Early Neolithic wine of Georgia in the South Caucasus

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Chemical analyses of ancient organic compounds absorbed into the pottery fabrics from sites in Georgia in the South Caucasus region, dating to the early Neolithic period (ca. 6,000–5,000 BC), provide the earliest biomolecular archaeological evidence for grape wine and viniculture from the Near East, at ca. 6,000–5,800 BC. The chemical findings are corroborated by climatic and environmental reconstruction, together with archaeobotanical evidence, including grape pollen, starch, and epidermal remains associated with a jar of similar type and date. The very large-capacity jars, some of the earliest pottery made in the Near East, probably served as combination fermentation, aging, and serving vessels. They are the most numerous pottery type at many sites comprising the so-called "Shulaveri-Shomutepe Culture" of the Neolithic period, which extends into western Azerbaijan and northern Armenia. The discovery of early sixth millennium BC grape wine in this region is crucial to the later history of wine in Europe and the rest of the world.

Neolithic | wine | viticulture | Georgia | Near East

Following the last Ice Age, the Neolithic period in the Near East (ca. 10,000–4,500 BC) was a hotbed of experimentation, especially in the mountainous region extending west to east from the Taurus Mountains of southeastern Anatolia through the South Caucasus and northern Mesopotamia to the Zagros Mountains of northwestern Iran (e.g., refs. 1 and 2, including pertinent references). As the climate moderated and precipitation levels increased, especially between ca. 6,200–4,200 BC (*SI Appendix*), humans established year-round settlements. Permanent habitation allowed for a host of recently domesticated plants—including the "founder crops" of barley, einkorn wheat, emmer wheat, chickpea, pea, lentil, flax, and bitter vetch—to be efficiently raised, harvested, and stored. These developments were crucial in jump-starting the millennia-long upheaval and changes in human subsistence and culture known as the "Neolithic revolution" (3, 4).

Sedentary life, made possible by new, assured plant resources, was also accompanied by advances in the arts and crafts, such as architecture, weaving, dyeing, stone working, and woodworking. The invention of fired clay (pottery) containers sometime during the early seventh millennium BC (5, 6) had profound implications for processing, serving, and storing food and drink.

Human exploitation and cultivation of plants was not confined to staple cereals and legumes during the Neolithic. Fruits, nuts, tubers, herbs, and tree products are well-attested at Neolithic sites throughout the larger region. Among the fruit species, the wild Eurasian grape (*Vitis vinifera* sp. *sylvestris*) stands out, because its domestication as *V. vinifera* sp. *vinifera* became the basis of a widespread "wine culture" throughout the Near East and Egypt (1), which later spread to east Asia and across the Mediterranean to Europe (7–9), and then later to the New World. Today, there are some 8,000–10,000 domesticated cultivars of wine, raisin, and table grapes, with a range of colors from black to red to white. These cultivars owe their origins to human selection and accidental crosses or introgression between the incoming domesticated vine and native wild vines. These varieties account for 99.9% of the world's wine production and include famous Western European cultivars such as Cabernet Sauvignon, Sangiovese, Tempranillo, and Chardonnay (10).

The Near Eastern uplands have been described as the "world center" of the Eurasian grape (11), based on where the wild plant thrived and achieved its greatest genetic diversity. Indeed, DNA studies have shown that the wild vine of Anatolia is genetically closer to Western European cultivars than its wild counterpart there (12–16). Many cultivars in Georgia also have a close relationship to those in the West, including Pinot Noir, Nebbiolo, Syrah, and Chasselas (12).

Two important questions remain to be answered. Can more narrowly defined mountainous areas of greater Mesopotamia and the Fertile Crescent be delimited where the Eurasian grape first began to be made into wine and where it was subsequently domesticated? If so, when did these developments occur?

Archaeological Samples Chosen for Analysis

Our investigation, part of a larger Georgian project (17), sought to answer these questions by focusing on two archaeological sites

Significance

The earliest biomolecular archaeological and archaeobotanical evidence for grape wine and viniculture from the Near East, ca. 6,000–5,800 BC during the early Neolithic Period, was obtained by applying state-of-the-art archaeological, archaeobotanical, climatic, and chemical methods to newly excavated materials from two sites in Georgia in the South Caucasus. Wine is central to civilization as we know it in the West. As a medicine, social lubricant, mind-altering substance, and highly valued commodity, wine became the focus of religious cults, pharmacopoeias, cuisines, economies, and society in the ancient Near East. This wine culture subsequently spread around the globe. Viniculture illustrates human ingenuity in developing horticultural and winemaking techniques, such as domestication, propagation, selection of desirable traits, wine presses, suitable containers and closures, and so on.

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that were occupied during the earliest Pottery Neolithic period in Georgia, the so-called "Shulaveri-Shomutepe Culture" (SSC), dated to ca. 5,900–5,000 BC (18–20). The two sites are Shulaveris Gora, which gives its name to the period together with Shomutepe approximately 50 km downstream on the Kura River, and Gadachrili Gora (21). These sites are located within 2 km of one another in the province of Kvemo (Lower) Kartli, roughly 50 km south of the modern capital of Tbilisi (Fig. 1). Each is a small village, approximately 1 ha in area, of closely spaced mudbrick circular structures, 1–5 m in diameter, with interspersed pits and courtyards. The buildings are believed to be domestic residences, and the pits assumed to be for storage and/or refuse.

Fertile, rolling hills surround the sites on a high plateau at an altitude of >1,000 m ASL. Gadachrili Gora is presently bifurcated by the Shulaveris Ghele, a seasonal tributary of the

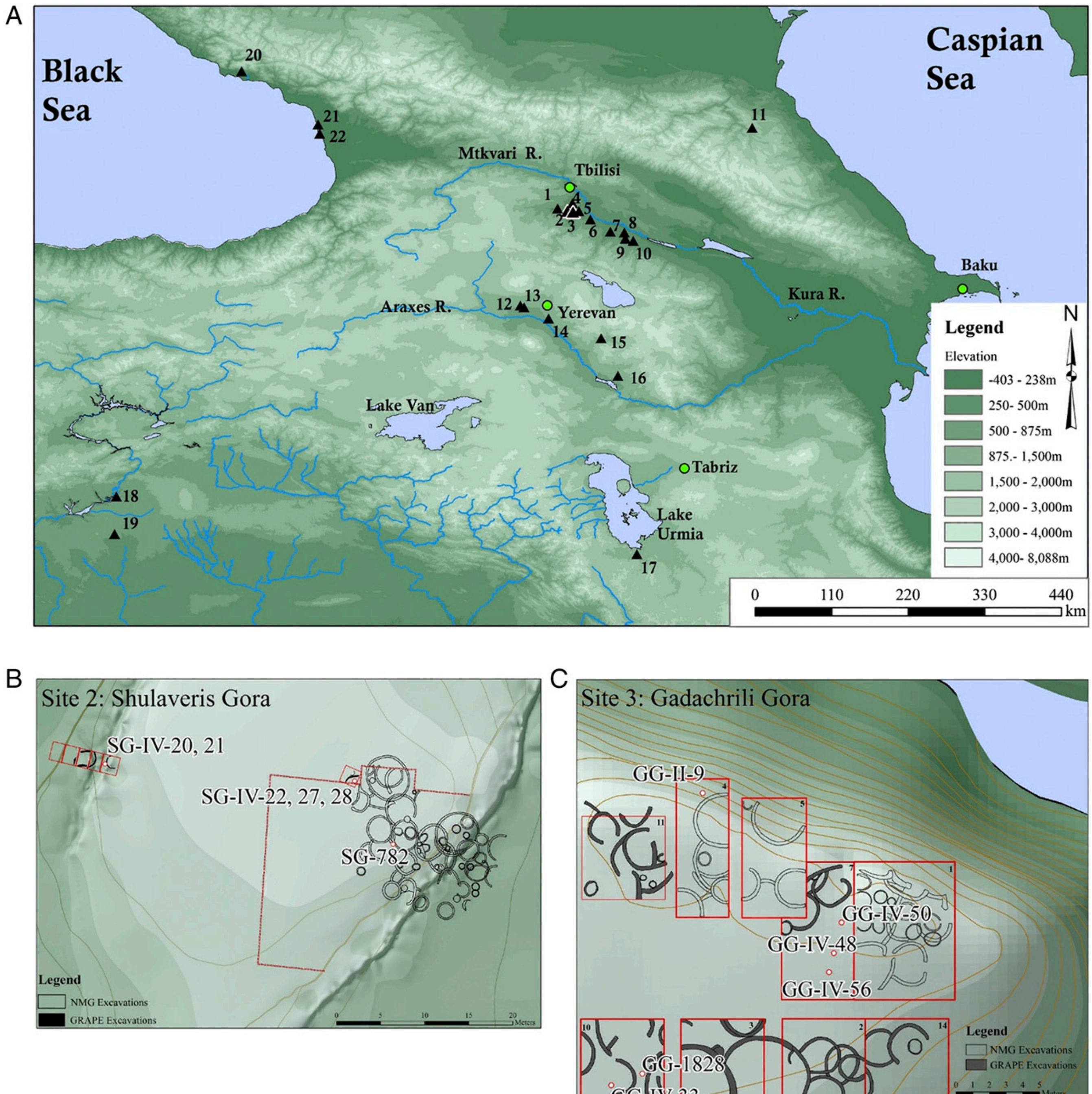

Fig. 1. Map of Shulaveri-Shomutepe Culture sites and other sites mentioned in the text (*A*) and the early Neolithic settlements of Shulaveris Gora (*B*) and Gadachrili Gora (*C*) showing the locations of the analyzed jar sherd samples that were positive for tartaric acid/tartrate. Site names: Arukhlo (1), Shulaveris Gora (2), Gadachrili Gora (3), Dangreuli Gora (4), Imeris Gora (5), Khramis Didi-Gora (6), Shomutepe (7), Haci Elamxali Tepe (8), Göytepe (9), Mentesh Tepe (10), Chokh (11), Aratashen (12), Aknashen (13), Masis Blur (14), Areni-1 (15), Kül Tepe (16), Hajji Firuz Tepe (17), Nevali Çori (18), Göbekli Tepe (19), Gudau River (20), Pichori (21), and Anaklia (22). GRAPE, Gadachrili Gora Regional Archaeological Project Expedition; NMG, National Museum of Georgia; R, river. Red lines indicate excavated areas and squares.

Khrami River that runs into the Kura, while Shulaveris Gora is roughly 0.5 km from the stream. The climate today is semiarid (steppe), with an annual rainfall of 350–550 mm and an average temperature of approximately 13 °C. Milder, better-watered conditions prevailed during the period ca. 5,900–5,000 BC (*SI Appendix*). The Eurasian grapevine was well adapted to the ancient climate and remains well adapted to the modern climate.

As is our standard practice in biomolecular archaeological investigations (22), we strove to obtain the best-dated, best-provenienced, and best-preserved samples possible. These criteria were met to a varying extent in this study. For example, we had previously analyzed two sherds (SG-16a and SG-782; Fig. 2 *B*–*C* and Table 1) from the 1960s excavations at Shulaveris Gora, which we designated as "borderline positives" for tartaric acid/tartrate (1), the principal biomarker of grape/wine in the Near East (*SI Appendix*), because of conflicting results from the less-sensitive chemical techniques that we used at that time. Moreover, the customary practice at that time was to "clean" sherds by washing them in dilute hydrochloric acid to remove calcium carbonate and other postburial accretions. In the process, ancient organics might well have been altered, even destroyed, to give "false positives." It was also later learned that the sherd with the highest apparent level of tartaric acid/tartrate (SG-16a) was collected from the surface of the site. Besides compromising the dating of this sherd, this also called into question the extent to which it had been subjected to environmental contamination and exposure to rain, which might have caused increased microbial activity and an elevated tartaric acid/tartrate content.

The opportunity to learn more and put the biomolecular archaeological investigation on a firmer, multidisciplinary foundation came when excavations at Gadachrili and Shulaveri were renewed in 2012–2013 and 2015–2016 (17). Many more radiocarbon dates from well-defined occupational contexts were obtained; coupled with advances in calibration curves and statistical evaluation, this has allowed for construction of a much tighter chronology for the early Neolithic than had been proposed in earlier publications (*SI Appendix*). Excavation and archaeobotanical techniques have also advanced since the 1960s, providing a finer-grained picture of how artifacts and ecofacts (i.e., plant and animal remains) were deposited and subjected to geological and chemical processes, as well as to human activity.

Fig. 2. (*A*) Representative early Neolithic jar from Khramis Didi-Gora (field no. XXI-60, building no. 63; depth, −5.45 to −6.25 m). (*B*) Jar base SG-16a, interior and cross-section. (*C*) Jar base SG-782, exterior. Note the textile impression on the base. (*D*) Jar base GG-IV-50, interior. (Photographs by Mindia Jalabadze and courtesy of the National Museum of Georgia.)

Table 1. **Georgian early Neolithic pottery positive for tartaric acid by LC-MS-MS and their associated soil samples**

Sample no.	Date (BC)	Provenience	Pottery type	Extract weight (mg)	Tartaric acid (ng/mg residue)*	Malic acid (ng/mg residue)*	Succinic acid (ng/mg residue)*	Citric acid (ng/mg residue)*
Gadachrili Gora								
GG-II-9, body sherd	ca. 5900-5750	Square BB-27, −2.73 m	Jar base sherd	NA	**134 ± 11***	**715 ± 86***	596 ±25*	**182 ± 3***
GG-II-9, soil	ca. 5900-5750	Square BB-27, −2.73 m	Associated soil	NA	20 ± 2*	491 ± 7*	630 ± 21*	10 ± 1*
GG-IV-33, disk base sherd	ca. 5700-5500	Square 10, Locus 4	Jar base sherd	1.2	**87 ± 6**	**998 ± 47**	**165 ± 13**	**186 ± 6**
GG-IV-62, soil	ca. 5700-5500	Square 10, Locus 4	Associated soil	0.8	7 ± 1	193 ± 33	32 ± 5	9 ± 0
GG-IV-50, pedestal base	ca. 5700-5500	Square 7, Locus 2	Jar base sherd	1.2	**17 ± 1**	**170 ± 13**	**31 ± 4**	**45 ± 1**
GG-IV-51, soil	ca. 5700-5500	Square 7, Locus 2	Associated soil	4.6	5 ± 0	91 ± 7	16 ± 0	5 ± 1
GG-IV-48, pedestal base	ca. 5700-5500	Square 7, Locus 2	Jar base sherd	4.3	**4 ± 1**	**50 ± 1**	**22 ± 1**	**6 ± 1**
GG-IV-54, soil	ca. 5700-5500	Square 7, Locus 2	Associated soil	4.5	1 ± 0	23 ± 1	7 ± 1	1 ± 0
GG-IV-56, flat base	ca. 5700-5500	Square 7, Locus 1	Jar base sherd	6.3	**39 ± 0**	**369 ± 22**	**54 ± 0**	**51 ± 0**
GG-IV-46, soil	ca. 5700-5500	Square 7, Locus 1	Associated soil	2.2	19 ± 0	312 ± 16	34 ± 4	20 ± 0
Shulaveris-Gora								
SG-16a, flat base	Early Neolithic	Surface	Jar body sherd	NA	**55 ± 1[†]**	**2028 ± 71[†]**	**198 ± 4[†]**	**58 ± 1[†]**
SG-782, pedestal base	ca. 5900-5750	Square BB, −0.8 m	Jar body sherd	NA	**8 ± 0[†]**	**387 ± 14[†]**	**56 ± 4[†]**	**15 ± 0[†]**
SG-IV-20, body sherd	ca. 5900-5750	Square 2, Locus 2	Jar base sherd	6.1	**4 ± 0**	**97 ± 2**	**12 ± 1**	**34 ± 0**
SG-IV-21, soil	ca. 5700-5500	Square 2, Locus 2	Associated soil	7.1	3 ± 0	56 ± 0	12 ± 1	5 ± 1
SG-IV-22, soil	ca. 5700-5500	Soil, Neolithic levels	Site soil	9.6	2 ± 0	17 ± 2	3 ± 0	1 ± 0
SG-IV-27, soil	ca. 5700-5500	Soil, Neolithic levels	Site soil	8.8	2 ± 0	18 ± 1	4 ± 0	1 ± 0
SG-IV-28, soil	ca. 5700-5500	Soil, Neolithic levels	Site soil	14.6	1 ± 1	9 ± 1	4 ± 1	1 ± 0

Numbers in bold highlight concentrations for ancient sherds that are higher than their corresponding soils. NA, not applicable.

