Towards Electron Spin Resonance dating of anthropogenic carbonates: ESR signals of ^{14}C-dated historical lime mortars

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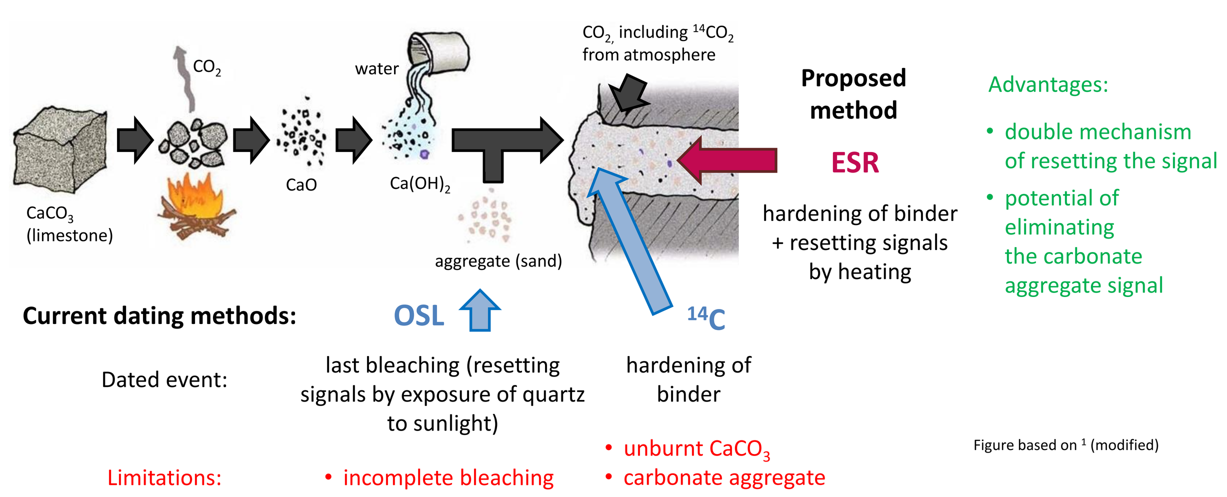
Introduction

This study presents the preliminary data of the Polish Returns NAWA project (2024-2027): *Radiation defects in anthropogenic carbonates: Towards Electron Paramagnetic Resonance dating of lime mortars and plasters (DANCER)*, which aims to establish Electron Paramagnetic Resonance (EPR) / Electron Spin Resonance (ESR) as a dating method for historical lime binders – mortars and plasters. This goal will be achieved by investigating the changes in concentration of radiation-sensitive paramagnetic centres with a dose of radiation in historical and modern anthropogenic carbonates: well-characterised archaeological samples dated by ^{14}C and OSL, and binders produced in laboratory conditions from various types of limestones. These analyses will provide a lower time limit of their ESR dating of carbonates and expend its range closer to the present time. ESR, together with OSL and TL, belongs to the so-called trapped charge dating methods, and dates the last bleaching (emptying the traps by heat or light) or crystal formation.



Mortars, as opposed to building blocks, cannot be reused, hence their age directly reflects the construction time of a building. Since carbonate crystals are formed during the mortar production, this moment can be regarded as a zero point for the accumulation of trapped charges, and their concentration in a measured sample should reflect the age of the mortar. In order to obtain the age of the samples the natural material must exhibit measurable ESR signals of the centres suitable for dating, however in the relatively young materials the signals may be very weak.

We present the ESR study of well-characterised samples from five different archaeological sites and verify the presence of suitable signals in order to assess the possibility of future dating by ESR spectroscopy. The samples have been previously dated by ^{14}C, which means they had undergone extensive characterisation and preparation, ensuring the selection of binder, which reflects the true age of the mortar. It should be noted, that as the sampling of the materials was done in accordance with the ^{14}C protocol used in ^{14}C and exposed to sunlight, which might have affected the concentration of paramagnetic centres. However, it can be reasonably assumed that the presence of measurable ESR signals in those samples would indicate that the material sampled and prepared in suitable conditions should provide the accurate information on the archaeological dose absorbed by the sample since the time of mortar production. As there are no data available on the annual dose at the location where the investigated samples were collected, it is not possible to date them by ESR, therefore, the goal of this work is a qualitative analysis of the natural signals found in a variety of mortars, assessing their potential suitability for dating.

