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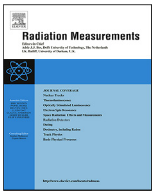

Electron Paramagnetic Resonance and petrographic analysis for dating Mesolithic and Neolithic pottery from Al Khiday (Sudan)

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HIGHLIGHTS

- Radiation-induced defects in prehistoric pottery were detected through pulsed EPR.
- Paleo-dose estimation in pottery through pulsed EPR was tempted.
- A correct trend of signal intensity vs. irradiation dose was obtained.
- Pulsed EPR paleo-dose was overestimated compared to SAR-TL.
- A relationship between quartz grain-size and signal intensity was found.

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ABSTRACT

Electron Paramagnetic Resonance (EPR) dating, like luminescence techniques, is based on the time-dependent accumulation of trapped charges at mineral defect centres. However, Fe(III) ions prevent the common Continuous Wave (CW-EPR) approach for dating pottery, which always contains iron. The Pulsed method (ED-EPR) allowed this limitation to be overcome, with recording of radiation-induced defect signals, as shown by increased signal intensity after artificial irradiation of samples. The method was applied to studying Mesolithic and Neolithic pottery from Al Khiday (Central Sudan), characterized by quartz-rich tempers and coming from dated contexts. As the occurrence of a natural ED-EPR signal was found to be related to the quartz grain size of the temper, a petrographic study was carried out. This first attempt at age determination of pottery by ED-EPR meant that experimental conditions and important parameters could be taken into account in developing a new dating procedure.

1. Introduction

Stylistic examination of shapes, surface treatments and decorations is the first and oldest method used for dating pottery. Recognizing stylistic changes through time or other attributes, and detecting variation trends is largely adopted for establishing relative chronology of artefacts (Bonsall et al., 2002). But this approach is empirically derived and does not provide by itself absolute ages. Different methods to the chronological topic are possible, being all functional to dating specific moments of the lifetime of a ceramic object, as the manufacture, the use or the burial. The choice of an absolute dating technique is in fact related to the archaeological event for which an age is required, as well as to the availability in terms of type and quantity of the material suitable for the specific analysis (Wagner, 1998). The radiocarbon dating on pottery is possible only in few cases, since it can be applied only in presence of organic residues, as food (Stott et al., 2003), and charcoal or seeds occurring in the ceramic surface or paste, respectively. However, pottery rarely has an organic content that could form a basis for radiocarbon dating, and when present there is always the risk of

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contamination by substances circulating in the soil and displacement of residues through the stratigraphic units. Especially in the case of buried artefacts, the migration of older or younger organic matter is a complication for radiocarbon age determination. In the absence of associated datable carbon-containing organic matter, pottery can be directly dated by other methods. A new approach is based upon the rehydroxylation (Wilson et al., 2009), a process which consists in the slow recombination of the fired clay material with the environmental moisture. But this dating method is strongly dependent from the mean lifetime temperature and humidity of the environment in which the sample was buried.

Archaeological pottery is often dated by luminescence methods, overall by thermoluminescence (TL) and Optically Stimulated Luminescence (OSL). These dating techniques are based on quantification of defects accumulating in quartz crystals and caused by radiation emitted during the decay of radioactive elements in the soil in which the pottery was buried (external exposure) or in minerals composing the ceramic paste itself (internal exposure). In more detail, in non-conductive minerals such as quartz, ionizing radiation due to the radioactive decay is responsible for producing free charges which can be trapped at lattice defects (Aitken, 1985; Ikeya, 1993). The number of trapped charges (called centres) is proportional to the dose to which the crystal was exposed to. Since the decay is time dependent, the quantification of the centres can be linked to the age of the material, going back to the beginning of accumulation. The phenomenon of luminescence (Aitken, 1985) is produced during recombination of trapped electrons within the charged vacancies under thermal or optical energy stimulation. The main drawback of these techniques is that information regarding accumulated dose is lost when the samples are stimulated.

