Sherd Trace Analysis Report

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1 Abstract

During the course of this project, trace analysis was carried out on pottery sherds that were found in the ruins of the ancient city of Alalakh in Hatay Province in Southern Turkey. Archaeologists sent us two large pottery sherds and samples of dirt from the site, which we extracted samples from for analysis. Scrapings from the ceramic sherds and dirt samples were processed using organic solvents, namely methanol and dichloromethane, and sent to a mass spectrometry lab. Before results returned from the lab, we identified potential trace organic compounds based on the agricultural products and flavoring agents consumed by people in this era and cultural region.

Our results showed traces of 4-Hydroxybutanoic acid, a molecule often produced during fermentation as well as traces of glucose. During the Late Bronze Age, numerous types of fruit grew and were cultivated in the Northeastern Region of the Mediterranean where Alalakh is located, leading us to believe that our sherds are from a pot that may have contained fruit that then fermented. However, our results did not definitively show the presence of wine or beer specifically.

2 History of Alalakh

The Alalakh excavation site is located on a mound that stands nine meters tall and covers 22 hectares, making it one of the largest mounds in the area. Seventeen strata have been identified at the site, although excavations have not reached the Neolithic layers.[1] The archaeological site, known as Tell Atchana,

[1] "Tell Açana / Alalakh." Accessed November 19, 2018. http://www.tayproject.org/TAYages.fm$Retrieve?CagNo=2839&html=ages_detail_e.html.

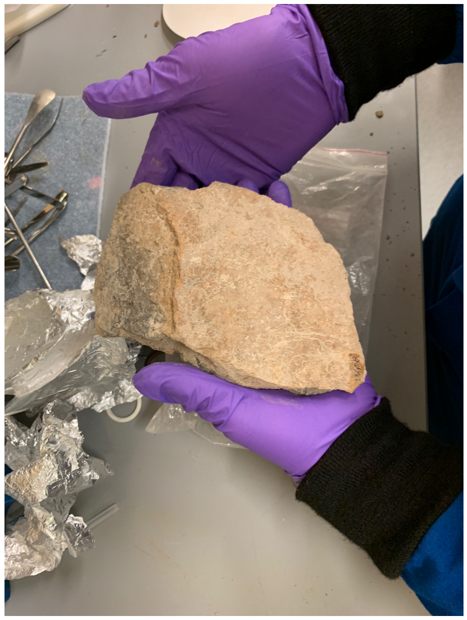

Figure 1: One of our two sherds

was first excavated by Leonard Woolley in 1936 on behalf of the Oriental Institute of the University of Chicago. Tell Atchana lies within the southernmost province of Turkey called the Hatay province. Numerous excavations have been carried out in the years since the initial 1936 dig, largely focusing on a large Late Bronze Age palace.[2]

The city of Alalakh was relatively wealthy in ancient times. The city expanded from a smaller, but still important, kingdom in the Middle Bronze Age into an even more important strategic site that sat on a nexus point of critically important trade routes between Mesopotamia, the Mediterranean, and Anatolia. During the Middle Bronze Age, we know that Alalakh was in trade relationships with Assur, Kanes, and Kultepe. By the Late Bronze Age, the surrounding region was dominated by the Hittite Empire, which maintained open trade.[3] This allowed Alalakh to become quite wealthy, allowing elites to accumulate many luxury goods such as elaborately painted pottery.[4] We know from McGovern that wine was traded as a luxury good along the Euphrates River. Kings and Queens would reserve the finest wines for themselves, importing them from other city-states and provinces through a complex network of

[2]Yener, K. Aslihan, J. David Schloen, and Amir Sumaka'i Fink. Expedition to Alalakh (Tell Atchana). N.p.: Oriental Institute, 2005.

[3]Yener, Kutlu Aslihan, ed. Tell Atchana, Ancient Alalakh. Istanbul: Koç Üniversitesi, 2010.

[4]Yener, K. Aslihan, J. David Schloen, and Amir Sumaka'i Fink. Expedition to Alalakh (Tell Atchana).N.p.: Oriental Institute, 2005.

