

Supplementary data

1. XRF characterisation of the clay

For chemical analysis of clayey materials, we performed wavelength dispersive X-ray fluorescence analysis on a Bruker S8 Tiger instrument (Bruker, Karlsruhe, Germany) with the detection limit of 0.1 ppm – 100 % and resolution (Mn-Ka) 35eV. X-rays were generated using a 3 kW rhodium anode X-ray tube under helium. The parameters of X-ray tube are 50 kV and 60 mA.

Two Shahumyan clay samples and the potter clay body (clay/sand 2:1 and water) hereafter referred as clay body were analyzed. For each, 5g of fine-grained homogenous sample was placed on single-use sample holder with a prolene membrane.

Results are presented in Table S1. The chemical composition of both clay samples are similar. The most abundant components in the samples are SiO₂, CaO and Al₂O₃. As expected, the amount of SiO₂ in clay body is higher than in the parent raw clay powders, and more interesting the obtained SiO₂ content in clay body is in agreement with the 2:1 clay/sand ratio claimed by the potter (according to SiO₂ concentrations of Table S1, a 2:1 mixture of sand/clay gives 75 % or 72 % of SiO₂ for Sh1 or Sh2 sample respectively). It should be noted that clay samples are characterized by a rather high content of calcium oxide (18 %), however, it does not affect the quality of the ceramics, because it is in a finely dispersed states (Abramyan and Martirosyan, 1970; Mkrtychyan *et al.*, 1966).

Table S1. Chemical components of two clay powders from Shahumyan deposit (Sh1 and Sh2) and a potter clay body (clay/sand 2:1 and water) obtained by XRF.

Composition	Concentration/%		
	Sh 1	Sh 2	Clay body
SiO ₂	62.78	58.21	73.77
CaO	15.04	21.93	9.69
Al ₂ O ₃	8.75	8.18	6.57
Fe ₂ O ₃	5.42	4.98	3.95
MgO	2.94	3.23	2.53
K ₂ O	1.95	1.49	1.53
Na ₂ O	1.15	0.83	1.05
TiO ₂	0.67	0.70	0.48
MnO	0.09	0.08	<0.01

SUPPLEMENTARY DATA

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2. Complete ICP-AES data

Table S2. Concentrations (mg/L) of elements released from ceramic to model wine determined by ICP-AES. The volume of model wine was 2.8 ml. Samples were aged from 1 hour (1h) up to 16 months (16m) ; h, d, m stand for hour, day, month, respectively. Sample 0 corresponds to model wine alone (without contact with the ceramic). The ratio R corresponds to the ratio of the volume of model wine to the surface of the tablet. The colour map highlights the concentration of elements from lowest value (red) to the highest value (green).

Samples	0	1h	2h	3h	4h	5h	6h	7h	8h	9h	10h	11h	2d	4d	8d	15d	2m	4m	8m	16m
Mass of the tablets (mg)	-	748	709	683	733	669	635	691	724	600	553	718	709	606	695	692	718	658	668	668
R (m)	-	0.0086	0.0090	0.0087	0.0102	-	0.0096	0.0094	0.0090	0.0086	0.0092	0.0088	0.0092	0.0091	0.0098	0.0091	0.0087	0.0093	0.0094	0.0088
Al	0.35	4.96	10.20	12.60	14.60	10.10	16.50	10.60	11.20	9.05	11.70	15.70	21.40	24.30	1.10	0.86	5.32	2.89	0.33	0.52
B	0.52	0.16	0.68	0.71	0.37	0.70	0.17	0.25	0.54	0.32	0.36	0.41	0.36	0.52	0.40	0.48	0.00	0.44	0.30	0.59
Ba	0.01	0.23	0.24	0.20	0.24	0.15	0.14	0.18	0.19	0.24	0.20	0.25	0.31	0.19	0.07	0.13	0.15	0.15	0.21	0.03
Be	0.03	0.06	0.03	0.03	0.03	0.03	0.06	0.03	0.03	0.03	0.03	0.03	0.06	0.03	0.03	0.03	0.05	0.03	0.03	0.03
Ca	0.34	95	129	142	152	140	167	148	164	149	149	193	106	33.7	34.1	33.3	109	91.7	79.9	11.5
Cd	0.01	0.01	0.01	0.03	0.04	0.01	0.01	0.01	0.05	0.04	0.01	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.03	0.02
Co	0.03	0.02	0.03	0.03	0.03	0.03	0.02	0.03	0.03	0.03	0.03	0.03	0.02	0.03	0.03	0.03	0.02	0.03	0.03	0.03
Cr	0.01	0.07	0.12	0.11	0.11	0.09	0.10	0.10	0.11	0.08	0.10	0.13	0.11	0.14	0.09	0.36	0.76	0.86	0.59	0.50
Cu	0.01	0.02	0.04	0.04	0.05	0.04	0.08	0.05	0.04	0.08	0.05	0.24	0.05	0.09	0.01	0.02	0.02	0.01	0.01	0.01
Fe	0.01	2.27	4.35	6.03	8.01	12.40	5.86	6.81	4.89	3.71	27.10	7.08	3.60	6.68	2.18	1.02	3.31	1.37	0.02	0.02
Hg	0.03	0.01	0.03	0.03	0.03	0.03	0.01	0.03	0.03	0.03	0.03	0.03	0.01	0.03	0.03	0.03	0.01	0.03	0.03	0.03

