GEOCHIMICA ED ARCHEOLOGIA

Lezione 13

Gianluca Sottili

AA 2021-22

Effetti dell'ambiente di conservazione sulle caratteristiche chimico-fisiche delle ceramiche

Il processo di degrado di una ceramica archeologica dipende dalle **caratteristiche chimico-fisiche del materiale costitutivo** (composizione chimica e mineralogica del corpo ceramico, porosità, metodo e condizioni di cottura), dall'**uso del manufatto** e dall'**ambiente** di conservazione (suolo, depositi vulcanici, detriti antropogenici, cavità sotterranee, acqua marina, acqua dolce).

- Ambiente lacustre
- Ambiente marino
- Suolo
- Ambiente museale (!)

L’acqua è la maggior responsabile del processo di degrado fisico e chimico.

Processi fisici legati alla presenza di acqua:

Abrasione e consunzione (nel caso di drenaggio veloce)

Cavillatura, ossia il reticolo di microfessurazioni che sono presenti nel rivestimento ceramico, in alcuni casi già presente nella fase di raffreddamento dopo la cottura, aumenta quando l’umidità determina l’espansione del corpo ceramico.

Fratturazione crioclastica, dovuta all’espansione dell’acqua liquida presente nei pori della ceramica per effetto delle gelate.

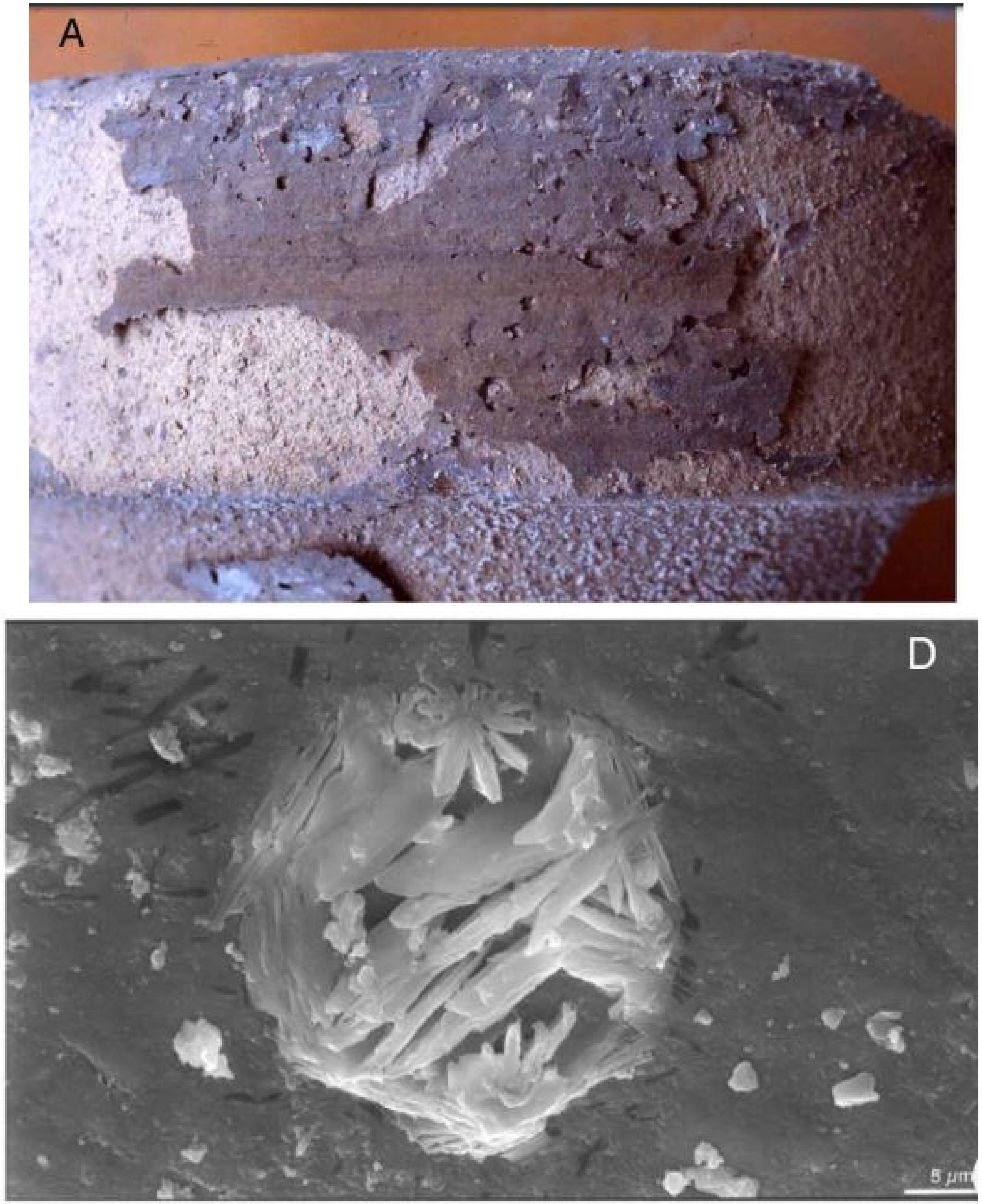
L’acqua è la maggior responsabile del processo di degrado fisico e chimico.

Processi chimici legati alla presenza di acqua:

Riargillificazione legata all’assorbimento di acqua (reidratazione) nelle frazioni meno resistenti (poco cotte) dei manufatti. Le ceramiche preistoriche, per la modalità di cottura che non determina una completa trasformazione chimica dell’argilla, sono le più suscettibili di riargillificazione.

Dissoluzione di sali presenti nella terracotta. Fenomeno che può avvenire in presenza di acqua acida circolante nel terreno, per dissoluzione e asportazione delle inclusioni calcaree. L’iridescenza negli smalti può derivare dalla dissoluzione degli elementi alcalini (sodio e potassio) dello smalto da parte dell’acqua.

Precipitazione di sali portati in soluzione dall’acqua nei pori delle terrecotte; la precipitazione e la cristallizzazione esercitano una pressione considerevole nei pori disgregando il materiale dalla superficie verso l’interno. Tra i sali solubili più comuni ci sono i cloruri, i solfati e i nitrati (cloruri spesso associati agli ambienti marini, i nitrati e i fosfati spesso derivanti dalla decomposizione di sostanze organiche). Negli ambienti ipogei si può avere la precipitazione di patine anche consistenti di carbonato di calcio. Incrostazioni brune o bruno rossastre di ferro o di manganese possono formarsi sulla superficie delle ceramiche.



Salt efflorescence on pottery in the Athenian Agora: A closer look (Paterakis & Steiger, 2015)

Lo “stato di equilibrio” di un manufatto ceramico

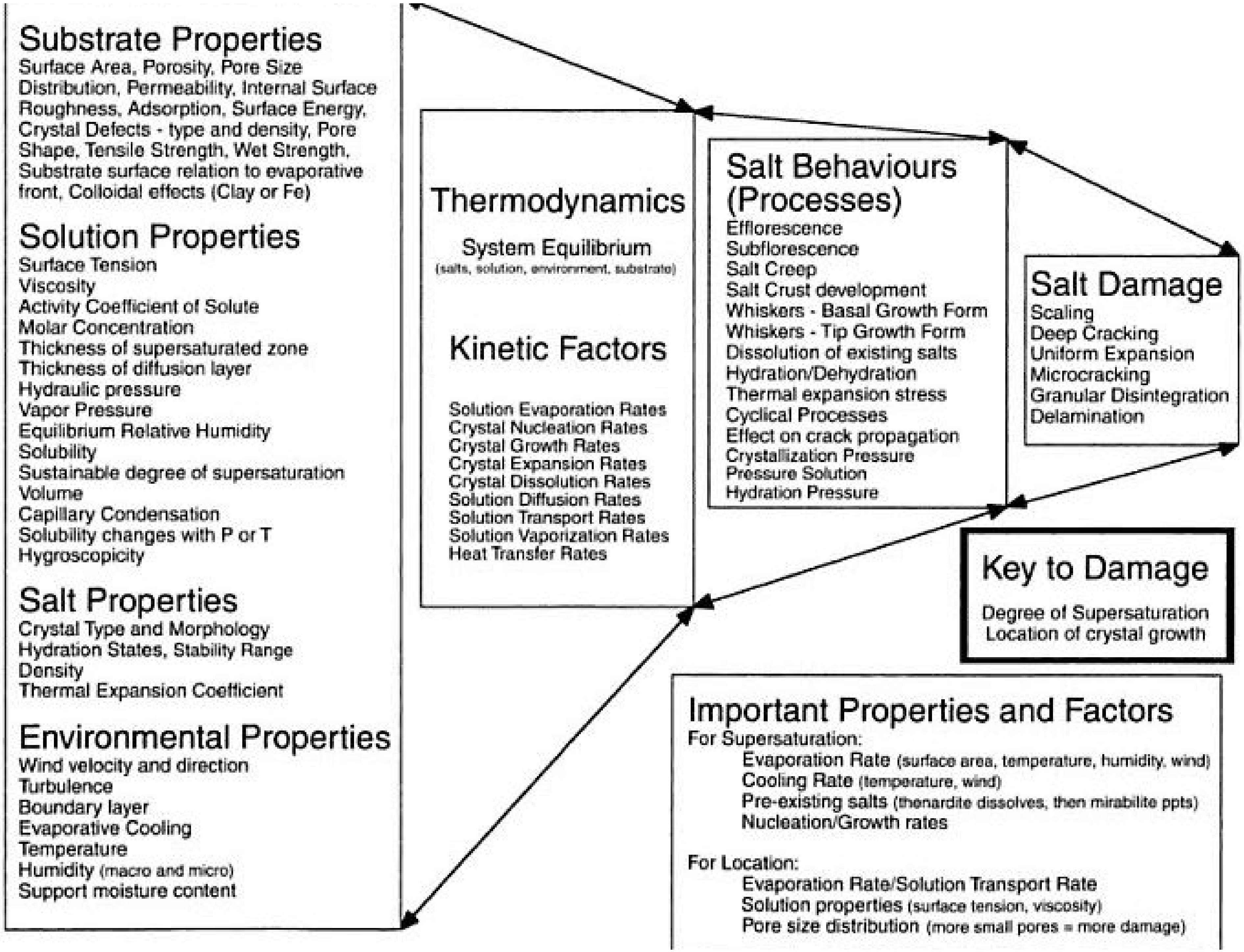
In genere, dopo una fase di rapido degrado iniziale, raggiunge quello che viene definito uno **stato di equilibrio** con l’ambiente di rinvenimento.

