[Supplementary material]

Hunter-fisher-gatherer pottery production and use at the Neolithic shell-midden of Riņņukalns, Latvia

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Petrographic fabric descriptions

Table S1. Riņņukalns: description of matrix, inclusions, temper and firing temperatures of Petro-fabrics 1–5 (potsherds and reference material).

Potsherds				
Petro-fabric (sample no.)	**Matrix**	**Inclusions**	**Temper**	**Firing temperature and notes on surface treatments**
Petro-fabric 1 (RK00134, 00344, 00399, 00574, 00179, 10032, 01217, 01937, 2419)	Reddish-brown (usually darker core), non-calcareous; most samples have oriented inclusions; sample RK10032 (unfired sample) has a more birefringent (anisotropic) matrix than the	Abundant: shell fragments (>20 per cent; mainly finer than 1.0mm up to 5.3mm, very occasional amphibole (RK00134, 00344). Common: fine and mainly well-sorted sub-angular quartz (~10 per cent; ~0.03 × 0.02mm; scattered coarser quartz inclusions, up to 0.15mm), iron-rich clay pellets (in some cases containing fine quartz inclusions), iron oxides	Shells	Below 750°C (shell microstructure perfectly intact, see Maritan *et al.* 2007); sample RK10032 was unfired; Surface treatments: RK00399 was polished and then impressed: circle-impressed decoration; RK01217 was probably polished; RK2419 was probably smoothed and then painted on both surfaces (thinner stroke visible on one surface); RK01937 was polished on one surface, there are some small traces of deposits, possibly paint/ochre (?); RK00344 has some ochre on one surface; RK00179 has an iron layer (ochre?), which is visible on scattered areas of one surface

	other samples examined in this group	Occasional: fine muscovite mica (1 per cent), plagioclase (1 per cent), k-feldspar (1 per cent), pyroxene (1 per cent), bone fragments (e.g. RK10032) Very occasional: biotite (sample RK01937), amphibole, polycrystalline quartz, stretched metamorphic quartz, zircon, a small fragment of microcline (RK00179), plant matter that did not burn out of the clay during firing (e.g. RK00134)		
Subgroup a (four samples: RK00173, 00630, 00902, 2394)	Dark red to brown-reddish, non-calcareous, and oriented (some have more oriented clay than others, e.g.	Abundant: crushed shells Common: quartz sand (<20 per cent; between 1.5 × 1.0 and 0.03 × 0.03mm), plagioclase (<2 per cent) Very occasional: amphibole (e.g. RK2394) and pyroxene, biotite, fine felsic rock fragments (from	Shells	Below 750°C (shell microstructure perfectly intact); Surface treatments: RK00173 has a nicely polished surface; Some post-depositional calcareous fragments

	RK2394 and 00173)	intrusive rocks – granite(?); e.g. quartz, plagioclase and epidote, sample RK00630), opaques (possible ilmenite), plant matter (e.g. RK00630)		
Petro-fabric 2 (three samples: RK00022, 01015, 10042)	Brown to reddish-brown, non-calcareous and oriented (except for sample RK10042)	Abundant: shell fragments (>20 per cent) with homogeneous structure and in some cases visible exterior walls, fine iron oxides. Sample RK00022 has coarser and more abundant shells than the other samples Common: fine quartz sand (<5 per cent; 0.02 × 0.02 mm), k-feldspar, plagioclase (weathered plagioclase) Occasional: muscovite mica	Shells	Mostly below 750°C (sample RK01015 was more highly-fired than the others); Surface treatments: RK10042 was smoothed/polished RK01015 and 00022 have possibly traces of ochre
Petro-fabric 3 (sample RK01043; a	Brown-reddish and non-	Common: well-sorted sub-angular to sub-rounded quartz (7–15 per cent; ~0.03 × 0.02mm),	Plant- and/or/ shell-	Firing temperature: approximately 800°C

decorated rim)	calcareous clay, starting to vitrify	fine muscovite mica (<2 per cent), iron-rich clay pellets, opaques, scattered voids probably left by plant matter Occasional: pyroxene, plagioclase Very occasional: iron oxides	tempered (?)	
Subgroup a (sample RK01155) an undecorated pot	Brown-reddish, non-calcareous, oriented clay, starting to vitrify	Abundant: planar voids (>20 pre cent); these might be due to shell and/or plant temper, or both Common: rather well-sorted quartz (20 per cent; 0.04 × 0.04mm), iron oxides, plagioclase, muscovite Very occasional: fine intrusive rock inclusions with micrographic texture (intergrowth of quartz with alkali feldspar?) (orthopyroxene?), biotite, amphibole.	Plant matter? and/or shells(?)	Firing temperature: ~750–800°C; Surface treatment: possibly polished surface, fine clay layer on the top of the surface

