Characterisation of grain extractions from Brazilian sand sediments using FT-IR, XRD, SEM/EDS, and ESR Methods

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1. INTRODUCTION

The characterisation of materials used in dating can be a great ally in further development, especially in ESR and OSL methods. Some of the main problems in dating by dosimetry are the dosimetric signal saturation and the repeatability of the results. Many of these problems may be related to the mineral types forming the sample and the impurities on the grain surface.

Therefore, the present study aimed to determine the chemical, physical, mineralogical characteristics of Brazilian sediment and the features of the paramagnetic centres.

2. SAMPLE AND METHODS

• Samples of sandy sediments are located in São Vicente on the coast of São Paulo state and were collected on the sand wall five kilometres from the nearest beach.

Figure 1 – The map shows the location of the collection point.

Figure 2 – The figure shows the sandy terrace wall.

• The grains were extracted by chemical treatment, optimized according to the composition of the sediment, and comprised the following stages: Attack with H_2O_2 (20%), HF (15%) and HCl (20%) (Figure 3a).

• The grains were further treated with EDTA solutions of 10-3 molar, pH 10 controlled by NH_4OH.

• The solution with EDTA and the grains were exposed to a 20 minutes ultrasonic bath at ambient temperature in a dark room and red light (Figure 3b).
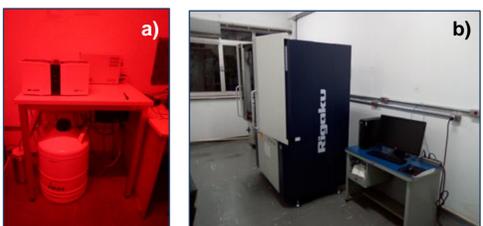

Figure 3 - The chemical treatment of the room and the red light.

Figure 4 - Spectrometer a) ESR b) XRD.

• The AMCSD and ICSD codes: quartz (62404); kaolinite (0017947); cerussite (0018859); palygorskite (9005566); titanite (0000500) and ferrihydrite (0012028).

3. RESULTS

The grains extracted from sediments were analysed using FT-IR methods. The spectrum shows fourteen vibration bands (Figure 5). A total of six minerals have been identified: quartz (777 cm-1), (1081 cm-1), (693 cm-1), (516 cm-1); kaolinite (3748 cm-1) and (3670 cm-1); cerussite (1384 cm-1); palygorskite (1631 cm-1); titanite (470 cm-1), ferrihydrite (1631 cm-1) and (693 cm-1) [1, 2, 3, 4, 5, 6].

Vibration bands of Si-O (1836 cm-1) bonds damaged by weathering effects have also been identified [2].
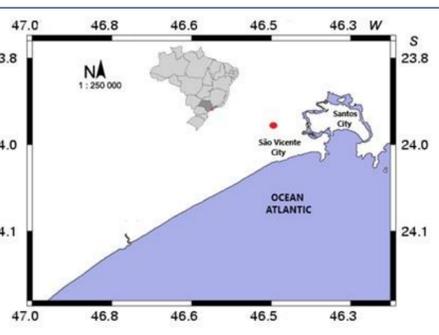

Figure 5 - FT-IR spectrum of grains.

Subsequently, the grain sample was investigated by XRD.

The minerals identified by FT-IR are used as candidates for the Rietveld refinement method (Figure 6).

Rwp and GOF values assess the quality of improvements. The refinement presented excellent accuracy. The values of these factors were less than 10% and 4%, respectively [7].

The refined Diffractogram shows that the grains extracted from sediments comprise 97% Titanite, 2.7% Quartz, and 0.3% other minerals.

Figure 6 - Diffractogram of grains.
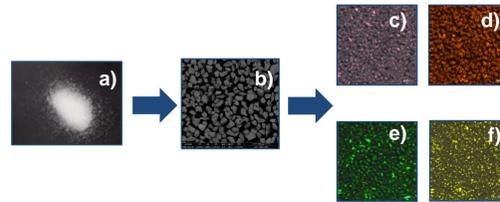
Figure 7 - Chemical mapping (SEM/EDS) of the grains sample (H_2O_2, HF and HCl) treatment (a) grains, (b) SEM grains image, (c) Ti, (d) K, (e) Ca and (f) Fe on the surface.
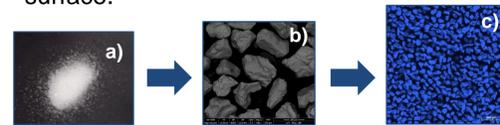
Figure 8 - Chemical mapping (SEM/EDS) of the grains sample (H_2O_2, HF, HCl and EDTA) treatment (a) grains, (b) SEM grains image and (c) Si.

