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Short communication

A single procedure for the accurate and precise quantification of the rare earth elements, Sc, Y, Th and Pb in dust and peat for provenance tracing in climate and environmental studies

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ABSTRACT

The geochemical provenancing of atmospheric dust deposited in terrestrial archives such as peat bogs using trace elements is central to the study of atmospheric deposition over the continents and at the heart of many climate and environmental studies. The use of a single digestion method on all sample types involved in such a study (dust archive and sources) minimizes the contribution of the total analytical error when comparing sample compositions and attributing a source to the deposited dust. To date, this factor is limiting progress in geographical areas where the compositional variations between the sources and within the archive are small. Here, seven microwave and hot plate digestion methods were tested on rock, soil and plant reference materials to establish a unique method optimizing precision and accuracy in all sample types. The best results were obtained with a hot plate closed-vessel digestion with 2 ml HF and 0.5 ml HNO_3 for 0.1 g of sample, which allowed the precise, accurate and low blank quantification of the trace elements La–Yb, Sc, Y, Th and Pb by ICP-MS. This method was tested in a climate study in central Asia and temporal changes in the dominant dust source were for the first time successfully linked to changes in atmospheric circulation patterns above this region.

1. Introduction

The geochemical characterization of mineral dust deposited in terrestrial or marine records is central to the study of changing atmospheric circulation as it allows the determination of past dust fluxes and the identification of the dominant dust sources through the quantification of suitable geochemical provenance tracers. The identification of variations in dust fluxes and sources through time is the only tool to retrieve information on past atmospheric circulation patterns and changes in wind strength and direction.

Ombrotrophic peat bogs and ice cores are the only archives which record mineral dust and aerosol deposition with a solely atmospheric origin [1–3]. However, unlike glacial ice, which reflects mostly integrated long-range inputs due to its location in polar regions or at high altitude, peat bogs also record dust supplied by local and regional sources, allowing the study of medium- and small scale climate variability. In the last two decades, peatlands have been increasingly used in climate and environmental studies to reconstruct human impacts on the deposition history of metal pollutants such as Pb [1,4–7], to identify and date cooling events in Europe and South East Asia [1,8] and to constrain the geochemical cycle of lithogenic elements worldwide during the Holocene [8–10].

Rare earth elements (REE) and trace elements such as Sc, Y, Th and Pb are established geochemical tracers to investigate the source of aeolian deposits [11–16] and have been increasingly applied in studies using peatlands [2,3,17,18]. Analyses of aeolian dust deposited in peat cores around the world have suggested that these elements are unlikely affected by post-depositional mobility [2,3,7,9] and their relative concentrations can be used to identify the source of the deposited dust and interpret changes in past atmospheric deposition and circulation patterns.

To establish a record of dust provenance in a peat archive, the geochemical composition of the peat samples must be compared to that of the potential dust sources. For this purpose, the use of a single dissolution method optimizing the precise and accurate recovery of the elements of interest in all relevant sample types (dust sources and receptors) minimizes the propagation of

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any uncertainty relating to the sample preparation and digestion procedures (acid types/volumes and associated blanks, laboratory environment and possible sources of external contamination). This becomes of great importance in dust studies as variability within the archive itself can be small and slight compositional differences must be resolved. A unique method will enable more accurate source identification and improve provenance tracing for environmental or climate studies.

Methods for the dissolution of loess and other aeolian deposits, notably samples with granitic matrices, widely use high pressure acid digestion [19–21] or alkali fusion decomposition [12,22] as they show improved dissolution of refractory mineral phases such as zircon. Both methods, however, present issues for source tracing studies in peat archives: fusion leads to high amounts of total dissolved solids (TDS) in solution, loss of analyte and high blanks. High pressure bomb techniques are time consuming, with analytical procedures taking up to 10 days per batch. This becomes problematic when paleoclimate studies require up to several hundred measurements to account for natural variabilities in the record. It is therefore of great interest to employ a precise, accurate and time-efficient method to determine trace element concentrations in geological samples for provenance studies. Both hot-plate and microwave-assisted dissolutions offer these advantages and an in-depth description of our recent evaluation of these methods for provenance tracing work is presented here.

To test whether these methods are applicable to samples from *both* the dust sources (inorganic-based samples) and the peat archive (organic-based samples), a series of certified reference materials (CRMs) representative of the range of sample compositions is needed, including the archive itself (receptor) and possible dust source regions (source). A previous study used the USGS reference material BCR-1 Basalt as quality control when investigating the origin of Argentinean loess and its potential as a dust source to Antarctica [22]. While this or a similar reference material can be used in such a study area where parent rocks and deposited dusts largely consist of material with a basaltic and andesitic composition, a basaltic CRM alone is less favourable in more general studies of dust transport where sources may have a different matrix richer in silica. If the geochemical composition of sources and archive are to be directly compared and analytical errors minimized, additional reference materials are needed to characterize more silica-rich source matrices and the matrix of the archive itself.

The constraints on a single digestion method applicable to trace element-based provenance tracing of dust in terrestrial archives are numerous, including (i) good recoveries for a wide range of elements; (ii) applicability to different sample types, from silica-rich to basaltic and organic-rich; (iii) enabling multi-element analysis at μg/g to ng g^{-1} levels, requiring low procedural blanks and an instrument with the ability to measure low concentrations of multiple elements, such as ICP-MS; (iv) small volumes of material; and (v) high sample throughput to allow the high-quality analysis of entire peat cores. To our knowledge, a method combining all of these considerations has not been developed to date. The aim of this work is therefore: (i) to test new and published dissolution methods and identify one reliable method enabling the accurate and precise determination of trace elements for provenance studies of dust deposited in terrestrial archives such as peat bogs; and (ii) to apply it to a real world setting, i.e. a peat core from the eastern Qinghai-Tibetan Plateau recording 9.5 kyr of Asian dust deposition [7,23]. For the first time, episodes of northerly cold front dominance above this region were identified, when the deposited dust was dominated by long-range particles from the aeolian deposits of northern China.