*Except for the GG-II-9 samples, which are reported as nanograms of organic acid per gram of sherd/soil material (ng/g or ppb), all concentrations are cited as ng/mg (ppm) of extracted residue.

[†]Sherds were extracted in toto.

Pottery is the essential starting point of many biomolecular archaeological investigations. Barring the recovery of discernible physical residues of natural products constituting a food or drink, pottery has the advantage of being porous and an ionic (zeolite-like) material that absorbs liquids in particular and preserves them from environmental contamination for millennia until they are chemically extracted (see below).

Pottery had some additional advantages for our study. The plasticity of the clay is ideal for producing vessel shapes suited to specific purposes, and once fired, the material is virtually indestructible. The beginning stages of pottery making in the Near East are attested at Gadachrili and Shulaveri. The pottery is well-made and functional, implying that it derives from even earlier industrial developments, possibly from a nearby mountainous region of Turkey, Mesopotamia, or Iran. Although the vessels were handmade, textile impressions on the bottoms of some bases indicated that they were probably turned on a slow wheel.

Fortunately, it has been possible to reconstruct in its entirety what is likely the principal jar type of the period. Large jars, like the one from Khramis Didi-Gora shown in Fig. 2*A*, are among the most common shapes in the pottery corpora of Gadachrili, Shulaveri, and other SSC sites. They can be very large; for example, the Khramis Didi-Gora specimen is nearly 1 m tall and 1 m wide, with a volume exceeding 300 L. Strangely, their bases, which are flattened or low disks or low pedestals, can be relatively small and seemingly unstable; the diameter of the Khramis Didi-Gora jar base is only one-quarter of its overall diameter at its widest point (*Discussion and Conclusions*).

Globules and strips of clay were sometimes applied as plastic decorations to the exterior surfaces of jars, especially very large ones. Fig. 2*A* shows 10–15 clay globules enclosed within semicircular strips at intervals around the mouth of the vessel. This motif has been interpreted as a schematic grape cluster. Small central indentations of individual globules on other jars might then represent the attachment points of bunches of berries to their pedicels. The larger knobs in the intervening spaces could indicate how a cover or lid made of an organic material (perhaps leather or cloth) was held down. Another jar from Khramis Didi-Gora is thus far unique in showing a stick-like figure with upraised arms beneath vertical lines of globules (*SI Appendix*, Fig. S1). Could this be a Neolithic rendition of a popular motif, seen on modern monuments and buildings throughout Georgia today, in which jubilant, dancing figures are seen cavorting under trellised grapevines? Chemical analysis was clearly needed as a check on any fanciful interpretations.

The pottery fabrics of all vessel types, including bowls and a range of different-sized jars with both narrow and wide mouths, are moderately well-fired, occasionally straw-tempered, and rarely polished (burnished) on their reddish-yellowish exteriors (Fig. 2 *B–D*). Interiors are generally blackish-grayish due to the narrow mouths of jars cutting off oxygen, and variously sized reduction splotches of the same colors on the exterior surfaces pointed to open-firing rather than kiln-firing (23). Interior reddish residues on the lower halves and bases of jar interiors were infrequently observed, but were suggestive of precipitates from liquid contents.

As might be anticipated, pottery was not produced on a large scale in the early Neolithic, and relatively little pottery has been recovered from these sites compared with later eras. Unlike undisturbed burials with intact vessels, human occupation, especially when a site has been intensely inhabited over centuries, usually results in whole vessels being broken into sherds and dispersed.

Based on considerations of good context and preservation, assured dating, special features such as decoration, and availability, 18 jars (6 body sherds and 12 base sherds) were sampled from the 2012–13 and 2014–2016 seasons at Gadachrili, along with one jar base sherd from the more limited 2016 season at Shulaveri. Bases were most desirable because materials settling out from a liquid were most likely to have accumulated on their interiors. Body sherds were less definitive, since they might come from the lower or upper part of a vessel. The sherds, which were not washed in the field, were accompanied by soil samples, collected from the same contexts but separated from the sherds, so as to provide a check on possible environmental contamination and background organic acid production by microorganisms.

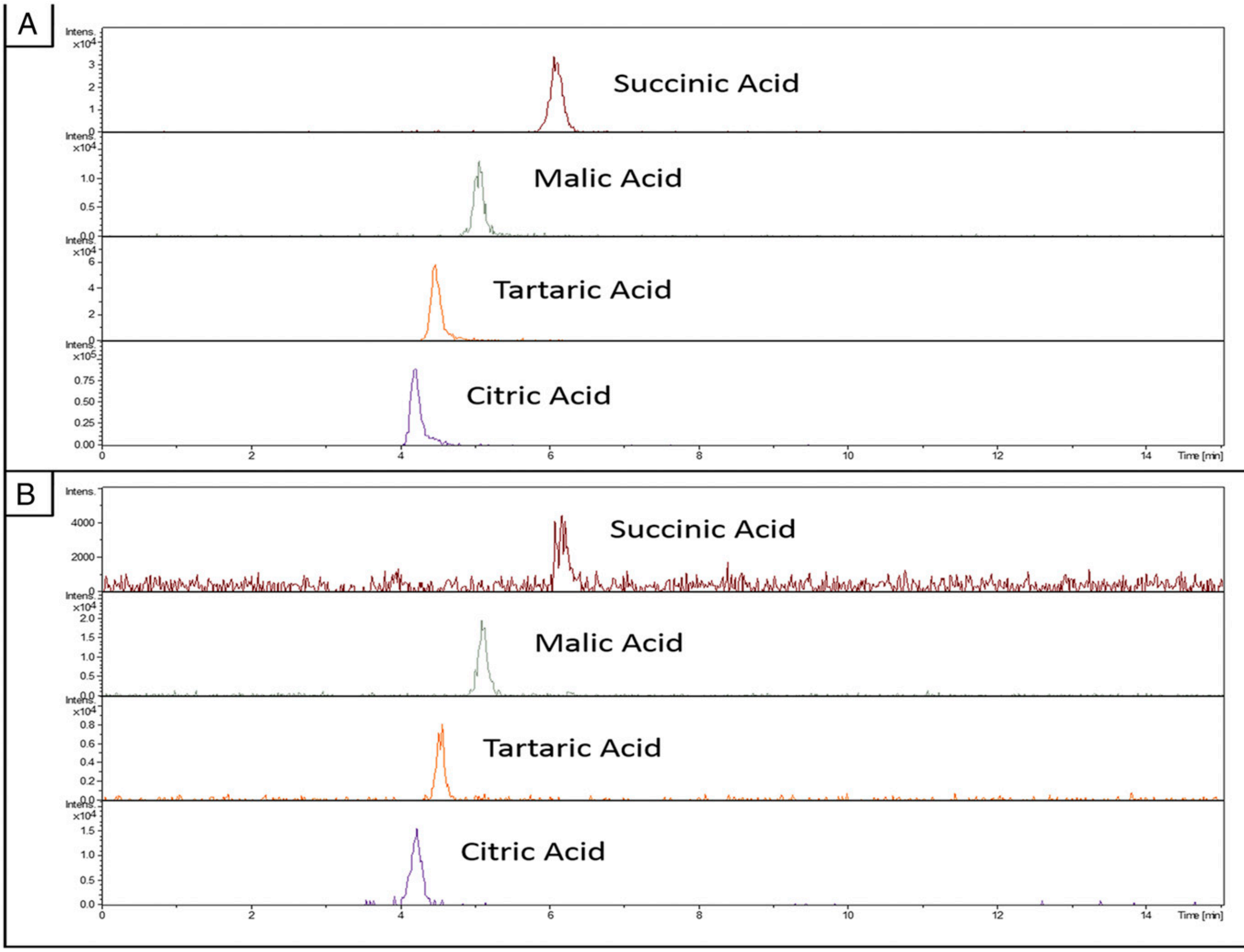

Fig. 3. Extracted ion chromatograms (±0.005-Da window) for 5 μM standard solutions (*A*), using the theoretical mass of deprotonated tartaric, malic, succinic, and citric acid, compared with jar sherd sample GG-IV-50 (*B*). All four organic acids were positively detected and quantified in this sample. Intens, intensity.

The two putative "positive" samples from the 1960s excavations at Shulaveri (one base sherd and one body sherd) were included in our analytical corpus for reanalysis with our stricter protocols and more sensitive instrumentation. Three general soil samples from Neolithic levels served as controls. Soils at both Shulaveri and Gadachrili were of the gray cinnamonic dark type.

Relative Chronology and Absolute Dating

Given our claim to have identified the earliest grape wine in the Near East (ca. 6,000–5,800 BC), it is crucial to put our findings on a solid chronological footing. Our primary reliance on short-lived botanical samples, well-defined archaeological contexts, and a Bayesian analysis of the composite data ensure that all of the analyzed samples from Shulaveris Gora and Gadachrili Gora belong to the first half of the sixth millennium BC.

Kiguradze (18) first developed a five-phase chronological model for the SSC based on the Kvemo Kartli group of sites in the Kvemo (Lower) Kartli province: Shulaveris Gora, Imeris Gora, and Khramis Didi Gora. His chronology of the relative phasing of the sites was anchored by 10 radiocarbon dates, which were carried out in the early days of the technique's development by Soviet laboratories (24). Renewed excavations at Gadachrili Gora in the same region provided an additional three calibrated dates to the corpus (21), and the 2016 excavation of Gadachrili and Shulaveris Gora added another nine calibrated dates (Datasets S2 and S3).

Even though different laboratories carried out the 22 analyses with different levels of precision and calibration, most of the dates approximated Kiguradze's original phasing and dating. A Bayesian analysis (25) of the determinations enabled Kiguradze's dates to be recalibrated with the most recent 2016 dates using OxCal v. 4. 3.2 and IntCal 13 (26–28), as shown in composite *SI Appendix*, Fig. S10 and Dataset S2. This analysis suggests that Kiguradze's fivefold model should be expanded to six phases, including an earlier phase 1 extending back into the seventh millennium BC, which is consistent with radiocarbon dates from Azerbaijan (29). Phase 1's upper limit remains to be defined by additional radiocarbon determinations.

Chemical Results

After sample extraction, ancient organic compounds were identified by a combination of chemical techniques, including Fourier-transform infrared spectrometry (FT-IR), gas chromatography-mass spectrometry (GC-MS), and liquid chromatography linear ion trap/orbitrap mass spectrometry (LC-MS-MS) (*SI Appendix*).

Our previous FT-IR results for base sherds SG-16a and SG-782 from the excavations at Shulaveris Gora in the 1960s had been promising for the presence of tartaric acid/tartrate. In 2016,

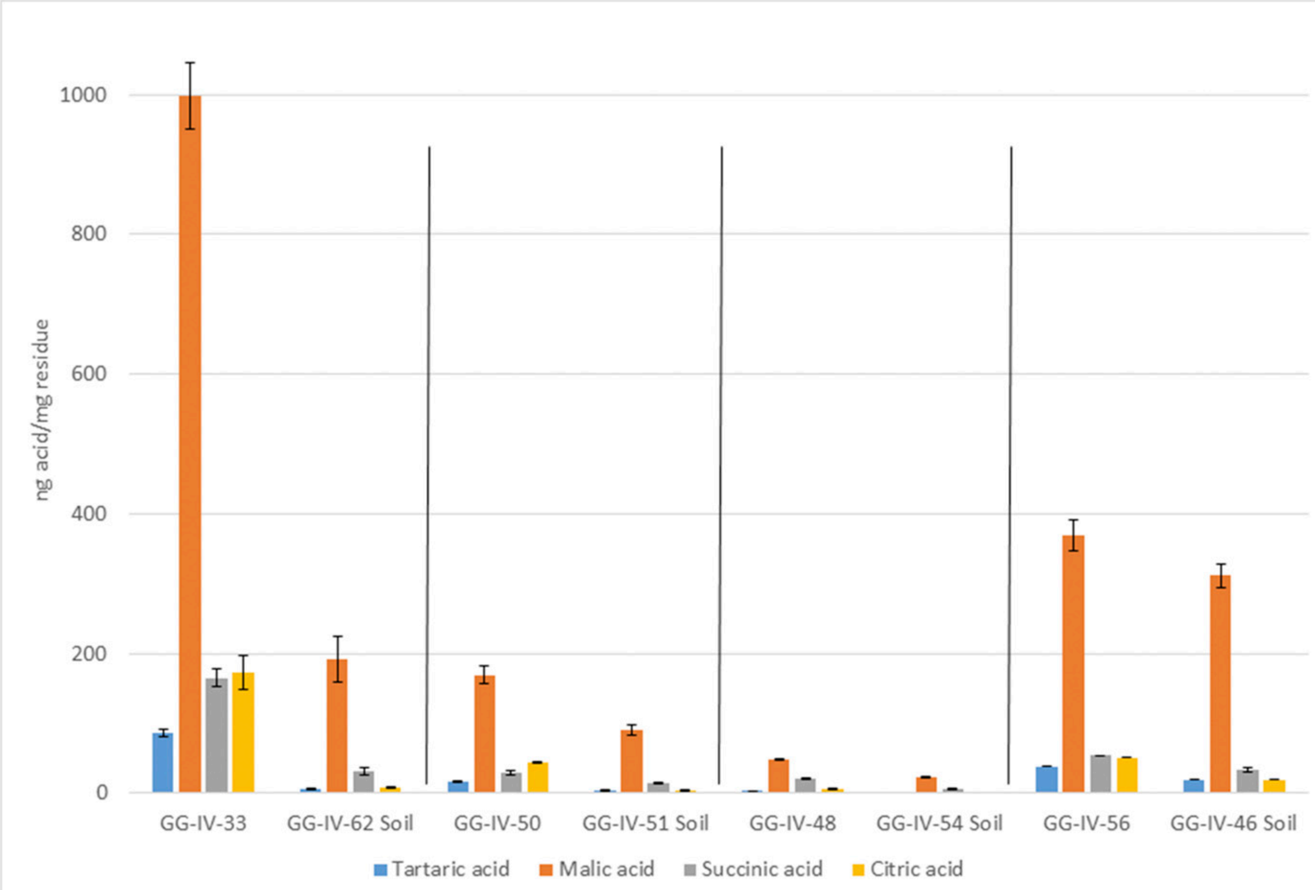

Fig. 4. Organic acid distribution for the LC-MS-MS–analyzed ancient jar base samples that were positive for tartaric acid/tartrate at Gadachrili Gora, compared with their associated soil samples. Concentrations are reported as nanograms of organic acid per milligram of extracted residue from sherd/soil material, and errors as the SD of two measurements. Note that the GG-II-9 samples (Table 1) are omitted from this graphical representation, because their data were reported as nanograms of organic acid per gram of extracted sherd/soil material.

we reran the samples, together with Neolithic soil samples from the site collected during the 2016 season. As shown in *SI Appendix*, Fig. S2, the spectrum of SG-782 had more pronounced straight-chain carbon-hydrogen stretch bond peaks at 2,920 and 2,850 cm^{-1} compared with soil, an indication that the extracted ancient sample is relatively richer in hydrocarbons. The characteristic tartaric acid doublet-carbonyl stretch bond peaks at 1,716 and 1,734 cm^{-1} were apparent for the ancient sherd, as was the hydroxyl bend at 1,452 cm^{-1}. Tartrate was identified by the carbonyl stretch bond peaks at 1,636 and 1,598 cm^{-1}, as well as the carboxylate stretch at 1,380 cm^{-1}. In contrast, the soil spectrum had very ill-defined absorptions in these regions, which might be variously interpreted.

