Research Question: sophisticated wine producing technologies had developed in the Fertile Crescent of the Near East before 4000 BCE (6000 years ago)

Materials and Methods:
- **Samples:** three potsherds from what appeared to be a wine producing facility, radio-carbon dated to around 4000 BCE, were collected.
- **SPE:** free syringic acid was removed using Agilent AccuBond ODS-C18 SPE cartridges; syringic acid eluted with the 10% methanol with the 50% organic fraction.
- **MS:** during negative ion ESI-MS/MS syringic acid fragments with calculated average masses of 197.2, 182.1 and 123.1 m/z.
- **Replicates:** over time malvidin polymers, which aids its preservation in archaeological contexts. In a strong alkaline environment it reobat syringic acid.
- **LC:** newly formed syringic acid was identified following the 197+182 and 187+123 m/z transitions using an AB MDS SCIEX 4500QTrap, with a Waters Nova-Pak C18 column in an Agilent 1200 LC system.

Results:
- **Controls:** Charles Shaw cabernet sauvignon and authentic syringic acid (Sigma-Aldrich 56881) were used as positive controls; new vessel in which dromedary milk was cooked as the negative control.

Discussion:
- **Sensitivity:** additional research was done on a PerkinElmer-SCIEX API III (QqQ), with a Waters Nova-Pak C18 column in a HP 1100 LC system, and on an Agilent 6460 QqQ, with an Agilent ZORBAX Rapid Resolution High Definition Eclipse Plus C18 column in an Agilent 1290 Infinity LC system.

Conclusions:
- The results for samples B2 and C3 are interpreted as the presence of malvidin (corresponding to >30 ml red wine) in the ancient vessels.
- This in turn is interpreted as the former presence of a grape or pomegranate product.
- If the malvidin is indeed from grapes, it could be associated with red wine, grape juice, raisins or alab满满 (pomegs).
- Given the archaeological context, the cave near Areni was likely a wine production site; our analysis corroborates this hypothesis.

Bibliography:

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