CHAPTER THIRTEEN
Analysis of Lipid Residues in Archaeological Artifacts: Marine Mammal Oil and Cooking Practices in the Arctic
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Pottery sherds, stone lamps and artifacts from archaeological sites in Alaska and Canada were selected from the archives of the National Museum of Natural History in Washington DC. Ancient organic residues were collected on the sherds, often incrusted as a thick layer. Lipids were extracted from these residues followed by derivatization and analysis by high temperature gas chromatography (HTGC) and combined gas chromatography mass spectrometry (GC/MS). Modern samples of whales and seals were also analyzed. Some of these fresh specimens were thermally degraded to simulate cooking and aging. Alkaline treatment was sometimes necessary to hydrolyze the insoluble lipid fraction.

Thousands of years ago, Eskimos settled on the American coasts around the Arctic Circle and developed a fascinating culture in one of the most extreme climates of the world.[1] The ancient inhabitants of the arctic and sub-arctic coastal areas adapted to an economy relying primarily on the sea. In regions where land mammals are rare and plant resources sparse, marine mammals (seals, whales and walruses) provide an essential source of raw materials: skins and furs for clothing, boots, kayaks and tents; bones and ivory for tools, weapons and decorative objects; meat and fat for food and fuel. The muscles and blubber of large sea mammals were important sources for lipids and proteins and one individual could feed a family for days.

Blubber is a thick layer of fat and connective tissue located between the skin and the muscle of marine mammals. Blubber functions as insulation and as an energy store. It has a complex structure of fat cells and structural fibers made of collagen and elastin embedded in the fat matrix to give it both rigidity and elasticity. It is a good source of lipids but also provides proteins. Lipids composing the blubber are subject to variation and depend directly on the source of food. Studies show seasonal and geographical variations as well as compositional differences by sex, age and stage of pregnancy and lactation (Dahl et al. 2000; Grahl-Nielsen et al. 2003; Hamilton et al. 2004; Lockyer et al. 1984; Olson and Grahl-Nielsen 2003; Pabst et al. 1995). The oil rendered from the blubber was also used for fueling lamps (Blumer 1997; Lucier and Vanstone 1991; Nelson 1899; Spencer 1959).

Cooking Practices in the Arctic Coastal Areas

The inhabitants of arctic and sub-arctic coastal areas relied heavily on sea mammals (walrus, seals and whales) for their subsistence (Dumond 1998). Carbohydrates were absent in the diet and had to be compensated for by increased consumption of lipids and proteins. For example, for a family of 10 people with 8 dogs at Point Barrow, 60 kg of meat were necessary every day (Spencer 1959). Fish, birds and other small games were a complementary source of food, as well as roots, berries and seaweeds. Caribou was hunted when available, but this could only be found inland and the migration patterns of caribou are more unpredictable than those of the sea mammals.

In Alaska, wooden dishes were used to store water, oil or fermented food (mixtures of meat, fat and berries); fish and meat could then be eaten raw, dipped in oil. Food was cooked by boiling or simmering, usually with oil

[1] The general term Eskimo refers to all groups inhabiting the Arctic and Sub-arctic regions from North Eastern Siberia to Greenland. With the Aleuts, occupying the Aleutian Islands, they form the Eskimo-Aleut family from which are derived the different language groups: Aleut in the Aleutian Islands, Yupik in Eastern Siberia and Southwestern Alaska, and Inupiaq-Inuktitut, a continuum of dialects spoken from the coasts of Northern Alaska and Canada to Labrador and Greenland. Inuit is the term in use for Arctic populations in Canada and Greenland.

rendered from blubber, in clay vessels to make stews and soups. Meat and fish were also roasted on an open fire when wood was available, or eaten frozen, dried or aged. 'Muktuk', a mix of skin and blubber that was consumed raw or cooked and that apparently tasted like coconut, was eaten with relish (Geist and Rainey 1936; Nelson 1899; Spencer 1959). Cooking by means of hot stones was practiced at Barrow (Reid 1990) and in southern Alaska (De Laguna 1956).

Open oil-burning lamps were an important utensil in daily life. Oil rendered from blubber provided fuel for the lamp. Made of clay or soapstone, the flat-bottom lamps were used for lighting, heating and cooking. On St. Lawrence Island a second pot fashioned of clay was hung above the lamp and used as a cooking pot. Another clay or wooden pot, in the shape of the lamp, could be placed under the wick to collect any dripping of oil (Collins 1937; Nelson 1899).

Oil-burning lamps were reproduced in the laboratory. Blubber was cut in 2 x 2 cm squares, placed in a modern clay saucer and lit with a straw wick. The blubber rendered oil and provided a constant flame for up to two hours (using about 10 ml of oil). A small cup was placed 5 cm above the lamp with 20 ml of water. The heat from the lamp was sufficient for the water to simmer but not to boil.

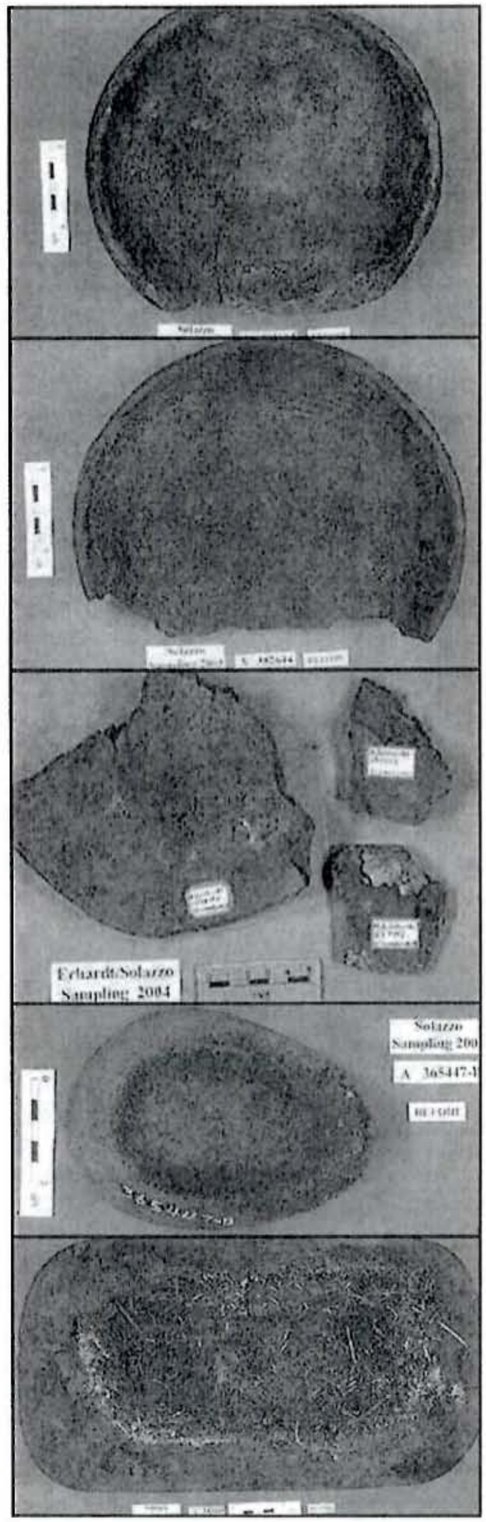

Figure 1: Examples of artifacts from which residues were taken. From top to bottom: saucer-shaped clay lamps numbers 382643 and 382644 from Nunivak Island, potsherds from Miyowagh on St. Lawrence Island, soapstone lamp number 365447 from Kodiak Island and wooden dish number 342583 from the vicinity of Wales.

The Artifacts

Pottery was developed in Alaska and western Canada as early as 1500 BCE and persisted until European contact and the historic period. Arctic pottery is made of a coarse black paste tempered with mineral or organic materials, depending on their availability. It is described as thick, crude and brittle. As it crumbles easily few complete vessels have been found. They were generally flat bottomed containers with thick walls and wide openings, compared to the size of the pot. Usually, oil-lamps were shallow with thick walls, while cooking pots were deeper and had thinner walls. Decorations are very rare (Ackerman 1961; Collins 1937; De Laguna 1947; Geist and Rainey 1936; Reid 1990; Spencer 1959; Stimmel and Stromberg 1986). Beach gravel was used as a mineral temper and could make up as much as 50% of the paste. Marine mammal blood and blubber were sometimes added to the temper. Fiber temper (animal hair, grass, wood, feathers and baleen) was responsible for the high porosity. Ceramics could be coated with burned grease and fat on both sides, sealing the pores before each use. The limited availability of wood restricted the firing to low temperatures. These types of vessels are good insulators, making them suitable for simmering, stewing or the rendering of oil by stone boiling (Reid 1990).

