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Journal of Archaeological Science 33 (2006) 1–13

Journal of Archaeological SCIENCE

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Chemical analyses of organic residues in archaeological pottery from Arbon Bleiche 3, Switzerland – evidence for dairying in the late Neolithic

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Received 23 April 2004; received in revised form 2 May 2005; accepted 18 May 2005

Abstract

Fatty acids distribution and stable isotope ratios (bulk $\delta^{13}C$, $\delta^{15}N$ and $\delta^{13}C$ of individual fatty acids) of organic residues from 30 potsherds have been used to get further insights into the diet at the Late Neolithic (3384–3370 BC) site of Arbon Bleiche 3, Switzerland. The results are compared with modern equivalents of animal and vegetable fats, which may have been consumed in a mixed ecology community having agrarian, breeding, shepherd, gathering, hunting, and fishing activities. The used combined chemical and isotopic approach provides valuable information to complement archaeological indirect evidence about the dietary trends obtained from the analysis of faunal and plant remains. The small variations of the $\delta^{13}C$ and $\delta^{15}N$ values within the range expected for degraded animal and plant tissues, is consistent with the archaeological evidence of animals, whose subsistence was mainly based on C_3 plants. The overall fatty acid composition and the stable carbon isotopic compositions of palmitic, stearic and oleic acids of the organic residues indicate that the studied Arbon Bleiche 3 sherds contain fat residues of plant and animal origin, most likely ruminant (bovine and ovine). In several vessels the presence of milk residues provides direct evidence for dairying during the late Neolithic in central Europe.

Keywords: Organic residue; Fatty acids; Potsherds; Gas chromatography-mass spectrometry; GC-MS; Stable carbon and nitrogen isotope ratios; Compound specific isotope analysis; CSIA; Neolithic; Dairying; Switzerland

1. Introduction

1.1. Archaeological residues

The Neolithic settlement of Arbon Bleiche 3 is situated on the southeastern shore of Lake Constance, Canton Thurgau, Switzerland (Fig. 1). From 1993 to 1995, rescue excavations of the site conducted by the Cantonal Archaeological Service found 27 houses, all built between 3384 and 3370 BC (dendrochronological dating), in the excavated area of about 1100 m^2 [34]. The cultural layer lies in the waterlogged zone, where the humidity helped the preservation of the archaeological organic material [30]. In the frame of a long-term project, with the aim to understand the economy and particularly food procurement strategies, preparation and consumption of Neolithic lake shore settlers in central Europe, a multidisciplinary approach, applying botanical, zoological and chemical methodologies to the material recovered from Arbon Bleiche 3 have been adopted [30]. Arbon Bleiche 3 is therefore the most

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doi:10.1016/j.jas.2005.05.013

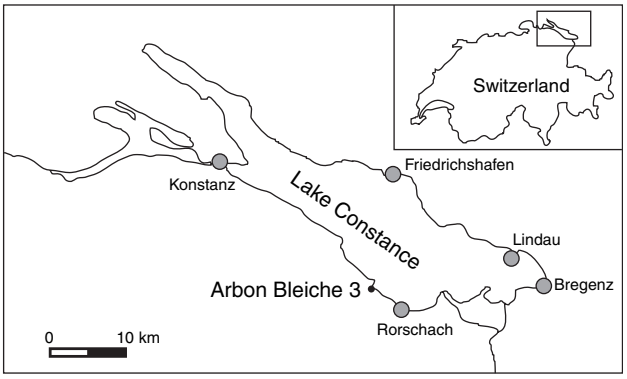

Fig. 1. Location of Arbon Bleiche 3, Lake Constance, Switzerland (adapted from [2]).

thoroughly investigated Neolithic lake shore settlement in central Europe. Among the cultural remains associated with the plant and animal relicts were abundant fragments of unglazed ceramic vessels [6,5]. Dark brown consolidated organic residues were recognized in the interior of some vessels [5], suggesting that they were used for storage and processing of food. Within these organic crusts rare relics of cereals and fish bones were preserved [5]. Mostly, the relics were too small to be visible with low magnification. A microscopic analysis shows that the organic residues contained regularly cereals and other plant tissues; however, no structures of tissues or bones of other animals were detected [36]. The investigations of faunal and plant remains (mammal and fish bones, teeth, seeds, fruits, twigs, pollen, and phytolites) and artifacts associated with food consumption provided evidence for the presence of domestic cows (*Bos taurus*), pigs (*Sus domesticus*), goats (*Capra hircus*), sheeps (*Ovis aries*), and dogs (*Canis familiaris*), and a wide range of wild animals such as red deer (*Cervus elaphus*), wild boar (*Sus scrofa*), brown bear (*Ursus arctos*), and frogs [10,11,26,27]. A further faunal diet component came from lacustrine resources, including Cyprinidae (e.g. *Rutilus rutilus*), Salmonidae (e.g. *Coregonus* sp.), pike (*Esox lucius*), catfish (*Silurus glanis*), and perch (*Perca fluviatilis*) [28]. Cultivated plants such as cereals (*Triticum div.* sp., *Hordeum* sp.), flax (*Linum usitatissimum*) and opium poppy (*Papaver somniferum*) were important food elements [26,27]. Many wild food plants were gathered in the surroundings of the settlement to complement the crops. These included hazelnut (*Corylus avellana*), strawberries (*Fragaria* sp.), blackberries (*Rubus fruticosus* s.l.), raspberries (*Rubus idaeus* s.l.), crab apple (*Malus sylvestris*), and sloe plum (*Prunus spinosa*). The diet of the domestic animals included silver fir (*Abies alba*), mistletoe (*Viscum album*), blackberry (*Rubus frulicosus* s.l.), alder (*Alnus* sp.) and hazel [1,2,32], suggesting their presence in the settlement mainly during wintertime.

1.2. Fat preservation

The main fatty acids found in plant and animal lipids are straight chain carboxylic acids (abbreviated as $C_{x:y}$, where "x" is the number of carbon atoms and "y" the number of double C–C bonds in the chain). The more abundant saturated fatty acids are the lauric ($C_{12:0}$), myristic ($C_{14:0}$), palmitic ($C_{16:0}$), and stearic ($C_{18:0}$) acid, and the unsaturated acids are palmitoleic ($C_{16:1}$), oleic ($C_{18:1}$), linoleic ($C_{18:2}$), and linolenic ($C_{18:3}$). During hydrolytic degradation of the lipids, the fatty acids are released from the triglycerides. The short- and medium-chain fatty acids (e.g., $C_{4:0}$ to $C_{14:0}$) are appreciably more water-soluble and volatile than the long-chain fatty acids. So, degraded fat is identified by high concentrations of palmitic and stearic acid. The survival of lipids in association with many archaeological materials is widely documented [15]. In subsequent studies Evershed et al. [17] have shown that the stable carbon isotopic composition of the main fatty acids preserved in unglazed archaeological pottery appears unaffected by diagenetic alteration during burial. Thus providing, by comparison with modern reference fats, a highly robust criteria to distinguish a range of commodities associated with the use of vessels in the past, including among others, animal fats [19,40], milk [14], plant oils [3], plant leaf waxes [16], and beeswax [18].

