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Measurement of corrosion content of archaeological lead artifacts by their Meissner response in the superconducting state; a new dating method

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Abstract. Meissner fraction in the superconducting state of lead archaeological artifacts is used to evaluate the mass of the uncorroded metal in the sample. Knowing the total mass of the sample, the mass of all corrosion products is established. It is shown that this mass correlates with the archaeological age of the lead artifacts over a time span of $\sim$2500 years. Well-dated untreated lead samples from Tel-Dor, the Persian period, Caesarea, the Byzantine and the Crusader periods as well as contemporary data were used to establish the dating correlation. This new chemical dating method is apparently applicable to lead artifacts buried in soils with pH > 6.5. In such soils the corrosion process is very slow and the corrosion products, mainly PbO and $PbCO_3$, accumulate over hundreds of years. The method presented is in principle non-destructive.
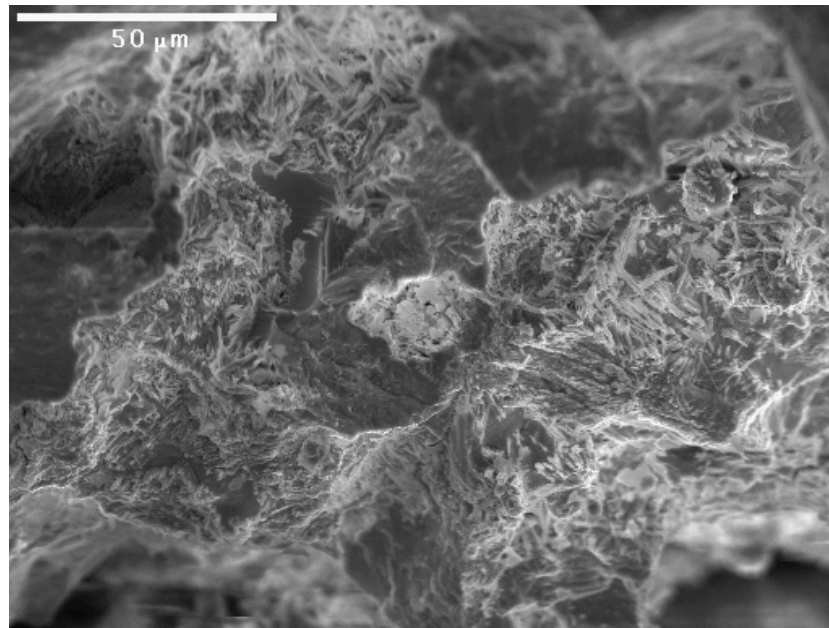
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Figure 1. SEM image of a corroded lead disc punched out from an archaeological artifact from the Persian period. $PbCO_3$ crystallites are present on the surface.

1. Introduction

Dating of metal artifacts is in most cases an unsolved problem. We propose a new chemical dating method for lead which is found quite frequently in archaeological excavations. In our method the corrosion extent on the surface of lead, used in antiquity for weights, pipes, claddings etc, is correlated with the burial time of the archaeological artifact. Conceptually our method is similar to the obsidian dating developed in 1960 by Friedman and Smith [1]; see also [2] for a review on chemical methods.

Lead metal at room temperature exhibits diamagnetic susceptibility of the same order of magnitude as its salts and oxide. However, when cooled below 7.2 K it enters into the superconducting state in which it exhibits the ideal diamagnetic susceptibility. The value of this susceptibility is 10^4–10^5 higher than that of its oxide and salts which are not superconductors (s.c.). The value of the volume susceptibility (χ_v) of lead in the Meissner state (see [3]), i.e. a state in which there is a total expulsion of the magnetic field from the volume of the lead sample, is $-1/4\pi = -0.0796$. This value translates to a molar susceptibility (χ_M) of $\chi_M = -1.453$ cgs. The molar susceptibility of lead oxide and lead salts is of the order of -10^{-5} to -10^{-4} cgs at room temperature [4] and down to cryogenic temperatures. Thus the contribution to the diamagnetic signal of these compounds at cryogenic temperatures is negligible in comparison to the diamagnetic signal of lead.

