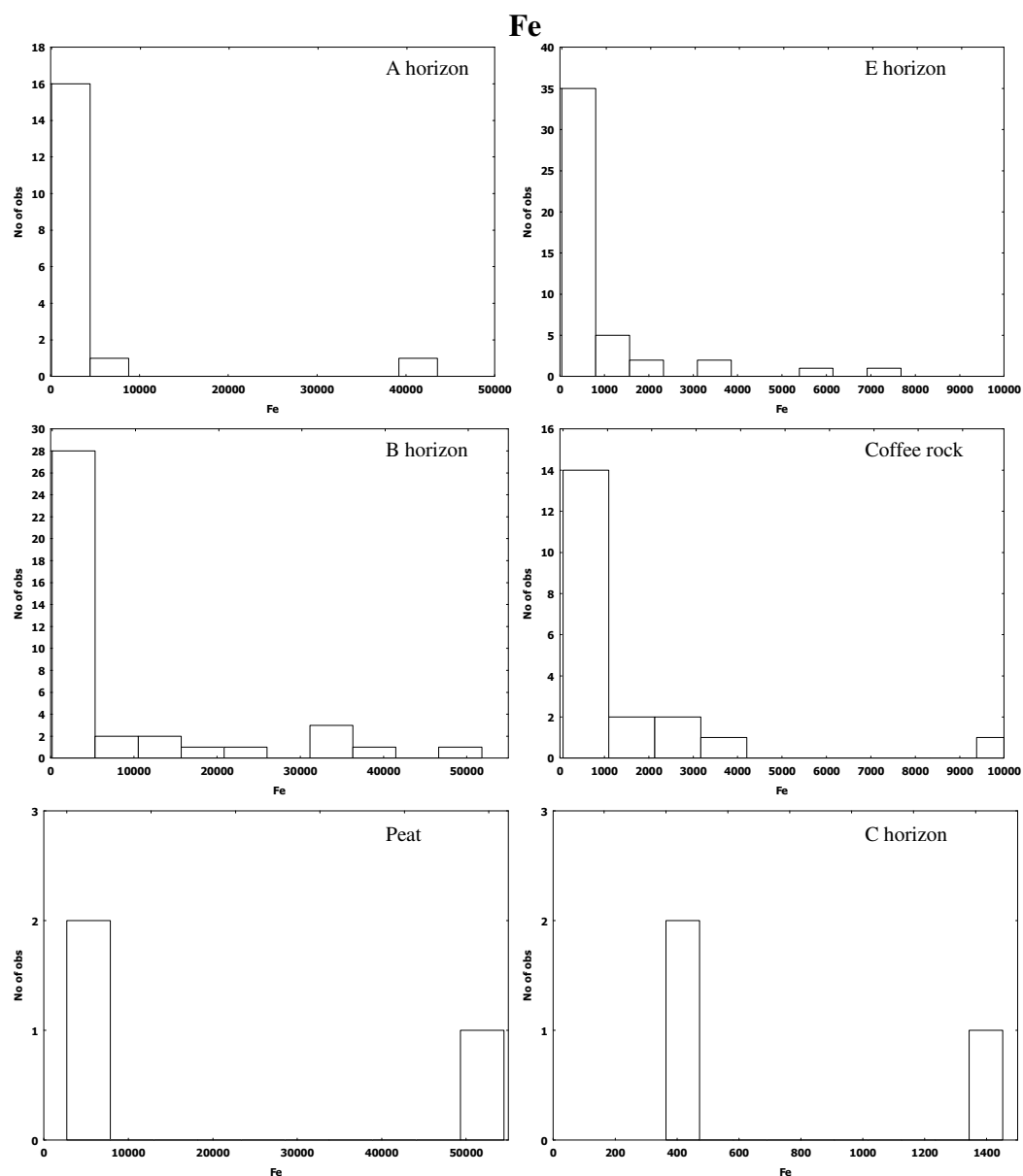
**Appendix Figure 26** Histograms for the concentration of silicon (Si) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (fusion acid digestion method; ICP-OES).  
\* Data are from Kabata-Pendias (2001), Essington (2004).

## Al



Horizon	Valid N	Median	Min	Max	Std. Dev.
A horizon	18	846	276	80116	18574
E horizon	46	1683	162	19930	4342
B horizon	39	6365	303	74968	20838
Coffee rock	20	10695	1201	33192	8406
Peat	3	2478	363	5547	2607
C horizon	3	8304	3542	11603	4053
Mean values for normal surface soils worldwide 10000-300000 mg kg <sup>-1</sup> *					

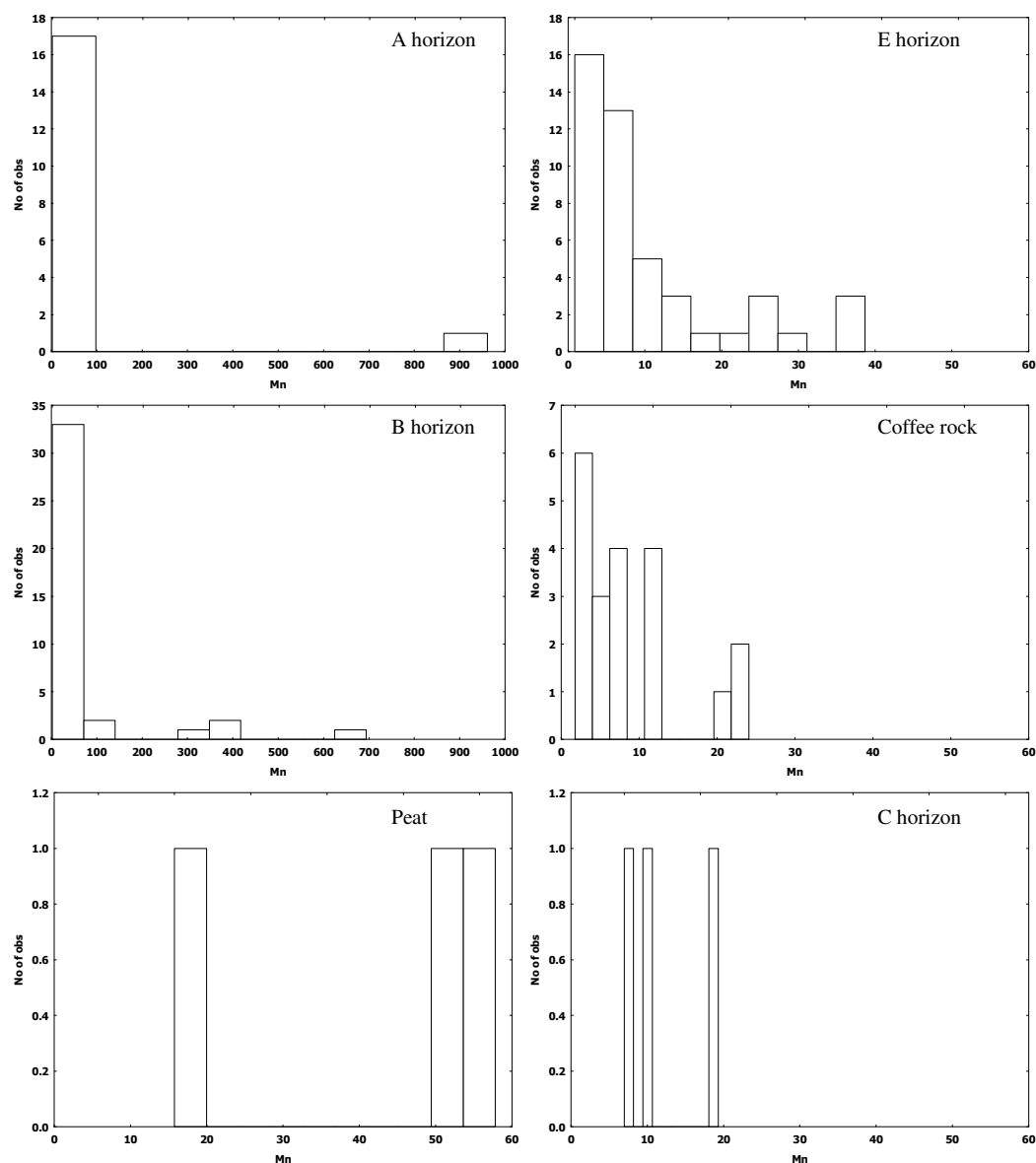
**Appendix Figure 27** Histograms for the concentration of aluminium (Al) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (fusion acid digestion method; ICP-OES).  
\* Data are from Kabata-Pendias (2001), Essington (2004).



Horizon	Valid N	Median	Min	Max	Std. Dev.
A horizon	18	315	106	43557	10154
E horizon	46	231	43	7677	1485
B horizon	39	1003	198	51808	13434
Coffee rock	20	694	67	10415	2283
Peat	3	4198	2699	54503	29486
C horizon	3	408	364	1452	616
Mean values for normal surface soils worldwide 2000-550000 mg kg <sup>-1</sup> *					

**Appendix Figure 28** Histograms for the concentration of iron (Fe) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (aqua regia method; ICP-OES). \* Data are from Kabata-Pendias (2001), Essington (2004).

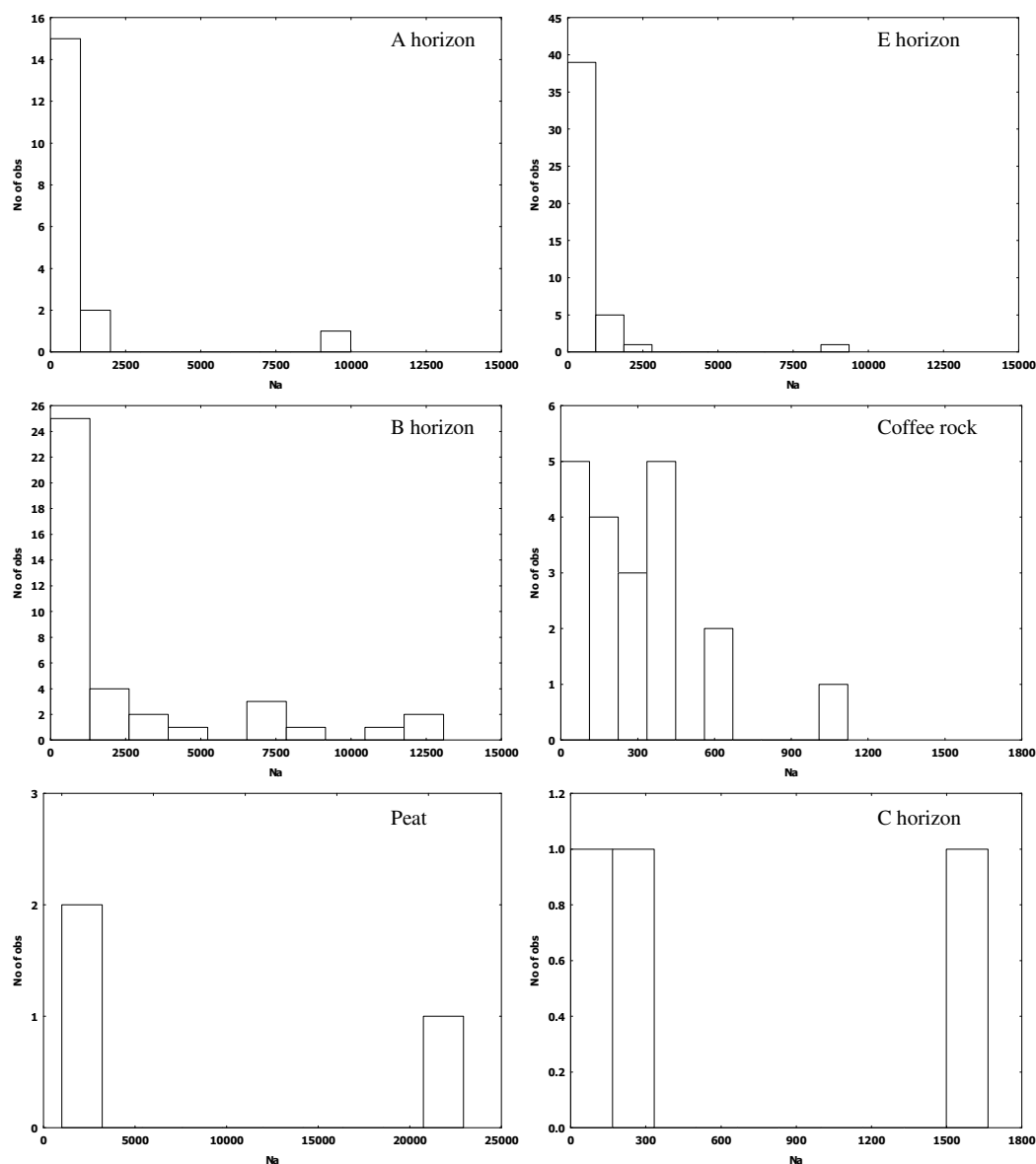
## Mn



Horizon	Valid N	Median	Min	Max	Std. Dev.
A horizon	18	6.8	2.0	961	225
E horizon	46	6.6	0.87	39	10
B horizon	39	13	2.3	694	139
Coffee rock	20	7.0	1.8	24	6.9
Peat	3	50	16	58	22
C horizon	3	10	7.0	19	6.4
Mean values for normal surface soils worldwide 270-530 mg kg <sup>-1</sup> *					
Critical soil concentration 1500-3000 mg kg <sup>-1</sup> **					

**Appendix Figure 29** Histograms for the concentration of manganese (Mn) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (aqua regia method; ICP-OES). \* Data are from Kabata-Pendias (2001), Essington (2004); \*\* Data are from (Alloway, 1995).

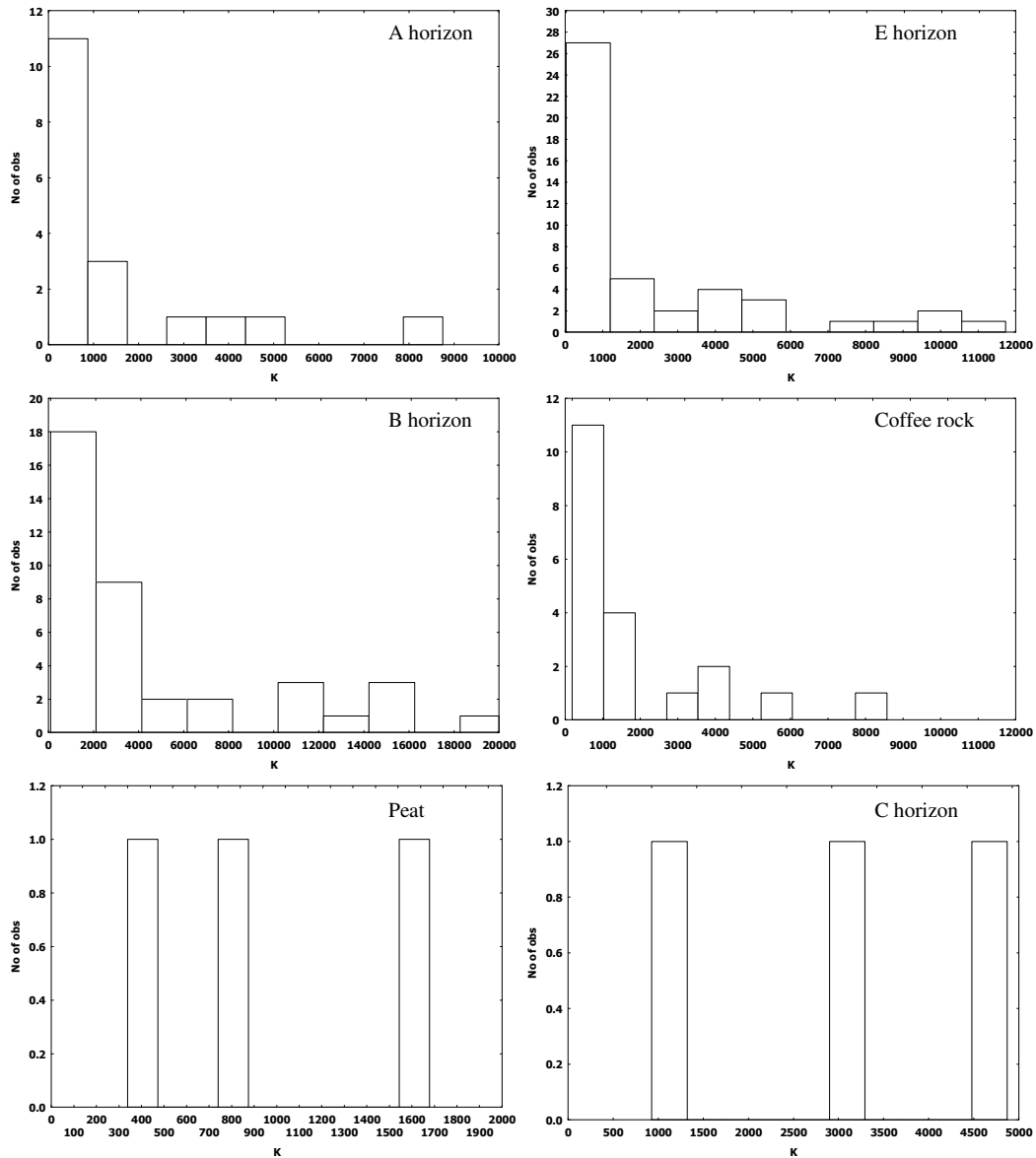
## Na



Horizon	Valid N	Median	Min	Max	Std. Dev.
A horizon	18	187	nd	9982	2315
E horizon	46	219	nd	9357	1425
B horizon	39	529	nd	13070	3756
Coffee rock	20	258	nd	1120	276
Peat	3	1488	1002	22932	12524
C horizon	3	300	nd	1666	888
Mean values for normal surface soils worldwide 150-25000 mg kg <sup>-1</sup> *					

**Appendix Figure 30** Histograms for the concentration of sodium (Na) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (fusion acid digestion method; ICP-OES).  
\* Data are from Kabata-Pendias (2001), Essington (2004).

## K

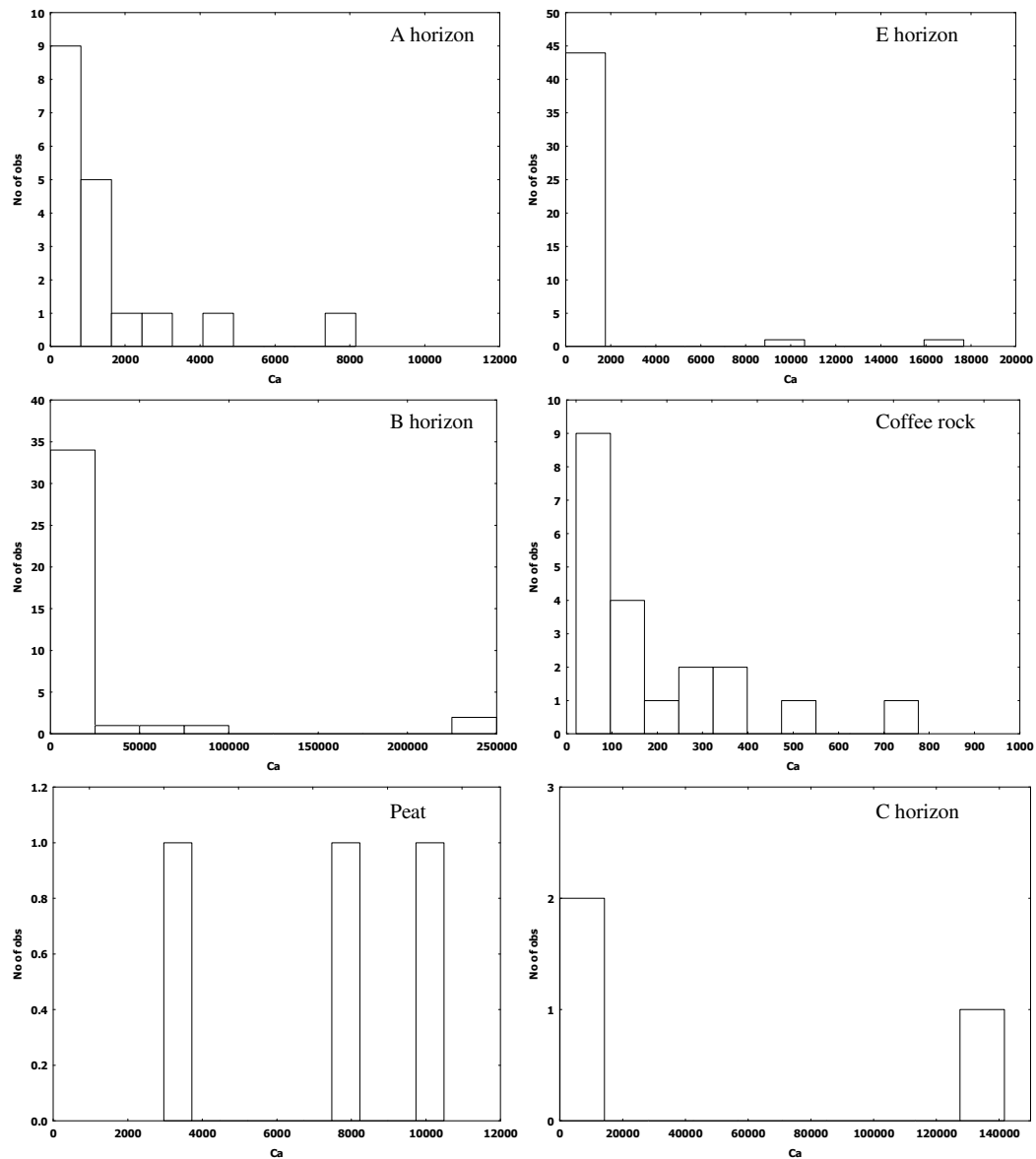


Horizon	Valid N	Median	Min	Max	Std. Dev.
A horizon	18	360	nd	8753	2268
E horizon	46	741	28	11731	3044
B horizon	39	2227	99	20288	5299
Coffee rock	20	899	188	8566	2200
Peat	3	842	339	1678	676
C horizon	3	2927	926	4873	1974
Mean values for normal surface soils worldwide 80-37000 mg kg <sup>-1</sup> *					

**Appendix Figure 31** Histograms for the concentration of potassium (K) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (fusion acid digestion method; ICP-OES). \* Data are from Kabata-Pendias (2001), Essington (2004).



