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# TL dating of sediments from Ilha do Mel, Brazil

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## article info

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## **ABSTRACT**

Twelve samples of sediments collected from Ilha do Mel in the eastern coast of the State of Paraná have been dated using thermoluminescence (TL) technique. Assuming that sunshine exposure zeroed the previously induced TL, somewhat overestimated ages have resulted. Residual TL has been inferred for each of the samples from laboratory UV bleaching and also from sunlight bleaching. The correction carried out using the ratio between naturally accumulated TL-value, TL<sub>0</sub>, and the residual TL<sub>p</sub>, has resulted in geologically expected ages for the sediment samples.

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## 1. Introduction

Ilha do Mel is located at the mouth of the Baía de Paranaguá estuarine complex at  $25^{\circ}$ S along the southern Brazilian coast ([Fig. 1\)](#page-1-0). The island is constituted by two geological-geomorphologic domains: (a) Precambrian to Mesozoic igneous and metamorphic rocks, which form the hills; and (b) Quaternary sand deposits, which form the coastal plains. According to [Angulo and](#page-7-0) [Souza \(2005\),](#page-7-0) the paleogeographic evolution of Ilha do Mel could be reconstructed from the Late Pleistocene. At the last interglacial maximum, when sea-level reached  $8 \pm 2$  m above the present level ([Martin et al., 1988\)](#page-7-0), the island was reduced to a rocky archipelago with a small sedimentary terrace between two rocky hills. During the last glacial period, the sea-level lowered more than 100 m and the island was attached to the mainland. During the postglacial period, the sea-level rose at high rates (ca. 10 mm/y) until  $8000-$ 7000 years before present (BP), and subsequently the rates diminished significantly  $(1.0-3.3 \text{ mm/y})$  [\(Pirazzoli, 1996](#page-8-0)). Since that time, the sea-level at southeast Brazilian coast has changed only 2-4 m [\(Angulo et al., 2006\)](#page-7-0). Sea-level stabilization allows the building up of coastal plains at positive sedimentary balance areas. Therefore, the ages of southeastern Holocene coastal plains of Brazil are younger than 7000 BP ([Angulo et al., 2006](#page-7-0)). The same is true for the Ilha do Mel Holocene coastal plain. [Angulo and Souza \(2005\)](#page-7-0) recognized five progradational Holocene stages [\(Fig. 1\)](#page-1-0). The morphology and spatial distribution of foredune-beach ridges suggest that during stages 2 and 3, progradation occurred mainly from west to east [\(Fig. 1\)](#page-1-0).

This work presents the dating of 12 samples collected from Ilha do Mel. These sediment deposits were chosen as they can help to reconstruct the latest Quaternary history of Ilha do Mel.

## 2. Materials and methods

Twelve samples have been collected for dating using 100 cm long and 5 cm diameter PVC tubes. Ten samples were taken from the cliffs along the northwestern and southwestern coasts of the island (Figs. [1](#page-1-0) and [2](#page-2-0)a). Two samples were taken from an outcrop of the dune ridge between the Morro do Miguel and Morro do Meio hills at the southern part of the island [\(Fig. 1\)](#page-1-0).

The samples were taken from three different sedimentary facies: massive sand (Sm), low-angle cross-stratified sand (Sl), and sigmoidal cross-stratified sand (Ss). These three facies were interpreted as deposited in different sedimentary environments: foreshore, flood tidal delta, foredune, and aeolian dune [\(Table 1](#page-1-0)). Sl facies is characterised by thick tabular and wedge-shaped beds, composed of fine to very fine and well to very well-sorted sand, and corresponds to the swash cross-stratification at the beach swash zone of the foreshore [\(Fig. 2](#page-2-0)b). Ss facies is characterised by thick tabular beds composed of fine to very fine, moderate- to wellsorted sand, and corresponds to straight-crest subaqueous dunes of a flood tidal delta [\(Fig. 2](#page-2-0)c). Sm facies is composed of fine to very fine well-sorted sand and corresponds to aeolian dunes identified