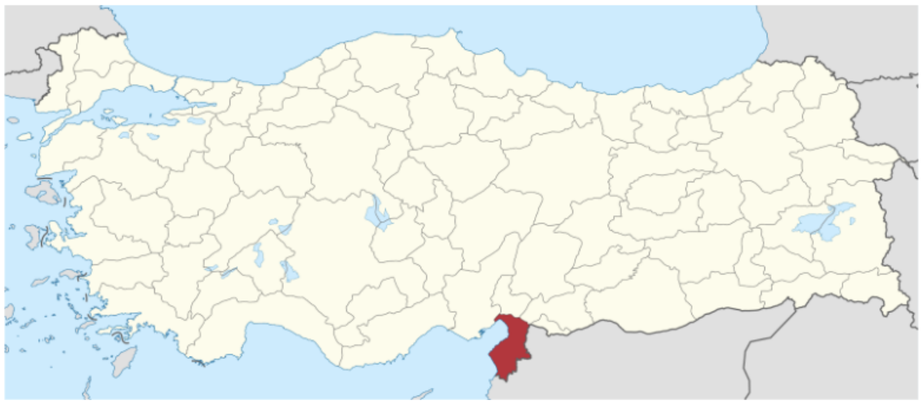

Figure 2: Location of Hatay Province within modern day Turkey

trade routes. The value of wine is demonstrated through the expensive process they went through to make it and the significant markup on vineyards over other types of agriculture.[5]

Figure 3: Tell Atchana archeological site

3 Climate and Fauna

Alalakh is located 30 miles east of the Mediterranean Sea near its northeastern corner. The Orontes River flows through the site which aided inhabitants in irrigating their fields, and left a thick layer of alluvium which further spurred agricultural growth in the area. Records of oxygen isotopes show that historically, the region of the Mediterranean in which Alalakh is located has shifted between a rainy, marshy wetland and a drier climate. The Late Bronze Age coincided with an warm, dry phase which some sources refer to as a drought,

[5]McGovern, P. (2003). Ancient Wine :The Search for the Origins of Viniculture. Princeton: Princeton University Press.

followed by an abrupt period of cooler temperatures.[6] There is no evidence that states that the Orontes River ever dried up during the period of drought.

Farmlands near rivers such as the Orontes are primed for the large scale cultivation of cereals such as wheat, since farmers could use the river to irrigate their fields and grow large swaths of crops. Specifically, archaeobotanical research evidence shows the consistent presence of free-threshing wheat and barley in the region over time. However, research shows that the warmer climate at the end of the Late Bronze Age allowed grapes and olives to grow in the region during this time period. Specifically, numerous samples of olive, grape, lentil, barley, and bitter vetch and their seeds have been found at Alalakh.[7] Texts found at Alalakh have described the site as one of the centers of olive production. Grapes were combined with olives to make olive oil as well as wine which was traded throughout the region.[8]

4 Viticulture

Wine production is believed to have developed around 6000 BCE in the area between the Black and Caspian Sea. Alalakh was one of the cities known for wine production and by the late 4th millennium BCE, wine was being traded extensively both overland and across waterways. Alalakh was significant in wine production due to its climate and geography. It had fertile soils and received plenty of rainfall, which made viticulture very popular. The growth of vines also made wine and beer production easily possible. During this time period, beer was processed through three main stages. The first stage involved using barley to prepare malt. During this stage, they soaked the barley, dried it in the sun for up to 3 weeks, and heated it in the oven. The result was then crushed and mixed with water or honey to make Sumerian Bappir. The second step involved mixing green malt, crushed bappir, and hulled barley with water to make a liquid known as Hymn to Nikasi. Finally, the third step was fermentation. During this stage, the beer produced from the first and second stages was placed in storage and transport vessels for either storage or sale and consumption. Processed and fermented beer was described and categorized according to its taste and color. They had beer types such as golden beer, dark beer, sweet dark beer, red beer, and strained beer.[9]

Beer played a very important role in the lives of the Mesopotamians; it was used in medicine, as a food ingredient, in celebrations, to conduct business, and as a substitute for water in homes where there was no water. While it is unclear how the beer technology developed, it is believed to have been developed earlier than writing.

