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The potential of lacquer-peel soil profiles for palaeo-geochemical analysis using XRF analysis

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ABSTRACT

This paper discusses the suitability of hand-held XRF analysis to extract palaeo-geochemical information from lacquer-peel soil sections that have been taken to document pedological information at geological and archaeological sites. This not only allows the study of sections from archaeological and geological sites that have since disappeared, but can also answer new archaeological questions on the nature of activities undertaken at such sites. Seven lacquer-peels, from different time-periods and different geogenetic backdrops, have been studied with hand-held XRF (Niton XL3t, GOLDD detector). Five of these lacquer-peels were studied to assess possible interference from mounting materials (glues, textiles and framing boards) used. Four of these lacquer-peels were studied for their palaeo-geochemical information. These lacquer-peels were taken from prehistoric agricultural plots and settlement sites, ranging in age from the Neolithic to the Iron Age. Values for Si, K, Al, Fe, Ti, Sr, Zr and Rb reflect lithogenetic and pedological processes. The contents of S, Ca and P were used as a proxy for anthropogenic influence. The lacquer-peels provided consistent and reliable geochemical readings with the hand-held XRF. Observed correspondence between pedological predictions, archaeological hypotheses and the measured results testifies to the suitability of hand-held XRF for palaeo-geochemical characterization. Interference from the primarily organic fixing- and mounting-agents used was absent. Consequently, hand-held XRF analysis allows extraction of palaeo-geochemical information from lacquer-peel soil sections, which opens-up a new potential data-set for reconstructing past pollution and to geochemically re-assess geological and archaeological sites from existent lacquer peels – adding a geochemical dimension to lacquer-peels of pedological, archaeological and geological sites.

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1. Introduction

Research that aims at understanding long-term soil development is hampered by the ongoing alteration of the earth's topsoil by biological, geochemical and anthropogenic processes. Archaeological fieldwork can be particularly disruptive to palaeosols, as during excavation formerly present soil properties such as stratigraphy and soil formation are disturbed and overturned. This transient nature of palaeosols renders studies that target previous conditions of soils (e.g. data collection for diachronic approaches in archaeology, climate studies or geology) particularly problematic. In archaeological research, bulk-, kubiena- and monolith tin-samples are generally not kept after study and final publication of a site, due to problems with long-term storage (e.g. fungal activity or drying-out of samples, and limited capacity of storage space). Lacquer-peel soil profiles

allow better long-term storage and allow for detailed study of entire sections (unlike kubiena or bulk samples). Consequently, it is argued in this study that lacquer-peel soil profiles represent a reliable resource for geochemical analyses of such former soils. The ample lacquer-peels created by soil-scientist and archaeologists provide a – thus far rarely exploited – data-set to be used in a variety of fields (e.g. reconstructions of sub-recent pollution, soil-degradation or archaeology).

The usage of lacquer-peels to preserve soil-profiles ex-situ started as a paleontological technique in the 1930s (Voigt, 1933) but witnessed more widespread application after the discussion of its methodology by Dumond (1963), Bouma (1969) and Goldberg (1974). Generally, polyvinyl acetate, cellulose nitrate in acetone, or polybutyl methacrylate resin (1:10) was used to bind sediments to carrier fabrics such as cotton, linen or canvas (Voigt and Gittins, 1979). The resulting flexible soil-section could either be wrapped around an axle for easy storage, or be glued to (ply) wood boards for display and storage purposes. To this day, soil lacquer-peel profiles are used in the Netherlands to study

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Table 1

Origins and main characteristics of the four lacquer-peel sections discussed in more detail in this study.

Zeijen-Noordse veld		Groningen - Winschoterdiep	
Archaeological context	Celtic Field	Archaeological context	Field (ard-marks)
Archaeological age	400–0 BC?	Archaeological age	3100–3000 BC
Geomorphological setting	Upland: boulder clay plateau with coversand	Geomorphological setting	Upland: boulder clay plateau
Geogenetic setting	Saale glaciation till with Late Weichsel coversand	Geogenetic setting	Saale glaciation till
Pedological structures	Podzol in top Celtic field ridge	Pedological structures	Ard-marks
Lacquer film created	1993	Lacquer film created	1985
Section or level?	Section	Section or level?	Level
Relevant publications	Spek et al. (2003)	Relevant publications	Kortekaas (1987), Lanting and Van der Plicht (2000, 67)
Swifterbant-S3		Oostwoud-Tuithoorn	
Archaeological context	Settlement	Archaeological context	Field (ard-marks) under barrow
Archaeological age	4300–3700 BC	Archaeological age	2500–2000 BC
Geomorphological setting	Wetland: creek system	Geomorphological setting	Wetland: creek system
Geogenetic setting	Inland active creek system	Geogenetic setting	Inland inactive creek system
Pedological structures	Anthropogenic layer with hearths on creek levee	Pedological structures	Ard-marks
Lacquer film created	1975	Lacquer film created	1956/1957
Section or level?	Section	Section or level?	Level
Relevant publications	Van der Waals (1977), De Roever (2004), Raemaekers (2011)	Relevant publications	Van Giffen (1961, 1962)

sedimentary (palaeo-)environments (e.g. Van Heijst et al., 2002; Schokker et al., 2005), document archaeological phenomena (e.g. Spek et al., 2003) and aid in soil-analyses (e.g. Van Dam and Schlager, 2002).

In order to determine whether the glues, fabrics and wooden panels used to fixate the various lacquer-peels can distort analyses of their geochemical composition, 17 hand-held XRF measurements on five different lacquer-peels have been taken. These measurements – targeting the glues, fabrics and wooden panelling underlying the lacquer-peels proper – allow evaluation of the extent to which hand-held XRF measurements solely reflect geochemical properties or whether distortion by these support materials may occur.

In addition, four lacquer-peel sections were selected for a study into their potential for palaeo-geochemical analysis. Specifically, lacquer-peel sections were selected that documented features for which specific geochemical hypotheses could be formulated and validated (e.g. leaching of elements in podzolic profiles, phosphorus accumulation in agricultural layers). To test such hypotheses, a subset of elements measured by XRF is selected (comprising Si, Ca, K, P, S, Fe, Al, Sr, Ti, Rb and Zr). These elements can be accurately determined with hand-held XRF and combine elements that accurately reflect lithology and pedogenetic processes (Si, Ca, K, S, Fe, Al, Sr, Ti, Rb and Zr) and elements that may reflect anthropogenic influence (P, S, Ca, K). If XRF measurements match geochemical predictions and display consistency, lacquer-peel preserved palaeo-environments can also be studied geochemically. This will open another dimension to the study of lacquer peels and allows for reconstruction of, for example, past pollution or effects of climate change by comparing time series of lacquer-peels, or to get insight into lithological or pedological changes caused by human influence.

2. Materials and methods

2.1. Materials

The Archaeological Institute of Groningen University houses many soil lacquer-peels from a wide geogenetic variety of Dutch landscapes, with the oldest lacquer-peel being taken in 1956 (Van Es, 1967) and the youngest being taken in 2007 (Huisman et al., 2009). These lacquer-peels originated mostly from archaeological excavations, but some lacquer-peels were taken solely for their pedological particularities. For this study 7 lacquer-peel sections were investigated by X-ray fluorescence analysis to determine their potential for palaeo-geochemical analysis. To ensure a good coverage

of potential sedimentary environments, archaeological contexts and method/age of lacquer-peel section fabrication, four panels were chosen reflecting this variability (Table 1).

The Zeijen-Noordse veld lacquer-peel was taken to document the cross-section of an Iron Age Celtic field bank (Spek et al., 2003). This lacquer-peel section was made in 1993 during a combined pedological and archaeological study of an Iron Age agricultural field system (so-called Celtic field) and covers the lower flank of an earthen bank – that once delimited an adjacent Iron Age field plot – from the 1993 surface level to a depth of 95 cm (Spek et al., 2003). At the location of the transect (Fig. 1), the base of the lacquer-peel film is formed by a 30 cm thick layer of glacial till, of which the top-most 10 cm represents a deflation zone (as is evident from the distribution of large boulders). The overlying 65 cm of sediment is anthropogenically influenced and represents a mixture of (1) local pre-Celtic field soil, ploughed out, (2) non-local soil (possibly sods from the nearby stream valley) and (3) settlement debris and (burned and unburnt) dung (Arnoldussen, 2012). This mixture ended up in or was used to construct the banks around the Iron Age fields. After the Celtic field plots and banks fell into disuse, podzolisation of the banks (and field plots) occurred. A total of 21 measurements were taken from the top of the Celtic fields bank down into the glacial till.

The Groningen-Winschoterdiep lacquer-peel (Fig. 2) shows darker discolourations interpreted as traces of a Neolithic plough or ard. In 1985, constructions works for a subterranean parking facility uncovered these ard-marks at 3.5 m below the street level of the Winschoterdiep in the city of Groningen. The ard-marks were visible as darker grey-brown streaks against the underlying yellowish-brown sediment, which consisted of Late Weichselian coversand (deposited on top of Saale period boulder clay (glacial till); Kortekaas, 1987, 115–117). The level in which the ard-marks were visible was superimposed by a layer of locally-grown peat, that was dated to c. 2430–2240 cal BC (GrN-13248: 3860 ± 60 BP; Kortekaas, 1987, 112), but dates from the arable layer itself suggest an age of 3100–3000 cal BC (Fokkens, 2008, 23 note 1; ref. to Lanting and Van der Plicht, 2000, 67).