The relative consumption of marine versus terrestrial foods or use of C_3- vs. C_4-plants based foods within terrestrial ecosystems can be inferred from stable carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotopic composition. The carbon isotope composition of plants and their products are linked to the processes of photosynthetic CO_2 fixation. The most important atmospheric CO_2-fixing reactions are the C_3 and C_4 pathways [41]. C_3 plants (plants adapted to temperate ecosystems, including most vegetables, fruit and wheat) use the Calvin cycle for CO_2 fixation, and the $\delta^{13}C$ values fall into the range -34 to $-22‰$ [48]. The C_4 plants use the Hatch–Slack cycle, and have lower isotopic fractionation compared to C_3 plants. C_4 plants are plants adapted to hot, arid environments, comprising most plants in the tropics, including millet, maize, sugar cane and savanna grasses, and are relatively enriched in ^{13}C (-16 to $-9‰$). Small shifts of $+1$ to $+2‰$ in $\delta^{13}C$ occur between the muscle tissue or whole body of a consumer and its food source [7,21]. Animals, including humans, who consume a great deal of C_4 plants (e.g., maize) can have $\delta^{13}C$ values close to or higher than $-12‰$. More negative $\delta^{13}C$ values, lower than $-22‰$, indicate that the food that the individual has consumed comes mainly from terrestrial C_3 plants environment, as well as from the flesh or milk of animals that also subsisted on only C_3 plants. In the region under consideration in this study, Neolithic terrestrial food chains are based on photosynthesis by C_3 plants. The diet of the domestic and herbivore prey

animals at Arbon Bleiche 3 consisted of a mixture of unknown proportions of C_3 plants.

Effect of cooking on the $\delta^{13}C$ and $\delta^{15}N$ values of modern C_3 and C_4 plant material has been reported by DeNiro and Hastorf [9]. These authors found that boiling, roasting, and carbonization of modern plant material resulted in random variations of $\pm 3‰$ in both $\delta^{13}C$ and $\delta^{15}N$ values. The isotope ratios of the prehistoric carbonized plants are not substantially altered, permitting the isotopic distinction of the type of plants in archaeological remains [9]. Therefore, the combination of $\delta^{13}C$ and $\delta^{15}N$ values of organic residues can give further information on the trophic level. Non-leguminous plants fix nitrogen from soil NO_3^-, and have $\delta^{15}N$ values ranging from 2–6‰. The $\delta^{15}N$ of animal tissues or a whole organism can indicate the trophic level along the food web, as there is 2–4‰ enrichment in ^{15}N each step up the food chain [8,38]. Therefore if plants have an average $\delta^{15}N$ of about 3‰, herbivores that consume those plants have $\delta^{15}N$ of about 6‰, and carnivores that consume those herbivores will have $\delta^{15}N$ of about 9‰.

Even when the presence of domestic cows is easy to deduce from the found artifacts and bones, the practice of dairying and the exploitation of the farm products remain one of the most difficult questions in the prehistoric agricultural practices. From the age distribution of the slaughtered bovine animals, based on the analyses of recovered bones, one can suggest some dairying practice at Arbon Bleiche 3 [10]. However, direct evidence of milk products exploitation is not available. We present here the results of a chemical study encompassing fatty acids distribution and stable isotope composition (bulk $\delta^{13}C$ and $\delta^{15}N$, and $\delta^{13}C$ of individual fatty acids) of organic residues from potsherds. These data serve to gain further insight into the dietary trends, and the farming activities at Arbon Bleiche 3.

2. Materials and methods

2.1. Samples

Organic residues samples from 30 potsherds of different geometries were obtained from excavations of the Arbon Bleiche 3 site, Canton of Thurgau, Switzerland. Full details, i.e. excavation, grid references and description of the ceramics are in de Capitani [5]. The material is a dark, black brownish amorphous solid deposited in the interior of the pottery vessels, supposed to have been used for storage and cooking of food (Table 1). The presence of sooting patterns as blackened exterior and dark brown crusts in the interior of the vessels [5] suggests that they were placed over a fire or hot ashes at some time. So it is likely that foods were cooked in some vessels.

Samples were prepared and analyzed at the Institute of Mineralogy and Geochemistry of the University of Lausanne. The potsherds were cleaned of visible foreign material and the organic residues collected by scraping the potsherds with an organic solvent cleaned sharp blade. Following removal of exogenous material with cleaned SS-forceps, the samples were manually ground and homogenized using agate mortar and pestle, weighed and stored in screw-cup sealed vials at −20 °C in the dark until use. The organic residues were grouped according to the geometry of the vessels described in de Capitani [5]. Fat samples of modern animals that have been fed exclusively on C_3 forage grasses were analyzed in order to test the origin of the fat in the archaeological ceramics. These reference fats include adipose samples of pig, cattle, calf, lamb, deer and fish, milk fat samples of cow, goat, and sheep (Table 2), and were obtained from organic farms and from markets supplying local food products. Vegetable fats from different origin were studied previously [43,44]. To complement that data set, samples of linseed and poppy seed were included in this study.

2.2. Sample preparation and analysis

All the solvents used were of a quality suitable for chromatography (Fluka, Switzerland) and were glass-distilled shortly before use. All the reagents were tested for purity by gas chromatography-mass spectrometry. All the glassware used for sample handling was thoroughly washed, rinsed with distilled water and heated at 480 °C for 4 h before use. An aliquot (~0.2–5 g) of the samples was refluxed with 100 ml of dichloromethane for 2 days, with change of solvent after the first 24 h. The solvents containing the extracted lipids were combined and reduced to 2 ml by rotary-evaporation. The solvent was then gently removed by passive evaporation in a good ventilated fume-hood. Carboxylic acids were isolated from the extracted lipids by alkaline hydrolysis with 1 N aqueous ethanolic potassium hydroxide at 60 °C for 3 h. After cooling to room temperature, nonsaponifiables were removed by washing with hexane aliquots. The sample was then acidified with 1 N HCl, and the acid lipids separated with hexane. The acid fraction was methylated (14% BF_3-methanol Fluka, 60 °C, 8 min) and the fatty acid methyl esters (FAME) were purified by elution with hexane. The FAME were stored with 1 ml hexane in 2 ml vials with PTFE-lined screw-caps at +4 °C until gas chromatographic analysis [44].

2.3. Gas chromatography-mass spectrometry (GC-MS)

Chemical characterization of the lipids was performed with an Agilent (Palo Alto, USA) gas chromatograph 6890 coupled to an Agilent 5973 quadrupole mass selective detector (GC-MS). The system was equipped

Table 1
C and N concentrations and bulk $\delta^{13}C$ and $\delta^{15}N$ values for organic residues in potsherds from Arbon Bleiche 3

Sample number	Location[a]			Description	C	N	C/N	$\delta^{13}C$	$\delta^{15}N$
	Board	Square-meter	House		(wt.%)	(wt.%)	(at.)	(‰, VPDB)	(‰, AIR)
ARB-30				Crust on single sherd	52.5	8.4	7.3	−25.4	5.2
ARB-101				Crust on single sherd	64.7	6.7	11.3	−25.2	3.1
ARB-103				Crust on single sherd	60.8	5.2	13.7	−27.2	4.2
ARB-106				Crust on single sherd	57.4	4.1	16.3	−25.3	2.4
ARB-114				Crust on single sherd	62.1	7.8	9.3	−24.8	3.2
ARB-115				Crust on single sherd	59.4	5.9	11.7	−26.0	2.4
ARB-3197				Crust on single sherd	35.0	3.4	12.1	−27.2	1.4
ARB-15524	20.4	66/232	9	Straight pot, >10 l	61.0	6.1	11.6	−25.0	2.5
ARB-16743	42.8	77/227	20	Pot of other form	49.5	5.9	9.8	−26.1	1.8
ARB-18244	28.11	75/214	5	Pot of other form	62.0	12.8	5.7	−25.7	4.3
ARB-18311	14.1	70/213	5	Curved pot, >20 l	54.9	7.2	8.9	−25.6	4.7
ARB-18833	35.6	66/217	4	Pot of other form	59.5	6.9	10.1	−27.4	3.6
ARB-18840	24.4	69/215	5	Straight pot, 5–10 l	54.4	5.1	12.5	−24.3	3.2
ARB-18854-A	12.2	67/213	5	Curved pot, >30 l	53.4	5.5	11.3	−27.1	9.6
ARB-18854-I	12.2	67/213	5	Curved pot, >30 l	56.3	8.6	7.7	−25.4	4.5
ARB-18865	23.2	67/211	3/5	Conical pot, 5–10 l	45.3	4.9	10.7	−27.9	4.7
ARB-18902	5.3	60/217	1	Curved pot, >20 l	45.1	6.5	8.1	−26.2	0.2
ARB-18925	21.9	63/215	1	Straight pot, 1–4.5 l	56.3	7.7	8.5	−26.3	4.8
ARB-18949	14.2	61/212	3	Curved pot, >20 l	52.8	4.3	14.5	−26.1	2.5
ARB-19610	12.4	76/206	24	Curved pot, >10 l	57.1	4.5	14.6	−26.1	2.1
ARB-19774	1.2	70/207	14	Curved pot, >10 l	54.7	6.8	9.4	−27.6	6.9
ARB-19775	24.5	73/205	24	Straight pot, 5–10 l	48.7	7.2	7.9	−26.5	5.2
ARB-20028	2.6	69/206	14/15	Curved pot, >20 l	64.3	6.5	11.5	−25.1	2.3
ARB-20031	12.3	69/206	14/15	Curved pot, >10 l	56.7	6.9	9.6	−25.9	2.8
ARB-20038	32.7	66/207	15	Curved pot, >10 l	51.6	7.6	7.9	−25.9	3.6
ARB-20047	22.2	66/209	3/15	Straight pot	55.4	6.1	10.6	−26.2	3.3
ARB-20204	36.3	61/209	3	Pot of other form	59.3	3.6	19.0	−26.2	3.0
ARB-20215	38.7	68/211	5	Pot of other form	49.6	6.8	8.5	−26.1	5.3
ARB-20221	38.4	63/209	3	Pot of other form	59.1	7.4	9.3	−26.6	3.2
ARB-20891	7.4	62/202	15	Curved pot, 5–10 l	52.4	7.7	7.9	−25.9	5.0

