Preparation of peat samples for inorganic geochemistry used as palaeoenvironmental proxies

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SUMMARY

This article provides a brief review of protocols used in peat inorganic geochemistry. We emphasise the key issues that could lead to inter-comparison problems. For each section (drying, grinding, non-destructive analyses, acid digestions and destructive analyses), recommendations are provided to guide the reader through an idealised protocol, which is the only workable approach for studies incorporating long-term comparisons.

KEY WORDS: acid digestion, freeze-drying, grinding, X-ray fluorescence.

1. INTRODUCTION

During recent decades, numerous techniques have been used to concentrate and analyse the inorganic components of peat samples (e.g. Kempter *et al*. 1997, Shotyk *et al*. 1998, Martinez-Cortizas *et al*. 1999, Mighall *et al*. 2002). These studies have generally aimed to reconstruct past human activities (e.g. Kempter & Frenzel 2000, Mighall *et al*. 2006), atmospheric pollution (e.g. Shotyk *et al*. 1998, Novák *et al*. 2003, De Vleeschouwer *et al*. 2010b) or environmental changes (e.g. Shotyk *et al*. 1998, Klaminder *et al*. 2003, Roos-Barraclough *et al*. 2004, De Vleeschouwer *et al*. 2009, Kylander *et al*. 2010). However, while these studies contribute greatly to accurately retrieving and better understanding the inorganic geochemical signals contained in peat records, no comprehensive review of the various existing geochemical protocols has been undertaken. Such an idealised protocol is much needed because some fluctuations in geochemical records may be artefacts of the analytical procedures used to obtain the information. A protocol paper dedicated to peat geochemistry, which focuses on metal contamination and minimising peat compression during coring, has already been published by Givelet *et al.* (2004). This paper also provides some methods for improving sampling resolution, and any researcher interested in the inorganic geochemistry of peat is encouraged to read it.

Since 2004, multidisciplinary studies, as opposed to investigations focusing solely on the geochemistry of major and trace elements in peat, have been achieved; and new projects combining biological and geochemical proxies have been launched. This article presents refinements of the protocol proposed by Givelet *et al.* (2004), but also different strategies depending on the inorganic geochemical proxies being studied.

2. PEAT DRYING

For all inorganic geochemical analyses, the samples must be dried before analysis. Usually, simple overnight oven drying at 105°C is performed. However, there is a major issue concerning such hot drying, as some elements are potentially volatile even at low temperatures. Therefore, we recommend freeze-drying following the procedure described below:

1. Freeze the sub-samples in their bags overnight at -20°C.

2. Also prepare ice cubes.

3. Place a series of bags upright in a plastic box that fits inside the freeze dryer.

4. Open the bags in such a way that they will remain slightly open during freeze-drying.

5. If some sub-samples are beginning to thaw after this operation, close the bags and place the whole box in the freezer for one hour, then retrieve the box and re-open the bags.

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6. Start the freeze dryer.

7. Place a couple of ice cubes in visible positions around the sample bags within the box, then place the box in the freeze dryer. The purpose of the ice cubes is to monitor the completeness of freeze-drying.

8. When the ice cubes have totally disappeared, stop the freeze dryer, remove the box and close the bags.

9. Inspect the sub-samples whilst still inside their closed bags. They should be easily crushable. If any of them (especially large ones) still have solid cores, it may be that some ice is still present. In that case the sub-samples should be re-processed, starting from Step 1 above.

Note that it is possible to measure peat density in conjunction with freeze-drying. If this is required, before Step 1 of the freeze-drying process:

a) Weigh the empty bags that will contain the sub-samples.

b) Precisely measure the volume of each sub-sample, following the instructions given by De Vleeschouwer *et al*. (2010a) and Chambers *et al*. (this volume).

c) Put the fresh sub-samples inside their individual bags and weigh again.

Then, after Step 9 of the freeze-drying process:

d) Weigh the freeze-dried sub-samples in their bags.