Le **azioni di messa in luce e recupero** determinano una brusca variazione delle condizioni chimiche e fisiche in cui si trova l’oggetto determinando delle sollecitazione che spesso ne compromettono l’integrità.

Inoltre, le possibili alterazioni chimiche e fisiche prodotte dalle operazioni di recupero possono **compromettere la possibilità di condurre alcune tipologie di ricerche archeometriche** (v. oltre).

È fondamentale che sin dall’atto del rinvenimento si operi seguendo alcune procedure (nella maggior parte dei casi anche piuttosto banali), per **impedire effetti negativi sui manufatti**.

Un **esame diagnostico preliminare** a campione aiuta a identificare il tipo di degrado presente, le sue cause e la sua estensione.


Substrate Properties
Surface Area, Porosity, Pore Size Distribution, Permeability, Internal Surface Roughness, Adsorption, Surface Energy, Crystal Defects - type and density, Pore Shape, Tensile Strength, Wet Strength, Substrate surface relation to evaporative front, Colloidal effects (Clay or Fe)
Solution Properties
Surface Tension
Viscosity
Activity Coefficient of Solute
Molar Concentration
Thickness of supersaturated zone
Thickness of diffusion layer
Hydraulic pressure
Vapor Pressure
Equilibrium Relative Humidity
Solubility
Sustainable degree of supersaturation
Volume
Capillary Condensation
Solubility changes with P or T
Hygroscopicity
Salt Properties
Crystal Type and Morphology
Hydration States, Stability Range
Density
Thermal Expansion Coefficient
Environmental Properties
Wind velocity and direction
Turbulence
Boundary layer
Evaporative Cooling
Temperature
Humidity (macro and micro)
Support moisture content
Thermodynamics
System Equilibrium
(salts, solution, environment, substrate)
Kinetic Factors
Solution Evaporation Rates
Crystal Nucleation Rates
Crystal Growth Rates
Crystal Expansion Rates
Crystal Dissolution Rates
Solution Diffusion Rates
Solution Transport Rates
Solution Vaporization Rates
Heat Transfer Rates
Salt Behaviours (Processes)
Efflorescence
Subflorescence
Salt Creep
Salt Crust development
Whiskers - Basal Growth Form
Whiskers - Tip Growth Form
Dissolution of existing salts
Hydration/Dehydration
Thermal expansion stress
Cyclical Processes
Effect on crack propagation
Crystallization Pressure
Pressure Solution
Hydration Pressure
Salt Damage
Scaling
Deep Cracking
Uniform Expansion
Microcracking
Granular Disintegration
Delamination
Key to Damage
Degree of Supersaturation
Location of crystal growth
Important Properties and Factors
For Supersaturation:
Evaporation Rate (surface area, temperature, humidity, wind)
Cooling Rate (temperature, wind)
Pre-existing salts (thenardite dissolves, then mirabilite ppts)
Nucleation/Growth rates
For Location:
Evaporation Rate/Solution Transport Rate
Solution properties (surface tension, viscosity)
Pore size distribution (more small pores = more damage)

Minerale	Composizione
Gesso (Gypsum)	$CaSO_4.2H_2O$
Alite (Halite)	$NaCl$
Epsomite (Sale di Epsom)	$MgSO_4.7H_2O$
Esaedrite (Hexahydrite)	$Na_2SO_4.6H_2O$
Mirabilite	$Na_2SO_4.10H_2O$
Blödite (Bloedite)	$Na_2SO_4.MgSO_4.4H_2O$
Celestina o Celestite	$SrSO_4$

archaeometry

Archaeometry **53**, 4 (2011) 809–829 doi: 10.1111/j.1475-4754.2010.00571.x

ALTERATION PROCESSES OF POTTERY IN LAGOON-LIKE ENVIRONMENTS*

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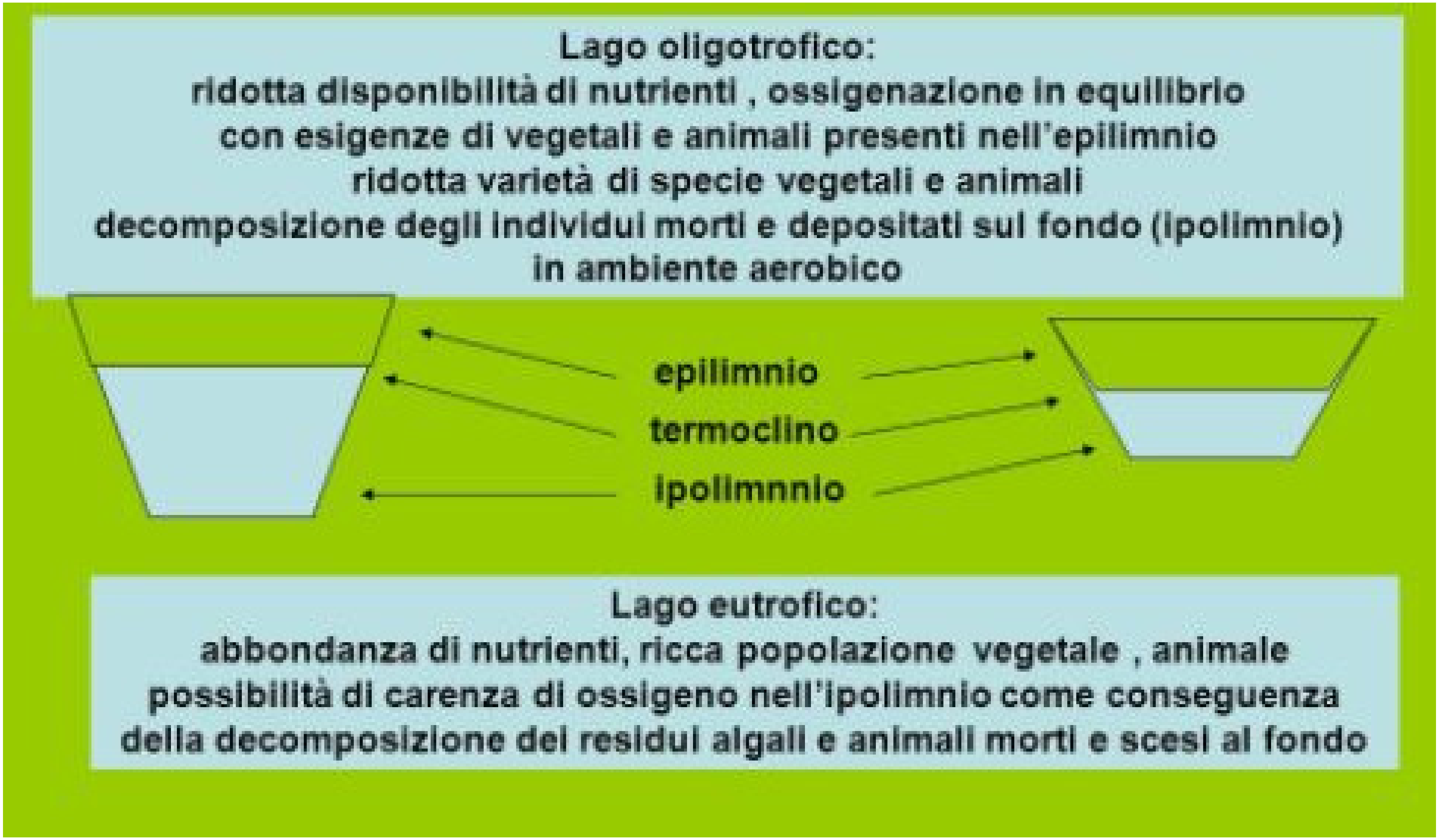
La conservazione delle ceramiche in ambienti lacustri

Stratificazione termica. Durante l'estate uno strato d'acqua superficiale (epilimnio) è riscaldato dalla radiazione solare e, a causa della sua minore densità, galleggia sopra uno strato più freddo (più denso) che si trova sul fondo (ipolimnio).