The third lacquer-peel film discussed was taken in 1975, during the excavation of the Early Neolithic activity areas on the active creek levees of Swifterbant S3 (Van der Waals, 1977, 17). The site known as S3 consists of an area of c. 20 by 30 m of anthropogenic deposits, situated close to several similar sites on the creek levees and river dunes of the Swifterbant creek system (Van der Waals, 1977, 16; De Roever, 2004, 7). A series of radiocarbon dates reliably dates activities at the Swifterbant S3 site to the period between c.

Fig. 1. Top: photograph of the lacquer-peel section taken in 1993 at Zeijen - Noordse veld (vertical section: panel height 100 cm; [Spek et al. 2003](#)), the locations of the XRF measurements are indicated by grey dots. Bottom: interpretation of the lacquer-peel section showing the podzol horizons that have formed in the top of the Celtic field ridge.

4450 and 4000 cal BC ([De Roever, 2004](#), 14 Table 2; 18), but calibration does not allow the identification of individual use-phases.

The archaeological remains at Swifterbant S3 are primarily preserved as a 40–80 cm thick anthropogenic ‘culture-’ or ‘occupation layer’ ([Van der Waals, 1977](#), 15 Fig. 11; [De Roever, 2004](#), 21), which has accumulated on top of the silty clay of the creek system’s levees, albeit that, occasionally, some flooding still occurred (as is evident from clayey inundation bands in the occupation layer; [Van der](#)

[Waals, 1977](#), 15 Fig. 11; [De Roever, 2004](#), 21). [Van der Waals \(1977, 15–16\)](#) describes the nature of the occupation layer as “...a complex of thin, irregular lenses of clay, intermixed with varying amounts of organic and/or charred material, and lenses of white ash”. Embedded in this layer were many finds of bone, pottery, flint and stones ([De Roever, 2004](#), 21).

Presumably, the creek’s levees were deliberately raised with layers of wood-chips and bundles of reed ([Van der Waals, 1977](#), 18;

Fig. 2. Left: Groningen - Winschoterdiep lacquer-peel section with the location of the XRF measurements indicated as grey dots (horizontal surface: panel width 115 cm, taken in 1985). Right: interpretation of the lacquer-peel section showing the location and direction of the main ard-marks.

Fig. 3. Top: Photograph of the Swifterbant - S3 lacquer-peel (vertical section; taken in 1975, c. 260 by 85 cm) with the XRF sample locations indicated as grey dots. Bottom: schematic interpretation of the main lithogenetic entities.

De Roever, 2004, 21; 41), which were occasionally set on fire. Situated on top of such layers of 'paving', occasionally clay hearth linings can be identified in the strata of organic materials (Van der Waals, 1977, 18; De Roever, 2004, 21). The lacquer-peel section here discussed (Fig. 3), was taken to document the presence of such hearth constructions (Van der Waals, 1977, 17; 19 Fig. 12b; De Roever, 2004, Bijlage 2). Tentatively, the S3 hearths may relate to a rectangular post structure interpreted as a hut that overlaps with

a series of stratigraphically separated hearths (De Roever, 2004, 34; Bijlage 1 & 3).

The fourth lacquer-peel film discussed was taken in 1956 or 1957 during the excavation of two Neolithic Bell Beaker period (c. 2500–2000 cal BC) barrows near Oostwoud, West-Friesland. Underneath both barrows, traces of prehistoric ploughs (ard-marks) were recognised (Van Giffen, 1962, Pl. 1; Lanting and Van der Plicht, 2000, 86–88). Based on the graves and the artefacts recovered (Van

Fig. 4. Left: Oostwoud Late Neolithic ard-marks (horizontal surface; panel width is 1,9 m) taken during fieldwork in 1957. The locations of the XRF measurements are indicated by grey dots. Right: interpretation of the lacquer-peel section showing the location and direction of the main ard-marks.

Giffen, 1961, 226, 1962, 204–207) and the various radiocarbon dates (see [Lanting and Van der Plicht, 2000, 86–88](#) and [Beckerman, 2012, 34; 52–56](#) for a discussion of the dates), barrow construction can be dated to between 2250 and 1900 cal BC. This means that the ard-marks date to this, or a slightly older period. Three distinct ard-marks from a lacquer-peel section underneath barrow I were analysed. At Oostwoud, linear streaks of darker soil clearly stand out against the lighter grey background of sandy clay ([Fig. 4; Van Giffen, 1961, 224; 226, 1962, 200](#)).

2.2. XRF measurements

The hand-held XRF device used was a Thermo Scientific Niton XL3t with the measurement of up to 25 simultaneous elements in the analytical range between sulphur (atomic number 16) and uranium (atomic number 92) as well as light elements (Mg, Al, Si, P, S and Cl). To optimise performance for light elements by preventing secondary X-ray absorption by air, the source and detector were purged with helium gas. All analyses were performed in bulk mode (“mining mode”). The device is factory calibrated and additional soil standards were measured for external standardization. Dutch sediment standards were measured (part of the ISE programme, but issued by Wageningen University (www.WEPAL.nl)), as these better reflect the full lithogenetic spectrum of Dutch soils.

Lacquer films were measured directly by hand using helium purge. Larger lacquer-peel sections were placed on a wooden support to exclude the possibility of reflection of heavier elements (that may reflect from depths greater than the 2–3 mm of the fixated sediment or the 5–10 mm of wooden board to which they are fixed). Measuring times were 80 s, using 4 different energy settings: light (Mg, Al, Si, P, S, Cl), low (Ca, K, Sc, Ti), main (K-lines from V until Ag and L-lines from Au until Pb) and high (Ag until Au). Apart from the measurable elements the XRF software also estimates the non-measurable part, “balance”, abbreviated “Bal”. The balance is composed of the oxide part of the compounds, organic matter and – if present – carbonate and water.

Measurement outcomes may be affected both by possible contamination from the board, glue or textile, and by measurement conditions. Ideally in XRF analyses the sample should be homogeneous and have “infinite” (sufficient) thickness. In order to avoid shadow effect of mineral grains and diffraction of X-rays by crystals, the grain size of the sample should be as small as possible ([Nielson, 1977](#)). Recent study into the minimal thickness of obsidian samples ([Davis et al., 2011](#)) revealed that for elements with a $Z > 22$ (Ti) was about 0.5 mm. For light elements (Mg to Cl), however, grain size and thickness effects on the measured results can be significant. Secondary X-rays will be easily absorbed by the matrix, and as a result, light elements are only measured at the surface of the sample. Therefore, inhomogeneity and grain size effects influence the light elements results. Furthermore, the XRF is factory “calibrated” with a Fundamental Parameter algorithm based programme. As this software is propriety software of the Niton company, it is not possible to discern how it compensates for variable sample thicknesses, irregular shaped surfaces or other matrix and geometric effects. However, as film thickness is more or less similar within an individual lacquer peel (although depending on the porosity of the soils and the viscosity of the used lacquer) variations in light element concentrations due to variability of sample thickness are most likely small.

3. Results

3.1. Possible contaminations: glues, fabrics and wood used

To test the possible effects that lacquer-peel glues may have on XRF analysis, eight measurements of patches of glue on four different lacquer-peel panels were undertaken ([Table 2](#)). The high value for

titanium (0.526wt%; [Table 2](#)) in measurement no. 2374 was caused by the presence of white paint on the underlying wood panel underneath the glue, and was absent in the duplicate measurement on a slightly different spot (no. 2376; [Table 2](#)). High values for sulphur ($>0.7\%$), which are to be expected if gelatine-based glue was used ([Section 4.1](#)), were absent in all but three measurements (nos. 2433, 2478 and 2488). These three measurements with higher sulphur readings have relatively high (3.8–28%) silica content, suggesting that the raised sulphur values may derive from sediment particles enclosed in the glue. Alternatively, the also somewhat elevated calcium readings on the Oostwoud (no. 2433, taken 1961) and Swifterbant-S3 (no. 2478, taken in 1975) lacquer-peels could suggest that secondary gypsum has precipitated at the surface of the peel, possibly caused by dust or SO_2 from the air. It must be remembered that until the late 1960s storage rooms were often heated by coal or heating fuel stoves resulting in high indoor SO_2 concentrations and sulphate-rich dust ([Kucera and Fitz, 1995](#)). The elevated calcium and sulphur values of the Neolithic field at Swifterbant (no. 2488), on a panel taken in 2007 and never subjected to such storage conditions, indicate that glue-encased sediment rather than sulphur precipitation is most likely causing the elevated sulphur values. Alternatively or additionally, three measurements from the boards to which the lacquer-peels are fixed, also show slightly higher (up to 1.2%; measurements 2435, 2375, 2405; [Table 2](#)) sulphur content, suggesting that sulphur is one of the hardboard constituents (*infra*).

As the textiles used to transfer lacquer-peels to the wooden boards were generally covered fully by either glue and/or sediment, only a single measurement of a fabric could be made (no. 2475; [Table 2](#)). The inorganic elements of the transfer cloths used (often linen, flax or jute; see [Section 4.1](#) for their inorganic composition) could in theory interfere with the XRF determination of the geogenetic composition. Calcium, magnesium and sulphur were however all below their detection limits, and phosphorus and potassium both very low ($<0.14\text{wt}\%$ and $0.03\text{wt}\%$ respectively; [Table 2](#)).