3. PEAT GRINDING

An environmental sample may be crushed in several different ways. The most widely used technique employs an automated planetary agate mortar ("ball mill"), which can crush rocks that have previously been reduced to a gravel grain-size. Each sample is placed in a separate agate jar, together with several small agate marbles. The jars are then rotated at high speed so that the movement of the marbles crushes the samples. This crushing method is highly efficient for non-fibrous peat, and in this case the crushing time can be reduced to ten minutes at 400 r.p.m. However, fibrous peat requires longer crushing times, sometimes up to one hour. The samples must be absolutely dry because even small quantities of residual water will cause the powder to clump and damage the device. After every crushing and before the next, each jar should be carefully cleaned with tap water and a synthetic brush, rinsed with ultra-pure water or acetone, and thoroughly dried using compressed air. Ideally, jars used for peat samples should not be used for other sample types such as rock, which may have very different elemental concentrations, in order to prevent any possibility of cross-contamination. An advantage of this crushing method is that one can control the theoretical grain size, which may be important for some non-destructive geochemical analyses such as X-ray fluorescence. A limitation is the amount of material needed; the pre-crushed sample should almost cover the agate marbles, which may be problematic depending on the size of the jars. For small samples, hand crushing using an agate mortar and pestle can be used as an alternative, but will not deliver the fine grain size obtained using the ball mill. Moreover, fibrous peat is difficult to crush by hand, and the overall procedure is time-consuming.

Because peat is composed mainly of plant remains, mills are good tools for pulverising peat samples. They can be crushed simply and quickly in an inexpensive coffee mill or herb grinder with an aluminium cup. However, possible contamination must be taken into account in a systematic way, especially for early Holocene peat with very low elemental contents. To our knowledge, the possibility of contamination from commercial mills has not been investigated.

A homogenous and fine preparation of the sample is normally necessary for geochemical analyses. However, first results on pre-industrial Belgian peat indicate quite homogenous trace element concentrations regardless of the method of preparation (Table 1). For investigation of volatile organic and metal pollutants, peat may be prepared using similar methods with the modification that liquid nitrogen is involved (Becker *et al.* 2006, Pugh *et al*. 2008).

4. NON-DESTRUCTIVE CHEMICAL ANALYSES BY X-RAY FLUORESCENCE

X-ray fluorescence (XRF) is an inexpensive, rapid and non-destructive technique which is used widely in geology to characterise the bulk geochemical composition of a variety of materials. Samples may be analysed as compressed powder, pellets or fused glass discs (see Potts 1987 and references therein). In the case of peat, the last of these is excluded because the quantity of ash residue remaining after fusion would be too small to be measurable. The

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Table 1. Measured concentrations (μg g^{-1}) of selected elements in three sets of replicate peat samples which were crushed using two different techniques. The variation between replicates is quite similar regardless of the crushing method used.

Sample Name	Al	K	Ti	V	Fe	Sb	La	Pb	U
in powder									
MIS20a	2146	1003	295	22.3	1899	9.21	3.83	632	0.607
MIS20b	1795	1006	297	22.1	1884	9.20	3.71	623	0.598
MIS20c	1763	986	300	21.5	1838	9.11	3.58	614	0.592
only hand crushed									
MIS135a	1216	190	125	1.32	247	0.07	0.77	1.97	0.068
MIS135b	1184	174	122	1.36	282	0.03	0.84	1.71	0.069
only hand crushed									
MIS140a	599	40	30	0.71	310	0.03	0.31	2.99	0.024
MIS140b	586	17	29	0.70	295	0.03	0.32	2.93	0.023

interaction of the primary X-ray with the sample causes ionisation (*i.e.* ejection) of discrete inner orbital electrons, causing re-arrangement of the remaining electrons accompanied by an emission of X-ray fluorescence whose characteristic wavelength is given by Moseley's law:

$$\frac{1}{\lambda} = k\,(Z - \sigma)^2 \qquad (1)$$

where λ is the wavelength, Z is the atomic number of the element, k is the orbital (K,L,M) constant and σ is a shielding constant.