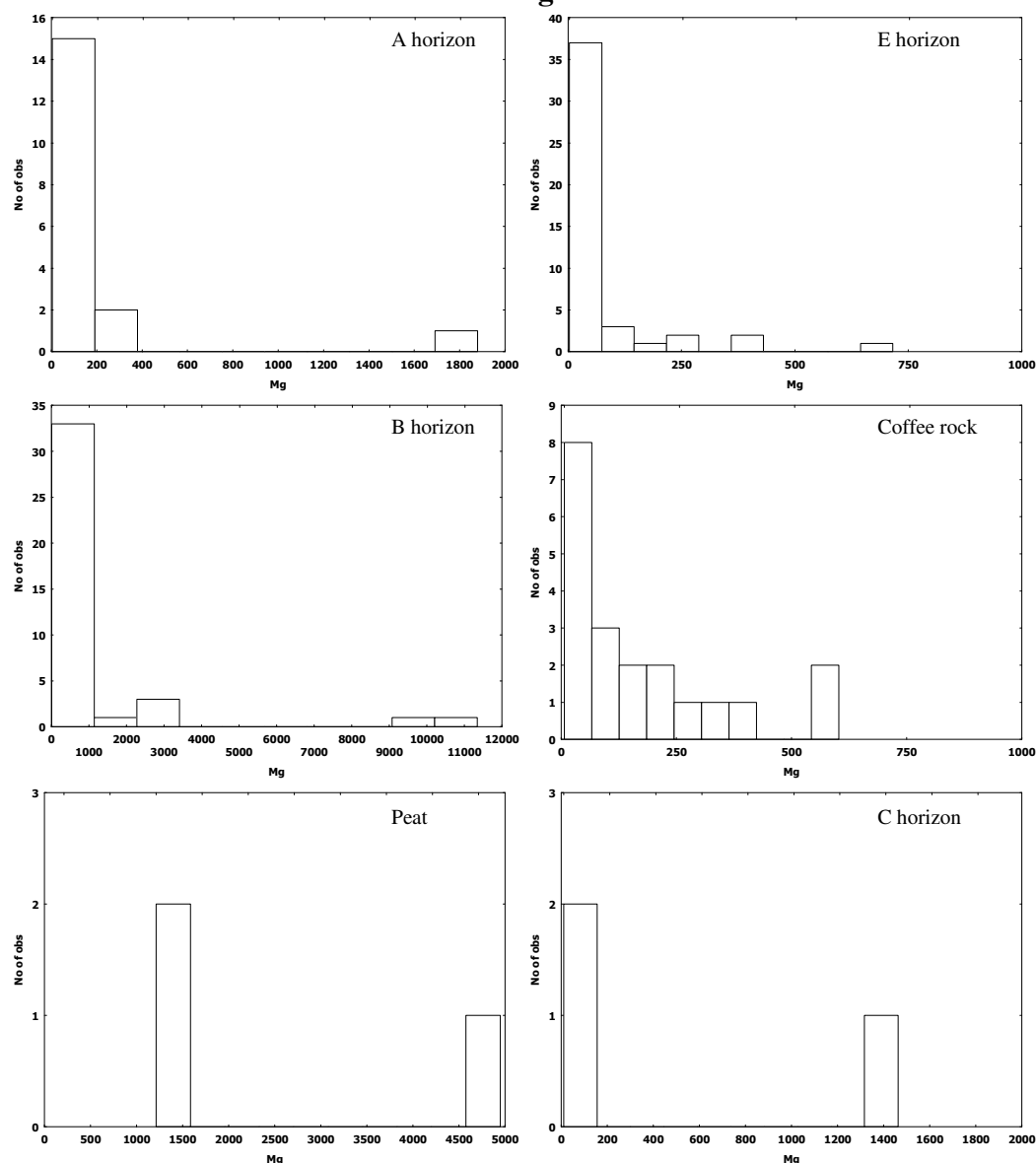
## Ca



Horizon	Valid N	Median	Min	Max	Std. Dev.
A horizon	18	642	nd	8155	2009
E horizon	46	28	nd	17689	2982
B horizon	39	225	11	249900	55932
Coffee rock	20	112	21	777	193
Peat	3	7622	2968	10479	3791
C horizon	3	30	24	141627	81753
Mean values for normal surface soils worldwide 700-500000 mg kg <sup>-1</sup> *					

**Appendix Figure 32** Histograms for the concentration of calcium (Ca) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (aqua regia method; ICP-OES). \* Data are from Kabata-Pendias (2001), Essington (2004).

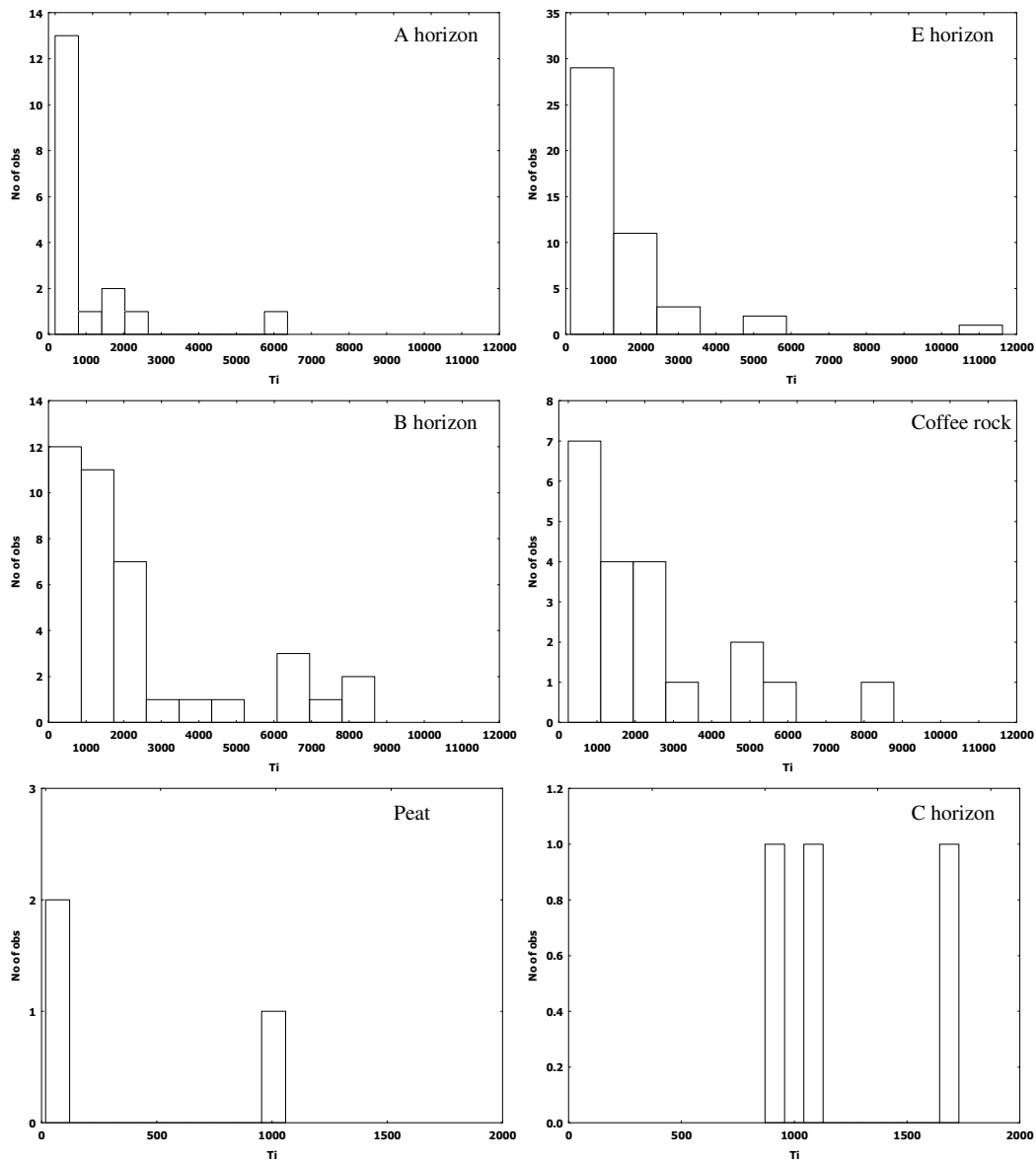
## Mg



Horizon	Valid N	Median	Min	Max	Std. Dev.
A horizon	18	77	4.3	1879	428
E horizon	46	15	2.8	716	137
B horizon	39	83	10	11338	2371
Coffee rock	20	105	6.7	603	175
Peat	3	1216	1212	4950	2157
C horizon	3	14	10	1462	837
Mean values for normal surface soils worldwide 400-9000 mg kg <sup>-1</sup> *					

**Appendix Figure 33** Histograms for the concentration of magnesium (Mg) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (aqua regia method; ICP-OES). \* Data are from Kabata-Pendias (2001), Essington (2004).

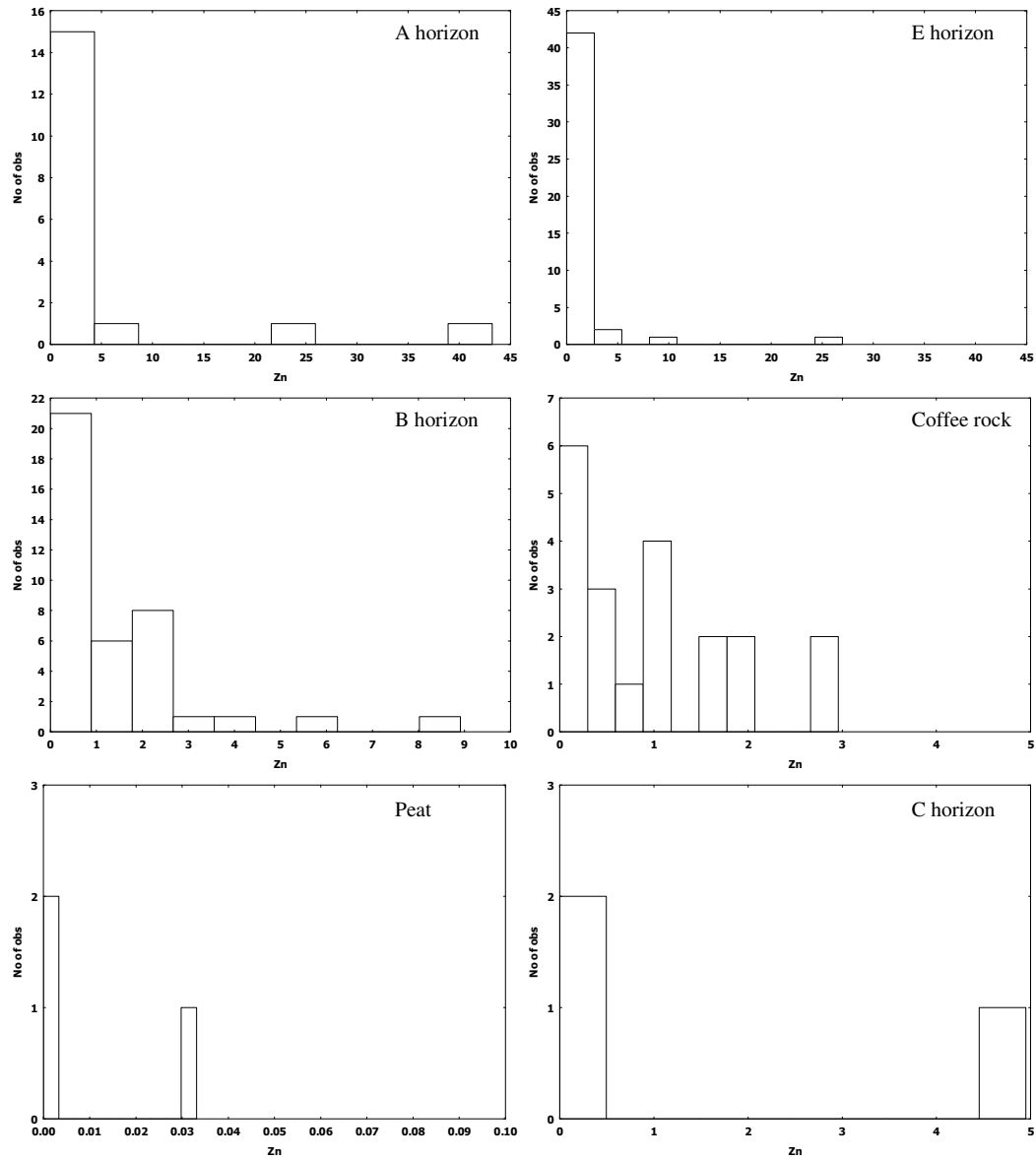
## Ti



Horizon	Valid N	Median	Min	Max	Std. Dev.
A horizon	18	614	179	6362	1441
E horizon	46	874	126	11621	1858
B horizon	39	1497	5.04	8681	2390
Coffee rock	20	1639	248	8773	2224
Peat	3	68	17	1058	587
C horizon	3	1098	871	1730	445
Mean values for normal surface soils worldwide 2300-26000 mg kg <sup>-1</sup> *					

**Appendix Figure 34** Histograms for the concentration of titanium (Ti) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (fusion acid digestion method; ICP-OES). \* Data are from Kabata-Pendias (2001), Essington (2004).

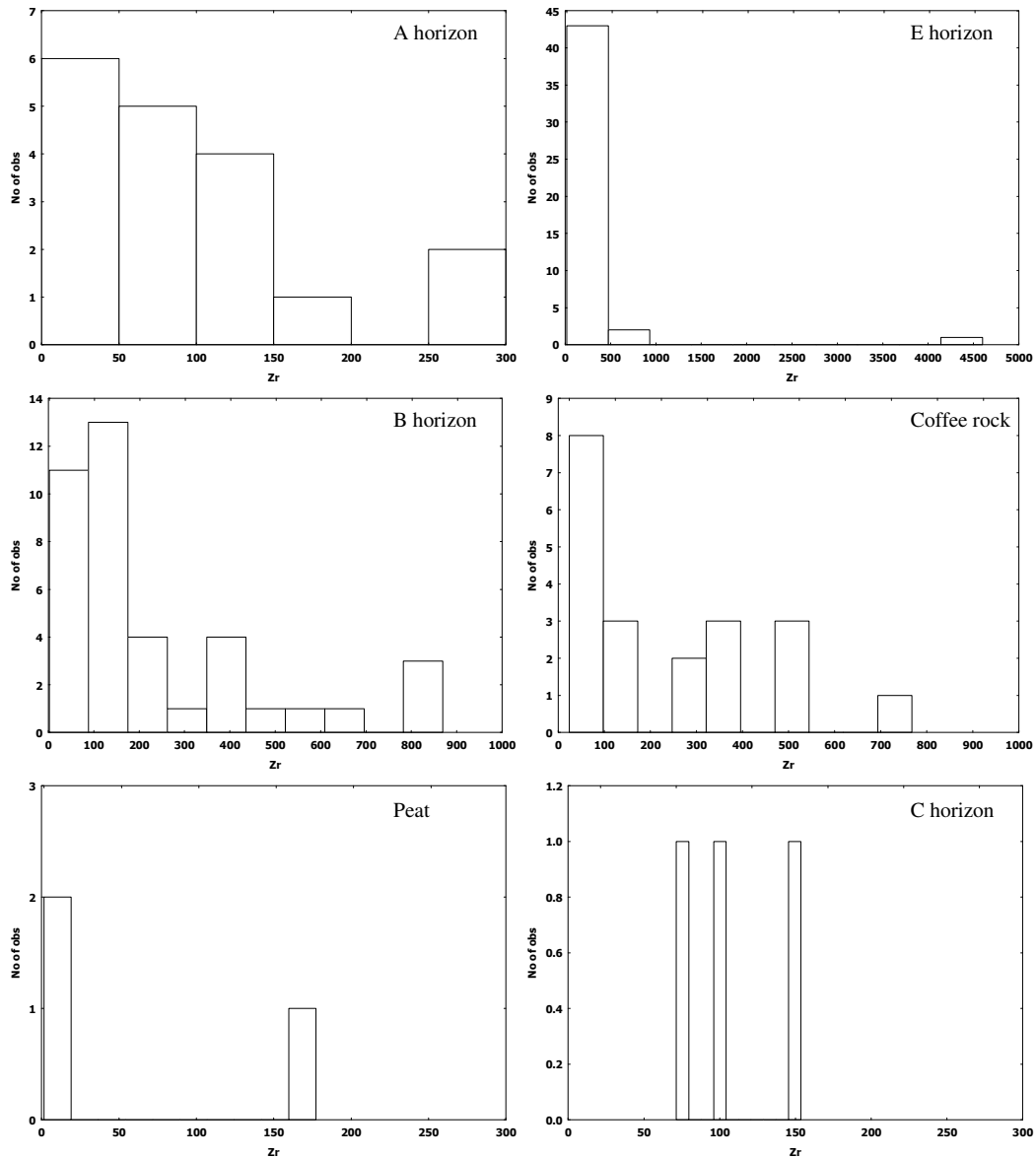
## Zn



Horizon	Valid N	Median	Min	Max	Std. Dev.
A horizon	18	0.98	nd	43	11
E horizon	46	0.23	nd	27	4.2
B horizon	39	0.54	nd	8.9	1.8
Coffee rock	20	0.93	nd	3.0	0.93
Peat	3	nd	nd	0.033	0.019
C horizon	3	0.34	nd	5.0	2.8
Mean values for normal surface soils worldwide 45-100 mg kg <sup>-1</sup> *					
Critical soil concentration 70-400 mg kg <sup>-1</sup> **					

**Appendix Figure 35** Histograms for the concentration of zinc (Zn) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (aqua regia method; ICP-OES). \* Data are from Kabata-Pendias (2001), Essington (2004); \*\* Data are from (Alloway, 1995).

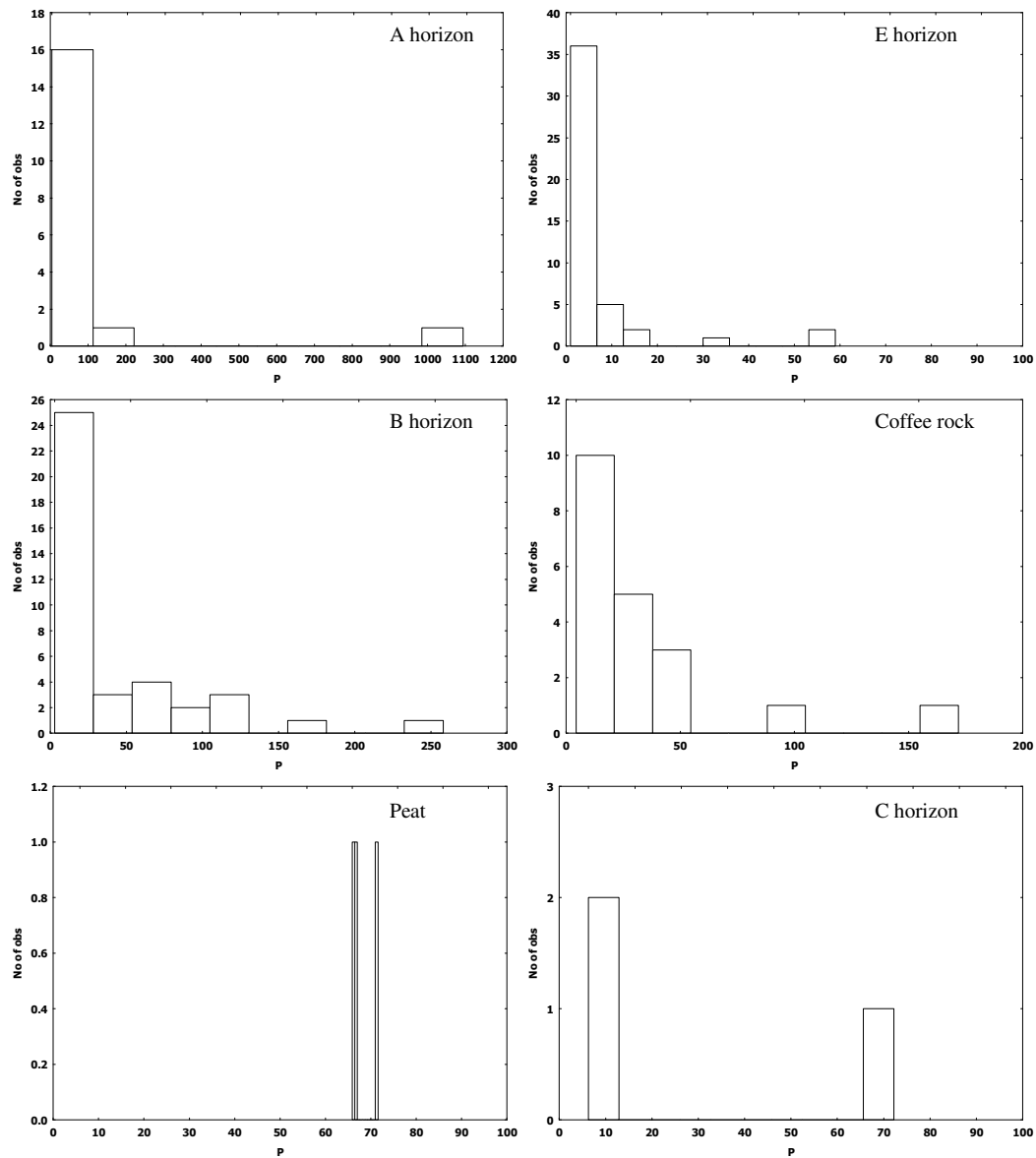
## Zr



Horizon	Valid N	Median	Min	Max	Std. Dev.
A horizon	18	69	15	279	79
E horizon	46	94	17	4600	672
B horizon	39	135	1.8	869	237
Coffee rock	20	136	24	768	210
Peat	3	7.9	1.6	177	100
C horizon	3	104	71	154	41

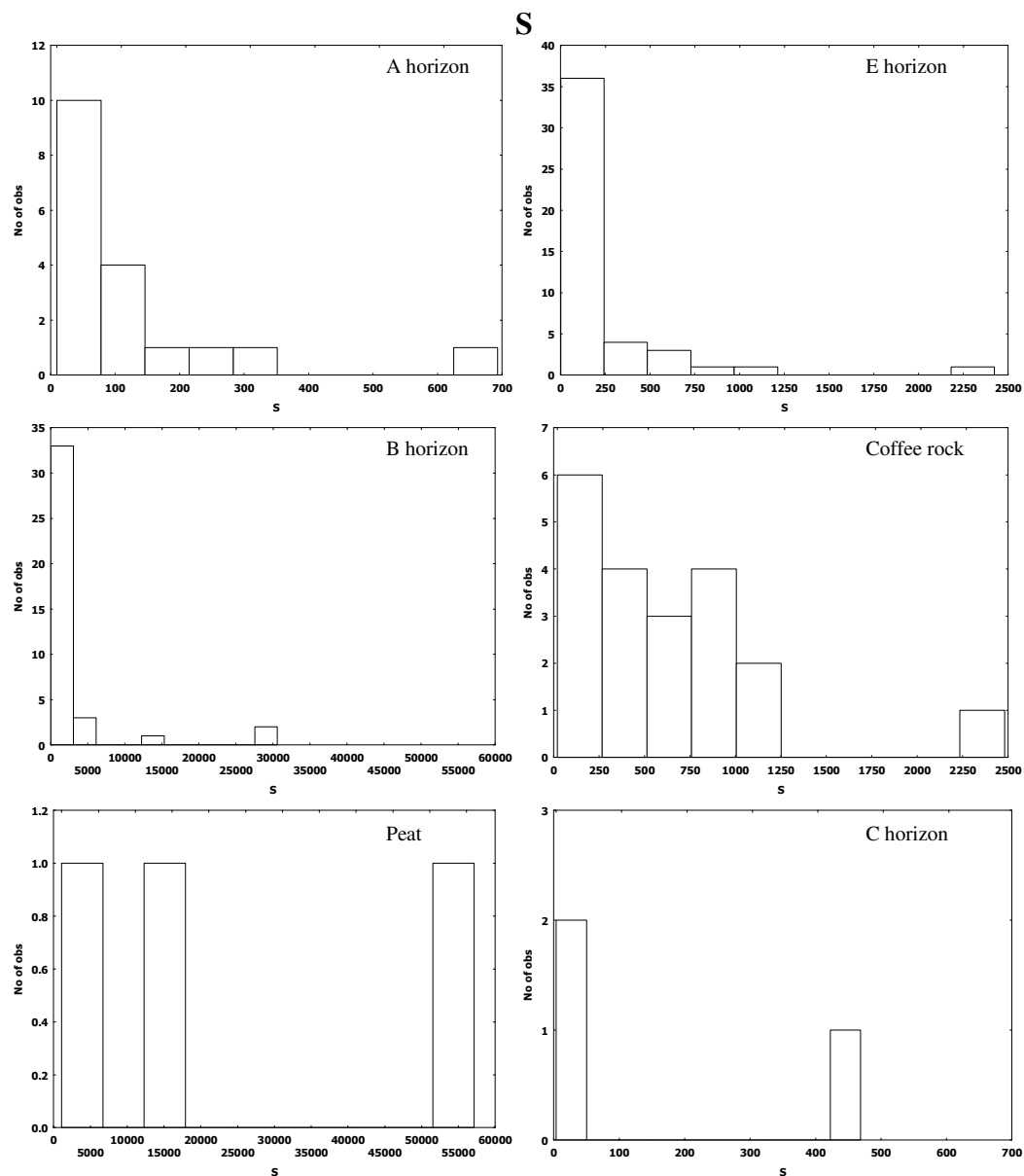
**Appendix Figure 36** Histograms for the concentration of zirconium (Zr) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (fusion acid digestion method; ICP-OES).