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<span id="page-1-0"></span>

Fig. 1. Location of the study area: (1) Hills supported by igneous and metamorphic rocks; (2) Pleistocene sedimentary terrace; (3) Holocene coastal plain; (4) foredune-beach ridges alignments; (a-e) older to younger Holocene stages of island progradation (after [Angulo and Souza, 2005\)](#page-7-0). 1 to 12 sample location.

by morphological characteristics (samples IM08, IM11 and IM12, [Fig. 2d](#page-2-0)) or to a pedogenetic horizon where sedimentary structures were eliminated by eluvial processes (sample IM01, [Fig. 2a](#page-2-0)). The samples were taken from E (eluvial), Bh (spodic), and C (Espodossolo) horizons. The E horizon is characterized by white structureless sand (sample IM01), the Bh horizon by brown sand with organic matter and iron sesquioxides, and the C horizon corresponds to white Sl sand sedimentary facies (sample IM07). The depth from the sample to the coastal plain surface that corresponds to the top of the original depositional surface was between 0.8 and 3.0 m (Table 1).

Sediment from the ends of each tube was discarded. About 50 g of the sample to be used for thermoluminescence (TL) measurements was dried and sieved to retain grains with diameters between 0.080 and 0.180 mm. These grains are natural and did not result from crushing of larger grains. These grains were subjected to chemical treatment to separate quartz grains. A wide range of concentrations of  $H<sub>2</sub>O<sub>2</sub>$ , HF and HCl acids and reaction times have been reported in the literature for the extraction of quartz. In the present study, it was decided to evaluate the efficacy of a method which uses these acids. [Watanabe et al. \(2008\)](#page-8-0) have concluded that the optimum reaction time when using a solution of 40% HF and







<sup>a</sup> The pairs of samples IM-03-04, 05-06 and 07-08 were collected at the same places at different depths.

b Depth is referred to the terrace surface that corresponds to the original depositional.

<sup>c</sup> Sm: massive sand; Sl: low-angle cross-stratified sand; Ss: sigmoidal cross-stratified sand.

<sup>d</sup> E: eluvial, Bh\*: spodic with incipient illuviation, Bh\*\* spodic well developed, C: parent material.

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Fig. 2. (a)- Cliff at the northwestern coast of the island where sample IM01 was taken (for location see [Fig. 1](#page-1-0)). Notice the white structureless sand of the eluvial (E) horizon where the sample was taken and de brown low-angle cross-stratified sand of the spodic horizon (Bh). (b)- Cliff at the southeastern coast of the island where sample IM07 was taken (for location see [Fig. 1](#page-1-0)). Notice the low-angle cross-stratified sand and the Espodossolo horizons: A, E, Bh and C. (c)- Cliff at the southeastern coast of the island where sample IM03 was taken (for location see [Fig. 1\)](#page-1-0). Notice the sigmoidal cross-stratified sand facies (Ss) corresponding the de paleo-flood tidal delta where the sample was taken, the low-angle crossstratified sand facies (Sl) and the well developed Bh horizon. (d)- Paleo-foredune where IM08 sample was taken. Notice the white structureless sand (for location see [Fig. 1](#page-1-0)).

37% HCl is 40 min. The present work utilized this method for extraction of quartz grains. The additive dose method was utilized for the evaluation of accumulated dose  $(D_{ac})$  (paleodose or equivalent dose).  $D_{ac}$  was also evaluated using  $(TL)_{ac}/TL_{u}$  where  $TL_{u}$ stands for TL value of the sample for unit dose.

The recommended procedure to evaluate annual dose rate (Dan), is to bury TL dosimeters in places where the sediment samples have been collected. In the present study, however, <sup>238</sup>U,  $232$ Th and  $40$ K- concentrations were measured using an ICP-MS mass spectrometer. Table 4.5 of [Ikeya \(1993\)](#page-7-0) was used to determine the annual dose rate. It was assumed that there was no interference in the equilibrium condition of radioactive decay of radioactive series due to any geological or climate change conditions since the beginning of sediment formation. Table 4.5 ([Ikeya,](#page-7-0) [1993\)](#page-7-0) was prepared taking into consideration the contribution of each daughter element in the series, such that the desired dose is known if the first radionuclide concentration of the series is known. Alpha contribution was not considered in the dose evaluation, as 40% HF etch was used in the preparation of the samples. As the largest grain size is 0.18 mm, the attenuation of  $\beta$ -rays was not considered. As all the samples have been collected at depths less than 100 cm below the surface, no attenuation has been considered for the cosmic ray contribution, about 0.25 mGy/y at sea level.