Comparable spectra were observed for the Gadachrili sherds (e.g., Fig. 2*D*) that were positive for tartaric acid by LC-MS-MS (Table 1).

Searches of our FT-IR databases also yielded excellent statistical "matches" of the ancient spectra from both sites to those of other ancient and modern wine samples and synthetic tartaric acid and tartrate (*SI Appendix*).

Our recent GC-MS analyses were uninformative about the original contents of the jars from both sites. Fatty acids predominated in all of the samples, especially palmitic and stearic acids. The chromatogram (*SI Appendix*, Fig. S3) of jar base GG-IV-50, which was positive for tartaric acid by LC-MS-MS, is representative. Branched and unsaturated fatty acids also might occur, together with the occasional alcohol, high-numbered hydrocarbon, hopane-related triterpenoid (generic to plant cell walls), C_9 and C_{10} dioic acids (breakdown products of oleic acid), and nonspecific stigmasterol (a plant steroid). Contaminants, such as phthalate (a plasticizer ingredient of the bags in which the sherds were stored) and behenic acid (used in hand moisturizers), were ever-present.

A comparison of the chromatogram of the ancient sherd (*SI Appendix*, Fig. S4) with that of its associated soil sample (GG-IV-51) shows that the soil is richer in organics, especially high-numbered hydrocarbons (C_{27}–C_{33}) at retention times exceeding 20 min. The soil compounds are likely of modern origin. Fatty acids and n-alkanes occur widely in plants and animals, and are produced by microorganisms; they are not definitive for a grape-derived product.

The LC-MS-MS analyses proved to be most productive. Altogether, five base sherds from Gadachrili and three from Shulaveri were shown to be positive for tartaric acid and other organic acids (malic, succinic, and citric acid) found in grape/wine.

The presence of the four acids in the ancient samples is demonstrated by the exact correspondence of retention times for their extracted ion chromatograms with those of modern standards (Fig. 3). As seen in Fig. 4 and Table 1, the tartaric acid content of the positive sherds from Gadachrili (GG-II-9, GG-IV-33, GG-IV-48, GG-IV-50, and GG-IV-56) exceeded that of their corresponding background soil samples by 3.4- to 12.4-fold. At Shulaveri (Fig. 5), the tartaric acid level of SG-16a was 44 times that of the average of three Neolithic soil samples (SG-22,

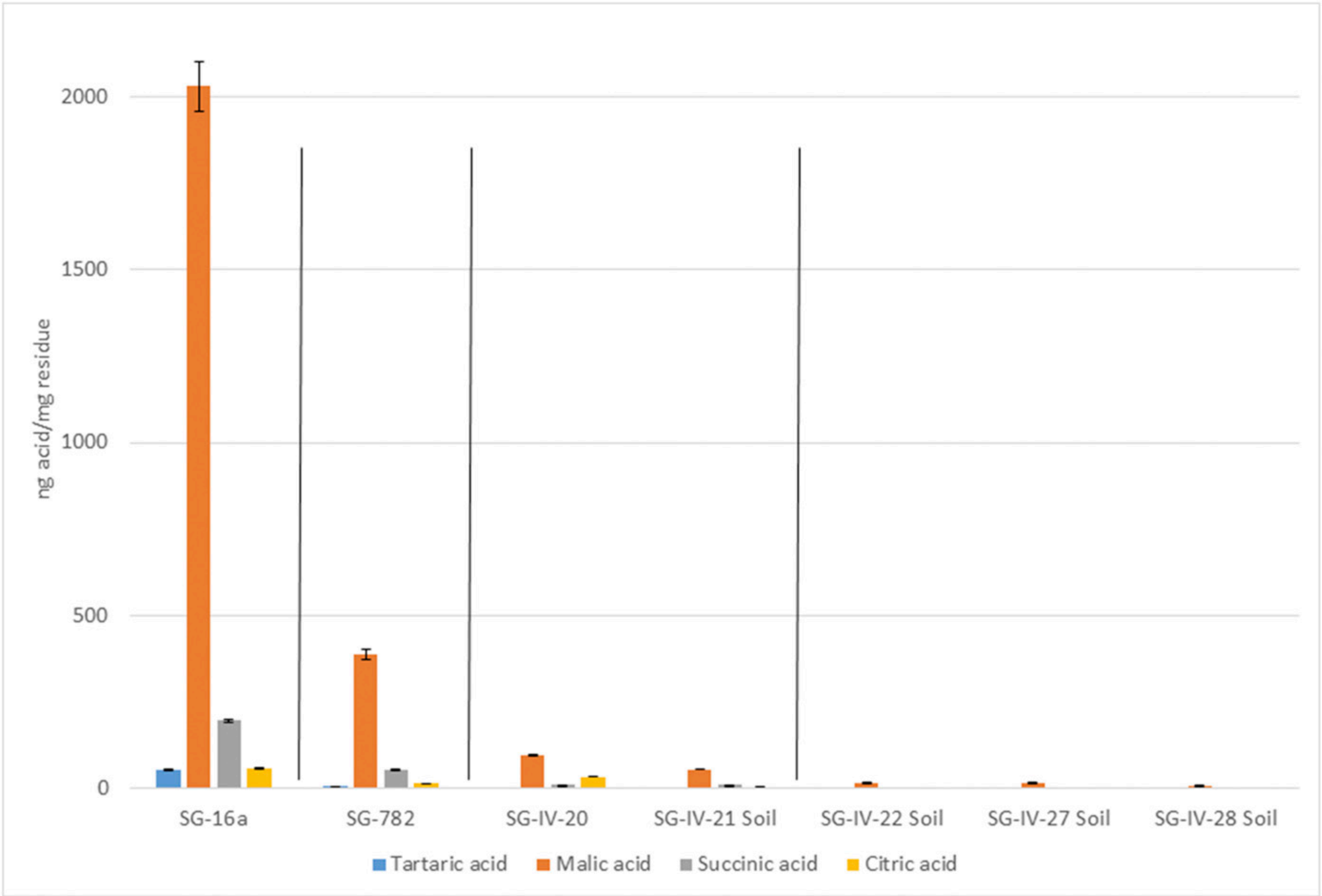

Fig. 5. Organic acid distribution for the LC-MS-MS–analyzed ancient jar base samples that were positive for tartaric acid/tartrate at Shulaveris Gora, compared with their associated soil samples. Concentrations are reported as nanograms of organic acid per milligram of extracted residue from sherd/soil material, and errors as the SD of two measurements.

SG-27, and SG-28). In contrast, the tartaric acid content of SG-IV-20 was only 1⅓ times that of its associated soil (SG-IV-21) and very low (4 ng/mg residue). Any variability in microbial soil activity (*SI Appendix*) might well lead to SG-IV-20 being classified as negative.

Negative results (not shown here) were also obtained, including 11 Gadachrili samples (five jar bases and six body sherds) with tartaric acid concentrations below those of their associated soil samples. Two other bases from this site, GG-IV-49 and GG-IV-60, did not contain any detectable levels of tartaric or the other organic acids.

Two of the bases from Shulaveris Gora (SG-16a and SG-782) were extracted as complete sherds (in toto), as was our customary procedure in the late 1990s, and were then analyzed by high-resolution LC-Orbitrap MS-MS (Table 1). The Shulaveri soils were markedly lower in abundance of the four organic acids than the soils at Gadachrili. Rainy conditions at the time of collection appear to have contributed to this difference (*SI Appendix*). High levels of tartaric acid, especially for SG-16a, provide very strong evidence for the presence of ancient grape/wine in this jar and others from Gadachrili (e.g., GG-IV-33).

Archaeobotanical Results

If grapes were exploited to make wine or used as a food source at Shulaveris Gora and Gadachrili Gora, as well as other SSC sites, then corroborative archaeobotanical evidence—seeds (pips), grapevine wood, even desiccated remains, such as skins—might be expected. Thus far, no grape pips, which have been confirmed to be Neolithic by radiocarbon dating, have been recovered from an SSC site. Those that have been excavated, including both uncarbonized and carbonized specimens, have been shown to be post-AD 1600, or "modern" in date (*SI Appendix* and Dataset S3). Only two later Middle Bronze pips were in accordance with their archaeological dating, one an uncarbonized seed with wild features per geometric morphometric analyses (ref. 24 and *SI Appendix*) from the site of Dicha Gudzuba in the port city of Anaklia and the other a carbonized pip from Pichori, north of Anaklia on the Black Sea Coast (Fig. 1), which has not yet been analyzed by geometric morphometry but appears to be of the domesticated type.

To date, the recovery of single carbonized grape pips appears to be the rule at SSC sites, including Mentesh Tepe (wild morphology; ref. 30), Göytepe (uncertain morphology; ref. 29), and Haci Elamxanli Tepe (uncertain morphology; ref. 29) in Azerbaijan. Only Aratashen in Armenia, with two pips (wild), has yielded more than one (31). Carbonized grape wood at Mentesh Tepe (30) points to grapevines growing at the site or in its environs. None of these specimens has been radiocarbon-dated, however. Possible explanations for the relative lack of grape seeds in the early Neolithic, especially given the prevalence of well-dated cereal grains from the period, are addressed below.

The archaeobotanical database for grapes at SSC sites was expanded to include evidence of pollen, starches, and phytoliths by analyzing soils and artifacts from the 2016 Gadachrili and Shulaveri excavations (*SI Appendix*). These data provide direct, contemporaneous evidence that grapes—whether wild or domesticated is not yet clear—were an important natural resource at these sites.

Grape pollen (*SI Appendix*, Fig. S7 *A* and *C*) is widespread and abundant in many of the excavated early Neolithic contexts at both sites (e.g., locus 9 at Shulaveri; *SI Appendix*, Fig. S8*A*), but is absent from the modern top soils of the sites (*SI Appendix*, Fig. S9). The nearest grapevines in the area today are several kilometers away, and it has been demonstrated that grape pollen is distributed by wind over a short distance (32, 33). It can be concluded that the pollen from the Neolithic level is ancient. Moreover, agglomerations of pollen (*SI Appendix*, Fig. S7*A*), which are best interpreted as the remains of grape flowers, imply that grapes were growing near or even at the sites in the Neolithic. Supporting evidence for these conclusions is provided by results that are consistent with grape starch (*SI Appendix*, Fig. S7*B*) and grapevine epidermis (*SI Appendix*, Fig. S7*D*).

Pollen, palynomorphs, and nonpollen microfossils were also extracted by standard palynological analysis combined with acetolysis (*SI Appendix*) from a jar body sherd (serial no. 1828) at Gadachrili. It was excavated from a sealed context (square 10, locus 7, lot 22) inside a circular Neolithic building. Its spectrum of tree, cereal, and herbaceous pollen (*SI Appendix*, Fig. S8*B*) is similar to that of a stone grinder fragment from nearby squares 2 and 3 (locus 35). Unlike the jar sherd, however, the grinder did not yield any grape starch, grapevine epidermis, or remains of fruit flies (*Drosophila melanogaster*) (*SI Appendix*, Fig. S7*E*), which are attracted to sugar and alcohol. It can be hypothesized that the jar once contained grape wine and/or beer (compare ref. 34). Grape juice readily ferments into wine (*SI Appendix*).

Based on this microbotanical evidence, two reasonable, parsimonious inferences can be made: that grapevines were growing close to the Georgian sites, possibly inside the villages, and that their fruit was used as a food source. Combined with the chemical evidence for a grape product inside several jars, which would have served well as liquid containers, grape wine was likely one of the intended products, especially in light of the "wine culture" that emerged later in this area and throughout the Near East and Egypt.

Discussion and Conclusions

Previously, the earliest evidence for grape wine in the Near East was from the early Neolithic village of Hajji Firuz Tepe in the northwestern Zagros Mountains of Iran, ca. 5,400–5,000 BC (1, 35). Six jars, two of which were analyzed and showed the presence of tartaric acid/tartrate and a tree resin, had been embedded in the earthen floor along one wall of a "kitchen" of a Neolithic mudbrick house. Each jar when full had a volume of approximately 9 L—altogether, approximately 55 L for an average household. If that amount of wine is multiplied many times over by the houses throughout the settlement, then the production level would have already been relatively large scale at this early date. Either wild grapes were plentiful in the area or the Eurasian grapevine was already being intentionally cultivated or even domesticated. Hajji Firuz lies within the ancient and modern distribution zone of the wild grape, as established by pollen cores from nearby Lake Urmia.

The Hajji Firuz jar shapes are also well suited for vinification and wine storage, implying that they are part of an earlier industrial tradition. Their narrow, high mouths could have been stoppered with clay (some possible examples with the same diameter as the mouths of the jars were found nearby) or covered.

Hajji Firuz is only approximately 500 km from Shulaveri and Gadachrili, and even closer to sites in Armenia and Azerbaijan. These sites also lie within the zone of the wild grape, as does the mountainous region of northern Mesopotamia and, farther afield, the Taurus Mountains of eastern Anatolia. Now that wine jars from as early as ca. 6,000 BC have been confirmed for Gadachrili and Shulaveri, preceding the Hajji Firuz jars by half a millennium, the question might be asked which region has priority in the discovery and dissemination of the "wine culture" and the domesticated grape. It is impossible to assign priority to any of these regions at this stage in the investigation; much more excavation and the collection of wild grapevines for DNA analysis are needed.

One disparity between the analyses of Hajji Firuz and Georgian jars is that the latter showed no signs of a tree resin or any other additive, according to the GC-MS analyses. Pine and terebinth saps were commonly added to wine throughout antiquity. They acted as antioxidants to keep the wine from going to vinegar, or barring that, to cover up offensive aromas and tastes. The tradition continues today only in Greece as retsina.

The Hajji Firuz jars were found partly buried in an earthen floor. No evidence has yet been found of how the Shulaveri and Gadachrili jars were positioned or whether they were partly or fully buried underground, as is the common practice for making so-called *qvevri* ("large jar") wine today in Georgia. The very small, flat bases of the ancient jars, often disks or low pedestals, seem inadequate to independently support a vessel full of liquid, so a case could be made for burying them. But then why even provide them with such unstable bases, unless these were decorative like the plastic decorations on some examples?