## P



Horizon	Valid N	Median	Min	Max	Std. Dev.
A horizon	18	12	4.3	1094	254
E horizon	46	3.8	1.0	59	12
B horizon	39	13	2.8	258	55
Coffee rock	20	21	4.4	172	39
Peat	3	67	66	72	3.0
C horizon	3	7.4	6.3	72	38
Mean values for normal surface soils worldwide 35-5300 mg kg <sup>-1</sup> *					

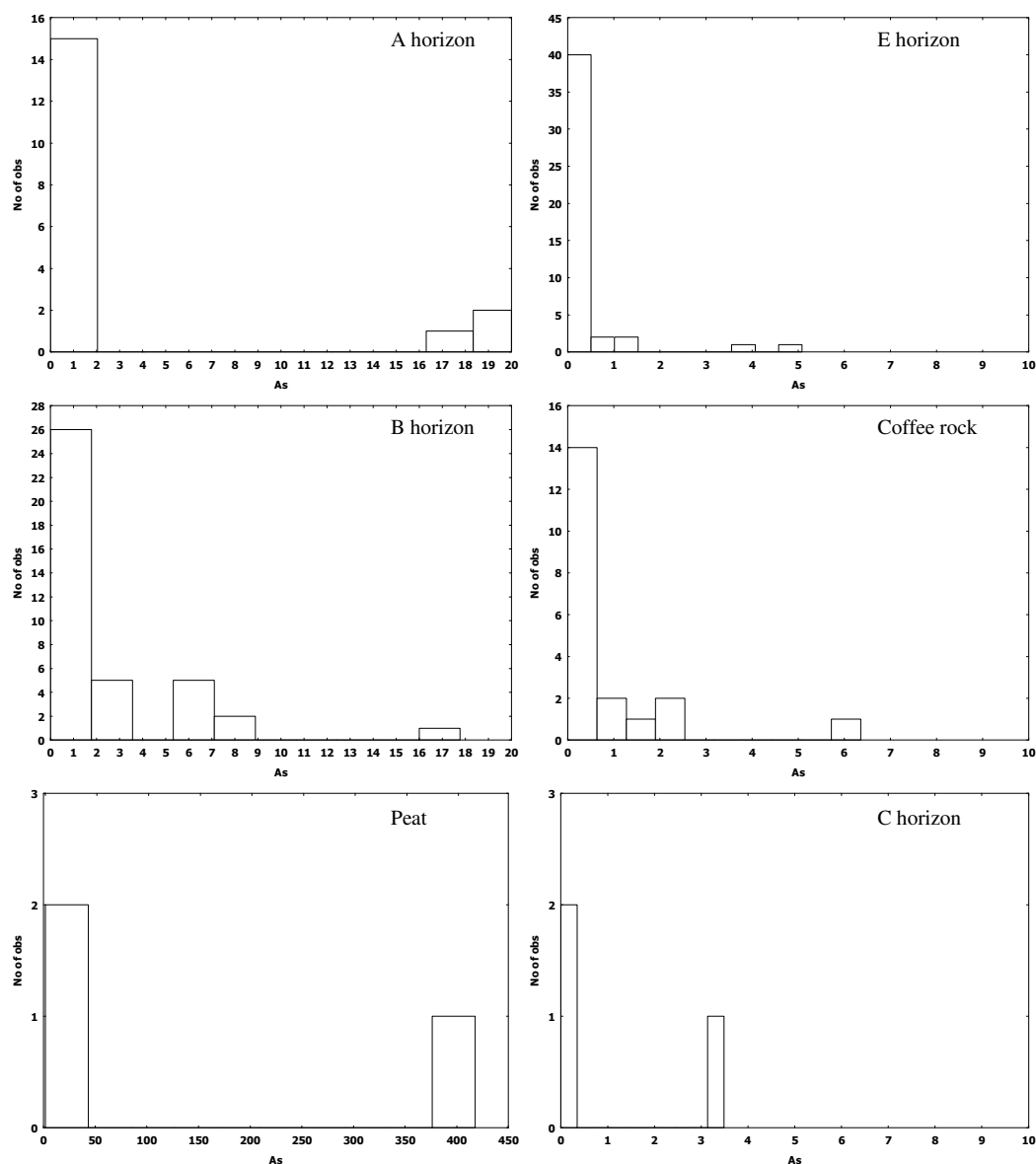
**Appendix Figure 37** Histograms for the concentration of phosphorus (P) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (aqua regia method; ICP-OES). \* Data are from Kabata-Pendias (2001), Essington (2004).



Horizon	Valid N	Median	Min	Max	Std. Dev.
A horizon	18	56	10	693	167
E horizon	46	37	1.3	2424	410
B horizon	39	308	17	30601	6860
Coffee rock	20	541	21	2482	559
Peat	3	12948	1102	57117	29521
C horizon	3	16	3.7	469	265
Mean values for normal surface soils worldwide 30-1600 mg kg <sup>-1</sup> *					

**Appendix Figure 38** Histograms for the concentration of sulfur (S) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (aqua regia method; ICP-OES). \* Data are from Kabata-Pendias (2001), Essington (2004).

## As

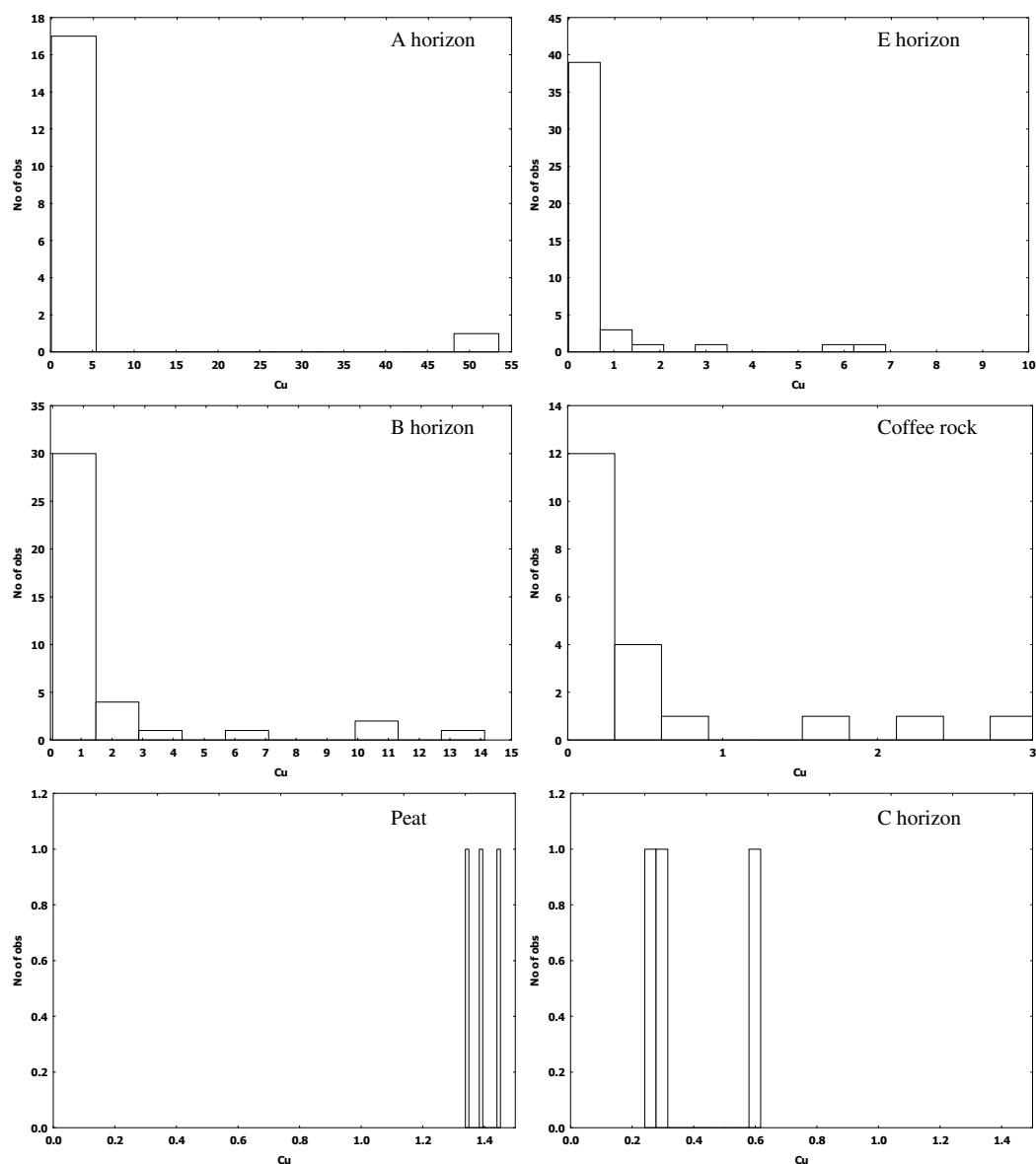


Horizon	Valid N	Median	Min	Max	Std. Dev.
A horizon	18	0.0021	nd	20	7.2
E horizon	46	0.070	nd	5.1	1.0
B horizon	39	0.29	nd	18	3.6
Coffee rock	20	0.20	nd	6.4	1.5
Peat	3	35	1.68	418	231
C horizon	3	nd	nd	3.5	2.0
Mean values for normal surface soils worldwide 4.4-9.3 mg kg <sup>-1</sup> *					
Critical soil concentration 20-50 mg kg <sup>-1</sup> **					

**Appendix Figure 39** Histograms for the concentration of arsenic (As) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (aqua regia method; ICP-OES). \* Data are from Kabata-Pendias (2001), Essington (2004); \*\* Data are from (Alloway, 1995).



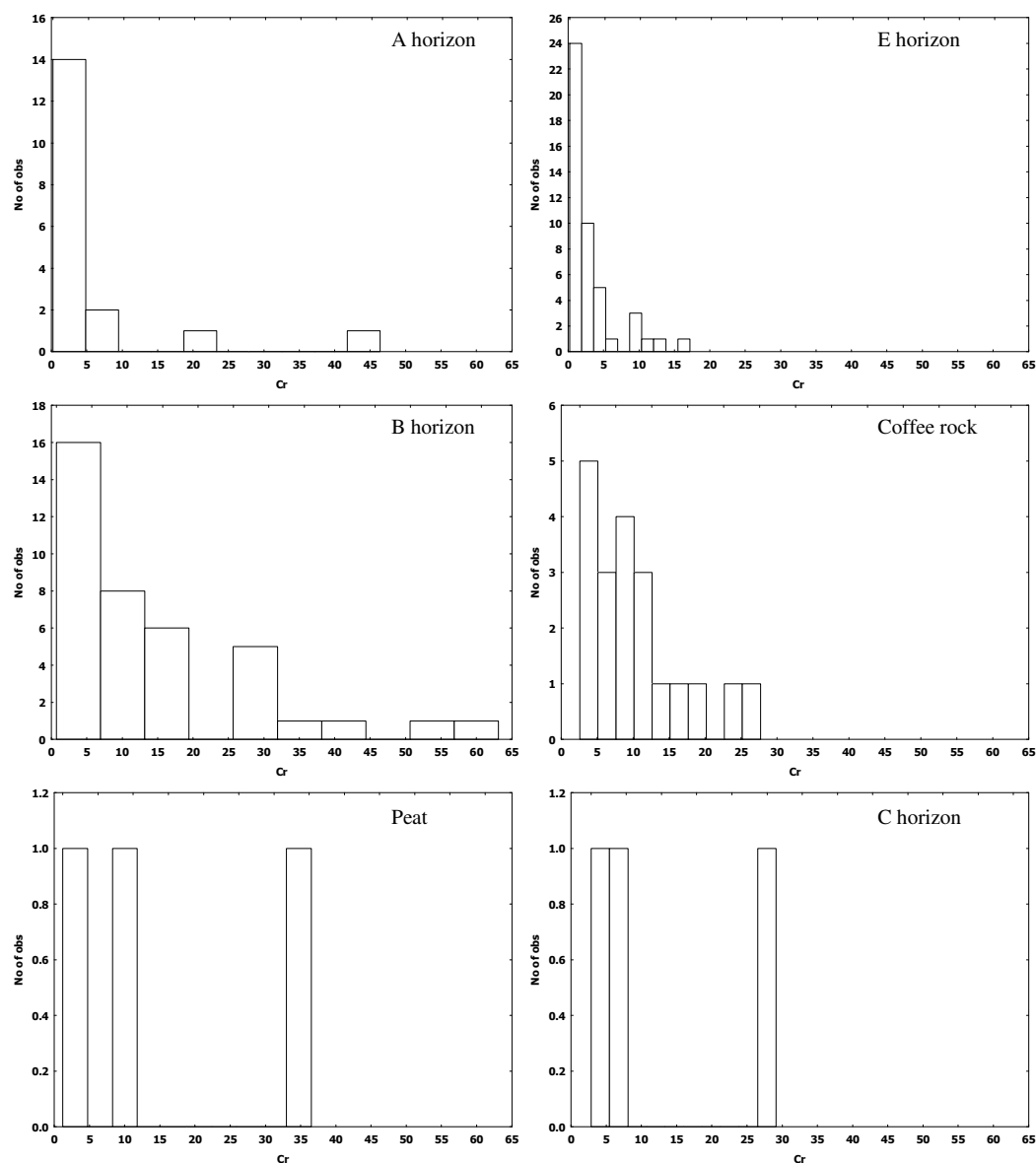
## Cu



Horizon	Valid N	Median	Min	Max	Std. Dev.
A horizon	18	0.73	0.11	54	12
E horizon	46	0.17	0.019	6.9	1.3
B horizon	39	0.40	0.069	14	3.2
Coffee rock	20	0.28	nd	3.0	0.79
Peat	3	1.4	1.34	1.5	0.057
C horizon	3	0.31	0.24	0.62	0.20
Mean values for normal surface soils worldwide 13-24 mg kg <sup>-1</sup> *					
Critical soil concentration 60-125 mg kg <sup>-1</sup> **					

**Appendix Figure 40** Histograms for the concentration of copper (Cu) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (aqua regia method; ICP-OES). \* Data are from Kabata-Pendias (2001), Essington (2004); \*\* Data are from (Alloway, 1995).

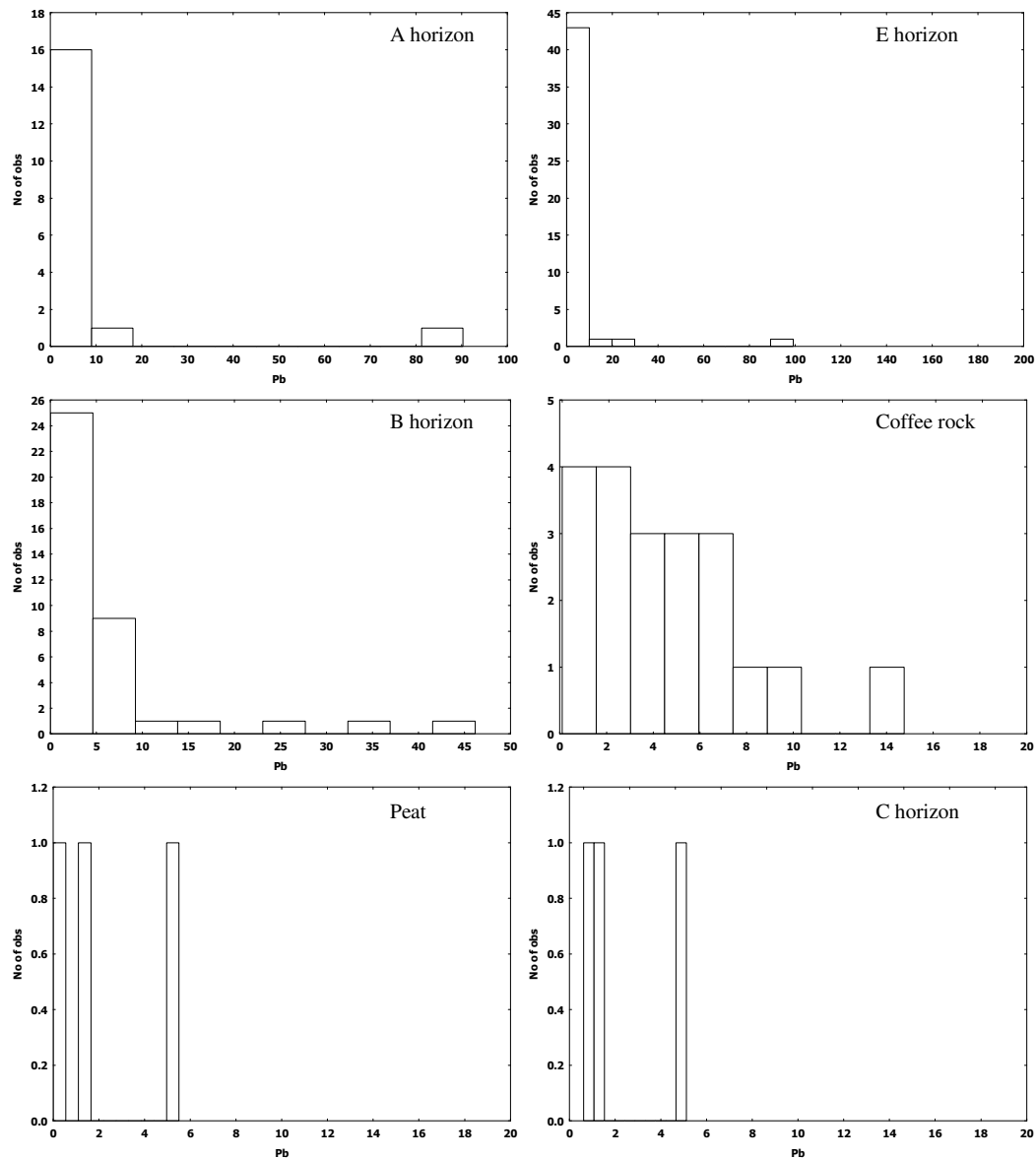
## Cr



Horizon	Valid N	Median	Min	Max	Std. Dev.
A horizon	18	0.89	0.23	46	11
E horizon	46	1.8	0.22	17	3.7
B horizon	39	10	0.70	63	15
Coffee rock	20	8.8	2.6	28	6.8
Peat	3	9.7	1.2	36	18
C horizon	3	7.2	2.8	29	14
Mean values for normal surface soils worldwide 12-83 mg kg <sup>-1</sup> *					
Critical soil concentration 75-100 mg kg <sup>-1</sup> **					

**Appendix Figure 41** Histograms for the concentration of chromium (Cr) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (aqua regia method; ICP-OES). \* Data are from Kabata-Pendias (2001), Essington (2004); \*\* Data are from (Alloway, 1995).

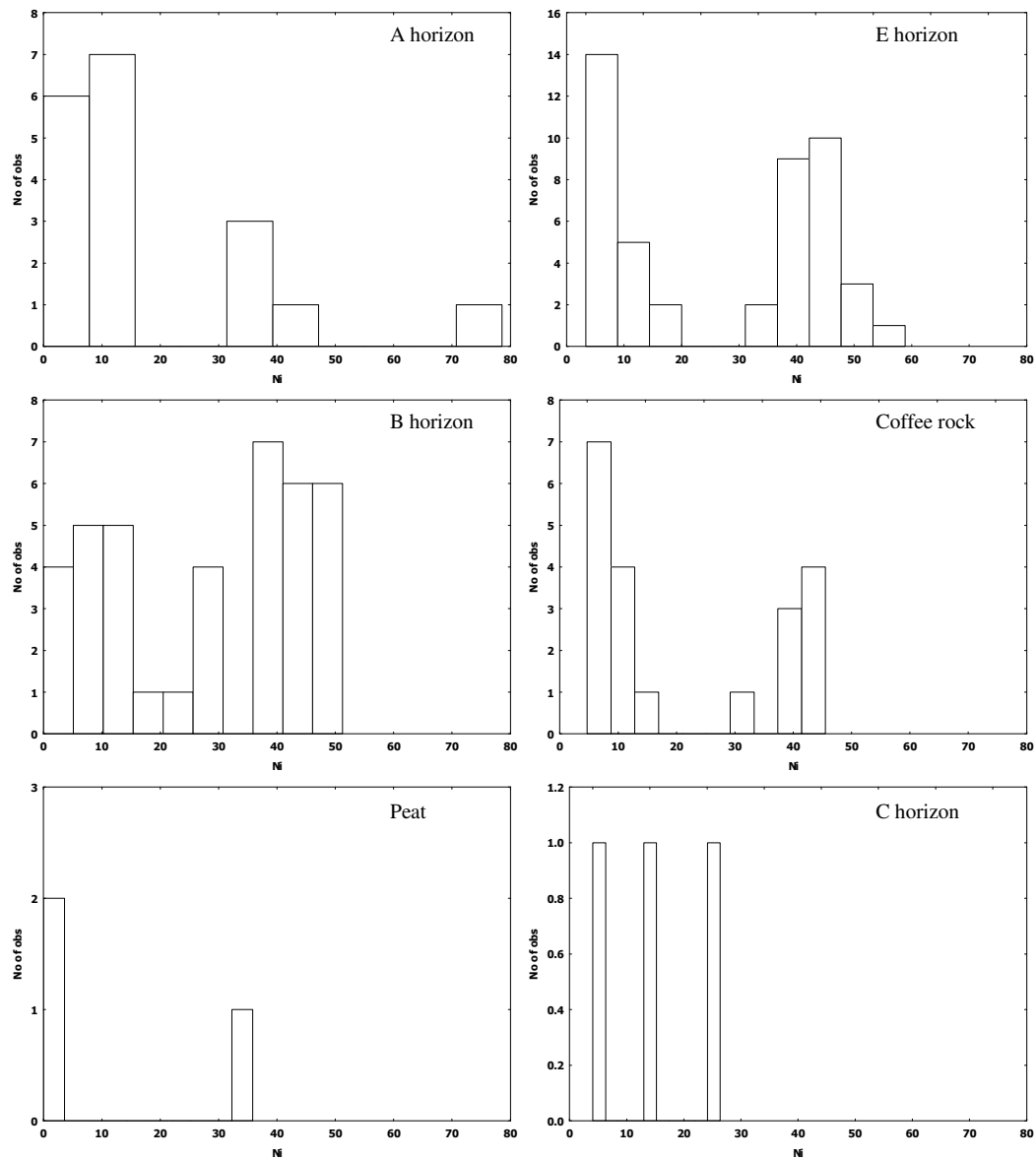
## Pb



Horizon	Valid N	Median	Min	Max	Std. Dev.
A horizon	18	0.69	nd	90	21
E horizon	46	0.68	nd	99	15
B horizon	39	1.9	nd	46	10
Coffee rock	20	4.2	0.10	15	3.6
Peat	3	1.3	nd	5.5	2.9
C horizon	3	1.1	0.62	5.1	2.5
Mean values for normal surface soils worldwide 22-44 mg kg <sup>-1</sup> *					
Critical soil concentration 100-400 mg kg <sup>-1</sup> **					

**Appendix Figure 42** Histograms for the concentration of lead (Pb) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (aqua regia method; ICP-OES). \* Data are from Kabata-Pendias (2001), Essington (2004); \*\* Data are from (Alloway, 1995).