Materials and methods

Samples from five archaeological sites, previously dated by ^{14}C were subjected to ESR analysis.

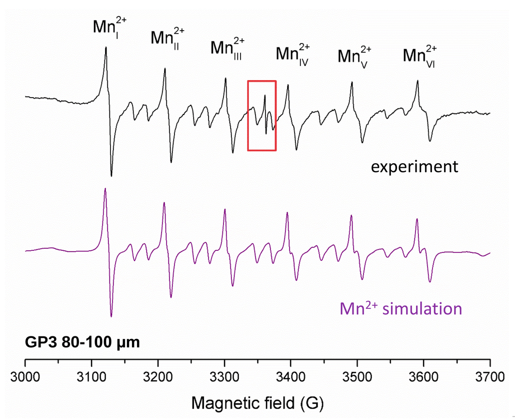
Sample	Site		^{14}C dating*	Ref.
Hip 8	Ancient settlement of Hippos (Sussita), east shore of the Sea of Galilee (Israel), North-West Church, 3rd cent. BC - 749 AD (earthquake)	lime plaster poorly compact, dusting, characterised by presence of elongated pores – straws traces	-	3-4
Hip 10		pure lime plaster, presence of large number of straw traces	Poz 1245 ± 35 BP Gd 1310 ± 45 BP	
MODIS 1 sample 2	Burial site at Cova S'Estora (Son Pellisser), Mallorca (Spain), 751-407 BC	lime conglomerate, macroscopically white, no aggregate, some not completely burned fragments of carbonate rocks; dolomitic, presence of hydromagnesite within the cracks	Poz 2380 ± 60 BP Poz 3045 ± 30 BP	5-7
MODIS 2 sample 1	Church of Saltvik on the Åland Islands (Finland); 14th century tower, dendrochronological dating 1381 AD	binder and aggregate have a carbonate character; most likely Ordovician calcitic limestone blocks were used for local lime production; limestone has macrofossils, especially trilobites	Poz 615 ± 30 BP Poz 555 ± 35 BP	8
MODIS 2 sample 3	Early Christian Basilica of Santa Eulalia in Mérida (western Spain); 304 AD (after Eulalia's death) - 570 AD (rebuilding)	dolomitic character of the lime and the aggregate; possible presence of young carbonate; dolomitic chemistry; little dead carbon contamination;	Poz 1870 ± 90 BP Poz 1835 ± 30 BP	9
GP 1	The Royal Castle in Poznań (Poland), Góra Przemysła; most likely built during the life of Przemysł II (1273-1296) as his residence	carbonate-clay binder, abundant and diverse aggregate, single fragments of unburnt limestone, evidence of recrystallisation	-	10
GP 2			ETH 576 ± 74 BP	
GP 3			-	
GP 4			-	

* for the samples from MODIS projects only the results obtained at the Poznań Radiocarbon Laboratory are reported

- Preparation for ^{14}C depending on the composition, including crushing, sieving, and separation of the binder in suspension through sequential dissolution[11] (for some samples); aiming at separating the binder and removing the aggregate
- Characterisation (petrography, SEM + EDS, XRD)
- Collected and prepared without protection from light, no annual dose rate data
- γ irradiation (Technical University of Łódź)
- ESR measurements on Bruker EMXPlus (X-band) spectrometer (UBB, Romania); measurement conditions: 3350 ± 75 G, modulation amplitude 0.5 G, microwave power 0.5024 mW
- ESR spectra simulations using EasySpin, an open-source MATLAB toolbox; simulation parameters similar to those reported in [12-14]

ESR spectra

Natural samples were investigated for presence of signals connected with the trapped charges, which appear in the centre of the manganese (Mn^{2+}) signal (between Mn^{2+}_{III} and Mn^{2+}_{IV}).