According to Beer-Lambert's law, the intensity of the secondary X-ray is given by:

$$I = I_0\, e^{-\mu x} \qquad (2)$$

where x is the finite thickness of the sample and μ is the mass attenuation coefficient. This coefficient is density dependent. In other words, the first limiting variable in XRF analyses of peat will be the density of the sample. A ~1.5 g dry pellet of a low-density material such as peat would require 3–5 g of powder for homogenisation reasons, and this in turn would be derived from 30–50 g of fresh peat on account of its high (~90 %) water content. This quantity of fresh material is difficult to obtain in conjunction with high-resolution sampling (*i.e.* 1 cm thick peat samples). However, Richardson *et al.* (1995) noted that quantity is not a limiting factor for peat mosses, as 3 g of dry peat is relatively homogenous (owing to compaction during the burial process) compared to, for example, 3 g of single plant leaves. Therefore, it is possible to sub-sample at depth intervals of one centimetre and analyse the resulting dry powder. Depending on the set-up of the XRF device, it may be necessary to press the powder into a pellet. This may require addition of a coherence agent (e.g. lucite), but our experience has shown that most peat powders can be pressed successfully without any additive. Moreover, many modern XRF devices can provide measurements on both pellets and powder. For organic samples, measurements on powder are generally preferred, especially as the samples can then be re-used for other analyses.

Quantitative analyses of theoretically infinitely thick samples bring to the fore a second problem, namely the matrix effects caused by the mineralogy and thickness of the pellet or the powder layer. This is especially critical when analysing low-density materials (*e.g.* plant, food, lichen or peat samples). Amongst these effects are the attenuation of the primary X-ray beam, the attenuation of the fluorescence radiation, the secondary fluorescence, and the tertiary fluorescence (Potts 1987). In rock analyses, the secondary absorption effect is dominant, primary absorption is less significant, and the last two effects are often ignored in correction procedures (Potts 1987). Thus, there is a critical maximum depth below the sample surface where X-rays can no longer penetrate and be detected by the spectrometer. However, in peat samples (and indeed more generally in organic samples), an inverse effect can be expected because, being composed primarily of C, H, and O, their mass absorption coefficients are very low. In fact, bulk organic material is so transparent to X-rays that minor concentrations of elements other than C, H, and O could bias the absorbency of the pellet. Again, it must be emphasised that the powder weight and pellet thickness should be sufficient for the bulk analyses required, especially in the case of heavy metals.

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To avoid transparency problems in plant leaves or lichen samples, Richardson *et al.* (1995) recommend the addition of a moderately light element such as Al or Si in order to increase the absorbency of the pellet, which they postulate renders XRF suitable for determining low levels (i.e. a few µg g^{-1}) of heavy metals such as Zn, Ni and Pb in plant material. Conversely, we do not recommend adding anything to the samples, as this amounts to contamination making them unusable for other purposes, and thus cancels out one of the main advantages of non-destructive XRF analyses. The most satisfactory method for circumventing the matrix effect is to calibrate the XRF properly by repeatedly measuring an adequate series of standards (*i.e.* with the same matrix as the samples). These standards are generally plant materials such as leaves, lichens, or sometimes coal. By calibrating the XRF using this series of standards, and by analysing the sample using the same procedure, the matrix effects can be prevented and good data can be acquired. Several environmental geochemists have now designed and optimised XRF devices for peat so that dry peat powder can be routinely analysed for major and trace elements (Cheburkin & Shotyk 1996, 1999, 2005). The detection limits and standard errors are variable but generally higher than for destructive techniques such as ICP-MS. They are suitable for a wide range of peat samples, and XRF has the great advantage of not requiring sample digestion. Also, new commercial XRF devices give promising detection limits which may possibly broaden their ranges to encompass low concentrations.