[6] Simone Riehl, Tell Atchana, Ancient Alalakh Vol.1 The 2003 2004 Excavations Seasons (Part 2), report, ed. Kutlu Aslıhan Yener, May 2010, 124-125, accessed October 29, 2018. https://www.academia.edu/1579633/Tell_Atchana_Ancient_Alalakh_vol.1_The_2003_2004_Excavations_Seasons_Part_2_.

[7] Ibid 128.

[8] Ibid.

[9] Ibid.

5 Cultural Importance of Alcohol

Wine and beer played important economic, religious, and cultural roles in the ancient Near East. The numerous depictions of wine drinking in ancient reliefs as well as the various vessels dedicated to wine hint at its importance. Just like in modern times, drinking and feasting in the ancient Near East was a social and bonding activity, and seals have been found depicting drinking scenes. In the Royal Cemetery of Ur, several cylinder seals were also found depicting men and women drinking wine.[10] The act of feasting with others, which alcohol was an integral part of, established and reinforced social status, feelings of loyalty, and alliances.[11] The best wine was saved for the king and queen, and as a result, wine also became seen as a symbol of status.[12] Wine was a valued good that could differentiate the elite from the others.[13]

Wine and beer were both meaningful in religion and various rituals. Both were given as offerings to the gods.[14] Vessels with animal-like shapes and other elaborately decorated vases, such as the Inandik vase, were used for holding wine at ceremonies, rituals, or celebrations. In many ways, wine takes on a meaning beyond its ability to simply provide enjoyment or quench thirst. The fact that vineyards were forty times more valuable than other agricultural lands exemplifies the value wine had in ancient Mesopotamian society. Vineyards were valuable because no wine to satisfy the gods could be made without them, and the gods' favor was necessary to ensure prosperity and health.[15] The wine trade was also very profitable, and wine was imported from other cities for the elite.[16]

Like wine, beer was also valued by ancient Mesopotamian society. A hymn to the Sumerian beer goddess Ninkasa praises her for creating beer and for the joy that drinking beer brings.[17] In the Epic of Gilgamesh, as part of Enkidu's process of becoming human, he drinks seven cups of beer. To the ancient Mesopotamians, it seems that beer is more than just a dietary staple - it was something that separated humans from the beasts.[18]

[10] Vidale, Massimo. "PG 1237, Royal Cemetery of Ur: Patterns in Death." Cambridge Archaeological Journal 21, no. 3 (2011): 446.

[11] Joffe, Alexander H., Dietler, Michael, Edens, Christopher, Goody, Jack, Mazzoni, Stefania, and Peregrine, Peter N. "Alcohol and Social Complexity in Ancient Western Asia." Current Anthropology: A World Journal of the Human Sciences 39, no. 3 (1998): 303.

[12] McGovern, Patrick E. Ancient Wine :The Search for the Origins of Viniculture. Princeton: Princeton University Press, 2003.

[13] Joffe, 302.

[14] Joffe, 300.

[15] McGovern, Patrick E. Ancient Wine :The Search for the Origins of Viniculture. Princeton: Princeton University Press, 2003.

[16] Joffe, 302.

[17] Oppenheim, and Oppenheim, A. Leo. Studies Presented to A. Leo Oppenheim : June 7, 1964 [from the Workshop of the Chicago Assyrian Dictionary]. Chicago, 1964.

[18] Homan, Michael M. "Beer and Its Drinkers: An Ancient near Eastern Love Story." Near Eastern Archaeology 67, no. 2 (2004): 3.

6 Methods

Based on the methods used last year, we were able to use a more efficient process. Previously, they used 100 mL of the solvents dichloromethane and ethyl alcohol to dissolve the compounds. They then used a Rotovap to distill the solvents and compounds out of the mixture. The combination of 100 mL solvent and ethyl alcohol yielded little success when run through the mass spectrometer. The volume of solvent reduced the accuracy of the analysis, and the ethyl alcohol was not effective in isolating organic compounds. They ended up repeating the extractions with 10 mL dichloromethane and methanol. Knowing this, we imitated their new method.