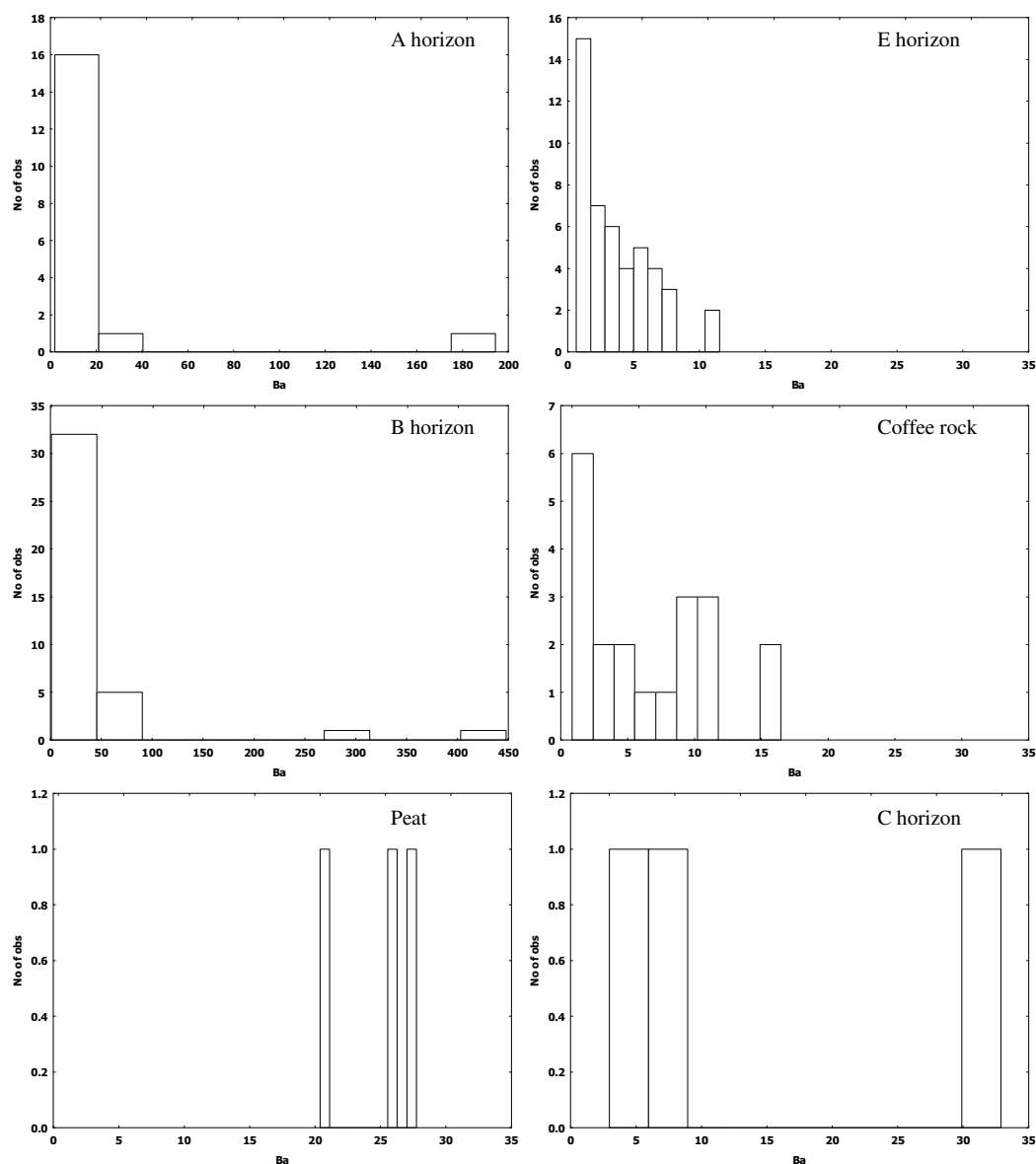
## Ni



Horizon	Valid N	Median	Min	Max	Std. Dev.
A horizon	18	9	nd	79	20
E horizon	46	36	3.3	59	18
B horizon	39	29	nd	51	18
Coffee rock	20	12	4.7	46	17
Peat	3	nd	nd	36	21
C horizon	3	13	4.1	26	11
Mean values for normal surface soils worldwide 13-34 mg kg <sup>-1</sup> *					
Critical soil concentration 100 mg kg <sup>-1</sup> **					

**Appendix Figure 43** Histograms for the concentration of nickel (Ni) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (fusion acid digestion method; ICP-OES). \* Data are from Kabata-Pendias (2001), Essington (2004); \*\* Data are from (Alloway, 1995).

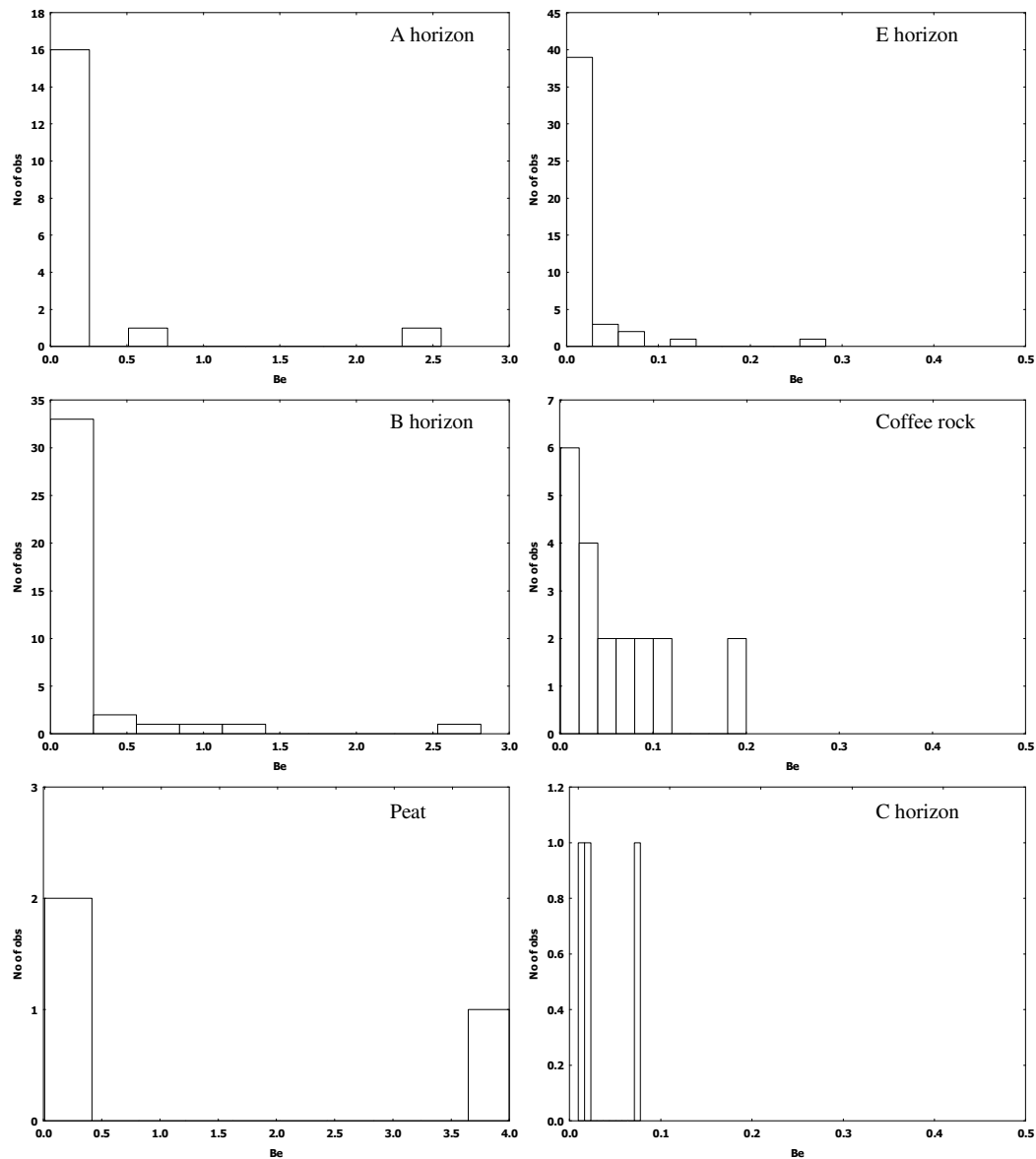
## Ba



Horizon	Valid N	Median	Min	Max	Std. Dev.
A horizon	18	4.5	1.9	194	45
E horizon	46	3.0	0.65	12	2.8
B horizon	39	8.8	0.82	448	83
Coffee rock	20	5.6	0.85	16	4.8
Peat	3	26	20	28	3.8
C horizon	3	8.2	3.0	33	16
Maximum barium content observed in soils 500-700 mg kg <sup>-1</sup> *					

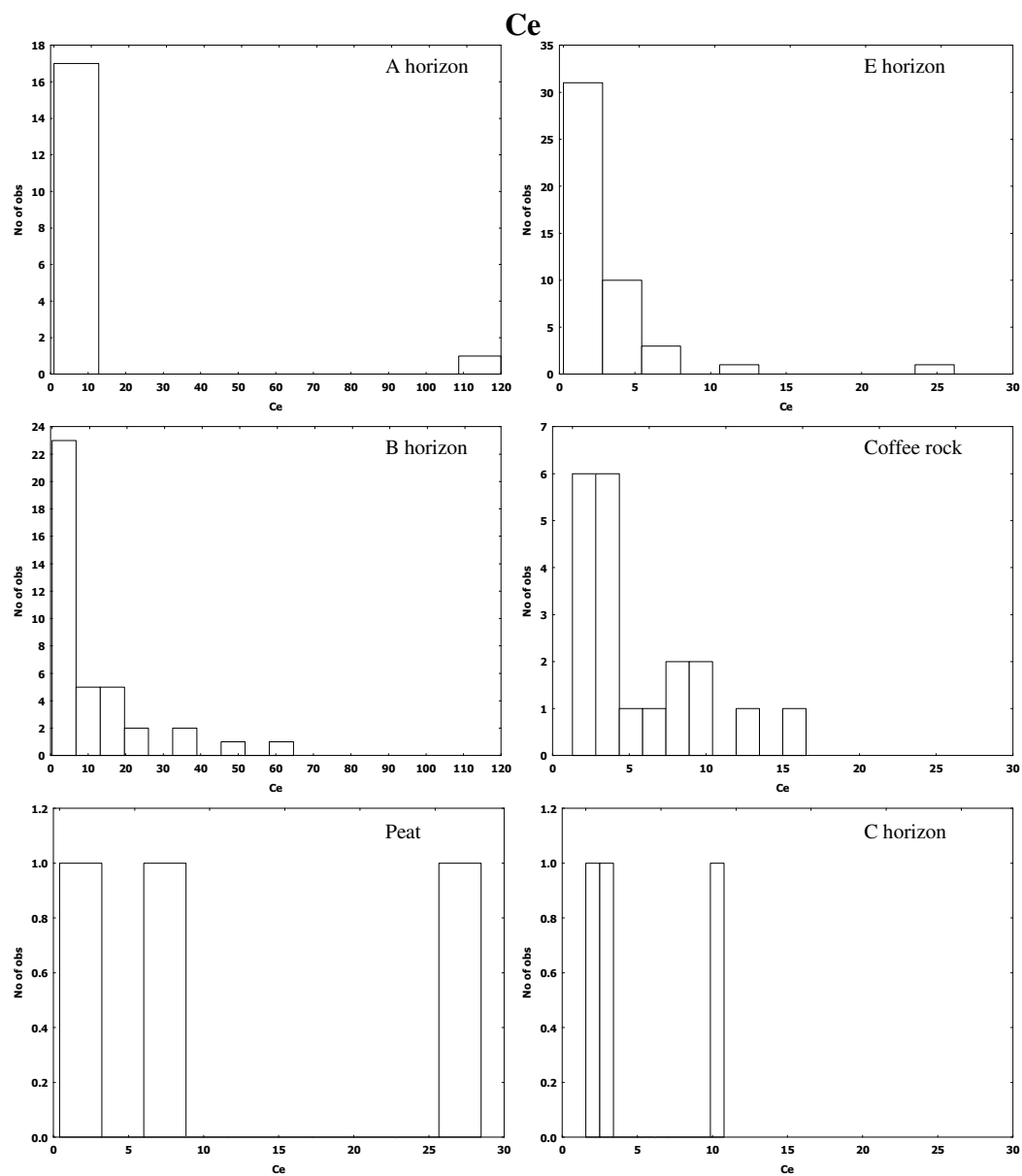
**Appendix Figure 44** Histograms for the concentration of barium (Ba) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (aqua regia method; ICP-OES). \* Data are from Crompton (2006).

## Be



Horizon	Valid N	Median	Min	Max	Std. Dev.
A horizon	18	0.0078	0.00029	2.6	0.61
E horizon	46	0.0047	nd	0.28	0.05
B horizon	39	0.032	nd	2.8	0.51
Coffee rock	20	0.044	0.00087	0.20	0.06
Peat	3	0.19	0.011	4.0	2.3
C horizon	3	0.017	0.010	0.078	0.04
Mean values for normal surface soils worldwide 0.35-3.52 mg kg <sup>-1</sup> *					

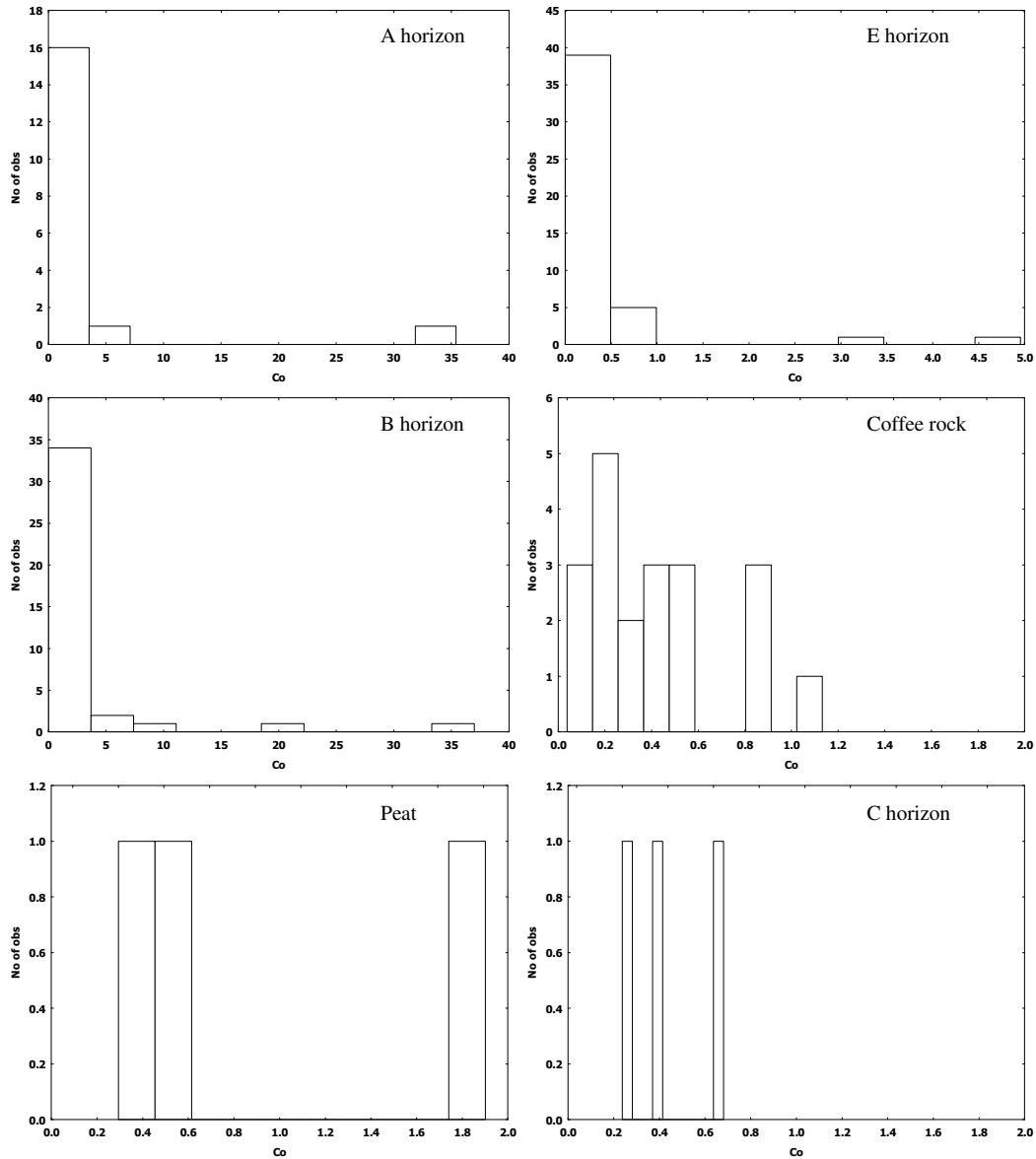
**Appendix Figure 45** Histograms for the concentration of beryllium (Be) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (aqua regia method; ICP-OES). \* Data are from Kabata-Pendias (2001), Essington (2004).



Horizon	Valid N	Median	Min	Max	Std. Dev.
A horizon	18	1.6	0.87	121	28
E horizon	46	1.8	0.27	26	4
B horizon	39	4.2	0.39	65	14
Coffee rock	20	3.7	1.3	17	4
Peat	3	8.2	0.41	28	14
C horizon	3	3.2	1.6	11	5

**Appendix Figure 46** Histograms for the concentration of cerium (Ce) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (aqua regia method; ICP-OES).

## Co

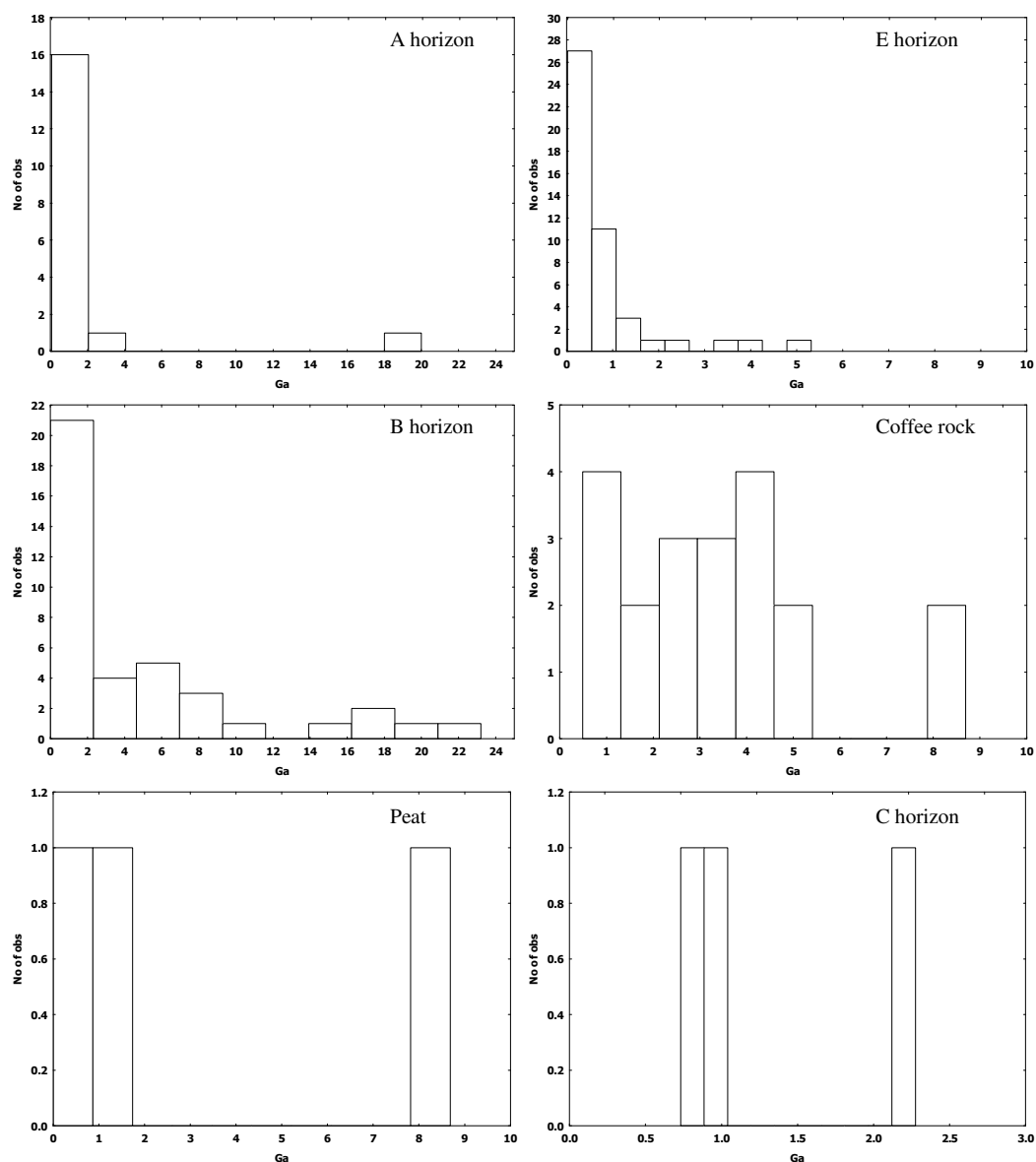


Horizon	Valid N	Median	Min	Max	Std.Dev.
A horizon	18	0.19	0.0066	35	8.3
E horizon	46	0.12	nd	5.0	0.84
B horizon	39	0.34	nd	37	6.7
Coffee rock	20	0.36	0.038	1.13	0.30
Peat	3	0.56	0.29	1.90	0.86
C horizon	3	0.38	0.24	0.68	0.23
Mean values for normal surface soils worldwide 4.5-12 mg kg <sup>-1</sup> *					
Critical soil concentration 25-50 mg kg <sup>-1</sup> **					

**Appendix Figure 47** Histograms for the concentration of cobalt (Co) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (aqua regia method; ICP-OES). \* Data are from Kabata-Pendias (2001), Essington (2004); \*\* Data are from (Alloway, 1995).