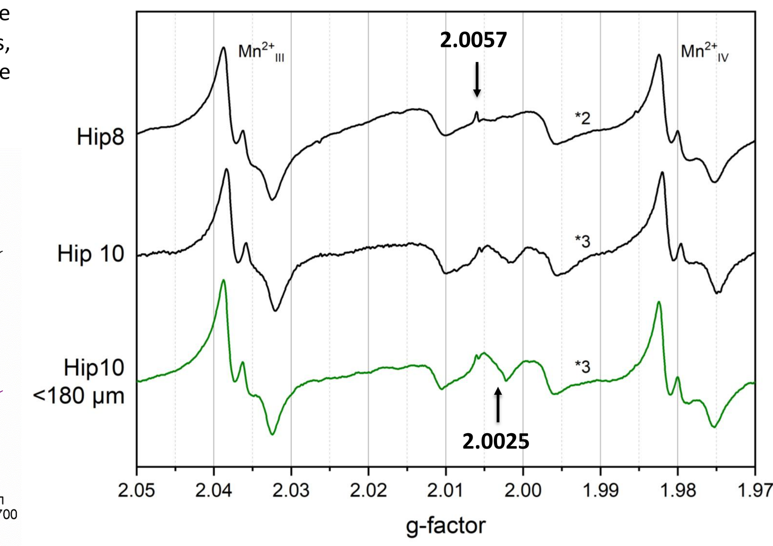


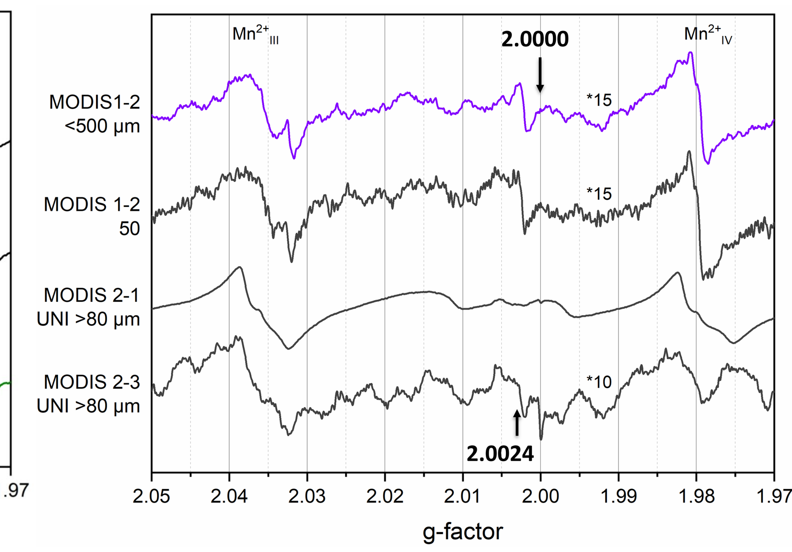
Ionizing radiation can generate various paramagnetic centres in calcite:

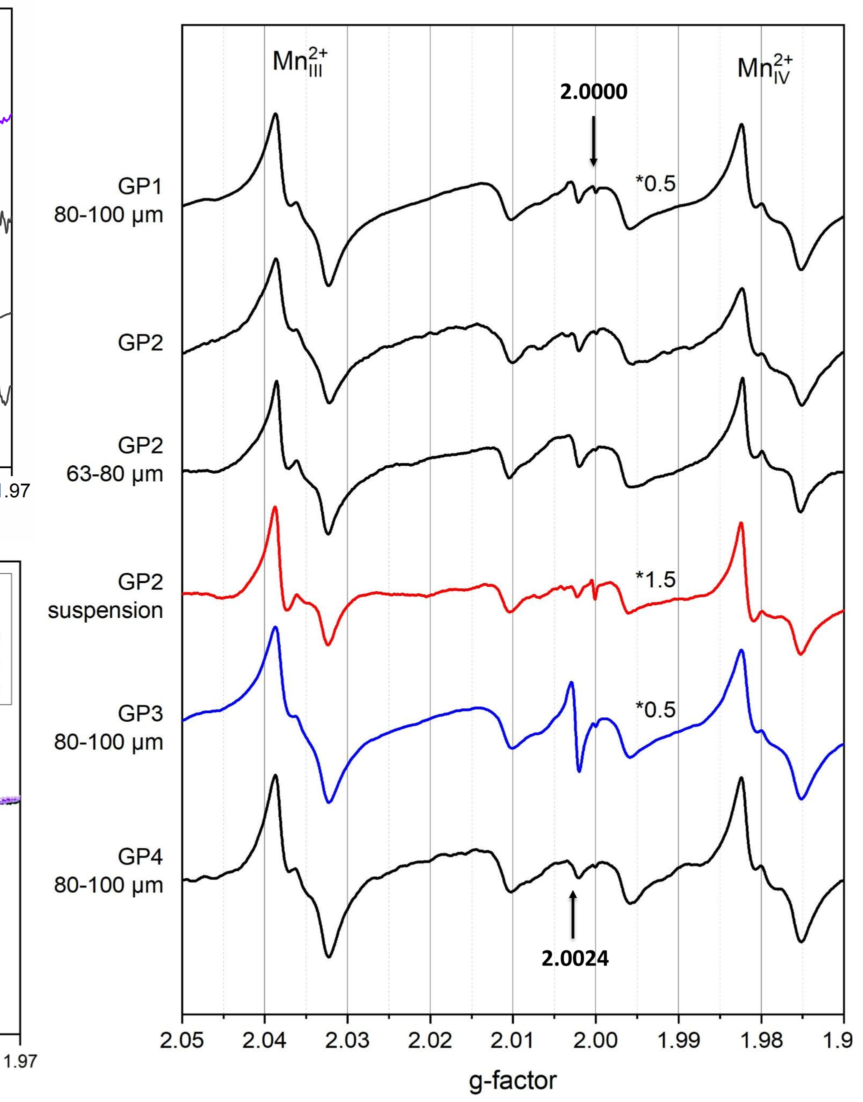
- carbonate defects, e.g. CO_2^-, CO_3^-, CO_3^{3-}
- non-carbonate defects, e.g. SO_2^-, SO_3^-, NO_3^{2-}, and NO_2^{2-}

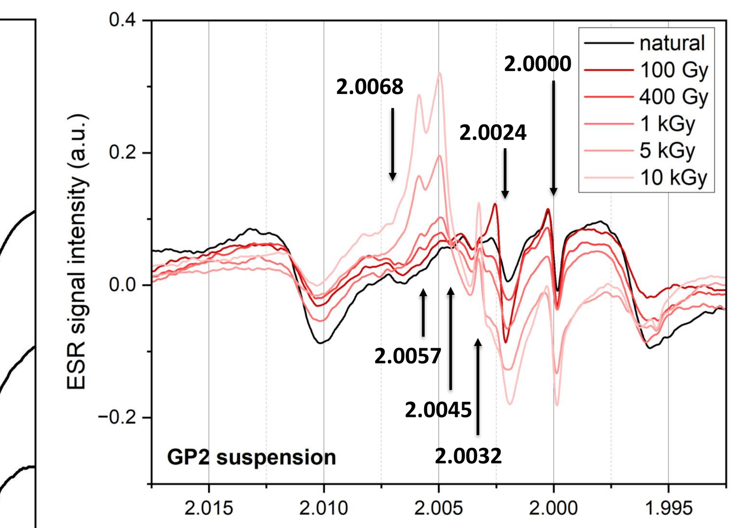
Depending on the environment those defects can exhibit different symmetry: orthorhombic, axial or isotropic.