[a] In [5].

with an Agilent free fatty acids phase (FFAP) fused silica capillary column (50 m length, 0.20 mm i.d.) coated with nitroterephthalic acid modified polyethylene glycol stationary phase (film thickness 0.33 μm). Helium was used as carrier gas (1 ml/min flow rate), and the manual injection was made splitless at a temperature of 200 °C. After an initial period of 2 min at 100 °C, the column was heated to 240 °C at 5 °C/min followed by an isothermal period of 30 min. The MS was operated in the electron impact mode at 70 eV, source temperature of 250 °C, emission current of 1 mA and multiple-ion detection with a mass range from 50 to 600 amu. Compound identifications were based on comparison of standards, GC retention time, and mass spectrometric fragmentation patterns. The abundances of FAME in the organic residues relative to total FAME were calculated from total ion chromatogram peak areas. Replicate GC-MS analyses ($n = 2–3$) were carried out for each sample. The GC-MS measurements of individual fatty acids and compounds distribution showed relative standard deviation within 5% of the mean. Octanoic ($C_{8:0}$) and nonanoic ($C_{9:0}$) acids are highly volatile components, which are expected to be reduced in abundance during sampling handling and analyses.

2.4. Isotopic analysis of bulk organic residue by EA-IRMS

The carbon and nitrogen isotope compositions, along with the percentage of C and N (and then the C/N atomic ratio), were determined by flash combustion on a Carlo Erba 1108 (Milan, Italy) elemental analyzer (EA) connected to a Thermoquest/Finnigan MAT Delta S (Bremen, Germany) isotope ratio mass spectrometer (IRMS) that was operated in the continuous helium flow mode via a Thermoquest/Finnigan Conflo II split interface. Flush combustion was in an O_2 atmosphere in a quartz rector at 1020 °C packed with Cr_2O_3 and $(Co_3O_4)Ag$ to form CO_2, N_2, NO_x and H_2O. The gases were then passed through a reduction reactor containing elemental copper and copper oxide at 640 °C to remove excess of oxygen and to reduce the non-stoichiometric nitrous products (NO_x) to N_2. Water was subsequently removed by anhydrous $MgClO_4$, and N_2 and CO_2 were than separated in a gas chromatograph with a packed column (Pora-PLOT Q, 5 m length, 1/4 inch i.d.) at 70 °C and were then analyzed for their isotopic composition on the IRMS. Reference N_2 and CO_2 gases were inserted in the He carrier flow as pulses of pure standard gases.

Table 2
Bulk $\delta^{13}C$ and $\delta^{15}N$ values for modern faunal and floral samples

Sample[a]	Site/Origin	$\delta^{13}C$ (‰, VPDB)	$\delta^{15}N$ (‰, AIR)
Pig adipose A	Local farm (Langebruck, CH)	−28.4	–
Pig adipose B	Local farm (Langebruck, CH)	−28.2	–
Cattle adipose A	Local farm (Buus, CH)	−28.6	–
Cattle adipose B	Local farm (Buus, CH)	−30.7	–
Calf adipose A	Local farm (Holstein, CH)	−26.9	–
Calf adipose B	Local farm (Olsberg, CH)	−27.0	–
Lamb adipose	Local bio-farm	−30.4	–
Deer adipose A	Local forest (Susch, CH)	−32.3	–
Deer adipose B	Local forest (Susch, CH)	−32.9	–
White fish adipose	Lake Constance	−30.0	–
Cow milk A	Local market	−25.9	–
Cow milk B	Local market	−25.0	–
Cow milk C	Local market	−24.6	–
Cow milk (de-hyd.)	Local market	−25.1	–
Cow milk cream A	Local market	−30.6	–
Cow milk cream B	Local market	−28.2	–
Cow milk cream C	Local market	−28.6	–
Cow milk cream D	Local market	−28.9	–
Cow milk butter A	Local farm	−28.5	–
Cow milk butter B	Local farm	−29.4	–
Cow milk butter C	Local farm	−26.8	–
Cow milk cheese	Local farm	−28.0	–
Sheep milk A	Local farm	−29.0	–
Sheep milk B	Local farm	−27.7	–
Sheep cheese	Local farm	−23.8	–
Goat cheese	Local farm	−25.2	–
Fresh goat cheese	Local farm	−23.4	–
C_3 vegetable oil[b]		−35 to −27	–
Linseed	Local market	−28.2	8.1
Poppy seed A	Local market	−29.2	2.8
Poppy seed B	Local market	−26.7	7.5

[a] A, B, C, D = different farm/supplier.
[b] $\delta^{13}C$ range of C_3 vegetable oil from [43] and [44].

The stable isotope composition of carbon and nitrogen are reported by delta (δ) notation as the per mil (‰) deviations of the isotope ratio relative to known standards:

$$\delta = \left[\left(R_{\text{sample}} - R_{\text{standard}}\right)/R_{\text{standard}}\right]1000$$

where R is the ratio of the heavy to light isotopes ($^{13}C/^{12}C$, $^{15}N/^{14}N$). For carbon the standard is Vienna Pee Dee Belemnite limestone (VPDB) and for nitrogen it is air. The repeatability and intermediate precision of the EA-IRMS method, defined as the observed variability from separately replicate analyses of laboratory standard materials (glycine, $\delta^{13}C = -26.1‰$ and $\delta^{15}N = 2.7‰$; urea, $\delta^{13}C = -43.1‰$ and $\delta^{15}N = -1.4‰$) and Arbon Bleiche 3 samples were better than 0.1‰ (1 SD) for both $\delta^{13}C$ and $\delta^{15}N$ values. The accuracy of the analyses was checked periodically by analyses of the international reference materials USGS-24 graphite (−15.9‰ $\delta^{13}C$), IAEA-PEF1 polyethylene foil (−31.8‰ $\delta^{13}C$), NBS-22 oil (−29.7‰ $\delta^{13}C$), and IAEA-NO_3 potassium nitrate (+4.7‰ $\delta^{15}N$). The carbon and nitrogen concentrations were determined from the peak areas of the major isotopes. Calibration was done periodically with organic standards. The repeatability was better than 0.2 wt.% for both carbon and nitrogen.