TL measurements were carried out using the Daybreak 1100 TL Reader. A heating rate of 4  $C^{\circ}/s$  was used for all TL measurements. An average of 4 mg was used for every reading. The intensity of the laboratory UV radiation was measured with a Delta OHM HD 9021 digital radiometer coupled with different sensors for the measurements of UV-A, UV-B and UV-C in the range of 315-400 nm,  $280-315$  nm and  $200-280$  nm, respectively.

ICP-MS analysis of the elements Na, K, Al, Ca, Ti and Fe, in weight %, was carried out for samples IM03 through IM12. Several other elements were found in less than 200 to 100 ppm concentrations. The largest concentrations of K (about 5 wt %) and Ca (about 2.2 wt %) were found in IM04. IM04 was divided into three parts, one for HCl etch and two others for 10% and 40% HF etch, followed by ICP-MS analysis.

For  $D_{\text{ac}}$  evaluation by additive method, eight portions (each one about 40 mg) of each sample were irradiated to 5, 10, 20, 50, 100, 125, 150 and 200 Gy gamma ray doses, and their TL-values were measured.

## 3. Results

[Fig. 3](#page-3-0) shows the TL glow curves for the sample IM03 which has been irradiated to different doses from 5 Gy to 200 Gy. Each glow curve represents an average of five measurements. The TL response of the samples IM03 and IM12 with radiation doses measured using the high temperature TL peak is given in [Fig. 4](#page-3-0). From these dose

<span id="page-3-0"></span>

Fig. 3. Glow curves of IM03 irradiated to 5 up to 200 Gy gamma-rays with peaks around 150, 220 and 350  $\degree$ C.

response curves, the respective accumulated doses have been estimated for the IM03 and IM12 samples.

Annual dose rates,  $D_{an}$ , have been estimated using the uranium, thorium and potassium concentrations derived from ICP-MS experiments. In these estimates, the cosmic ray contribution has been added.  $D_{ac}$ ,  $D_{an}$  and ages of samples are given in Table 2. The ages shown in the third column are somewhat overestimated as compared to geological ages. This overestimation is due to residual TL, which each sample exhibits after bleaching due to sunlight exposure. It is therefore essential to estimate this residual TL for each sample by exposing them to long term exposure to sunlight as well as exposure to ultraviolet light from a calibrated 60 W mercury lamp in the laboratory.



Fig. 4. TL response curve vs. radiation dose of the samples IM03 and IM12 to find the accumulate dose,  $D_{ac}$ . Each point represents an average of five measurements.

The UV source has three components: UV-A (315-400 nm), UV-B (280 $-315$  nm) and UV-C (200 $-280$  nm). At point E in [Fig. 5](#page-4-0), the energy of these components is 0.152  $W/m^2$ , 0.269  $W/m^2$  and 8.09  $W/m^2$  for UV-A, UV-B and UV-C components respectively. A board with a 2 cm hole was placed such that the sample at E was exposed to UV through this hole. In a separate experiment, an optic filter that absorbs UV-C component of light was placed in the hole.

[Fig. 6](#page-4-0) shows the solar spectrum outside Earth's atmosphere, spectrum on the Earth's surface at sea level, and a black body spectrum [\(Seinfeld and Pandis, 1998](#page-8-0)). This is referred as the standard reference spectrum. The solar spectrum changes throughout the day and also with location and the time of the year. The solar UV components below 300 nm are very small, and the largest parts lie in the interval  $315-400$  nm.

## Table 2

Accumulate dose, annual dose and age (years before present) with and without  $TL<sub>r</sub>$  into account.