2. Experimental

2.1. Materials and equipment

Four reference materials were used to represent the chemical diversity in potential dust sources as well as archives. USGS BCR-1 Basalt and USGS G-2 Granite represent geological extremes of potential source composition, from silica-poor to silica-rich. NIST 2711 Montana soil can represent both a potential terrestrial dust source and an archive. NIST 1515 Apple leaves represents peat as a dust archive and organic-based matrix. In the absence of a certified peat reference material, the plant reference material NIST 1515 is commonly used for quality control [24,25].

Hot plate and microwave-assisted dissolution methods were tested. For hot plate digestions, all work was undertaken under clean laboratory conditions with protective clothing and footwear to avoid sample contamination.

2.2. Chemicals and spike materials

All laboratory ware was cleaned in turn with 1 M HCl, 1.5 M HNO_3 and ultrapure (Milli-Q) H_2O on a hot plate at 120 °C for 24 h each. For hot plate digestions, HF was of Aristar® (VWR) grade, $HClO_4$ of Suprapur® (Merck) grade and HNO_3 was purified by sub-boiling distillation. For microwave-assisted digestions, H_2O_2 was of Suprapur® grade and acid addition was carried out under clean laboratory conditions. Microwave vessels were pre-cleaned with 5 ml HNO_3 and 5 ml Milli-Q H_2O for 20 min at 150 °C in the microwave. Acid concentrations for the digestions were as follows: $\sim$15 M HNO_3, 48% (v/v) HF, 70% (v/v) $HClO_4$ and 30% (v/v) H_2O_2.

External calibration solutions for the ICP-MS (0.1–200 μg L^{-1} in 0.3 M HNO_3) were prepared by diluting multi-elemental standard solutions CCS-1 (Inorganic Ventures Inc.) containing 100 mg L^{-1} Sc, Y, REE, Th, U and CCS-6 including 100 mg L^{-1} Pb, and single element Rb standard (VWR Aristar® 10,000 mg L^{-1}). Internal standard solutions were prepared using 1000 mg L^{-1} Rh and In (Alfa Aesar Specpure®) standard solutions. Multi-elemental external calibration solutions for the ICP-AES (0.1–100 mg L^{-1} Al, Cu, Fe, Pb, Rb, Ti and Zn in 0.3 M HNO_3) were prepared by mixing and diluting single element standards (Alfa Aesar Specpure® 10,000 mg L^{-1}).

2.3. Instrumentation

The accurate and precise determination of trace element concentrations in dust samples requires an analytical technique with low detection limits for many elements and rapid multi-element measurement capabilities. The REE and selected trace elements were therefore determined by inductively coupled plasma mass-spectrometry (ICP-MS) using a Varian 810 quadrupole instrument. Immediately before the analysis, 1 ml of sample digest was diluted in 0.3 M HNO_3 to 9.9 ml and 0.1 ml of a solution containing 100 ng ml^{-1} Rh and 100 ng ml^{-1} In was added as an internal standard. ^{103}Rh was chosen as a preferred internal standard for isotopes with masses below 103 atomic mass units (amu) due to its low abundance in most natural samples. ^{115}In was chosen as a preferred internal standard for isotopes with masses heavier than 103 amu due to its low abundance in most natural samples and good stability in solutions at low concentrations. Indium was found to be a satisfactory internal standard for all heavier masses up to ^{238}U and the use of heavier isotopes as internal standards was not more advantageous due to potential problems (e.g. Re isotopes suffer from REE oxide interferences and Tl is routinely determined at low levels in the laboratory).

The soil and plant reference materials used in this study are not certified for the REE and other trace elements of interest for provenance tracing of deposited dust. The efficiency of the digestions was

Table 1
Hot plate and microwave-assisted digestion methods tested on USGS BCR-1 Basalt, USGS G-2 Granite, NIST 2711 Montana soil and NIST 1515 Apple leaves.

Method	Acids	Reference material	Weight	Time	Digestion step 2
A	3 ml HF, 2 ml HNO_3	BCR-1, G-2	0.25 g	24 h	2 ml HCl
B[a]	2 ml HF, 0.5 ml HNO_3	BCR-1, G-2	0.1 g	48 h	2 × 1 ml HNO_3
C	5 ml HF, 2 ml HNO_3, 1 ml $HClO_4$	BCR-1, G-2	0.25 g	48 h	2 × 1 ml HNO_3
D	2.535 ml HF, 0.635 ml HNO_3	G-2	0.1 g	48 h	2 × 1 ml HNO_3
E	2 ml HF, 0.5 ml HNO_3	G-2	0.1 g	48 h	1 ml HNO_3, 0.5 ml $HClO_4$

Method	Acids	Reference material	Weight	Final ramp T (°C)
MW1[b]	4 ml H_2O, 6 ml HNO_3, 0.16 ml HF	NIST 2711, NIST 1515	0.05 g, ashed	165
MW2	2 ml H_2O, 3 ml HNO_3, 3 ml H_2O_2, 0.8 ml HF	NIST 2711, NIST 1515	0.3 g, unashed	210

[a] [29].
[b] [32].

thus tested on those elements presented in the certificate: Al, Cu, Fe, Pb, Rb, Ti and Zn. Soil and plant reference materials were analysed by ICP-AES (Varian Vista-Pro Axial) to allow the determination of major element concentrations.

The limits of quantification (LoQ) for the quadrupole ICP-MS were calculated after each run based on the intensity and standard deviation measurements of the calibration standards and calibration blank and were generally at or below a few tens of ng g^{-1} for Pb, Sc, Y and the light REE La–Gd and lower than a few ng g^{-1} for Th and the heavy REE Tb–Lu. These were at least two orders of magnitude below the lowest concentrations measured for Pb, Sc, Y, Th and the REE La–Er and Yb and one order of magnitude for the low abundance heavy REE Tm and Lu.