No pottery was manufactured in the Aleutian Islands. Its absence is due to the lack of suitable clay and the abundance of easily carved volcanic rock (McCartney 1970). The lamps have thick walls and are ovoid, narrowing at one end where the wick was placed (DeLaguna 1956; Laughlin 1980). Figure 1 presents a few of the artifacts chosen for analysis.

Archaeological residues were collected from artifacts excavated in Alaska and Canada and kept by the National Museum of Natural History of the Smithsonian Institution. Because of their geographical context it is fairly certain that the ceramic pots and the soapstone lamps must have contained primarily marine products. Lipids analysis was conducted using chromatographic techniques. Lipids usually survive well in archaeological contexts because of their hydrophobic nature. The conservation of fatty acids appeared particularly enhanced by the specific conditions of the Arctic. The composition of the fatty acid profile resulting from hydrolyzed and oxidized acylgycerides, observed after processing and burial of fats and oils, was characterized. Biomarkers, such as products of the oxidation of cholesterol and isoprenoid acids, were also observed.

Archaeological Samples

Archaeological soapstone lamps from Canada as well as clay, wooden and stone artifacts from archaeological sites in Alaska were examined for the presence of lipids. A series of 18 sherds, between 1000 and 1500 years old, were selected from the archaeological site of Miyowagh near Gambell in the northwestern part of the St. Lawrence Island.[2] Miyowagh is the second most ancient village at Gambell and dates back from the Old Bering Sea culture and the beginning of the Punuk. At this time, the hunting of walrus and seals was well developed; whales were obtained from stranded animals (Collins 1937). St. Lawrence Island is situated at 63°N in the Bering Sea, about 150 km (100 miles) from the coast of Alaska and 60 km (40 miles) from Siberia. The terrestrial fauna is restricted to arctic foxes, arctic squirrels and sometimes polar bears; the island is often frequented by birds. Because of its isolated location (St. Lawrence Island is encircled by the ice more than half the year) the inhabitants relied essentially on marine animals for subsistence: whales, seals and in particular walrus, abundant in the north of the island (Collins 1933; 1937; Dumond 1998; Geist and Rainey 1936).

Twelve clay sherds, eight stone lamps and tools, one wooden dish and one bone scraper from the coast of Alaska between Point Barrow and the Aleutian Islands were also sampled. At 71°N Point Barrow is the northernmost point of Alaska, protruding into the Beaufort Sea. St. Lawrence Island and Point Barrow are located along sea mammal migration routes and are still active whaling villages. Coastal Eskimos would hunt along the shore, chiefly in search of bowhead whales during their spring migration (Spencer 1959). The Aleutian Islands are situated west of Alaska. The archipelago consists of about 100 islands spread out over 1450 km (900 miles). The water around the islands is particularly rich in sea mammals attracted by the milder weather (Laughlin 1980). The other localities from which samples were investigated include the Seward Peninsula, Norton Sound, Nunivak Island and Kodiak Island (Figure 2, Table 1).

As described in the available archaeological literature the clay potsherds were made from a coarse and crude paste. The walls of the vessels varied from 0.5 to 2.7 cm and the surfaces were smoothed and undecorated. Most of the vessels had a high porosity and were certainly subjected to low temperature firing. They were tempered with mineral and vegetal matter like grass, feathers and maybe mammal hair (Collins 1937; Oswalt 1955). These sherds preserved amorphous organic residues on the inner or the outer surface, or both. In the latter case both sides were sampled when possible. The residues on the potsherds were thick, carbonized deposits. Two sherds (U1 and SL6) did not have a visible residue. In these cases the entire sherds were ground and any absorbed organic residue extracted. The stone lamps contained a thin layer of residue, strongly adhering to the surface.

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[2] The name Miyowagh was introduced by Collins (1937), other designations include Mayughwaaq (Badten et al. 1987) and Miyowaghameet (Collins 1932).

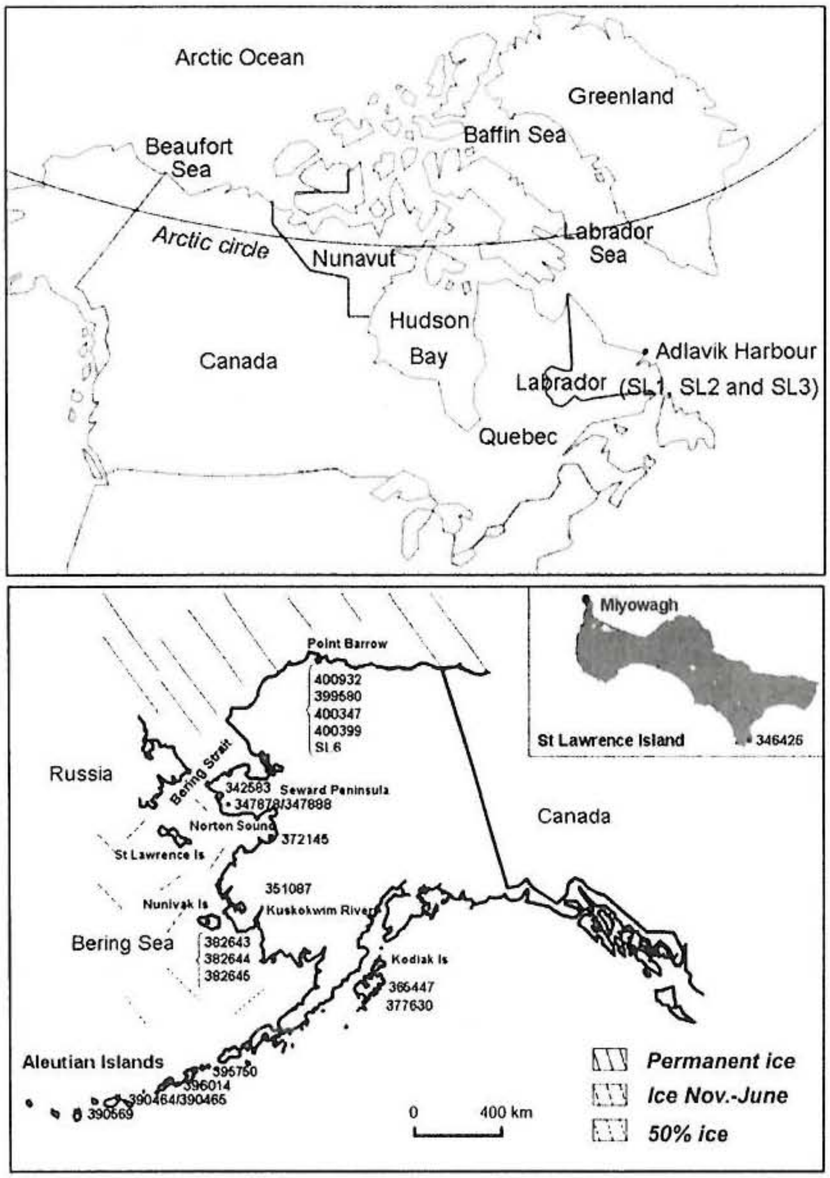

Figure 2: Maps showing the archaeological sites and provenance of the artifacts sampled in Alaska and Canada.

Three other objects were also sampled: a stone 'bola' (used to kill seals), a wooden dish and a bone scraper. The first two were covered with a thick layer of decomposing fat, still fresh and mixed with grass in the dish. The bone scraper was covered with a black material that proved difficult to remove. Three additional samples were taken from soapstone vessels excavated at Adlavik Harbour, a coastal Inuit community (dated to about 1750 CE) in Labrador at 55°N. The samples were of a brown waxy material. The Thule people, who are the ancestors of the Inuit in Arctic Canada, began using soapstone lamps and pots about 1000 to 500 BCE.

The samples from St. Lawrence Island were excavated in 1930 and 1931 by Collins (1937); the other samples from Alaska were collected in the first half of the 20th century CE for the National Museum of Natural History and were stored at the Smithsonian Institution, most recently in an environment-controlled storage area. The samples from Labrador were unearthed between 1999 and 2004 and were stored in plastic bags and wooden drawers at the Smithsonian Arctic Studies Center.