5. DESTRUCTIVE PEAT ANALYSES: PEAT DIGESTION FOR ELEMENTAL AND ISOTOPIC GEOCHEMISTRY

5.1 Microwave system

The different protocols for peat digestion have been comparatively described and discussed in detail by Krachler *et al.* (2001, 2002a, 2002b, 2004) and others (Weiss *et al.* 1999). Recently developed microwave ovens and autoclaves enable the digestion of peat samples under high pressure and high temperature. The advantages of microwave systems are speed and the smaller volumes of acid required. Mixture recipes include ultrapure HNO_3 and HF or HBF_4 to digest minerals and HCl and/or H_2O_2 to dissolve organic matter through oxidation. Krachler *et al*. (2001) show that HBF_4 can be used instead of the more harmful HF in microwave systems.

5.2 Mixed ashing-acid digestion procedure

When a microwave oven or autoclave is not available for digesting the peat samples, it is still possible to process them with some minor adaptations to the digestion protocol. Direct digestion of 200 mg samples of peat powder can be carried out in dedicated 15 ml vials made from Teflon® or carbon glass using a mixture of HNO_3-HCl and HF, possibly with H_2O_2, on a hotplate or in a warm waterbath. The main problem that arises in digesting peat in concentrated acid is that the high organic matter content causes a strongly exothermic reaction. Moreover, the reaction of bulk peat with acids is relatively 'dirty' and this often leads to incomplete digestion, reagent consumption, or a long time requirement. An easy way to circumvent these problems is to ash the peat before acid digestion. The ashing should ideally be performed in ceramic crucibles topped with ceramic caps, under oxidative environment, at 550°C for four hours. The ash residue needs to be handled with great care and its transfer to the Teflon® vials should be performed in a room without air turbulence; firstly because the ash is very volatile, and secondly because only a small fraction of the initial volume of powder will remain as residue. Moreover, the reaction of organic matter with HNO_3 is strongly exothermic and causes a lot of degassing, leading to potential health hazards. A step-by-step procedure for digesting peat samples without an autoclave or microwave oven is given below:

1. Mark the bottom of each crucible using a graphite pen (graphite will survive the high ashing temperature).

2. Weigh the crucibles with their caps.

3. Weigh one crucible without its cap and reset the scale to zero.

4. Pour and weigh precisely 100 mg of dry peat powder into this crucible, and put the cap on it.

5. Alternatively, as 100 mg of dry peat powder will yield 1–10 mg of ash, and therefore a very small quantity of material to be transferred into the Teflon® vial, 1–2 g can be weighed and burned, and then an aliquot of the resulting ash can be weighed into the Teflon® vial.

6. Repeat the operation for all the samples.

7. Put the crucible in a muffle furnace and set the time to four hours and the temperature to 550°C.

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8. Once the oven has cooled, place the crucibles in a desiccator or desiccator cabinet (this will remove any water adsorbed by the ash during cooling of the oven).

9. Re-weigh each closed crucible and calculate the loss on ignition by deducting the weight of the empty crucible; Chambers *et al*. (this volume) give a precise protocol for this measurement.

10. Mark all the Teflon® vials, on both vials and caps, with waterproof pen (this operation may be repeated during the digestion process as the markings will progressively disappear).