La conservazione delle ceramiche in ambienti lacustri



Formation of pyrite

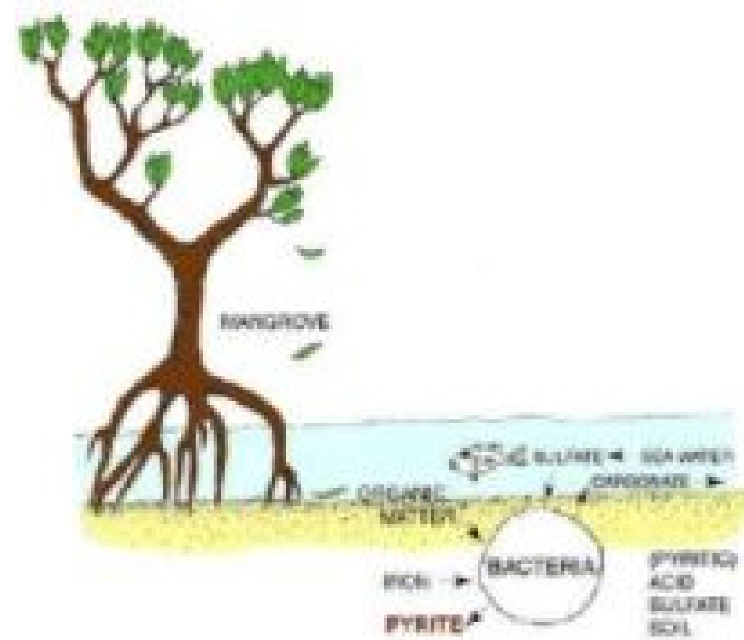
FeS_2

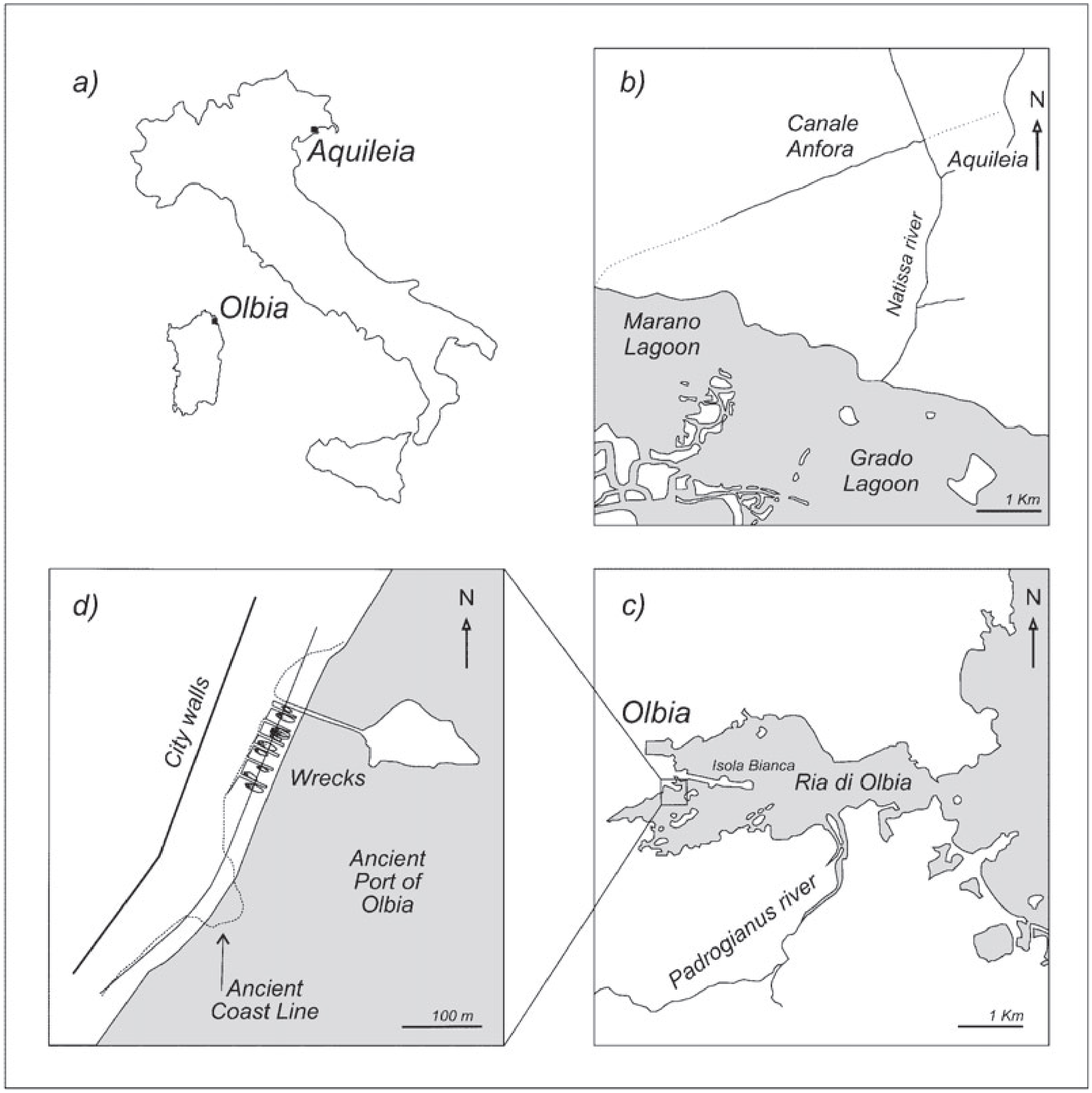
Certain anaerobic bacteria produce pyrite when there are more favourable conditions for these bacterias

$$Fe_2O_3 + 4H_2S \rightarrow 2FeS_2 + 3H_2O + H_2$$

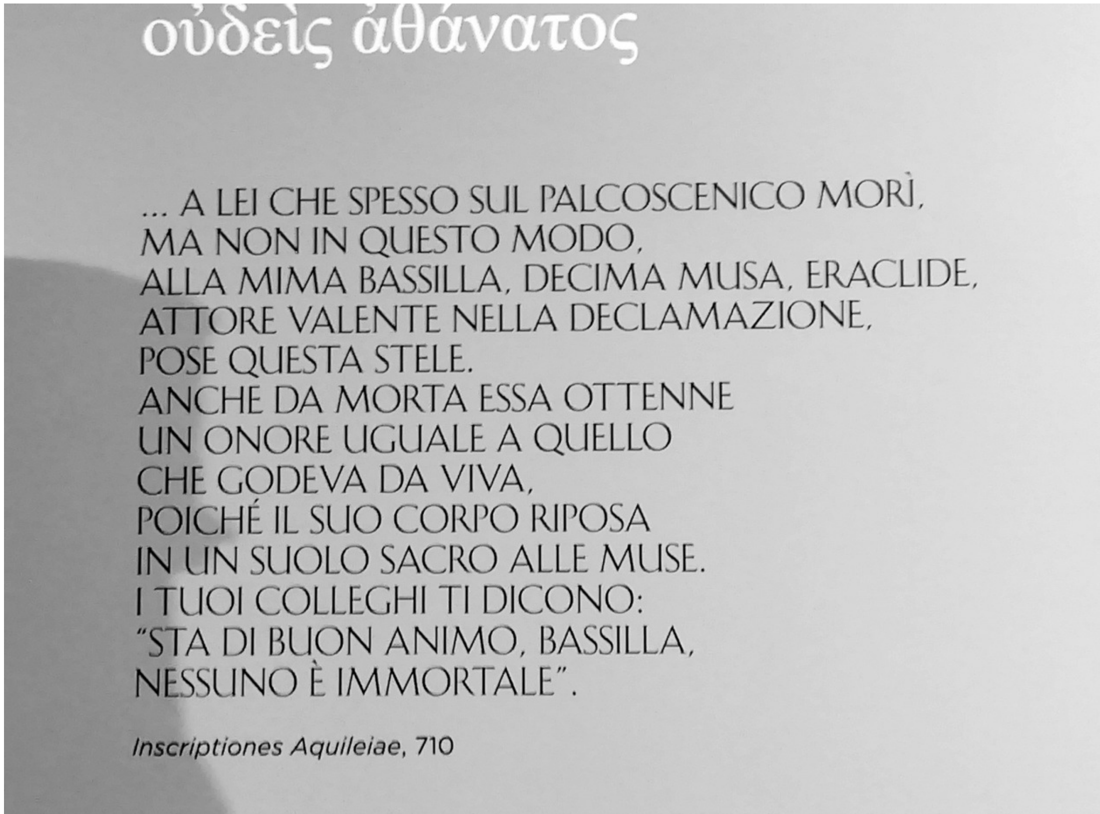
For pyrite to form, it requires

- a supply of sulphur (usually from seawater)
- anaerobic (oxygen free) conditions
- a supply of energy for bacteria (usually rotting organic matter e.g. mangrove leaves)
- a system to remove reaction products (e.g. tidal flushing of the system)
- a source of iron (most often from terrestrial sediments)
- temperatures greater than 10^0C

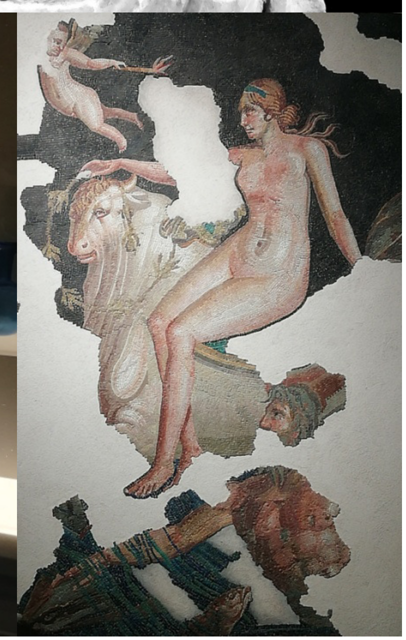




Although the two archaeological sites of Aquileia and Olbia are apparently located in two different environmental contexts - the former inland, the latter on the coast —they are characterized by very **similar chemico-physical burial conditions**.