Modern Specimens

Some species that are traditionally hunted, or otherwise obtained, by the Eskimos were studied as reference. These included ringed seal, harbour seal, grey seal, beluga whale and narwhal (narwhal and grey seal are native to eastern Canada). In order to compare these fresh specimens with the archaeological samples they were subjected to high temperature storage to reproduce aging. By analyzing cooking residues from Arctic archaeological contexts the degradation of organic compounds resulting from the processing of foodstuffs can be understood and correlated with the anthropological data. Samples were taken from the blubber of a *Phoca hispida* (ringed seal), provided by the National Zoo of Washington DC; from the blubber, meat and skin of a *Phoca vitulina* (harbour seal) and a *Halichoerus grypus* (grey seal), hunted in Canada in 2005 and provided by the Vertebrate Zoology Department of the National Museum of Natural History; from the blubber and skin of the neck of a male *Delphinapterus leucas* (beluga whale) from the Churchill River (Manitoba, Canada) and conserved at the Smithsonian Institution; and from the blubber near the ear of a female *Monodon monoceros* (narwhal) stranded in Alaska in 2005. All samples were stored frozen.

Sample	Location on the excavation site	Material	Remarks
352986	Miyowagh Cut 1M Section 6	Clay potsherd	Flat, thick with a rim, sand and gravel tempered
353010	Miyowagh (no information)	Clay potsherd	Slightly curved, thick
353036	Miyowagh Cut 1M Section 8	Clay potsherd	Slightly curved with a low curved wall
353109	Miyowagh Cut 2M Section 4	Clay potsherd	Flat, thick, sand and gravel tempered
353140-1	Miyowagh Cut 2M Section 6	Clay potsherd	Curved, thick
353140-2	Miyowagh Cut 2M Section 6	Clay potsherd	Curved, thick, shaped as a saucer, sand and gravel tempered
353197	Miyowagh Cut 3M Section 4	Clay potsherd	Flat, thick with a low, curved wall (rim), sand and gravel tempered
353233-1	Miyowagh Cut 3M Section 7	Clay potsherd	Slightly curved, thick, sand and gravel tempered
353233-2	Miyowagh Cut 3M Section 7	Clay potsherd	Slightly curved, thick, sand and gravel tempered
353274	Miyowagh Cut 3M Section 10	Clay potsherd	Flat, thick, sand and gravel tempered
353356	Miyowagh Cut 4M Section 5	Clay potsherd	Slightly curved, thick
353917	Miyowagh Cut 11M Section 5	Clay potsherd	Flat, thick
353961	Miyowagh Floors 1, 2, Cuts 8,11,13	Clay potsherd	Flat, thick
354168	Miyowagh above roof timbers of entrance to House B, Cut 15M, Section 5	Clay potsherd	Flat, thick with a curved and low wall, sand and gravel tempered
354380	Miyowagh Cut 9(a), Cache site East of House B, below level of House B	Clay potsherd	Slightly curved, thin
U1-U5	Miyowagh	Clay potsherds	---
346426	Cape Kialegak, St. Lawrence Island	Clay potsherd	Curved, thin rim, sand and gravel tempered
347878	Seward Peninsula Kowieruk, 3 miles east of Imaruk Basin	Clay potsherd	Curved, thin rim, sand, gravel and grass tempered
347888	Seward Peninsula Kowieruk, 3 miles east of Imaruk Basin	Clay potsherd	Curved, thin rim, sand, gravel and grass tempered

372145	Whale Island, St. Michael, Norton Sound	Clay potsherd	Curved, thin, sand, gravel and grass tempered
351087	Kuskokwim River	Clay potsherd	Curved, thin rim, sand, gravel and grass tempered
382643	Old Eskimo burials on Nunivak Island	Earthenware lamp / bowl	Diameter 22 cm, thick
382644	Old Eskimo burials on Nunivak Island	Earthenware lamp / bowl	Diameter 22 cm, thick
382645	Nunivak Island, Old Eskimo burials	Clay potsherd	Thick, big pot with high walls
365447	'Our site', Jones point, Uyak Bay, Kodiak Island	Stone lamp	14 x 10 cm
377630	'Our point', village site on Uyak Bay, Kodiak Island	Stone lamp	19 x 15 cm
390463	Atka Island, Andreanof group, Aleutian Islands	Stone lamp	15 x 13 cm
390464	Atka Island, Andreanof group, Aleutian Islands	Stone lamp fragment	20 x 12 cm
390569	'Site C', east end of Sweeper Cove, North of road (shell and bone heap), Adak Island, Aleutians, Andreanof group	Hearth stone fragment	Flat slab 21 x 9 cm
395750	Amaknak Island, northeast end of Unalaska, Fox Island, Aleutians group	Stone lamp	19 x 16 cm
396014	Umnak P-A Fox Island group	Stone vessel fragment	Curved thick wall with beginning of bottom
342583	Wainwright Mitliktavik site, 22 miles northeast of Wales	Wooden dish	45 x 25 cm, crystals and grass
400347	From a locality in the southern part of Utkiavik, Point Barrow, purchased	Bone kayak bailer-scraper	---
400399	From a place in south end of Utkiavik, Point Barrow, purchased	Stone bolas	Diameter 7 cm
399580	Piginik (Barrow Birnick site), Mound J, cut 1, southwest corner of house A	Clay potsherd	Curved, thick, sand and gravel tempered
400932	Nunagiak (Barrow Nunakiat?), above house X	Clay potsherd	Curved, thick, sand and gravel tempered
SL6	School Collection, from Point Barrow, Alaska	Clay potsherd	Rim, gravel tempered
SL1	Adlavik Harbour-1 House-1 Unit 29	Soapstone (steatite) body vessel sherd, appears to be a lamp fragment	---
SL2	Adlavik Harbour-1 House-1 Test-Pit#2 Cut#2	Soapstone (steatite) body vessel sherd, vessel type indeterminable	---
SL3	Adlavik Harbour-1 House-1 Unit 3a	Soapstone (steatite) body vessel sherd, side of a large cooking kettle	---

Table 1 (on this and the previous page): Description of the collection of artifacts sampled for analysis.

Because archaeological samples have suffered severe conditions through time, it is necessary to try and reproduce an artificial degradation of fresh samples. Cooking pots are exposed to heat during their use and modifications of organic molecules will also occur during the long-term burial of the artifacts. The usual method for reproducing the degradation of foodstuffs in ceramic is to store them at high temperatures as heat accelerates the oxidation process (Copley et al. 2005; Malainey et al. 1999a; b). Samples of seal and whale products in modern clay saucers were artificially aged in an oven at an average temperature of 100°C (Patrick et al. 1985). A few grams of blubber and meat were boiled with water in saucers for two hours at 100°C and left in the oven for several weeks. Residues were sampled each week. The saucer that contained meat of beluga whale was cut in pieces and one of them was ground and treated as the ancient samples.

Analytical Methods

Fatty acid standards, *n*-tetratriacontane ($C_{34}H_{70}$) and the derivatization agent N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA), containing 1% trimethylchlorosilane (TMCS), were purchased from Supelco; chloroform, methanol and diethyl ether from Sigma-Aldrich. Archaeological samples as well as modern specimens were extracted in a 2:1 mix of chloroform and methanol. When enough material was available, 10 mg of the fresh specimens and 150 mg of the carbonized residues were mixed with 0.5 ml of the extraction solution. After sonication for 40 min and centrifugation for 20 min, the supernatants were concentrated to a volume of 0.5 ml, the total lipid extract (TLE). Of this, 50-100 µl was derivatized by trimethylsilylation. 20 µl *n*-tetratriacontane was added to the extracts and, after evaporation of the solvent under nitrogen, the samples were heated for 30 min at 70°C with 50 µl of BSTFA. Another 50 µl of the TLE was saponified with 0.5 ml 2N KOH in methanol for one hour at 70°C (Colombini 2002). Acidified with HCl (pH = 3), the acid fraction was recovered with diethyl-ether, evaporated under nitrogen and derivatized as described above.