Subgroup b (sample RK01164)	Red, non-calcareous and starting to vitrify	Abundant: planar voids left by the burning of plant matter and/or in some cases shells Common: well-sorted quartz (>10 per cent; 0.04 × 0.03mm, with some coarser quartz inclusions), fine muscovite Occasional: papules, pyroxene Very occasional: weather feldspar	Plant matter (?)	Firing temperature: ~750–800°C A plant impression on the surface; Polished/smoothed surface; Iron infills some of the planar voids
Petro-fabric 4 (sample RK02392)	Dark red, non-calcareous with some orientation; clay filaments starting to vitrify	Abundant: mainly sub-angular sand (30 per cent; 0.6 × 0.4 and 0.03 × 0.02mm; some of the quartz is sub-rounded) Common: plagioclase, muscovite, pyroxene Occasional: fine polycrystalline quartz, fine elongated voids possibly left by the burning of plant matter, which might have been naturally occurring in the raw material	Added sand (?)	Firing temperature: ~750–800°C; Decorated with fine impressions

		Very occasional: fine intrusive rock inclusions		
Petro-fabric 5 (sample RK01284)	Red, non-calcareous, with some orientation	Abundant: poorly-sorted quartz sand (20 per cent; 1.2 × 1.0 and 0.03 × 0.02mm), plagioclase Common: some rock fragments (up to 1.8mm) including hornblende, plagioclase and quartz, and apatite) Occasional: K-feldspar, amphibole, biotite with thick lamellae, a clay pellet. Altered hornblende and biotite, possible because of the heating and biotite is oxidised (P. Raase *pers. comm.*).	Sand and rock temper	Firing temperature: ~750°C; The surface of the vessel was smoothed

		Very occasional: fine planar voids left by the burning of plant matter (naturally present in the clay)		
Reference material				
Sample RK10033 (unfired clay; flotation residue, trench 1B)	Brown-reddish and non-calcareous	Abundant: iron-rich pellets (occasionally containing some fine quartz inclusions), iron-rich pellets (up to 0.63mm) Common: not very well-sorted mainly fine sub-angular quartz (0.03 × 0.02 and 0.1 × 0.05mm), stretched metamorphic quartz Occasional: papules, fine microcline, apatite and quartz, irregular-shaped voids (naturally present in the soil) Very occasional: amphibole, opaques, clay pellets, plagioclase,		Unfired

		fine muscovite, biotite, a rounded igneous inclusion		
Sample RK00216 (hand collection, clay; trench 1A)	Brown-reddish and non-calcareous	Abundant: sub-angular ton sub-rounded poorly-sorted quartz (20–40 per cent [in some regions]; between 0.03 × 0.04 and 0.2 × 0.15mm); the sand is concentrated in some regions (as in sample RK00379) Common: plagioclase (some of which is zoned), iron oxides, fine bone fragments, clay pellets, opaques Occasional: polycrystalline quartz, green amphibole, k-feldspar (possibly from granite), muscovite mica, biotite (similar		Unfired

		to that in RK1284; P. Raase *pers. comm.*), microcline, post-depositional(?) calcite, plant matter, polycrystalline limestone infilling the voids (post-depositional?) and some post-depositional calcareous material on the surface of the sample		
Sample RK00379 (clay, hand collection, trench 1A)	Brown-reddish and non-calcareous	Abundant: poorly-sorted sub-angular to sub-rounded quartz (between 0.03 × 0.03 and 2.0 × 1.6mm), large clay fragments Common: biotite, bone fragments, iron oxides, muscovite, plagioclase (some of which is zoned), albite Very occasional: amphibole, biotite, pyroxene, a calcite fragment, felsic rock fragment (from granite?)		Unfired; poorly mixed clay with sand

SEM-EDX instrumental setup

SEM-EDX analyses were run at an accelerating voltage of 20kV, with a count rate of 10 000cps, and a 150s counting time. Oxford Instruments AZtec software was used to quantify 10 elements (Na, Mg, Al, Si, P, K, Ca, Ti, Mn, and Fe), and the results converted into oxide percentages. These percentages were normalised (oxygen by stoichiometry) to take into account the fact that oxygen and carbon are not measured (Table 3). No other oxides were detected; detection limits for each element vary, but are typically 0.1–0.4 per cent.