Another method based on similar principles is the Electron Paramagnetic Resonance (EPR). It differs from the luminescence methods in that it can detect paramagnetic centres non-destructively. EPR records the absorption of microwaves by unpaired electrons in an applied magnetic field without any recombination, and several measurements can be made on the same sample. EPR is well attested for age determinations in geology and palaeo-anthropology, although it cannot yet be applied to dating of recent materials such as archaeological artefacts (Rink, 1997). In particular, although EPR can be used in pottery dating, the presence of iron as a constituent of the ceramic paste represents an important limiting factor, due to the strong background recorded in Continuous Wave EPR (CW-EPR) spectra, overlapping the weaker radiation-induced signals. Several chemical treatments to eliminate the contribution of iron by dissolution have been tested, but none of them resulted to be very effective. Even when reduced, the iron background is recorded because of the sensitivity of EPR to small numbers of metal ions (Campos et al., 2011; Watanabe et al., 2008). Very innovative in this sense is the pulsed technique of Echo-Detected EPR (ED-EPR), which does not record the signals of transition metal ions according to their short relaxation times. The technique, only recently and preliminarily applied to archaeological pottery (Zoleo et al., 2011), has proved to be efficient in identifying radiation-induced defects and was tested here in order to verify its potential as a dating method, confirming the dependence of the signal on dose and testing its reliability in equivalent dose estimation.

In this research, a set of potsherds from a radiocarbon-dated archaeological stratigraphic sequence is studied by ED-EPR in order to define if the radiation-induced defects can be easily assessed and their measure used to date the pottery. The choice ended up on the Mesolithic and Neolithic pottery (Fig. 1) from the sites of Al Khiday (Khartoum, Sudan), since these ceramic materials both are old in age to guarantee that the EPR signal can be recorded (Mesolithic: 7050–6500 BC, Neolithic: 4450–4230 BC) (Salvatori et al., 2011; Salvatori, 2012), and the quartz-predominant pastes lack in mineral phases which can cause internal radiation and induce defects (Dal Sasso et al., 2014a). Also from an archaeological point of view, the possibility of dating pottery in a geographic region in which the old stratigraphic sequences were disturbed by Meroitic and post-Meroitic graves and partially eroded from the action of wind, represents an important goal in the absolute chronology of the prehistoric sequence. Moreover, the arid climate conditions which characterise this region from the sixth millennium BC (Williams et al., 2015) and the post-depositional diagenetic processes, mainly related to the consumption of organic matter (collagen in bones, and organic residues) and the precipitation of secondary phases (calcite and manganese oxides) (Dal Sasso et al., 2014b), make the dating difficult, if not impossible. Fortunately, in the case of Al Khiday sites, the well preserved stratigraphic sequence allowed us to define both a relative and absolute chronology (radiocarbon dates on charcoal and shells) (Salvatori et al., 2011), so that the ceramic materials can be linked to specific phases of life of these sites.

The study was therefore addressed to the applicability of ED-EPR analysis to date archaeological pottery and to understand the influence of the textural feature of the ceramic paste, especially of the inclusion grain size in the accumulation of defects and therefore on the quality of the ED-EPR signal.

2. Materials and methods

Eleven prehistoric potsherds from the archaeological site 16-D-5, located on the western bank of the White Nile at Al Khiday (Omdurman, Khartoum, Central Sudan) were studied. The site revealed an extraordinary situation: a desert archaeological environment with materials still preserved in their original stratigraphic deposit (Usai et al., 2010; Salvatori et al., 2011; Zerboni, 2011). Radiocarbon dating could be applied to these units, since materials such as charcoal and shells in primary deposits had never been disturbed after their deposition. The data allowed us to establish a reference chronology for the pottery samples. Petrographic analyses of a large number of samples (Dal Sasso et al., 2014a) provided an essential base for selecting the most suitable ceramic paste for testing the EPR technique. In detail, only quartz-rich ceramic pastes lacking mineral phases producing important internal radiation (e.g., feldspar) were chosen. Due to their very basic composition (quartz-predominant pastes) and ancient age, the pottery studied here represents the best choice for testing EPR. Five potsherds were chosen from Mesolithic stratigraphic units (7050–6500 BC) and six from Neolithic ones (4450–4230 BC) (Salvatori et al., 2011; Salvatori, 2012), in order to evaluate the applicability of EPR also to materials belonging to more recent prehistoric periods such as the Neolithic. After the external surface of the samples had been removed with a microdrill, they were carefully crushed in an agate mortar to break up the matrix and temper without damaging the quartz inclusions. Disrupted samples were then dry-sieved and EPR measurements were carried out on the most frequent grain-size fraction, as determined by petrographic analysis of 30 μm thin sections according to the method of Whitbread (1995). In order to describe the quartz grain-size distribution quantitatively, computerized analysis of digital images (DIA) was performed on a set of 5–6 images for each sample (covering almost the whole section of each) under a polarized light optical microscope in crossed-polar conditions. The images were then processed with the ImageJ graphic software package (1.44p National Institute of Health, USA). After pre-processing, all images were segmented by means of an unsupervised classification mode by MultiSpec (version 3.3, Purdue Research Foundation). Grey tones were assigned to a set of 25 arbitrary classes, covering the whole