



Chemical process to separate iron oxides particles in pottery sample for EPR dating

S. Watanabe^{a,*}, T.M.B. Farias^a, R.F. Gennari^a, G.M. Ferraz^a,
R. Kunzli^b, J.F.D. Chubaci^a

^a Instituto de Física, Universidade de São Paulo, São Paulo, Brazil

^b UNESP, Presidente Prudente, Brazil

ARTICLE INFO

Article history:

Received 9 November 2007

Received in revised form 19 February 2008

Accepted 19 March 2008

Keywords:

Dating

EPR

Chemical treatment

Brazilian ceramic

ICP-MS

ABSTRACT

Ancient potteries usually are made of the local clay material, which contains relatively high concentration of iron. The powdered samples are usually quite black, due to magnetite, and, although they can be used for thermoluminescence (TL) dating, it is easiest to obtain better TL reading when clearest natural or pre-treated sample is used. For electron paramagnetic resonance (EPR) measurements, the huge signal due to iron spin–spin interaction, promotes an intense interference overlapping any other signal in this range. Sample dating is obtained by dividing the radiation dose, determined by the concentration of paramagnetic species generated by irradiation, by the natural dose so as a consequence, EPR dating cannot be used, since iron signal do not depend on radiation dose. In some cases, the density separation method using hydrated solution of sodium polytungstate [$\text{Na}_6(\text{H}_2\text{W}_{12}\text{O}_{40})\cdot\text{H}_2\text{O}$] becomes useful. However, the sodium polytungstate is very expensive in Brazil; hence an alternative method for eliminating this interference is proposed.

A chemical process to eliminate about 90% of magnetite was developed. A sample of powdered ancient pottery was treated in a mixture (3:1:1) of HCl, HNO₃ and H₂O₂ for 4 h. After that, it was washed several times in distilled water to remove all acid matrixes. The original black sample becomes somewhat clearer. The resulting material was analyzed by plasma mass spectrometry (ICP-MS), with the result that the iron content is reduced by a factor of about 9. In EPR measurements a non-treated natural ceramic sample shows a broad spin–spin interaction signal, the chemically treated sample presents a narrow signal in $g=2.00$ region, possibly due to a radical of $(\text{SiO}_3)^{3-}$, mixed with signal of remaining iron [M. Ikeya, New Applications of Electron Spin Resonance, World Scientific, Singapore, 1993, p. 285]. This signal increases in intensity under γ -irradiation. However, still due to iron influence, the additive method yielded too old age-value. Since annealing at 300 °C, Toyoda and Ikeya [S. Toyoda, M. Ikeya, *Geochem. J.* 25 (1991) 427–445] states that E'_1 -signal with maximum intensity is obtained, while annealing at 400 °C E'_1 -signal is completely eliminated, the subtraction of the second one from 300 °C heat-treated sample isolate E'_1 -like signal. Since this is radiation dose-dependent, we show that now EPR dating becomes possible.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Iron is an element found in most of places on earth, particularly in sediments and clays. It is, therefore, expected that this element is to be found in smaller or larger amount in ceramics. Brazilian soil is very rich in iron minerals and most of ancient potteries found in this country contains relatively large amount of magnetite.

The presence of iron does not, however, preclude the dating by thermoluminescence (TL) and optical stimulated luminescence (OSL) techniques, although light output becomes smaller. On the other hand, Fe³⁺ EPR signal around $g=2.0$ is large enough to hide other signals, for instance, that of E'_1 -center contained in quartz grains. Hence, in most cases, EPR dating is not possible and it is not used in dating of ancient potteries.

Similar situation is seen in the EPR study of ionic crystals containing enough concentrations of Fe. For example, most of natural silicate minerals contain iron impurity in several hundreds of ppm concentration. The Fe³⁺ signal around $g=2.0$, very often interferes with other signal in this region.

* Corresponding author at: Instituto de Física, Universidade de São Paulo, R do Matão, Travessa R, 187, CEP 05508-090 São Paulo, SP, Brazil.
Tel.: +55 11 30916990; fax: +55 11 30312742.

E-mail address: watanabe@if.usp.br (S. Watanabe).



Fig. 1. A fragment of ceramics found in an archaeological site in Presidente Prudente, SP, Brazil.

2. Experimental

2.1. Sample

Fig. 1 shows a ceramic fragment of about 20 cm × 25 cm uncovered at archaeological site in the vicinity of the town of Presidente Prudente, Brazil. It was identified as PP. A ceramic piece was crushed and sieved in order to select grains size between 0.080 and 0.180 mm. This sample was used to obtain EPR spectrum. Fig. 2 shows the spectrum with a very large signal around $g=2.33$. It was interpreted being due to Fe^{3+} magnetic dipolar interaction [3]. Similar signal has been obtained in rhodonite [4], in which large amount of MnO, that is part of crystal lattice, presents Mn^{2+} dipolar interaction.