3.2. Zeijen-Noordse veld

To test whether geochemical information obtained from XRF analysis of lacquer-peels conformed to pedological hypotheses, it was decided that a lacquer-peel visually showing clear podzolisation would be targeted ([Fig. 1](#)). As the process of podzolisation is relatively well-known and well-studied for both the Netherlands (e.g. [Mokma and Buurman, 1982; Nierop and Buurman, 1998; Buurman et al., 2008](#)) and beyond (e.g. [McKeague et al., 1983; Courchesne and Hendershot, 1997; Lundström et al., 2000; Tyler, 2004](#)), the relative geochemical signatures of the A-, E- and B-horizons can be predicted to a reliable degree (e.g. [Courchesne and Hendershot, 1997, 239; Tyler, 2004, 283 Table 2, Van der Salm et al., 2000; Van Breemen and Buurman, 2002, 274 Table 11A](#)), which enables us to compare the measured outcomes to such predictions. The formation of B-horizons in podzols is ‘dominated by accumulation of iron and aluminium compounds, and by root-derived organic matter’ ([Buurman and Jongmans, 2005, 80, cf. Lundström et al., 2000, 99](#)). Similarly, E-horizons occur when iron oxides and clay minerals are removed (e.g. [Tyler, 2004, 281](#)) and as a result no longer offer protection to previously accumulated iron complexed organic matter ([Buurman and Jongmans, 2005, 80–81](#)).

Although a much wider spectrum of elements was measured for each section, here a subset of elements related to podzolisation and anthropogenic factors are discussed (Fe, Al, P, S, Ca; [Fig. 5](#)). First and foremost, iron and aluminium contents reflect the (relative degree) of displacement of (organically bound) sesquioxides from the Ah- and E-horizons into the B-horizon and downwards ([Courchesne and Hendershot, 1997, 238; Van Breemen and Buurman, 2002, 272; Buurman and Jongmans, 2005, 79](#)). Phosphate

Table 2

XRF measurements of glue, fabric and board for six lacquer-peel panels. All measurements taken in mining mode (60 seconds), main elements listed (for more elements see Appendix II). Elements below detection limit: Mg (<6000ppm), Sn (<80 ppm), Cr (<600ppm), Ag (<90 ppm), Ni (<90ppm), Sb (<60ppm), Au (<50ppm), Se (<10ppm), W (<230 ppm), Bi (<15 ppm), Pd <20 ppm). Note: Totals are more than 100% as the balance (Bal; non measurable components) includes the oxide part of the compounds (O₂ in SiO₂ etc). Values for oxides as percentages, other elements as PPM. ENEO = Early Neolithic, MNEO = Middle Neolithic, LNEO = Late Neolithic, ROM = Roman Period.

No.	Site of origin	Objective	Bal	SiO ₂	CaO	P ₂ O ₅	K ₂ O	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MnO	S	Cl	Co	Comment
2488	Swifterbant (MNEO field)	Glue, yellow thick patch	77.133	23.311	4.226	0.475	0.853	0.334	0.306	6.726	0.071	14174.300	985.560	<256	With traces of soil (high Si)
2478	Swifterbant (MNEO settlement S3)	Glue	91.736	9.461	0.932	0.413	0.412	0.647	0.098	1.197	0.046	8338.090	2823.100	<98	With traces of soil (high Si)
2433	Oostwoud (LNEO ardmaks)	Glue	95.069	3.815	0.281	<0.156	0.127	<0.3	0.051	1.019	0.022	13423.610	3215.980	<143	With traces of soil (high Si)
2434	Oostwoud (LNEO ardmaks)	Glue, possibly also measuring wood	98.385	1.362	0.285	<0.033	0.024	0.074	0.008	0.056	0.015	5680.850	531.800	<30	With traces of soil (high Si)
2374	With traces of soil (high Si)	Glue, possibly measuring wood as well	98.346	1.461	<0.099	0.437	0.035	0.142	0.526	0.075	<0.008	2186.940	457.180	<31	With traces of white paint (high Ti)
2376	Wijster Looveen (driftsand underneath ROM site)	Glue, possibly measuring wood as well	98.383	1.462	0.158	0.428	0.038	0.261	0.011	0.081	<0.008	3540.240	439.950	<30	
2378	Wijster Looveen (driftsand underneath ROM site)	Glue, yellow thick patch	91.993	15.207	<0.094	0.061	0.154	0.471	0.038	0.097	<0.008	2980.570	620.950	<33	With traces of soil (high Si)
2403	Wijster Looveen (driftsand underneath ROM site)	Glue	89.867	18.284	0.291	0.381	0.257	0.352	0.046	0.150	<0.009	5303.130	1010.270	<40	With traces of soil (high Si)
2475	Swifterbant (MNEO settlement S3)	Cloth (linen or cotton)	98.836	1.233	<0.097	0.139	0.027	<0	0.010	0.100	<0.008	2191.100	1512.500	<34	
2489	Swifterbant (MNEO field)	Wooden board, front (multiplex)	98.989	0.252	0.857	<0.026	0.026	<0	<0.004	<0.005	<0.008	655.050	835.540	<21	
2476	Swifterbant (MNEO settlement S3)	Wooden board, front (hardboard)	98.970	1.088	<0.1	0.397	0.026	<0	0.033	0.068	<0.008	1434.480	580.950	<28	
2435	Oostwoud (LNEO ardmaks)	Wooden board, front (hardboard)	98.061	0.629	0.251	<0.04	0.019	0.082	<0.006	0.055	0.013	12326.090	877.640	<29	
2375	Wijster Looveen (driftsand underneath ROM site)	Wooden board, back (hardboard)	98.407	0.316	0.208	<0.037	0.014	0.135	<0.005	0.053	<0.008	10661.740	864.580	<28	
2377	Wijster Looveen (driftsand underneath ROM site)	Wooden board, back (hardboard)	99.172	0.257	0.154	<0.029	0.010	0.137	<0.004	0.047	<0.008	4291.750	567.620	<28	
2404	Wijster Looveen (driftsand underneath ROM site)	Wooden board, front (hardboard)	97.400	3.504	0.351	0.227	0.054	0.085	0.012	0.049	<0.009	3535.040	910.150	<27	
2405	Wijster Looveen (driftsand underneath ROM site)	Wooden board, back (hardboard)	98.205	0.292	0.444	<0.037	0.040	<0.1	<0.005	0.055	0.018	11238.790	625.620	<29	
2454	Winschoter Diep (MNEO posthole)	Wooden board, back (hardboard)	98.529	0.624	0.578	<0.035	0.035	0.072	<0.006	0.080	0.021	4644.340	747.110	<32

Fig. 5. XRF measurements for calciumoxide, phosphorus, siliciumoxide, potassiumoxide, aluminiumoxide, ironoxide, and titaniumoxide (as percentages, with error margins (2σ element measurement error)) and content of strontium, rubidium, zirconium and sulphur (in ppm, with error margins (2σ element measurement)) for the Zeijen - Noordse veld lacquer-peel. Note that all soil formation in samples 1–13 has formed in anthropogenic (Celtic field ridge) sediment. The Y-axis denotes depth from top of profile in cm (left) and sample numbers (right). For the location of the samples see Fig. 1.

similarly leaches and is transported downwards (Borggaard et al., 1990; Buurman and Jongmans, 2005, 79), but can – if derived from human or animal excrements – be used as an anthropogenic tracer (overview in: Holliday and Gartner, 2007). Sulphide soil compounds oxidise easily in aerobic conditions (and are thus susceptible to considerable leaching-out; Tyler, 2004, 283) but have been incorporated because S could (a) potentially reflect glues used to fix the lacquer-peel sections (*supra*), (b) can reflect recent admixtures from atmospheric sources (pollution; Rühling and Tyler, 2001), or (c) reflect recently added fertilizers. Calcium is incorporated as a tracer for the natural calcium content of the original soils, but also to track soil acidification and decalcification depths.

To test whether the typical geochemical patterns predicted for podzolisation have been preserved in lacquer-peel sections, a lacquer-peel sample from Zeijen (province of Drenthe, The Netherlands) was analysed with hand-held-XRF.

The podzol that formed near the top of the Zeijen-Noordse veld Celtic field ridge (Fig. 1) is well reflected in the geochemical composition as derived from the lacquer-peel section. Measurements 2 to 4, which were visually identified as an eluvial horizon, show the lowest values for aluminium-oxide (below 0.9wt% of the entire section). Secondary proxies for clay minerals such as titanium and rubidium have their lowest values in those exact same locations (samples 2–4; Fig. 5). These observations tie in with the interpretation as a podzol by Spek et al. (2003, 154), based on organic matter content and studied thin sections.

The visually identified iron-oxide surface water gley stains (Fig. 1; measurements 12–14) are reflected as high values for iron oxide (0.487–1.16wt%, versus 0.315wt% mean in the overlying parts of the section; Fig. 5). Noteworthy is that the values for sulphur and iron show identical trends across the section, suggesting that coupled mobilisation of iron and sulphur caused the fossilization as iron–humic–sulphur complexes throughout the section. In any case, the observed conformity indicates that this sulphur is indeed sediment-borne, and does not reflect a signal caused by adhesives or composition of the board to which the lacquer-peel film is fixed.

Remarkable is the fact that phosphorus peaks near the base (sample 11; Fig. 5) of the anthropogenic layer (Celtic field ridge) and gradually decreases towards present-day surface level. Traditional models for the origin and agricultural usage of Celtic fields suppose an intensification of Celtic field agriculture that is reflected by an increase in phosphorus in the final (upper) stages of the Celtic field (banks; e.g. Gebhardt, 1976, 97–99; Spek et al., 2003, 147–149; 167–168; Spek, 2004, 149). Evidently, the

traditionally supposed increased intensification cannot – based on our more detailed analysis of the vertical distribution of phosphorus in Celtic field banks (Section 3.1; Arnoldussen, 2012, 56, cf. Scheele and Arnoldussen, 2012, 26–28) – be identified. Considering the low concentrations of phosphorus in the top part of the section (0–50 cm; samples 1–10; Fig. 5), it seems improbable that leaching of phosphorus from higher parts of the profile has inverted a phosphorus distribution that was originally highest near the top of the section. Rather, the fact that iron compounds peak higher-up in the section (around 35 cm: sample 8; Fig. 5), the second, higher, peak at 63 cm (sample 12; Fig. 5) reflecting pseudo-gley rather than illuviation patterns, confirms that the distribution observed is not related to iron–phosphorus coupling, and reflects an originally higher phosphate content lower in the section. This argues against models that assume increased manuring of the Celtic field banks in the final stages of use.