Sample	$U$ (ppm)	Th (ppm)	$K(\mathcal{X})$	$D_{ac}$ (Gy)	$D_{an}$ (mGy)	Age (without $TLr$ )
<b>IM01</b>	$0.08 + 0.01$	$0.32 + 0.04$	$1.27 + 0.22$	$21.9 + 1.5$	$3.8 + 0.3$	$5754 + 500$
<b>IM02</b>	$0.05 + 0.01$	$0.26 + 0.03$	$2.15 + 0.38$	$35.2 + 2.5$	$3.8 + 0.3$	$9273 + 650$
IM <sub>03</sub>	$0.04 + 0.01$	$0.06 + 0.01$	$2.41 + 0.43$	$31.7 + 2.3$	$3.8 \pm 0.3$	$8324 + 650$
<b>IM04</b>	$0.18 + 0.02$	$0.53 + 0.06$	$3.53 + 0.63$	$29.5 + 2.1$	$6.1 + 0.5$	$4806 + 350$
<b>IM05</b>	$0.13 + 0.02$	$0.24 + 0.03$	$1.03 + 0.18$	$26.7 + 1.8$	$3.3 + 0.3$	$8095 \pm 600$
<b>IM06</b>	$0.03 + 0.004$	$0.09 + 0.01$	$2.33 + 0.42$	$24.2 + 1.6$	$3.8 + 0.3$	$6367 + 450$
IM <sub>07</sub>	$0.09 + 0.01$	$0.07 + 0.01$	$0.82 + 0.14$	$17.9 + 1.5$	$3.0 + 0.2$	$5980 + 520$
<b>IM08</b>	$0.06 + 0.01$	$0.43 + 0.05$	$1.35 + 0.24$	$16.2 + 1.4$	$4.4 + 0.4$	$3675 + 250$
<b>IM09</b>	$0.03 + 0.004$	$0.03 + 0.003$	$1.42 + 0.26$	$26.4 + 1.8$	$3.2 + 0.3$	$8178 + 600$
<b>IM10</b>	$0.11 \pm 0.01$	$0.14 + 0.02$	$2.47 + 0.44$	$15.5 + 1.1$	$4.1 + 0.3$	$3795 + 220$
<b>IM11</b>	$0.12 + 0.01$	$0.83 + 0.10$	$1.68 + 0.30$	$39.2 + 2.2$	$3.7 + 0.3$	$10.675 \pm 850$
IM12	$0.17 \pm 0.02$	$0.17 \pm 0.02$	$1.83 \pm 0.33$	$33.4 \pm 2.4$	$2.7 \pm 0.3$	$12.344 \pm 900$

## 4. Residual TL measurements

Solar radiation bleaching of sediment erases previously induced TL. However, a residual TL persists which cannot be removed by solar radiation, and this affects the dating result, leading to an overestimation of ages. To understand the presence of residual TL, bleaching was conducted using a 60 W fluorescent mercury lamp which has been calibrated with a Delta OHM HD 9021 [\(Fig. 5\)](#page-4-0).

The accumulated dose,  $D_{ac}$ , is obtained from the triangle ABO shown in [Fig. 7.](#page-4-0) Here,  $BO = TL_0$ , the TL value of the as received sample,  $AO = D_{ac}$ ,  $BC = TL<sub>r</sub>$ , the residual TL. The accumulated dose after corrected for the residual TL is obtained from the following equation:

$$
D_{a,c,r} = D_{a,c} \frac{T L_0 - T L_r}{T L_0} = D_{a,c} \left( 1 - \frac{T L_r}{T L_0} \right)
$$
 (1)

<span id="page-4-0"></span>

Fig. 5. Fluorescent Hg lamp, 60 W, used for UV bleaching of sediments.

#### 4.1. Results of  $TL<sub>r</sub>$  measurements

Fig. 8 shows the residual TL glow curve of the natural IM07 sample after exposure to laboratory UV light for 24 h (Fig. 8a) and the curve of the chemically treated IM07 sample exposed for 24 h to laboratory UV light (Fig. 8b). The figure also shows the curve of the natural IM07 sample after exposure to sunlight for 24 h (Fig. 8c).