The volume magnetic susceptibility measured in the s.c. state of a corroded lead sample is

$$-1/4\pi = \frac{M}{H_0} \frac{\rho}{m_{Pb}} (1 - \eta) \tag{1}$$

where M is the magnetic moment in emu; $\rho = 11.34$ g cm^{-3} the density of lead, m_{Pb} is the mass of the lead metal in the sample and η is the demagnetizing factor. η is shape dependent and its
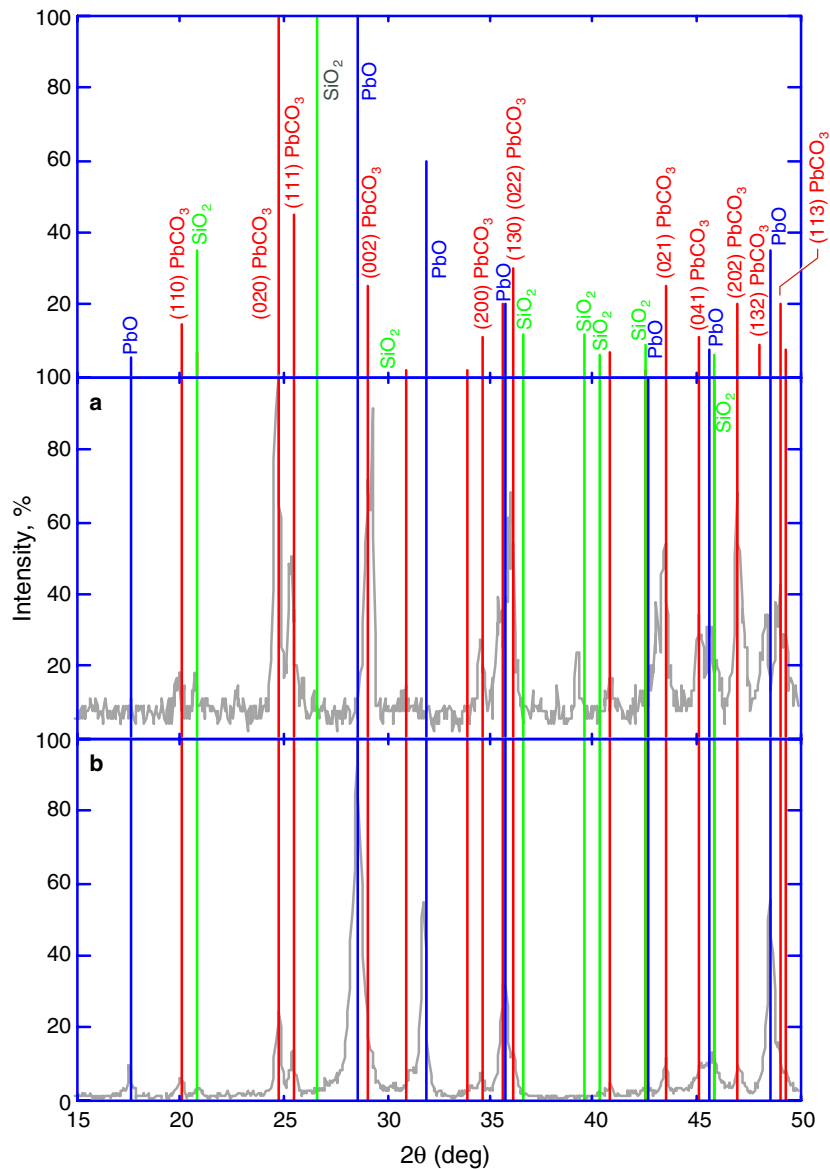
Figure 2. XRD spectra, Cu K_α radiation; (a) spectrum from the corrosion on the surface of a disc, (b) spectrum from homogenized corrosion powder scraped off the surface of the disc. The sample is from the Persian period.

measurement is presented later. H_0 is the value of the external magnetic field. Substituting the measured experimental values of M, H_0 and η into equation (1) we solve for the mass of the lead metal m_{Pb}. We thus use the magnetic measurement of the corroded sample to determine the mass of the uncorroded lead. This procedure yields the total mass of lead in the sample and does not depend on the spatial distribution of the corrosion materials in the sample, their connectivity and shape, provided this corrosion is on top of a continuous sheet of lead.