HTGC was performed in a 6890N Agilent instrument with a J&W DB-1HT fused-silica capillary column (15 m × 0.32 mm, 0.10 µm) with a 100% dimethylpolysiloxane stationary phase. Set at an initial oven temperature of 50°C, the temperature was increased to 380°C at 10°C/min and held at 380°C for 5 min. CC/MS analysis was performed on a Finnigan Trace GC 2000 Thermo-electron with AS2000 Autosampler, coupled with a PolarisQ Ion Trap GC/MSn. The GC was equipped with an Rtx®-5MS fused-silica capillary column (30 m × 0.25 mm, 0.25 µm) with a 5% diphenyl/95% dimethyl-polysiloxane stationary phase. The oven temperature was programmed for a 2.5 min isothermal at 80°C, then increased to 260°C at 10°C/min, held at 260°C for 0.1 min, then increased to 300°C at 5°C/min and finally held at 300°C for 10 min.

Fatty Acid Profiles in the Modern Specimens

Whale and seal blubber is mainly composed of triacylglycerides (TAGs). Because of post-mortem hydrolysis, free fatty acids and mono- and diacylglycerides (DAGs) were recovered in addition to TAGs. TAGs ranged from 44 to 62 total acid carbons, with a peak at 50 or 52 for all species except for grey seal for which TAGs ranged from 44 to 66 and reached a maximum at 56. DAGs ranged from 28 to 40, with two main peaks at 34 and 36. Unsaturated fatty acids were also present in small amounts, including C14:1, C16:1, C18:1, C20:1, C20:4, C20:5, C22:1, C22:5 and C22:6.

Alkaline treatment of the fresh samples allowed identification of the saturated fatty acids as their trimethylsilylester derivatives. The fatty acids and their relative proportions for the studied seal and whale species are presented in Table 2. Fish oil and blubber are rich in unsaturated fatty acids, characteristic of their marine origin (Morgan 1983). Eicosapentaenoic acid (EPA, C20:5ω3) and docosahexaenoic acid (DHA, C22:6ω3) are the major polyunsaturated fatty acids. Other fatty acids found in marine oils are gadoleic (C20:1ω11), gondoic (C20:1ω9), erucic (C22:1ω9), cetoleic (C22:1ω11), arachidonic (C20:4ω6), clupadonic (22:5ω3) and selacholic (C24:1) acids and to a lesser extend nisinic (C24:6), shibic (C26:5) and thynnic (C26:6) acids (Dahl et al. 2000; Grahl-Nielsen et al. 2003; Olsen and Grahl-Nielsen 2003).

After hours at an average temperature of 100°C, polyunsaturated fatty acids are the first components to oxidize. Table 2 also shows the changes in fatty acid composition of the species tested in the laboratory. Depending on the species, the results show that polyunsaturated fatty acids disappear in the first hours or days, leaving the monounsaturated as the main components. For grey seal (12 days) and ringed seal (7 days), for example, monounsaturated fatty acids have higher levels. This may be caused by the saturation of the polyunsaturated fatty acids (Malainey et al. 1999a; b; Morgan 1983). Only after one or two weeks the relative levels of monounsaturated fatty acids start to decrease while the percentage of saturated fatty acids increase. In the tests on beluga whale products, only monounsaturated and saturated fatty acids, ranging from C12:0 to C18:0, are left after 24 hours. Dicarboxylic acids with 4-9 carbon atoms and short-chain saturated fatty acids appeared after 7 days. At the same time the concentration of monounsaturated fatty acids reduced dramatically (Table 2, Figure 3a). Polyunsaturated fatty acids can also oxidize to form diacid (dicarboxylic acids) by oxidative cleavage of the double bonds of unsaturated fatty acids. Different mechanisms lead to the formation of different diacids from unsaturated fatty acids (Colombini et al. 2005; Copley et al. 2005; Passi et al. 1993; Regert et al. 1998). The most common transformation is the oxidation of oleic acid, or any other fatty acid with a double bond in position 9, generating azelaic acid (C9 diacid). Diacids with 9 or 7 carbon atoms can be formed from polyunsaturated fatty acids, such as linoleic acid (C18:2ω6) and linolenic acid (C18:3ω3), or oleic (C18:1ω9) and palmitoleic (C16:1ω7). Diacids with 5 carbons can be formed from EPA with 4 carbons from DHA (Passi et al. 1993). Long-chain monounsaturated fatty acids (such as gadoleic, cetoleic and erucic acids with double bonds in position 11 or 13) are the primary source for diacids with more than 9 carbons.

Compound	Grey seal blubber	Grey seal blubber (12 days)	Harbor seal blubber	Harbor seal blubber (50 days)	Ringed seal blubber	Ringed seal blubber (7 days)
C8:0	0.124	0.067	--	0.205	--	--
C9:0	0.290	0.074	--	0.245	--	--
C10:0	0.184	0.085	--	0.202	--	--
C11:0	--	--	--	0.541	--	--
C12:0	0.508	0.118	--	0.553	--	--
C13:0	--	--	--	1.392	--	1.018
C14:0	16.968	9.677	5.156	10.286	2.297	4.609
C15:0	--	0.971	0.327	1.201	0.400	1.302
C16:0	31.462	11.556	14.458	27.683	3.759	11.218
C17:0	--	--	--	1.357	0.547	1.072
C18:0	2.378	0.533	1.558	6.876	1.565	6.617
C20:0	--	3.949	--	--	0.665	--
C14:1	1.949	2.078	2.495	1.535	2.485	1.814
C16:1	4.481	17.588	34.823	17.760	21.048	25.939
C18:1 (ω9)	10.794	31.302	36.667	16.762	27.51	24.060
C18:1 (ω7)	--	--	--	--	3.051	11.253
C20:1	10.160	11.866	2.273	5.549	6.615	8.343
C22:1	4.073	5.345	--	1.462	0.715	1.376
C24:1	--	--	--	0.240	--	--
C20:4	1.529	0.670	--	--	--	--
C20:5	7.824	1.282	2.243	--	10.796	0.288
C22:5	2.496	0.247	--	--	5.243	--
C22:6	2.928	0.440	--	--	13.302	--
C4 diacid	--	--	--	0.932	--	--
C5 diacid	0.449	0.234	--	0.269	--	--
C6 diacid	--	0.177	--	0.284	--	--
C7 diacid	0.652	0.210	--	0.383	--	0.724
C8 diacid	--	0.216	--	0.841	--	0.366
C9 diacid	0.745	1.317	--	0.756	--	--
Total diacids	1.846	2.154	--	3.465	--	1.090
Total monounsaturated fatty acids	31.457	68.179	76.258	41.773	52.813	72.785
P/S ratio	13.226	2.926	9.277	4.026	2.401	1.695

Compound	Narwhal blubber	Narwhal blubber (50 days)	Beluga whale blubber	Beluga whale blubber (1 day)	Beluga whale blubber (7 days)	Beluga whale blubber (90 days)	Archaeological samples
C8:0	--	0.557	--	--	0.973	0.777	**0<A<4**
C9:0	--	0.693	--	--	--	0.968	**0<A<4**
C10:0	0.073	0.759	--	--	1.749	1.192	**0<A<2**
C11:0	--	1.165	--	--	--	2.099	**0<A<2**
C12:0	0.820	2.330	1.522	0.836	4.189	2.112	**0<A<1**
C13:0	--	2.318	--	--	1.048	--	**0<A<1**
C14:0	5.529	13.094	9.100	9.630	15.057	12.517	**4<A<11**
C15:0	0.484	1.573	0.815	--	0.851	1.746	**0<A<2**
C16:0	9.530	22.515	10.248	11.933	15.958	15.168	**10<A<35**
C17:0	--	3.393	0.459	--	0.403	1.522	**0<A<1**
C18:0	2.135	11.369	0.880	1.810	4.461	4.175	**5<A<10**
C20:0	0.885	--	0.260	--	0.414	1.135	**0<A<2**
C14:1	1.350	0.650	3.225	2.178	1.193	1.507	**trace**
C16:1	22.788	10.505	23.056	40.022	17.404	18.021	**<8**
C18:1 (ω9)	28.449	8.939	27.389	22.766	13.306	12.470	**7<A<14**
C18:1 (ω7)	--	--	2.583	--	--	--	
C20:1	15.229	4.846	12.974	8.896	6.603	7.035	**5<A<10**
C22:1	5.799	2.453	4.843	1.929	6.641	4.908	**2<A<8**
C24:1	0.119	0.911	0.483	--	--	1.690	**trace**
C20:4	0.348	--	--	--	--	--	--
C20:5	1.955	--	0.860	--	--	--	--
C22:5	0.688	--	0.373	--	--	--	--
C22:6	1.644	--	0.929	--	--	--	--
C4 diacid	--	2.167	--	--	0.848	--	--
C5 diacid	--	0.530	--	--	1.090	0.243	--
C6 diacid	--	--	--	--	1.036	0.880	--
C7 diacid	--	0.676	--	--	1.617	1.998	--
C8 diacid	0.821	1.385	--	--	2.714	5.817	--
C9 diacid	1.349	3.171	--	--	9.747	2.019	--
Total diacids	2.17	7.929	--	--	8.656	10.957	**3<A<40**
Total monounsaturated fatty acids	73.734	28.304	74.07	75.791	45.147	45.631	--
P/S ratio	4.464	1.980	11.652	6.593	3.577	3.633	--

Table 2 (on this and the previous page): Relative percentage composition of fatty acids in marine mammal blubber after simulated decomposition; in the last column the range is given of the fatty acids found in the archaeological samples (A). Diacids are dicarboxylic fatty acids; P/S ratio = C16:0/C18:0.