The residual TL glow curve of the natural IM08 sample after exposure to laboratory UV light for 24 h is shown in [Fig. 9a](#page-5-0). [Fig. 9b](#page-5-0) shows the residual glow curve of the IM08 sample after 24 h exposure to sunlight. The residual glow curve of the IM08 sample irradiated to 500 Gy  $\gamma$ -rays and later exposed to laboratory UV light for 24 h is displayed in [Fig. 9](#page-5-0)c.

[Fig. 10](#page-5-0) shows the residual TL glow curve of the natural IM09 sample after exposure to laboratory UV light for 24 h ([Fig. 10](#page-5-0)a) and also the residual glow curve of the natural IM09 sample subjected to 24 h exposure to sunlight [\(Fig. 10](#page-5-0)b).

[Fig. 11](#page-5-0) shows the residual TL glow curves of the natural IM03 sample irradiated to 500 Gy  $\gamma$ -rays and then exposed to laboratory UV light for 15, 60, 120, 180 and 300 min, and a plot of the residual TL intensity as a function of exposure time to laboratory UV light. This curve was fitted to the equation:  $y = y_0 + A \exp(-R_0 \cdot x)$ , where  $R_0$  is the decay rate per minute; t is the exposure time,  $y_0$  is the residual TL after more than 300 min.

The shapes of glow curves of laboratory UV light irradiated sample and sunlight bleached samples are different. They differ as sunlight bleaches low temperature peaks. A difference is observed



Fig. 6. Solar spectrum outside the atmosphere and at Earth's surface taken from the work of [Seinfeld and Pandis \(1998\)](#page-8-0).



Fig. 7.  $D_{ac}$ -and  $D_{ac}$ -values in the additive method: TL<sub>0</sub> = BO is the TL-value of the natural sample given by 350 °C peak;  $BC = TL$  is the residual TL-value.

in the 330 $\degree$ C peak height. The residual peak is larger under sunlight bleaching. [Fig. 9c](#page-5-0) shows that the residual peak of 500 Gy gammaray irradiated sample is larger by a factor 9 compared to the laboratory UV bleached sample and by a factor 5 compared to the sunlight bleached sample. Chemical treatment is found to increase the residual TL peak slightly. [Fig. 11](#page-5-0) shows the decay curve of the 500 Gy irradiated peak submitted to UV light for times varying from 15 to 300 min. TL decays very rapidly in the first  $120-180$  min. For later times, it is observed to be almost constant. Therefore, the observed TL after five hours bleaching with UV light is considered as the residual TL.

The following experiments were subsequently carried out. In the first experiment, a board with a 2 cm diameter hole to focus the UV beam on to the sample was used. In the second experiment, an optical filter that absorbs UV-C light was inserted in the hole. [Fig. 12](#page-5-0)



Fig. 8. (a) Glow curve of the sample IM07 bleached in the laboratory UV light for 24 h, (b) of the same sample now chemically treated and bleached also in the laboratory light, (c) of the sample IM07 bleached in sunlight for 24 h.

<span id="page-5-0"></span>

Fig. 9. Glow curves of IM08: (a) bleached in the laboratory UV light, (b) bleached in sunlight, (c) irradiated to 500 Gy gamma-rays and then bleached in laboratory UV light.

shows the residual TL glow curve of a sample exposed to UV light at position E. It also shows the glow curve of the sample illuminated with focused UV light and the glow curve obtained after using a UV-C filter. The glow curve of a sample which has not been exposed to light is added for comparison.

Laboratory UV light produces residual low and high temperature peaks, whereas sunlight produces only a high temperature residual peak with an intensity which is about three times greater. The filtered UV light produces a low temperature as well as a high temperature residual TL peak, which are closer to the sunlight produced residual peak.



Fig. 10. Glow curves of IM09: (a) after 24 h exposure to laboratory UV light, (b) after 24 h exposure to sunlight.