Potential isobaric interferences need to be quantified when determining elemental concentrations by quadrupole ICP-MS, as they cause spurious data and affect the accurate comparisons between different samples. $^{135}Ba^{16}O^+$, $^{137}Ba^{16}O^+$ and $^{140}Ce^{16}O^1H^+$ can interfere with $^{151}Eu^+$, $^{153}Eu^+$ and $^{157}Gd^+$, respectively. Previous studies have shown the importance of such corrections for the accurate quantification of the REE, notably for ^{157}Gd [26–28]. In the final stages of the method development, solutions of Ba and Ce were placed at the beginning and end of each run to measure the proportion of the signal at masses 151, 153 and 157 formed by oxide and hydroxide molecular species and apply the relevant interference corrections.

2.4. Digestion procedures

2.4.1. Hot plate digestion of USGS BCR-1 and USGS G-2

The reference materials USGS BCR-1 and USGS G-2 were digested using five different hot plate digestion protocols (Table 1), including one published method previously applied to geological (though not biological) reference materials such as USGS G-2 (method B [29]) and four variations of this method (methods A, C–E). Hot plate-assisted dissolutions present the advantage of achieving high temperatures in a clean environment while maintaining relatively rapid digestion times and moderately elevated pressures. They are less effective, however, in breaking down heavy mineral phases like zircons and apatites than lengthier methods such as high-pressure bomb dissolutions.

The procedures were designed to examine the efficiency of varying proportions of HF and HNO_3, reaction times and post-HF acid additions. Aliquots of both materials were weighed into 14.7 ml screw top Savillex PTFE vessels and digestions were carried out on a hot plate at 120–150 °C. The REE can react with F^- in solution or co-precipitate with CaF_2 to form insoluble fluorides which can lower the REE recovery. Samples were therefore evaporated to dryness after the digestion times noted and a second acid step was carried out to dissolve solid residues and fluorides that formed due to excess HF. Methods A, B and C tested different digestion times, acid combinations and HF/HNO_3 ratios. As USGS G-2 contains appreciable amounts of refractory minerals, which concentrate heavy REE (Ho–Lu) but are difficult to fully dissolve, methods D and E were designed to investigate whether the total amount of HF (to improve the breakdown of heavy mineral phases) or the use of $HClO_4$ in the post-digestion step (to re-dissolve fluorides) improved elemental recovery. For methods B–E, all solutions were placed in an ultrasonic bath at the beginning of the digestion and after 24 h and 48 h. After the digestion, samples were made up in 1.5 M HNO_3 to 10 ml or 25 ml (in proportion with initial sample mass).

2.4.2. Microwave and hot plate digestion of NIST 1515 and NIST 2711

Recent studies have shown that microwave autoclave digestion techniques are appropriate for the determination of trace elements in peat and plant matrices [30–32] and NIST 1515 and NIST 2711 were initially digested using two microwave-assisted methods (MW1 and MW2, Table 1), including a method previously developed for the determination of Pb in peat (method MW1 [32]). Determination of the REE in plant matrices requires the mineralization of organic matter by dry or wet ashing. Material for dry ashing (method MW1) was weighed into acid cleaned porcelain crucibles and dried at 105 °C for 12 h. The dry weight was recorded and the crucibles placed in a furnace at 450 °C for a further 12 h. The ash content was determined and the ash collected and digested in a mixture of HF–HNO_3–H_2O in TFM Teflon XP-1500 Plus^{TM} vessels in a CEM MARSx microwave oven (CEM Corporation, USA). Material for wet ashing (method MW2) was left to react with 3 ml H_2O_2 for 1 h before introducing the remaining acids. After digestion, solutions were transferred to Savillex beakers and evaporated to dryness. One millilitre of HNO_3 was added and evaporated twice to dissolve any solid residue. Samples were then made up in 1.5 M HNO_3 to 5 ml or 30 ml for method MW1 and MW2, respectively, in proportion with initial sample mass.

Finally, 0.1 g of dry ashed peat and soil samples were digested following the hot plate procedure which produced the best results for USGS BCR-1 and USGS G-2, to compare the potential of microwave-assisted and hot plate methods for the digestion of plant and soil samples and investigate the potential of a single method applicable to all sample types.

2.4.3. Procedural blanks

Procedural blank solutions were prepared with similar acid mixtures and under identical experimental conditions as the samples in each batch. Blank concentrations were below or equal to LoQs for all REE, Sc, Y, Th and Pb and generally at least three orders of magnitude lower than sample concentrations. External contamination under the clean laboratory conditions is therefore negligible.

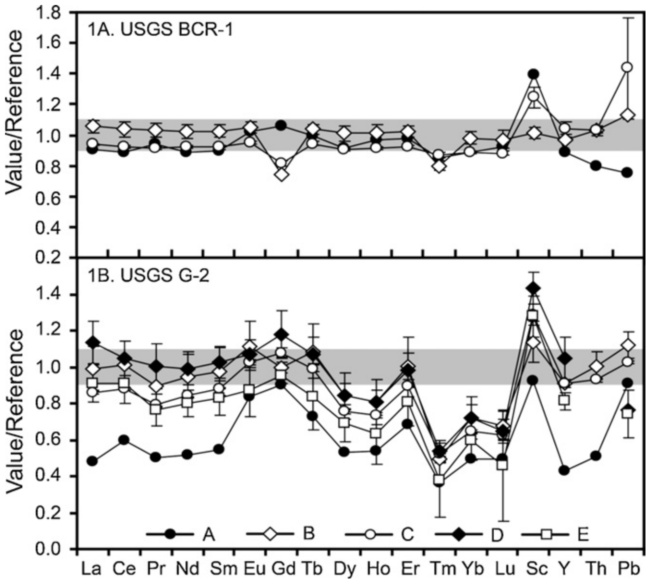

Fig. 1. Recovery of the REE, Sc, Y, Th and Pb (value/reference) for the certified reference materials USGS BCR-1 and USGS G-2 using the hot plate dissolution methods A–E (Ref. [38]). The shaded area represents the acceptable 100 ± 10% accuracy range. Errors are given at the 2σ-level or as the range of values when $n = 2$.