2.5. Isotopic analysis of individual fatty acids by GC-C-IRMS

The compound specific stable carbon isotope analyses ($\delta^{13}C$ values) of the fatty acids were obtained by the use of an Agilent 6890 GC coupled to a Thermoquest/Finnigan MAT Delta S isotope ratio mass spectrometer by a combustion (C) interface III (GC-C-IRMS) under a continuous helium flow [25]. The combustion interface consists of two ceramic furnaces. An oxidation reactor with CuO/NiO/Pt wires at 940 °C and a reduction reactor with Cu wires at 600 °C. Water was removed from the effluent gas by passing a Nafion tube (Perma Pure, Toms River, NJ, USA) with an annular back-flow of He. The IRMS ion source pressure is lower than 6×10^{-6} bar. The GC was operated with the same type of column and temperature program used for GC-MS analyses. The background subtraction and $\delta^{13}C$ values were calculated using the Thermoquest/Finnigan ISODAT 7.2 software. The repeatability and intermediate precision of the GC-C-IRMS procedure, and the performance of the GC and combustion interface were evaluated every 5 analyses by injection of an in-house mixture of *n*-alkanoic acids (UNIL-FAME MIX) of known isotopic composition ($\delta^{13}C_{10:0} = -31.1‰$, $\delta^{13}C_{12:0} = -29.7‰$, $\delta^{13}C_{14:0} = -29.2‰$, $\delta^{13}C_{16:0} = -29.6‰$, $\delta^{13}C_{18:0} = -29.2‰$, $\delta^{13}C_{12:0} = -27.6‰$, $\delta^{13}C_{20:0} = -29.4‰$, $\delta^{13}C_{21:0} = -28.6‰$, $\delta^{13}C_{22:0} = -28.4‰$), and at least three replicate analyses of the Arbon samples. The standard deviations for repeatability ranged between 0.05 and 0.4‰ for the main FAME and for intermediate precision between 0.3 and 1.1‰. The accuracy of the GC-C-IRMS analyses was checked every 10 analyses by injection of a FAME isotope standard (icosanoic acid methyl ester, $\delta^{13}C_{20:0} = -25.4‰$) prepared by A. Schimmelman from the Biogeochemical Laboratories at Indiana University, USA.

The isotopic shift due to the carbon introduced in the fatty acid methylation was corrected by a mass balance equation [43]:

$$\delta^{13}C_{FAME} = f_{FA}\delta^{13}C_{FA} + f_{MeOH}\delta^{13}C_{MeOH}$$

where $\delta^{13}C_{FAME}$, $\delta^{13}C_{FA}$, and $\delta^{13}C_{MeOH}$ are the carbon isotope compositions of the fatty acid methyl ester, the fatty acid, and the methanol used for methylation of the fatty acid, respectively, and f_{FA} and f_{MeOH} are the carbon fractions in the fatty acid methyl ester due to the alkanoic chain and methanol, respectively. The variability introduced by this correction was determined by GC-C-IRMS measurements of replicate derivatized aliquots of palmitic ($C_{16:0}$) and stearic ($C_{18:0}$) acids of known isotopic composition. The differences of the measured and calculated $\delta^{13}C_{FA}$ values are much smaller than the standard deviation for repeatability of GC-C-IRMS analyses of FAME from similar C-chain length.

3. Results and discussion

3.1. Carbon and nitrogen contents

The C and N concentrations and the bulk $\delta^{13}C$ and $\delta^{15}N$ values for the organic residues are given in Table 1. The mean C and N concentrations of the organic residues are ~55 wt.% (most between 45 and 65 wt.%) and ~15 wt.% (most between 3 and 9 wt.%), respectively. The relatively high total nitrogen content (3.4–12.8 wt.% N) suggests processed/altered protein-rich food.

3.2. Bulk C and N isotope composition

The carbon and nitrogen isotope composition of the organic remains in pottery vessels used for cooking of food may reflect the average $\delta^{13}C$ and $\delta^{15}N$ of the degraded food material during vessel use and burial. This may provide insights into the types of food consumed, and particularly whether the diet was animal or plants (C_3 and C_4) based. The average and standard deviation for all samples of organic residues from potsherds are $-26.1 \pm 0.8‰$ and $+3.7 \pm 1.8‰$ for $\delta^{13}C$ and $\delta^{15}N$, respectively (Table 1, Fig. 1). The analyzed modern animal materials provide reference isotopic data. The herbivores (cow, sheep, goat, and deer) and lake fish fats have $\delta^{13}C$ values of −30.7 to −26.7‰ (Table 2). The nitrogen content of the animal adipose is very low, which made the measurement of the N isotope ratios impossible. Terrestrial C_3 plants have $\delta^{13}C$ values between −30 and −23‰ and $\delta^{15}N$ between −7 and 6‰ [42]. Thermal degradation and microbial reworking of organic matter may cause selective loss of more reactive organic compounds, creating an isotopic shift of 1–5‰ [9]. The small variations of the $\delta^{13}C$ values (between −27.9 and −24.3‰) within the range expected for degraded animal and plant tissues is consistent with the archaeological evidence of C_3 plants and animals, whose subsistence was mainly based on C_3 plants. There is no evidence of a significant correlation of the $\delta^{13}C$ and $\delta^{15}N$ values with the geometry of the vessels. However, the highest $\delta^{15}N$ values (up to 9.6‰) of organic residues in sherds from some curved vessels could be related to a preferential cooking of low-protein/high-fibre food. In summary, the variations of the carbon and nitrogen concentrations and isotope ratios support animal and plant food diversity, and omnivory in the Arbon Bleiche 3 community.

3.3. Fatty acid distribution

The organic residues from Arbon Bleiche 3 potsherds contain a significant amount of extractable lipids, consisting almost entirely of free and bonded fatty acids identified by their methyl ester (FAME) mass spectra (Fig. 2). Representative total ion chromatograms of the acid fraction of the lipids extracted from the Arbon Bleiche 3 organic residues are shown in Fig. 2. The gas chromatograms show a series of FAME of straight chain carboxylic acids in the C_9–C_{24} carbon number range, excluding C_{21} and C_{23}. The main saturated fatty acids are the lauric ($C_{12:0}$), myristic ($C_{14:0}$), pentadecanoic ($C_{15:0}$), palmitic ($C_{16:0}$), margaric ($C_{17:0}$), and stearic ($C_{18:0}$) acids, maximizing at C_{16} and C_{18}. These fatty acid distributions are typical of degraded fats, and have a strong biological signature (maximum at $C_{16:0}$ with markedly greater abundance than $C_{18:0}$). Small to trace amounts of capric ($C_{10:0}$), tridecanoic ($C_{13:0}$), and arachidic ($C_{20:0}$) acids occur in all samples. The only unsaturated acids identified and quantified were palmitoleic ($C_{16:1}$) and oleic ($C_{18:1}$). Terminally branched *iso* and *anteiso* b-$C_{15:0}$ acids elute between $C_{14:0}$ and $C_{16:0}$. Apart from trace amounts of linoleic ($C_{18:2}$) no polyunsaturated fatty acids were detectable. This is to be expected since the polyunsaturated fatty acids would have decomposed under the oxidative conditions during vessel use and subsequent burial at the archaeological site.