The deflation level suggested visually by the presence of a band of larger boulders at c. 70–80 cm depth (Fig. 1, cf. Spek et al., 2003, 150) is also, albeit weakly, reflected geochemically. Deflation zones are typically enriched in zirconium due to gravitational sorting (cf. Taylor et al., 1983; Schaetzl and Loope, 2008, 292; Scheib and Lee, 2010, 8). Consistent with this geochemical prediction, the highest value for zirconium is found at this depth (measurement 17; Fig. 5). This deflation zone represents the (hiatus of the) post-Saalian erosion of the boulder-clay sediment, transforming the original glacial till sediment into a (more sandy, less loamy) mixture known locally as *keizand* (cf. Rappol, 1984, 12; De Mulder et al., 2003, 338).

3.3. Groningen-Winschoterdiep

The Groningen-Winschoterdiep lacquer-peel displays several ard-marks. The visibility of ard-marks relies on the visually distinct contrast and composition of (a) the main agricultural layer (generally the ploughed original top-soil), enriched in organic material (normal plant decay, and/or anthropogenically added compost or manure) and homogenized by processes of crop-cultivation such as hoeing and ploughing, and (b) the (decapitated) original soil, which is less affected by soil-formation and not affected by anthropogenic processes of homogenisation. During ard-ploughing, the tip of the ard can penetrate into the underlying ('b') layer, causing this 'scar' to be in-filled with material from the overlying agricultural ('a') layer (cf. Klammm, 1993, 100–108; Huisman and Deeben, 2009, 158–159 Fig. 82a). If during archaeological excavation the depth of the exposed surface is set at, or some centimetres below, the interface of layers 'a' and 'b', ard-marks are generally visibly as streaks

Fig. 6. XRF measurements for calciumoxide, phosphorus, siliciumoxide, potassiumoxide, aluminiumoxide, ironoxide, and titaniumoxide (as percentages, with error margins) and content of strontium, rubidium, zirconium and sulphur (in ppm, with error margins (2σ element measurement error)) for the Groningen - Winschoterdiep lacquer-peel. Measurements plotted in the grey band concern ard-mark, measurements outside the gray bands represent the surrounding matrix outside the ard-marks. The Y-axis denotes the sample numbers. For the location of the samples see Fig. 2.

of darker material from layer 'a' against a generally lighter background of layer 'b'.

Two clearly visible ard-marks were measured with the XRF, as well as two measurements of the natural matrix to each of their sides (Fig. 2, nos. 1–6). This way, two readings for the composition of the anthropogenic ard-marks proper could be compared to four readings of the local surrounding matrix. The location of the samples is indicated in Fig. 2. It should be stressed, however, that the presently low number of samples for ard-marks and direct vicinity analysed do not allow for statistically sound validation or generalisation.

The hypothesis was that the ard-marks could show signs of tillage, most notably in (a) an increase in phosphorus due to manuring (which can be up to factor 2.79 in fields; Wilson et al., 2008, 415 Table 3, cf. Jacobson et al., 2003, 27; Guttman et al., 2004, 58–59; Holliday and Gartner, 2007, 303; Shahack-Gross, 2011, 212), and (b) a relative higher organic content (mostly C–H and O), resulting in a dilution of measurable elements, and (c) an increased mobilisation of iron oxides (due to iron reducing conditions causing the conversion of non-soluble iron to soluble iron, facilitated by an originally increased organic matter content; cf. Van Breemen and Buurman, 2002, 64–67). The results of the XRF analyses of the main elements are listed in Fig. 6.

Although the values for phosphorus appear to be highest within the ard-marks proper (samples 2 and 4; Fig. 6), this difference is most likely not significant (error margins in ppm for phosphorus range between 13 and 23%). However, the significant slightly higher

calcium oxide values in the ard-marks could indicate that in this case the difference is significant (error margins in ppm for calcium during measuring 4–11% (relative)). This could indicate that the ard-marks are enriched with a Ca–P compound such as ash or bone. Moreover, values for sulphur also peak within the ard-marks proper (error margins in ppm for sulphur during measuring 2–5%). This concurrent elevation of sulphur and calcium – and, albeit tentatively, phosphorus – suggests that the different composition of the ard-mark fills to the natural sediment is geochemically traceable, but that phosphorus (alone) is no reliable tracer of this feature-type here. Although calcium-enrichment of arable soil can occur (mainly due to addition of manure, ash or vegetal matter), it is not a defining trait of arable soils (Wilson et al., 2008, 415 Table 1 note a factor of 1.4 to 2.3 increase in calcium for arable, but at one site the arable was decalcified (factor 0.67)). Arable layers are also prone to sulphur enrichment, due to the fossilization of original organic sulphur (factor 1.8 to 3.6 of S-enrichment of arable versus control samples; Zhao et al., 2006, 1001 Table 1, cf. Scherer, 2001, 87). Particularly organic materials rich in S such as straw, can – if added to a soil – add to the immobilisation of sulphur (Chapman, 1997; Scherer, 2001, 87–88), but long-term preservation is poor as most sulphate compounds are soluble in water. Combined, the raised values for Ca and S in the ard-marks versus their encasing sediment are consistent with other analyses of arable soils, but their geochemical identification remains tentative due to the marginal differences observed.

Fig. 7. XRF measurements for calciumoxide, phosphorus, siliciumoxide, potassiumoxide, aluminiumoxide, ironoxide, and titaniumoxide (as percentages, with error margins (2σ element measurement error)) and content of strontium, rubidium, zirconium and sulphur (in ppm, with error margins (2σ element measurement error)) for the Swifterbant - S3 lacquer-peel. The Y-axis denotes depth from top of profile in cm (left) and sample numbers (right). For the location of the samples see Fig. 3.

Fig. 8. XRF measurements for calciumoxide, phosphorus, siliciumoxide, potassiumoxide, aluminiumoxide, ironoxide, and titaniumoxide (as percentages, with error margins (2σ element measurement)) and content of strontium, rubidium, zirconium and sulphur (in ppm, with error margins (2σ element measurement error)) for the Oostwoud - Tuithoorn lacquer-peel. Measurements plotted in the grey band concern ard-mark, measurements outside the gray bands represent the surrounding matrix outside the ard-marks. The Y-axis denotes the sample numbers. For the location of the samples see Fig. 4.

The second prediction, that the ard-marks are characterized by relatively high organic content, resulting in an increased dilution of measurable elements, is not evident from the geochemical data. The values for 'balance' (reflecting lighter (organic) elements that cannot be detected with the XRF used) of the ard-marks (78.9 and 80.8% balance) overlaps with the range observed for the natural sediment (78.4–80.5% balance; Appendix I). Moreover, the balance is calculated by the XRF software by subtracting all measured components, expressed as oxides from 100% and is not directly measured. A consistent drop in elemental concentration for the ard-marks locations versus the natural sediment cannot be identified. The observed low values for strontium in the ard-marks have no significance due to the large margin of error for individual measurements (error margins in ppm for Sr during measuring 10–16%). The third prediction of increased mobilisation of iron-oxide due to original organic content of the ard-marks, also cannot be validated (values for iron-oxides in the ard-marks are lower as well as higher than the surrounding sediment; Fig. 6). It seems that the ard-marks therefore can, in addition to visual differences caused by very small increases in resistant organic matter, only be identified geochemically by their Ca–P–(S) compounds.

3.4. Swifterbant-S3

A total of 14 measurements was taken from the top of the dark 'occupation layer' down into the underlying creek levee's clay at Swifterbant-S3 (Fig. 3). The measured transect cuts across two overlying but stratigraphically separated clay hearths (cf. Van der Waals, 1977, 17; 19 Fig 12b) and a thin band of fluvial clay sedimentation that was deposited during the early stages of anthropogenic raising of the bank with reed bundles (Van der Waals, 1977, 18; Fig. 11; De Roeve, 2004, 21; 41). The variable lithogenesis of the sediments of the S3 lacquer-peel allows formulating several testable hypotheses on the geochemical composition. First, the archaeologically documented hearths can be identified by raised levels of phosphates (up to factor 12.3; Wilson et al., 2008, 415 Table 3, cf. Holliday and Gartner, 2007, 307) as well as raised levels of potassium (Holliday and Gartner, 2007, 307; Oonk et al., 2009, 41) and possibly magnesium (Oonk et al., 2009, 38 Table 1 with references). The inorganic content of ash (burned wood, peat, or cow dung) comprises mainly the oxides of calcium, phosphorus, potassium and silicium (Braadbaart et al., 2012). Second, the main lithogenetic intercalation of the occupation layer(s) – of partly carbonised, anthropogenic organic materials – and naturally deposited clay may be reflected in different dominances of Al, Ti and Rb (all proxies for clay content).