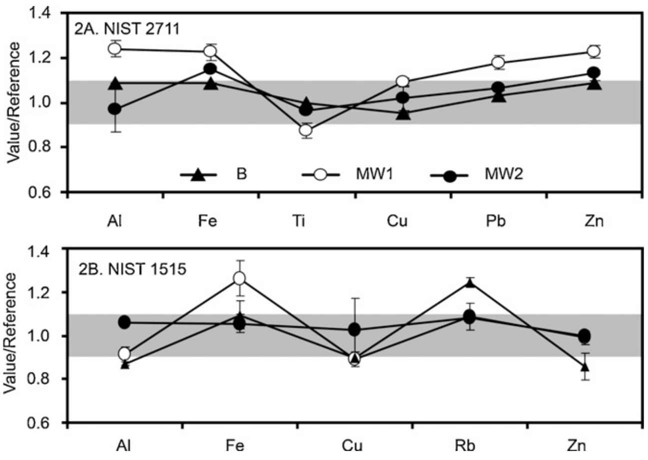

Fig. 2. Recovery of certified elements (value/reference) for the reference materials NIST 2711 and NIST 1515 (Refs. [39,40]) using microwave-assisted dissolution methods MW1 and MW2 and hot plate method B. The shaded area represents the acceptable 100 ± 10% accuracy range. Errors are given at the 2σ-level or as the range of values when $n = 2$.

3. Results and discussion

3.1. Hot plate digestion of USGS BCR-1 and USGS G-2

Elemental recoveries for the REE, Sc, Y, Th and Pb in USGS BCR-1 and USGS G-2 using the hot plate dissolution methods are shown in Fig. 1 and elemental concentrations in Table 2. Recovery is calculated as a percentage of the certified or recommended value for each element presented in the certificate.

USGS BCR-1 is readily dissolved by all digestion methods, as illustrated by the high recoveries observed for most elements (Fig. 1). This is expected as refractory heavy minerals such as rutile and zircons are absent and SiO_2 content is low (54.11%). Nevertheless, method B gives the best results with 15 out of 18 elements within 5% of the certified value, in agreement with published results [29].

Results for the same three methods on USGS G-2 show that method A is not suitable for the digestion of granites, with most REE recoveries not exceeding 60%. This is likely due to the short digestion time and lower HF content and HF:HNO_3 ratio. Methods B and C both show a decrease in elemental recovery with increasing atomic number but method B values are closer to the certified or recommended values for most elements (recoveries for light and middle REE La–Dy vary from 84% to 112% for method B and 75% to 108% for method C and heavy REE Ho–Lu from 50% to 100% and 53% to 90%, respectively). The use of 2 ml HF and 0.5 ml HNO_3 for 0.1 g of sample is therefore suitable for the digestion of basalts and granites (Table 1).

Method D was designed to determine whether increasing the total amount of HF while maintaining a similar HF:HNO_3 ratio improved the recovery of the heavy REE by facilitating the dissolution of refractory mineral phases. The amount of HF was increased in proportion with the excess SiO_2 in USGS G-2 compared to USGS-BCR-1, for which method B produced nearly 100% recovery of the heavy REE. The results show that increasing the amount of HF does not improve the accuracy of the heavy REE results for G-2 and recoveries are overall equal or lower than method B, notably for Lu (68% with method B and 65% with method D), which is probably lost through fluoride formation caused by the excess HF introduced. Similarly, taking up the samples in $HClO_4$ after digestion (method E) does not seem to improve the digestion results, suggesting that most residual material is best re-dissolved with HNO_3 only. Additionally, perchloric acid is difficult to evaporate with conventional hot plate methods due to the high temperatures required and remaining perchloric acid and perchlorates may cause additional polyatomic interferences during ICP-MS analysis [33]. Method B, with 2 ml HF and 0.5 ml HNO_3 for 0.1 g of sample, therefore produces results which best agree with reference values.

Bomb dissolutions or alkali fusion decomposition methods have been used to digest granitic rocks such as USGS G-2 and produced good recoveries [34–36]. However, as mentioned previously, both methods present drawbacks for provenance studies of dust deposited in terrestrial archives (higher blanks, high amounts of TDS, lengthy procedures). In addition, method B described in this work presents better accuracy for USGS G-2 than these studies for the elements Ce: 1% error against 3–11%; Ho: 19% against 22%; and Er: <1% against <2–5% [35,36]. Bomb methods produce better results for Yb and Lu but method B results in faster, cleaner and accurate determination of the majority of elements of interest.

3.2. Microwave and hot plate digestion of NIST 1515 and NIST 2711

Microwave and hot plate methods are both adequate for the digestion of NIST 2711 but method B displays yet again the best results, with all elements within 10% of the certified value (Fig. 2 and Table 3). This is in agreement with published results suggesting that microwave digestion of soils is optimized only if a hot plate predigestion step is included [37]. Additionally, reproducibility with this method is superior, with relative standard deviations of <1% for Al, Fe, Pb and Ti and <3.5% for Cu and Zn at the 2σ-level. Results are less clear for NIST 1515. Microwave-assisted methods produce good results in agreement with published work [30]. Method B also achieves accurate results for most elements although Zn recoveries are slightly lower. Zinc is not an element widely used in dust studies due to its potential to suffer post-depositional mobility in acidic environments such as typically present in peatlands, so this result does not affect the viability of the hot plate digestion for the purpose of dust provenance tracing in peat archives.

Table 2

Digestion results for USGS reference materials BCR-1 Basalt and G-2 Granite. Elemental recovery (Rec) is calculated as a percentage relative to the recommended and certified values.[a] Measured concentrations exceeding that of the reference material result in recoveries greater than 100%. Errors given at the 2σ-level (95% confidence interval) or as the range of measured values when $n = 2$.