In the aged samples of beluga whale, the formation of diacids is clearly the result of the degradation of polyunsaturated fatty acids. Although the polyunsaturated fatty acids quickly decompose, in 24 hours, diacids appear only after 7 days at 100°C. The profile observed at 24 hours is an intermediate between the beginning of decomposition and its final stage. Before 7 days, diacids must be present only as their, partially oxidized, precursors still attached to the glycerol molecule.

The P/S ratio (C16:0/C18:0) can be an indicator to discriminate between categories of residues. The ratio calculated from the modern sample of beluga whale is relatively high, more than 11. It progressively decreases with the time of exposure to heat to reach a value of 3.6 after 7 days at 100°C and seems to stabilize after that. In all species, this ratio decreases to values between 1.7 and 4.0. Although a general pattern was observed, it is not possible to distinguish between species, or even between seals and whales. Basically the same profile was obtained for all kinds of marine oils and fats. Other species, such as walrus, should be tested and added to this study.

HTGC Results of the Archaeological Samples

In the archaeological samples polyunsaturated fatty acids and TAGs appeared to have degraded. DAGs were rarely detected, but monoacylglycerides (MAGs), such as monopalmitin and monostearin, were encountered frequently. High amounts of glycerol were found in many samples. Its presence indicates hydrolysis over time. Monounsaturated fatty acids with an even carbon chain from 14 to 22, and sometimes 24, were detected. Although the gas chromatographic method used does not separate gadoleic from gondoic acid, or erucic from cetoleic acid, the presence of long-chain monounsaturated fatty acids must be considered evidence for a marine origin.

The observed degradation of the lipids in fresh specimens demonstrated that polyunsaturated fatty acids can oxidize in a couple of hours at 100°C or higher, and in a couple of days at lower temperatures. This is followed by the formation of diacids. These were found in abundance in all archaeological samples. The profile of diacids was similar in most samples, ranging from 4-14 carbon atoms with azelaic acid (C9 diacid) the most abundant. Azelaic acid is the primary degradation product in mammal fat, due to the abundance of C18:1, C18:2 and C16:1. Longer chain diacids are from the degradation of long-chain monounsaturated fatty acids, such as C20:1 and C22:1, also abundant in marine mammal fat. Oxidizing conditions or high temperatures are responsible for the cleavage of the double bond in unsaturated fatty acids (Colombini et al. 2005; Copley et al. 2005; Regert 1998).

Cooking or burning of the fat has probably occurred repeatedly. Tests in our laboratory reproducing a blubber-burning lamp showed that the heat above the flame reached a temperature of about 200°C. Although some contamination may occur from the surroundings after immediate discarding, the high concentration of polyunsaturated fatty acids in marine fat are certainly responsible for most diacids. The conditions of preservation of the archaeological samples in permafrost can provide an explanation for the excellent recovery of diacids, preventing them from leaching into the soil. The P/S ratio in all archaeological samples is lower than in the fresh mammal samples, but similar to the degraded samples (Tables 2 and 3). The process of degrading mammal blubber by heating appears to lower this ratio to reach about the same value as the archaeological residues.

GC/MS Results of the Archaeological Samples

When possible, samples were also analyzed by GC/MS. Diacids were observed ranging from 4 to 14 carbon atoms and saturated fatty acids from C6:0 to C18:0, and in some cases also C20:0 and C22:0. Even and odd middle-chain fatty acids were also present, mostly C6:0 to C13:0. C15:0 and C17:0, present in small quantities in animal and marine mammal fat, were also detected. The short- and middle-chain fatty acids may result from the oxidation of unsaturated long-chain fatty acids. For instance, C9:0 is a product of the oxidative scission of oleic acid. A few oxidation products were identified by GC/MS: 2-hydroxydecanoic acid, 3-hydroxydecanoic acid and 12-hydroxyoctadecanoic acid. 12-hydroxyoctadecanoic acid is formed from monounsaturated fatty acids with the double bond in position 11, such as gondoic acid or cetoleic acid. Both are present in lipids from marine mammals after oxidation and dehydration.

Phytanic acid (3,7,11,15-tetramethyl-hexadecanoic acid) was also encountered (Table 3). This compound is found in fish and marine mammals and it could be an important biomarker. Two other isoprenoid fatty acids are considered characteristic of oils from marine mammals: 4,8,12- trimethyltridecanoic acid (TMTD) and pristanic acid (2,6,10,14-tetramethylpentadecanoic acid). All three are proposed to come from the phytoplankton and krill ingested by marine mammals (Ackman 1968; 1989; Hansen 1970). These isoprenoid compounds are found in higher concentrations in marine than in terrestrial animals. Their detection in pots can be used as a good biomarker to prove the presence of a marine source of food, especially whale oil (Hansen 1970). Pristanic acid and TMTD have been detected in only a few samples, which may be due to the naturally higher abundance of phytanic acid (Copley et al. 2005). Cholesterol has been detected, as well as two of its oxidation products: cholesta-3,5-dien-7-one and cholest-5-en-7-one.

Cholesta-3,5-dien-7-one is known to be thermally derived from 7-ketocholesterol, which is often the main product of auto-oxidation of cholesterol (Rose-Salin 1996). It has been shown that the auto-oxidation of polyunsaturated TAGs accelerates the oxidation of cholesterol (Kim and Nawar 1991; Osada et al. 1993). These unstable compounds are quickly oxidized and produce radicals that accelerate the oxidation of cholesterol (peroxidation of the TAGs by heating).

The Samples from Miyowagh

Archaeological residues from Miyowagh, St. Lawrence Island, are probably the oldest samples analyzed in this study. They were found in kitchen middens from a 1500 year old site on a gravel beach. Residues are characterized by monounsaturated fatty acids, especially monounsaturated fatty acids with 20 carbon atoms, gadoleic acid (C20:1ω9) and gondoic acid (C20:1ω11); and with 22 carbon atoms, erucic acid (C22:1ω9) and cetoleic acid (C22:1ω11). A variable amount of C22:1 was present, with an average of 4.5% of the total composition in fatty acids. C20:1 was quite abundant, from 5% to 10% of all fatty acids. Only two samples had low levels of C20:1 (354380-2(E) and 353274), these did not contain C22:1. C18:1 varied from 7% to 14%. Palmitoleic acid, C16:1 was present at a maximum of 8% of all fatty acids. C16:1 is less stable than C18:1 and during degradation its quantity is more likely to decrease and palmitoleic acid will disappear first. C16:0, with an average of 22% of all fatty acids, varied between 35% in sample 354380-2(E) and 9%, 10% and 12% in samples 353961(I), U3(I) and U5(E) respectively. Stearic acid had an average relative abundance of 7% and appeared more consistent among the samples tested. In the last column of Table 2 the ranges of percentages of fatty acids found in all archaeological samples (A) is presented and compared to those found in sea mammals.