οὐδεὶς ἀθάνατος
... A LEI CHE SPESSO SUL PALCOSCENICO MORÌ,
MA NON IN QUESTO MODO,
ALLA MIMA BASSILLA, DECIMA MUSA, ERACLIDE,
ATTORE VALENTE NELLA DECLAMAZIONE,
POSE QUESTA STELE.
ANCHE DA MORTA ESSA OTTENNE
UN ONORE UGUALE A QUELLO
CHE GODEVA DA VIVA,
POICHÉ IL SUO CORPO RIPOSA
IN UN SUOLO SACRO ALLE MUSE.
I TUOI COLLEGHI TI DICONO:
"STA DI BUON ANIMO, BASSILLA,
NESSUNO È IMMORTALE".
Inscriptiones Aquileiae, 710





The occurrence of **secondary mineral phases and variations in the pristine chemical composition** of the pottery represent the best evidence of chemico-physical **alterations of archaeological finds during burial**.

This suggests **caution when interpreting archaeometrical data in provenance studies and when estimating firing conditions**, and provides constraints on the chemico-physical conditions of burial and interaction processes between potsherds and fluids in post-depositional environments.

The research aimed at determining the **alteration processes of pottery found in transitional environments by studying the textural, microchemical and mineropetrographic** features of two sets of **ceramic** materials (**transport amphorae and tableware**), the colours of which had clearly changed from the original ones.

These potsherds come from the archaeological sites of **Aquileia** (Udine, northeastern Italy) and **Olbia** (northeastern Sardinia, Italy), respectively.

Both are characterized by **burial conditions intermediate between land-based and marine environments**, and they therefore represent suitable case studies for modelling post-depositional alteration effects and processes in **lagoon-like environments**

The potsherds from Aquileia were found in the eastern buried segment of the 6 km long **artificial ship canal named *Canale Anfora*** (Scotti Maselli 2005), which linked the centre of Aquileia to the Lagoon of Marano in Roman times (Fig. 1).

This canal was probably dug at the same time as the **foundation of the Roman colony (second century bc).** The easternmost segment of the canal towards the city of Aquileia remained active until the **middle of the third century AD**, when it was filled with sediments, whereas the westernmost one, towards the Lagoon of Marano, is still part of a present-day regional drainage system.

The chemico-physical conditions of burial were periodically affected by **sea-level rise and subsidence, which produced sea ingressions and changes in salinity.**

The samples from Olbia were found during the excavation of the **ancient Roman city harbour**. This site is located at the western end of the *Ria di Olbia*, an inlet on the western shoreline of the Gulf of Olbia, originating from the **submerged estuary of an ancient river**, due to the sea-level rise after the Pleistocene climate changes.

Geomorphological features mean that the **chemico-physical conditions of the Olbia harbour resemble those of a lagoon environment** (Ginesu 1999).

The harbour was active until the middle of the **fifth century AD**, when it was probably destroyed by a Vandal attack. This event caused the **sinking of 13 transport ships**, all found at the same depth in shallow water parallel to each other, perpendicular to the shoreline and with their prows in the same direction, suggesting that they were moored at the moment of the disaster.

Both archaeological sites can therefore be called **lagoon-like environments**, which are generally characterized by **high salinity, and basic and reducing water conditions**. **Salinity is generally higher than in freshwater, lower than in the open sea**, and may vary significantly over time, depending on different freshwater versus seawater contributions, the evolution of local geomorphological features, and hydrology.

A set of 27 potsherds were selected among those showing colour changes from the original colours.
Six samples are fragments of northern Adriatic-type transport amphorae (four **Dressel 6B** and two funnel-necked) collected from the *Canale Anfora* (Aquileia), and 21 are of **African Red Slip** ware (ARS), also known as African ***terra sigillata*** (types C and D), collected from the ancient harbour of Olbia.

For better understanding of the alteration processes that affected these potsherds, three unaltered fragments of amphorae were also collected from the *Canale Anfora* and archaeometrically characterized.

Two fragments of the same type of ARS were sampled from the coeval site of Nora (Cagliari, southern Sardinia) and analysed for comparison.

•Dressel 6B describes a class of amphorae used to transport oil that where produced in the Cisalpine and Istria regions (northwestern Croatia) between the end of Republican Roman times and the early third century AD.

The funnel-necked type is a class of amphorae probably used for oil transport and characterized by a wide flared mouth, produced in Istria since the early second century ad (Mazzocchin and Pesavento Mattioli 1993).

Courtesy of Dr. Tamás Bezeczky
Tamás Bezeczky

The ***terra sigillata*** is a type of fine tableware produced from the first century bc to the seventh century ad and characterized by a red slip. From the second century ad, Italic and Gallic production was supplanted by ARS manufacture.
According to morphological features and production areas, Hayes (1972) and Bonifay (2004) distinguished five main groups: A, A/D, C, D and E. The samples examined here belong to ARS types C and D, and were produced in **Bizacena** (central Tunisia) from 230 ad onwards and in northern Tunisia between the third and seventh centuries ad, respectively (Bonifay 2004).

Nuove presenze di terra sigillata africana ad Aquileia

Foto di Ella Zulini

FIGURA 12
Forma chiusa con decorazione a ramo di palma
(CA)
(foto dell'Autore)

In **thin section**, the samples from Aquileia contain **micro-sized secondary opaque minerals** in the micro-pores within the altered margins, and secondary calcite with geode- and mosaic-type microstructure in meso- and macro-pores, mainly along the margins.
Secondary **opaque minerals** also occur in the meso- and micro-pores of the altered external layer in the Olbia samples.

XRD analysis of the Aquileia samples indicates that the cores are mainly composed of quartz, associated with plagioclase, mica (muscovite/illite), hematite, calcite and in some cases also K-feldspar. This mineral assemblage represents the **pristine mineral composition of the ceramic ware**, with the exception of calcite, which represents a **secondary phase**.
Altered margins are mainly composed of quartz, associated with plagioclase, mica (muscovite/ illite), calcite, pyrite and in some cases also K-feldspar. Hematite is absent, whereas pyrite is the main Fe-bearing mineral phase.

Microstructural analysis by **SEM** on the Aquileia samples indicates the presence of aggregates of **secondary calcite in the meso- and macro-pores of the altered margins**. Micro-sized euhedral crystals of **pyrite** are dispersed in the micro-pores-

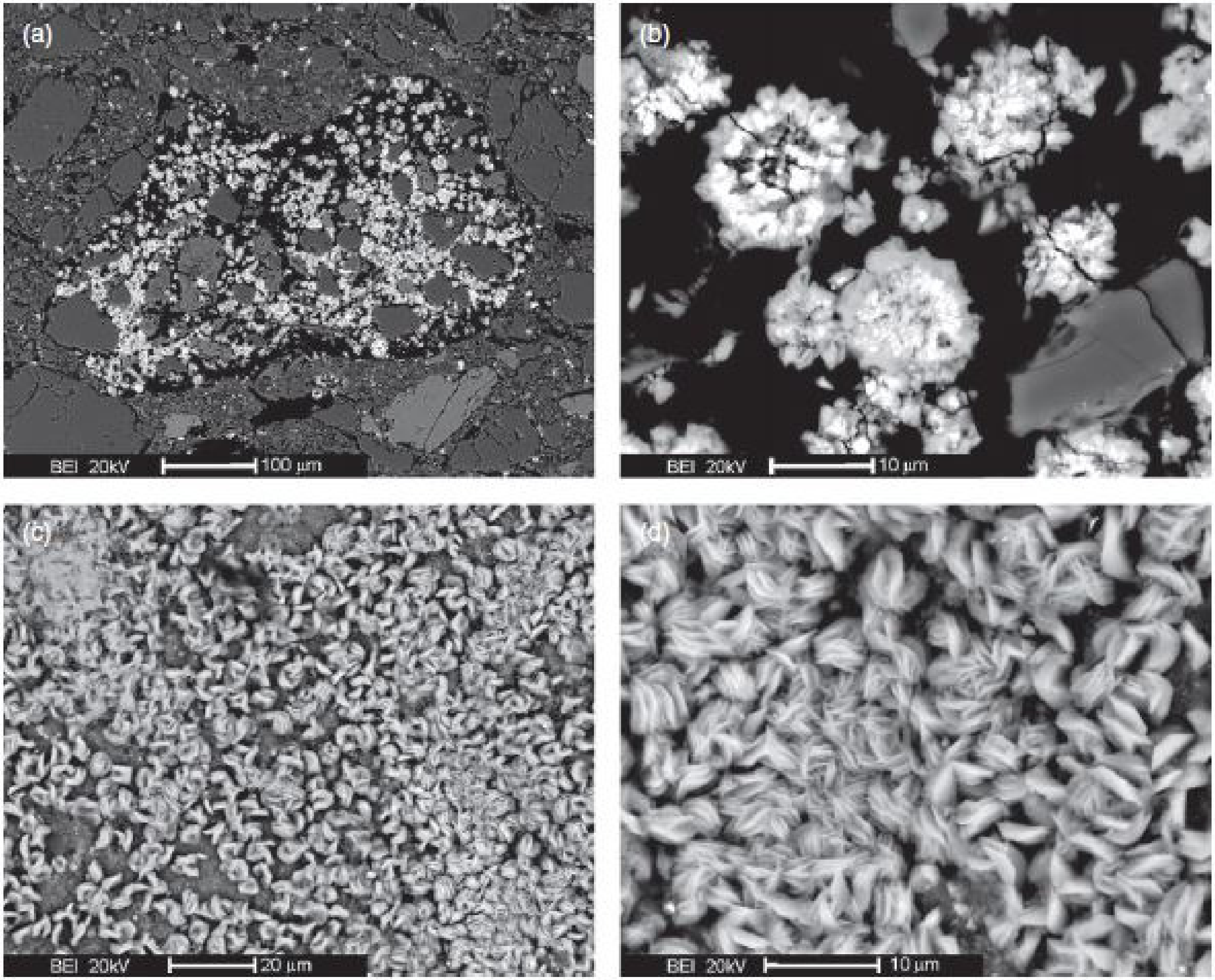


Figure 4 *SEM–BSE images of secondary phases in samples from Olbia: (a) framboidal aggregates (centre) and dispersed euhedral micro-sized crystals of pyrite; (b) a detail of framboidal aggregate, showing a core of euhedral crystals of pyrite surrounded by a jarosite rim; (c) very dense aggregates of jarosite on the sample surface; (d) a detail of jarosite crystals, with the characteristic bladed rosette habit.*