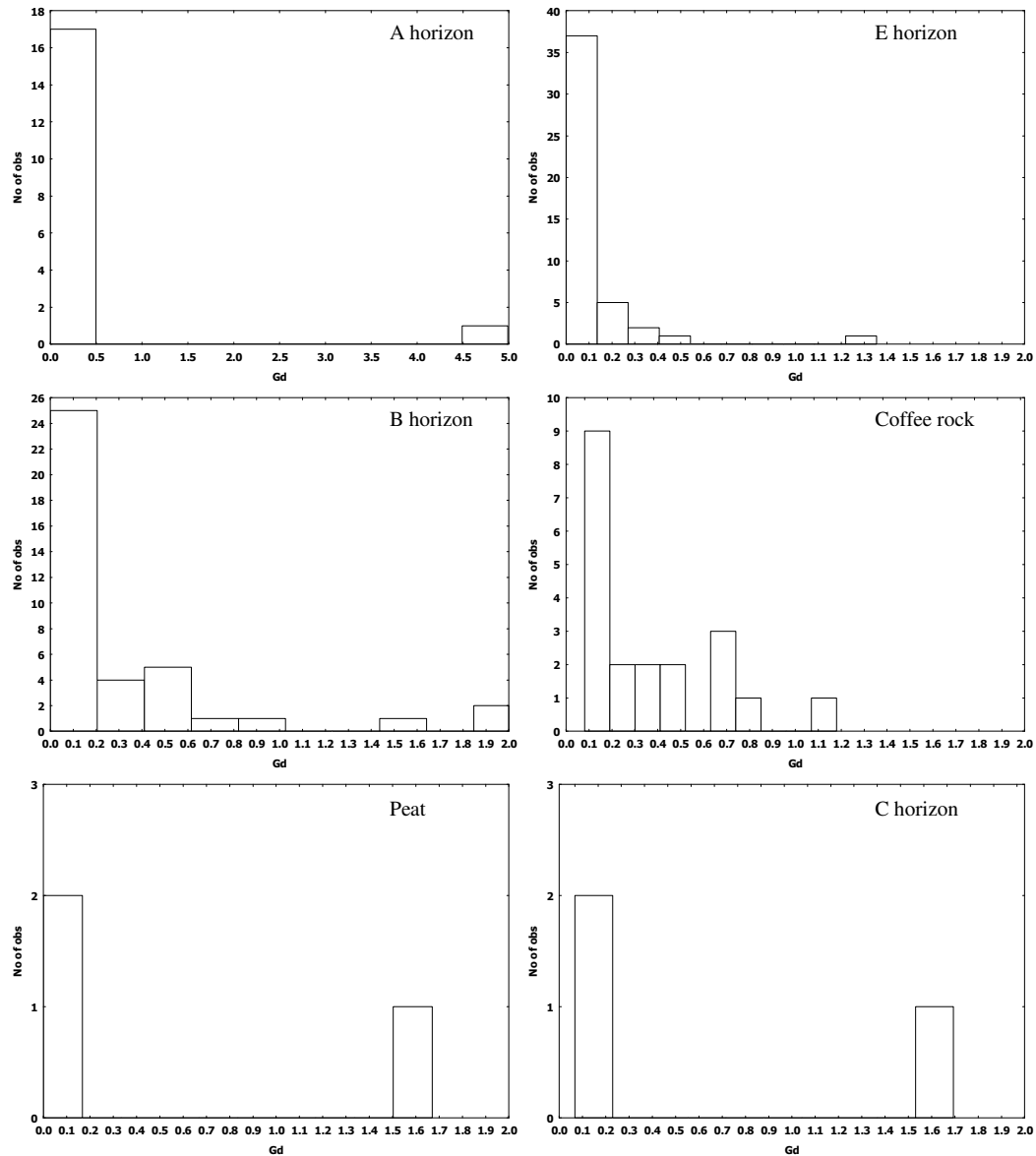
## Ga



Horizon	Valid N	Median	Min	Max	Std.Dev.
A horizon	18	0.26	0.064	20	4.7
E horizon	46	0.43	0.017	5.3	1.1
B horizon	39	1.5	nd	23	6.0
Coffee rock	20	3.4	0.49	8.7	2.2
Peat	3	1.49	nd	8.7	4.6
C horizon	3	1.0	0.73	2.3	0.8
Mean values for normal surface soils worldwide 1-70 mg kg <sup>-1</sup> *					

**Appendix Figure 48** Histograms for the concentration of gallium (Ga) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (aqua regia method; ICP-OES). \* Data are from Kabata-Pendias (2001), Essington (2004).

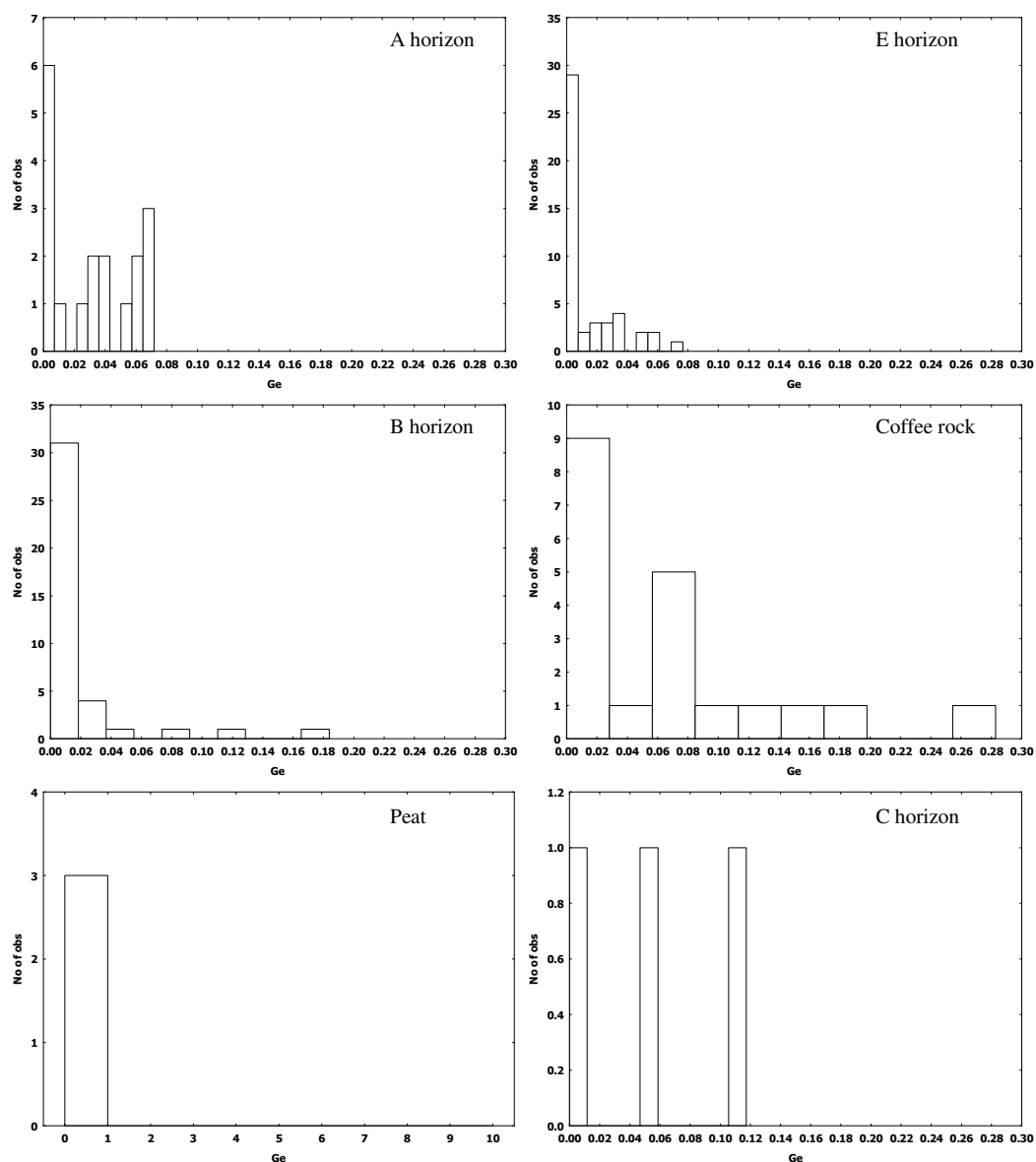
## Gd



Horizon	Valid N	Median	Min	Max	Std.Dev.
A horizon	18	0.082	nd	5.0	1.2
E horizon	46	0.076	nd	1.4	0.20
B horizon	39	0.089	nd	2.1	0.52
Coffee rock	20	0.21	0.081	1.2	0.30
Peat	3	nd	nd	1.7	0.96
C horizon	3	0.10	0.067	1.7	0.93

**Appendix Figure 49** Histograms for the concentration of gadolinium (Gd) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (aqua regia method; ICP-OES).

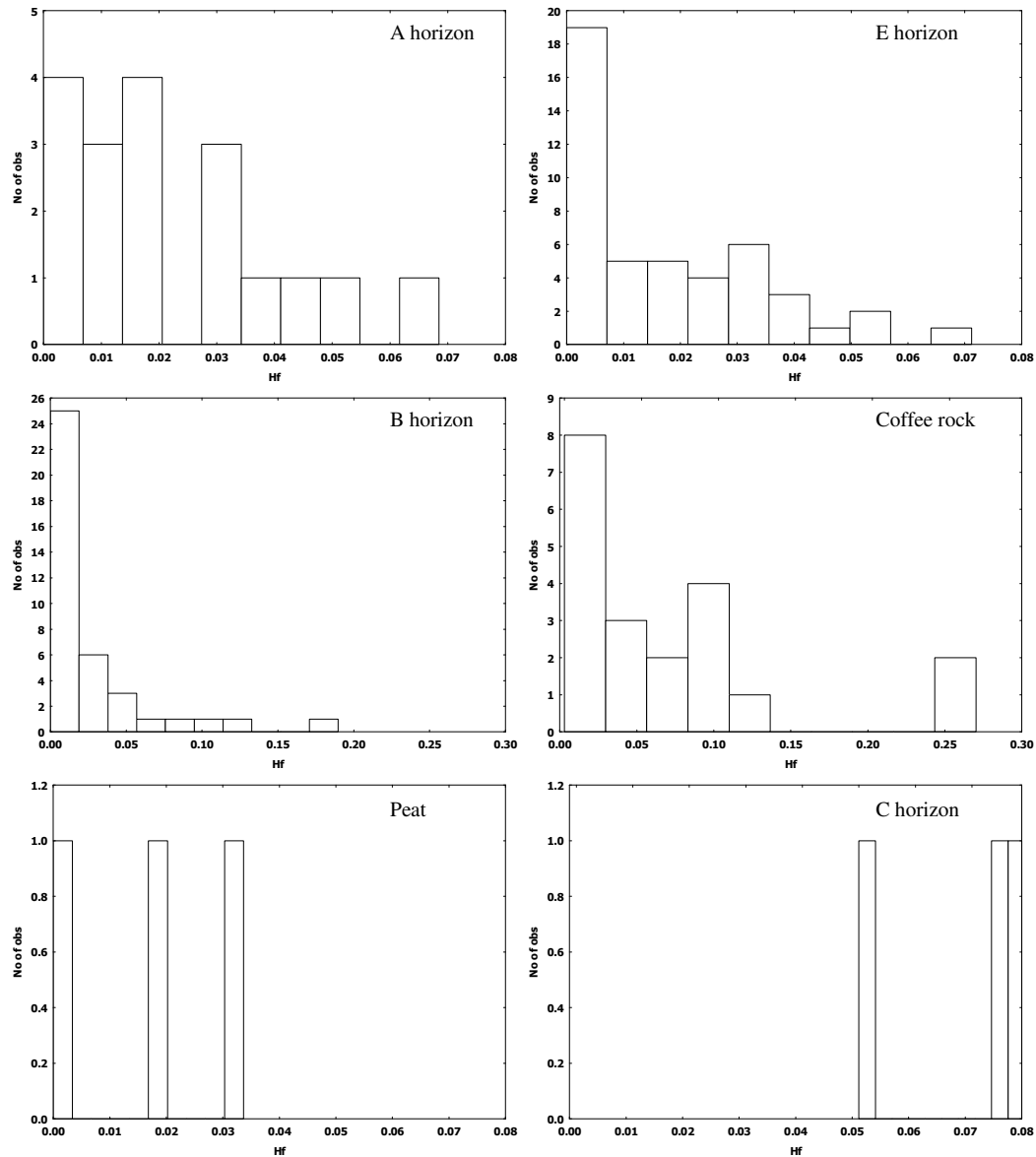
## Ge



Horizon	Valid N	Median	Min	Max	Std.Dev.
A horizon	18	0.033	nd	0.072	0.028
E horizon	46	0.000010	nd	0.077	0.020
B horizon	39	nd	nd	0.18	0.037
Coffee rock	20	0.055	nd	0.28	0.076
Peat	3	nd	nd	nd	nd
C horizon	3	0.052	nd	0.12	0.059

**Appendix Figure 50** Histograms for the concentration of germanium (Ge) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (aqua regia method; ICP-OES).

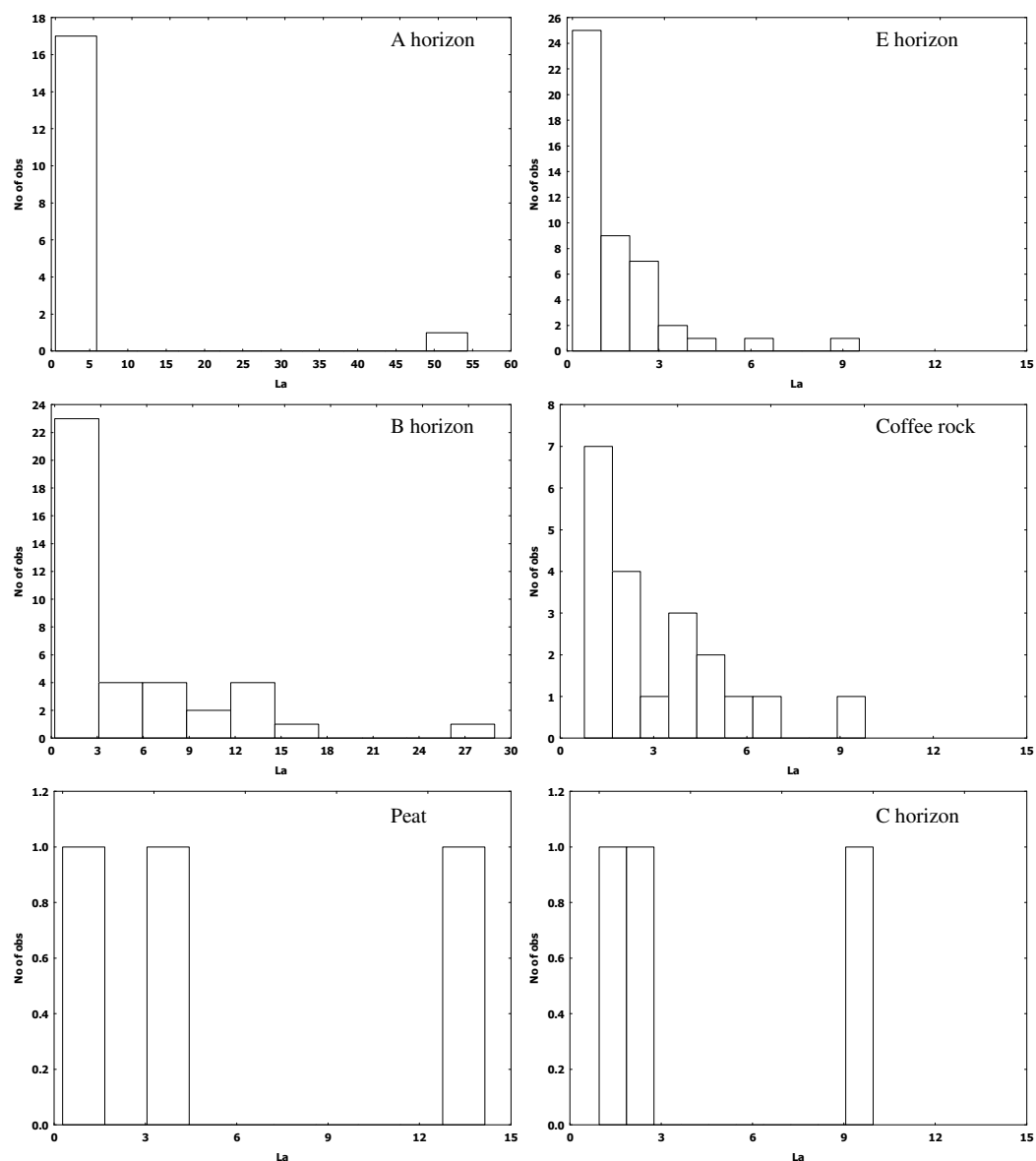
## Hf



Horizon	Valid N	Median	Min	Max	Std.Dev.
A horizon	18	0.022	0.015	nd	0.069
E horizon	46	0.017	0.011	nd	0.071
B horizon	39	0.025	0.008	nd	0.19
Coffee rock	20	0.072	0.045	0.0031	0.27
Peat	3	0.018	0.019	nd	0.034
C horizon	3	0.069	0.076	0.051	0.081
Maximum hafnium content observed in soils 0.6-4.1 mg kg <sup>-1</sup> *					

**Appendix Figure 51** Histograms for the concentration of hafnium (Hf) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (aqua regia method; ICP-OES). \* Data are from Crompton (2006).

## La

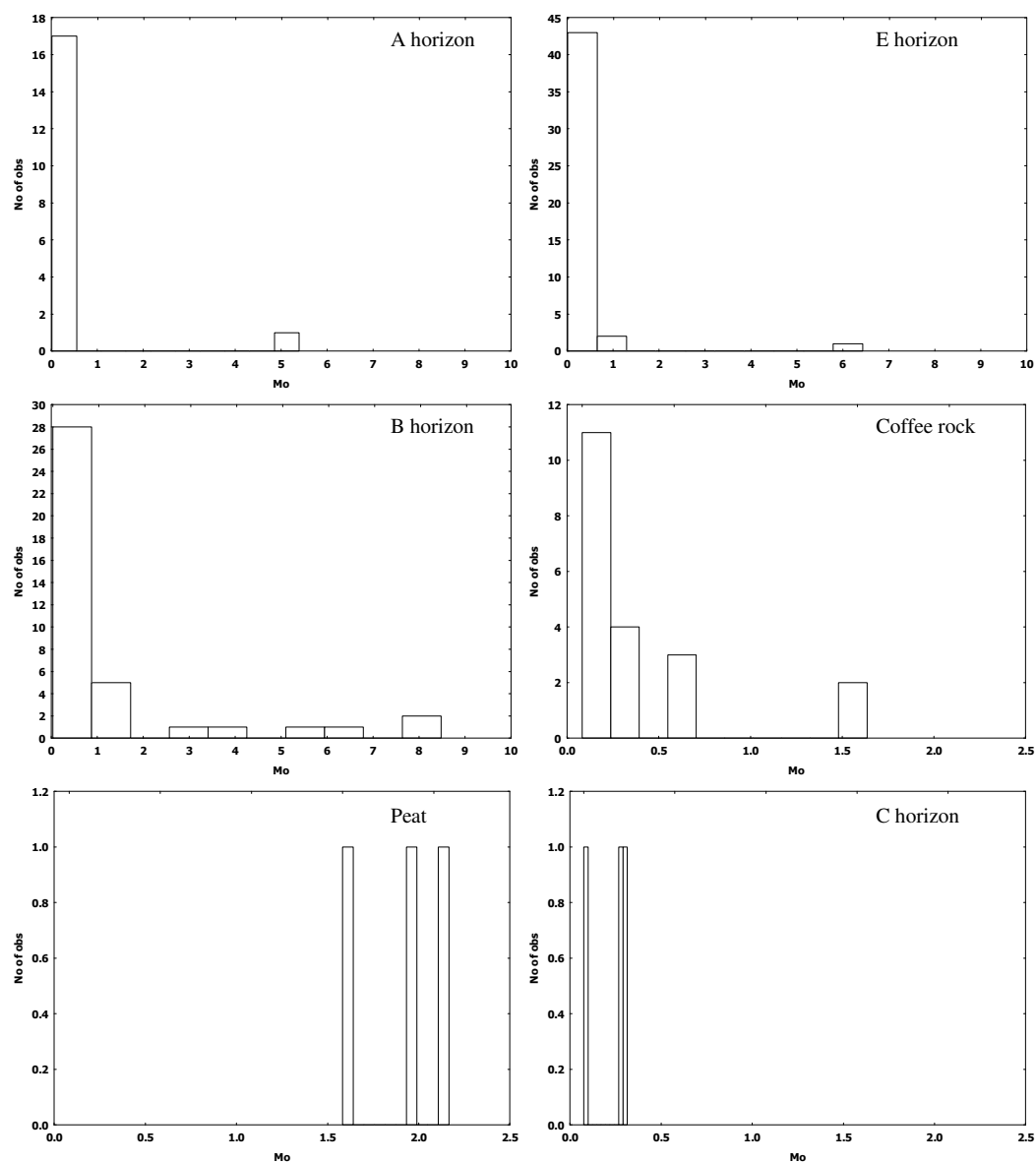


Horizon	Valid N	Median	Min	Max	Std.Dev.
A horizon	18	1.03	0.52	54	13
E horizon	46	1.03	0.18	10	1.7
B horizon	39	2.4	0.23	29	5.9
Coffee rock	20	2.3	0.77	10	2.4
Peat	3	4.3	0.28	14	7.1
C horizon	3	2.1	0.96	10	4.9

Maximum hafnium content observed in soils 15-47 mg kg<sup>-1</sup>\*

**Appendix Figure 52** Histograms for the concentration of lanthanum (La) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (aqua regia method; ICP-OES). \* Data are from Crompton (2006).

## Mo

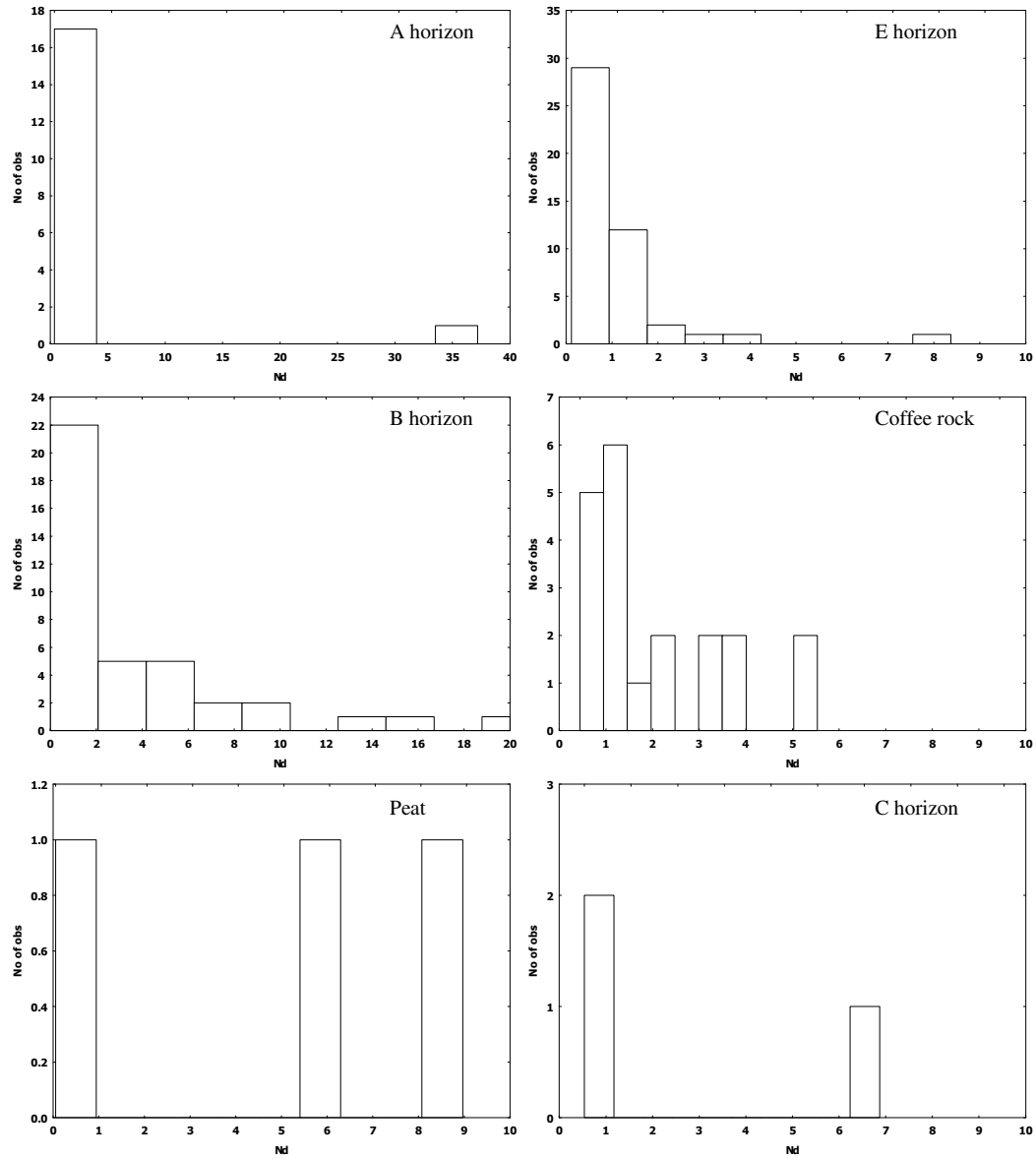


Horizon	Valid N	Median	Min	Max	Std.Dev.
A horizon	18	0.13	0.013	5.4	1.24
E horizon	46	0.095	0.013	6.4	0.95
B horizon	39	0.34	0.034	8.5	2.18
Coffee rock	20	0.20	0.083	1.6	0.44
Peat	3	1.9	1.6	2.2	0.29
C horizon	3	0.28	0.075	0.31	0.13

Maximum hafnium content observed in soils 0.2-437 mg kg<sup>-1</sup>\*

**Appendix Figure 53** Histograms for the concentration of molybdenum (Mo) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (aqua regia method; ICP-OES). \* Data are from Crompton (2006).