Knowing the total mass of the sample, m, the mass m_c of the corrosion products is determined:
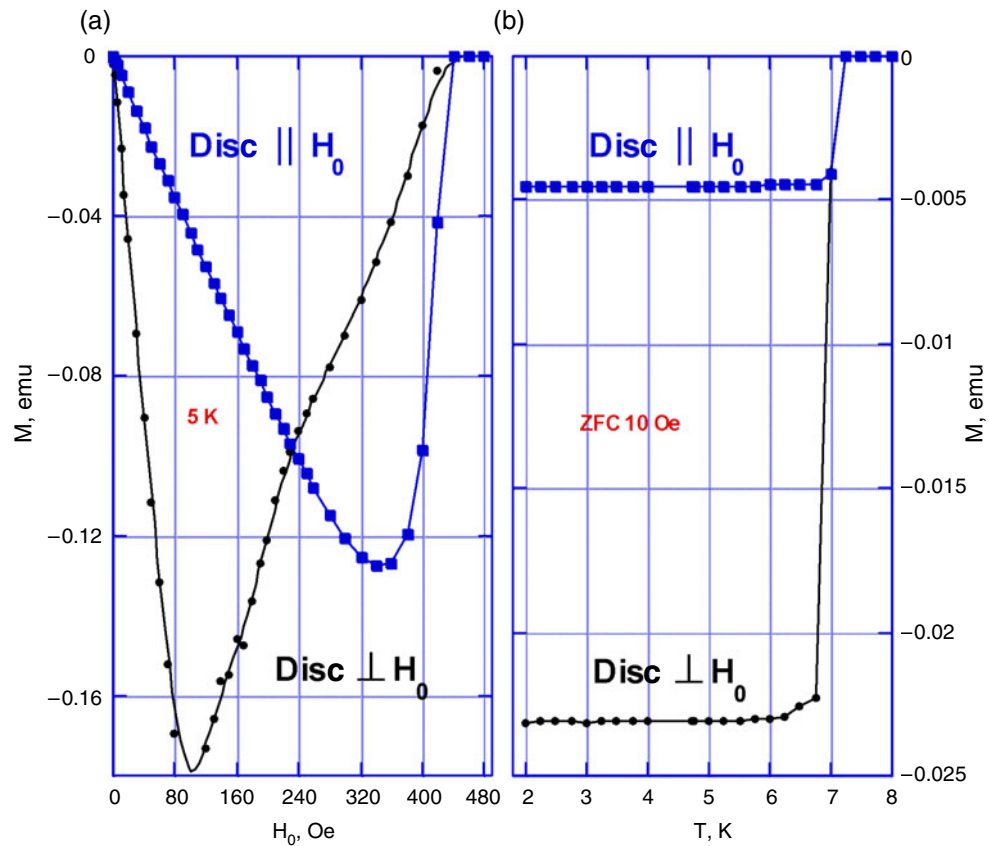
Figure 3. (a) Magnetization versus field of a corroded lead disc from the Persian period measured at 5 K. The disc is measured in two configurations; parallel and perpendicular to the external magnetic field. (b) Magnetization versus temperature for two configurations measured in an external magnetic field of 10 Oe in a zero field-cooled experiments.

$$m_{\mathrm{c}} = m - m_{\mathrm{Pb}}. \tag{2}$$

Experimentally we find that this procedure has an accuracy of $\sim 1\%$ in samples of ~ 100 mg.

By measuring the transition temperature to the s.c. state we can distinguish between the relatively pure lead metal phase, $T_{\mathrm{c}} = 7.2$ K, and homogeneous lead alloy phases which exhibit different values of T_{c}. Inclusions of a diamagnetic non-superconducting phase in the lead phase will not affect the T_{c} value.