A model is proposed here to describe **post-depositional alteration** in potsherds buried in lagoon like environments, based on the **occurrence of secondary minerals** and the **sequence of crystallization** determined microstructurally.

Bacterial activity resulting from varying amounts of organic matter causes pyrite to grow either as euhedral crystals or framboidal aggregates by different sequences of reactions.

- **Microstructural analysis may reveal the evolution of environmental burial conditions over time**.

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Journal of the European Ceramic Society 33 (2013) 2031–2042
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Archaeological ceramic amphorae from underwater marine environments: Influence of firing temperature on salt crystallization decay

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Received 13 January 2013; received in revised form 11 March 2013; accepted 12 March 2013
Available online 30 March 2013

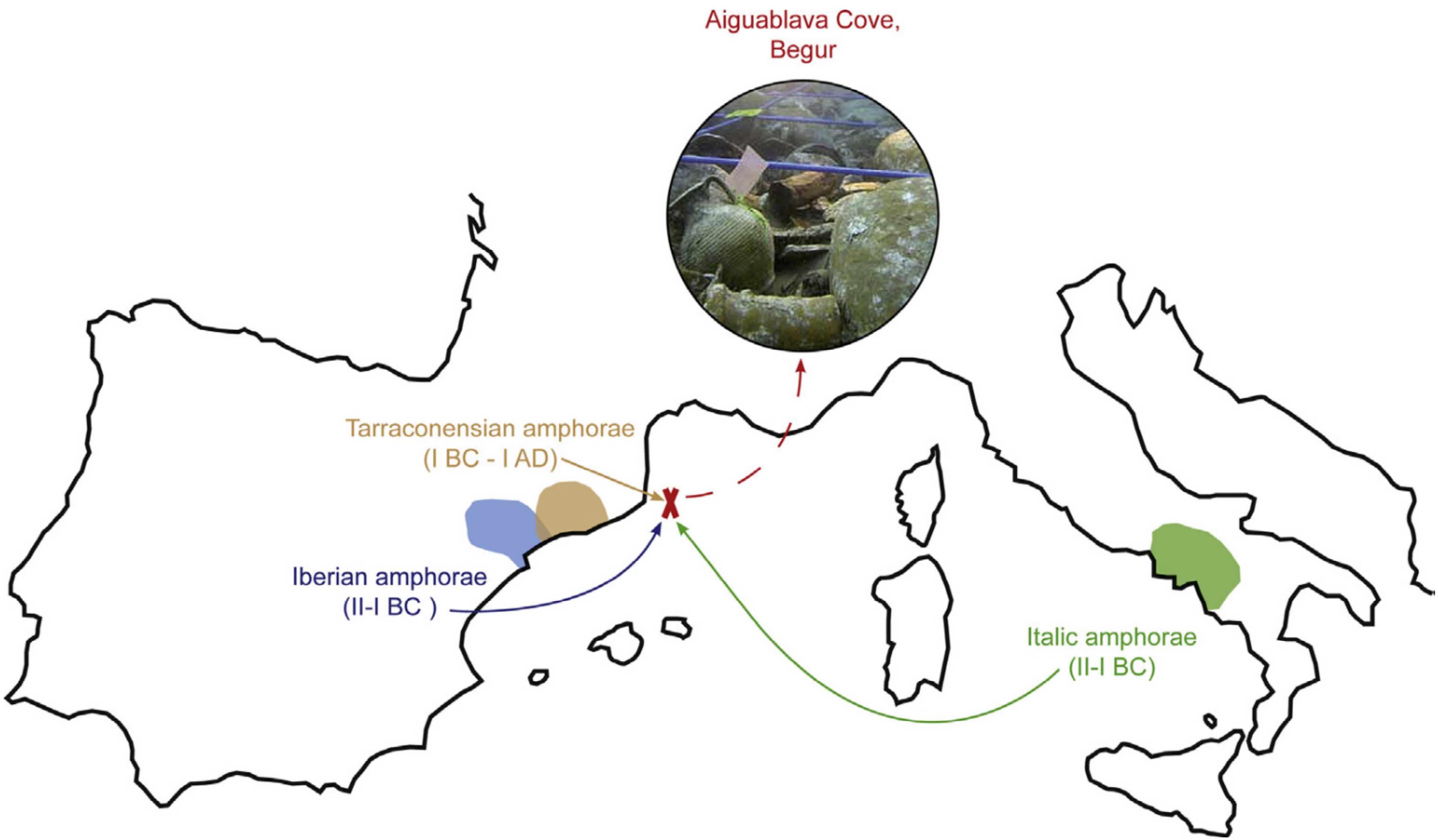
Non-desalinated and desalinated fragments of Iberian, Italic and Tarraconensian amphorae sherds, found in different underwater marine environments, were compared to determine the **decay caused by salt crystallization**.

Polarizing light and fluorescence optical microscopy, scanning electron microscopy coupled to energy dispersive X-ray spectroscopy, X-ray diffraction, ion chromatography and mercury intrusion porosimetry tests were conducted on the samples.

Non-desalinated samples exhibit a variety of signs of degradation, especially those samples fired at **lower temperature**. Sherds fired at **higher temperatures** have a lower surface area and less connected porosity, which entail a lower absorption of soluble salts containing water and eventually less decay than those fired at lower temperatures.

The **composition and texture reached with the firing temperature is a key factor on salt crystallization decay** and hence on the durability of these artefacts.

This should be taken into account during desalination procedures that have to be optimized in order to be successful.


Aiguablava Cove,
Begur
Tarraconensian amphorae
(I BC - I AD)
Iberian amphorae
(II-I BC)
Italic amphorae
(II-I BC)

The underwater marine ceramic amphorae fragments analysed in this study varied in origin and some of them were subjected to post-extraction desalination process.

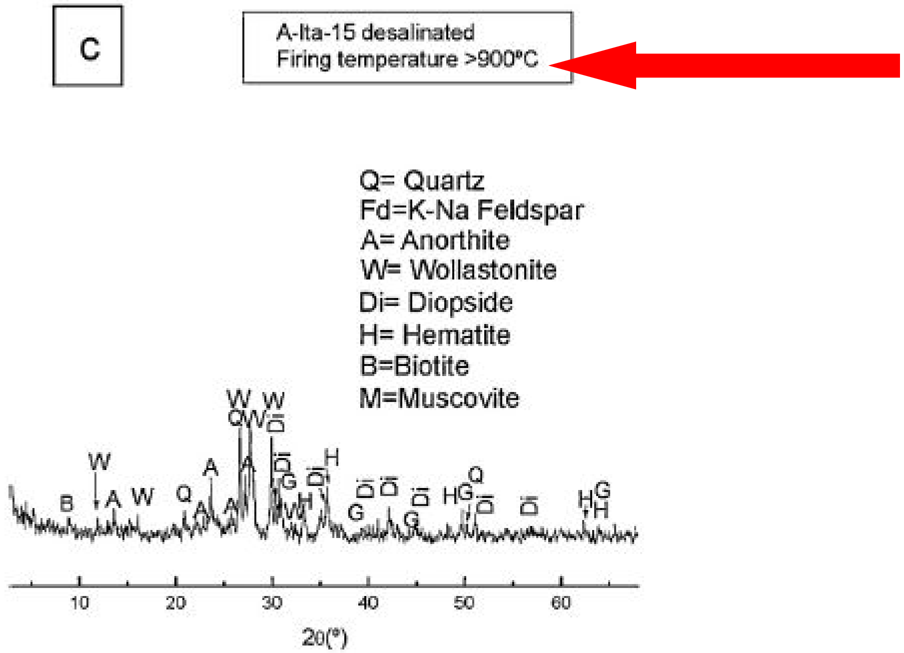
- Samples AIbe- 1, A-Ita-15 and A-Tar-24 were taken from the Cala de Aiguablava classic era anchorage ground at Begur, in the region of Catalonia (Fig. 1).
All the samples from this site have been subjected to a **desalination** process after their extraction from the archaeological site.