Table S2. Riņņukalns: compositional data from SEM-EDX analysis of the fabrics of Riņņukalns samples (italicised rows show the mean of four bulk analyses) and standard deviation (s.d.). Grey rows: SEM-EDX results of the red pigments on sample RK2419. Results are reported as normalised oxides; - indicates below detection limit.

Sample/standard deviation	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**K_2O**	**CaO**	**TiO_2**	**MnO**	**FeO**	**Petro-fabric**
RK10032	*0.8*	*2.1*	*15.4*	*61.8*	*4.5*	*9.4*	*0.8*	*0.0*	*5.3*	1
s.d.	0.0	0.0	0.5	2.1	0.2	1.3	0.0	0.0	0.2	
RK2419	*0.7*	*2.5*	*16.8*	*56.2*	*4.0*	*12.9*	*0.9*	*0.0*	*6.1*	1
s.d.	0.0	0.1	0.5	1.5	0.1	1.5	0.1	0.0	0.1	
RK01043	*0.9*	*1.7*	*15.9*	*65.5*	*4.0*	*2.9*	*0.8*	-	*7.9*	3
s.d.	0.1	0.1	1.0	1.3	0.3	0.6	0.0		1.2	
RK01155	*1.2*	*2.0*	*17.4*	*64.5*	*4.4*	*3.4*	*0.8*	*0.0*	*6.3*	3*a*
s.d.	0.1	0.1	0.3	0.7	0.2	0.2	0.1	0.0	0.6	
RK00173	*0.8*	*2.8*	*14.6*	*57.1*	*3.9*	*14.3*	*0.7*	-	*5.7*	1*a*
s.d.	0.1	0.0	0.5	0.8	0.2	1.3	0.0		0.2	
RK01284	*0.9*	*2.0*	*16.1*	*67.8*	*4.1*	*1.9*	*0.8*	*0.2*	*6.3*	5
s.d.	0.1	0.1	0.8	1.6	0.2	0.2	0.0	0.0	0.4	
RK00022	*0.6*	*3.1*	*16.7*	*45.0*	*3.1*	*24.8*	*0.8*	-	*5.8*	2
s.d.	0.0	0.3	0.8	2.8	0.2	4.3	0.1		0.3	
RK01015	*0.8*	*2.3*	*18.3*	*48.1*	*4.2*	*19.0*	*0.9*	-	*6.5*	2
s.d.	0.0	0.0	0.3	1.7	0.3	2.3	0.0		0.2	
RK10042	*0.7*	*1.8*	*20.9*	*53.8*	*4.1*	*10.3*	*1.0*	*0.0*	*7.3*	2
s.d.	0.1	0.2	1.2	1.6	0.2	0.8	0.1	0.0	0.6	

RK00134	*0.7*	*2.3*	*18.1*	*56.2*	*3.6*	*10.8*	*1.0*	-	*7.3*	1
s.d.	0.1	0.0	0.9	2.0	0.3	1.0	0.1		0.3	
RK01164	*0.7*	*2.8*	*18.2*	*60.7*	*4.6*	*2.2*	*0.9*	-	*9.7*	3*b*
s.d.	0.1	0.1	0.6	2.5	0.2	0.7	0.1		1.8	
RK00630	*0.9*	*2.4*	*15.2*	*66.2*	*4.0*	*5.4*	*0.8*	*0.0*	*5.2*	1*a*
s.d.	0.1	0.1	0.5	1.3	0.1	0.6	0.0	0.0	0.2	
RK02392	*0.9*	*1.7*	*15.0*	*68.6*	*3.8*	*2.5*	*0.8*	*0.0*	*6.6*	4
s.d.	0.2	0.2	0.1	0.4	0.2	0.1	0.1	0.0	0.2	
RK00902	*0.7*	*2.5*	*15.4*	*55.4*	*4.0*	*14.3*	*0.9*	-	*6.7*	1*a*
s.d.	0.1	0.1	0.7	2.0	0.1	1.3	0.1		0.2	
RK2394	*1.0*	*1.4*	*14.6*	*64.5*	*4.1*	*9.0*	*0.7*	-	*4.6*	1*a*
s.d.	0.1	0.2	0.2	1.2	0.2	1.1	0.1		0.1	
RK00179	*0.9*	*2.3*	*14.9*	*60.0*	*3.9*	*11.5*	*0.8*	*0.0*	*5.8*	1
s.d.	0.0	0.1	0.1	0.2	0.2	0.7	0.1	0.0	0.2	
RK00399	*0.9*	*3.4*	*15.6*	*61.8*	*4.3*	*7.3*	*0.8*	*0.0*	*6.0*	1
s.d.	0.1	0.1	0.3	0.3	0.1	0.3	0.1	0.0	0.1	
RK01937	*0.9*	*3.1*	*15.5*	*60.4*	*4.2*	*9.7*	*0.8*	-	*5.3*	1
s.d.	0.1	0.3	1.0	1.7	0.1	0.6	0.0		0.2	
RK00574	*0.7*	*2.7*	*16.9*	*55.4*	*4.3*	*13.1*	*0.8*	-	*6.0*	1
s.d.	0.0	0.3	0.5	1.2	0.1	0.8	0.0		0.3	
RK01217	*0.8*	*2.6*	*16.9*	*56.0*	*4.1*	*11.9*	*0.9*	-	*6.7*	1
s.d.	0.1	0.4	0.8	1.5	0.1	1.1	0.1		0.3	
RK00344	*0.9*	*2.7*	*15.1*	*63.2*	*4.5*	*7.3*	*0.8*	-	*5.5*	1
s.d.	0.1	0.1	0.4	1.5	0.1	1.8	0.1		0.2	
RK2419 Paint on exterior surface (mean of 6 bulk analyses ×550)	0.5	1.7	4.0	13.1	0.8	10.9	0.0	0.5	68.3	Pigment
s.d.	0.1	0.2	0.3	1.0	0.1	0.9	0.0	0.1	0.5	
RK2419 Red colour on interior surface	0.4	1.1	6.6	15.6	0.7	13.3	0.2	3.3	59.0	Pigment