The earliest archaeological evidence for *qvevri* winemaking in Georgia is Iron Age in date, specifically the eighth to seventh centuries BC By Roman and Byzantine times, *qvevris* had become very popular throughout the Near Eastern and Mediterranean worlds; for example, excellent examples have been unearthed at Pompeii. Strangely, however, no examples of large jars buried underground like those at Areni in Armenia have been found in Georgia for the 5,000-y period from the Neolithic period to Iron Age times.

Based on ancient Egyptian frescoes, the earliest pictorial record of winemaking in the world, fermenting wine in medium-sized jars (amphoras) totally above ground was the preferred method since ca. 3,000 BC (1, 36). Given that Canaanites introduced viticulture, winemaking, and the amphora ("Canaanite jar") to Egypt, it can be assumed that they performed vinification and storage of wine, as the Phoenicians did later, in the same way.

The breakthrough came when numerous underground jars were found inside caves at Areni in a mountainous region of Armenia (37). Desiccated (uncarbonized) grapevine wood, dating to ca. 4,000 BC, together with pips and chemical evidence by LC-MS-MS of tartaric acid/tartrate and the red pigment malvidin, left no doubt that we now had partial evidence for the previously "empty" transitional period. The technology was ingenious: humans had laid out plaster floors for pressing the grapes and running the unfiltered juice into underground jars. Whether similar evidence will eventually be found in Georgia and Azerbaijan, elsewhere in the SSC area, or in the extended mountainous region remains to be seen.

The prominence of cereals in the early Neolithic SSC sites was likely due to a combination of factors. Barley and the wheats (einkorn and emmer) were domesticated very early in the Near East, perhaps by ca. 10,000 BC. They provided the all-important ingredients for beer and bread, staples that were produced in quantity in succeeding periods. The probable later domestication of the grapevine, combined with the fact that it takes a minimum of 3 y to establish a vine to bear fruit, meant that grapes would have been a rarer commodity than grain.

What makes the domesticated vine so desirable for larger-scale production is that it is hermaphroditic, with both the male and female reproductive organs contained within a single flower, where fertilization readily occurs. The wild vine is dioecious, with separate male and female plants, so that it is dependent on the wind and, to a lesser extent, insects for pollination. Only a portion of the wild vine population—the female individuals—can produce fruit, and even then, not all flowers are pollinated. Consequently, wild vines produce far less fruit than domesticated vines.

Wine making also does not make direct use of the seeds, as do beer making and bread making. Because of their bitterness, pips were usually considered waste to be discarded. In contrast, whole, unprocessed cereal grains in a bread or beer are not necessarily detrimental to the end product, and might even be considered to provide more body and taste.

Grape pressing and winemaking were generally done near where the grapes grew in antiquity, to avoid heavy transportation and conserve space within the settlement. The dense concentration of circular buildings at Shulaveri and Gadachrili would have left little room for growing grapes. Small numbers of pips might have made their way to the bottoms of the wine jars, to be disposed of later within the settlement. To date, however, no jar with seeds has been recovered from an SSC site.

Moreover, bread making and beer making require heating installations for the best results. Simply placing a mixture of ingredients under a hot sun can work, but is less reliable and efficient. Open firings around jars for beer mashing (saccharification of grain starches into sugars for fermentation) have been excavated in proto-Dynastic Egypt, ca. 3,500 BC (2, 38). Pit-firing installations associated with flat stones for possibly drying, malting, and/or baking bread or making beer are attested as early as the Pre-Pottery Neolithic period, ca. 8,700–6,500 BC, in the Near East (39). Even earlier firing installations, associated with barley starch embedded in a basalt grinding stone, have been excavated at Ohalo II, located along the southwestern shore of the Sea of Galilee and dating to the Epipaleolithic period, 23,000 y ago (40, 41). Eurasian wild grape seeds also have been reported from this site (40). Inevitably, if the processing of cereals for bread, beer, and/or another product was done nearby, some grains might have fallen into the fire or been overheated, and thus carbonized. Spent cereal grains might also have been used as fuel.

Grape fermentation does not require a heat source; in fact, a cool environment, such as a cave or burying jars underground, is best. We can conclude that bread making/beer making and winemaking occurred in different places in ancient sites, the former of which contributed to the production of masses of carbonized grains, which are well-preserved, and the latter of which resulted in low amounts of carbonized seeds.

Cereals could be dried and stored in a settlement for easy use when needed throughout the year. Grapes could be dried as raisins, but like uncarbonized pips, they generally degraded and have disappeared from the archaeological record. Grapes also can be preserved by concentrating them down into a syrup, but if this was the intended product, then pottery vessels from the SSC sites should show signs of carbon splotches due to exposure to fire on their exteriors. None do.

These considerations lead to the conclusion that the jars excavated at Shulaveri and Gadachrili, which provide chemical and archaeobotanical evidence for grape, probably originally contained wine. If their contents were high enough in alcohol, they would have provided much more than year-round sustenance for early Neolithic inhabitants. Much like Georgia's wine culture today, wine likely also served as a medicine, social lubricant, mind-altering substance, and highly valued commodity. As such, it became the focus of religious cults, pharmacopoeias, cuisines, economies, and society in general.

This "working hypothesis" (22), while buttressed by new archaeological, chemical archaeobotanical, and climatic/environmental data, is only a beginning. We may now have evidence that at least two SSC sites in Georgia, Shulaveris Gora and Gadachrili Gora, were making grape wine as much as a half millennium earlier than Hajji Firuz Tepe in Iran. However, many other regions of the Near East, especially the broad arc of mountainous terrain bordering the Fertile Crescent on its north, remain to be investigated and studied scientifically.

Thus far, we have focused on jar residues from the Pottery Neolithic period, but a Pre-Pottery period preceded it, going back to ca. 10,000 BC. During the ensuing four millennia, the first permanent settlements, sustained by the founder crops, were established. Sites of this period are yet to be discovered and excavated in the SSC region of eastern Georgia, but they are well represented westward and southward in other mountainous regions.

With their extraordinary monumental architecture and artwork, Göbekli Tepe (42) and Nevali Çori (43) in the Taurus Mountains of southeastern Anatolia stand out among Pre-Pottery Neolithic sites. The domestication of three founder plants—einkorn wheat (44), chickpea, and bitter vetch—has been traced to this region. It has been proposed that wheat to make beer was the incentive that drew humans here and led to the grain's domestication. Fermentation might have been carried out in large limestone vats at Göbekli Tepe, which are the focus of ongoing chemical analyses (42). Stone bowls and goblets have also been excavated at the sites; as precursors of examples in pottery, and they were ideally suited for serving and drinking a fermented beverage. Chlorite, the stone they were made of, is a highly absorbent clay mineral that retains ancient organic compounds like pottery. The vessels are now being extracted and chemically analyzed (45).

But did the people of Göbekli Tepe and Nevali Çori limit their alcohol quaffing to wheat beer? Perhaps they experimented with wild Eurasian grape wine or honey mead. We hope to learn more about the beginnings of viniculture by the careful excavation of more archaeological sites, the fullest recovery of the micro and macro remains of our largely lost and destroyed past, and the application of the most exacting scientific techniques.

Finally, it should be noted that Jiahu in the Yellow Valley of China still has the distinction of having produced the earliest chemically confirmed grape wine in the world, as early as ca. 7,000 BC (46). This wine was probably made from a local, high-sugar wild species there. However, this early Neolithic fermented beverage was not purely a grape wine, like that in the South Caucasus appears to have been, but was combined with hawthorn fruit wine, rice beer, and honey mead.

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Supporting Information

Sample Preparation and Extraction

The jar sherds were first examined macroscopically and under low magnification. Soil adhering to the sherds was then physically removed, followed by light washing with distilled water. Although some sherds had a darker coloration on their interiors due to the restricted availability of oxygen inside small-mouthed jars, no visible residues were noted. Exterior reduction splotches also appeared to be due to the original firing rather than later exposure to burning. Even in the absence of visible residues, the aluminosilicate structure of pottery is ideal for absorbing and retaining ancient organic compounds, especially if they are polar (22, 47).

The interior surfaces of the sherds were then ground down to a depth of 1-2 mm with a Dremel rotary grinder with a tungsten-carbide burr, to produce a powder. To remove and discard this interior surface, as some researchers do (48), would have been largely to destroy the samples. It should also be noted that prior to any breakage, the interior of a narrow-mouthed jar is generally less exposed to ground-water contamination than its exterior.

The powdered samples were approximately divided in half for FT-IR and GC-MS analyses by our laboratory and for LC-MS-MS extractions and analyses at the Chemistry Department of Boise State University (Idaho).

To prepare the samples for FT-IR and GC-MS analyses, we extracted the powdered samples in a 1:1 chloroform/methanol solvent solution by boiling 70 mL for 30 min in borosilicate glassware, while vigorously stirring with a magnetized stirring bar to maximize sample/solvent contact. The soluble portion was decanted by pipette into beakers, and sat overnight to allow settling out of the undissolved inorganic pottery fines. The solvent had mostly evaporated by the next day, and a remaining small amount of fines, which had been suspended in the soluble portion, was visible at the bottom of the beaker. The remaining solvent was transferred to watch glasses, and evaporated down to solid residues with a yellowish-whitish hue. This extraction procedure was used only in the final phase (IV) of our investigation for the last 10 sherds and their accompanying soils. In earlier phases (I-III), we experimented with other approaches. We tried using more of the solvents (125-150 mL), boiling, and filtering out the insoluble fines. The extra glassware and increased handling for boiling and filtering, however, appeared to enhance contamination for the small residue extracts. We also tried a recommended procedure in the literature (49) by using much less of the solvents (5 mL) and small initial sample amounts (about 0.2 g), sonicating with minimal heating, and filtering. We obtained very little residue by this method, probably because of small starting amounts and poor mixing of sample and solvent.

The non-filtration method with 70 mL of boiling solvents proved best, as implied by the recovery of tartaric acid and the other organic acids of grape for 4 out of 10 samples. Only one (GG-II-9: Table 1) of 8 sherds, which had been extracted by the other methods, was positive for tartaric acid.

With starting samples of 1±0.1 g for the non-filtration method, we recovered residue extracts of 1-4 mg. The highly sensitive FT-IR, GC-MS, and LC-MS-MS analyses required smaller amounts (0.1-0.2 mg).

FT-IR Analyses, Databases, and Searches

The FT-IR data were obtained on Thermo Nicolet spectrometers at the Penn and Winterthur museums, both by diffuse-reflectance on samples either mixed with KBr (Penn) or on neat (unmixed) samples run using a diamond cell (Winterthur). The FT-IR spectra were searched for "matches" against large databases of relevant natural products and processed organic materials, synthetic compounds, modern wine samples, and "ancient wine reference samples." The latter are residues from ancient vessels which likely originally contained wine, based on strong archaeological criteria or exterior inscriptions which recorded their contents. Samples of special interest are those that provide matches to ancient and modern wine samples, to a high level of probability (90 or above on a scale of 100, according to Thermo Scientific's proprietary OMNIC algorithm). All spectra were deresolved at 4 cm^{-1} wavenumber.

The primary IR data are not presented here (except for jar base SG-782 and soil SG-IV-22 from Shulaveris Gora), because of limitations of space. Moreover, the pertinent compounds are much more exactly characterized by GC-MS and LC-MS-MS.

GC-MS Extractions and Analyses

For the liquid-injection GC-MS analyses, the extracted samples were taken up in a 1:1 mixture of chloroform and methanol and then the soluble portion evaporated to dryness and derivatized by methylation with Alltech II Me-Prep derivatization agent. The resulting mixture was heated for 1 hour at 60°C. Then, one-microliter samples were injected splitless onto a 30 m×250 μm×0.25μm film thickness HP-5MS column (5% phenyl methyl siloxane) of an Agilent HP 6890 GC, run at a 1.5 mL/min flow rate. A HP 5973 mass selective detector was used with the injector port at 325°C. The oven temperature was held at 50°C for 2 min, then programmed to increase at 10 °C/min to 325 °C where it was held for 10.5 min for a total run time of 40 min. The transfer line to the mass spectrometer was at 300°C. Mass spectra were acquired in electron ionization (EI) mode at 70 eV. Compound identification was made by retention time and mass spectrum comparison using the National Institute of Standards and Technology (NIST) 05 mass spectral library.

LC-MS-MS Extractions and Analyses

Our LC-MS-MS method has been optimized for the identification and quantitation of four organic acids: tartaric, malic, succinic, and citric acid, which were previously detected in other ancient samples and associated with grape wine (8). Accurate mass measurements are used to determine molecular formulae (usually parent mass compounds because of soft ionization methods). Due to the mass spectrometer's excellent mass accuracy, usually only one formula is possible for organic compounds ($m/z < 200$ Da, composed of C, H, N, and O). Together with chromatographic retention time and product ion spectra (MS/MS), unambiguous identification of organic acids can be accomplished. Furthermore, with very high mass accuracy and mass resolution, extracted ion chromatograms are typically very clean, which leads to greatly improved quantitation. LC-MS-MS has been applied to the study of highly complex organic samples of other kinds, including those found in meteorites (50).

In earlier phases (I-III) and for, sample analysis was carried out at the NASA Goddard Space Flight Center (Greenbelt, Maryland) using a Thermo Scientific Accela LC coupled to a LTQ (linear trap quadrupole) Orbitrap XL hybrid mass spectrometer. HPLC (high-performance liquid chromatography) separation was achieved with a Phenomenex Rezex ROA column (4.6 mm x 150 mm with SecurityGuard column) maintained at 40 °C and a flow rate of 200 μL/min. Mobile phase (A) was 0.1% formic acid and mobile phase (B) was acetonitrile. The LC separation was isocratic, 90% (A), 10% (B), for 15 min. A 10 μL sample injection was used. Full scan mass spectra in *negative ion* mode were acquired over a mass range of m/z 50 to 250. To maintain a high number of data points across chromatographic peaks, a mass resolution setting of 30,000 (at full-width-half-maximum for m/z 400) was used. Typical mass accuracy was <3 ppm error. For MS/MS measurements, parent mass selection, collision induced dissociation (CID, 28%), and fragment mass detection all occurred in the ion trap.

For the later Shulaveri and Gadachrili samples (phase IV), analysis was carried out under similar conditions using a Dionex Ultimate 3000 HPLC coupled to a Bruker maXis quadrupole time-of-flight (Q-TOF) mass spectrometer at Boise State University (Boise, Idaho). The electrospray ionization (ESI) source was operated under the following conditions: negative ion mode; nebulizer pressure: 1.2 bar; drying gas (N_2) flow rate: 8 L/min; 8 L/min; drying gas temperature: 200 °C; voltage between HV capillary and HV end-plate offset: 3800 V to 500 V; mass range was set from m/z 80 to 800; and the quadrupole ion energy was 4.0 eV. Sodium formate was used to calibrate the system in the mass range. To enhance ionization efficiency, a post-column infusion of 100% isopropyl alcohol at 33.3 μL/min was used. A 10 μL sample injection was used. Standard curves for tartaric acid, malic acid, succinic acid and citric acid were generated at concentrations of 1, 5, 10 and 50 μM. Data was analyzed using the Bruker Compass Data Analysis software package. Extracted ion chromatograms (EIC) were generated for tartaric acid, malic acid, succinic acid and citric acid using the following mass windows: 149.0092±0.005, 133.0142±0.005, 117.0193±0.005 and 191.0197±0.005, respectively.

Tartaric acid, malic acid, succinic acid, and citric acid in the sample extracts were identified by (1) correlating sample compounds with known standards at the experimentally determined chromatographic retention times; (2) comparing accurate mass measurements with theoretical exact masses for the organic acids; and (3) comparing product ion spectra (or selected fragments) with known standards when possible.