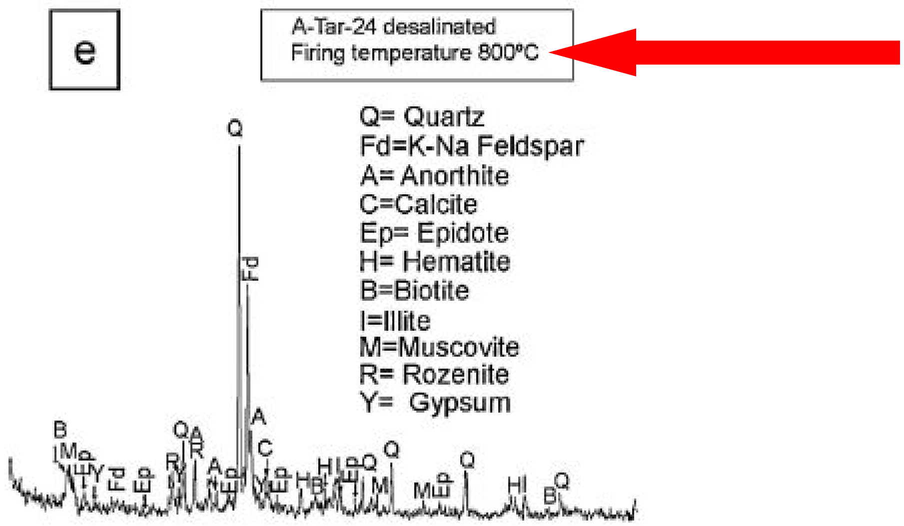
- By other hand, samples AIbe-31, A-Ita-33 and A-Tar-32 are **non desalinated** underwater sherds, with an unknown location since these were extracted in the 1970s by fishermen and divers.

In this case, these fragments of amphorae have the same historical provenance than the former mentioned desalinated samples, and these were used in this research in order to carry out **comparative studies**.

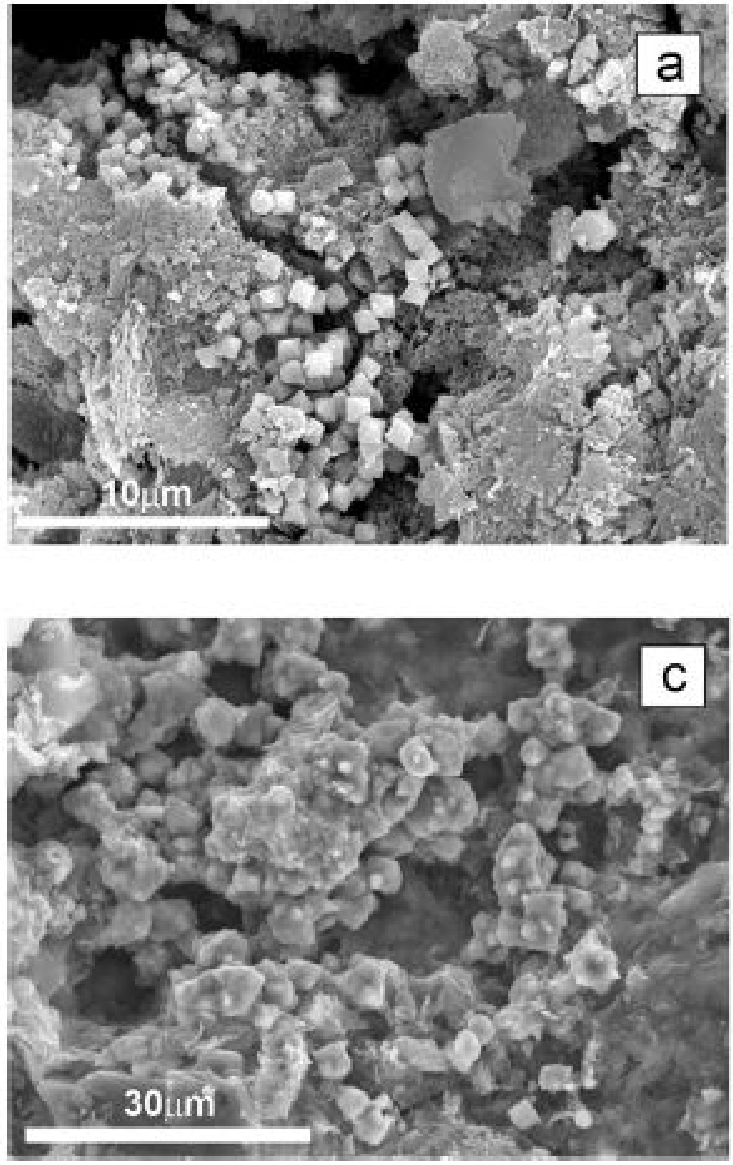
Tarraconensian sample A-Tar-32 (non-desalinated)

X-ray diffraction (XRD)





Scanning electron microscopy (SEM-EDS)



This study shows that both **soluble salts absorption** and their elimination after the desalination procedure is **closely related to ceramic firing temperature** and, hence, to the surface area and porosity generated during firing.

Ceramics fired at **temperatures over 900 ◦C show small amounts of soluble salts** (characteristic of marine environments), while the **materials fired at 800 ◦C or lower have more soluble salts and gypsum sub-efflorescences.**

The **composition and texture reached with the firing temperature is a key factor on salt crystallization decay and hence on the durability of these artefacts**.

Therefore in order **to optimize a desalination** procedure is necessary to previously **know the intrinsic characteristics of the artefacts, since their pore network can make difficult the desalination**.

The use and effectiveness of desalination treatments are keys to the future conservation of ceramics artefacts.

Corrosion Science 89 (2014) 268–274

Contents lists available at ScienceDirect

Corrosion Science

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Research into water-soluble salts in efflorescent pottery during long-term storage in a museum

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[d] Anhui Architecture University, Hefei 230022, PR China
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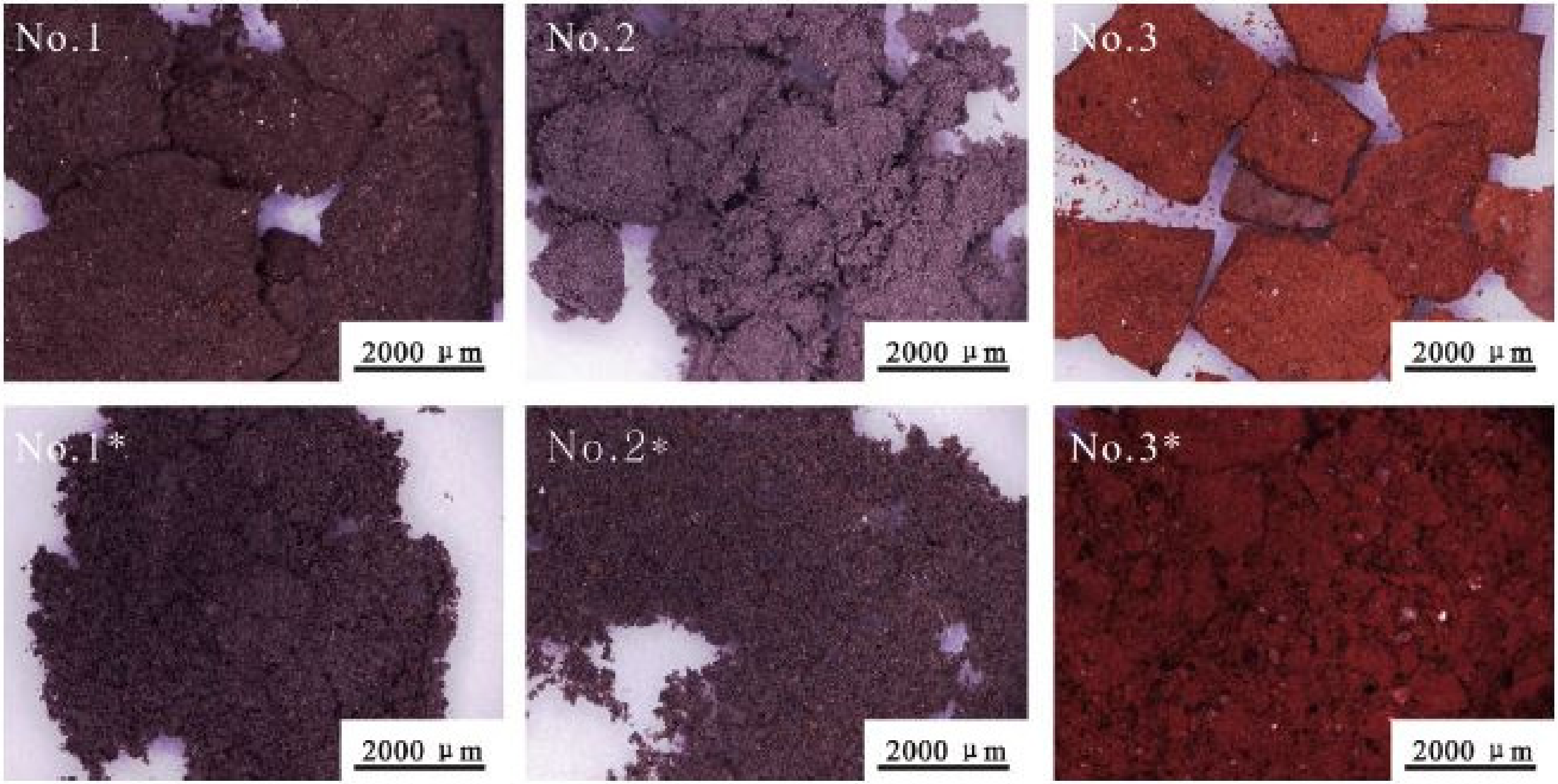
Baoji city, Shaanxi Province