2.2. Chemical treatment

To eliminate iron particles, besides magnetic separation method (which is not very effective), bromoform and sodium polytungstate ($\text{Na}_6(\text{H}_2\text{W}_{12}\text{O})\cdot\text{H}_2\text{O}$) are also used. Both compounds are liquid with a density of circa 2.75 g/cm³. Since density of quartz is approximately 2.65 g/cm³ and the magnetite is around 5.16 g/cm³, with ceramic powders immersed in the liquid sodium polytungstate, quartz grains float and magnetic particles sink. Unfortunately, these

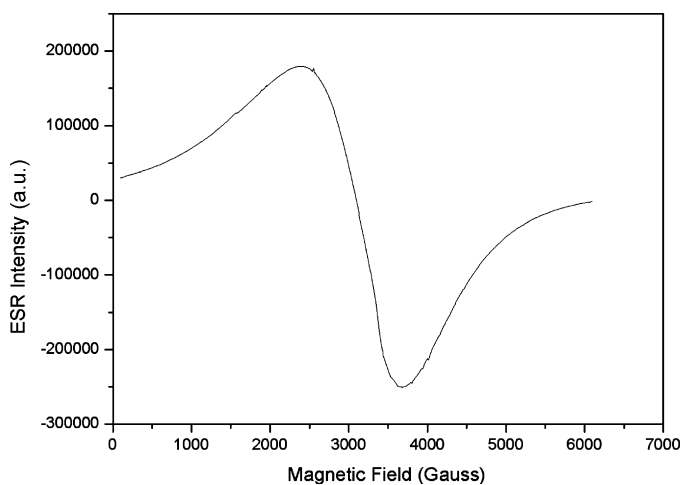
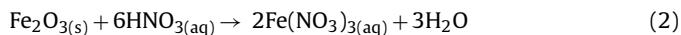
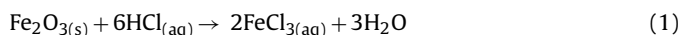


Fig. 2. EPR spectrum of a sample of PP showing a huge Fe^{3+} dipolar interaction of around $g=2.0$.

liquids are expensive for Brazilian standard; and besides that the bromoform is also hazardous to human health and for the environment.

There are in the literature several chemical methods for sample treatment (for instance [5–8]) however, many of them includes overnight steps. The main goal of this study is to propose a simple, relatively quick and cheap procedure so a chemical reaction procedure (CRP) to separate magnetite particles was devised. It is based on the two following reactions:



Hydrochloric acid is used because it has the formation constant of iron chloride higher than that of iron nitrate, however, the reaction (1) is not complete in the sense that, a considerable amount of iron oxide does not react with hydrochloric acid. The addition of nitric acid helps the effectiveness of the first reaction. Aqua-regia, a proportion of 3–1 of acids previously mentioned, in general, it is useful to leach or even digest the samples which contains high iron content. Despite that, hydrogen peroxide solution was added to eliminate the undesirable compounds which could be generated during aqua-regia treatment. Both iron salts are water soluble, therefore, they can be washed out.

Trace metal grade reagents (HNO_3 , HCl and H_2O_2) used are from Merck. All standards and sample solutions were prepared using high purity de-ionized water (Gehaka water system ($\Omega = 18.2 \text{ M}\Omega$)).

Around 700 mg sample of powdered ancient pottery was treated in a mixture (3:1:1) of $\text{HCl}(\text{conc.})$, $\text{HNO}_3(\text{conc.})$ and $\text{H}_2\text{O}_2(\text{conc.})$. The pulverized powder was firstly leached in 6 ml of the HCl solution, washed with high purity de-ionized water, then leached with 2 ml of HNO_3 solution, washed with high purity de-ionized water, leached with 2 ml of H_2O_2 solution, and finally washed several times in high purity de-ionized water to remove all acid matrixes. The sample was kept in each leaching solution for around 40 min. Different time periods were tested however, they were not effective or had caused a partial sample solubilization. The original black sample becomes somewhat clearer. The leaching procedure was done step by step instead of using the mixture of all acids together because the acid mixture causes a sample heating and this can affect the EPR signal.

The proposed CRP cannot be used for large mass of sample each time. It is limited to 1.5–2 g, since larger mass requires larger acid volumes and the sample had been rendered passive [9]. This phenomenon is not desirable once it promotes an appearance of a protective layer, so further reactions are not possible. Nevertheless, this chemical reaction process is much less expensive than the other methods already mentioned and separation is far more effective.

The chemical treatment always must be done before the dose irradiation once it eliminates the α and β particles. The presence of these particles increases the original accumulated dose, so an error on dating appears [1].

2.3. Instrumental apparatus

An electron paramagnetic resonance spectrometer (EPR-Bruker EMX RPE X range) was used. The EPR measurements were carried out using amplitude of 0.8 G, microwave power of 0.5 mW and operating at frequency of 100 kHz. Exactly 100 mg of powdered sample were inserted in the quartz sample cell (inner diameter between 4 and 5 mm and length of 270 mm), where the magnetic vector of the electromagnetic wave is a maximum.

For iron concentration determination it was used a plasma mass spectrometer (ICP-MS, PerkinElmer, Elan 6100). Iron content was

Download English Version:

<https://daneshyari.com/en/article/1233851>

Download Persian Version:

<https://daneshyari.com/article/1233851>

[Daneshyari.com](https://daneshyari.com)