	BCR-1 – Basalt					
	Method A		Method B		Method C	
	µg/g ($n = 1$)	Rec (%)	µg/g ($n = 3$)	Rec (%)	µg/g ($n = 2$)	Rec (%)
La	22.6	91	26.3 ± 1.0	105	23.4 (23.2–23.5)	94
Ce	47.5	88	55.7 ± 2.7	104	49.7 (49.3–50.1)	93
Pr	6.39	94	6.99 ± 0.30	103	6.19 (6.13–6.26)	91
Nd	25.5	89	29.5 ± 1.2	102	26.6 (26.4–26.8)	92
Sm	5.88	89	6.76 ± 0.28	103	6.05 (5.99–6.12)	92
Eu	2.00	103	2.04 ± 0.07	105	1.86 (1.84–1.87)	95
Gd	7.07	106	4.94 ± 0.07	74	5.46 (5.33–5.58)	82
Tb	1.04	99	1.09 ± 0.03	104	0.991 (0.976–1.01)	94
Dy	5.81	92	6.40 ± 0.32	101	5.75 (5.69–5.81)	91
Ho	1.22	97	1.28 ± 0.06	102	1.15 (1.14–1.16)	91
Er	3.56	98	3.71 ± 0.14	102	3.34 (3.30–3.38)	92
Tm	0.474	85	0.447 ± 0.017	80	0.487 (0.477–0.497)	87
Yb	3.00	89	3.32 ± 0.14	98	3.00 (2.95–3.04)	89
Lu	0.472	93	0.494 ± 0.030	97	0.450 (0.441–0.458)	88
Sc	45.5	139	33.0 ± 1.1	101	40.6 (38.4–42.8)	125
Y	33.8	89	37.0 ± 0.6	97	39.7 (38.1–41.3)	105
Th	4.78	80	6.19 ± 0.15	104	6.15 (5.94–6.35)	103
Pb	10.2	75	15.4 ± 0.1	113	19.6 (15.1–24.0)	144

	G-2 – Granite									
	Method A		Method B		Method C		Method D		Method E	
	µg/g ($n = 1$)	Rec (%)	µg/g ($n = 3$)	Rec (%)	µg/g ($n = 2$)	Rec (%)	µg/g ($n = 2$)	Rec (%)	µg/g ($n = 4$)	Rec (%)
La	42.7	48	88.3 ± 11.0	99	76.7 (75.7–77.7)	86	101 (90–111)	113	80.8 ± 9.1	91
Ce	94.9	59	162 ± 20	101	140 (139–142)	88	167 (153–182)	105	146 ± 17	91
Pr	9.08	50	16.1 ± 2.1	89	14.2 (14.1–14.4)	79	18.0 (15.8–20.2)	100	13.7 ± 1.6	76
Nd	28.3	51	52.2 ± 6.8	95	46.4 (46.1–46.7)	84	54.4 (49.4–59.4)	99	44.2 ± 4.0	80
Sm	3.93	55	7.00 ± 0.94	97	6.34 (6.32–6.37)	88	7.40 (6.76–8.03)	103	5.97 ± 0.70	83
Eu	1.17	84	1.56 ± 0.19	112	1.44 (1.42–1.45)	103	1.50 (1.39–1.61)	107	1.23 ± 0.21	88
Gd	3.88	90	4.28 ± 0.12	99	4.64 (4.50–4.77)	108	5.08 (4.54–5.61)	118	4.08 ± 0.17	95
Tb	0.350	73	0.521 ± 0.071	109	0.476 (0.467–0.485)	99	0.513 (0.467–0.558)	107	0.403 ± 0.087	84
Dy	1.28	53	2.02 ± 0.31	84	1.81 (1.78–1.84)	75	2.02 (1.86–2.19)	84	1.66 ± 0.24	69
Ho	0.216	54	0.323 ± 0.049	81	0.294 (0.288–0.300)	74	0.322 (0.293–0.350)	80	0.253 ± 0.066	63
Er	0.632	69	0.923 ± 0.150	100	0.824 (0.813–0.834)	90	0.906 (0.821–0.991)	98	0.741 ± 0.118	81
Tm	0.066	37	0.090 ± 0.005	50	0.095 (0.091–0.098)	53	0.097 (0.086–0.107)	54	0.068 ± 0.037	38
Yb	0.394	49	0.578 ± 0.094	72	0.517 (0.509–0.524)	65	0.575 (0.514–0.636)	72	0.478 ± 0.090	60
Lu	0.054	49	0.075 ± 0.009	68	0.069 (0.066–0.071)	62	0.071 (0.064–0.078)	65	0.050 ± 0.033	45
Sc	3.22	92	3.98 ± 0.40	114	4.51 (4.31–4.70)	129	5.02 (4.71–5.33)	143	4.47 ± 0.39	128
Y	4.72	43	10.0 ± 0.2	91	10.0 (9.73–10.3)	91	11.5 (10.2–12.8)	105	8.94 ± 0.53	81
Th	12.6	51	24.8 ± 2.1	100	23.0 (22.9–23.1)	93	–	–	–	–
Pb	27.3	91	33.6 ± 1.1	112	30.8 (30.5–31.0)	103	23.0 (22.8–23.1)	77	22.2 ± 2.0	74

[a] [38].

3.3. Summary of results using method B

Overall, the hot plate-based dissolution method B, with 2 ml HF and 0.5 ml HNO_3 for 0.1 g sample, provided accurate results for all reference materials. Major, trace and REE concentrations in all four reference materials prepared following this method are summarized in Table 4. All trace elements and REE with the exception of Gd, Tm and Pb are within 5% of the values presented in the certificate for BCR-1. The light and middle REE La to Tb fall within 12% of the certificate value for G-2, with most elements within 5%. Heavy REE values display lower recoveries. Concentrations of all elements determined in this study for which certified values exist are within 9% of the certificate value for NIST 2711 and within 14% of the reference value for NIST 1515 except Rb.

3.4. Optimum digestion time for REE recovery using method B

The effect of digestion time on the recovery of the REE, Sc, Y, Th and Pb using method B was tested on the reference material USGS G-2. G-2 was chosen for it is notoriously difficult to fully dissolve by hot plate acid digestion and the results produced therefore provide a conservative estimate of analytical uncertainty and accuracy. Three 0.1 g aliquots of USGS G-2 were weighed into PTFE Savillex beakers and the HF/HNO_3 mixture was added to each sample. The three beakers were left with their lids closed for 2, 3 and 7 days, respectively, on the hot plate. Recoveries were compared to previously published data [33], which may provide more accurate estimates of the composition of reference materials than presented in the certificate thanks to improved instrumentations and understanding of polyatomic interferences.