Samples 2 and 4 – identified as hearths based on the archaeological description – conform in their geochemical composition to the predictions of calcium- and phosphorus-enrichment of hearths (*supra*). Values for calcium oxide in samples 2 and 4 (2.9%; Fig. 7) are only surpassed by those of the underlying – naturally calcareous creek levee sediments (samples 12–14; Fig. 7). In this respect, it is notable that the sedimentary clay layer investigated in sample 9 formed the surface-level for sufficient time to become decalcified. The values for phosphorus are even clearer, with values of over 2% P only occurring with the hearths (samples 2 & 4; Fig. 7). Based on XRF analyses of nearby site Swifterbant S2, the effect of locally natural occurring ferrous phosphates (vivianite: $\text{Fe}_3(\text{PO}_4)_2$), is smaller than c. 0.58% phosphate (Huisman et al., 2008, 41–42; 56), supporting the interpretation of a phosphorus enriched man-made hearth. Furthermore, the potassium content in the hearths ranges between a factor 1 to 4 times higher than that of their encasing organic deposits (samples 1, 3, 5–8, 10–11; Fig. 7), pointing towards the presence of ash. Evidently, the preservation conditions at Swifterbant were sufficiently good to have preserved ash and its constituent elements.

The second hypothesis, that the XRF measurements should reflect the differences in lithology and lithogenesis (anthropogenic layers of phytoliths (possibly partly charred; cf. Huisman et al., 2009, 190–192)) versus natural clayey sedimentation, is also substantiated by our data. As was expected, the 'balance' signal (reflecting lighter (organic) elements that cannot be detected with the XRF used), was higher for the organic layers than for the natural sediments (anthropogenic layers mean: 83.8%, clay sedimentation mean 79.6%, hearths 79.9%; Appendix I). Within the detectable elements, aluminium provides the most prominent proxy for clayey sediments, with Al values above 1% only registered for one of the hearths (sample 4, built from clay; cf. De Roeve, 2004, 21), the intercalated clay layer (sample 9) and the underlying creek ridge sediments (samples 12–14; Fig. 7). Similarly, clay proxies such as titanium oxide values over 0.1% and detectable rubidium contents are again limited to one of the hearths (sample 4), the intercalated clay layer (sample 9) and the underlying creek ridge sediments (samples 12–14; Fig. 7).

The remarkably high values for sulphur (up to 3.7%; Fig. 7) do not originate from the board, cloth or adhesives used, as the maximum sulphur content measured in these was c. 0.8% (Table 2; measurements 2475; 2476; 2478). The high sulphur values most likely represent the presence of pyrite. From the 12th century AD onward (Huisman et al., 2008, 36–43), the local landscape changed dramatically due to large floods and subsidence caused by reclamation with ditches of former peatlands, allowing for the formation of an inland sea (Zuiderzee). As

a results, downward transport of sulphate-containing sea water caused pyritization of the underlying organic rich anthropogenic deposits, implying that the high sulphur values as such have no relevance for the archaeological period (Neolithic; c. 4000 cal BC) for which the lacquer-peel section was created.

3.5. Oostwoud-Tuithoorn

As with the Groningen-Winschoterdiep ard-marks (Section 3.2), the quantitatively limited data-set calls for cautiousness in generalisation, yet here too the hypothesis was that the ard-marks would show (a) an increase in phosphate, (b) have a relatively high organic content, resulting in an increased dilution of measurable elements, and (c) an increased mobilisation of iron oxides (*supra*). To test these assumptions, three individual ard-marks were measured with the hand-held XRF. For each suspected ard-mark, a measurement located centrally in the darker discolouration was accompanied by a measurement to either side of it. This way, the contrast between the geochemical signal of the 'b' layer (the underlying natural clayey and sandy creek deposits; Van Giffen, 1962, 199) and of the 'a' (agricultural) layer could be studied. The results for the various elements are listed below (Fig. 8).

As with the Groningen-Winschoterdiep lacquer-peel, phosphorus could not readily be used to discriminate between ard-marks and natural sediment. Although two of the three ard-marks have yielded the only observable values for P (Fig. 8: measurements 2 and 8, otherwise below detection limit), the large error margin during measurement (error margins in ppm for phosphorus during measuring 35–124%) indicates that these are not significant values.

In contrast to the Groningen-Winschoterdiep lacquer-peel, values for calcium within the ard-marks are here – significantly and consistently – lower than that of the surrounding sediment. This is probably due to the difference between a naturally calcareous underlying sandy-clayey sediment (*supra*) and the superimposing less calcareous arable layer. The lower calcium content in the ard-marks could be the effect of decalcification of the soil surface during the formation of the ard-marks. Effectively, the arable layers could still be enriched in Ca (compared to their original composition; *supra*), but any such rise in calcium is overshadowed by the much more prominent geochemical contrast of underlying natural calcareous sediment and overlying arable soil.

None of the other elements listed in Fig. 8 show a consistent correlation with the ard-marks, with values for K-, Al-, Fe- and Ti-oxides and Sr, Zr and S of the ard-marks overlapping with the ranges observed in the natural sediment. Evidently, no enhanced mobilisation of Fe within the ard-marks can be outlined. Moreover, the ard-marks do not show a significantly different percentage of 'balance', suggesting that their organic content is not significantly different from the underlying sediment. In conclusion, only by a difference in calcium content and colour could the Oostwoud-Tuithoorn ard-marks be differentiated from the underlying sediment.

4. Discussion

4.1. Factors potentially affecting the geochemical measurements of lacquer-peels with hand-held XRF

The geochemical signal obtained for the lacquer-peel sections can potentially be affected by reflections (of particularly the heavier elements) from glue, supporting textile and wooden frames used. The commonly used adhesives (polyvinyl acetate, cellulose nitrate in acetone, or polybutyl methacrylate resin) contain no elements measurable with XRF analysis (and solely contribute to the 'balance' signal) and thus pose no risk.

Gelatine-based glues (made from animal tissue; Horie, 1987; Nicholson et al., 2002) could potentially – if used – have raised the calcium, sulphur and phosphorus values (due to their presence

in the tissues and bones used for glue preparation). XRF-analysis by Fens (2010) has however shown that gelatine-based glues used in Dutch archaeology around c. 1940–1970 are prone to show only an increase in sulphur and chlorine, when applied to bone. Both sulphur and chlorine are used in the production of gelatine-based glue (Nicholson et al., 2002), with hydrochloric acid being used to remove the calcium phosphate (apatite) from the glue, and sulphuric acid being used to lighten the colour of the glue at the final stages of production and prevent its putrification (Fens, 2010). Although the gelatine-based glues studied contained between 1.9–2.6% S and 1.3–4% Cl, on the bone samples onto which such glues were applied studied by Fens (2010), values of c. 0.7–13.7% for S and only 0.04–0.3% Cl were documented. Maybe part of the chloride from the hydrochloric acid was washed out during the manufacturing process.

Regardless of the small risk of soil-incorporation into the glue fragments measured, tracers for gelatine-based glues such as chlorine and sulphur (*supra*) are invariably low for even the samples probably containing traces of sediment (Cl invariably lower than 0.32%, S invariably lower than 1.42%; Table 2), indicating that on the panels measured, gelatine-based glues were not used. In addition, the fact that cobalt values remained below detection limit (<260 ppm; Table 2), shows that epoxy resins using cobalt naphthenate catalysts (cf. Stoakley and St. Clair, 1986; Hawkins, 2001, 86; Ambrogi et al., 2002, 19; 24) were also not used. Rather, it appears that solely synthetic glues – such as polyvinyl acetate ((C₄H₆O₂)_n) or polyester glues – were used and that, consequently, contamination of the values for calcium, sulphur and phosphorus due to the use of gelatine-based glues can be excluded for the studied lacquer-peel films.

Generally, after a section of sediment is covered in glue, a layer of cloth is applied to aid in flexibly transferring (hence: peeling) the glue-trapped sediment to a more rigid wooden panel. Potentially, such fabrics used for the removal of glue-trapped sediment could affect the XRF signal as well. The textiles used to transfer the glue-impregnated soil sections generally consist of linen, cotton or jute. As these are all natural fibres (from *Linum usitatissimum*, *Gossypium spec.* and *Corchorus spec.* respectively) comprising mainly cellulose, hemicellulose, pectin and lignin (Vassilev et al., 2010, Table 5), they largely fall within the unobserved spectrum ('balance signal') of the XRF device utilized. Quantities of potassium (0.83wt%), phosphorus (0.62wt%), magnesium (0.43wt%), calcium (0.24wt%) and other elements (Cu, Fe, Mn, Na, Zn, all < 0.02wt%) within flax (Morris, 2007, 19 Table 6, cf. Heikal et al., 1980, 26; Beke and Volkmar, 1995, 401 Fig. 1) are invariably lower than 0.84wt% and unlikely to interfere, particularly as they are light elements (excluding deep penetration/reflection) and were never in direct exposure to the XRF beam (i.e. always covered by glue and sediment). The inorganic composition of jute fibres consists mainly of calcium (0.2wt%), iron (0.05wt%), aluminium (0.04wt%), magnesium (0.03wt%), with all other elements lower than 0.03wt% (Del Rio, unpublished). Similarly, the cotton seeds that produce the fibres used in textiles show comparable values for potassium (0.8–1.1wt%), phosphorus (0.59wt%), magnesium (0.08–0.32wt%), calcium (0.16–0.22wt%) and several other elements (Na, Cl, Fe, Zn, Mn, all < 0.12wt%; Doğan et al., 2012, 17 Table 1; Mujahid et al., 2000, 353).

The dominant inorganic elements for linen and flax (potassium) and jute (calcium) were in this study either undetected (calcium) or very low (potassium < 0.03wt%; measurement no. 2475 in Table 2), suggesting that the fabrics involved will not significantly affect the measurements of the sediments of the lacquer-peel films. In addition, because the textiles and the wooden frames used are situated underneath the analysed soil material, secondary X-rays from light elements (< K) will not be able to reach the detector.