The ESR method of grains (H_2O_2, HF, HCl) can identify the titanite and E'1 defects centres (Figures 9 and 10).

Figure 9 shows the spectrum of Fe^{3+} and V^{4+} paramagnetic centres [8].

Figure 10b shows the spectrum of the paramagnetic centre E'1. Furthermore, it was inversely observed that E'1 was correlated with the added gamma dose in the laboratory (Figure 10a).

SEM/EDS maps of the chemical composition surface were used. This component found the existence of iron (Figure 7f), calcium (Figure 7e), potassium (Figure 7d), and titanium (Figure 7c) on the surface of grains. The electron-beam range of the SEM is 10 nm.

After the chemical treatment of EDTA grains, chemical maps of the grain's surface were made (Figure 8). Fe, Ti, K, and Ca are absent. Silicon (Si) is the only element observed in the SEM/EDS method.

Figure 9 – ESR spectrum of Titanite centre.

Figure 10 – ESR spectrum of E'1 centre.

• The ESR spectrometer parameters for identifying the centre of titanite are 0.1mT field, 10mW microwave power, and 100 to 600 mT scan.

• The parameters were used to identify the paramagnetic centre E'1: field of 0.05 mT, microwave power of 0.001 mW, and scan from 335.5 to 339.5 mT.

• Parameters of the diffractometer: Angular range of 10 to 60° with a step of 0.02° and angular speed of 0.4°/min.
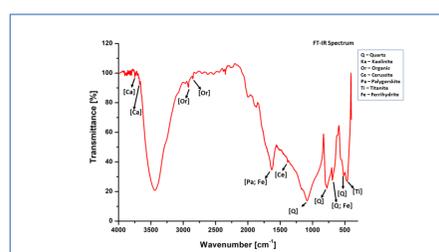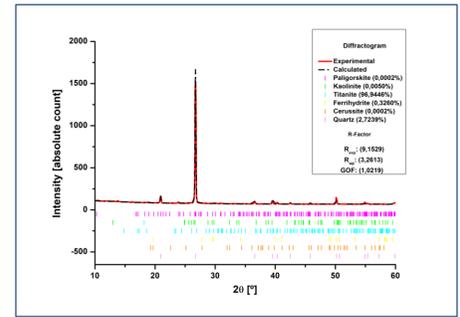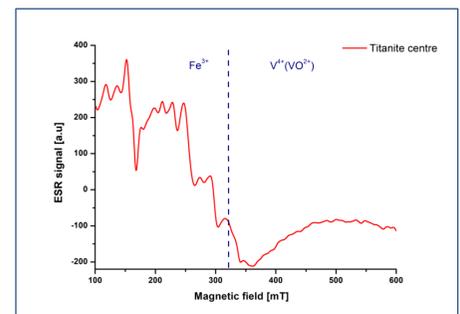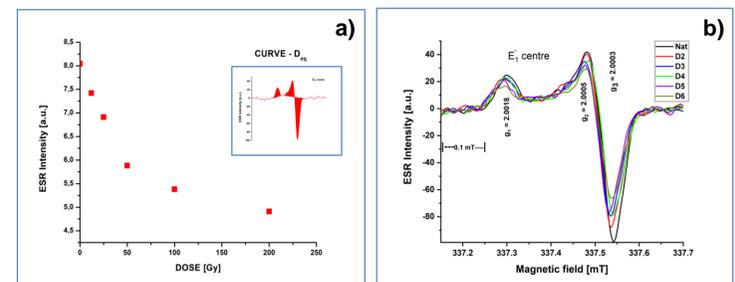
4. CONCLUSIONS

The FT-IR spectrum shows six minerals (quartz, ferrihydrite, cerussite, titanite, palygorskite and kaolinite). The mineral has been quantified, indicating that the grain samples are mainly formed through titanite. The grain's surface (depth of 10 nm) is composed of Fe, Ca, Ti, and K elements. The EDTA solution has shown efficiency in extracting chemical elements. The paramagnetic centre of the Titanite has been identified. The E'1 signal is inversely proportional to the addition of gamma dose. Therefore, the chemical characterisation of grains has proven to be very important in determining mineral dates. Chemical treatments using EDTA are being studied to analyze grain using the OSL dating method.

5. REFERENCES

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