Lead's corrosion resistance accounts for its successful use in many environments when exposed to the atmosphere, soil, fresh water and sea water (see [5]). Its good resistance in contact with many corrodents is due to the formation of relatively insoluble films of corrosion products deposited on the metal in the initial stages of exposure, which then protect it from further attack. The resistance to corrosion of lead in soils is usually good and it varies with the acidity of the soil. In a controlled corrosion experiment of lead pipes in a number of soils for periods up to 10 years (see [6]) it has been found that for soils with pH above 6.5 the rate of corrosion was between 4×10^{-5} and 6×10^{-5} cm year^{-1}. In acidic soils pH 4–5 the rate was about 50 times higher. Thus we may assume that lead buried in sites with similar low value of acidity will
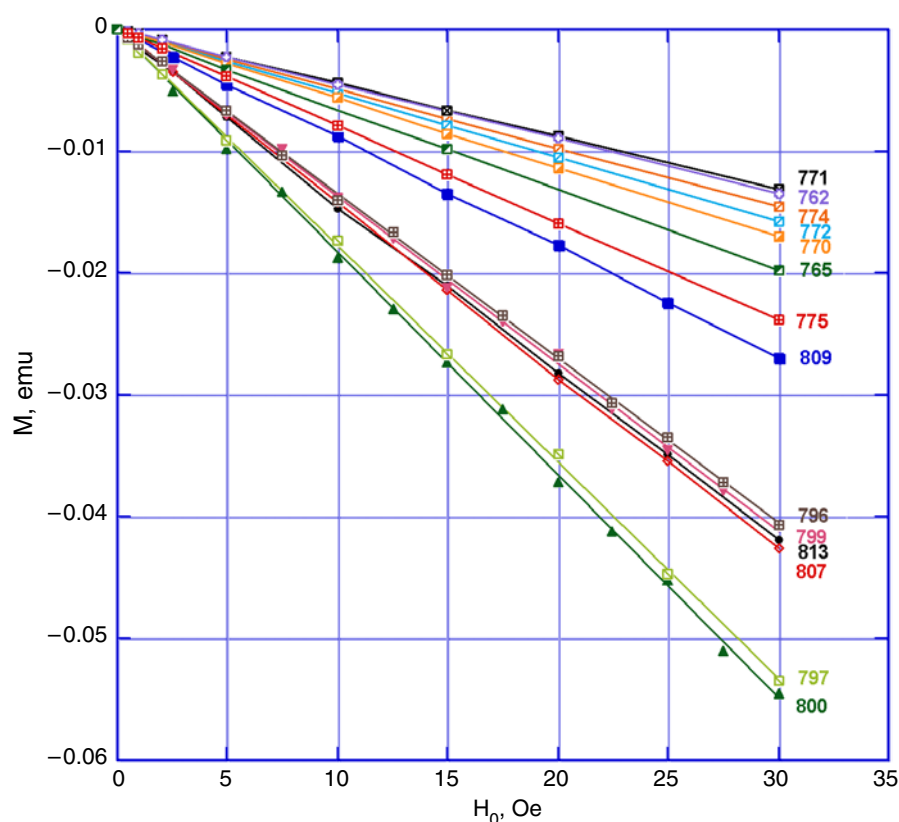
Figure 4. Magnetization of corroded discs from different periods. Discs are parallel to the external magnetic field and measured at 5 K. The numbers refer to table 1. Note that the slopes of these straight lines are proportional to the mass of the lead metal in the samples and inversely proportional to $(1 - \eta_\parallel)$, where $\eta_\parallel$ is the demagnetizing factor for the parallel configuration.

have a comparable rate of corrosion over very long time periods. Also it is assumed that the geological conditions such as soil conductivity and water table must have remained relatively constant throughout the archaeological time.

The corrosion products of lead in soil are mainly lead oxide, PbO, and lead carbonate, $PbCO_3$. The solubility of these compounds in water at room temperature is very low, 2.3×10^{-3} and 1.1×10^{-4} g/100 ml respectively, thus the accumulation of these products on the surface of archaeological artifacts in soil over hundreds of years could be expected.

2. Experimental details and results

In our study the sampling of lead artifacts is done by punching out discs in a corroded untreated lead sheet or ribbon. These discs are 0.5–2.5 mm in thickness and are 4.0 mm in diameter. The punching procedure is performed with a hard steel shearing cylindrical knife.