Our sherd and dirt samples collected from the Hayak Excavation site in the Hatay Province, Reyhanli District, Turkey in 2015. Each sample was presumably collected with proper procedure, including using gloves to minimize contamination. Each sample was taken out of packaging, photographed, and the sherds' total weight was measured and recorded. About two to three grams of each dirt sample were measured and put into vials labeled with the identification number. Each was then mixed with 10 mL dichloromethane (DCM) to dissolve the organic residues. The resulting mixture was then sonicated for one minute to break up any large portions of dirt. It was then gravity filtered through filter paper to isolate the compounds dissolved in the DCM, and collected in another labeled vial. Next, 10 ml of methanol was added to the remaining dirt samples to dissolve organic molecules not dissolved by the DCM. The same process of sonication and gravity filtration was repeated with the methanol mixture and collected in an additional labeled vial. This process was repeated for each of the five dirt samples.

A similar process was completed with the sherds. To get a sample of the sherd, the "inside" of the sherd was scraped with a metal spatula to remove a layer of clay. This was collected in a labeled vial and put through the same extraction process as the dirt samples.

Each sample was then examined with both Liquid Chromatography Mass Spectrometry (LCMS) and Gas Chromatography Mass Spectrometry (GCMS). The LCMS did not yield any conclusive results. We believe that the solution was not concentrated enough and the machine was not sensitive enough to find any of the compounds we were looking for. LCMS is typically used to detect heavier compounds because larger compounds are much more difficult to get into a gaseous state for the GCMS. We ran a sample from Sherd #2.

7 Results

As seen in the table above, four compounds found in the sherds that did not also appear in the dirt were phthalic acid, pinacol, dianhydrosorbitol, and mannose/glucose. phthalic acid is found in beer and wine, but considering its low concentration in the sherds, it isn't possible to draw any conclusions from its presence. Pinacol was found at high concentrations in both sherds, but we were

ID	Weight	Notes
AT24759	2.6g	
AT5204	2.68g	Some rocks
AT24772	2.79g	
AT24753	2.4g	Location does not match # at top of card
Sherd #1: AT23408	2.4g	Total mass: 171.2g
Sherd #2	7.0g	Possibly base of a vase (total mass 480.2g)

Figure 4: Lab notebook observations

unable to find a likely source. Dianhydrosorbitol and mannose/glucose are of special interest to us because they were found in high concentrations in the sherds but not in the dirt. Mannose and glucose are both sugars with the same molecular formula and thus the same molecular weight, so they cannot be distinguished using mass spectrometry. All three of these molecules could have potentially come from fruits. 4-Hydroxybutanoic acid was also found, although also present in low concentrations in the dirt, and suggests the possibility of fermenting fruits as is formed in the fermentation process, although it is unclear whether the fruits were purposefully fermented or not. Lactic acid, malic acid, octadecanoic acid, azelaic acid, and glycerol were also found in the sherds and could potentially be indicative of both beer and wine; however, all of these molecules were also present in the dirt samples, so their presence doesn't necessarily indicate that the molecules came from the pottery whose sherds we tested.

8 Conclusion

Based on the results obtained from the mass spectrometer, it seems likely that there was fruit present in the pots and that the fruits may have been fermenting in the pots. While 4-Hydroxybutanoic acid suggests that there may have been fermenting fruits, it is possible that the fruits were being inadvertently fermented in the vessels or if they were purposefully being fermented for some other sort of fermented fruit product, such as date wine. While we did find some compounds consistent with the presence of wine, like malic acid and lactic acid, those compounds were also found in comparable concentrations in the dirt, so it seems unlikely that either of the sherds came from vessels containing beer or wine. Other compounds like resveratrol, oxalic acid, or tartaric acid, which would suggest the presence of wine, were not found at all in the sherds or in the dirt. Instead, we found significant amounts of glucose and other sugars, that suggest the presence of fruit. As mentioned earlier in this report, we found that this region is known to have produced grapes, olives, and dates. Therefore, the presence of fruit in these sherds seems consistent with the types of foods these people would have been storing and transporting throughout the region. It is difficult to draw any definitive conclusions from these data, especially consid-