Ancient Grape Pips from Neolithic and Early Bronze Georgian Sites

The proposal that grape pips from Neolithic contexts of SSC sites were indeed Neolithic in date was advocated by Revaz Ramishvili, a prominent ampelographer at the Georgian Agricultural University, based on their morphological characteristics (51). He reported six uncarbonized pips of the "domesticated" type from Neolithic Shulaveris Gora (30). Laurent Bouby, an archaeobotanist and co-author on this paper, followed up by radiocarbon-dating one of the seeds, with funding from the larger Georgian project (17). It proved to be post-1600 A.D or "modern" (Dataset S2).

Uncarbonized grape pips from other Georgian Neolithic sites were also dated recently, including one of eight specimens from Dangreuli Gora and two from a Gudau River deposit believed to be of Neolithic date. These uncarbonized seeds were also "modern." As already indicated, one uncarbonized seed from Anaklia and another carbonized specimen from Pichori proved to be truly "ancient," having consistent archaeological and radiocarbon datings in the Middle Bronze Age. The only other carbonized seed in the corpus that was "ancient" was from Arukhlo, but rather than belonging to the Neolithic period, as its archaeological context suggested, it was radiocarbon-dated to the Iron Age.

The finding of two uncarbonized grape pips during the 2016 excavation at Gadachrili Gora highlights the problem in assuming that if a seed is excavated from a Neolithic level, it is necessarily Neolithic in date. Careful excavation of the context from which the two pips were recovered showed that they came from an animal burrow or tunnel dug down into Neolithic levels, 1.5 m below the surface. They were associated with many other seeds, including wheat and barley, both carbonized and uncarbonized. The grape seeds are currently being radiocarbon-dated; two uncarbonized pips from the 2012-13 excavation of the site (Dataset S3) proved to be "modern."

In general, it is highly improbable that uncarbonized botanical material could survive 8000-7000 years in a temperate climate, with moderate rainfall and possible exposure to groundwater, which reached a maximum ca. 4000-2000 B.C.. Archaeological contexts under low-oxygen and/or low-humidity conditions, including bogs, ice, deserts, and humanly contrived "hermetically sealed" environments such as some tombs and mummification, usually provide the best conditions for ancient organic preservation. None of these circumstances applied to the uncarbonized Georgian samples including the Anaklia pip. Judgment must similarly be reserved on the dating of pips from earlier excavations, such as Shomutepe in Azerbaijan and Chokh in Dagestan (19, 20), which were not reported as being carbonized or uncarbonized.

Ancient Climate Reconstruction for Shulaveris Gora and Gadachrili Gora

The Eurasian grape (*Vitis vinifera* L.) is adapted to temperate climates (Köppen's group C59). Based upon its modern distribution in Europe and the Mediterranean, its growth and survival is limited by (a) a 6-7 month maturation period; (b) an average annual temperature between 8°C and 20°C; (c) a Winkler index between 850° and 3000°C days, calculated by summing up the average temperature for each day, minus 10, during the growing season (52; also see Ref. 53) and excluding values less than 0; (d) an absolute minimum temperature above -15°C/-18°C in winter for well-hardened vines; and (e) sufficient water resources, exceeding 50% according to the plant's P/ET0 ratio: the annual precipitation (P) received by a rain-fed vineyard divided by its potential evapotranspiration (ET0) times 100 (as calculated by the Hargreaves and Samani method: Ref. 54). Lower levels of precipitation are tolerated in soils that allow for deep rooting and access to the water table (e.g., alluvial soils with shallow water tables).

Following this set of criteria, the modern climate for Shulaveri, Gadachrili, and other nearby SSC sites, is fully suitable for viticulture, with a mean annual temperature of about 13°C, a Winkler index of 1880-2054°C, very low risk of temperatures below -15/-18°C (about 2-3 times per century), and a P/ET0 ratio of 59% (mean of the five sites).

To determine whether similarly favorable conditions for the Eurasian grapevine prevailed during the early Neolithic period (*ca*. 6000-5000 B.C.), timberline data from a mountainous region of Abkhazia on the eastern Black Sea (55) were used to estimate paleo-temperatures for the SSC sites, about 350 km away. On the assumption that a l00-m increase in the timberline translates into an average 0.5°C temperature increase in mid-latitudes, the mean annual temperature of ancient Shulaveri and Gadachrili during the Holocene varied between 9-12°C, staying constantly above the minimum for grapevine viability except for a short period from *ca.* 7800-7300 B.C. (Fig. S5).

Mean annual temperatures during the period *ca.* 6000-5000 B.C. were within a degree of those today. Similarly, thermal resources, as expressed by the Winkler index, were in the 1738-2154°C range (Dataset S1), nearly the same as current values.

No data are available for determining whether the absolute temperatures fell below the critical threshold of -15/-18°C. However, the Greater Caucasus Mountains to the north of the Kura River basin, extending 1200 km from the Black Sea to the Caspian Sea and reaching a height of 5642 m should have shielded the Kura River basin from intrusions of Arctic and polar continental air, as it does today.

Levels of precipitation during the early Neolithic period were based on proxy sediment data from Lake Van in eastern Anatolia, about 350 km distant from SSC sites (56). Analyses of the sediments showed that the climate gradually ameliorated during the early Holocene, going from a very dry phase (Younger Dryas) at the end of the last Ice Age, *ca.* 10,900-9,700 B.C., to a relatively wet phase between *ca.* 6200-4200 B.C., reaching a pluviometric maximum from *ca.* 4000-2000 B.C., and returning thereafter to drier conditions that continue up until today.

Records of annual rainfall from 1974-2013 show that Tbilisi, which is representative of the weather at ancient Shulaveri and Gadachrili, has received on average about 42% more rain than Lake Van. Since we know that *V. vinifera* was present in the Van basin throughout the Holocene (57) and assuming a comparable precipitation difference between the SSC sites and Van in antiquity, then it is highly likely that the grapevine was growing at Shulaveri and Gadachrili *ca.* 6000-5000 B.C. If the current level of precipitation prevailed during this period, then the P/ET0 ratio for Shulaveri and Gadachrili would have been 57-61.

This scenario has now been confirmed by a new study (57) based on the sedimentary pollen profile of the Nariani wetland, about 100 km west of the SSC sites at a higher elevation (2058 mamsl). This work highlights an abrupt transition from steppic vegetation (*ca.* 10,700-8,500 B.C.) to a wet phase with forest around 7000 B.C. and continuing down to *ca.* 3000 B.C., which would have been fully suitable for viniculture.

The reconstructed ancient temperatures, precipitation levels, Winkler indices, evapotranspiration amounts, and P/ET0 ratios for Shulaveri and Gadachrili are summarized in Dataset S1. As can be seen by plotting the Winkler indices for the greater Tbilisi area (Fig. S6), the necessary environmental conditions for the Eurasian grape were met during the early Neolithic period (*ca.* 6000-5000 B.C.), as they continue to be today. Particularly noteworthy is the fact that the ancient Winkler indices for Shulaveri, Gadachrili, and other SSC sites are comparable to current values for the premium viticultural zones of Montalcino (Tuscany in central Italy) and Montpellier (Languedoc in southern France).

Archaeobotanical, Palynological, Starch, and Microfossil Analysis
Macrobotanical remains were collected by flotation in the field, and identified microscopically in the National Museum of Georgia's laboratory, using a Dino-Lite Digital Microscope, with zoom mode, at 4X-48X magnification. Mainly carbonized materials were recovered. Size and morphology were the principal criteria in comparison to our in-house reference collection.

Geometric Morphometric Analysis of Grape Pips
Grape seeds were well-discriminated as wild or domesticated by Elliptic Fourier Transform (EFT) analysis of their dorsal and lateral outlines (58, 59). Linear Discriminant Analysis (LDA) enabled direct comparison of an ancient pip with a reference collection of 4854 pips from modern wild grapevines and cultivars, originating from various areas of Europe, the Mediterranean, and the Caucasus. Leave-one-out cross-validation of the LDA results gave a 96.1% probability that a modern pip was correctly classified as wild or domesticated.

The so-called Stummer index, using a simple breadth-to-length ratio, was long used as the standard method to determine whether an ancient Eurasian grape seed was wild or domesticated. Even when many specimens from a well-stratified context are measured, however, positive assignment is uncertain.

Palynology and Acetolysis
Soils and artifacts were processed in the palynological laboratory of the Institute of Palaeobiology of the National Museum of Georgia, following standard procedures (60). Samples were first cleaned by boiling in a 10% potassium hydroxide solution for 5-10 min. Note that ancient samples need more than 3 min, the usual time for modern samples, because they have had long-term exposure to possible contaminants. After rinsing with distilled water, the material was centrifuged in heavy liquid cadmium to separate the organic material from fine mineral particles. After removing the separated organic material from the cadmium liquid, it was re-rinsed with distilled water, after which it was soaked in distilled water in a test tube (4 parts water to 1 part sample) for a minimum of 24 hrs.

The organic material was then removed from the bottom of the test tube, dried, and subjected to acetolysis (61, 62). The sample was added to a 9:1 solution of acetic anhydride and concentrated sulfuric acid, which was heated in a 90°C water bath for three min to dissolve all non-sporopollenin compounds except those of interest (starch and tissue remnants). After re-centrifugation, the sample was rinsed with acetic anhydride and dried. The resulting organic material will have been stained a brownish color. Glycerol was added to the material, and one drop of the solution was placed on a glass slide and examined at high magnification under an Olympus BX43 light microscope. Identifications of starch particles were double-checked by comparing results with those under a polarizing microscope. Additional slides were prepared if the concentration of palynomorphs was low. Photographs were obtained by the microscope's camera attachment.

Methodological Approach to Identifying an Ancient Grape Product as Wine
Tartaric acid/tartrate, together with associated organic acids (succinic, malic and citric), must first be unambiguously identified by LC-MS-MS in an ancient sample. Tartaric acid/tartrate serves as a biomarker for the Eurasian grape (*Vitis vinifera* L.) in the Near East, because it occurs

there only in this fruit at a relatively high level of 4000 mg/L (63). Other plants with high tartaric acid–e.g., hawthorn fruit and star fruit from east Asia, tamarind from the Indian sub-continent, and yellow plum from the New World—can be ruled out, because trade relations with those parts of the world did not exist in the Neolithic period.

Narrow-mouthed jars, such as those reported on here, are ideal for preserving tartaric acid/tartrate. The soluble acid will be absorbed into the pottery, depending on its porosity, and form ionic bonds with the clay, thus helping to preserve the compound. Tartaric acid also readily precipitates out of wine as the potassium bitartrate salt, which makes up part of the wine lees. In the calcareous *terra rossa* soils of the Kvemo (Lower) Kartli province of Georgia, tartaric acid also would have been readily converted to insoluble calcium tartrate, further assuring a residue accumulation and/or absorption into the pottery. These precipitates collect either as a residue on interior jar bases, which were targeted in this study, or are absorbed into the pottery fabric.

Once the Eurasian grape has been established as the source for the tartaric acid/tartrate, then several other archaeological and enological factors must be assessed, to determine whether the intended product was wine and not another grape product. A syrup, produced by heating grape juice and concentrating it down, was unlikely for the jars from Shulaveris Gora and Gadachrili Gora, because to make this product, the grape juice must be boiled down. However, no exterior carbon deposits have yet been observed on pottery from these sites. Minimally, then, the ancient jars, best suited for containing a liquid, had come in contact with grape juice. But any juice would not have remained non-alcoholic for long in the temperate climate of the Kvemo-Kartli province of Georgia, especially given the slow pressing methods used in antiquity. Grape juice naturally ferments to wine in several days, because yeast (*Saccharomyces cerevisiae*) is always present on some grape skins. These microorganisms thrive in grape juice, which is an ideal medium of water and nutrients for their multiplication, and convert the sugars in the juice into alcohol and carbon dioxide. While some vinegar for culinary purposes might have been intentionally produced, wine in quantity was needed to sustain the Near Eastern "wine culture."

The Possible Effects of Microbe Activity and Extraction Method on Soil Backgrounds

One proviso should be made vis-à-vis the soil samples serving as background controls for the extracted residues from the ancient pottery. The soil backgrounds for both the chemical and archaeobotanical results are dependent upon the specific climatic conditions--rainfall, temperature, soil type, possible groundwater movement, etc.—in antiquity as well as at the time of their collection. For example, more precipitation and higher temperatures might well result in larger microbial populations. Depending upon the production, metabolism, and interaction of numerous microorganisms--yet to be determined--more or less tartaric and other organic acids of the Eurasian grape might be detected in the soil.

Groundwater percolation, which might have affected both soils and ancient sherds, was probably minimal at Shulaveri and Gadachrili. Geomorphological evidence for water movement is lacking in the excavated areas, and a semi-arid climate has prevailed for the past 10,000 years. Anaerobic conditions underground also generally result in more consumption than production of organic acids by microorganisms (64). Since acids absorbed into a sherd are chemically bound by the ionic forces of the clay and more protected from environmental conditions, they would have been less prone to microbial attack, thereby accentuating any original differences in acid contents between sherds and soils.

The soils associated with the ancient sherds were collected under different climatic conditions. The first eight sherds (phases I and II), which were negative for tartaric acid, and soils were collected during a rainy period, whereas the final ten sherds (phases III and IV), five of which were positive for tartaric and the other organic acids (Table 1 and Figs. 4 and 5), and their soils were excavated during a dry period. The unusually wet conditions, contributing to greater microbe activity, probably account for the high ratio (approximately 1.3) of succinic to malic acid for the first group's soils, which in turn explain a similarly high ratio for its sherds (e.g., Table 1: sample no. GG-II-9, body sherd and soil). By contrast, the ratio of about 0.15 both for the sherds and soils of the final group is in keeping with the relative contents of the two acids in grape wine. A higher ratio might result from malic acid being converted to lactic acid during malolactic fermentation, but cannot explain the very high ratio of the first group. If succinic acid is to be used as a "fermentation marker" (66), then any contribution from the soil microbe activity must first be ruled out by running soil samples. The better extraction methods for the final ten sherds could also help explain why the succinic to malic acid ratios for those samples better accords with expectation.

It should also be noted that the tartaric acid and citric acid contents of all soils for Phases I-IV showed minor variations under different environmental conditions, and their ratios to malic acid were consistent for all the sherd and soil samples.

The Proto-Indo-European (PIE) Origin of Ancient and Modern Words for "Wine"

Nikolai Vavilov (67), who first advanced the hypothesis that the mountainous regions of the Near East, specifically Transcaucasia, was the "world center" of the domesticated Eurasian grape, also made a profound linguistic observation. The word for "wine" (PIE **woi-no* or **wei-no*, the asterisk indicating a reconstructed form) is shared by a host of languages, Indo-European and non-Indo-European, ancient and modern. The English word "wine," for example, clearly derives from Latin *vinum*, which also accounts for Italian *vino* and French *vin*. Old Irish *fín*, German *Wein,* and Russian *vino* (along with other Slavic forms) appear to have a more ancient pedigree.

Additionally, the same PIE root is well-documented in the dead languages of the ancient Near East, including the primary languages of Anatolia (Hattic *windu* and Hittite **wijana*), Mesopotamia (Akkadian *īnu*), the Levant (Ugaritic *yn*, proto-Semitic **wajnu*, and Early Hebrew *yayin*), Greece (Linear B *wo-no* and Homeric Greek *oînos*), and Egypt (Old Kingdom **wnš*). The equivalent in Kartvelian, a family of ancient languages in the South Caucasus and eastern Anatolia, denoted Kartvelian is **γwino*, which is still the spoken word for "wine" in modern Georgian.