11. Carefully transfer the ash into the Teflon® vials.

12. The remaining steps should be performed in a high-quality clean laboratory (at least class 100) using high-purity reagents (bidistilled or commercial *suprapur*®, or *ultrapur*®);

13. Add 1 ml of *distilled cleaned (or commercially suprapur or AnalaR)* HNO_3 and 4 ml *suprapur or AnalaR* HF;

14. Put the closed vials on a hotplate at 120°C for 48 hours;

15. Remove the vials from the hotplate and let them cool down;

16. Open the vials and slowly evaporate at 90°C;

17. Add 2 ml of *suprapur* HCl and close the vials;

18. Put the closed vials on a hotplate at 100°C for 24h;

19. Remove the vials from the hotplate and let them cool down;

20. Open the vials and slowly evaporate at 75°C (the low temperature guarantees that the residue will not burn and will therefore be easily dissolved again);

21. Add a known amount of diluted *suprapur* HNO_3 (or the appropriate carrier for the further analysis);

22. Put the closed vials on a hotplate at 75°C for six hours;

23. Remove the vials from the hotplate and let them cool down;

24. Proceed to analysis.

25. If the analytical session is not scheduled to immediately follow digestion, it is better to store the residues dry and dissolve them in diluted HNO_3 at the last moment before analysis.

26. The precise powder weight and the precise diluted HNO_3 weight will allow calculation of the dilution factor, which must be applied to the results obtained subsequently.

5.3 Lead isotope analysis

Lead (Pb) isotopes are commonly measured in digested peat samples, either directly (Krachler *et al.* 2004) or indirectly (Weiss *et al.* 2004) after resin extraction (Table 2). Measurements using multi-collection instruments (MC-ICP-MS, TIMS) need preliminary Pb purification (Weiss *et al.* 2004). This purification can be affected if the digestion is not complete. Using digested peat samples directly, some problems have been encountered during resin extraction and filament loading for TIMS, perhaps because of remaining soluble organic material. Thus, in order to get better measurements on early Holocene peat, we suggest digesting the peat samples again using microwave systems or after ashing.

Table 2. Ion exchange column procedure for separating Pb from the sample matrix (Weiss *et al*. 2004). The columns used here were made in-house from Teflon tubing and packed with 600 µl of EiChrom Sr-resin, resulting in a bed height of about 0.5 cm.

Stage	**Acid strength of HCl and volume used**
1. Cleaning step	6 M (6 × 1 ml)
2. Conditioning step	2.4 M (2 × 0.5 ml)
3. Sample loading step	2.4 M (1 × 1.5 ml)
4. Matrix elution step	2.4 M (4 × 1 ml)
5. Pb elution step	6 M (3 × 1 ml)
6. Cleaning step	6 M (3 × 1 ml)

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6. TECHNIQUES IN PROSPECT

6.1 Impregnated peat

Resin impregnation is classically used in micromorphology of soils (e.g. Murphy 1986, Tippkotter & Ritz 1996) and to stabilise lake sediments (e.g. Lamoureux 1994, Lotter & Lemke 1999, Boës *et al.* 2005). A review of the different polymer impregnation techniques is given by Boës & Fagel (2005). The main laboratory steps are: (1) water removal (*i.e.* dehydration), (2) polymer impregnation and (3) drying and thin-section preparation. Dehydration is achieved by various methods, namely: full water substitution by acetone in liquid (e.g. Pusch 1999) or vapour phase (e.g. Camuti & McGuire 1999), water evaporation by oven-drying or freeze-drying (e.g. Francus 1998, Boës & Fagel 2005, De Vleeschouwer *et al.* 2008b). Impregnation is generally achieved by acetone-resin-exchange under vacuum (e.g. Boës & Fagel 2005). Several polymers have been used to accomplish impregnation (e.g. Tippkotter & Ritz 1996), depending on the purpose of the analyses; the most widely used are epoxy polymers (e.g. Francus 1998).

The high water and organic contents of peat render it especially difficult to impregnate, and few laboratories have developed specific techniques (e.g. Mackenzie & Dawson 1961, Takeda 1988, De Vleeschouwer *et al.* 2008b). Water removal must be performed by freeze-drying because simple oven drying will lead to shrinkage; and full water-acetone exchange cannot be performed, as acetone causes physical stress within the peat by dissolving organic matter and weakening plant cells. As this technique is described prospectively here, we do not report the laboratory steps in full; instead, we direct the reader to De Vleeschouwer *et al.* (2008b), where the methodology is described step-by-step along with the main problems encountered (sample size, type of peat, freeze-drying of large sections, polymer viscosity, acetone content).