The fabrics with the glued-on sediments are fixed to wooden panels to prevent damage from warping and handling. For this purpose, plywood, chipwood and hardboard panels were used from the 1950s

onwards (e.g. Van Baren and Bomer, 1979, 8; Bowyer, 2000, 176; Barahona and Iriarte, 1999, 306). Due to the composite nature of these materials (consisting mostly of wood chips and wood pulp of unknown species and various kinds of glue; Chapman, 2006), there can be no adequate prediction of their inorganic composition. Therefore, the measurements for the five different panels analysed in this study (Table 2) are discussed to determine whether their composition could interfere with the measurements of the main elements (P, S, Fe, Al, Ca and K) used to test the suitability of lacquer-peel sections for geochemical analyses.

Foremost, the high 'balance' reading (invariably above 97%) testifies to the low inorganic content of the wooden panels used (one plywood panel; no. 2489 and four hardboard panels; Table 2). Sulphur ranges between 0.06 and 1.23wt% (Table 2), which – considering the invariably low (<0.092wt%) content of chlorine – cannot be attributed to the use of gelatine-based glues. Calcium comprises up to 0.9wt% and measurements for aluminium (up to 0.14wt%), iron (up to 0.08wt%) and potassium (up to 0.4wt%) are consistently low. The values for phosphorus are below the detection limit (<0.09wt%) for all but two measurement (no. 2476; 0.4wt% and no. 2404; 0.23wt%).

Considering the fact that the wood panels are separated from the sediments by additional layers of glue and fabric, it is unlikely that reflections from the wood panels proper may interfere with the geochemical composition as determined with the XRF. Only in the case of sulphur, which is present in somewhat higher amounts (0.06–1.23wt%), is there a cause for caution in interpreting the XRF readings. However the source of sulphur may not be the wood itself but may be caused by the historic indoor air quality (supra). Notably, the only plywood panel investigated (Table 2; no. 2489) has the lowest sulphur content, which could relate to its later date of manufacture (>1980, lacquer-peel fixed in 2007, limiting its exposure to SO₂ containing air) or to the fact that other adhesives or components were for its fabrication.

Despite the above argumentation that the inorganic composition of the boards, glues and transfer fabrics used are unlikely to have influenced the geochemical signatures as measured by hand-held XRF, one risk has remained undiscussed. When measuring concentrations, there is a risk that the organic components of the boards, glues and cloth used indirectly influences the 'balance' signal and consequently the absolute concentrations. In this study, this risk has proven minimal: (a) predominantly lighter elements were studied that have very shallow secondary X-rays penetration depth, and (b) by hand-picking the sample locations areas of poor sediment adhesion (causing greater risk of unwanted reflections from underlying materials) could easily be avoided.

4.2. Potential of palaeochemical analysis of lacquer-peel sections with hand-held XRF

All four lacquer-peel sections discussed here proved to have retained geochemical information extractable through hand-held-XRF analysis. Whereas before-hand interference from inorganic elements in the adhesives, cloth and wooden board used for fixture was expected, none of the lacquer-peel sections demonstrably showed such effects. This is caused by the fact that (a) no gelatine-based glues were used, (b) that the materials (linen, cotton, flax, hardboard and plywood) used are primarily organic in origin (contributing only to the balance signal), and (c) the fact that sediment coverage and thickness of the sediments encased in the lacquer-peel films was sufficient to prevent reflections from materials deeper down.

The age, or period of fabrication, of the panels does not seem to affect the suitability for geochemical analysis with XRF, as panels dating from 1957 as well as lacquer-peel sections made in 2007 yielded predictable and reliable outcomes. Also, lacquer-peel sections from wetland and upland context showed comparable suitability: lithologically varied sediments (Table 1) such as glacial till, coversand, creek deposits and anthropogenic layers all yielded reliable and consistent results. Noteworthy, however, is that the geochemical resolution of the vertical

(i.e. soil section) lacquer-peels proved more suitable to test hypotheses than the horizontal (i.e. level) lacquer-peels (ard-marks). This difference is related to (a) the larger number of measurements taken for the vertical sections, (b) the larger geogenetic and lithological variability generally reflected in vertical sections, and (c) the suitability to test a combination of hypotheses on both soil-formation and archaeologically observable phenomena.

The selection of elements chosen for discussion here (comprising Si, Ca, P, K, S, Al, Fe, Ti, Sr, Rb and Zr) proved suitable to (a) determine basic lithology and lithogenesis, (b) analyse processes of soil-formation (e.g. podzolisation), and (c) trace specific anthropogenic processes (element enrichment of hearths and arable layers). Noteworthy is that while phosphorus is often used in archaeology as a tracer for anthropogenic interference (signalling manuring and/or occupation; Holliday and Gartner, 2007), in this study it proved an unreliable indicator for arable if used in isolation (low phosphorus content of ard-marks in the Groningen and Oostwoud lacquer-peels). In lacquer-peel films with ard-marks, a combination of calcium, sulphur and phosphate should be studied to geochemically characterize or identify ard-marks. Phosphorus content did, however, prove a reliable indicator for hearths and could be used to disprove theories on supposed increased manuring of Celtic field banks.

The proven suitability of hand-held XRF analysis of lacquer-peel films underlines an enduring importance of lacquer-peel films beyond mere visual documentation and representation of archaeological and geological sites studied in the past. Unlike with strategies of discontinuous sampling such as bulk- or kubiena samples, sections are preserved completely – allowing for stratigraphically more detailed or continuous geochemical sampling. Moreover, the fact that various pedogenic processes are visually identifiable (e.g. gley stains), allows researchers to target or avoid parts of the lacquer-peel sections if desired. This allows for a combined, selective, continuous assessment of visual, textural and geochemical parameters that cannot be achieved with other sample types (e.g. thin sections).

5. Conclusions

This study has demonstrated the suitability of lacquer-peel films for palaeo-geochemical analysis using hand-held XRF. First, analyses undertaken of (a) the adhesives used, (b) the cloths used in transfer, and (c) the wooden panels to which the lacquer-peels films were fixed, have shown that their organic content is unlikely to interfere with the geochemical signal as extractable by hand-held XRF. Only if gelatine-based glues have been used, can values for sulphur and chlorine become artificially elevated (Section 4.1). Second, proof of concept was demonstrated by the sequential consistency of the geochemical signals in the Zeijen-Noordse veld lacquer-peel section. Third, and more importantly, the geochemical information obtained through hand-held XRF analysis of the lacquer-peel sections proved consistent with pedological predictions and archaeological hypotheses. This means that within lacquer-peels, geochemical properties have retained contextual relevance. Specific hypotheses compiled for each of the four lacquer-peel films proved testable. Moreover, the suitability of the lacquer-peel sections to XRF geochemical analysis was shown to be good regardless of the ages (from the 1950s to the 2000s) of the lacquer-peel films and irrespective of the geological area of origin (e.g. wetland versus upland geogenesis). In short, lacquer-peel films have shown to represent a valuable resource for (palaeo-)geochemical study.

This is particularly relevant for the field of archaeology, whose research method is inherently destructive: the excavated parts of sites are forever destroyed and lost. Lacquer-peel sections from old excavations are thus a prime resource for geochemical analyses of sites that no longer exist. Moreover, the fact that older lacquer-peel films proved to have retained their geochemical information value, allows the study of the geochemical composition of such long-gone sites with modern-day techniques. Therefore, in addition to representing an ex-situ

treasury of 1-to-1 representation of site characteristics such as stratigraphy and contexts, lacquer-peel films document the lithology, pedology and – as shown in this study – geochemistry of key locations for future research questions. Far from being an obsolete method, we argue that – based on the observed geochemical potential and documentary properties – new lacquer-peel sections should be taken at archaeological and geological excavations and call for more intensive study of lacquer-peel films in various archaeological or geological depots.

Although we have argued that possibility for geochemical analysis of (old) lacquer-peel sections is particularly of importance to the

field of archaeology, its merits evidently extend further. Particularly in the field of environmental studies, the archives of soil-sections taken by archaeologists and geologists may prove one of the most reliably dated data-sets to trace topsoil pollution during the last 50–70 years.

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Appendix I

XRF measurements for calciumoxide, phosphorus, siliciumoxide, potassiumoxide, aluminiumoxide, ironoxide, and titaniumoxide (as percentages, with error margins between brackets) and content of strontium, rubidium, zirconium and sulphur (in ppm, with error margins between brackets for all samples. Note: Totals are more than 100% as the balance (Bal; non measurable components) includes the oxide part of the compounds (O₂ in SiO₂ etc).