(bulk analysis ×1.0k)										
RK2419 Red colour on interior surface (bulk analysis ×1.0k)	0.0	0.7	5.3	14.7	0.5	10.6	0.0	2.1	66.1	Pigment

Lipid residue analysis: instrumental setup

For estimating general preservation and quantity of lipids GC with flame ionization detector (FID) was employed at the Institute of Chemistry (University of Tartu) using the same Agilent 7890 A Series gas chromatograph and DB5-MS (5%-phenyl)-methylpolysiloxane column. Injected sample size was 1µl. The splitless injector was used at 300°C with helium 6.0 carrier gas at constant flow rate at 3 ml min^{-1} (31.3 psi). The temperature was set at 50°C for 2 min, with the gradient of 10°C/min up to 325°C and the latter maintained for 15 min with the total run time of 44.5 min. FID was kept at 300°C with hydrogen flow of 30 ml min^{-1}, air flow of 400 ml min^{-1}, and makeup gas (nitrogen) flow of 25 ml min^{-1}.

GC-MS analysis was conducted at the Institute of Chemistry (University of Tartu) with Agilent 7890A Series gas chromatograph and Agilent 5975C Inert XL mass-selective detector with a DB5-MS (5%-phenyl)-methylpolysiloxane column (30m × 0.25mm × 0.25µm). Injected sample size was 1µl. The splitless injector and interface were maintained at 300°C and 280°C, respectively, helium 6.0 was used as the carrier gas at a constant flow. The GC column was inserted directly into the ion source of the mass spectrometer. The ionization energy was 70 eV and spectra were obtained by scanning between *m/z* 50 and 800 amu. The temperature program was set as follows: 50°C for 2 min, thereafter a gradient of 10°C/min up to 325°C and kept there for 6.5 min with the total run time of 36.5 min. Compounds were identified with Agilent Chemstation software using also NIST mass spectral library.

GC-C-IRMS analysis was conducted at the York BioArCh facility using acid extracted samples to estimate the $^{13}C/^{12}C$ ratio in two most abundant $C_{16:0}$ and $C_{18:0}$ fatty acids. Despite somewhat low lipid concentration in some samples (following the criteria of 100µg g^{-1} in food crust or 5 µg g^{-1} in ceramic powder; Evershed 2008), GC-C-IRMS analysis was conducted for all samples, although the samples below threshold lipid yield should be taken with caution. The samples were analysed using a Delta V Advantage isotope ratio mass