The P/S ratios varied little, from 1.2 to 4 with an average value of 2.9, a range typical of mammal fat. Only 353274 has a relatively high ratio of 7.2. MAGs were detected in all but three samples. When present, monostearin was the main MAG, usually accompanied by mono-olein. Monopalmitin was sometimes identified by HTGC, but can be confused with C22:1. GC/MS is more sensitive and allows the identification and separation of monopalmitin and monomyristin. When comparing all ceramics sampled on both interior and exterior, 353917, 353961, 354380-1, U2 and U3 have more degraded organic residues towards the inside (Table 4). These results corroborate the assumption that these sherds are from oil-burning lamps. The oil burning formed a layer of accumulated soot exposed to repeated heating. The residues found on the exterior were either spilled from inside the lamp or applied to create a waterproof coating. This fat was certainly exposed to a less intense heat.

Sample	Mass (g)	Glycerol	Mono acyl-glycerides	Mono unsaturated fatty acids	Diacids	Iso-prenoid acids	Sterols	P/S ratio
Miyowagh, Gambell, St. Lawrence Island								
352986 I	0.011	8.311	3.614	26.111	16.264			1.889
353010 E	0.100	0.239	2.109	32.636	7.091	*	*	2.919
353036 I	0.019	6.100	6.213	24.051	17.29			2.468
353109 E	0.152	4.353	0.609	25.996	20.134			2.586
353140-1 E	0.163	3.781	3.392	36.707	10.853	*	*	2.847
353140-2 E	0.152	10.188	5.418	24.515	21.200	*	-	2.557
353197 E	0.159	5.776	3.331	39.872	10.338			2.802
353233-1 E	0.152	12.554	4.552	31.809	10.997	*	*	2.858
353233-2 E	0.150	4.553	5.082	33.274	14.037	*	*	2.768
353274 E	0.152	19.916	0	5.238	17.053			7.163
353356 E	0.157	5.664	2.988	34.898	10.888			3.616
353917 E	0.150	3.976	0.670	30.991	11.997			3.268
353917 I	0.052	4.251	0.090	21.768	22.140			4.042
353961 E	0.152	4.338	8.348	28.863	13.408	*	*	3.154
353961 I	0.028	13.632	1.843	15.262	31.813			1.223
354168 E	0.153	3.944	3.550	30.884	14.485	*	-	3.207
354380-1 E	0.150	4.008	2.556	28.365	14.908			3.280
354380-1 I	0.050	5.280	4.309	26.59	24.167			2.885

354380-2 E	0.081	2.316	0	12.936	12.195			3.277
354380-2 I	0.108	2.314	3.340	23.692	13.144			3.122
U1 Ceramic	0.948	2.307	1.842	18.556	17.829			2.959
U2 E	0.165	4.441	1.219	29.739	17.051	*	*	3.748
U2 I	0.101	4.917	0	24.999	29.151			3.898
U3 E	0.154	4.120	4.786	34.268	14.537	*	*	2.671
U3 I	0.100	10.765	5.785	24.167	24.466			1.818
U4 E	0.150	6.096	1.817	23.177	10.548	*	*	3.672
U5 E	0.153	2.115	2.197	24.114	31.911	*	*	1.954
Kialegak, St. Lawrence Island								
346426 CLAY	0.040	2.038	0	44.443	11.304	*	*	2.409
Seward Peninsula								
347878 CLAY	0.035	12.146	2.881	29.073	16.116	-	-	2.222
347888 CLAY	0.100	10.717	6.786	25.486	18.778	-	-	3.252
372145 CLAY	0.042	7.865	11.478	35.659	7.982	-	-	2.116
Kuskokwim River								
351087S1 CLAY	0.100	6.989	4.307	36.971	9.810	*	*	2.176
351087S2 CLAY	0.104	10.139	2.335	28.465	11.390			2.817
Nunivak Island								
382643 CLAY	0.093	11.447	3.236	14.997	31.535	*	-	3.782
382644 CLAY	0.090	19.159	0.925	29.475	17.948	*	*	3.720
382645 CLAY	0.145	11.983	8.152	30.546	12.651	*	*	2.636
Kodiak Island								
365447 STONE	0.034	7.871	36.217	16.507	6.042	-	-	2.769
377630 STONE	0.033	7.710	13.2	20.689	10.425	*	*	3.272
Aleutian Islands								
390463 STONE	0.019	4.128	18.293	19.579	7.524	*	-	3.260
390464 STONE	0.060	33.157	0	18.052	10.282			3.603
390569 STONE	0.113	0.676	12.138	20.232	16.354	-	-	1.381
395750 STONE	0.033	10.713	35.237	14.863	4.904			2.196
396014 STONE	0.093	0.697	3.038	18.738	4.846	-	*	4.46

Northern Alaska								
342583 WOOD	0.023	1.335	4.875	41.473	10.293	-	-	7.648
Point Barrow								
400347 WOOD	0.034	1.344	28.859	11.754	42.883	*	-	1.605
400399 STONE	0.030	0.778	5.384	11.631	27.339	*	-	3.149
399580 CLAY	0.100	5.104	21.640	31.925	8.734			2.415
400932 CLAY	0.100	2.744	7.062	26.67	10.620	-	-	1.506
SL6 CLAY	0.156	1.106	2.750	25.062	4.979	*	*	2.552
Adlavik Harbour								
SL1 STONE	0.150	11.029	8.018	24.752	19.715			2.282
SL2 STONE	0.150	12.983	13.603	42.984	3.265			2.572
SL3E STONE	0.150	11.113	30.404	13.927	17.080			1.196
SL3I STONE	0.150	11.835	13.719	23.212	14.354	*	*	1.721

Table 3 (above and on the previous pages): Fatty acid profiles of the archaeological samples. Glycerol, monoacylglycerides, monounsaturated fatty acids, diacids and the P/S-ratio (C16:0/C18:0) were calculated from HTGC data. The values indicate the relative percentages calculated from the sum of all detected fatty acids. Isoprenoid acids and sterols (cholesterol and products of oxidation) were positively detected (*) or not (-) by GC/MS (blanks indicate that GC/MS was not performed).

DAGs were found in only two samples from St. Lawrence Island. U5 contained diacids, mostly C8 and C9, with reduced amounts of monounsaturated fatty acids, C16:0 and C18:0. Because the hydrolysis of the DAGs was incomplete, monounsaturated fatty acids and C14:0, C16:0 and C18:0 are less abundant as free fatty acids. It seems that the decomposition of the residue is less advanced; this vessel may have been used to collect dripping oil instead of being used as a cooking pot or a lamp.

Artifacts from the Coasts of Alaska

The artifacts from coastal archaeological sites in Alaska were classified according to their geographic origin and their material (clay, stone, wood or bone). HTGC chromatograms of a clay potsherd (399580) and the bone scraper (400347) are shown in Figures 3b and 3c, GC/MS chromatograms of a soapstone lamp (SL3), the bola (400399) and the wooden dish (342583) are shown in Figures 3d, e and f. Samples from ceramics found at Kialegak, Seward Peninsula, Kuskokwim River, Nunivak Island and Point Barrow had a composition similar to the samples described above. On average, the P/S ratio is 2.6. One sample seems to be more degraded: 382643 from Nunivak only had 14.7% unsaturated fatty acids, but more than 30% diacids. Independent of their geographical provenance, all clay vessels have the same fatty acids profile, and the slight differences can be explained by a more or less advanced degradation or slight differences in the initial lipid composition. The latter can be due to the species or the feeding period, factors that can not be accounted for by this kind of analysis.

Samples from stone artifacts from the Aleutian Islands are distinguished from the samples of clay artifacts as they have much less C18:1, C16:1 and diacids while MAGs are abundant. Possibly, residues have less adherence on stone and some components may leach out more easily, especially in the milder climate of the Aleutian Islands. Another possibility is that the oil used on the Aleutian Island comes from different marine mammals than further north. However, the P/S ratio is normal for a marine source with an average 3.26. Figure 4 shows the percentage of monounsaturated fatty acids plotted against the percentage of diacids in these artifacts.