Extending the duration of the closed-vessel HF–HNO_3 step had little effect on elemental recoveries (Fig. 3). Concentrations of the light REE La–Gd were nearly identical in all three aliquots. The recovery of Yb was slightly increased from 91% to 94% between 48 and 72 h while a digestion time of 7 days increased heavy REE recoveries by between 1% and 3% compared to the 2 and 3 day digestions. Given the negligible increase in REE recoveries with longer digestion times and the need for a high sample throughput in peat core analyses, these results demonstrate the adequacy of method B for the determination of trace elements in dust deposited in terrestrial archives.

Table 3

Digestion results for NIST reference materials 2711 Montana Soil and 1515 Apple Leaves. Elemental recovery (Rec) is calculated as a percentage of the certified values[a] and errors are given as the range of measured values for $n = 2$.

	NIST 2711 – Montana soil					
	Method MW1		Method MW2		Method B	
	μg/g ($n = 2$)	Rec (%)	μg/g ($n = 2$)	Rec (%)	μg/g ($n = 2$)	Rec (%)
Al	80,956 (78,596–83,315)	124	63,162 (56,674–69,651)	97	71,051 (71,027–71,076)	109
Fe	35,422 (34,384–36,461)	123	33,227 (33,013–33,440)	115	31,422 (31,412–31,433)	109
Ti	2679 (2578–2782)	88	2950 (2938–2962)	96	3054 (3051–3057)	100
Cu	125 (123–127)	109	116 (110–122)	102	109 (108–110)	96
Rb	–	–	–	–	–	–
Pb	1369 (1332–1405)	118	1235 (1227–1244)	106	1199 (1195–1203)	103
Zn	430 (420–439)	123	397 (395–400)	113	380 (376–385)	108

	NIST 1515 – Apple leaves					
	Method MW1		Method MW2		Method B	
	μg/g ($n = 2$)	Rec (%)	μg/g ($n = 2$)	Rec (%)	μg/g ($n = 2$)	Rec (%)
Al	261 (252–270)	91	302 (300–305)	106	249 (247–252)	87
Fe	105 (98–111)	126	87 (84–91)	105	91 (85–96)	109
Ti	–	–	–	–	–	–
Cu	5.02 (4.83–5.22)	89	5.78 (4.94–6.61)	102	5.06 (4.98–5.14)	90
Rb	11.1 (10.4–11.7)	109	11.0 (10.9–11.1)	108	12.7 (12.4–12.9)	124
Pb	–	–	–	–	–	–
Zn	12.4 (12.0–12.8)	99	12.4 (12.3–12.6)	100	10.7 (9.93–11.5)	86

[a] [39,40].

Table 4

Certified and recommended[a] concentrations and recoveries of elements for the four reference materials studied to represent potential dust source (USGS BCR-1 Basalt and USGS G-2 Granite) and terrestrial archive (NIST 2711 Montana soil and NIST 1515 Apple leaves) matrices, digested using method B. Elemental recovery (Rec) is calculated as a percentage of the recommended and certified values and errors given at the 2σ-level (95% confidence interval) or as the range of measured values when $n = 2$.

	USGS BCR-1		USGS G-2		NIST 2711		NIST 1515	
	μg/g ($n = 3$)	Rec (%)	μg/g ($n = 3$)	Rec (%)	μg/g ($n = 2$)	Rec (%)	μg/g ($n = 2$)	Rec (%)
Al	69,258 ± 483	96	81,478 ± 2526	100	71,051 (71,027–71,076)	109	249 (247–252)	87
Fe	87,454 ± 828	93	16,848 ± 285	91	31,422 (31,412–31,433)	109	91 (85–96)	109
Ti	11,053 ± 171	82	2626 ± 60	91	3054 (3051–3057)	100	–	–
Cu	–	–	–	–	109 (108–110)	96	5.06 (4.98–5.14)	90
Rb	–	–	–	–	–	–	12.7 (12.4–12.9)	124
Pb	15.4 ± 0.1	113	33.6 ± 1.1	112	1199 (1195–1203)	103	–	–
Zn	–	–	–	–	380 (376–385)	108	10.7 (9.93–11.5)	86
La	26.3 ± 1.0	105	88.3 ± 11.0	99	–	–	–	–
Ce	55.7 ± 2.7	104	162 ± 20	101	–	–	–	–
Pr	6.99 ± 0.30	103	16.1 ± 2.1	89	–	–	–	–
Nd	29.5 ± 1.2	102	52.2 ± 6.8	95	–	–	–	–
Sm	6.76 ± 0.28	103	7.00 ± 0.94	97	–	–	–	–
Eu	2.04 ± 0.07	105	1.56 ± 0.19	112	–	–	–	–
Gd	4.94 ± 0.07	74	4.28 ± 0.12	99	–	–	–	–
Tb	1.09 ± 0.03	104	0.521 ± 0.071	109	–	–	–	–
Dy	6.40 ± 0.32	101	2.02 ± 0.31	84	–	–	–	–
Ho	1.28 ± 0.06	102	0.323 ± 0.049	81	–	–	–	–
Er	3.71 ± 0.14	102	0.923 ± 0.150	100	–	–	–	–
Tm	0.447 ± 0.017	80	0.090 ± 0.005	50	–	–	–	–
Yb	3.32 ± 0.14	98	0.578 ± 0.094	72	–	–	–	–
Lu	0.494 ± 0.030	97	0.075 ± 0.009	68	–	–	–	–
Sc	33.0 ± 1.1	101	3.98 ± 0.40	114	–	–	–	–
Y	37.0 ± 0.6	97	10.0 ± 0.2	91	–	–	–	–
Th	6.19 ± 0.15	104	24.8 ± 2.1	100	–	–	–	–

[a] [38–40].