Although the "homeland" of the proto-Indo-Europeans is still hotly contested, strong linguistic cases have been made for the South Caucasus and/or eastern Anatolia (67, 68**)**. The stable correspondences of "wine" and its cognates in many different language groups of Europe and the Near East might then point to the extreme antiquity of **woi-no* or **wei-no* as a "migratory term." At some very early stage in the formation of PIE, this word was transferred to other languages and adapted to the dialects developing in other regions. Moreover, the PIE word often was linked etymologically to words for "grape," "vineyard," "edible fruit" in general, and compound words such as "grape cluster" and "wine steward."

A relative chronology of when daughter languages split off from PIE can only be established imprecisely on linguistic grounds. Correspondences of words for "wine" and "grape" in ancient texts from archaeological sites, which have been dated absolutely by radiocarbon, occur as early as *ca.* 3000 B.C. In prehistoric times, inferences must be made from the mute archaeological remains. Since agriculture, metallurgy, and other crafts are well represented in the PIE vocabulary, the earliest "migrations" by agriculturalists of the South Caucasus and eastern Anatolia with these skills would have been *ca.* 5000 B.C. If this reconstruction is correct, they headed eastward toward Iran, southward to Egypt, and westward to the Balkans and Europe (69**)**. They already tended the grapevine and enjoyed its principal product, wine.

Radiocarbon Dating

Dataset S2 provides the ^{14}C (radiocarbon) ages and their calibrated dates ranges ±1σ and ±2σ (i.e., ±1σ or ±2 standard deviations, indicating that there is, respectively, a 68.2% or 95.4% probability that the true age is included within the specified limits) for grape pips from Neolithic and later Georgia. Radiocarbon ages are reported in years before present (BP), which is 1950 A.D. according to international convention (70). All calculated radiocarbon ages have been corrected for the naturally occurring fractionation of carbon isotopes, based on the standard $\delta^{13}C$ value of -25‰ for wood. Calibrated ages in calendar years have been obtained from the tables in Reference 72 using OxCal v. 4.2 (26; also see Refs. 27 and 28).

Figure S10 is based on Dataset S2. Bayesian analysis (25) was used to construct the phasing of multiple SSC sites from earliest to latest. Since the samples are from different sites, a stratigraphic approach could not be used. The temporal limits of each sequence represent minimum dates. As can be seen, the minimum dates for viniculture during the early Neolithic period in Georgia at Shulaveris Gora and Gadachrili Gora is in the first century of the 6th millennium B.C. More precisely, there is a 68.2% probability (±1σ) that the dates fall within the range of 5980 B.C.-5900 B.C. or 6020 B.C.-5890 B.C. at a 95.4% probability (±2σ). The "old wood effect" in which botanically unidentified charcoal samples might come from inner tree rings and thus be older than the archaeological context does not apply for this analysis, since all the short-lived samples are earlier than the charcoal samples (perhaps indicating that any wood was from a branch or an outer ring).

The currently available radiocarbon dates for uncarbonized and carbonized grape pips from Neolithic SSC sites are summarized in Dataset S3. It will be noted that two Gadrachili samples were not assigned a calibrated date, because they belong to the nuclear age when radiocarbon has greatly increased in the atmosphere; their percent modern carbon (pMC) is given instead. Interestingly, one of these samples (RTD-7600) was prepared using two different procedures— acid-base-acid (72, 73) and cellulose extraction—and each gave the same radiocarbon age.

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Fig. S1. Plastic decoration on the exterior of an early Neolithic jar, possibly showing a stick-figure with upraised arms beneath a grape arbor. Courtesy of National Museum of Georgia, Tbilisi, no. XIII-69, length *ca.* 16 cm. Photograph by P. E. McGovern.

Fig. S2. FT-IR spectra for Shulaveris Gora jar base SG-782 (top) and Neolithic soil SG-IV-22 (bottom).

Fig. S3. GC-MS chromatogram for jar base GG-IV-50.

Fig. S4. GC-MS chromatogram for soil GG-IV-51.

Fig. S5. Average annual temperatures for a geographic cluster of six SSC sites including Shulaveris Gora and Gadachrili Gora during the Holocene Epoch. The dark green and gray areas mark the deviation above and below the lower thermal limit (8°C) for the Eurasian grape, as shown on left ordinate axis. + = B.C.; - = A.D.

Fig. S6. Winkler index for geographic cluster of six SSC sites (circled), *ca.* 6000-5000 B.C.: 1 = Arukhlo; 2 = Shulaveris Gora; 3 = Imiris Gora; 4 = Gadachrili Gora; 5 = Dangreuli Gora; 6 = Khramis Didi-Gora.

Fig. S7. Representative agglomerations of grape pollen (*A*), a grape starch particle (*B*), grape pollen grains (*C*), grapevine epidermal cells (*D*), and *Drosophila melanogaster* hairs (*E*) from early Neolithic contexts at Gadachrili Gora (2016 season). Photomicrographs by E. Kvavadze.

Fig. S8. (*A*) Arboreal pollen spectrum from early Neolithic contexts at Shulaveri Gora (2016 season); (*B*) Arboreal pollen spectra comparing that of pottery jar no. 827 with that of a stone grinding stone fragment, both from early Neolithic contexts at Gadachrili Gora (2016 season).

Fig. S9. Arboreal pollen spectra of modern soils in the vicinity of Gadachrili Gora (2016 season).

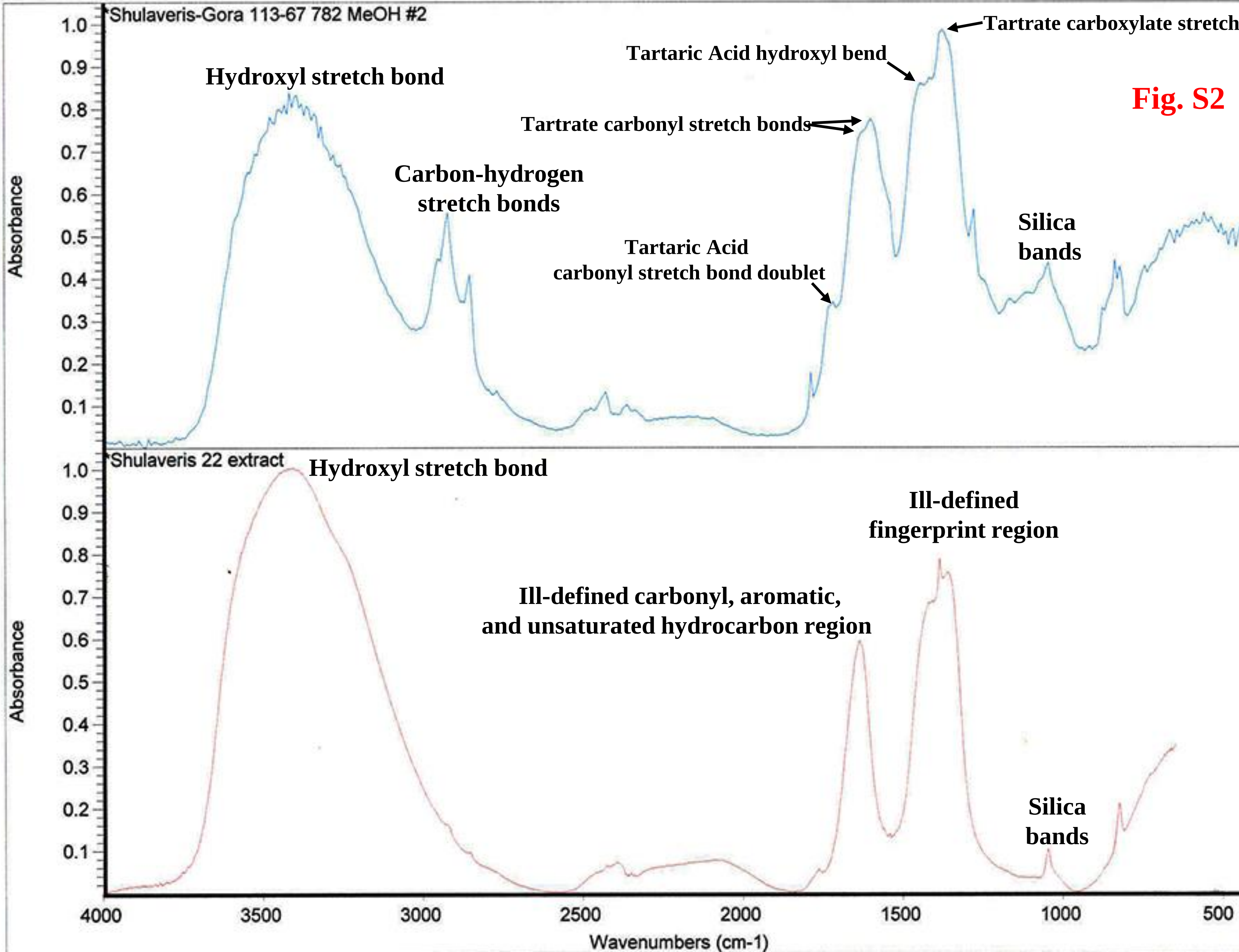
Fig. S10. Bayesian Modeling of Sequence and Phases for Radiocarbon Dates and Phasing for Kvemo-Kartli Sites, based on Dataset S2. Date ranges, shown in green, denote short-lived samples.

Dataset S1. Mean annual temperatures, Winkler indices, and other measurements during the modern period (1974-2013), as compared with the early Neolithic period (ca. 5900-5000 B.C.) for Lake Van and the geographic cluster of six SSC sites, including Shulaveris Gora and Gadachrili Gora.

Dataset S2. Radiocarbon Dates and Phasing for Early Neolithic Kvemo (Lower) Kartli Sites.

Dataset S3. Select Radiocarbon-Dated Grape Pips from Neolithic and Early Bronze Sites in Georgia.

Fig. S1


Shulaveris-Gora 113-67 782 MeOH #2
Hydroxyl stretch bond
Carbon-hydrogen stretch bonds
Tartaric Acid carbonyl stretch bond doublet
Tartrate carbonyl stretch bonds
Tartaric Acid hydroxyl bend
Tartrate carboxylate stretch
Silica bands
Fig. S2
Shulaveris 22 extract
Hydroxyl stretch bond
Ill-defined carbonyl, aromatic, and unsaturated hydrocarbon region
Ill-defined fingerprint region
Silica bands
Absorbance
Wavenumbers (cm-1)

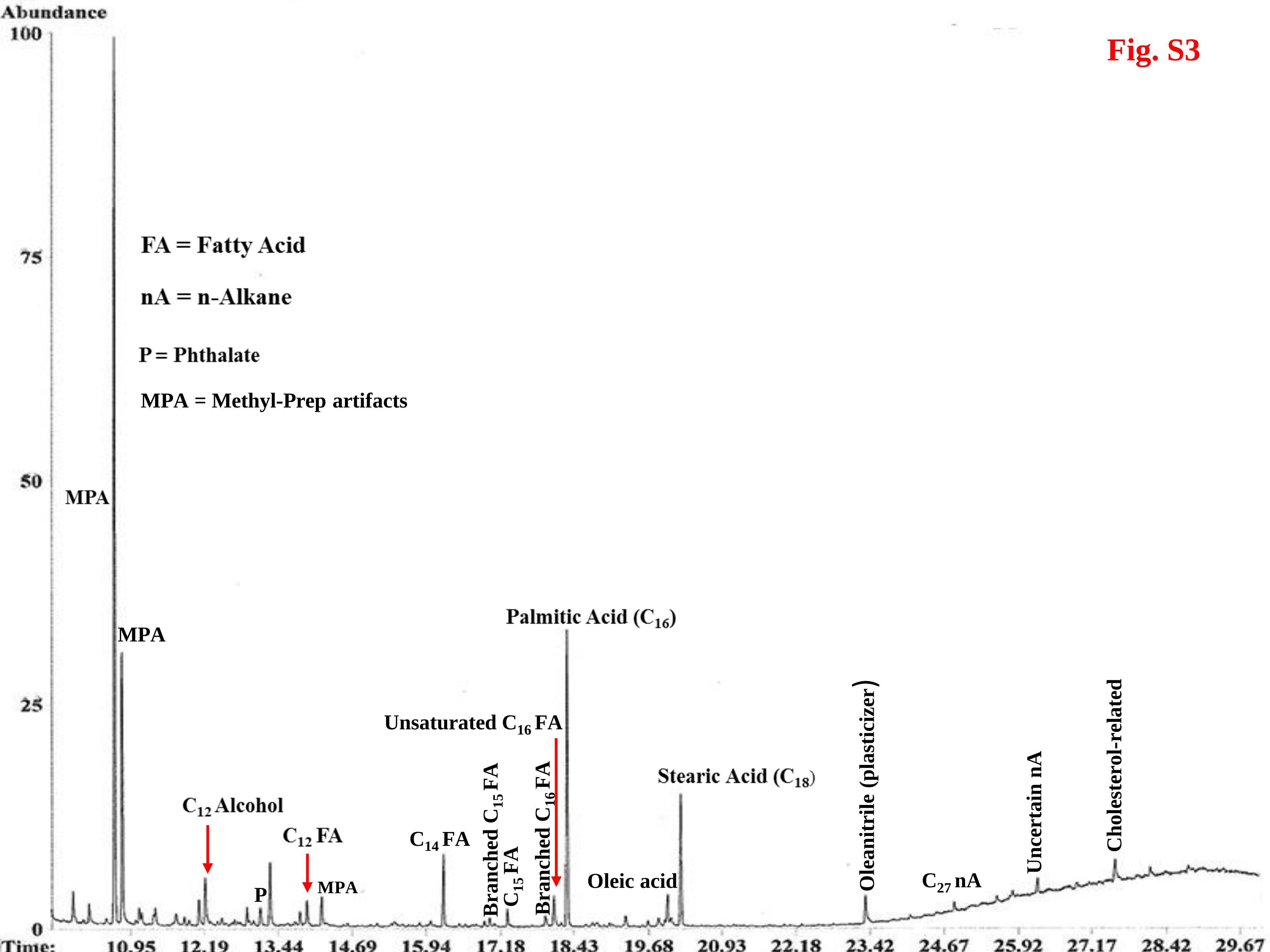


Fig. S3
Abundance
100
75
50
25
0
Time:
10.95
12.19
13.44
14.69
15.94
17.18
18.43
19.68
20.93
22.18
23.42
24.67
25.92
27.17
28.42
29.67
FA = Fatty Acid
nA = n-Alkane
P = Phthalate
MPA = Methyl-Prep artifacts
MPA
MPA
C_{12} Alcohol
P
C_{12} FA
MPA
C_{14} FA
Branched C_{15} FA
C_{15} FA
Branched C_{16} FA
Unsaturated C_{16} FA
Palmitic Acid (C_{16})
Oleic acid
Stearic Acid (C_{18})
Oleanitrile (plasticizer)
C_{27} nA
Uncertain nA
Cholesterol-related