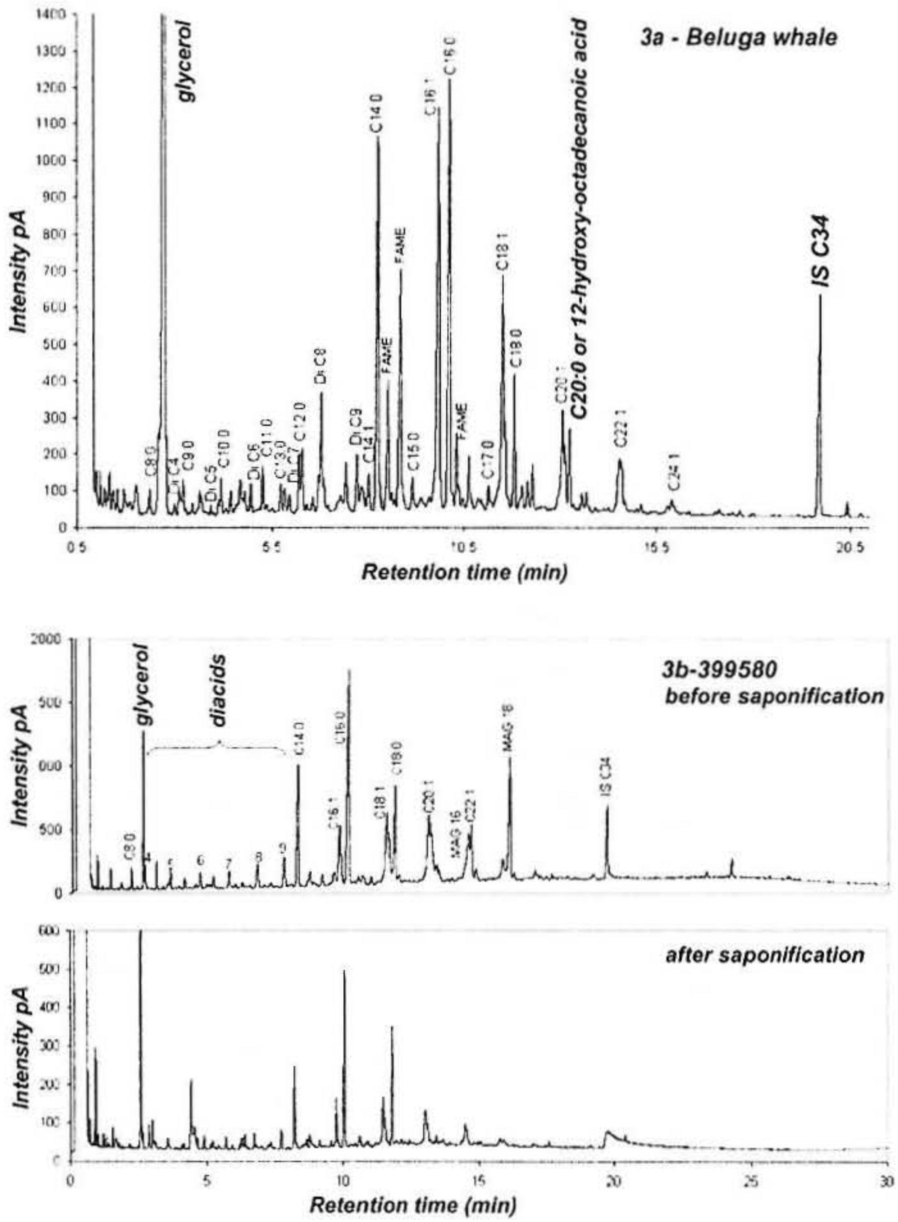

Figure 3a and 3b: High temperature gas chromatograms of Beluga whale blubber (a) and clay potsherd 399580 (b).

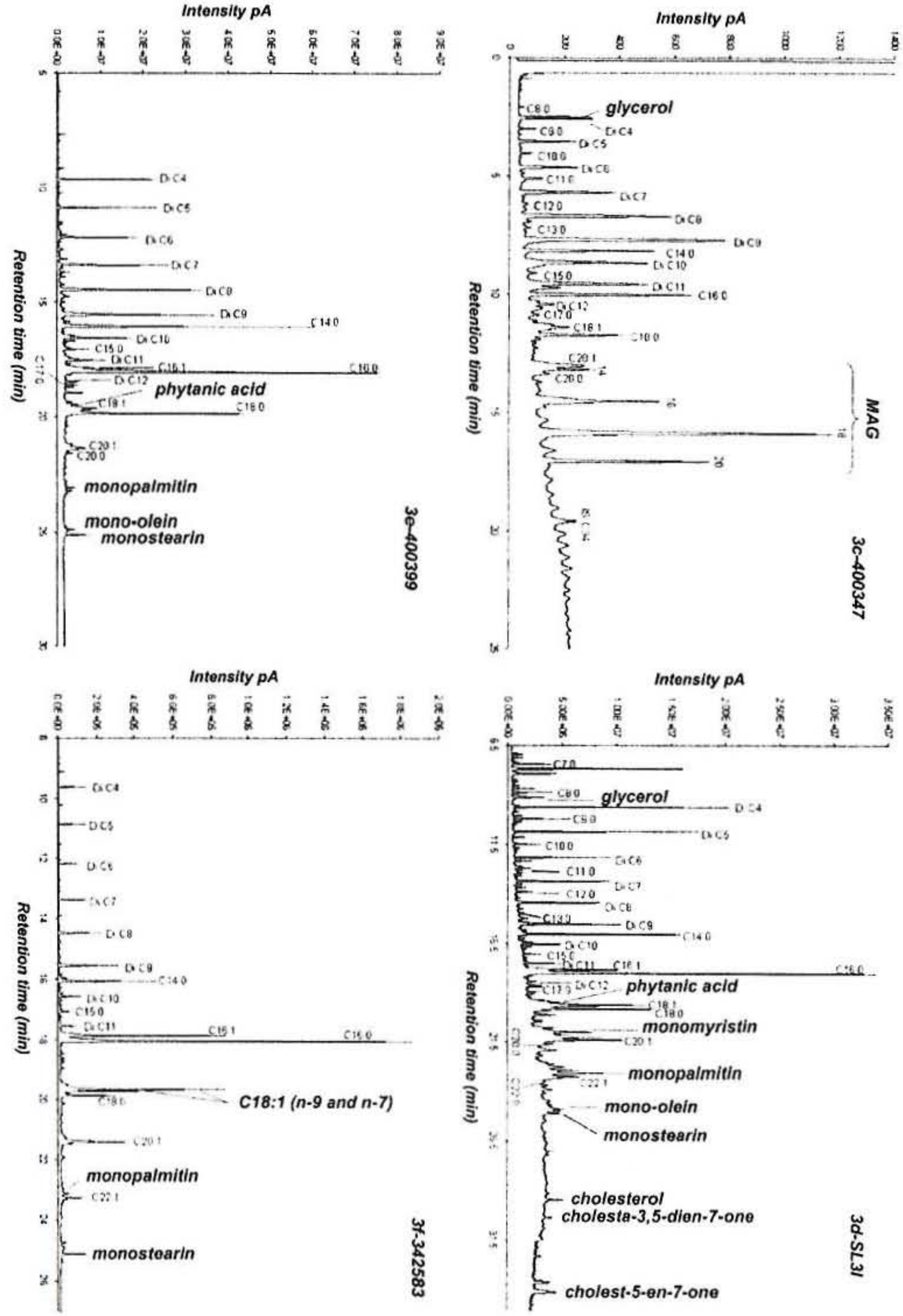

Figure 3c-f: High temperature gas chromatogram of bone scraper 400347 (c) and GC/MS chromatograms of soapstone lamp SL3 (d), bola 400399 (e) and wooden dish 342583 (f).

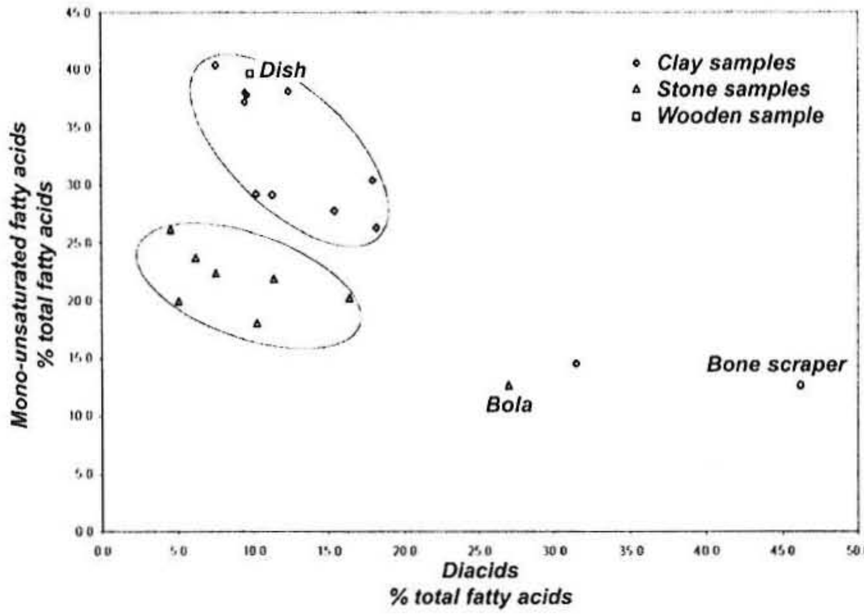

Figure 4: Monounsaturated fatty acids plotted versus dicarboxylic fatty acids for artifacts from coastal Alaska.