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K	0.17	2.20	4.65	6.67	8.17	7.84	8.66	8.95	10.60	9.91	9.20	12.60	13.00	14.90	11.20	13.30	30.60	34.00	45.50	64.90
Li	0.01	0.02	0.03	0.04	0.06	0.05	0.19	0.06	0.06	0.05	0.08	0.07	0.13	0.15	0.19	0.15	0.15	0.14	0.13	0.15
Mg	0.18	7.09	12.00	14.30	12.70	12.10	12.50	12.40	13.20	12.40	13.00	16.80	32.10	38.90	9.41	4.88	4.44	2.63	0.17	0.17
Mn	0.01	0.10	0.16	0.18	0.21	0.17	0.22	0.16	0.17	0.17	0.18	0.23	0.48	0.45	0.01	0.01	0.06	0.03	0.01	0.01
Mo	0.03	0.02	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.02	0.03	0.03	0.04	0.07	0.07	0.07	0.05
Na	1.41	7.03	16.10	16.40	17.50	17.40	41.90	19.00	22.80	20.60	20.00	25.60	25.30	35.20	34.00	39.60	27.90	30.20	26.20	30.00
Ni	0.01	0.02	0.02	0.02	0.02	0.02	0.03	0.15	0.02	0.23	0.06	0.04	0.04	0.04	0.01	0.01	0.02	0.01	0.01	0.01
P	0.47	0.14	0.38	0.49	0.56	0.55	0.62	0.51	0.46	0.70	0.54	0.58	0.27	0.67	0.47	0.46	0.24	0.46	0.41	0.42
Pb	0.03	0.03	0.03	0.03	0.03	0.03	0.02	0.03	0.03	0.03	0.03	0.03	0.02	0.03	0.03	0.03	0.02	0.03	0.03	0.03
S	0.17	1.58	2.94	3.18	3.15	2.81	14.50	3.12	3.49	2.87	3.20	4.23	2.75	2.91	2.53	2.91	3.22	4.95	4.22	3.05
Sr	0.01	0.25	0.38	0.42	0.44	0.42	0.45	0.44	0.47	0.43	0.44	0.57	0.63	0.62	0.28	0.25	0.37	0.36	0.34	0.09
Ti	0.01	0.04	0.08	0.10	0.15	0.08	0.15	0.07	0.08	0.08	0.08	0.13	0.01	0.01	0.01	0.02	0.07	0.02	0.01	0.01
V	0.01	0.05	0.09	0.09	0.08	0.07	0.08	0.08	0.09	0.06	0.09	0.11	0.12	0.14	0.18	0.24	0.14	0.08	0.04	0.05
W	0.03	0.00	0.03	0.03	0.03	0.03	0.00	0.03	0.03	0.03	0.03	0.03	0.00	0.03	0.03	0.03	0.00	0.03	0.03	0.03
Zn	0.01	0.05	0.14	0.12	0.12	0.11	0.31	0.12	0.10	0.17	0.15	0.13	0.21	0.23	0.01	0.01	0.02	0.02	0.01	0.01