Seicento bimbi intossicati dal piombo Presa d'assalto una fonderia cinese

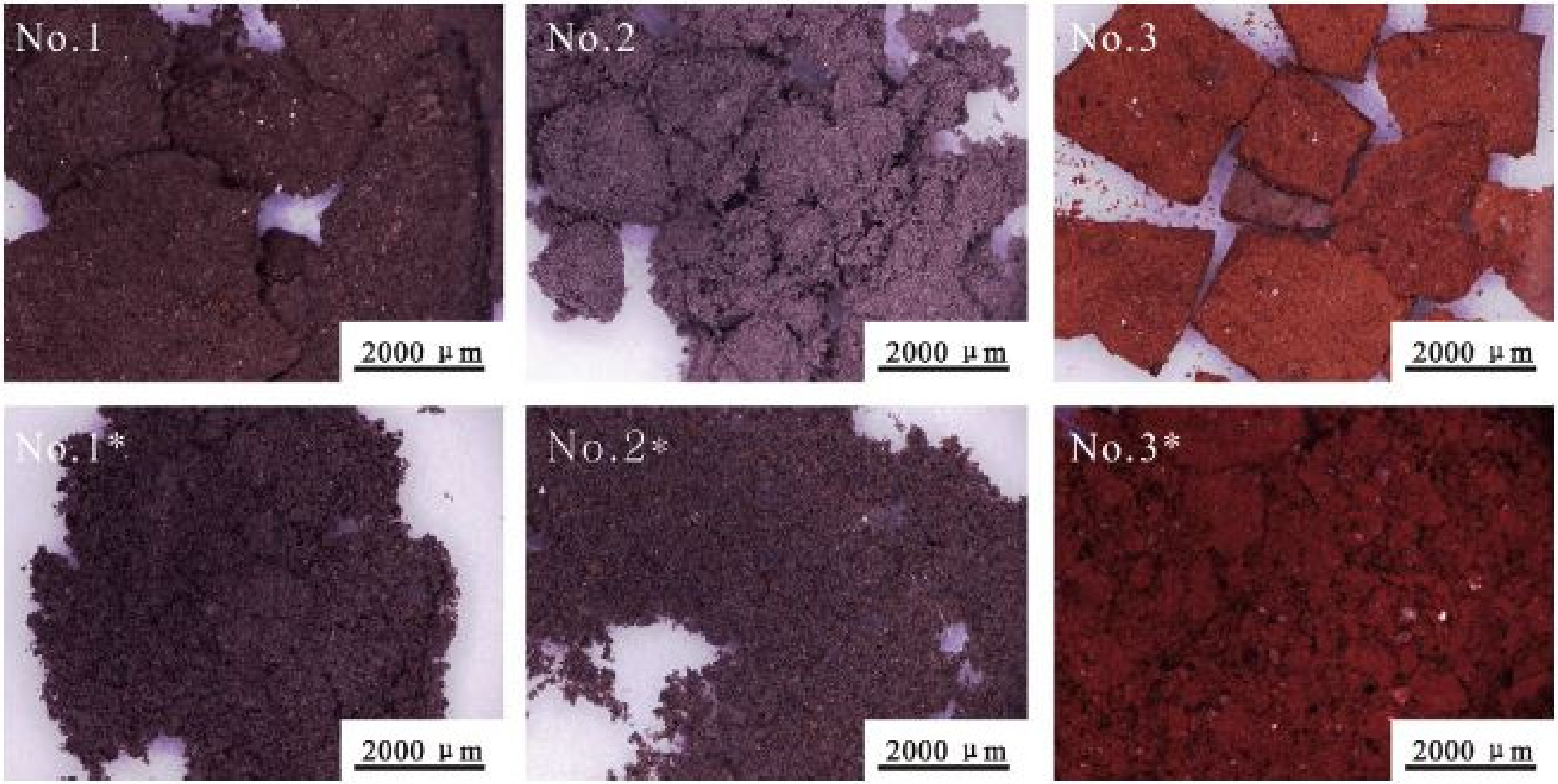
Centinaia di persone fanno irruzione in un impianto dello Shaanxi, nella città di Baoji. Intervenute decine di agenti

PECHINO - Centinaia di persone hanno fatto irruzione in una fonderia dello Shaanxi, nel nord-ovest della Cina, ritenuta responsabile dell'intossicazione da piombo di 615 bambini, pari all'80% dei 731 bambini che vivono in due villaggi vicino all'impianto per la fusione di metalli della Dongling. Di questi, 150 si trovano in ospedale.