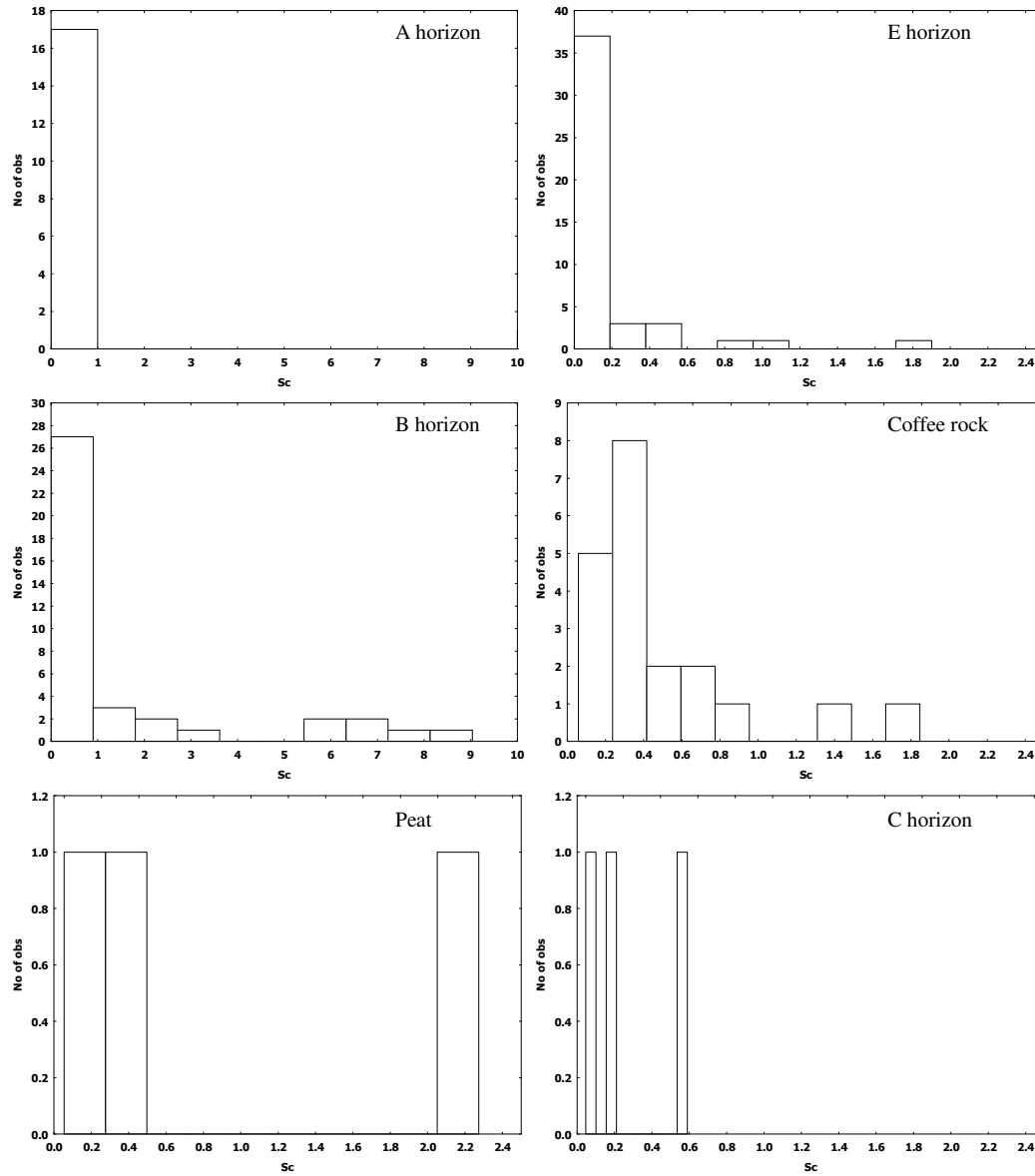
## Nd



Horizon	Valid N	Median	Min	Max	Std.Dev.
A horizon	18	0.60	0.35	37	8.6
E horizon	46	0.65	0.11	8.4	1.3
B horizon	39	1.5	nd	21	4.7
Coffee rock	20	1.4	0.44	5.5	1.6
Peat	3	5.4	0.054	9.0	4.5
C horizon	3	1.0	0.54	6.9	3.5

**Appendix Figure 54** Histograms for the concentration of neodymium (Nd) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (aqua regia method; ICP-OES).

## Sc

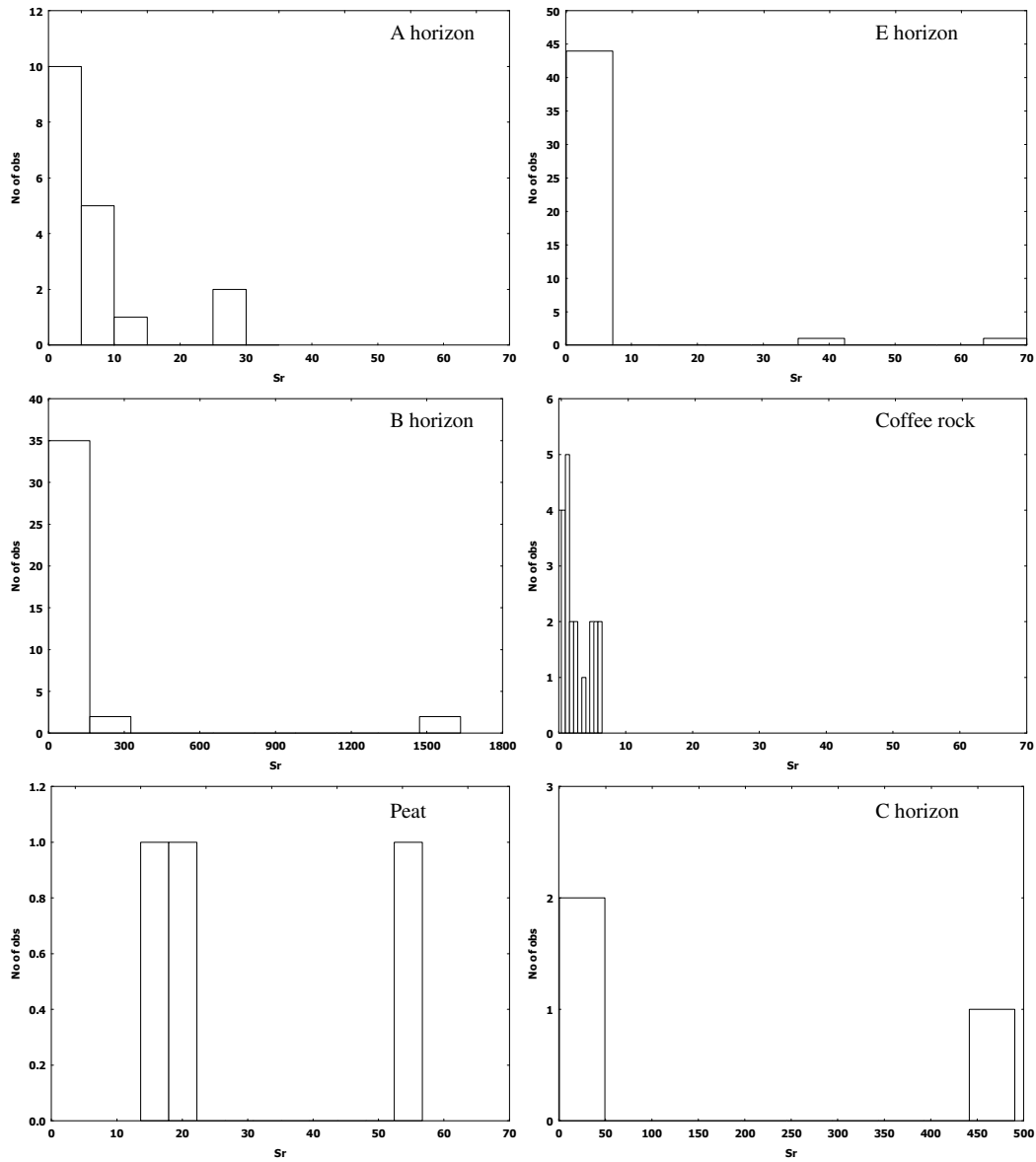


Horizon	Valid N	Median	Min	Max	Std.Dev.
A horizon	18	0.042	0.0030	10.1	2.4
E horizon	46	0.051	nd	1.9	0.34
B horizon	39	0.23	nd	9.0	2.5
Coffee rock	20	0.29	0.058	1.8	0.45
Peat	3	0.38	0.054	2.3	1.2
C horizon	3	0.17	0.046	0.59	0.29

**Appendix Figure 55** Histograms for the concentration of scandium (Sc) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (aqua regia method; ICP-OES).



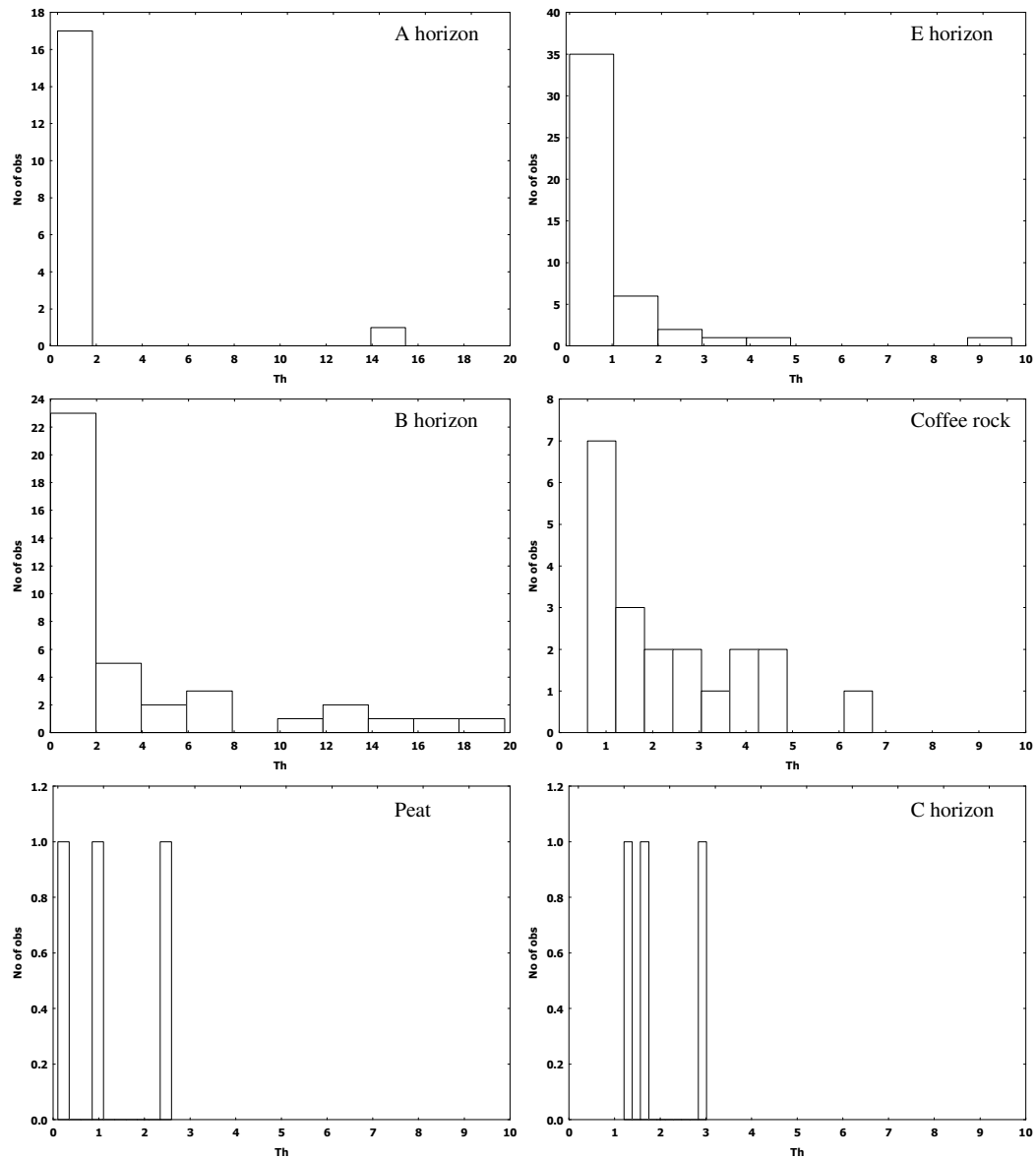
## Sr



Horizon	Valid N	Median	Min	Max	Std.Dev.
A horizon	18	4.5	0.29	29	8.1
E horizon	46	0.40	0.11	70	12
B horizon	39	1.9	0.28	1634	356
Coffee rock	20	1.8	0.38	6.5	2.09
Peat	3	20	14	57	23
C horizon	3	1.08	0.56	490	283
Mean values for normal surface soils worldwide 87-210 mg kg <sup>-1</sup> *					

**Appendix Figure 56** Histograms for the concentration of strontium (Sr) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (aqua regia method; ICP-OES). \* Data are from Kabata-Pendias (2001), Essington (2004).

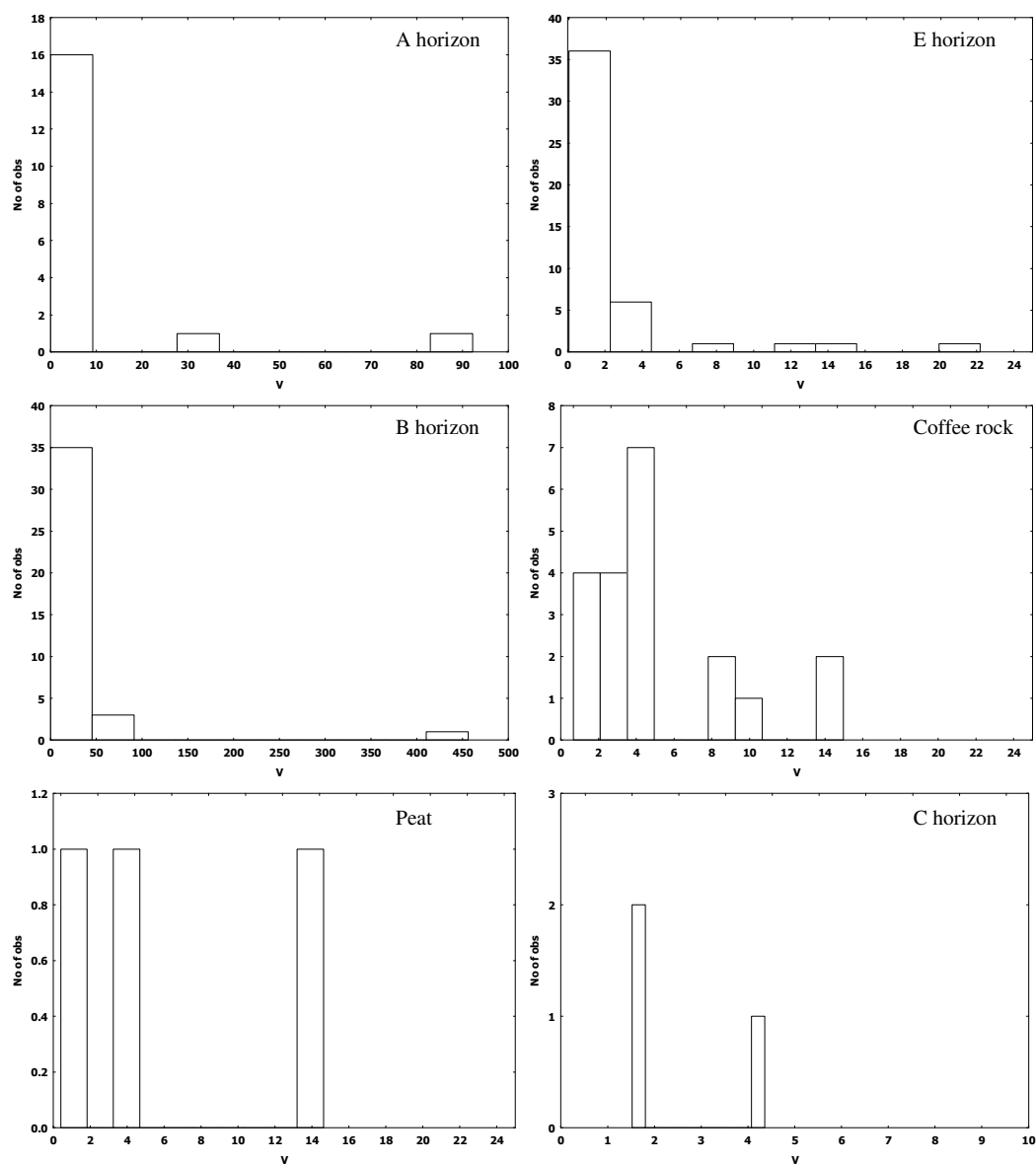
## Th



Horizon	Valid N	Median	Min	Max	Std.Dev.
A horizon	18	0.48	0.32	15	3.5
E horizon	46	0.58	0.074	10	1.5
B horizon	39	1.3	0.011	20	5.2
Coffee rock	20	1.7	0.60	6.7	1.7
Peat	3	1.1	0.10	2.6	1.3
C horizon	3	1.6	1.2	3.0	0.9

**Appendix Figure 57** Histograms for the concentration of thorium (Th) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (aqua regia method; ICP-OES).

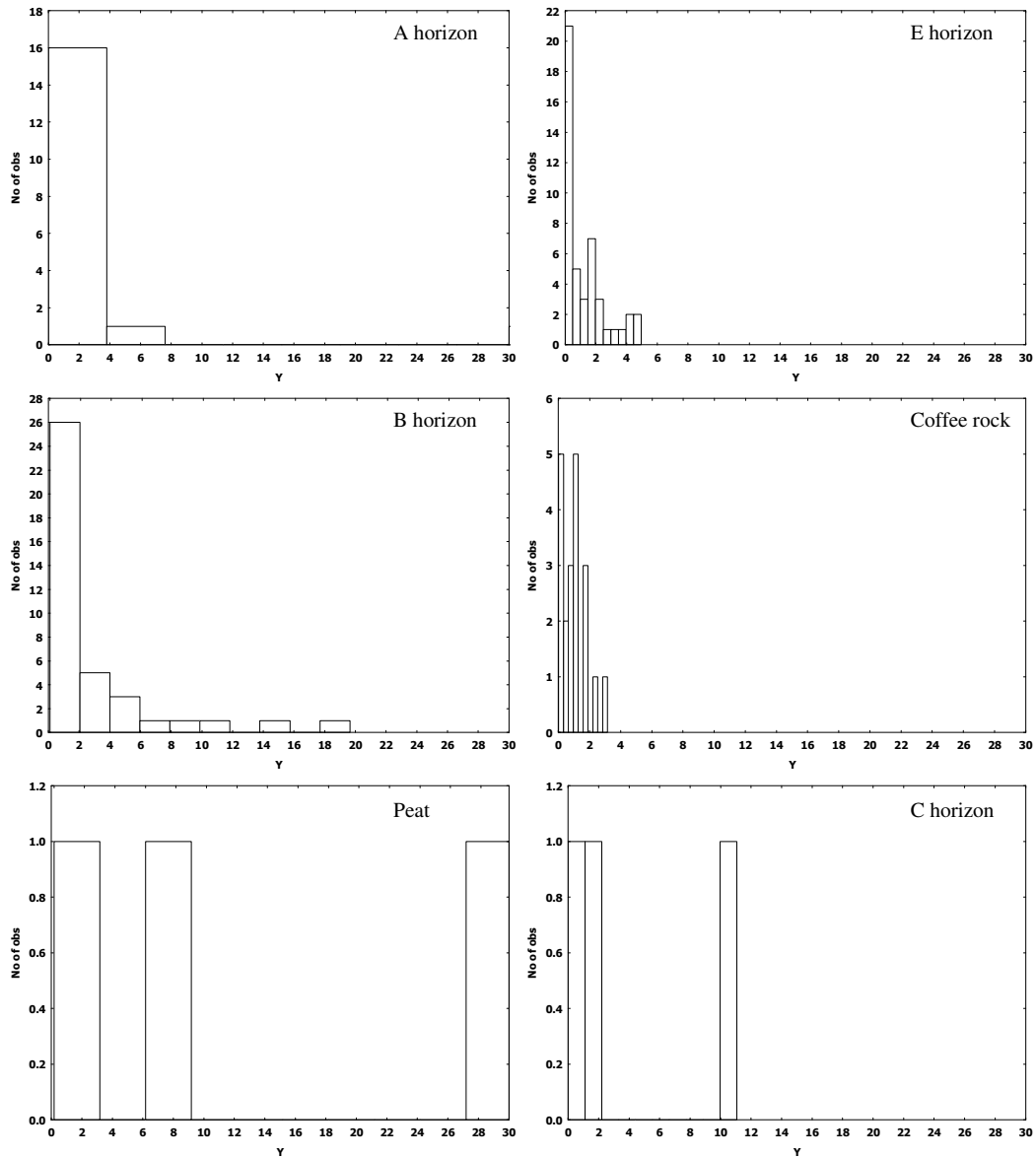
## V



Horizon	Valid N	Median	Min	Max	Std.Dev.
A horizon	18	0.90	0.015	92	22
E horizon	46	1.05	0.076	22	4.1
B horizon	39	2.3	nd	456	74
Coffee rock	20	4.0	0.66	15	4.04
Peat	3	4.2	0.41	15	7.4
C horizon	3	1.8	1.5	4.4	1.6
Mean values for normal surface soils worldwide 18-115 mg kg <sup>-1</sup> *					
Critical soil concentration 50-100 mg kg <sup>-1</sup> **					

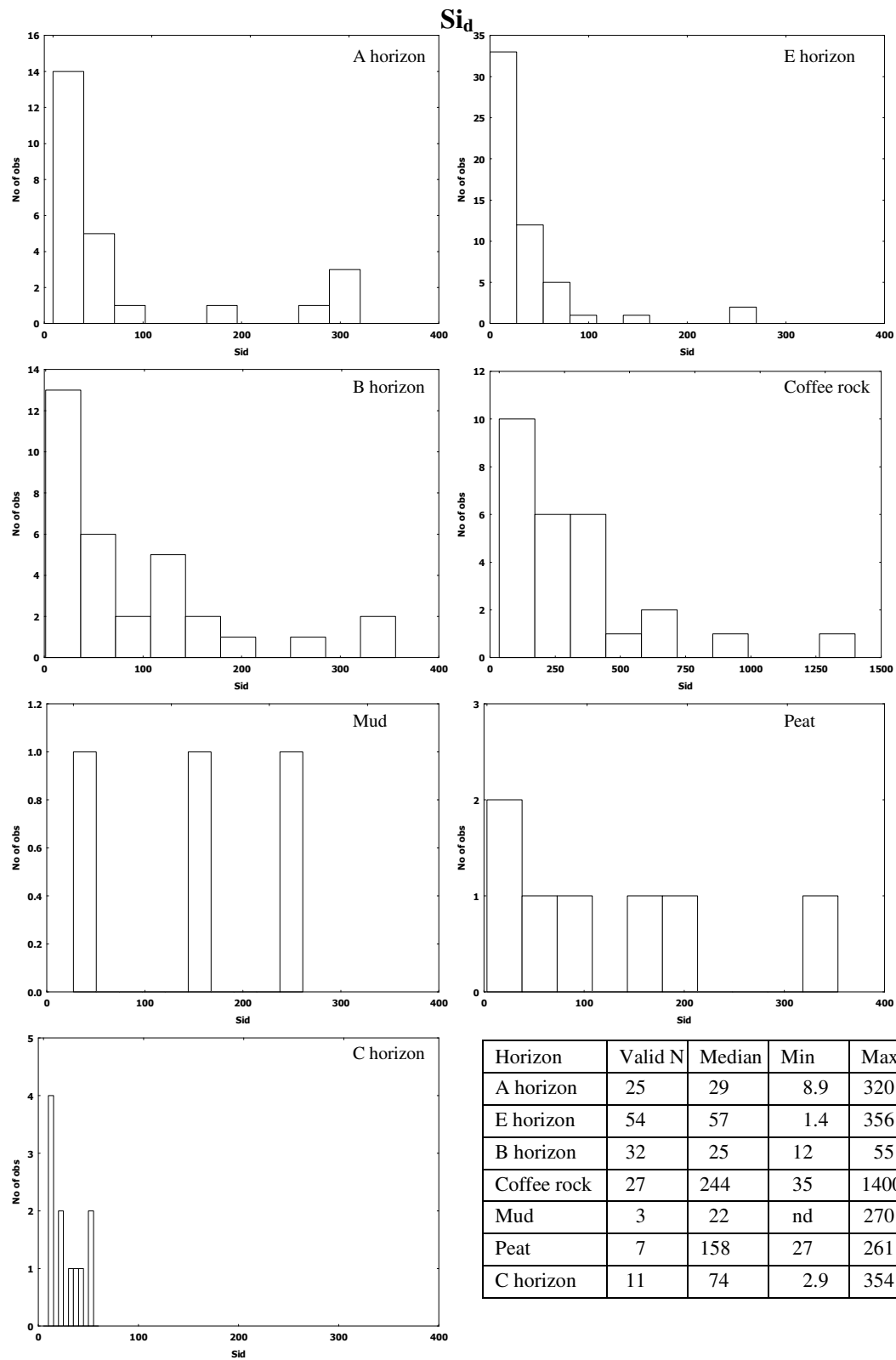
**Appendix Figure 58** Histograms for the concentration of vanadium (V) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (aqua regia method; ICP-OES). \* Data are from Kabata-Pendias (2001), Essington (2004); \*\* Data are from (Alloway, 1995).