3.4. Stable carbon isotope composition of individual fatty acids

The $\delta^{13}C$ values of the main fatty acids of the lipids extracted from the organic residues vary between −37.0 and −26.7‰. Mean $\delta^{13}C$ values for $C_{14:0}$, $C_{15:0}$, $C_{16:0}$, $C_{18:0}$, and $C_{18:1}$ are −29.2, −31.8, −30.1, −31.7, and −30.1‰ respectively, and have an average standard deviation of 1.7‰. Since the precision, including the overall analytical error for sample preparation and isotopic analyses is <1.1‰, the predominant factor in the standard deviations (1.3–2.3‰) is real archaeological variability. Most $\delta^{13}C_{16:0}$ and $\delta^{13}C_{18:1}$ values are lower than the $\delta^{13}C_{18:0}$ values (Fig. 3). The differences

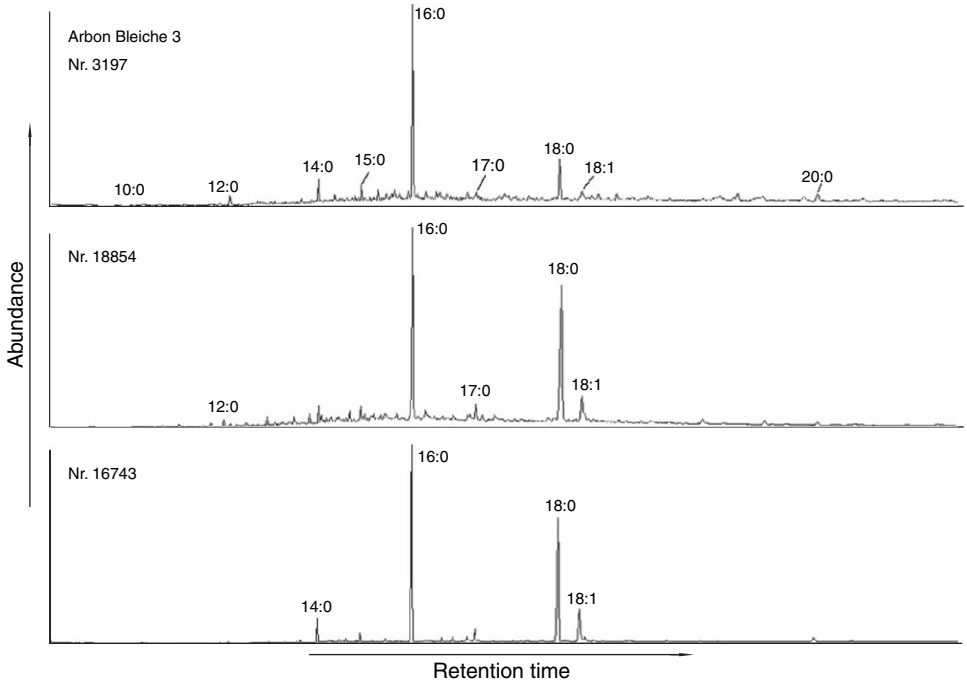

Fig. 2. GC-MS total ion chromatogram of the fatty acid methyl esters in lipids extracted from organic residues of potsherds from Arbon Bleiche 3. The fatty acids are the capric (10:0), lauric ($C_{12:0}$), myristic (14:0), pentadecanoic (15:0), palmitic (16:0), margaric (17:0), stearic (18:0), oleic (18:1), and arachidic (20:0) acids.

between the $\delta^{13}C$ values of the main fatty acids vary from −5.9 to +1.8 (average and standard deviation: $-1.6 \pm 1.9‰$) for $\Delta^{13}C_{18:0-16:0}$ and from −4.6 to +1.3 ($-1.7 \pm 1.4‰$) for $\Delta^{13}C_{18:0-18:1}$, indicating different biological sources and degrees of thermal and microbial degradation of the organic residues (see below). Some isotopic trends between pottery vessels of different geometry suggest that they may have had different use (Fig. 3). Particularly, the fatty acids extracted from the organic residues in curved pots are in average the isotopically heaviest.

3.5. Origin of lipids in the organic residues

The origin of lipids preserved in the archaeological ceramics can be assessed by comparison with modern

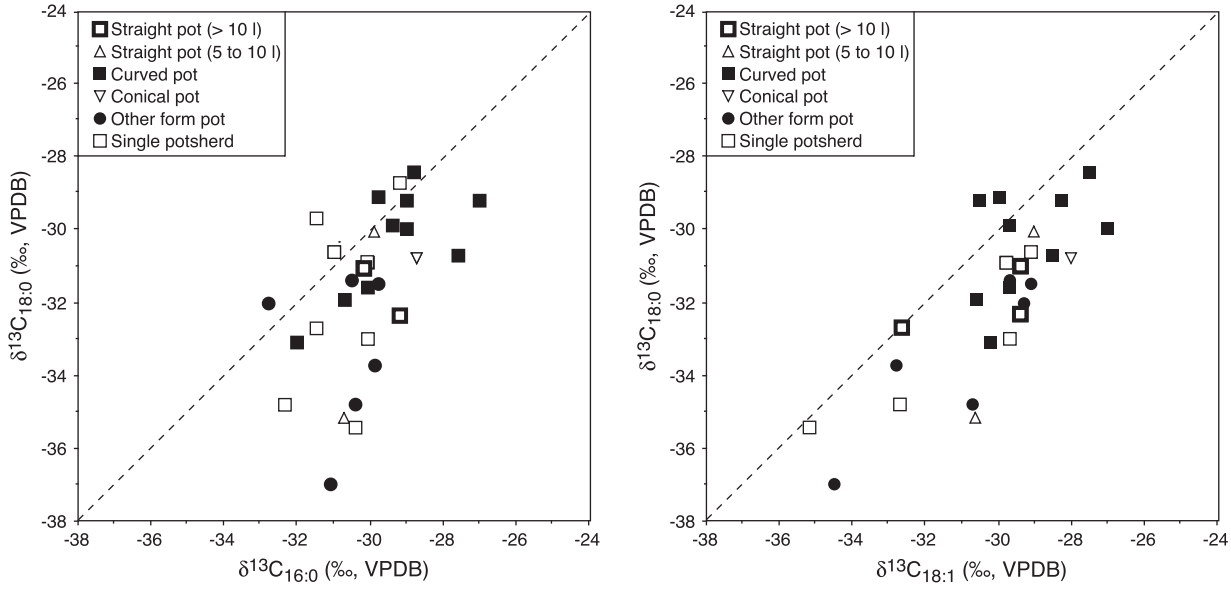

Fig. 3. Carbon isotope composition of stearic acid ($\delta^{13}C_{18:0}$) versus palmitic ($\delta^{13}C_{16:0}$) and oleic ($\delta^{13}C_{18:1}$) of the organic residues from Arbon Bleiche 3.

edible oils and fats. The modern animal and plant fats show a distinctive distribution in the carbon isotopic composition of the main fatty acids, reflecting their different biosynthetic origin (Fig. 4). The $\delta^{13}C$ values of the major fatty acids in oils from C_3 plants vary from -36.5 to $-27.5‰$, and plot near the 1:1 line in the $\delta^{13}C_{16:0}$ vs. $\delta^{13}C_{18:0}$ diagram [43,44]. To explain this relationship, one has to consider fatty acid synthesis in plant cells. The reactions of fatty acids biosynthesis are essentially the same in all plants [31,33]. In the endoplasmic reticulum a multienzyme complex catalyzes the key reaction sequence by which the longer chains of fatty acids are assembled. Elongation of carbon chains occurs in the same way as their synthesis, but differs in the enzymatic set which catalyzes the reactions. The product formed by addition of one acetyl group to palmitic acid ($C_{16:0}$) is stearate ($C_{18:0}$). At the same site of the plant tissue oxidative reactions catalyzed by fatty acyl-coenzyme A (CoA) desaturase introduces the unsaturation to the fatty acids. One can safely assume that the isotopic discrimination between the first biosynthesized fatty acid ($C_{16:0}$) and the first elongation and unsaturation products ($C_{18:0}$, $C_{18:1}$) is less than the analytical error [43,44].