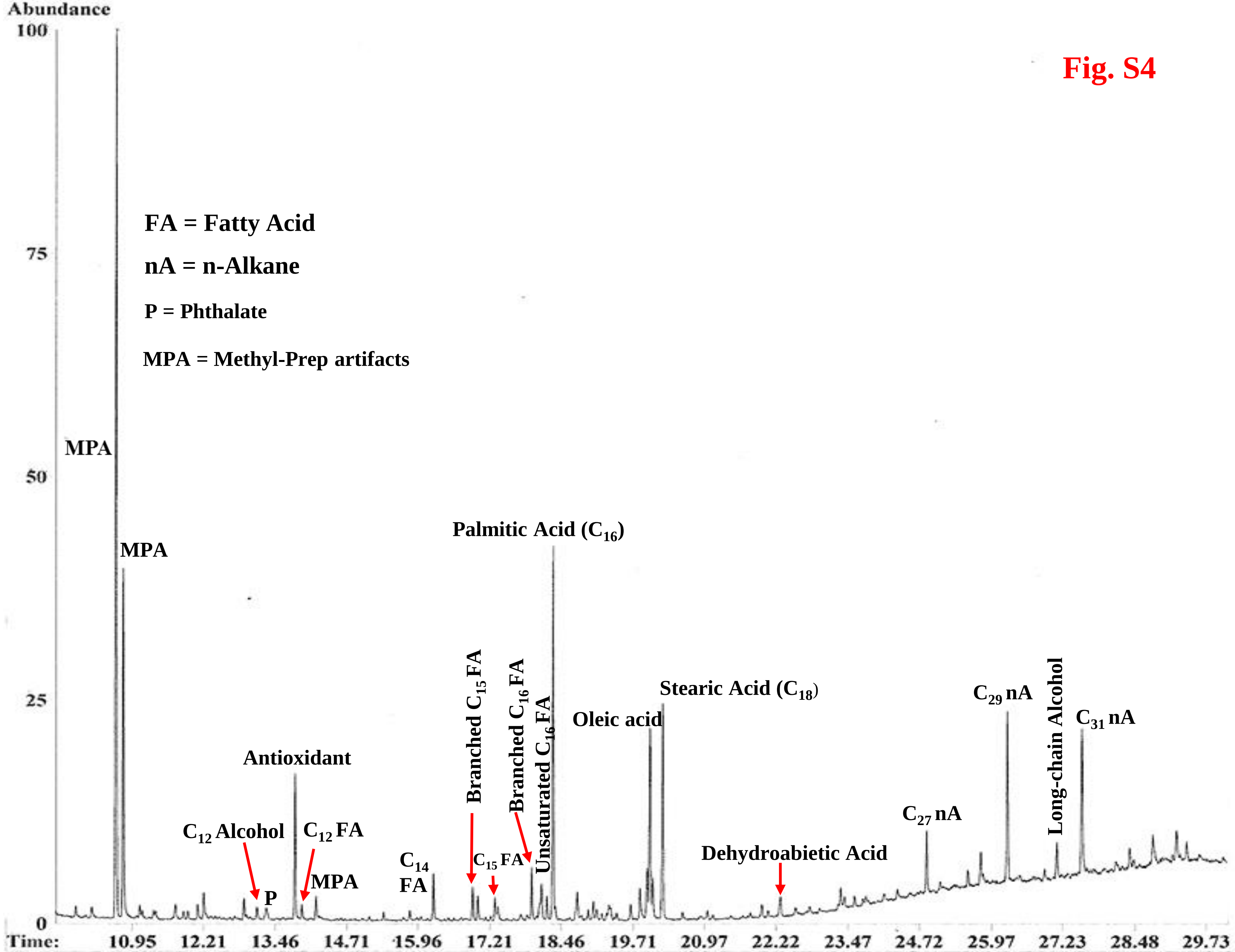
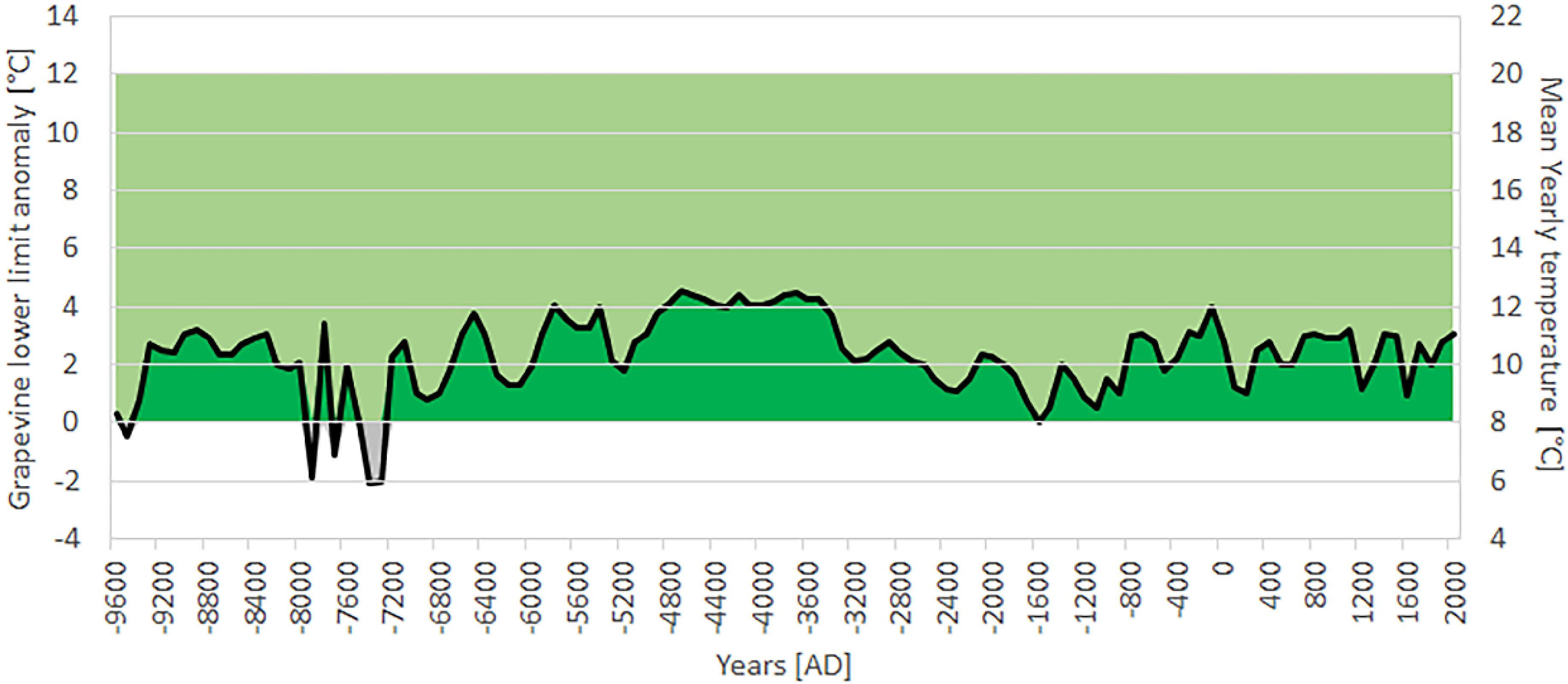


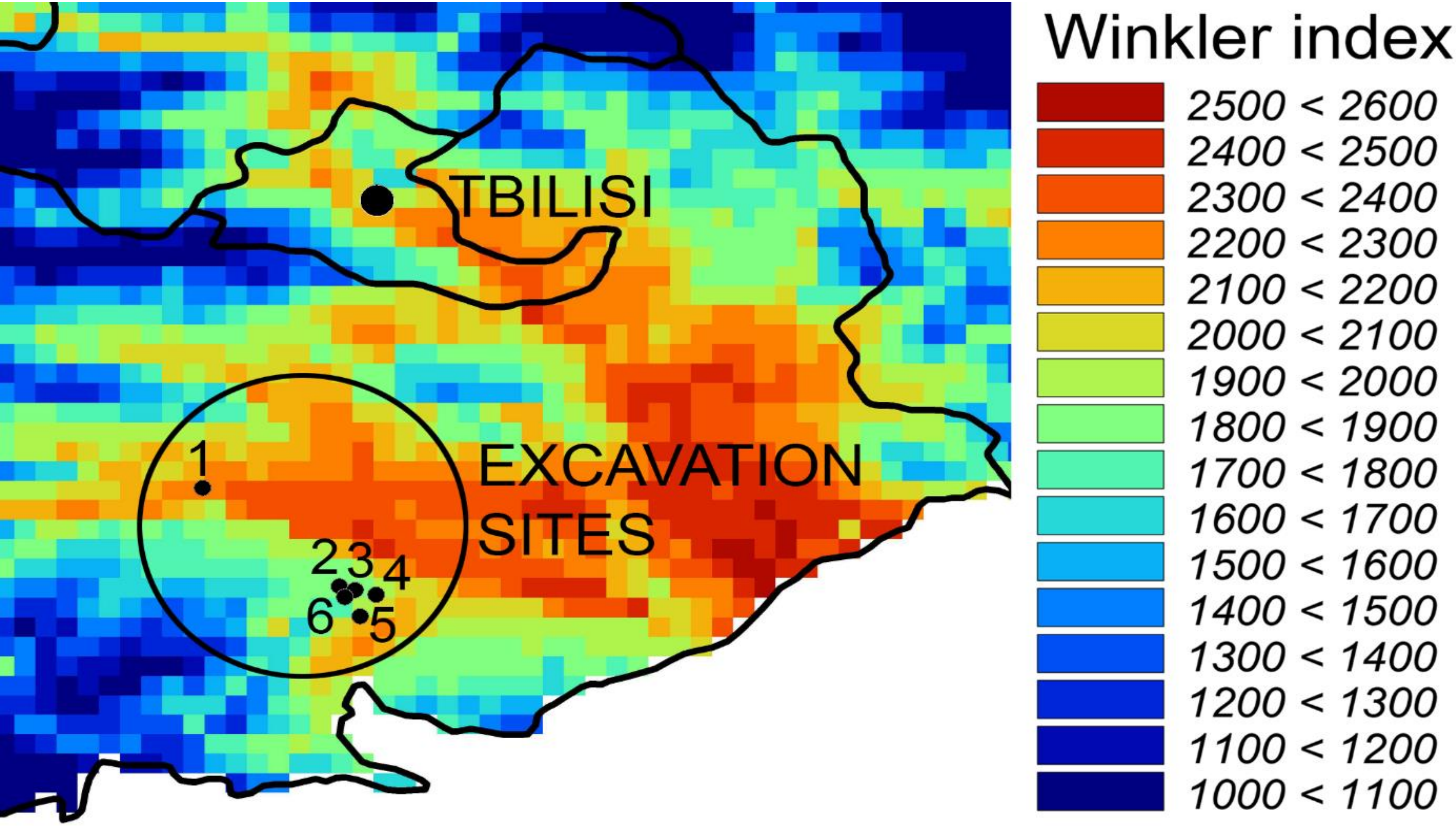
Fig. S4
Abundance
100
75
50
25
0
Time:
10.95
12.21
13.46
14.71
15.96
17.21
18.46
19.71
20.97
22.22
23.47
24.72
25.97
27.23
28.48
29.73
FA = Fatty Acid
nA = n-Alkane
P = Phthalate
MPA = Methyl-Prep artifacts
MPA
MPA
Palmitic Acid (C_{16})
Stearic Acid (C_{18})
Oleic acid
Unsaturated C_{16} FA
Branched C_{16} FA
Branched C_{15} FA
C_{15} FA
C_{14} FA
Antioxidant
C_{12} Alcohol
C_{12} FA
P
MPA
Dehydroabietic Acid
C_{27} nA
C_{29} nA
Long-chain Alcohol
C_{31} nA

Fig. S5



Grapevine lower limit anomaly [°C]
Mean Yearly temperature [°C]
Years [AD]
14
12
10
8
6
4
2
0
-2
-4
22
20
18
16
14
12
10
8
6
4
-9600
-9200
-8800
-8400
-8000
-7600
-7200
-6800
-6400
-6000
-5600
-5200
-4800
-4400
-4000
-3600
-3200
-2800
-2400
-2000
-1600
-1200
-800
-400
0
400
800
1200
1600
2000

Fig. S6



TBILISI
EXCAVATION
SITES
1
2
3
4
5
6
Winkler index
2500 < 2600
2400 < 2500
2300 < 2400
2200 < 2300
2100 < 2200
2000 < 2100
1900 < 2000
1800 < 1900
1700 < 1800
1600 < 1700
1500 < 1600
1400 < 1500
1300 < 1400
1200 < 1300
1100 < 1200
1000 < 1100