The impregnation of peat deposits can reveal information concerning their state of preservation, vegetation type, and the presence of charcoal or mineral particles. More specifically, their subsequent study in thin section using various techniques allows a broad range of observations which are useful for better understanding peat accumulation, compression and decomposition; and also to give a visual counterpart to geochemical analyses.

6.2 Continuous core scanning

X-ray fluorescence (XRF) core scanning has been widely used in studies of marine and lacustrine sediments (Jansen *et al.* 1998, Haug *et al.* 2001, Brown *et al.* 2007, Francus *et al.* 2009) and provides rapid, non-destructive analyses of split sediment cores for a broad range of major, minor and trace elements (Jansen *et al.* 1998, Richter *et al.* 2006). A mean spatial resolution of 1 mm can be achieved, potentially allowing for detection of fine structures and tackling of high-frequency signals. The XRF logging results are presented as number of XRF counts, tracing down-core geochemical variability in the sediment column. The first weakness of XRF core scanning of peat sections is that quantitative geochemical interpretation of bulk sediment data has not yet been attempted for this type of deposit. This is a major problem because further geochemical calculations, e.g. of elemental fluxes or dust concentrations, are often performed on the basis of elemental concentrations. The calibration of an XRF core scanner would require (1) corrections for sediment porosity, which is high in peat deposits and likely to be variable at a small spatial scale; (2) calibration based on standards with a similarly organic-rich matrix; and (3) validation by destructive quantitative analyses at selected depths. Attempts have been made to calibrate XRF core scanners (Weltje & Tjallingii 2008), but this is a time-consuming procedure requiring careful checks which is applicable to only one type of sediment and selected chemical elements, so that the calibration is more a case-by-case problem than an easily applicable procedure. It is hoped that further efforts will be made to solve this major difficulty. The second major problem of applying this technique to peat cores is that the split cores must be carefully flattened in order to reduce high noise:signal ratio arising from surface irregularities. Flattening is difficult in the case of peat, which is composed of various plant macrofossils, roots and fine material. Nonetheless, XRF scanning of fresh peat cores has sometimes been conducted successfully (e.g. Caseldine *et al.* 1999). Surface roughness problems may be avoided by stabilising the peat sections in resin (see Swindles *et al*. this volume) and polishing each impregnated block to obtain a perfectly smooth surface. However, the chemical composition of the resin must be critically assessed. The limited response depth of elements to incoming X-ray radiation should also be taken into account (Richter *et al.* 2006 and references therein), because the XRF scanning method will not 'detect' grains far below the surface of the impregnated core section. An example of successful XRF core scanning of impregnated peat sections is described in De Vleeschouwer *et al.* (2008a), who applied the technique to investigate geochemical trends in mineral-rich peat sections from Iceland and to

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attempt to detect cryptotephras. The major conclusions were that, although substantial tephra layers leave a clear signature in XRF logging records, cryptotephras cannot be detected; and that minor variability in elemental geochemical records can be interpreted only if microscopic observations of corresponding thin sections are carried out. Therefore, XRF core scanning of impregnated peat sections has potential for a wide range of chemical investigations, but there are problems regarding data acquisition.

6.3 Non-traditional stable isotopes and platinoids

Non-traditional stable isotopes (Hg, Cu, Zn, Sn *etc*.) are promising tracers of environmental processes and human influences, and of sources of metal in the environment (Weiss *et al.* 2007). Also, Rauch *et al.* (2004, 2010) have recently described a protocol specifically dedicated to the characterisation of platinoid and Os isotopes in peat. However, owing to the complexity of the peat matrix and because of possible volatility, further research is needed before a clear protocol can be provided for these measurements.

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