Before the disc is cut, the corroded lead sheet is sandwiched between two paraffin films, which keep the brittle corrosion encapsulated on the sample. After the punching procedure the mass of the disc is measured. A SEM image of the surface of a sample from the Persian period is presented in figure 1. Note the $PbCO_3$ plate-like crystallites on the surface. XRD spectra taken
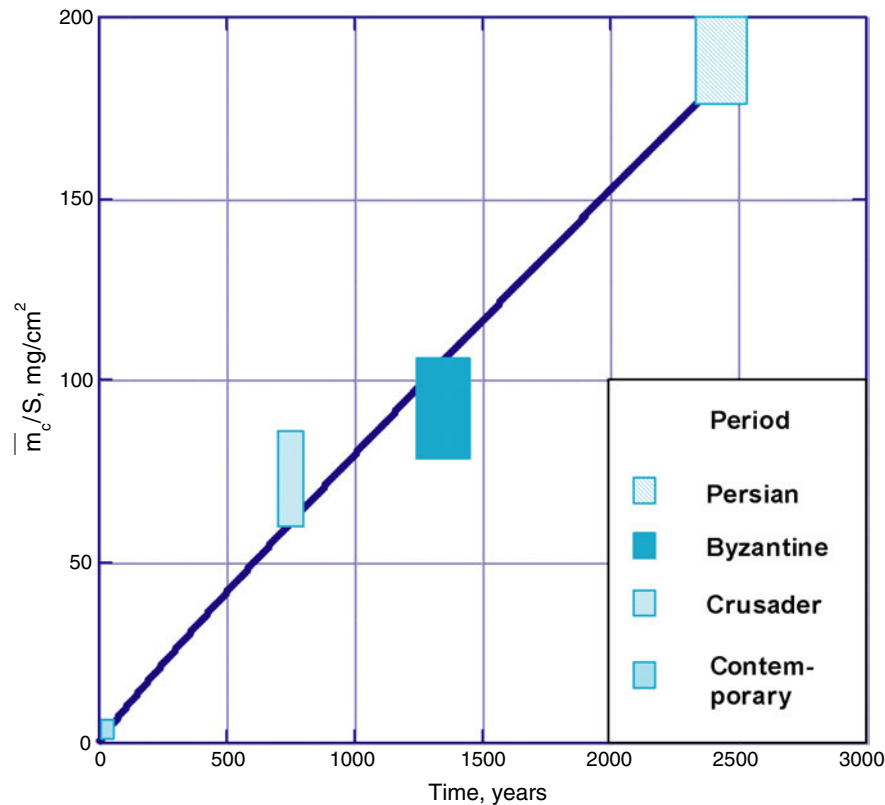
Figure 5. Average corrosion mass $\bar{m}_c$ per unit nominal surface area of the discs as function of time. The power law curve is the best fit to the experimental points.

from the surface of the artifact from the Persian period show the following composition: 80 vol% of cerussite, $PbCO_3$, 5 vol% of litharge, PbO; the rest are inclusions in the corrosion layer of SiO_2 and some other minerals. After scraping off the corrosion layer from the lead artifact and homogenenizing its content in a mortar the XRD spectrum was measured again. This time we observed 20 vol% of $PbCO_3$ and 75 vol% of PbO. This result shows that the surface of the corroded lead artifact is preferentially covered with cerussite as the XRD technique probes at most 1 μm deep into the artifact. The cerussite mineral, which is practically insoluble, provides a good barrier for the accumulation of litharge in the corrosion layer (figure 2).

Magnetization versus field and versus temperature for the disc samples is measured in a SQUID MPMS$_2$ magnetometer. Magnetization versus field at 5 K and versus temperature in a field of $H_0 = 10$ Oe for lead artifacts $\sim$2500 year old, Persian period, excavated in Tel Dor are shown in figure 3. The critical field H_c and the critical temperature, T_c, are the same as those measured in contemporary samples. To calculate the demagnetizing factor, η, the magnetization in small enough fields, O $\leq H_0 \leq$ 30 Oe, is measured in two configurations: discs parallel and perpendicular to H_0. Figure 4 presents data for 14 discs cut out from seven artifacts.

It can be shown that for thin enough discs (see [7])

$$m_{Pb} = -4\pi\rho\chi_{exp\parallel}/(1 + \chi_{exp\parallel}/2\chi_{exp\perp}) \tag{3}$$

where

$$\chi_{exp\parallel} = \frac{M_\parallel}{H_0}; \qquad \chi_{exp\perp} = \frac{M_\perp}{H_0}$$

Table 1. Data for archaeological and contemporary lead artifacts.