	STD available	Origin	Area					
			MeOH			DCM		
			Sherd 1	Sherd 2	Dirt	Sherd 1	Sherd 2	Dirt
Compounds of interest								
Cinnamaldehyde		wine	NF	NF	NF	NF	NF	NF
Eugenol		wine	NF	NF	NF	NF	NF	NF
Ferulic acid		wine	NF	NF	NF	NF	NF	NF
Humulone		wine	NF	NF	NF	NF	NF	NF
Lactic acid	x	wine	5E+05	6E+05	NF	2E+05	2E+05	2E+05
Limonene		wine	NF	NF	NF	NF	NF	NF
Malic acid	x	wine	3E+03	1E+04	NF	3E+04	3E+04	3E+04
Malvidin		wine	NF	NF	NF	NF	NF	NF
Myrcene		wine	NF	NF	NF	NF	NF	NF
Octadecanoic acid		wine	3E+06	5E+07	1E+03	5E+06	8E+06	2E+07
Oxalic acid		wine	NF	NF	NF	NF	NF	NF
p-Coumaric acid		wine	NF	NF	NF	NF	NF	NF
Phtalic acid		wine	2E+03	1E+03	NF	7E+02	NF	NF
Resveratrol		wine	NF	NF	NF	NF	NF	NF
Safranal		wine	NF	NF	NF	NF	NF	NF
Syringic acid		wine	NF	NF	NF	NF	NF	NF
Tartaric acid	x	wine	NF	NF	NF	NF	NF	NF
Azelaic acid		Beer	8E+03	9E+03	NF	3E+03	1E+04	8E+03
Benzoic acid		Beer	NF	NF	NF	NF	NF	NF
Butanedioic acid		Beer	NF	NF	NF	NF	NF	NF
Glycerol	X	Beer	1E+07	6E+07	4E+03	4E+04	4E+04	4E+04
Hydrocinnamic acid		Beer	NF	NF	NF	NF	NF	NF
Myristoleic acid		Beer	NF	NF	NF	NF	NF	NF
Pimelic acid		Beer	NF	NF	NF	NF	NF	NF
Squalene		Beer	NF	NF	NF	NF	NF	NF
Suberic acid		Beer	NF	NF	NF	NF	NF	NF
Other compounds found with difference from the Dirt samples								
Pinacol?			1E+05	5E+05	NF	1E+04	5E+03	NF
4-Hydroxybutanoic acid?			2E+04	3E+04	NF	1E+03	7E+02	5E+02
Dianhydrosorbitol			3E+05	9E+05	NF	NF	NF	NF
Lauric acid			2E+05	1E+05	NF	3E+04	1E+04	2E+04
Mannose or Glucose			6E+04	4E+05	NF	NF	3E+03	NF
other isomer manose or glucose	q		1E+05	4E+05	NF	NF	8E+03	NF

Figure 5: Mass Spectrometer Results

ering the fact that we had to identify compounds we wanted to look for before testing. The absence of many of the compounds we expected to find from wine and beer suggest that these sherds probably did not come from pots containing beer or wine, but it is hard to conclusively propose an alternative because the presence of glucose alone does not mean fruit was definitely in these pots. More data would be required to come up with a more viable hypothesis. One direction for future inquiry would be a more in depth look at potential unique and identifying compounds and molecules in all of the different fruits found in the region, especially grapes, olives, and dates as this regions is known to have produced these. If the potsherds did, in fact, contain any of these fruit or some food product made from them, such as date wine (as potentially suggested by the 4-Hydroxybutanoic acid), we could check both our mass spectrometry report for any reads on masses of those fruit-unique molecules as well as look for them specifically in any additional sherds from the excavation site. Another possibility is that the soil or the pot sherds were simply contaminated somehow over the thousands of years they spend in the ground. With more information about the specific location that that these sherds were found, we might be able to tell what sorts of contamination we could expect. For example, if the pots were found among the ruins of a collapsed building, there might be certain compounds that came from the building rather than from the contents of the pots. By scraping the pots for our samples, we tried to get deeper than surface level to mitigate our chances of contamination, but a lot can happen over thousands of years.

9 Sources

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