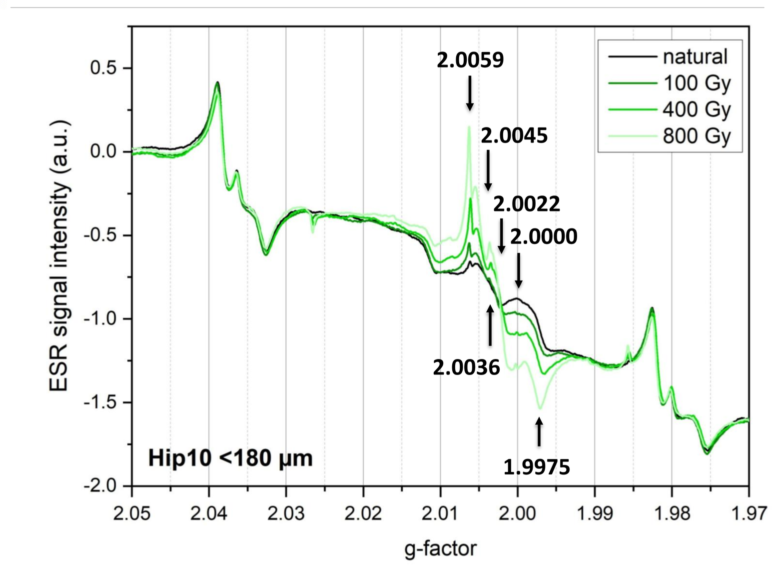
Natural samples investigated in this study show presence of weak ESR signals in this area. Based on the spectra and the availability of material samples Hip10, MODIS 1-2, GP3, as well as GPS2-suspension were selected for irradiation. The intensity of the signals grows with the dose of radiation.