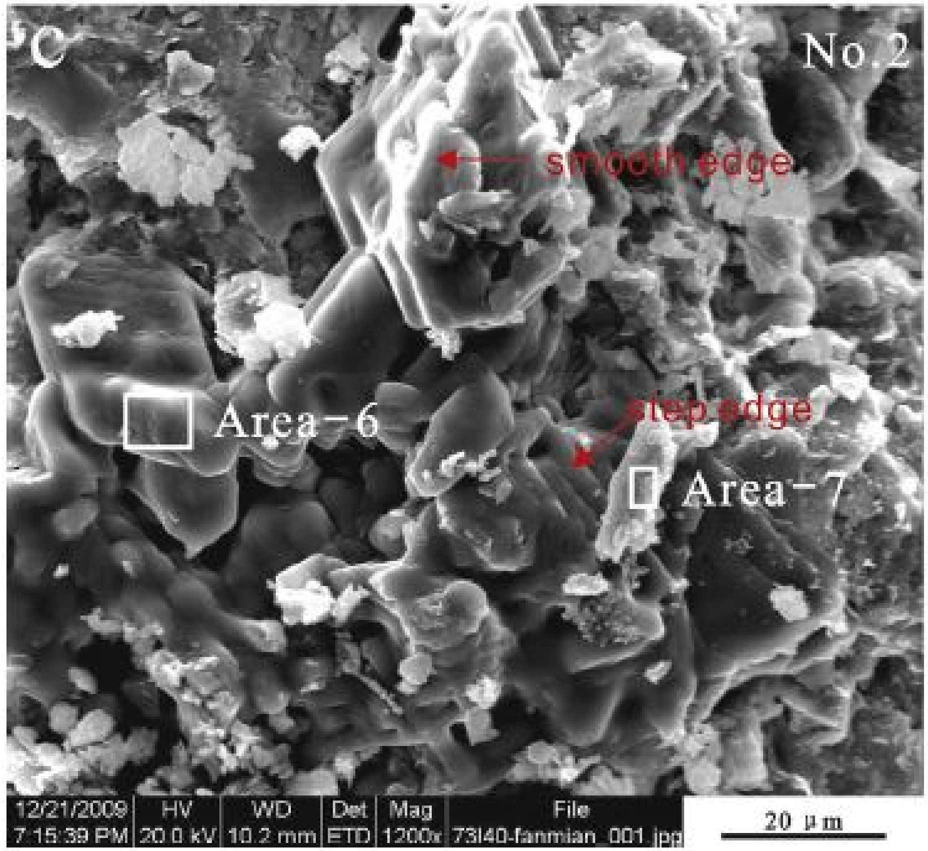

a
b
c
5cm



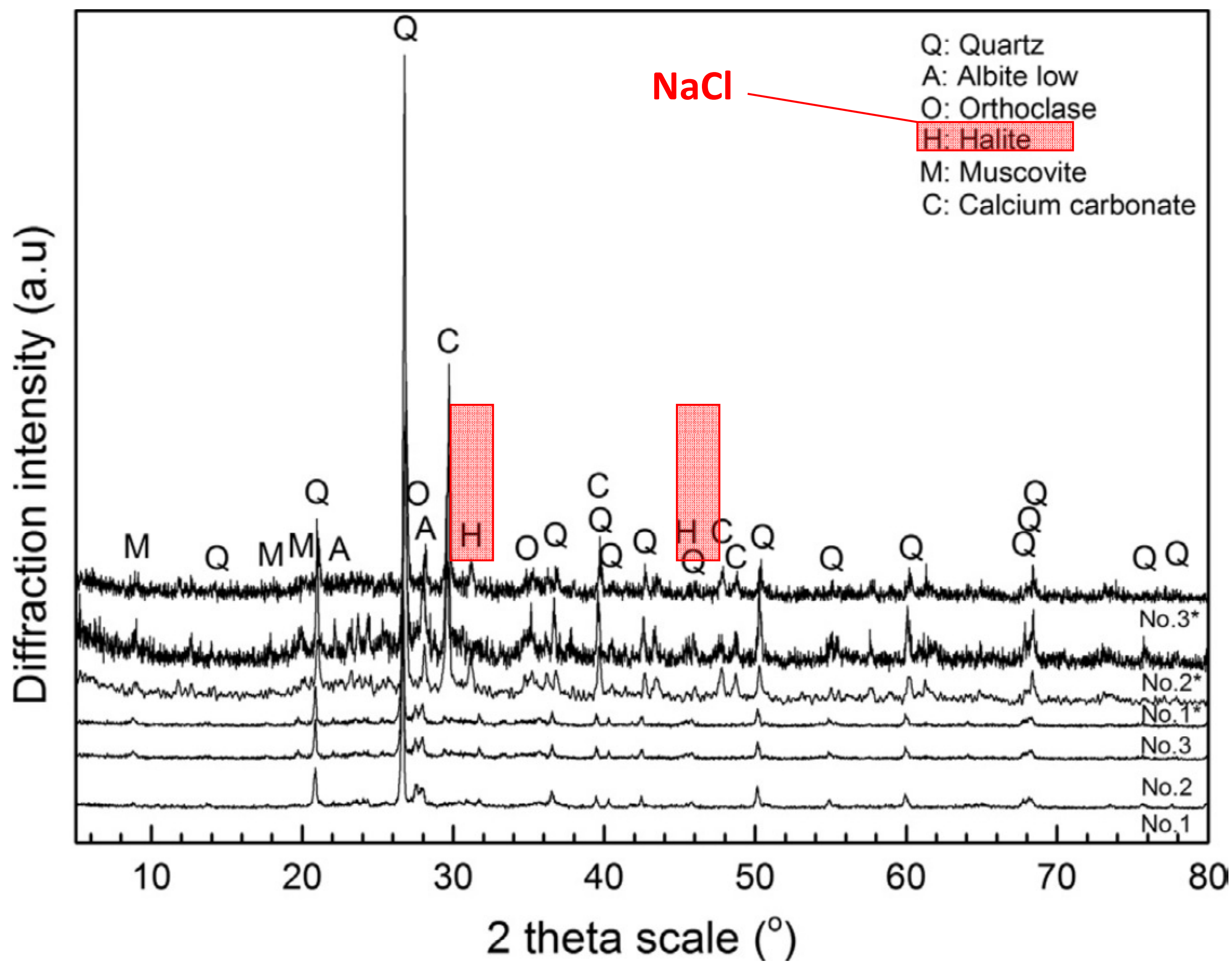
....It may be essential understanding the mechanism through which corrosion occurs and establishing proper protective methods. Consequently, efflorescent products, namely a recently excavated pottery fragment, buried soil and storeroom dust, were collected to explore the origin of the water-soluble salts in these damaged pottery specimens. The recently excavated pottery fragment and buried soil sample were used to evaluate the postdepositional process, and the storeroom dust sample was expected to supply some information regarding the local historical atmospheric environment.



All of the samples were analysed by scanning electronic microscopy (SEM), X-ray fluorescence analysis (XRF), ion chromatography (IC), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).


C
No.2
smooth edge
step edge
Area-6
Area-7
12/21/2009 7:15:39 PM
HV 20.0 kV
WD 10.2 mm
Det ETD
Mag 1200x
File 73l40-fanmian_001.jpg
20 μm

Phase identification by XRD



It is a noteworthy phenomenon that much ancient pottery has endured efflorescence in **northern Chinese museums**. The morphological changes of the efflorescent samples investigated in this study reveal a **gradual corrosion process** transforming a compact structure into a powdery structure during **long-term storage**.

Some reports have revealed the presence of many water-soluble ions from the atmospheric fallout in Xi’an…Among these ions, emissions from the burning of fossil fuels can spread widely via dust, air and precipitation.

As they are directly exposed to the atmosphere, porous pottery can absorb dust and gases, which are converted to soluble salts to produce large crystallisation stress during sharp changes in temperature and moisture.

Moreover, **the chemical reactions between atmospheric pollutants and minerals in pottery also cause corrosion**.
As a consequence, when considering ancient pottery conservation, the evaluation of preservation condition are useful and meaningful for them, including the **species and concentrations of water-soluble salts, atmospheric corrosive characteristics, temperature and humidity trends.**

The development of dairying in Europe: potential evidence from food residues on ceramics

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*Providing evidence of **dairying** is crucial to the understanding of the development and intensification of **Neolithic farming practices in Europe**, beyond the early stages of domestication.*
*Until recently, research in this field had been **limited to traditional archaeological methods, such as the study of pottery styles, faunal remains and specialised material artefacts**.*

Although suggestive, these methods are unable to provide direct evidence of dairying.

***Advances in biomolecular methods now allow the identification of remnants of dairy products on ceramic vessels** and the application of these methods to Neolithic ceramic assemblages across Europe is underway.*
There is no doubt that these new methods offer much scope for investigating hypotheses such as the 'secondary products revolution', but there are limitations.

*The cost of analyses prohibits indiscriminate sampling and differential survival is likely to prevent direct comparison of samples from different sites. Only by **incorporating these techniques within the wider frameworks of archaeological research may theories be properly tested**. Approaches to achieve this goal are discussed.*

Identification of the original contents of archaeological pottery has fascinated archaeologists and scientists alike throughout the 20th century. In fact, it was **Johannes Gruss** who in 1933, first identified an amorphous black residue on a ceramic vessel from the Hallstatt period, as overcooked milk by conducting some basic chemical tests (*Gruss 1933*). Although these analyses may have lacked the necessary rigor, which is now demanded from archaeological scientific investigations, this early work helped pioneer a **new approach to artifact analysis**.

In the last decade, the development of biochemical techniques such as gas and liquid chromatography, mass spectrometry, immunology and stable isotopic analysis have provided much greater scope for the reliable identification of residues. Issues of contamination from the burial environment have been addressed by **careful sampling methods**.

DEVELOPMENT OF DAIRYING IN EUROPE: THE POTENTIAL OF RESIDUE ANALYSIS

There is no doubt that the successful identification of milk residues on ceramics may contribute to the study of the origins and impacts of dairying, but at present only limited studies have been undertaken.

Milk residues have been detected at a number of UK sites: milk proteins in Late Bronze Age/Early Iron sites in the Western Isles of Scotland (*Craig et al. 2000*), milk lipids in Iron Age and Early Medieval ceramics from Northamptonshire (*Dudd & Evershed 1998*) and Late Neolithic sherds from the Welsh borders (*Dudd et al*. *1999*).

Journal of Archaeological Science

Volume 33, Issue 1, January 2006, Pages 1-13

Chemical analyses of organic residues in archaeological pottery from Arbon Bleiche 3, Switzerland – evidence for dairying in the late Neolithic

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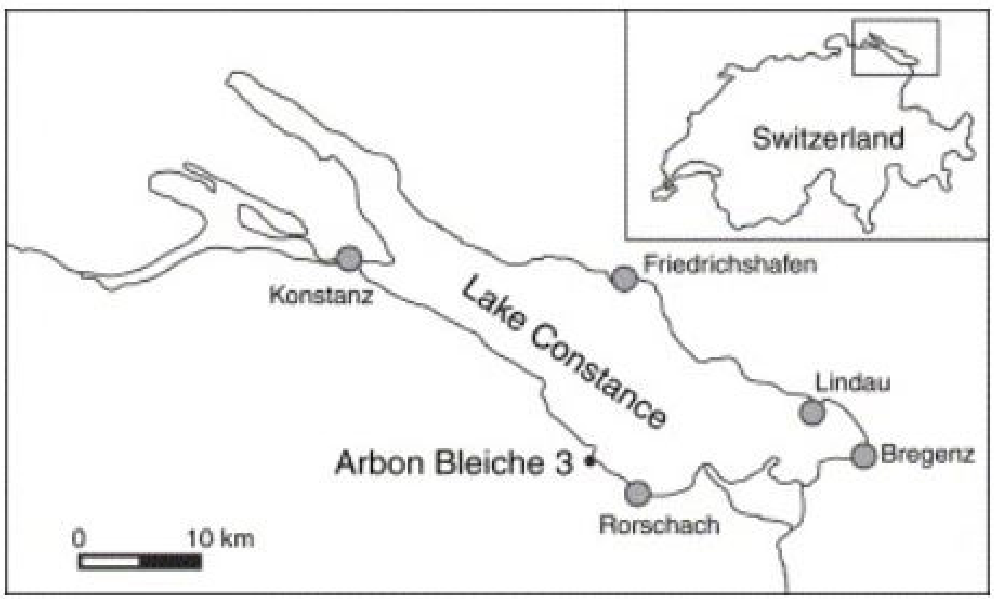

Samples were prepared and analyzed at the Institute of Mineralogy and Geochemistry of the University of Lausanne.

The potsherds were **cleaned of visible foreign material and the organic residues collected by scraping the potsherds with an organic solvent cleaned sharp blade**. Following removal of exogenous material with cleaned SS-forceps, the samples were manually ground and homogenized using agate mortar and pestle, weighed and stored in screw-cup sealed vials at −20 °C in the dark until use.

Fat samples of modern animals that have been fed exclusively on C3 forage grasses were analyzed in order to test the origin of the fat in the archaeological ceramics. These reference fats include adipose samples of pig, cattle, calf, lamb, deer and fish, milk fat samples of cow, goat, and sheep, and were obtained from organic farms and from markets supplying local food products. Vegetable fats from different origin were studied previously. To complement that data set, samples of linseed and poppy seed were included in this study.

Fat residues from plant, cattle adipose and ruminant milk were identified in almost all potsherds. This chemical evidence, combined with indirect archaeological observations, mainly from the age distribution of ruminant bones, indicate **meat consumption and farming practices for a sustainable dairying**. Given the **short life of milk**, which after leaving the ruminant udder quickly becomes colonized with lactobacilli, we can postulate that **Arbon Bleiche 3 settlers were consuming fermented milks**. Most likely the Neolithic settlers at Arbon were making relatively long life milk products, such as today's natural yoghurt, butter, and cheese, which could be stored and consumed at much later dates. **Our chemical data provide direct proof of dairying in late Neolithic settlements in central Europe**.