3.5. *Accuracy and reproducibility of method B*

Fourteen separate USGS G-2 digestions were carried out over a period of several months in order to characterize the long-term reproducibility of the digestion procedure for the major elements, REE, Sc, Y, Th and Pb (Table 5 and Fig. 4). All REE but Gd, Tb and Lu are within 10% of published values [33], with most within 4%, and the concentrations of the heavy REE Dy–Yb agree remarkably well. Thorium, Y and Pb concentrations are also in good agreement with certificate and published values [33,38] and Sc concentrations are within error of the certificate values [38]. The RSD at the 2σ-level is below 8% for most elements, 10% for heavy REE Er–Yb and 11% for Lu. The RSD can be applied to peat and dust measurements in provenance tracing studies to provide a quantitative estimate of the precision errors involved.

3.6. *Quantifying polyatomic interferences on Gd and Tb concentrations*

The middle REE Gd and Tb are the only two elements presenting poor accuracy results with respect to both certificate and published values (Table 5). The fact that measured concentrations are

Table 5
Major element ($n = 14$) and rare earth element (REE), Sc, Y and Th ($n = 12$) concentration data for USGS G-2 Granite using method B and accuracy (recovery in %) and precision (RSD at the 2σ-level) data of the results. Elements in italic represent those which are only assigned recommended values in the certificate. Values in brackets for Gd and Tb represent recoveries calculated after the effect of estimated PrO$^+$ and NdO$^+$ interferences were taken into account.

	Concentration[a] (µg/g)	Accuracy (%)		RSD (2σ, %)
		Govindaraju [38]	Dulski [33]	
Al	84,714	104	–	5.4
Ca	12,803	91	–	4.8
Fe	18,511	99	–	5.1
K	33,749	91	–	3.3
Mg	4484	99	–	9.9
Ti	2695	94		4.7
La	84.1	95	97	7.9
Ce	155	97	98	6.2
Pr	*15.8*	*88*	*97*	*8.1*
Nd	53.3	97	103	5.6
Sm	7.41	103	109	6.7
Eu	1.40	100	99	5.9
Gd	5.54 (4.26)	*129 (99)*	135 (104)	4.0 (3.2)
Tb	0.582 (0.460)	*121 (96)*	119 (94)	6.1 (6.0)
Dy	2.19	91	105	6.5
Ho	0.359	*90*	103	7.2
Er	0.879	*96*	100	8.1
Tm	0.111	*62*	95	9.2
Yb	0.679	85	94	9.7
Lu	0.090	*82*	75	10.9
Sc	4.13	118	–	8.0
Y	9.50	86	101	6.0
Th	25.7	104	–	4.2
Pb	30.6	103	109	6.3

[a] Average values include the three aliquots digested for 2, 3 and 7 days.

higher than expected suggests the production of interfering molecular oxide species in the plasma. The formation of $^{141}\mathrm{Pr}^{16}\mathrm{O}^{+}$ and $^{143}\mathrm{Nd}^{16}\mathrm{O}^{+}$ could have interfered with the correct measurement of ^{157}Gd and ^{159}Tb during the analysis. The production rate of these two oxides was not measured during the runs themselves but an informative correction was applied to the Gd and Tb concentrations determined in USGS G-2 based on the long-term measurement of these two oxides in subsequent runs.

Solutions containing 100 ng ml^{-1} Pr or 1000 ng ml^{-1} Nd or Ce were analysed at the start and end of 16 different ICP-MS runs to determine the long-term proportion of the signal at masses 157 and 159 formed by $^{141}\mathrm{Pr}^{16}\mathrm{O}^{+}$ and $^{143}\mathrm{Nd}^{16}\mathrm{O}^{+}$ and long-term rate of $^{140}\mathrm{Ce}^{16}\mathrm{O}^{1}\mathrm{H}^{+}$ production in our instrument (Table A-1). As $^{140}\mathrm{Ce}^{16}\mathrm{O}^{1}\mathrm{H}^{+}$ was also determined in the USGS G-2 run, the long-term average $^{141}\mathrm{Pr}^{16}\mathrm{O}^{+}/^{140}\mathrm{Ce}^{16}\mathrm{O}^{1}\mathrm{H}^{+}$ and $^{143}\mathrm{Nd}^{16}\mathrm{O}^{+}/^{140}\mathrm{Ce}^{16}\mathrm{O}^{1}\mathrm{H}^{+}$ rates could be calculated in the subsequent runs and applied to determine an empirical production rate of $^{141}\mathrm{Pr}^{16}\mathrm{O}^{+}$ and $^{143}\mathrm{Nd}^{16}\mathrm{O}^{+}$. Accounting for the effect of $^{141}\mathrm{Pr}^{16}\mathrm{O}^{+}$ and $^{143}\mathrm{Nd}^{16}\mathrm{O}^{+}$ on the Gd and Tb concentrations of USGS G-2 based on this average production rates improves the accuracy of the measurements, with final concentrations within 4% and 6% of the certificate [38] and published [33] values, respectively (Table 5). These corrections can only produce an information value but they show both: (1) the suitability of the dissolution method for the determination of the REE in dust samples; and (2) the importance of accounting for inter-REE polyatomic interferences when determining the REE by ICP-MS.

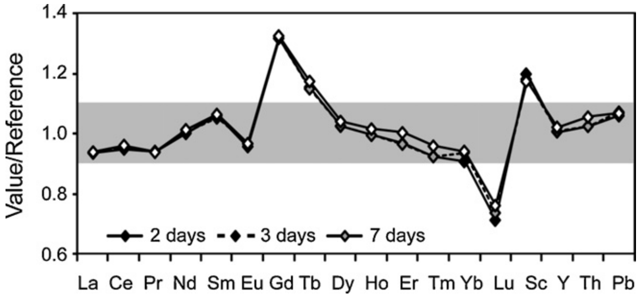

Fig. 3. Effect of digestion time on the recovery of the REE, Sc, Y, Th ad Pb in USGS G-2 using hot plate dissolution method B. Ref. [33] for La–Lu, Y and Pb and [38] for Sc and Th, not reported by Dulski [33]. The shaded area represents the acceptable 100 ± 10% accuracy range.