3. XRD diffractogram

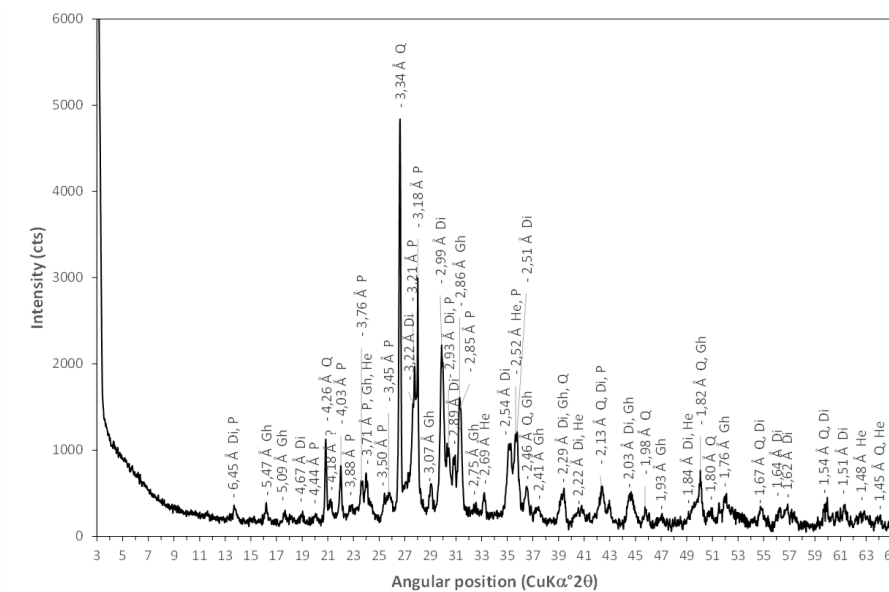


Figure S1. X-ray diffractogram of the ceramic. Minerals: (Di) Diopside, (Gh) Gehlenite, (P) Plagioclase, (Q) Quartz, (He) Hematite.

4. Relaxivity of paramagnetic aquaions

Table S3. Relaxivity of aquaions at 20 MHz, 25 °C (in water). Grey cells report non-majoritarian forms. It is worth noting that at a lower magnetic field (1 MHz or lower) or different temperature the relaxivity may strongly vary particularly for Mn²⁺ and V⁴⁺. (a) in 1M perchloric (Bertini *et al.*, 1997)

Aquaion	Fe ³⁺ (a)	Mn ³⁺	Mn ²⁺	Cr ³⁺	Cu ²⁺	Ti ³⁺	V ⁴⁺	Ni ²⁺	Fe ²⁺	V, V ²⁺ , V ³⁺	Cd ³⁺
Relaxivity (s ⁻¹ mM ⁻¹)	15	15	10	5	1	1	0.8	0.7	0.38	-	-

(Bertini *et al.*, 1997) reports that the relaxation rate of Fe³⁺ aqua ions decreases markedly above pH 3, as a result of the formation and precipitation of a variety of hydroxides.