Sample no	m (mg)	m_{Pb} (mg)	m_c (mg)	m_c/S (mg cm^{-2})	Shape of artifact	Archaeo-logical site	Period	Approximate time of corrosion (years)
762	118.63	58.6	60.0	240.0	Pb sheet	Tel Dor soil's	Persian	2430 ± 100
765	120.00	82.9	37.1	148.4	corrosion	pH of the	—	—
770	121.81	72.7	49.1	196.4	on both	archaeological	—	—
771	114.80	57.7	57.1	228.4	sides	stratum: 8.23	—	—
772	110.33	67.7	42.6	170.4		Surface site	—	—
774	98.42	63.3	35.1	140.4		control: 8.17	—	—
775	151.81	97.6	54.2	216.8				
	Average			191.5				
	Standard error			14.8				
807	105.3	82.6	22.7	90.8	Pb ribbon	Caesarea	Byzantine	1350 ± 100
809	124.0	107.2	16.8	67.2	corrosion	soil's pH	—	—
813	178.8	159.9	28.9	115.6	on both	of the	—	—
					sides	archaeological		
						stratum: 7.96		
						Surface site		
						control: 8.51		
	Average			91.2				
	Standard error			14.0				
796	176.73	155.8	20.9	83.6	Pb ribbon	Caesarea	Crusader	750 ± 50
797	210.41	200.9	10.5	42.0	corrosion	soil's pH	—	—
799	184.00	158.4	25.6	102.4	on both	of the	—	—
800	219.7	203.8	15.9	63.6	sides	archaeological	—	—
						stratum: 7.96		
						Surface site		
						control: 8.51		
	Average			72.9				
	Standard error			13.0				
				5.0	Pb pipes	Data from Gilbert (1946), soil's pH > 6.5	Contem-porary	10

$$\eta_\parallel = \frac{1}{2}\frac{U}{1+\frac{1}{2}U}; \qquad \eta_\perp = 1 - \frac{U}{1+\frac{1}{2}U}; \qquad U \equiv \frac{\chi_{exp\parallel}}{\chi_{exp\perp}}.$$

The m_c cm^{-2} values for these discs as calculated from equations (3) and (2) are shown in table 1. The archaeological site, the pH of the soil (see [8]) at the site, the archaeological dating of the

sampled objects (see [9]) and an estimated corrosion time are presented for samples from the Persian, the Byzantine and the Crusader periods. Contemporary samples are detailed in table 1 as well.

In figure 5 we present the corrosion extent for the above samples as a function of the estimated corrosion time. The power law curve $y(t) = \bar{m}_c(t)/\text{cm}^2 = Kt^{(1/(\alpha+1))}$, $\alpha = 0.07$, $K = 0.12$, is the best fit to the experimental points.

3. Discussion

A power law dependence of y on t is reasonable (see [10]). In a very general way the act of corrosion is based on the local existence of an electrochemical cell, which comprises a junction of a metallic oxide to a metal surface on the one hand and to oxygen and water on the other. This cell is characterized by certain potential difference, ε, that drives a current, I, through the cell:

$$\frac{dy}{dt} \sim I = \frac{\varepsilon}{R(y)}; \qquad \text{assuming } R(y) \sim y^\alpha \text{ we get}$$

$$y^\alpha \, dy = K_1 \, dt \rightarrow \frac{y^{\alpha+1}}{\alpha+1} = K_1 t + K_2$$

since at

$$t = 0 \ y = 0 \rightarrow K_2 = 0 \qquad y = Kt^{(1/(\alpha+1))}; \qquad K = (\alpha+1)K_1.$$

The power law fit is close to a rectilinear line. Such a behaviour is characteristic for a corrosion process in which the continuity of a thin protective layer of oxide on the surface of the metal is controlled by stress. When the layer reaches a certain thickness it breaks down and the metal surface is re-exposed to the environment. More oxide is then formed in contact with the metal, and, after a similar time interval, the thin film of corrosion is again disrupted, and then the process is repeated. The net result of such behaviour is the production of an oxidation curve, which is virtually a straight line (see [10]). This curve may serve for the approximate dating of lead archaeological artifacts buried in soils of relatively high pH, such as carbonate buffered soils, where the corrosion rate is comparable and relatively slow so that time averaging of external condition does occur.

As the relevant corrosion signal grows in time the relative dating accuracy should improve with the age of the sample. Thus the 2500 year span, dictated by the availability of samples, is not an upper limit of our method.

The new method presented here for the determination of lead metal content in a nonmagnetic artifact is in principle non-destructive as it does not require any chemical or mechanical separation of the corrosion products from the lead metal. Thus, for example, lead inclusions in copper, silver and gold ancient coins can also be studied.

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