4. Application to the Hongyuan peat core and the study of past atmospheric deposition in China

Ninety three peat samples from a 6.2 m core from the Hongyuan peatland, eastern Qinghai-Tibetan Plateau, and samples from potential local and long-range dust sources were digested using method B [7,23,41] to reconstruct the dominant sources of dust deposited in the core and to assess changes in atmospheric circulation patterns and Asian monsoon dynamics above this region during the Holocene. The trace elements La–Yb, Sc, Y, Th and Pb were determined in all samples [7,23,41]. A series of provenance

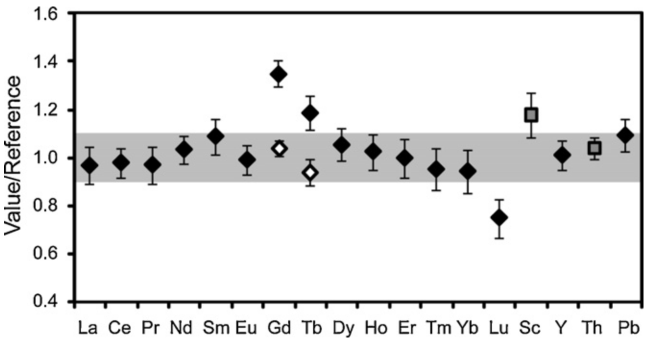

Fig. 4. Final precision (2σ standard deviation) and accuracy (value/reference) results for the REE, Sc, Y, Th and Pb using hot plate dissolution method B. Ref. [33] for La–Lu, Y and Pb (black diamonds) and [38] for Sc and Th, not reported by Dulski [33] (grey squares). Results for Gd and Tb are shown for the original ICP-MS run (black diamonds) and after post-run corrections for interfering oxides (white diamonds). The shaded area represents the acceptable 100 ± 10% accuracy range.

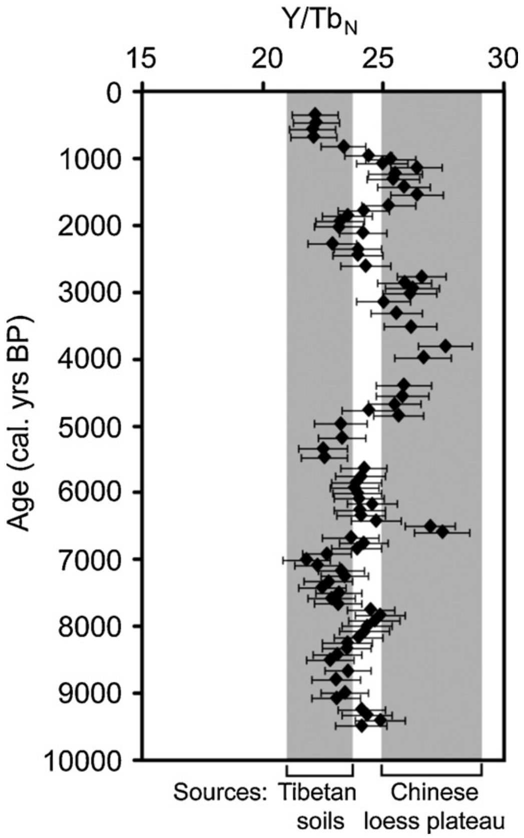

Fig. 5. Y/Tb$_N$ composition of dust deposited in the Hongyuan peat core during the Holocene. The error bars indicate the propagated precision error based on the 1σ relative standard deviation of the repeat USGS G-2 measurements presented in Table 5. The grey areas indicate the spread of values of samples from two proposed dust sources: the local Tibetan soils ($n = 9$, excluding one anomalous sample) and the long-range Chinese loess plateau ($n = 5$), including the propagated 1σ precision error of the ratio Y/Tb$_N$. The N subscript denotes that REE values were normalized to Post-Archean Australian Shale average values [42].

tracing ratios based on these elements was established to investigate the source of the dust deposited in the peat core, including rare earth element-based tracers such as La/Yb, Y/Tb, La/Th, Y/Er, Sc/La, Th/Sc and Th/ΣREE [23,41] as well as Pb isotopic ratios [7]. The ratio Y/Tb proved to be the most useful provenance tracer in this geographical setting, allowing to distinguish dust of local (eastern Qinghai-Tibetan Plateau) and long-range (Chinese loess plateau) origin [41]. This ratio is therefore chosen here to illustrate the efficacy of the digestion method B.

Fig. 5 shows the down-core Y/Tb composition of the peat samples as well as the compositional range of the local dust source (Tibetan soils) and of long-range samples from the Chinese loess plateau of northern China. The results show that: (1) the two dust sources can be distinguished geochemically within error; (2) the dissolution method allows the identification of compositional variations within the core and therefore enables the accurate distinction of periods when dust deposition was dominated by long-range dust from the vast aeolian deposits of northern China. Dust transport from these deposits is associated with cold fronts linked to the westerly jet and winter monsoon and the results therefore provide means to study changing atmospheric circulation above this region through time [23]. The full geochemical results and climatic implications of this study are detailed elsewhere [23].

5. Conclusions

A hot plate-based dissolution method using 2 ml ∼40% (v/v) HF and 0.5 ml ∼15 M HNO_3 for 0.1 g sample [29] was found to be the most appropriate for the digestion of rock, soil and plant reference materials and can thus be applied to mineral dust samples from a range of origins, including both dust sources (sand, soil) and dust archives (peat, soil). This method allows the precise and accurate determination of the major elements and trace elements La–Yb, Sc, Y, Th and Pb, improving provenance tracing work applied to climate or environmental studies. This single sample preparation method can be applied to trace element-based dust provenance tracing in terrestrial archives such as peat cores and ensures the accurate comparison between dust source and dust receptor for the reconstruction of past atmospheric circulation patterns. Using this method, it was possible to distinguish for the first time local from long-range dust input in a peat core from the Hongyuan peatland on the eastern Qinghai-Tibetan Plateau and subsequently allow the identification of phases of northerly cold front dominance linked to the westerly jet and winter monsoon above this region.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2012.01.052.

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