# Y

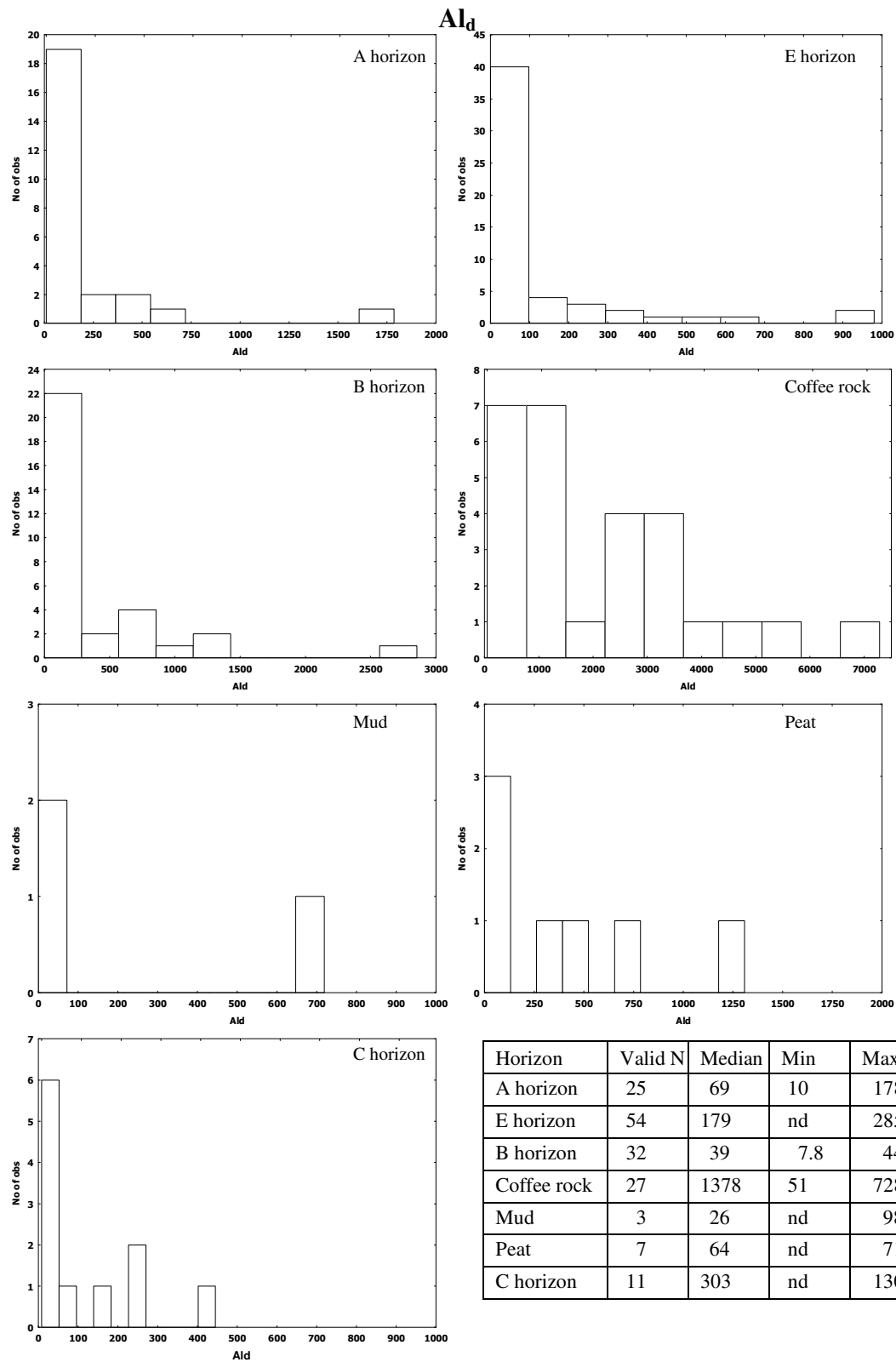


Horizon	Valid N	Median	Min	Max	Std.Dev.
A horizon	18	1.5	nd	38	8.7
E horizon	46	0.59	nd	5.0	1.4
B horizon	39	1.5	0.10	20	4.4
Coffee rock	20	0.97	0.019	3.2	0.82
Peat	3	6.8	0.17	30	16
C horizon	3	1.7	nd	11	6.0

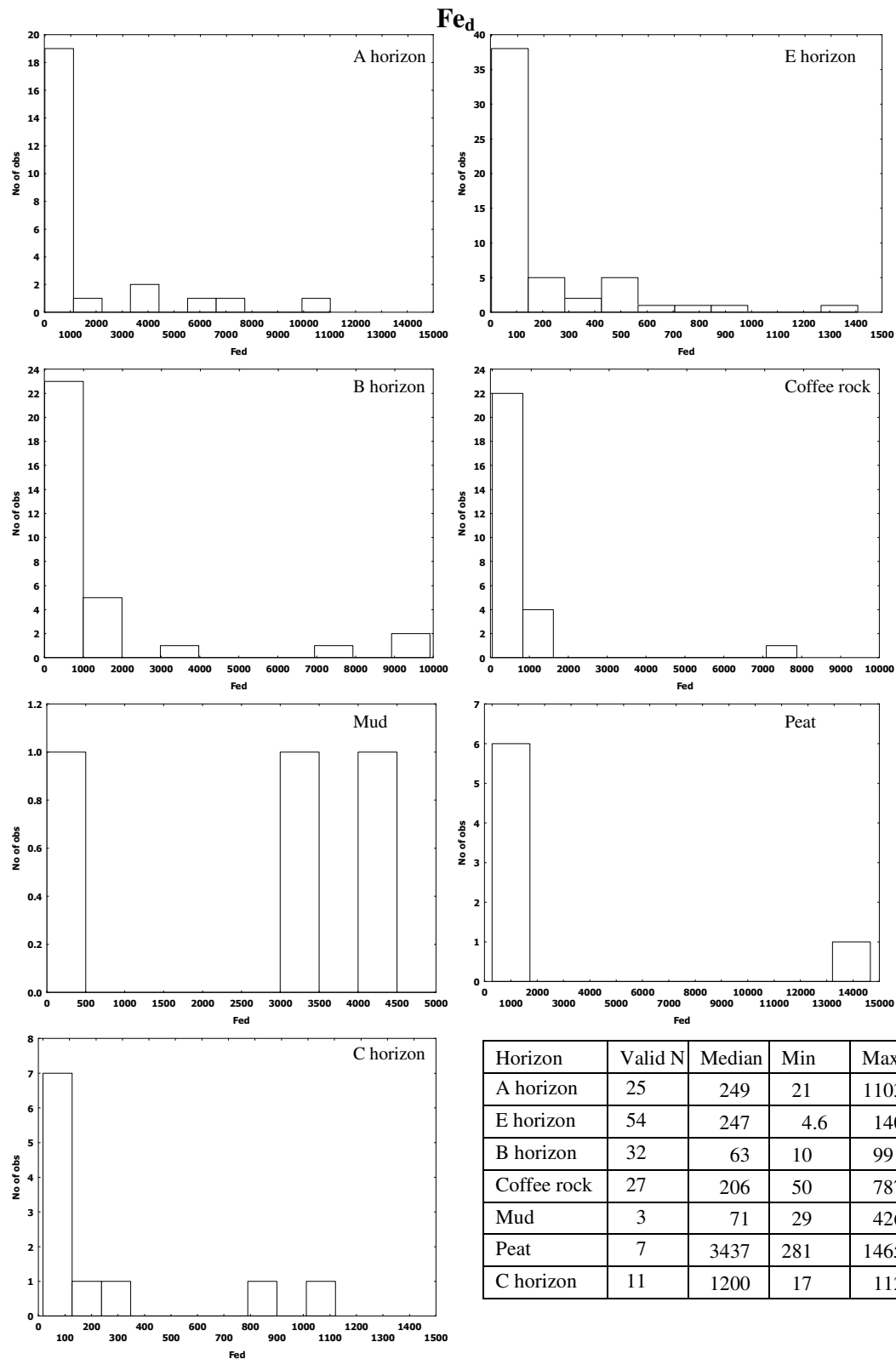
**Appendix Figure 59** Histograms for the concentration of yttrium (Y) in A, E, B, coffee rock, peat and C horizon materials (in mg kg<sup>-1</sup> unit) (aqua regia method; ICP-OES).



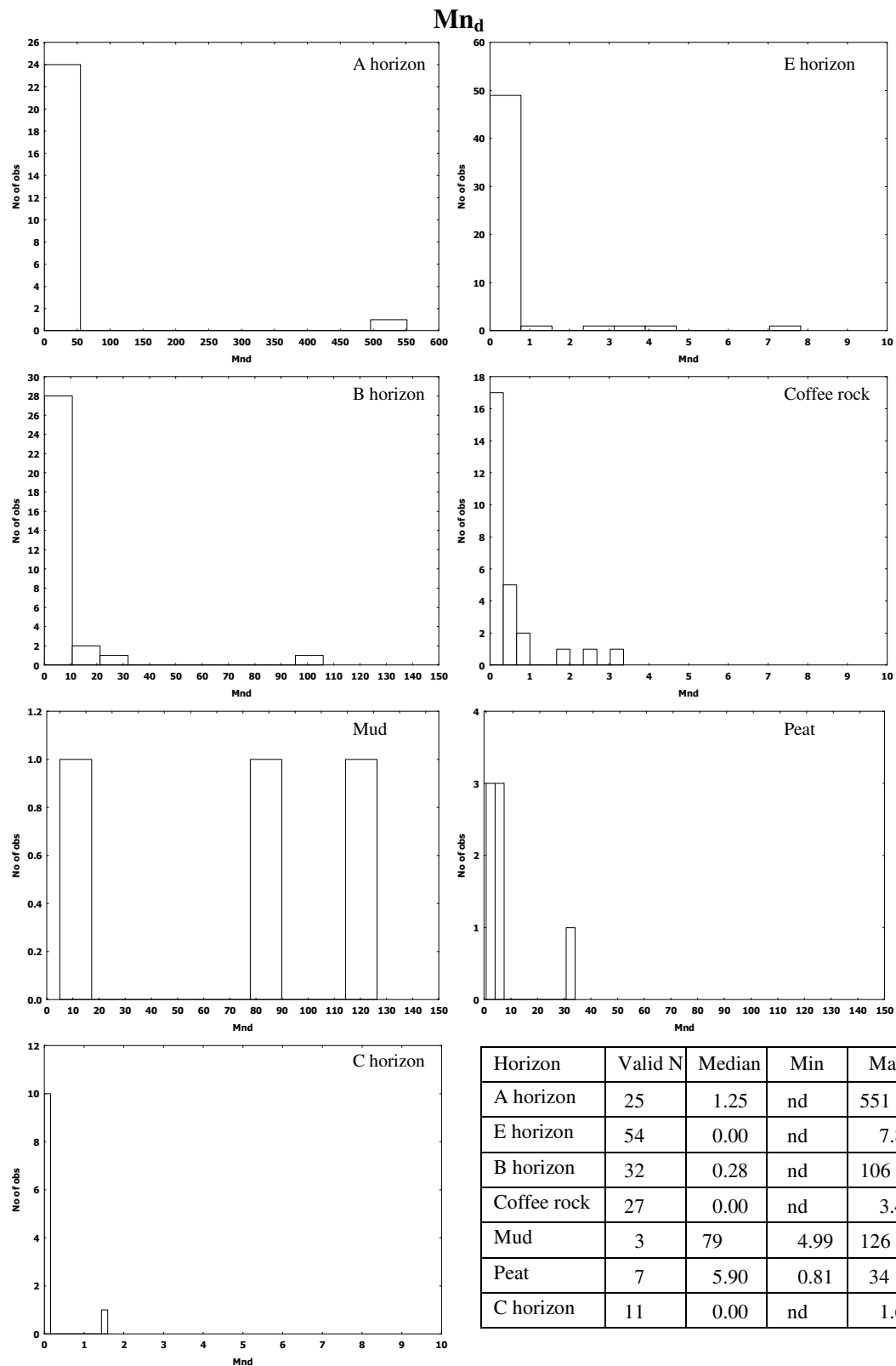
**Appendix Figure 60** Histograms for the concentration of silicon extracted by dithionite citrate bicarbonate (Sid) for A, E, B, coffee rock, mud, peat and C horizons (in  $\text{mg kg}^{-1}$  unit).



**Appendix Figure 61** Histograms for the concentration of aluminium extracted by dithionite citrate bicarbonate (Ald) for A, E, B, coffee rock, mud, peat and C horizons (in  $\text{mg kg}^{-1}$  unit).

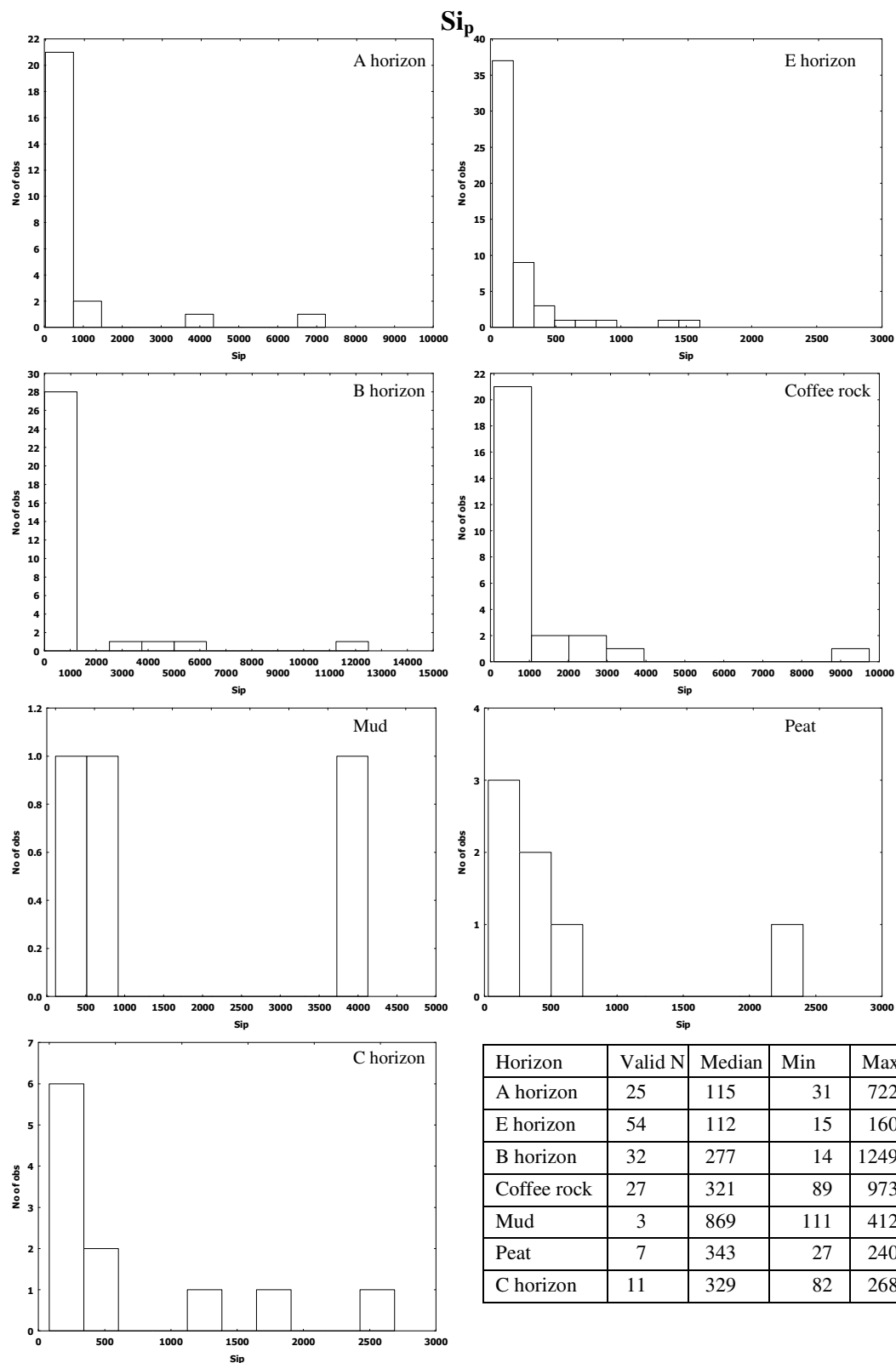


**Appendix Figure 62** Histograms for the concentration of iron extracted by dithionite citrate bicarbonate (Fed) for A, E, B, coffee rock, mud, peat and C horizons (in mg kg<sup>-1</sup> unit).

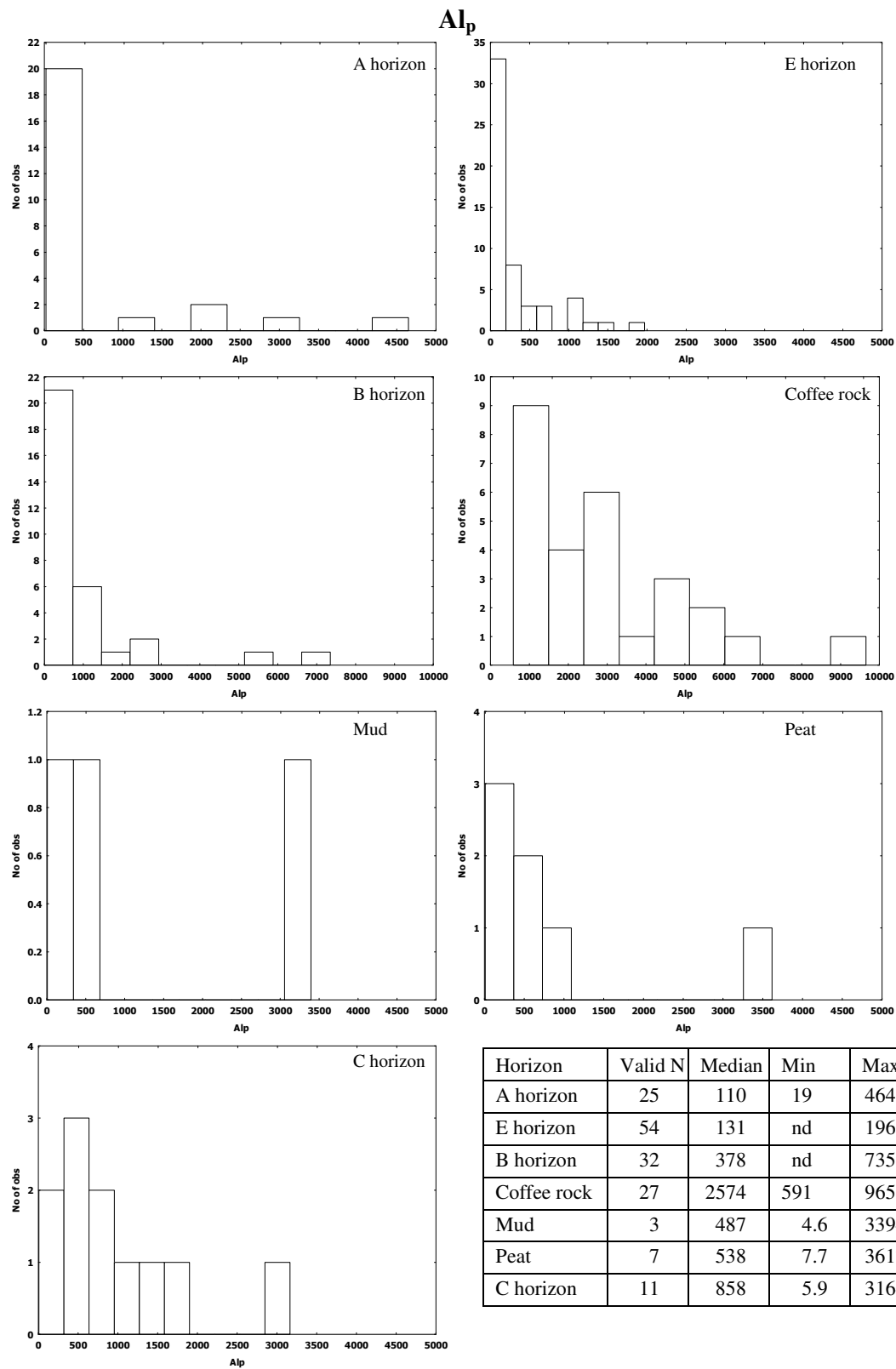


**Appendix Figure 63** Histograms for the concentration of manganese extracted by dithionite citrate bicarbonate (Mnd) for A, E, B, coffee rock, mud, peat and C horizons (in  $\text{mg kg}^{-1}$  unit).