The differences in isotopic composition between individual animal fatty acids (Fig. 4) may be due to isotopic fractionation occurring during biosynthesis and different rates of their metabolic turnover. The isotope effects between biogeochemical fractions in animals and plants are well known: $\delta^{13}C_{lipid} < \delta^{13}C_{total\ organic\ matter}$, $\delta^{13}C_{lipid} < \delta^{13}C_{carbohydrate}$, $\delta^{13}C_{lipid} < \delta^{13}C_{protein}$ [7]. Fatty acids are depleted in ^{13}C relative to carbohydrates by $4–6‰$ [37]. In species with extensive foregut fermentation, such as ruminants (e.g., cow, goat, and sheep) the plant lipids ingested by the animal undergo extensive microbial transformations in the rumen, including hydrolysis of sterified plant lipids and subsequent hydrogenation of the unsaturated fatty acids [23]. Short-chain fatty acids are the main end products of dietary carbohydrates fermentation in the rumen [23,24]. Glucose and other monosaccharides are liberated by microbial degradation of cellulose from plant material ingested by the ruminant. Furthermore, in the rumen bacteria and protozoa can incorporate or synthesize de novo C_{15} to C_{18} fatty acids [13]. Thus, the circulating fatty acids in tissues will not reflect the diet due to extensive biochemical transformations in the rumen. In ruminant adipose tissues the metabolic pathways of fatty acids include direct uptake of dietary free or sterified fatty acids and de novo fatty acid synthesis. The carbon precursor in fatty acid synthesis may be acetate (or C_2 equivalents) and/or glucose. Cow, sheep, and goats utilize acetate as the main carbon source for synthesis of palmitic, stearic and oleic acids [47]. In monogastric mammals (non-ruminants, e.g., pig) ingested triglycerides are hydrolyzed in the stomach and small intestine, and re-esterified during the transport to tissues. Thus, dietary fatty acids essentially remain intact through digestion and incorporation into the adipose tissues of non-ruminants. Pigs resemble ruminants in adipose as the main site of de novo fatty acids synthesis, but differ from them in the carbon source, as they incorporate carbon from both, acetate and glucose. Young (suckling) calfs, lambs, and goats mainly utilize glucose carbon for fatty acid synthesis, due to the high sugars content in the mother's milk [47]. The similar

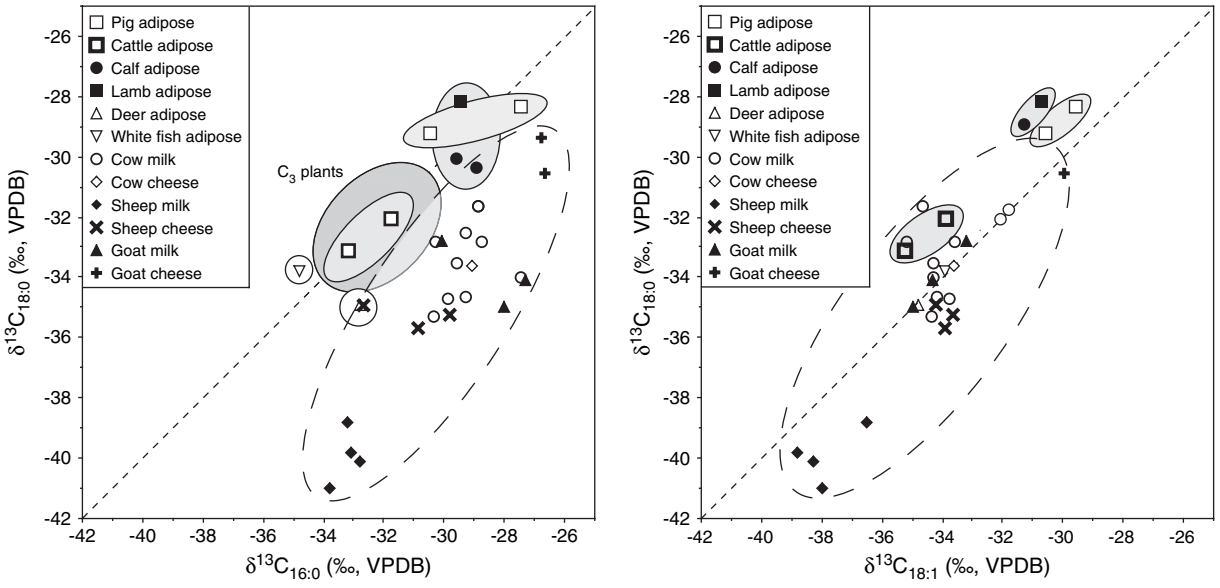

Fig. 4. Carbon isotope composition of stearic acid ($\delta^{13}C_{18:0}$) versus palmitic ($\delta^{13}C_{16:0}$) and oleic ($\delta^{13}C_{18:1}$) of reference modern animal and plant fats. The measured values were used to determine the fields for present-day animal fats. The field for European C_3-vegetable oil lipids is from [43] and [44].

carbon source (acetate and glucose) for fatty acid synthesis explains why calf and lamb adipose plot near the field for pig adipose in the $\delta^{13}C_{16:0}$ vs. $\delta^{13}C_{18:0}$ and $\delta^{13}C_{18:1}$ vs. $\delta^{13}C_{18:0}$ diagrams (Fig. 4). The measured ^{13}C-enrichment ($\approx 4‰$) of the palmitic, stearic and oleic acids from pig, calf and lamb adipose relative to the same fatty acids in cattle adipose and C_3 plants is due to the different carbon precursor ($\delta^{13}C_{acetate} < \delta^{13}C_{glucose}$). A similar ^{13}C-enrichment (up to 4.8‰) of the same fatty acids in pig tissue relative to the dietary plant fatty acids was observed in controlled feeding experiments [46]. The separation of the fatty acids from deer and fish adipose from the 1:1 line in the $\delta^{13}C_{16:0}$ vs. $\delta^{13}C_{18:0}$ diagram is due to admixture of fatty acids from different origins, probably related to diet diversity of the wild animals (deer) and a different metabolism of aquatic organism (white fish).

The ruminant dairying fats (milk, butter and cheese) plot below the 1:1 line in the $\delta^{13}C_{16:0}$ vs. $\delta^{13}C_{18:0}$ diagram, and have higher $\delta^{13}C_{16:0}$ and $\delta^{13}C_{18:0}$ values than those of adipose fats (Fig. 4). The distinct metabolic pathways of milk fatty acids can explain this isotopic difference [4,14]. Fatty acids in milk may derive from: (1) direct uptake of circulating dietary fatty acids, (2) de novo synthesis of fatty acids by mammary gland from metabolites (e.g., acetate or C_2 equivalents) until C_{14} or C_{16} chain length is attained, and (3) further modification of fatty acids within the gland (e.g., desaturation or elongation) [29]. Palmitic acid is the major fatty acid synthesized from C_2 precursors produced from fermentation of dietary sugars [22]. In contrast, the C_{18} fatty acids ($C_{18:0}$, $C_{18:1}$, and $C_{18:2}$) are derived largely from the dietary plant fatty acids. The different carbon source (carbohydrates vs. fatty acids) explains up to 6.7‰ lower $\delta^{13}C$ values of $C_{18:0}$ compared to $C_{16:0}$ measured in the dairying products. Furthermore, in the dairying products the $C_{18:1}$ acid is enriched in ^{13}C (up to 1.7‰) compared to $C_{18:0}$. It is not known if desaturation and elongation of C_{16} fatty acids in the mammary cells can occur in both, the dietary plant and the de novo synthesized $C_{16:0}$ [22]. In C_3 and C_4 plants the $C_{16:0}$ acid is generally more depleted in ^{13}C than the C_{18} fatty acids [51,43–45]. A ^{13}C-enrichment of $C_{18:1}$ compared to $C_{18:0}$ acid was measured in vegetable oils [44]. This would support that both C_{18} acids in milk originate from fatty acids in dietary plants. The main fatty acids in sheep and goat cheese samples are enriched in ^{13}C by ~4‰ compared to the raw milk samples. This isotopic shift most likely reflects the bacterial degradation of the long-chain fatty acids during cheese making and storage.