5. Titration of ferric ions concentration in a model wine

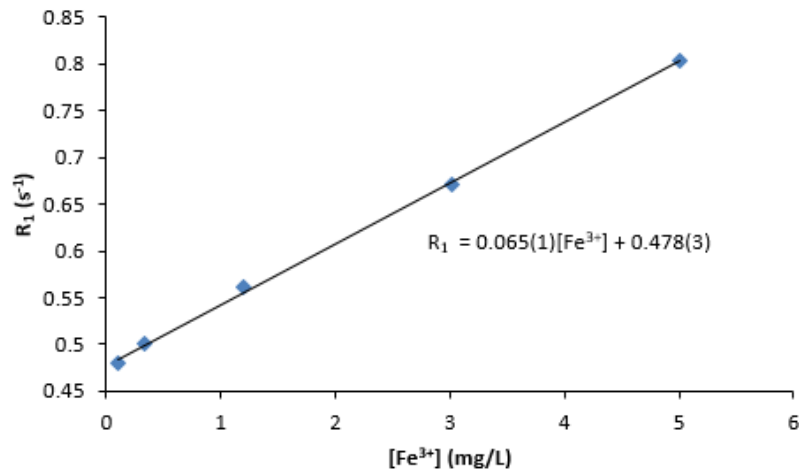


Figure S2. Titration of ferric ions concentration in a model wine. Each point was obtained by an independent dissolution of FeSO₄.7H₂O, (no dilution of a stock solution was used). Numbers in brackets are the incertitude given by the linear regression on the previous digit.

6. Ceramics covered with beeswax

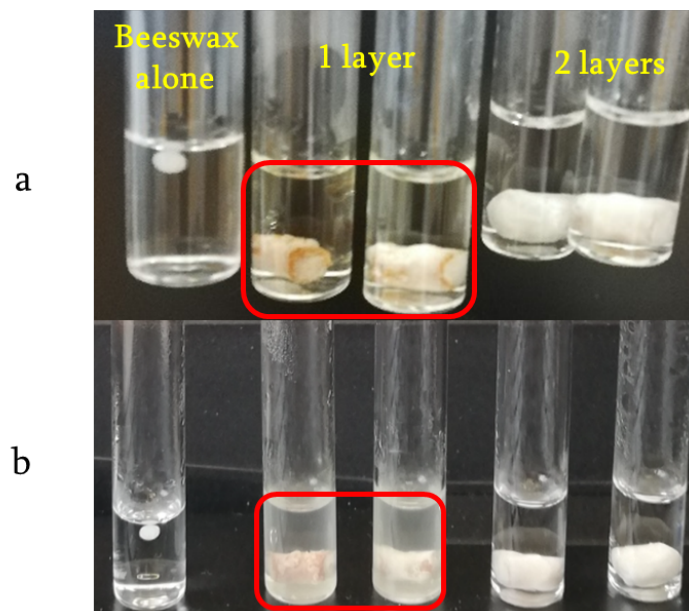


Figure S3. Model wine aged with ceramic covered beeswax. a) 3 months aged, b) 1 year aged.

During the aging of the samples for one year, changes were observed related to both the colour of the model wine and the texture of beeswax (Figure S3). After three months (Figure S3 (a)), the samples coated with one layer of beeswax turned yellow but remained transparent and the texture of beeswax was slightly damaged. It should also be noted that no yellow or white precipitate or crystals were formed, which is typically observed with uncoated samples. A year later, the model wine in contact with one layer coated ceramic become hazy and the texture of beeswax continued to deteriorate (**Figure S3(b)**). In samples coated with two layers of beeswax and beeswax alone in model wine none of these changes (crystallization, precipitation, haze formation, change in colour) were observed. This allow to conclude that the changes occur in sample with one layer of beeswax are associated with the effect of ceramics, it means that, at least for the noted period of time, relatively big amount of beeswax limited the acidic attack of model wine on the ceramic.

7. References

Abramyan, G. M., and Martirosyan, A. O. (1970). *A report on the results of exploration work carried out by the Shahumyan party at the Shahumyan clay deposit in the Artashat region of the Armenian SSR in 1969 with a calculation of reserves for 1970.* (p. 145).

Bertini, I., Donaire, A., Luchinat, C., and Rosato, A. (1997). Paramagnetic relaxation as a tool for solution structure determination: Clostridium pasteurianum ferredoxin as an example. *Proteins: Structure, Function, and Genetics*, 29(3), 348–358.
[https://doi.org/10.1002/\(SICI\)1097-0134\(199711\)29:3<348::AID-PROT8>3.0.CO;2-6](https://doi.org/10.1002/(SICI)1097-0134(199711)29:3<348::AID-PROT8>3.0.CO;2-6)

Mkrtchyan, S. S., Gabrielyan, A. A., Vardanyants, L. A., Maghakyan, I. G., and Paffenholc, K. N. (1966). *Geology of Armenian SSR: Vol. VII.* Academy of Science Armenian SSR.