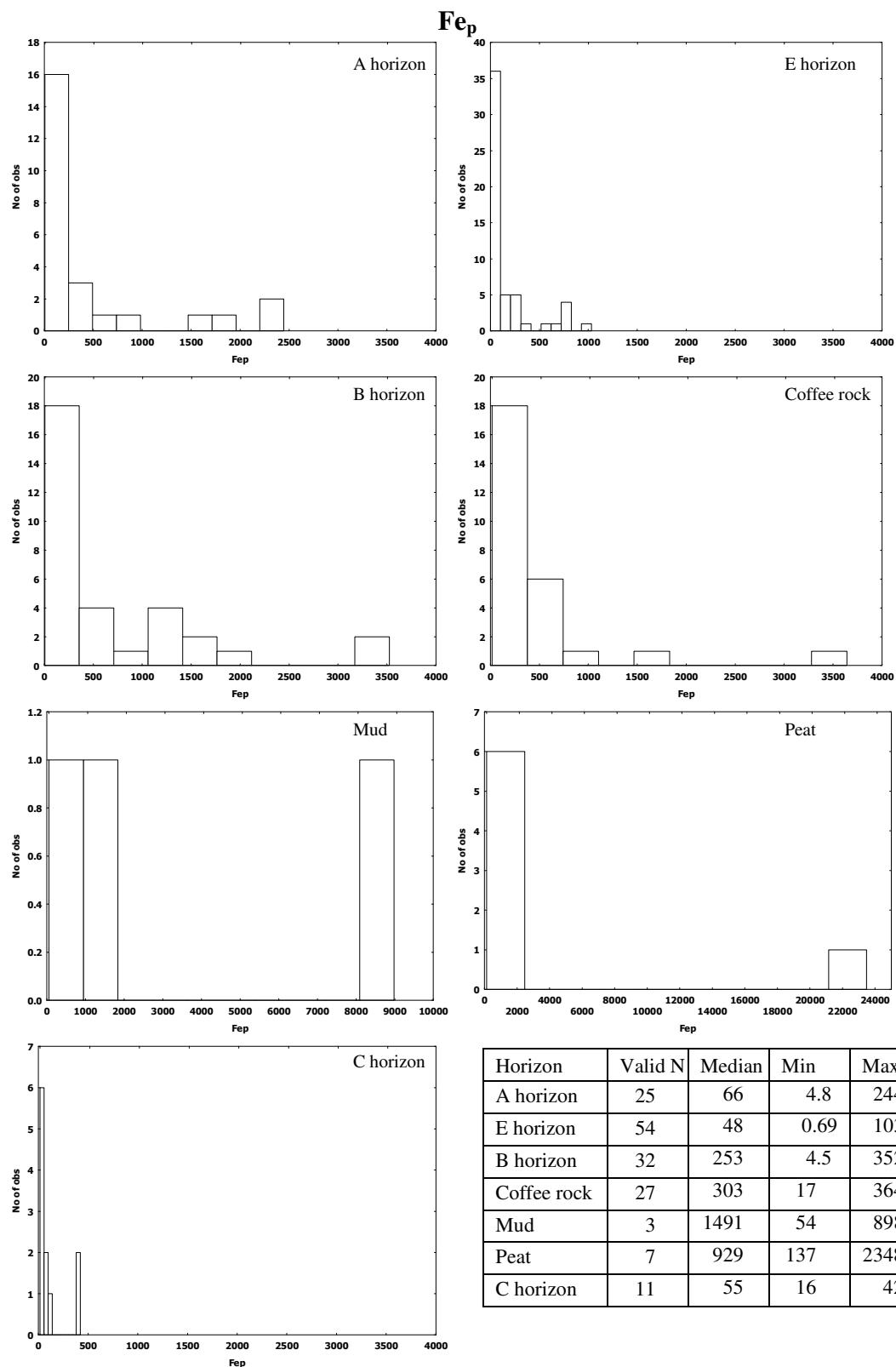




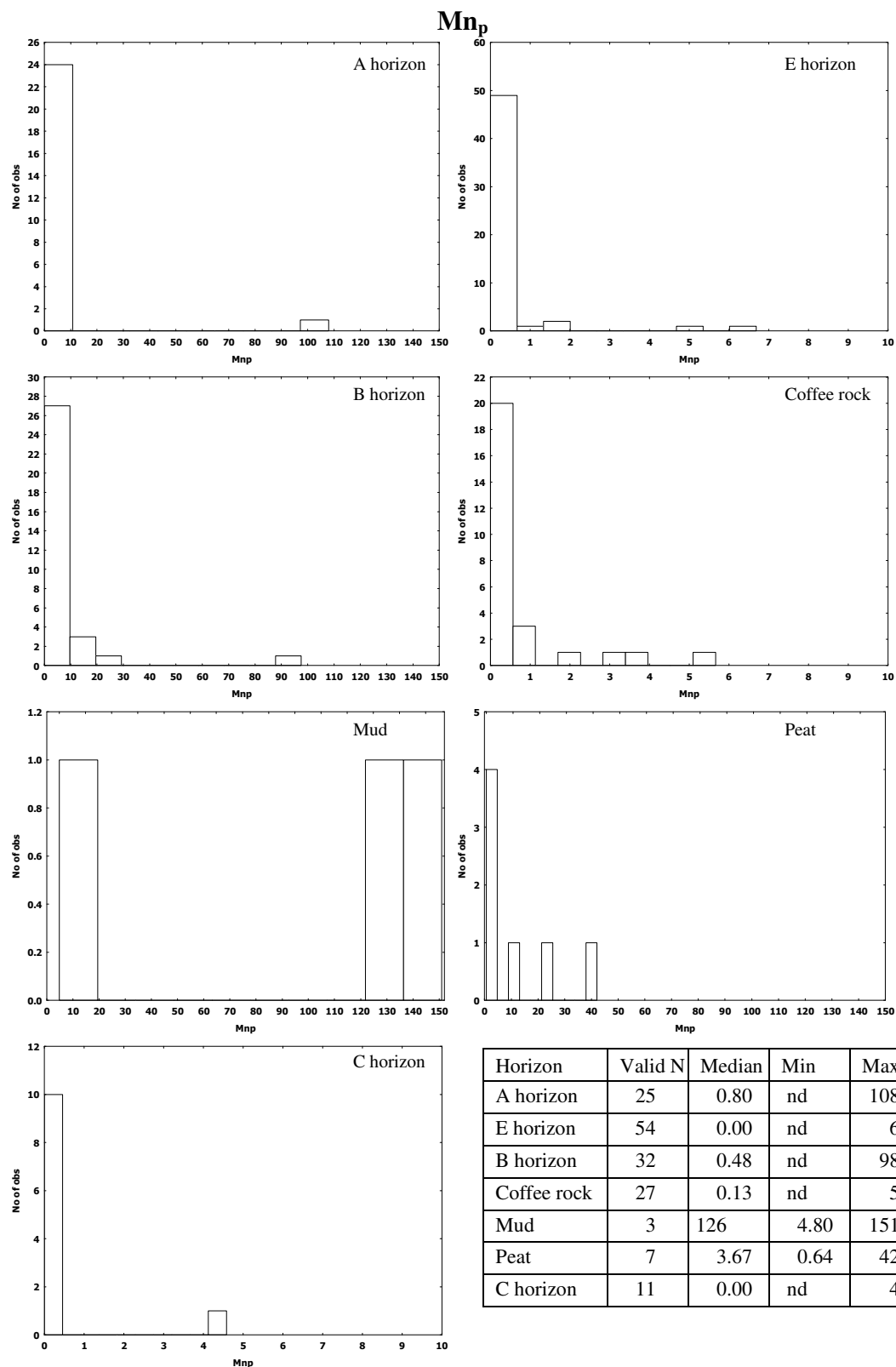
**Appendix Figure 64** Histograms for the concentration of silicon extracted by Na-pyrophosphate (Sip) for A, E, B, coffee rock, mud, peat and C horizons (in mg kg<sup>-1</sup> unit).



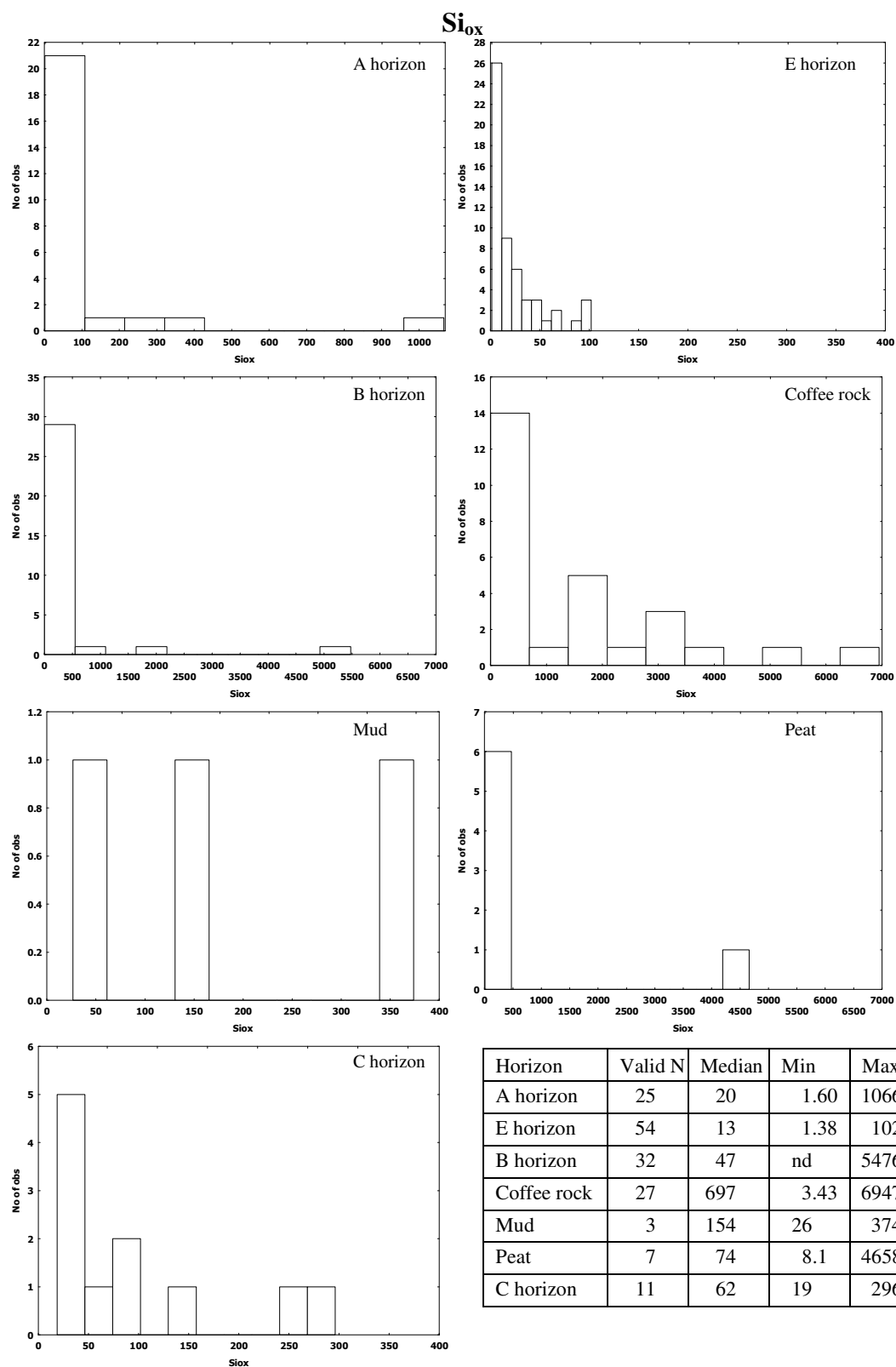
**Appendix Figure 65** Histograms for the concentration of aluminium extracted by Na-pyrophosphate (Al<sub>p</sub>) for A, E, B, coffee rock, mud, peat and C horizons (in mg kg<sup>-1</sup> unit).



**Appendix Figure 66** Histograms for the concentration of iron extracted by Na-pyrophosphate (Fep) for A, E, B, coffee rock, mud, peat and C horizons (in  $\text{mg kg}^{-1}$  unit).

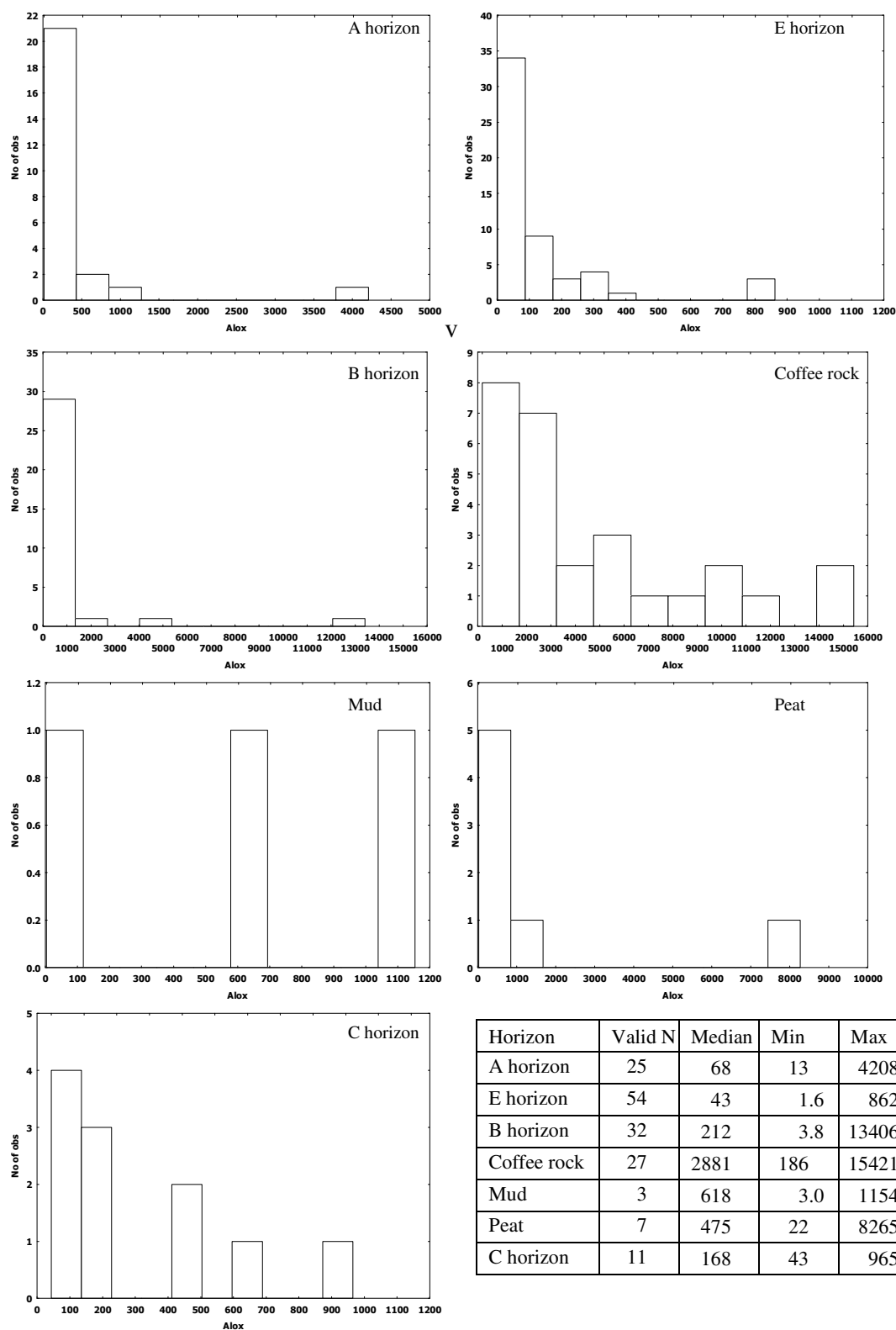


**Appendix Figure 67** Histograms for the concentration of manganese extracted by Na-pyrophosphate (Mnp) for A, E, B, coffee rock, mud, peat and C horizons (in mg kg<sup>-1</sup> unit).



**Appendix Figure 68** Histograms for the concentration of silicon extracted by oxalic acid (Si<sub>ox</sub>) for A, E, B, coffee rock, mud, peat and C horizons (in mg kg<sup>-1</sup> unit).

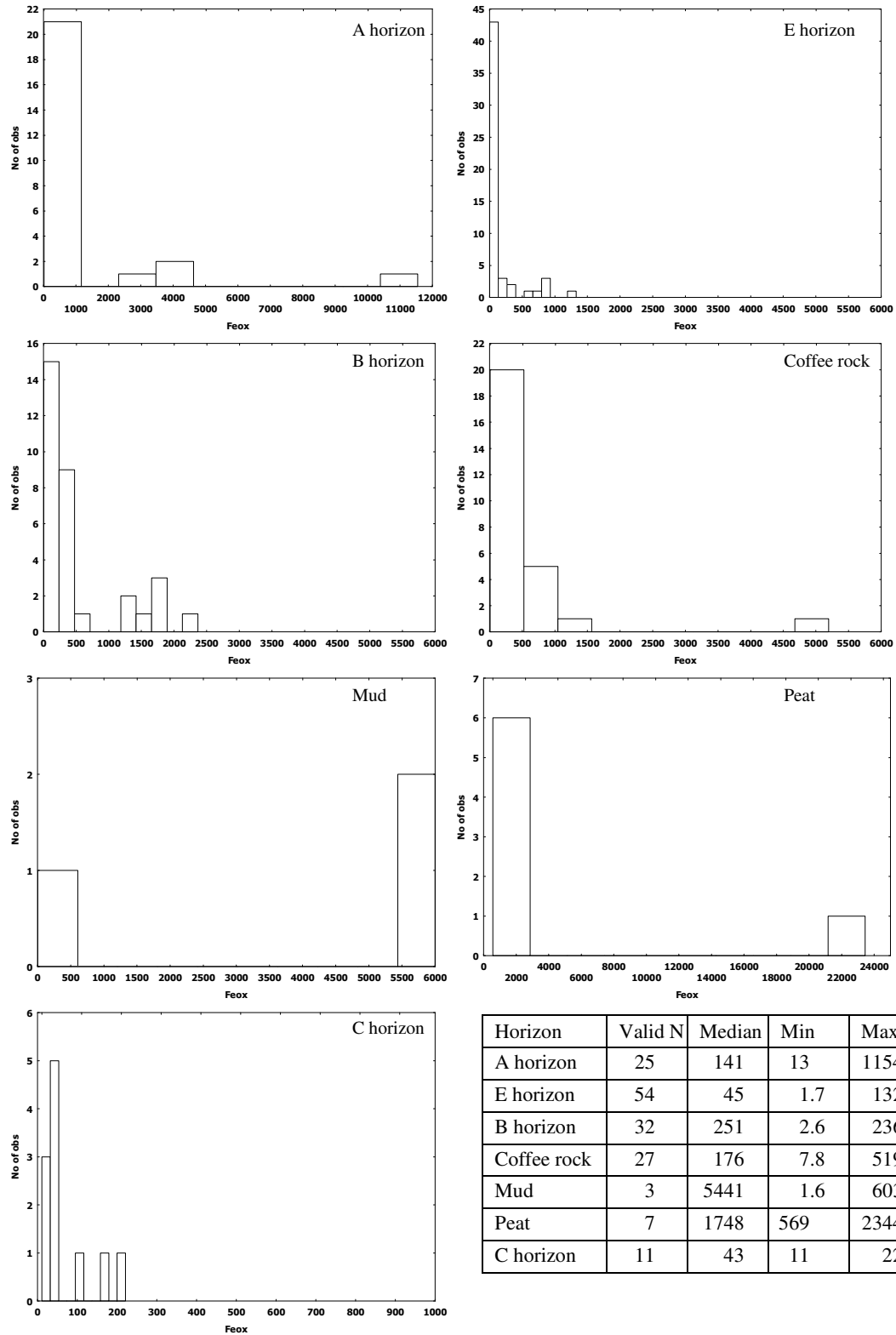
$Al_{ox}$



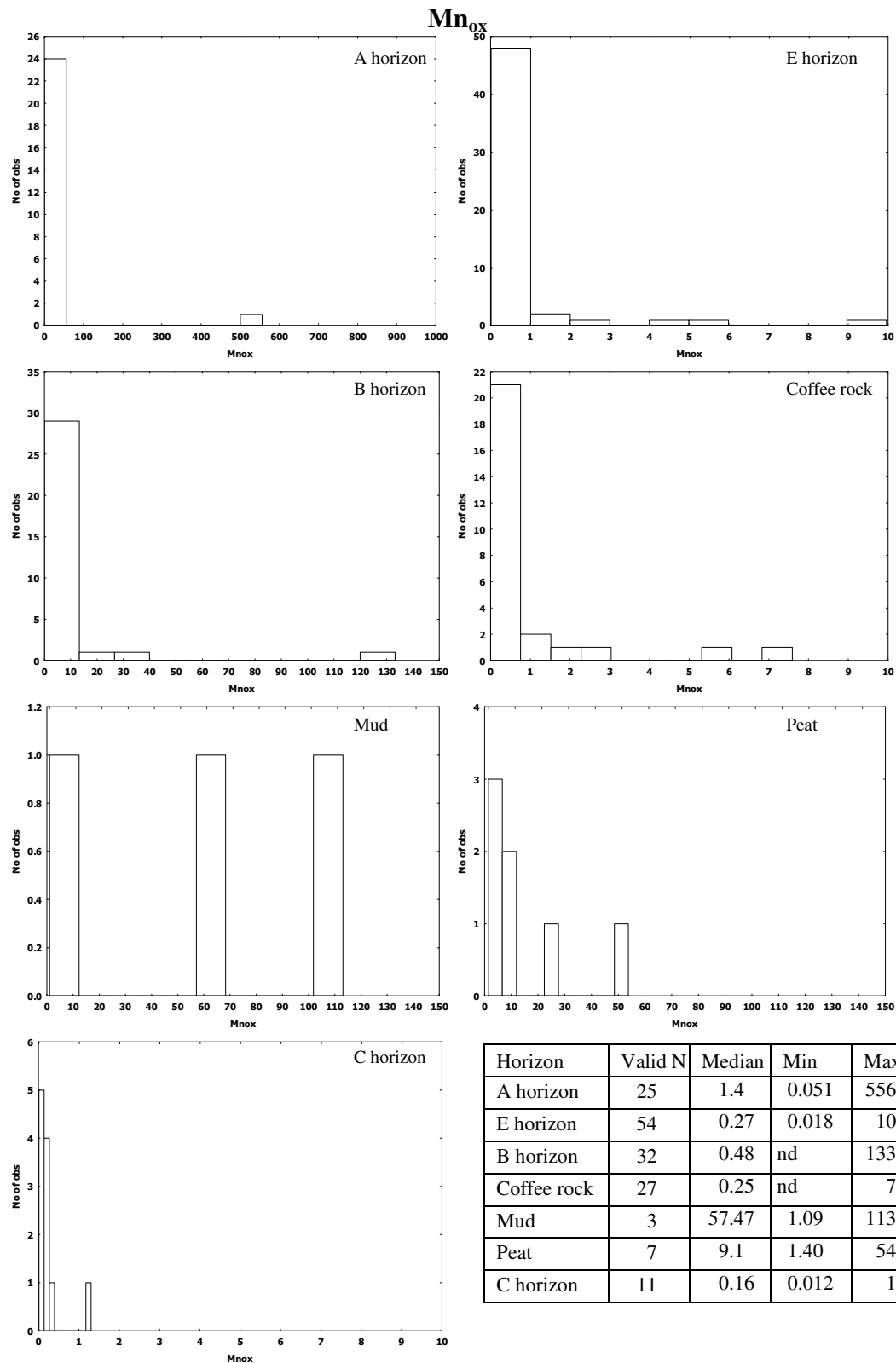
Horizon	Valid N	Median	Min	Max	Std.Dev.
A horizon	25	68	13	4208	844
E horizon	54	43	1.6	862	201
B horizon	32	212	3.8	13406	2461
Coffee rock	27	2881	186	15421	4526
Mud	3	618	3.0	1154	576
Peat	7	475	22	8265	2993
C horizon	11	168	43	965	299

**Appendix Figure 69** Histograms for the concentration of aluminium extracted by oxalic acid ( $Al_{ox}$ ) for A, E, B, coffee rock, mud, peat and C horizons (in  $mg\ kg^{-1}$  unit).

### Fe<sub>ox</sub>



**Appendix Figure 70** Histograms for the concentration of iron extracted by oxalic acid (Fe<sub>ox</sub>) for A, E, B, coffee rock, mud, peat and C horizons (in mg kg<sup>-1</sup> unit).



**Appendix Figure 71** Histograms for the concentration of manganese extracted by oxalic acid (Mn<sub>ox</sub>) for A, E, B, coffee rock, mud, peat and C horizons (in mg kg<sup>-1</sup> unit).