Most samples of organic residues in archaeological vessels plot in the $\delta^{13}C_{16:0}$ vs. $\delta^{13}C_{18:0}$ and $\delta^{13}C_{18:1}$ vs. $\delta^{13}C_{18:0}$ fields of milk products, and calf/lamb and pig adipose (Fig. 5A–B). Several samples are between the fields of plants and animal fats, suggesting admixture of fats of different origins and different degrees of degradation. No samples plot in the fields of fish or deer fats.

3.6. Change of the carbon isotope composition of archaeological lipids

For classification of the archaeological fats, we used $\delta^{13}C$ values of individual fatty acids from modern plant and animal fats. Some differences in the $\delta^{13}C$ values of modern and archaeological lipids may result from: (1) different isotopic composition of the primary carbon source, (2) alteration during cooking by the prehistoric people, and (3) diagenetic alteration of the food remains during burial at the archaeological site.

The stable carbon isotopic composition of lipids absorbed into the porous structure of the archaeological pottery appears unaffected by diagenetic alteration during burial (e.g., [17]). Some isotopic variations in the organic residues may be related to different isotopic compositions of the primary carbon source. The pre-industrial atmospheric CO_2 was isotopically heavier (by ~1.6‰ between 1800 and 1980, [49]) than in present time. The carbon isotopic composition of plant and animal (primary producers and consumers) fats depends on the $\delta^{13}C$ value of the atmospheric CO_2 fixed into organic compounds by photosynthesis. Therefore, by assuming that the isotopic fractionation in the pre-industrial (e.g., 230 AC) biogeochemical carbon cycle was determined by the today's known photosynthetic mechanisms and metabolic pathways, we could expect the $\delta^{13}C_{16:0}$ vs. $\delta^{13}C_{18:0}$ and $\delta^{13}C_{18:0}$ vs. $\delta^{13}C_{18:1}$ covariation fields for plants and consumers at that time to be slightly shifted (by ~1.6‰) toward more positive $\delta^{13}C$ values. With this correction, significantly more samples from Arbon Bleiche 3 are included in the so corrected $\delta^{13}C_{16:0}$ vs. $\delta^{13}C_{18:0}$ and $\delta^{13}C_{18:0}$ vs. $\delta^{13}C_{18:1}$ fields for pre-industrial plants, cattle adipose, and dairying products (Fig. 5C–D).

The effects of cooking in ceramic pots on the lipid composition of meat, fish and plants from Western Canada were studied by Przylski and Sheriff [35]. These authors found that thermal decomposition reduces the number of fatty acids in food sample and the concentrations of saturated fatty acids increase while of unsaturated fatty acids decrease. Such compositional transformations may explain up to ±3‰ change of the bulk $\delta^{13}C$ values of modern C_3 and C_4 plants material by heating, boiling and roasting onto ceramic vessels, reported by DeNiro and Hastorf [9]. Some cooking experiments in ceramic vessels are being performed to simulate ancient cooking practices at Arbon Bleiche 3 (Urs Leuzinger from the Cantonal Archaeological Service at Thurgau, *personal communication*). Here we present the results of a preliminary study of the $\delta^{13}C$ variation in cooked milks. For this study fresh raw cow,

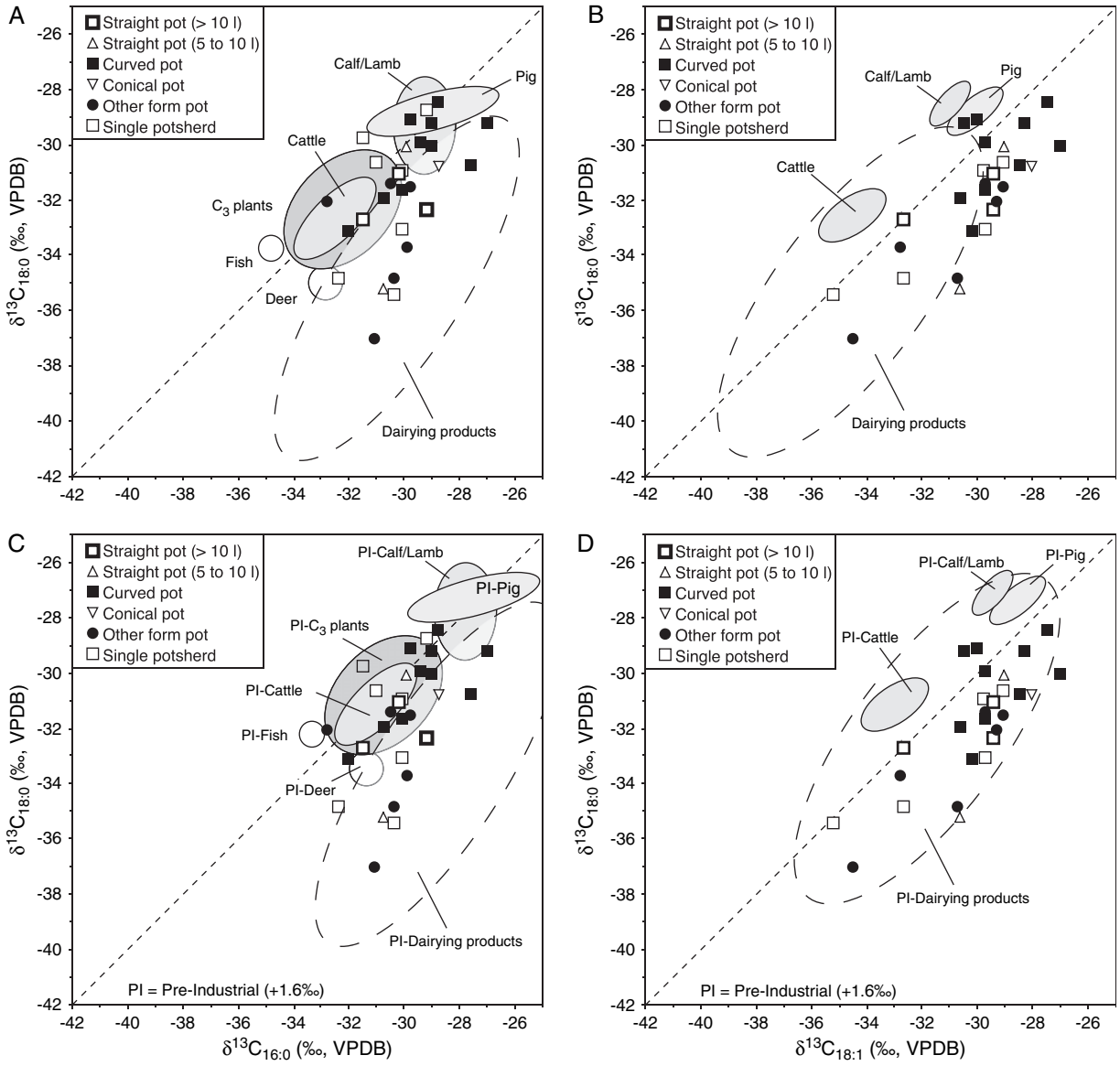

Fig. 5. Comparison of the carbon isotope composition of stearic acid ($\delta^{13}C_{18:0}$) versus palmitic ($\delta^{13}C_{16:0}$) and oleic ($\delta^{13}C_{18:1}$) of the organic residues from Arbon Bleiche 3 with those of modern (A, B) and pre-industrial animal and plant fats (C, D). The isotopic fields for pre-industrial (PI) animal and plant fats were determined assuming an atmospheric CO_2 enriched in ^{13}C by ~1.6‰ than in present time.