The stone bola 400399 from Point Barrow was covered with a thick layer of decomposed fat, low in palmitoleic and oleic acid, but very high in diacids. This is remarkable as the object was probably not exposed to heat, but used to kill seals. The presence of diacids could be due to biodegradation by micro-organisms of the fresh remains before the object was discarded. The sample from bone scraper 400347 from Point Barrow was similar to the bola, high in diacids (about 40%) and low in C16:1 and C18:1. It was also low in C16:0 and C18:0. On the chromatogram (Figure 3c), the high concentration of MAGs is striking. MAG-C18:0 is the most abundant, although C16:0 is the main free fatty acid. Scrapers were used to remove fat from intestines and skins from seals, caribous or small land mammals. The sample from wooden dish 342583 from northern Alaska had a very high amount of monounsaturated fatty acids and a quite high P/S ratio of 7.6. This sample was collected in 1929 when it was described as a 'flat wooden dish used beneath stone lamp to catch drippings, found in place in an abandoned house'. The blubber was still fresh, which may explain the high P/S ratio (typical of fresh blubber).

	353917		353961		354380-1		U2		U3	
	E	I	E	I	E	I	E	I	E	I
MAGs	0.670	0.090	8.348	1.843	2.556	4.309	1.219	---	4.786	5.785
Monounsaturated fatty acids	30.964	21.768	28.863	15.262	28.365	26.59	29.739	24.999	34.268	24.167
Diacids	11.997	22.140	13.408	31.813	14.908	24.167	17.051	29.151	14.537	24.466
P/S ratio	3.268	4.042	3.154	1.223	3.280	2.885	3.748	3.898	2.671	1.828

Table 4: Comparison between samples taken from the exterior (E) and from the interior (I) of the sherd. MAGs are monoacylglycerides; diacids are dicarboxylic fatty acids; P/S ratio = C16:0/C18:0.

Discussion

The archaeological residues recovered in the coastal arctic regions proved to have been remarkably well preserved, most likely due to a particularly favorable environment. To summarize, our samples were characterized by the presence of high concentrations monounsaturated fatty acids and diacids, a P/S ration of about 3 and the presence of MAGs as well as phytanic acid. Archaeological residues showed important similarities with the fat of marine mammals. Most potsherds did not retain a recognizable shape that would enable to recognize them as fragments of a lamp or a cooking pot. Lamps are likely to have contained marine mammal fat exclusively; cooking pots may occasionally have been used to prepare land mammal meat, for example caribou. It was not possible to test samples from such species, but if land mammals were used, palmitic, stearic and oleic acids would be more abundant (Malainey et al. 1999 a; b).

In the Northern Slope of Alaska, caribou could be encountered during its migration. It was also bartered for sea mammal oil with the land Eskimos. Two samples from clay vessels from Point Barrow had about twice the average percentage of C18:0 (7%): SL6 with 13.57% and 400932 with 14.87%. In SL6 myristic and palmitic acids were also much more abundant than in any other archaeological sample. In these two samples, terrestrial mammal meat could have been mixed with sea mammal fat. Indeed, long-chain monounsaturated fatty acids were more abundant in these samples compared to the other artifacts tested.

Many factors influence the biochemical modifications of foodstuffs. Were they cooked, fried or stored? How and where were they discarded? Repeated exposure to heat, biodegradation by micro-organisms, contamination by the surroundings and leaching of the residue are some of the processes that may take place over the hundreds of years before the artifacts are eventually unearthed. Decomposition of lipids occurs through hydrolysis and oxidation. Low temperatures and an anaerobic environment can temporarily protect compounds from extensive degradation.

Even though the lipid profiles in most of our samples are typical of burned blubber, the species that provided the fat still have to be determined. It may not be possible to determine what kind of oil was used in the lamp as it is likely that both seal and whale oil were used, depending on their availability. Diacids are exceptionally abundant, meaning that the residues were not leached by water. Detailed information of the archaeological context is lacking for many samples, especially of those artifacts obtained as gifts or bought from Eskimos. Even though this means that the period of use and the nature of the soil in which they were buried may remain unclear, the extreme cold of Alaska and northern Canada evidently provides an ideal environment for the biochemical study of their former contents.

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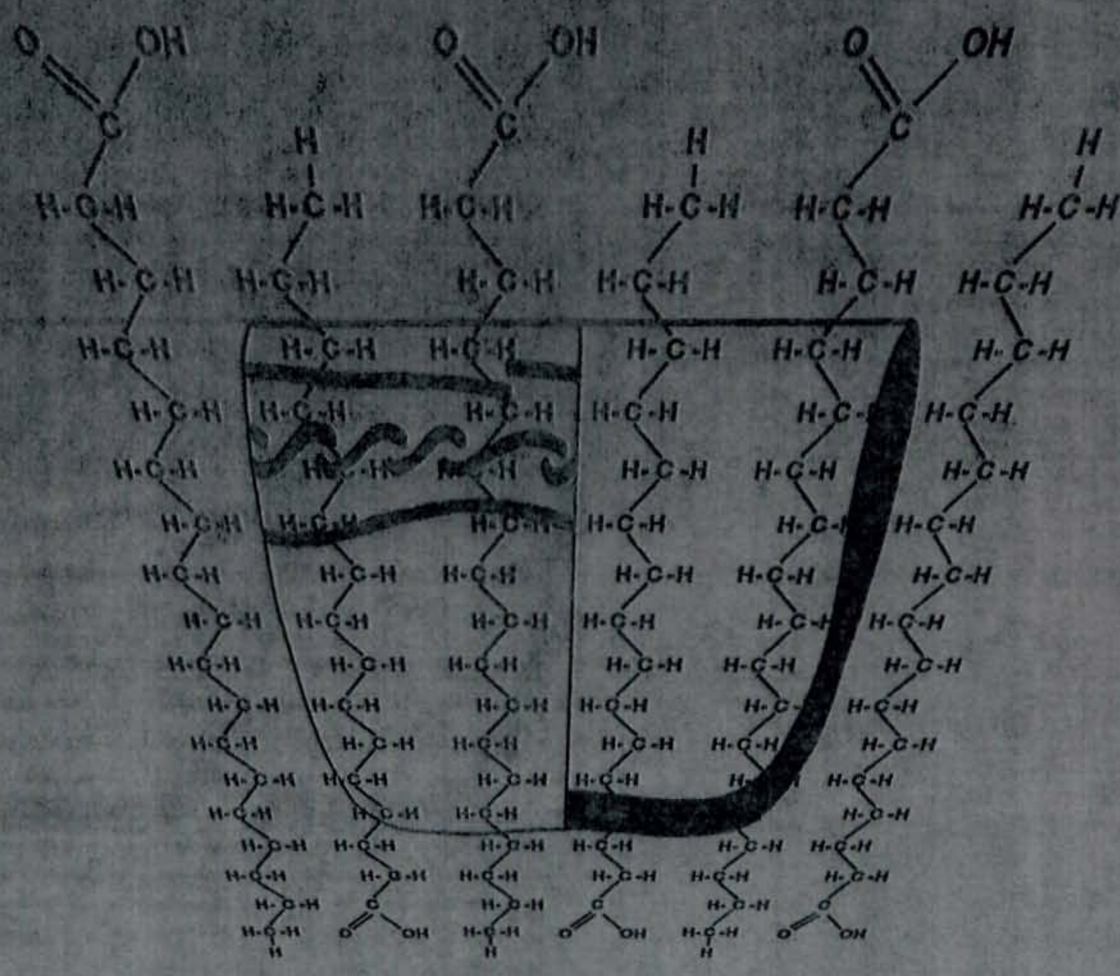

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