spectrometer (Thermo Fisher, Bremen, Germany) linked to a Trace Ultra 1310 gas chromatograph (Thermo Fisher) with a GC Isolink II interface (CuO combustion reactor held at 850°C). Parallel acquisition of the molecular data was achieved by deriving a small part of the flow to an ISQ mass spectrometer (Thermo Fisher). All samples were diluted with hexane and subsequently 1µl of each sample was injected into a DB-5MS UI fused-silica column (PN 122-5562UI; 60m × 250µm × 0.25µm; J&W Scientific technologies, Folsom, CA, USA). The injector was operated in Splitless mode. The temperature was set at 50°C for 0.5 min and raised by 25°C min^{-1} to 175°C, then raised by 8°C min^{-1} to 325°C where it was held for 20 min. Ultra high-purity-grade helium with a flow rate of 2 ml/min was used as the carrier gas. Eluted products were combusted to CO_2 and ionized in the mass spectrometer by electron impact. Ion intensities of m/z 44, 45, and 46 were monitored in order to automatically compute the $^{13}C/^{12}C$ ratio of each peak in the extracts. Computations were made with Isodat (version 3.0; Thermo Fisher) and IonOS Software (Isoprime, Cheadle, UK), and were based on comparisons with a repeatedly measured standard reference gas (CO_2). The results are reported in ‰ relative to an international standard (V-PDB). The accuracy and precision of the instrument was determined on *n*-alkanoic acid ester standards of known isotopic composition (Indiana standard F8-3, 6 measurements). The mean ± S.D. values of these were −30.02±0.07‰ and −23.24±0.08‰ for the methyl ester of $C_{16:0}$ (reported mean value vs. VPDB −29.90±0.03‰) and $C_{18:0}$ (reported mean value *vs.* VPDB −23.24±0.01‰) respectively. Each sample was measured in duplicate (mean of S.D. 0.11‰ (range of 0.05–0.4) for $C_{16:0}$ and 0.11‰ (range of 0.06–0.26) for $C_{18:0}$). Values were also corrected subsequent to analysis to account for the methylation of the carboxyl group that occurs during acid extraction. Corrections were based on comparisons with a standard mixture of $C_{16:0}$ and $C_{18:0}$ fatty acids of known isotopic composition processed in each batch under identical conditions.

Table S3. GC-MS and GC-C-IRMS results from Riņņukalns pottery. Ci = ceramic powder (interior); Fi = food crust interior; P/S = palmitic acid/stearic acid ratio; TMTD = 4,8,12-trimethyltridecanoic acid; pri = pristanic acid; phy = phytanic acid.

Sherd ID	Sample type	Lipid concentration ($\mu g/g^{-1}$)	P/S ratio	ω-(o-alkylphenyl) alkanoic acids	Isoprenoids	Cholesterol (derivatives)	$\delta^{13}C_{16:0}$	$\delta^{13}C_{18:0}$
RK00134	Ci	19.9	0.71	-	-	Yes	−28.13	−26.63
RK00173	Ci	9.7	1.86	C_{18}	-	Yes	−31.94	−30.68
RK00179	Ci	21.6	0.74	-	TMTD	Yes	−28.70	−27.55
RK00182	Ci	56.2	2.04	$C_{16\text{-}22}$	phy, TMTD	Yes	−34.86	−32.70
RK00182	Fi	254.4	1.80	$C_{16\text{-}22}$	phy, TMTD	Yes	−31.24	−31.57
RK00219	Ci	2.8	0.69	-	-	-	−26.96	−26.24
RK00282	Ci	7.9	1.03	C_{18}	-	Yes	−27.19	−26.89
RK00344	Ci	18.1	0.70	-	-	Yes	−28.47	−26.95
RK00358	Ci	7.7	0.82	-	-	Yes	−28.16	−27.06
RK00399	Ci	10.2	0.78	-	TMTD	Yes	−28.04	−26.33
RK00574	Ci	31.6	0.57	-	-	Yes	−30.16	−31.04

RK00662	Ci	35.1	1.15	$C_{16, 20}$	prist	Yes	−30.88	−29.38
RK00569	Ci	2956.1	3.39	$C_{16\text{-}22}$	TMTD	Yes	−35.28	−34.34
RK00569	Fi	122.2	1.51	$C_{16\text{-}20}$	phy, TMTD	Yes	−34.21	−33.29
RK01031	Ci	28.0	1.11	-	prist	Yes	−33.91	−31.72
RK01031	Fi	170.2	2.27	-	phy	Yes	−31.96	−30.97
RK01164	Ci	14.2	0.93	-	prist	Yes	−27.86	−27.05
RK01155	Ci	8.1	1.23	-	prist	Yes	−26.68	−26.49
RK01217	Ci	3.5	0.99	-	-	Yes	−27.39	−26.39
RK01284	Ci	22.3	1.46	C_{18}	phy, prist, TMTD	-	−31.83	−28.67
RK02392	Ci	1.6	0.81	-	-	-	−28.52	−27.81
RK02419	Ci	3.9	0.80	-	phy, prist?	Yes	−27.20	−25.90
RK10042	Fi	131.3	1.51	$C_{16\text{-}22}$	phy	-	−27.20	−26.00

References

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