	SiO ₂	CaO	P ₂ O ₅	K ₂ O	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	S	Zr	Sr	Rb	Balance
	%	%	%	%	%	%	%	ppm	ppm	ppm	ppm	%
<i>Zeijen: sample</i>												
1	38 (0.32)	0.10 (0.09)	0.09 (0.04)	0.58 (0.011)	1.21 (0.08)	0.20 (0.006)	0.25 (0.01)	1579 (108)	177 (4.40)	20 (1.76)	19 (2.51)	80.28
2	24 (0.25)	0.10 (0.09)	0.08 (0.08)	0.43 (0.009)	0.43 (0.06)	0.17 (0.006)	0.26 (0.01)	1977 (124)	134 (3.95)	16 (1.68)	17 (2.51)	87.60
3	39 (0.31)	0.09 (0.09)	0.13 (0.04)	0.41 (0.008)	0.69 (0.07)	0.17 (0.006)	0.15 (0.01)	1837 (108)	126 (3.66)	15 (1.55)	11 (2.51)	80.42
4	46 (0.39)	0.10 (0.10)	0.11 (0.11)	0.55 (0.013)	0.86 (0.09)	0.18 (0.006)	0.12 (0.01)	1250 (124)	155 (4.41)	17 (1.80)	14 (2.51)	76.86
5	56 (0.40)	0.10 (0.10)	0.22 (0.06)	0.75 (0.015)	1.89 (0.10)	0.23 (0.007)	0.24 (0.01)	1108 (104)	188 (4.58)	21 (1.81)	24 (2.51)	71.32
6	43 (0.35)	0.10 (0.10)	0.10 (0.05)	0.62 (0.013)	1.68 (0.10)	0.22 (0.007)	0.31 (0.01)	1376 (113)	140 (4.02)	17 (1.72)	25 (2.51)	77.87
7	40 (0.34)	0.12 (0.08)	0.25 (0.05)	0.53 (0.012)	1.75 (0.10)	0.17 (0.006)	0.41 (0.01)	1944 (127)	97 (3.48)	19 (1.76)	18 (2.51)	78.96
8	44 (0.33)	0.14 (0.08)	0.27 (0.05)	0.65 (0.013)	2.18 (0.10)	0.19 (0.006)	0.45 (0.01)	1641 (109)	113 (3.51)	18 (1.65)	21 (2.51)	76.78
9	45 (0.36)	0.11 (0.08)	0.23 (0.05)	0.69 (0.014)	2.32 (0.11)	0.21 (0.007)	0.40 (0.01)	1687 (120)	161 (4.31)	27 (2.00)	27 (2.51)	76.27
10	40 (0.33)	0.11 (0.08)	0.29 (0.05)	0.79 (0.016)	2.77 (0.11)	0.24 (0.007)	0.44 (0.01)	1345 (108)	142 (4.05)	26 (1.95)	27 (2.51)	78.19
11	47 (0.35)	0.14 (0.08)	0.44 (0.05)	0.82 (0.015)	3.48 (0.12)	0.25 (0.007)	0.43 (0.01)	1835 (117)	155 (4.09)	27 (1.93)	27 (2.51)	74.51
12	45 (0.35)	0.11 (0.08)	0.35 (0.05)	0.76 (0.016)	3.30 (0.12)	0.22 (0.007)	0.72 (0.02)	1592 (111)	130 (3.90)	20 (1.78)	23 (2.51)	75.30
13	40 (0.33)	0.12 (0.08)	0.20 (0.05)	0.66 (0.014)	2.65 (0.11)	0.19 (0.006)	0.49 (0.01)	1224 (111)	152 (4.20)	22 (1.86)	21 (2.51)	78.53
14	49 (0.35)	0.11 (0.08)	0.26 (0.05)	0.87 (0.018)	3.70 (0.12)	0.24 (0.008)	1.16 (0.02)	2224 (110)	145 (3.99)	22 (1.79)	22 (2.51)	72.65
15	48 (0.36)	0.12 (0.08)	0.18 (0.05)	0.75 (0.015)	2.97 (0.12)	0.20 (0.007)	0.66 (0.02)	1615 (112)	123 (3.77)	22 (1.83)	20 (2.51)	74.49
16	45 (0.36)	0.14 (0.08)	0.21 (0.05)	0.76 (0.015)	3.12 (0.12)	0.21 (0.007)	0.60 (0.02)	1722 (118)	130 (3.95)	22 (1.87)	22 (2.51)	75.50
17	46 (0.37)	0.13 (0.08)	0.18 (0.05)	0.78 (0.016)	3.48 (0.13)	0.18 (0.006)	0.65 (0.02)	1765 (120)	236 (5.31)	28 (2.09)	26 (2.51)	74.70
18	31 (0.30)	0.11 (0.08)	0.09 (0.09)	0.65 (0.015)	1.92 (0.10)	0.16 (0.006)	0.53 (0.01)	946 (113)	105 (3.71)	18 (1.81)	16 (2.51)	82.87
19	53 (0.39)	0.19 (0.08)	0.11 (0.11)	0.88 (0.017)	3.58 (0.13)	0.21 (0.007)	0.82 (0.02)	1874 (123)	184 (4.66)	32 (2.16)	30 (2.58)	71.52
20	53 (0.39)	0.24 (0.09)	0.11 (0.11)	1.05 (0.021)	3.26 (0.13)	0.24 (0.008)	0.85 (0.02)	2822 (141)	426 (7.45)	37 (2.42)	37 (2.89)	71.22
21	56 (0.40)	0.10 (0.10)	0.11 (0.11)	0.83 (0.017)	2.85 (0.12)	0.16 (0.006)	0.57 (0.01)	1063 (107)	123 (3.85)	25 (1.94)	21 (2.51)	70.57
<i>Groningen: sample</i>												
1	42 (0.30)	0.26 (0.08)	0.18 (0.04)	0.47 (0.007)	0.84 (0.06)	0.09 (0.004)	0.14 (0.01)	3189 (108)	64 (2.73)	12 (1.41)	12 (2.51)	78.47
2	37 (0.28)	0.29 (0.08)	0.24 (0.04)	0.39 (0.005)	0.85 (0.06)	0.09 (0.003)	0.12 (0.01)	3752 (114)	63 (2.69)	11 (1.36)	6.67 (2.51)	80.80
3	47 (0.32)	0.23 (0.08)	0.23 (0.04)	0.44 (0.006)	1.03 (0.07)	0.09 (0.004)	0.11 (0.01)	2911 (106)	82 (2.97)	15 (1.48)	9.52 (2.51)	76.32
4	42 (0.30)	0.22 (0.08)	0.23 (0.04)	0.43 (0.006)	0.89 (0.06)	0.12 (0.004)	0.12 (0.01)	2514 (100)	76 (2.90)	12 (1.41)	9.38 (2.51)	78.94
5	41 (0.28)	0.25 (0.08)	0.26 (0.04)	0.42 (0.006)	0.98 (0.06)	0.10 (0.004)	0.29 (0.01)	5221 (123)	34 (2.24)	10 (1.31)	5.74 (2.51)	78.90
6	39 (0.28)	0.18 (0.08)	0.23 (0.04)	0.37 (0.004)	0.87 (0.06)	0.08 (0.003)	0.10 (0.01)	2065 (86)	58 (2.60)	11 (1.34)	8.42 (2.51)	80.55
<i>Swifterbant S3: sample</i>												
1	25 (0.20)	2.88 (0.10)	0.78 (0.04)	0.29 (0.007)	0.68 (0.06)	0.06 (0.004)	0.32 (0.01)	18315 (236)	4.96 (1.84)	71 (2.57)	4.90 (4.90)	82.66
2	34 (0.27)	2.94 (0.11)	2.67 (0.06)	0.37 (0.012)	0.24 (0.07)	0.05 (0.004)	1.88 (0.03)	11359 (217)	3.57 (3.57)	224 (5.23)	4.90 (4.90)	76.97
3	31 (0.24)	1.77 (0.10)	0.90 (0.04)	0.28 (0.007)	0.44 (0.06)	0.07 (0.004)	0.50 (0.01)	12471 (203)	10 (2.01)	64 (2.57)	4.90 (4.90)	81.14
4	18 (0.18)	2.93 (0.11)	2.17 (0.05)	0.60 (0.018)	1.06 (0.07)	0.14 (0.007)	1.99 (0.03)	19927 (274)	12 (2.13)	70 (2.79)	5.24 (2.51)	82.95
5	17 (0.16)	2.03 (0.10)	1.14 (0.04)	0.15 (0.003)	0.08 (0.08)	0.01 (0.002)	0.92 (0.02)	11548 (185)	4.28 (1.83)	62 (2.44)	4.90 (4.90)	87.63
6	23 (0.20)	2.38 (0.10)	1.50 (0.04)	0.29 (0.006)	0.16 (0.05)	0.03 (0.003)	0.57 (0.01)	11209 (182)	3.69 (3.69)	70 (2.59)	4.90 (4.90)	84.14
7	26 (0.20)	0.79 (0.09)	0.81 (0.03)	0.19 (0.005)	0.08 (0.04)	0.01 (0.003)	1.21 (0.02)	14324 (193)	5.33 (1.82)	46 (2.15)	4.90 (4.90)	84.08
8	29 (0.26)	1.26 (0.10)	0.65 (0.05)	0.23 (0.007)	0.16 (0.06)	0.04 (0.004)	1.05 (0.02)	15390 (256)	8.09 (2.05)	61 (2.63)	4.90 (4.90)	81.93
9	22 (0.19)	1.58 (0.09)	0.26 (0.03)	0.62 (0.012)	1.75 (0.07)	0.16 (0.006)	0.68 (0.01)	14106 (200)	19 (2.11)	36 (2.02)	10 (2.51)	84.47
10	17 (0.16)	1.06 (0.09)	0.26 (0.03)	0.26 (0.008)	0.49 (0.05)	0.05 (0.004)	2.09 (0.03)	27671 (285)	4.49 (1.77)	28 (1.80)	4.90 (4.90)	85.94
11	24 (0.19)	1.93 (0.10)	0.45 (0.03)	0.34 (0.009)	0.86 (0.06)	0.07 (0.005)	1.14 (0.02)	21824 (251)	9.30 (1.85)	38 (1.98)	4.90 (4.90)	82.86
12	26 (0.20)	3.49 (0.11)	0.59 (0.04)	0.82 (0.021)	3.03 (0.10)	0.23 (0.008)	1.89 (0.02)	31549 (325)	12 (1.97)	41 (2.11)	6.48 (2.51)	77.02
13	25 (0.20)	3.18 (0.11)	0.73 (0.04)	0.80 (0.020)	2.63 (0.09)	0.20 (0.008)	1.95 (0.03)	23346 (270)	22 (2.20)	48 (2.31)	15 (2.51)	78.77
14	22 (0.21)	5.38 (0.13)	0.10 (0.04)	0.77 (0.021)	2.43 (0.11)	0.18 (0.008)	0.85 (0.02)	37367 (410)	15 (2.19)	49 (2.44)	8.61 (2.51)	78.30
<i>Medemblik: sample</i>												
1	22 (0.19)	3.36 (0.10)	0.06 (0.03)	0.56 (0.010)	1.11 (0.06)	0.12 (0.005)	0.52 (0.01)	6370 (135)	28 (2.18)	34 (1.92)	11 (2.51)	84.47
2	26 (0.20)	1.59 (0.09)	0.08 (0.05)	0.54 (0.011)	1.53 (0.06)	0.13 (0.005)	0.46 (0.01)	6160 (123)	21 (1.98)	15 (1.41)	5.12 (2.51)	83.87
3	19 (0.17)	4.33 (0.11)	0.05 (0.05)	0.48 (0.010)	1.12 (0.06)	0.12 (0.005)	0.66 (0.01)	6590 (132)	46 (2.49)	42 (2.12)	9.31 (2.51)	84.83
4	25 (0.22)	5.86 (0.13)	0.07 (0.07)	0.71 (0.017)	1.63 (0.08)	0.16 (0.007)	0.84 (0.02)	7473 (168)	51 (2.80)	68 (2.78)	17 (2.51)	79.83
5	38 (0.30)	3.00 (0.11)	0.09 (0.09)	0.93 (0.022)	2.09 (0.11)	0.25 (0.009)	1.01 (0.02)	8279 (201)	65 (3.03)	42 (2.34)	21 (2.51)	75.67
6	43 (0.31)	6.07 (0.13)	0.09 (0.09)	0.80 (0.019)	1.95 (0.10)	0.17 (0.007)	0.68 (0.02)	7020 (175)	187 (4.80)	129 (4.03)	29 (2.53)	71.33
7	25 (0.20)	3.47 (0.11)	0.06 (0.06)	0.55 (0.010)	1.38 (0.07)	0.12 (0.005)	0.52 (0.01)	5902 (131)	31 (2.27)	39 (2.06)	10 (2.51)	83.01
8	25 (0.20)	1.89 (0.10)	0.08 (0.03)	0.52 (0.011)	1.56 (0.06)	0.13 (0.005)	0.51 (0.01)	6525 (126)	22 (2.03)	19 (1.53)	6.72 (2.51)	83.95
9	35 (0.28)	5.31 (0.12)	0.08 (0.08)	0.72 (0.016)	1.66 (0.09)	0.17 (0.007)	0.76 (0.02)	11495 (218)	110 (3.79)	86 (3.26)	22 (2.51)	75.48