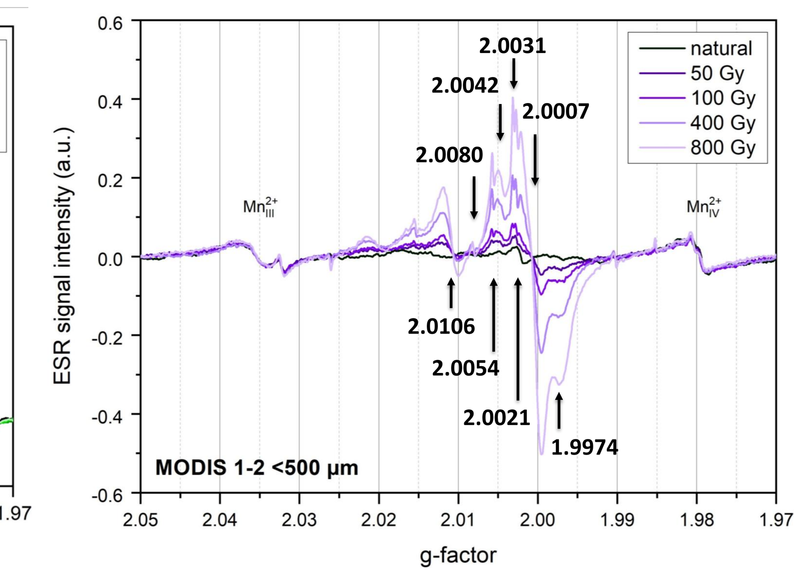


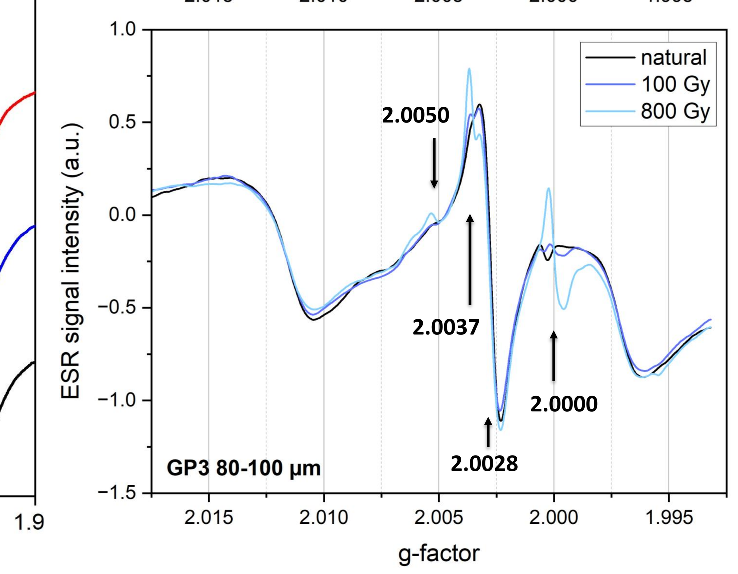












ESR simulations

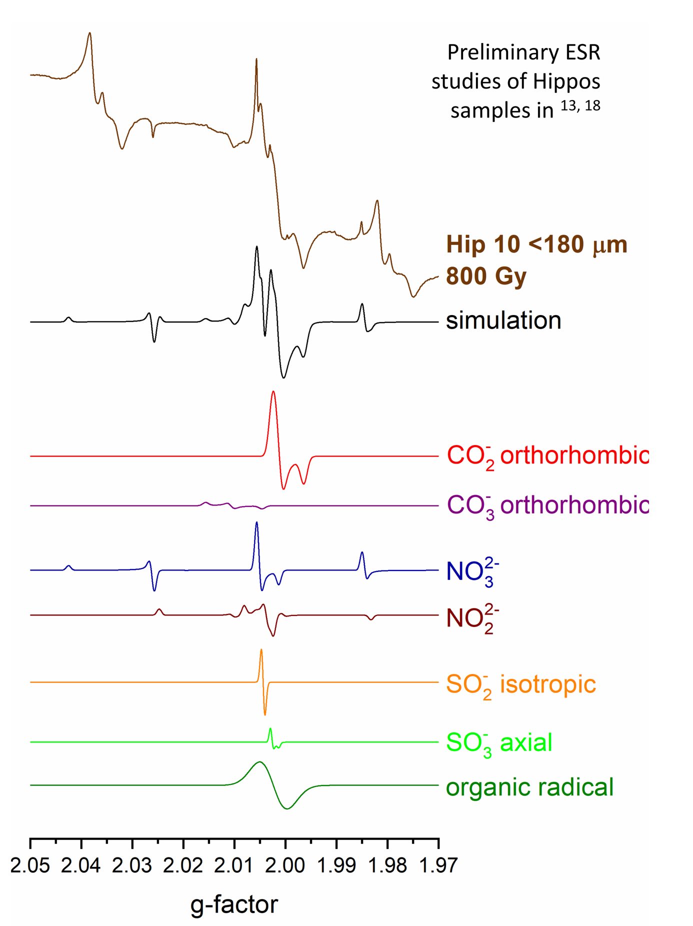
Simulations allowed for separating the individual components of the complex ESR spectra.

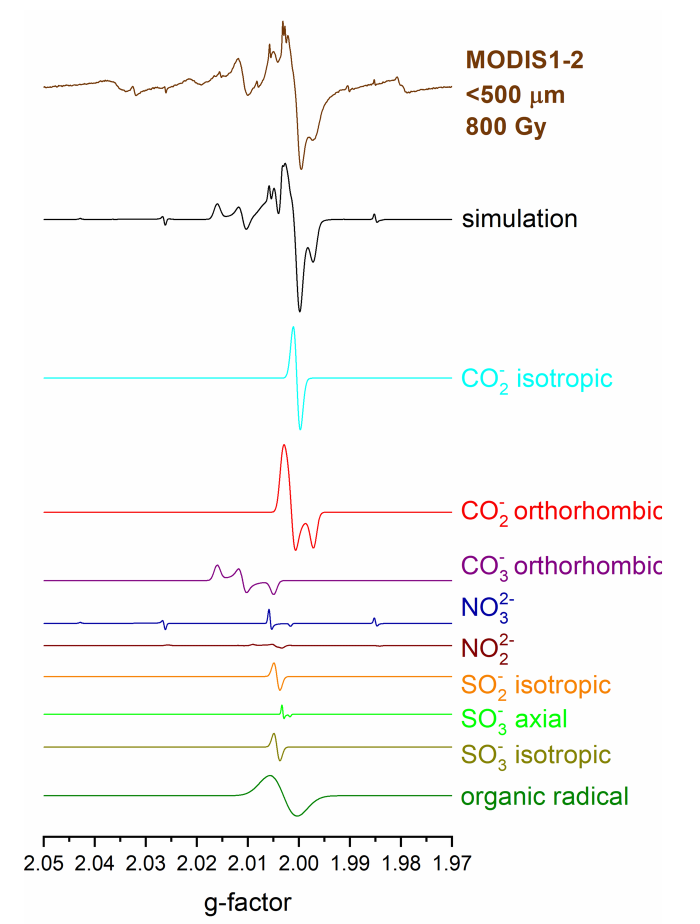
Signals assigned to isotropic CO_2^-, orthorhombic CO_2^-, isotropic SO_2^-, axial SO_3^-, which are generally considered suitable for dating[15-17], were identified in samples Hip10 and MODIS 1-2.