Fig. S7

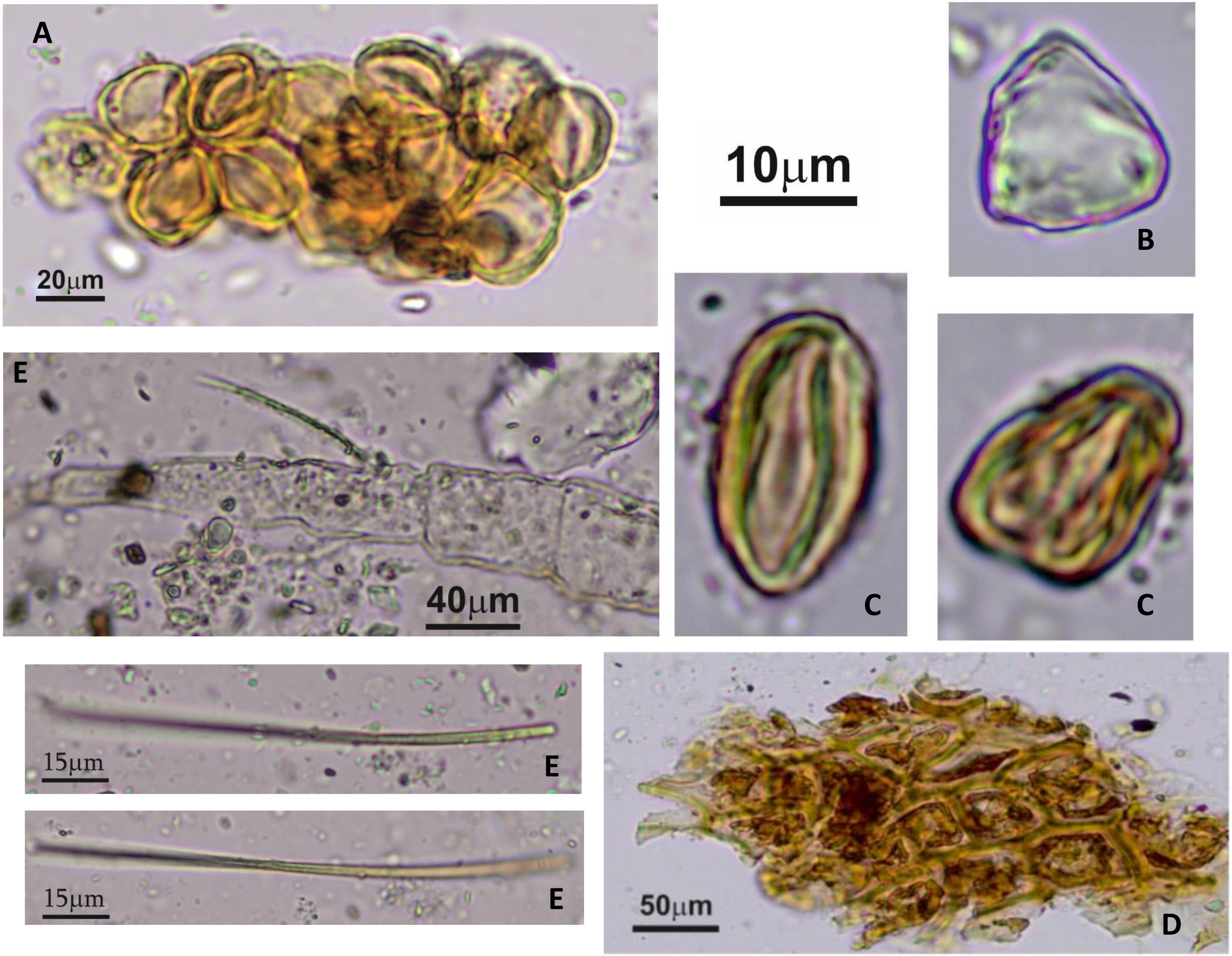


Fig. S8

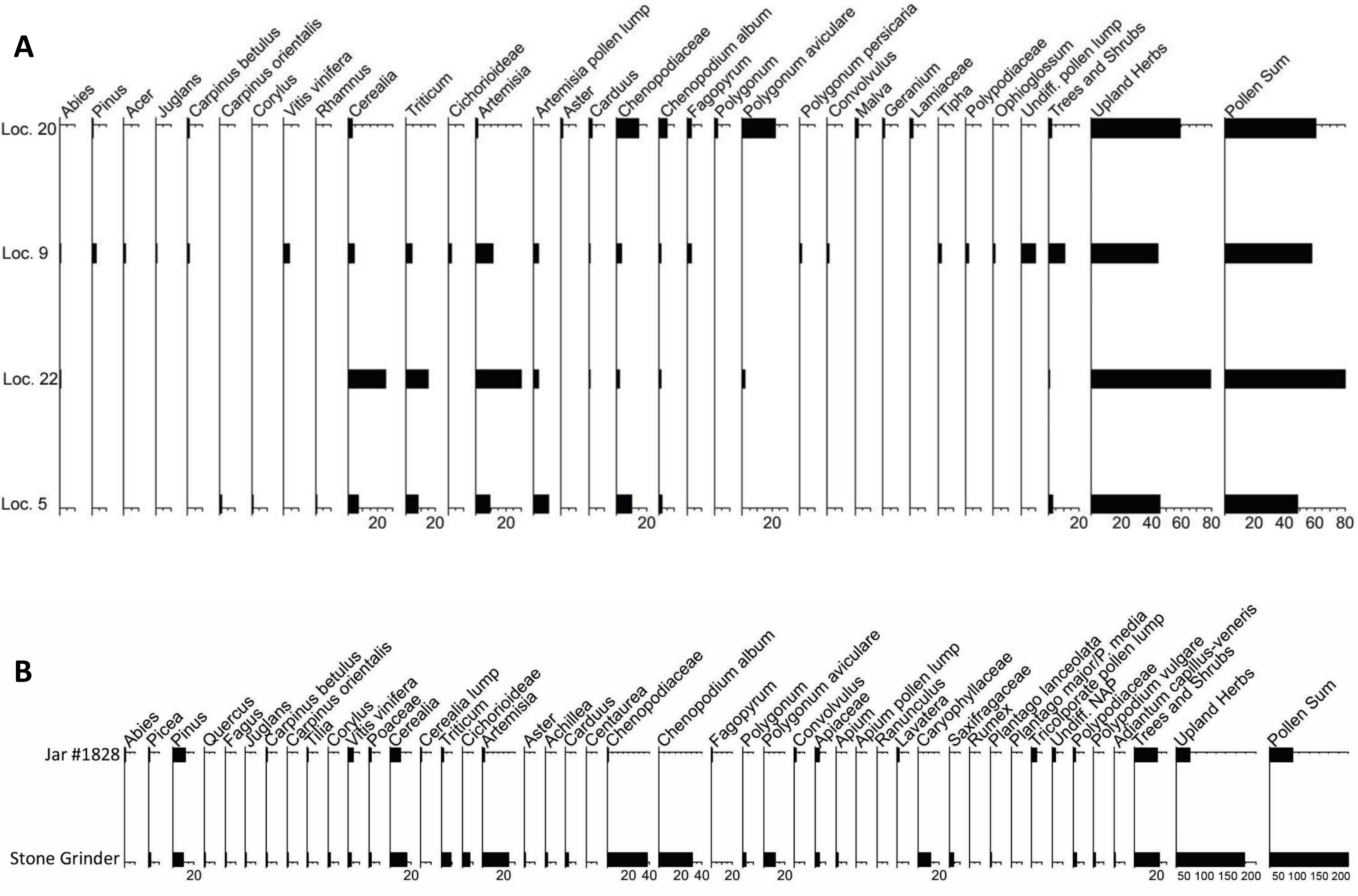
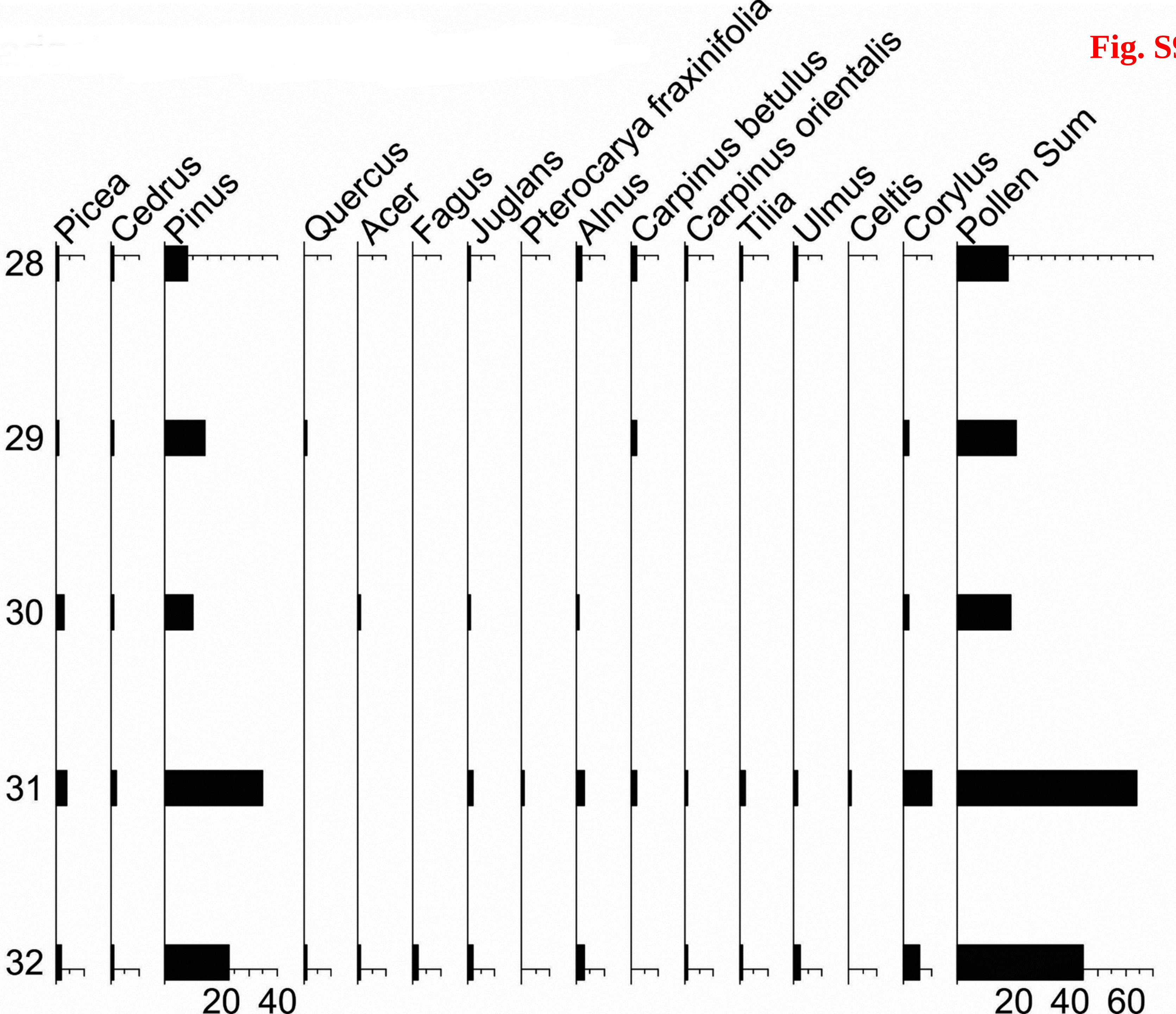
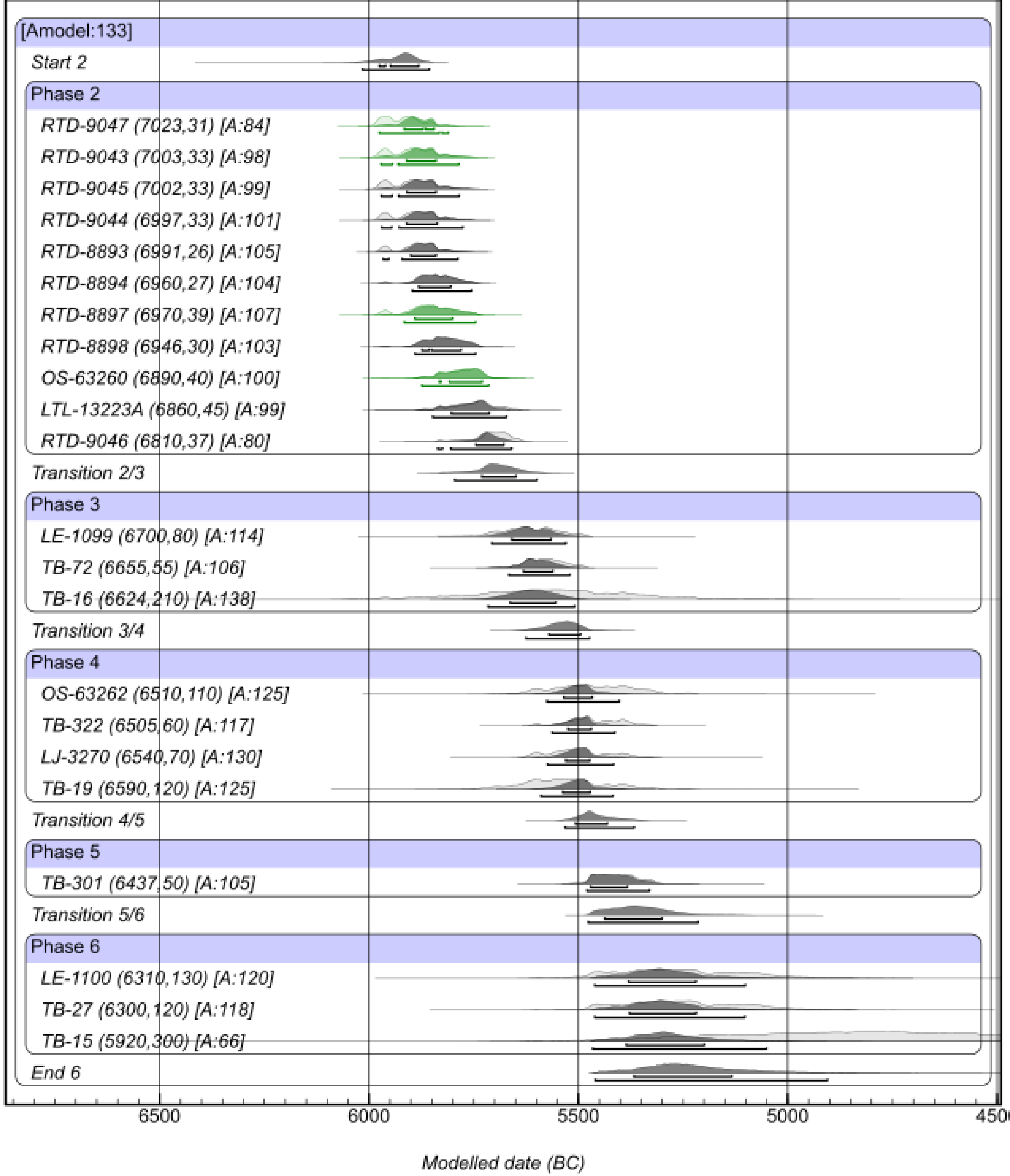

A
Abies
Pinus
Acer
Juglans
Carpinus betulus
Carpinus orientalis
Corylus
Vitis vinifera
Rhamnus
Cerealia
Triticum
Cichorioideae
Artemisia
Artemisia pollen lump
Aster
Carduus
Chenopodiaceae
Chenopodium album
Fagopyrum
Polygonum
Polygonum aviculare
Polygonum persicaria
Convolvulus
Malva
Geranium
Lamiaceae
Tipha
Polypodiaceae
Ophioglossum
Undiff. pollen lump
Trees and Shrubs
Upland Herbs
Pollen Sum
Loc. 20
Loc. 9
Loc. 22
Loc. 5
20
20
20
20
20
20
20 40 60 80
20 40 60 80
B
Abies
Picea
Pinus
Quercus
Fagus
Juglans
Carpinus betulus
Carpinus orientalis
Tilia
Corylus
Vitis vinifera
Poaceae
Cerealia
Cerealia lump
Triticum
Cichorioideae
Artemisia
Aster
Achillea
Carduus
Centaurea
Chenopodiaceae
Chenopodium album
Fagopyrum
Polygonum
Polygonum aviculare
Convolvulus
Apiaceae
Apium
Apium pollen lump
Ranunculus
Lavatera
Caryophyllaceae
Saxifragaceae
Rumex
Plantago lanceolata
Plantago major/P. media
Tricolporate pollen lump
Undiff. NAP
Polypodiaceae
Polypodium vulgare
Adiantum capillus-veneris
Trees and Shrubs
Upland Herbs
Pollen Sum
Jar #1828
Stone Grinder
20
20
20
20 40
20 40
20
20
20
20
50 100 150 200
50 100 150 200

Fig. S9



Picea
Cedrus
Pinus
Quercus
Acer
Fagus
Juglans
Pterocarya fraxinifolia
Alnus
Carpinus betulus
Carpinus orientalis
Tilia
Ulmus
Celtis
Corylus
Pollen Sum
28
29
30
31
32
20
40
20
40
60

Fig. S10



[Amodel:133]
Start 2
Phase 2
RTD-9047 (7023,31) [A:84]
RTD-9043 (7003,33) [A:98]
RTD-9045 (7002,33) [A:99]
RTD-9044 (6997,33) [A:101]
RTD-8893 (6991,26) [A:105]
RTD-8894 (6960,27) [A:104]
RTD-8897 (6970,39) [A:107]
RTD-8898 (6946,30) [A:103]
OS-63260 (6890,40) [A:100]
LTL-13223A (6860,45) [A:99]
RTD-9046 (6810,37) [A:80]
Transition 2/3
Phase 3
LE-1099 (6700,80) [A:114]
TB-72 (6655,55) [A:106]
TB-16 (6624,210) [A:138]
Transition 3/4
Phase 4
OS-63262 (6510,110) [A:125]
TB-322 (6505,60) [A:117]
LJ-3270 (6540,70) [A:130]
TB-19 (6590,120) [A:125]
Transition 4/5
Phase 5
TB-301 (6437,50) [A:105]
Transition 5/6
Phase 6
LE-1100 (6310,130) [A:120]
TB-27 (6300,120) [A:118]
TB-15 (5920,300) [A:66]
End 6
6500
6000
5500
5000
4500
Modelled date (BC)