goat and sheep milk samples were obtained from local farmers. Two hundred milliliters milk aliquot was heated in glass vessel at 100 °C for 5 h. A sample of the heated milk was taken, and the milk further heated in a muffle at 250 °C for 1 h. Aliquots of the raw and heated milks were stored in the dark at −20 °C until analyses. Heating causes milk to turn slightly brown and to produce caramel flavors. This browning of milk results from a series of complicated reactions, such as caramelization, involving sugars dehydration, break down, and polymerization, and Maillard reactions between sugars (mainly lactose) and proteins [20]. The bulk and fatty acids stable $\delta^{13}C$ values were obtained as described previously, and are presented in Fig. 6. The bulk cow milk and the main fatty acids are generally enriched in ^{13}C by heating (Fig. 6A). This isotopic shift is due to preferential release of isotopically light, more volatile and thermally and chemically less stable compounds (e.g., carbohydrates, lipids, proteins, and vitamins) during the heat treatment [50]. In particular, heating enhance hydrolysis and degradation of lipids, and the volatilization of short-chain carboxylic acids. The ^{13}C-enrichment of $C_{18:0}$ and $C_{18:1}$ during heat treatment of milk is most likely due to preferential cleavage of the ^{12}C–^{12}C single or double bonds and loss of ^{12}C-rich moieties. A similar isotopic shift was observed during thermal treatment of olive oil [43]. In all the milk samples, the myrstic and palmitic acids have significantly higher $\delta^{13}C$ values compared to stearic and oleic acids. The $C_{14:0}$ and $C_{16:0}$ acids in goat and sheep

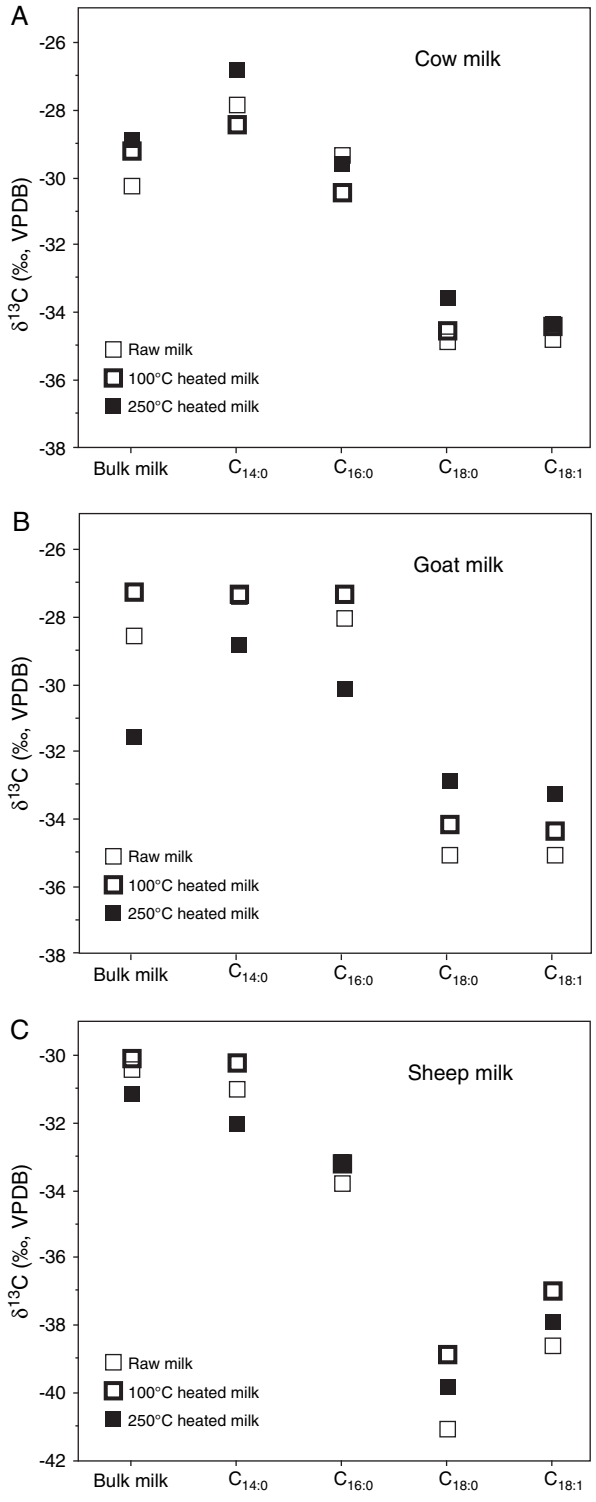

Fig. 6. Bulk and fatty acids carbon isotope composition of cow (A), goat (B) and sheep (C) raw and heated milk.

milk have lower $\delta^{13}C$ values with heat treatment (Fig. 6B–C). This ^{12}C-enrichment in the most heated samples is attributed to a contribution of isotopically light ($C_{14:0}$ and $C_{16:0}$) fatty acids. In raw milk, oleic acid is depleted in ^{13}C by up to ~6‰ compared to palmitic acid. A pathway in oleic acid degradation involving chain shortening with loss of a C_2 moiety and double bond reduction, could explain the ^{12}C-enrichment of short chain (C_{16} and C_{14}) fatty acids. To the best of our knowledge, the mechanisms of palmitic and oleic acids degradation in milk during heat treatment were not studied. Further experiments, using ^{14}C-labeled and natural fatty acids, are required to assess the pathways for the degradation of these compounds during cooking of milk.

The bulk goat and sheep milks show a distinct isotopic trend compared to cow milk, with a ^{12}C-enrichment during heating. This isotopic shift can be explained by the marked differences in milk composition among these ruminants. In general, goat and sheep milks are less rich in lactose, fats and proteins than cow milk, and have significantly higher concentrations of short-chain acids (butyric, C_4; caproic, C_6; caprylic, C_8; and capric, C_{10}). For example goat milk may contain up to 27% $C_{4:0}$–$C_{12:0}$ acids [29]. The milk fats (primarily as triglycerides) are hydrolyzed during heating and the released more volatile short-chain acids may escape by evaporation. As the carboxyl moieties in organic acids are enriched in ^{13}C (by up to 8‰) relative to the alkyl carbons [12,39], the loss of the highly abundant relatively ^{13}C-rich C_4–C_{12} acids, may explain the lower $\delta^{13}C$ values of the heated goat and sheep milks.

In summary, the data indicate that the animal fat preserved in the organic residues originates from plants, ruminants, and/or milk, thus providing direct evidence of dairying at Arbon Bleiche 3. This is in line with the interpretation of the distribution of bones from ruminant animals of different ages [10]. Most of the bones correspond to very young suckling calves or senile, non-lactating cows. This is a well-known slaughter practice to keep up the supply of milk in the farm.

4. Conclusions

Fat residues from plant, cattle adipose and ruminant milk were identified in almost all potsherds. This chemical evidence, combined with indirect archaeological observations, mainly from the age distribution of ruminant bones, indicate meat consumption and farming practices for a sustainable dairying. Given the short life of milk, which after leaving the ruminant udder quickly becomes colonized with lactobacilli, we can postulate that Arbon Bleiche 3 settlers were consuming fermented milks. Most likely the Neolithic settlers at Arbon were making relatively long life milk products, such as today's natural yoghurt, butter, and cheese, which could be stored and consumed at much later dates. Our chemical data provide direct proof of dairying in late Neolithic settlements in central Europe.

Acknowledgements

We thank Silvia Martinez (University of Basel) for helping in sampling of the organic residues, and Valérie Schwab and Torsten Vennemann (University of Lausanne) for providing reference samples from farms in the Cantons of Vallais and Vaud. This study benefited from financial support of the Swiss National Science Foundation (grant 1253-036539.00/1 to J. Bürgi, S. Jacomet and J. Schibler, grant 2100-066739.01/1 to J. E. Spangenberg) and the University of Lausanne. We thank the *Journal of Archeological Science* reviewers for constructive criticism.

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