Appendix II

XRF measurements of glue, fabric and board for six lacquer-peel panels. All measurements taken in mining mode (60 seconds). Elements below detection limit: Mg (<6000 ppm), Sn (<80 ppm), Cr (<600 ppm), Ag (<90 ppm), Ni (<90 ppm), Sb (<60 ppm), Au (<50 ppm), Se (<10 ppm), W (<230 ppm), Bi (<15 ppm), Pd (<20 ppm). Values for oxides as percentages, other elements as PPM. Note: Totals are more than 100% as the balance (Bal; non measurable components) includes the oxide part of the compounds (O₂ in SiO₂ etc). ENEO = Early Neolithic, MNEO = Middle Neolithic, LNEO = Late Neolithic, ROM = Roman Period.

no.	Site of origin	Objective	Bal	SiO ₂	CaO	P ₂ O ₅	K ₂ O	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MnO	S	Cl
2488	Swifterbant (MNEO field)	Glue, yellow thick patch	77.133	23.311	4.226	0.475	0.853	0.334	0.306	6.726	0.071	14174.300	985.560
2478	Swifterbant (MNEO settlement S3)	Glue	91.736	9.461	0.932	0.413	0.412	0.647	0.098	1.197	0.046	8338.090	2823.100
2433	Oostwoud (LNEO ardmarks)	Glue	95.069	3.815	0.281	<0.156	0.127	<0.3	0.051	1.019	0.022	13423.610	3215.980
2434	Oostwoud (LNEO ardmarks)	Glue, possibly also measuring wood	98.385	1.362	0.285	<0.033	0.024	0.074	0.008	0.056	0.015	5680.850	531.800
2374	With traces of soil (high Si)	Glue, possibly measuring wood as well	98.346	1.461	<0.099	0.437	0.035	0.142	0.526	0.075	<0.008	2186.940	457.180
2376	Wijster Looveen (driftsand underneath ROM site)	Glue, possibly measuring wood as well	98.383	1.462	0.158	0.428	0.038	0.261	0.011	0.081	<0.008	3540.240	439.950
2378	Wijster Looveen (driftsand underneath ROM site)	Glue, yellow thick patch	91.993	15.207	<0.094	0.061	0.154	0.471	0.038	0.097	<0.008	2980.570	620.950
2403	Wijster Looveen (driftsand underneath ROM site)	Glue	89.867	18.284	0.291	0.381	0.257	0.352	0.046	0.150	<0.009	5303.130	1010.270
2475	Swifterbant (MNEO settlement S3)	Cloth (linen or cotton)	98.836	1.233	<0.097	0.139	0.027	<0	0.010	0.100	<0.008	2191.100	1512.500
2489	Swifterbant (MNEO field)	Wooden board, front (multiplex)	98.989	0.252	0.857	<0.026	0.026	<0	<0.004	<0.005	<0.008	655.050	835.540
2476	Swifterbant (MNEO settlement S3)	Wooden board, front (hardboard)	98.970	1.088	<0.1	0.397	0.026	<0	0.033	0.068	<0.008	1434.480	580.950
2435	Oostwoud (LNEO ardmarks)	Wooden board, front (hardboard)	98.061	0.629	0.251	<0.04	0.019	0.082	<0.006	0.055	0.013	12326.090	877.640
2375	Wijster Looveen (driftsand underneath ROM site)	Wooden board, back (hardboard)	98.407	0.316	0.208	<0.037	0.014	0.135	<0.005	0.053	<0.008	10661.740	864.580
2377	Wijster Looveen (driftsand underneath ROM site)	Wooden board, back (hardboard)	99.172	0.257	0.154	<0.029	0.010	0.137	<0.004	0.047	<0.008	4291.750	567.620
2404	Wijster Looveen (driftsand underneath ROM site)	Wooden board, front (hardboard)	97.400	3.504	0.351	0.227	0.054	0.085	0.012	0.049	<0.009	3535.040	910.150
2405	Wijster Looveen (driftsand underneath ROM site)	Wooden board, back (hardboard)	98.205	0.292	0.444	<0.037	0.040	<0.1	<0.005	0.055	0.018	11238.790	625.620
2454	Winschoter Diep (MNEO posthole)	Wooden board, back (hardboard)	98.529	0.624	0.578	<0.035	0.035	0.072	<0.006	0.080	0.021	4644.340	747.110

Appendix II (continued)

no.	Zn	Cu	Co	Pb	Zr	Sr	Rb	As	Ba	V	Cd	Mo	Nb	Comment
2488	66.064	<22	<256	<12	177.905	301.899	72.239	14.94	290.78	113.794	<32	<7	13.22	With traces of soil (high Si)
2478	21.355	<10	<98	<7	22.511	34.074	15.024	<5	<133	<25	<22	6.01	7.5	With traces of soil (high Si)
2433	2519.480	102.708	<143	44.38	92.136	93.879	36.201	<13	<206	<89	<37	26.78	31.27	With traces of soil (high Si)
2434	145.949	12.087	<30	<6	12.915	11.066	<5	<4	<90	<23	25.84	13.61	17.58	with traces of soil (high Si)
2374	26.924	<10	<31	<8	12.994	9.968	<5	<4	<91	<29	19.41	11.27	16.35	With traces of white paint (high Ti)
2376	<16	17.955	<30	<6	11.719	7.666	<5	5.57	<83	<19	25.66	11.52	14.8	
2378	<16	<8	<33	<6	54.887	8.020	<5	<5	<110	<17	<18	<5	6	With traces of soil (high Si)
2403	<17	<9	<40	<9	41.265	10.181	8.109	<5	<134	<17	<23	7.06	6.49	With traces of soil (high Si)
2475	<16	<6	<34	<5	9.477	8.587	<5	<3	<89	<18	19.11	11.43	12.7	
2489	<13	<8	<21	<5	11.181	23.095	<5	<3	<88	<20	20.3	12.38	13.71	
2476	<16	<8	<28	<6	10.463	10.122	<5	<3	<92	<19	<16	11.64	13.73	
2435	134.569	15.624	<29	<7	28.430	20.805	6.577	<3	<89	<26	29.33	19.37	19.9	
2375	<17	37.958	<28	<5	87.493	13.085	7.415	<4	<94	<23	28.6	16.61	18.6	
2377	<16	18.227	<28	<5	12.117	10.110	6.051	<4	<87	<21	21.11	13.39	15.88	
2404	27.950	<9	<27	<6	9.676	10.523	<5	<3	<100	<18	17.97	11.16	11.86	
2405	33.285	31.158	<29	<6	42.281	18.633	6.003	<3	<91	<25	21.33	18.57	22.99	
2454	30.319	9.921	<32	<6	48.241	19.188	7.104	<3	<90	<26	24.48	16.53	19.64	

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