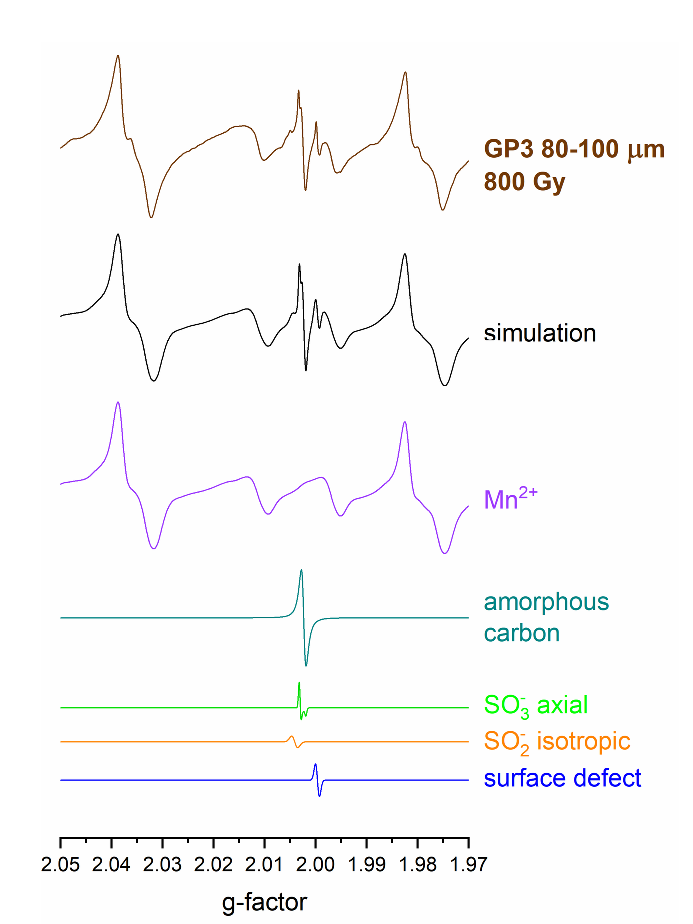
Sample GP3 shows absence of carbonate signals and presence of sulphate signals, as well as an amorphous carbon signal (presumably due to pyrolysis), which precludes dating. However, this signal is much less pronounced in sample GP2-suspension, showing the importance of sample preparation.

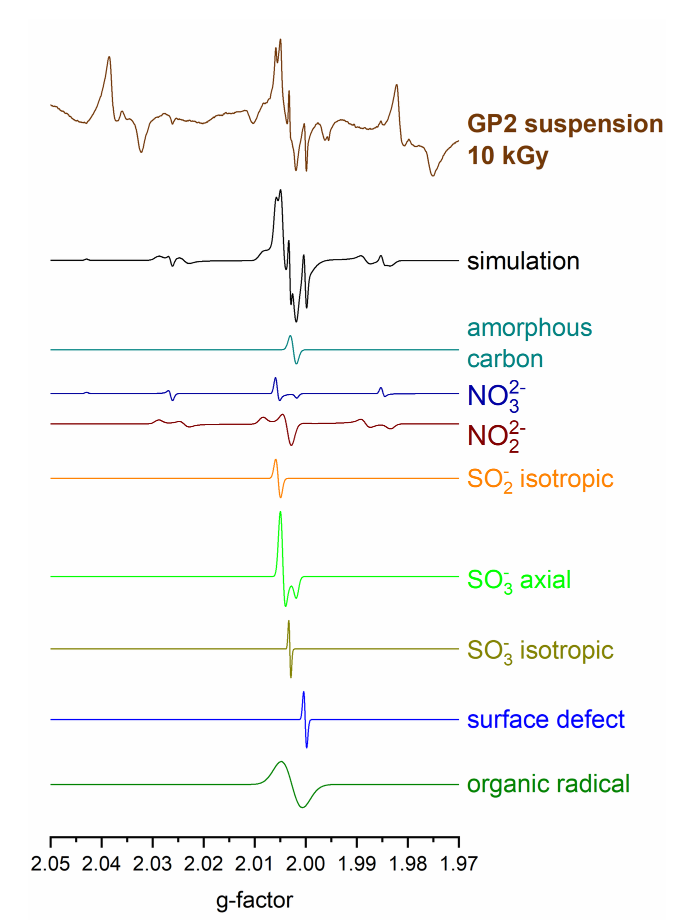
Example g-factor values of the signals[13, 16]:

Signal	g-factor, A (mT)
CO_2^- isotropic	2.0006
CO_2^- orthorhombic	2.0030 2.0016 1.9975
CO_3^- orthorhombic	2.0174 2.0098 2.0052
NO_3^{2-}	2.0063 2.0024, 3.450 6.800
NO_2^{2-}	2.0083 2.0033 2.0029, 0.380 3.480 0.330
SO_2^- isotropic	2.0057
SO_3^- axial	2.0038 2.0019
SO_3^- isotropic	2.0031
surface defect	2.0000
amorphous carbon	2.0027
organic radical	2.0035

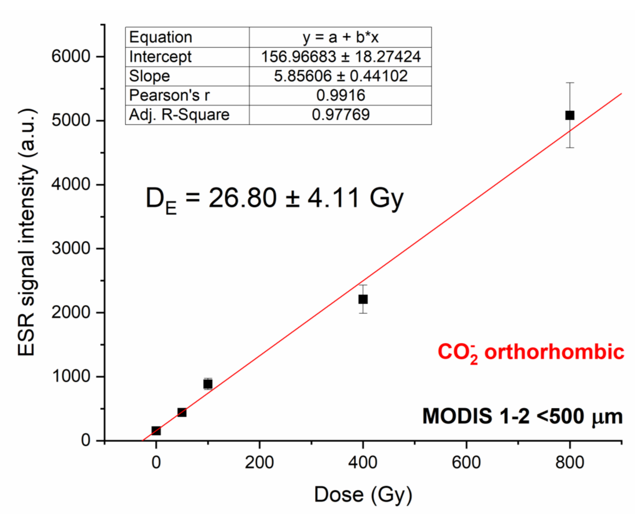








Dose response curve



The obtained equivalent dose (D_E) is likely underestimated, as samples were exposed to light before the measurements. No dose rate data is available for the samples.

The intensity was obtained through a double integration of the simulated signal, therefore the dose response curve represents the behaviour of a specific centre. This method allows for avoiding the interference from the overlapping signals, which often affects the estimation of signal intensity through the measurement of peak-to-peak amplitude in the complex spectra.

Based on the calculated D_E = 26.80 ± 4.11 Gy and the expected age of the lime burial of Cova S'Estora (751-407 BC[6]), the estimated dose rate ranges between 8 and 10 Gy/ka.

Dose rate calculated for quartz aggregate in OSL-dated mortars is typically in the range of 1 – 10 Gy/ka [19-24]. However, these values do not take into account the alpha component, as the outer part of the quartz grains which was affected by it is etched during the sample preparation. As no similar procedure is employed for the carbonate samples the alpha component cannot be ignored, therefore the dose rate values will automatically be higher.

Conclusions

- Lime mortars from five archaeological sites, previously dated with ^{14}C and well-characterised, were investigated by ESR.
- Natural samples exhibit weak signals in the area of the spectra connected with the trapped charges used for dating.
- Signals generally considered suitable for dating, such as isotropic CO_2^-, orthorhombic CO_2^-, isotropic SO_2^-, axial SO_3^- were identified in the irradiated samples and separated using ESR simulations.
- Simulations allow for quantifying individual components of the spectrum and avoiding interference from overlapping signals.
- Dose response curve for CO_2^- orthorhombic signal in MODIS 1-2 < 500 μm sample was plotted and yielded D_E = 26.80 ± 4.11 Gy
- Based on the D_E and the expected age of MODIS 1-2 sample, the dose rate for calcite was estimated as 8-10 Gy/ka, in the upper part of the range reported for quartz aggregate in mortars.
- **Establishing ESR as a new method of dating historical carbonate binders will allow us to overcome the difficulties of the currently used approaches.**
- **ESR studies of anthropogenic carbonates will extend the time range of ESR dating closer to the present.**

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