Fig. 11. Glow curves of the sample IM03 irradiated to 500 Gy gamma-rays and then bleached in the laboratory UV light for 15 up to 300 min. In inset, the 350  $\degree$ C TL peak height as function of the time of exposure to UV light.

## 4.2. Corrections due to residual TL values

The residual TL values obtained by bleaching samples using laboratory UV light were used to determine the corrected ages. The residual TL-values, TL<sub>r</sub> and the corrected ages are listed in [Table 3.](#page-6-0) Long-duration exposure to sunlight of IM07, IM08 and IM09 was carried out. Their residual TL-values obtained by bleaching by laboratory UV light as well as sunlight are given in [Table 4](#page-6-0). There is a considerable difference between the two values. Peak height values as well as areas under glow curves show that sun bleaching leaves larger residual TL. Sunlight retains only high temperature TL



Fig. 12. Glow curve of IM03 sample: (a) as received; (b) Bleached in laboratory bare UV light for 10 h; (c) Bleached in laboratory UV light collimated thought a 2 cm diameter hole drilled in a board; (d) Bleached in laboratory UV light with an optical filter that absorbs 180-200 nm light.

<span id="page-6-0"></span>peaks, while laboratory UV light also retains the low temperature peaks. In order to calculate the ratio  $(TL_f/TL_0)$  for age correction, peak height has to be used in one case and the area under the glow curve in the other. The corrected ages of samples IM07, IM08 and IM09 are given in Table 5.

#### Table 3

Ratios between TL<sub>r</sub> and TL<sub>0</sub>; correction factor  $1 - (TL_r/TL_0)$ ;  $D_{ac,r}$  and age corrected for TLr. TLr here refers to residual TL after bleaching in the laboratory UV.

Sample	$TL_r/TL_0$	$1 - (TL_r/TL_0)$	$D_{\text{ac.r}}$	Age without TL,	Age with TL <sub>r</sub> (years)
<b>IM01</b>	0.53	0.47	$10.211 \pm 1$	$5754 + 500$	$2244 + 200$
<b>IM02</b>	0.53	0.47	$16.562 \pm 2$	$9273 + 650$	$4080 + 280$
IM03	0.36	0.64	$20.234 \pm 1$	$8324 + 620$	$5310 + 310$
<b>IM04</b>	0.15	0.85	$25.202 \pm 1$	$4806 + 350$	$4104 + 220$
<b>IM05</b>	0.25	0.73	$19.446 \pm 1$	$8095 + 600$	$5893 + 390$
<b>IM06</b>	0.16	0.84	$20.274 \pm 1$	$6367 + 450$	$5335 + 360$
IM <sub>07</sub>	0.34	0.76	$13.616 \pm 1$	$5980 + 520$	$4539 + 250$
<b>IM08</b>	0.75	0.25	$3996 + 1$	$3675 + 250$	$904 + 80$
<b>IM09</b>	0.28	0.72	$19.607 \pm 1$	$8178 + 600$	$5904 + 380$
<b>IM10</b>	0.10	0.90	$14.006 \pm 1$	$3795 + 220$	$3427 + 150$
<b>IM11</b>	0.06	0.94	$36.818 \pm 2$	$10.675 \pm 850$	$10.045 \pm 800$
<b>IM12</b>	0.15	0.85	$28.433 \pm 2$	$12.344 \pm 900$	$10.492 \pm 810$

#### Table 4

Residual TL-values of the samples IM07, IM08 and IM09.

Sample	Residual TL-values				
	Using peak heights (a.u.)		Using areas glow curve $(a,u)$		
	Lab. UV light	Sunlight	Lab. UV light	Sunlight	
$IM-07$	2.2	5.9	6.4	9.2	
$IM-08$	0.5	3.1	3.0	5.0	
IM-09	2.1	3.4	4.3	5.0	

#### Table 5

Ages (in years) of sample IM07, IM08 and IM09, corrected for residual TL-values obtained under 4 different conditions.

Samples	Laboratory UV bleaching		Solar bleaching		
	Peak height	Area/glow <b>CULLA</b>	Peak height	Area/glow curve	
$IM-07$	$4539 + 250$	$2110 + 160$	$837 + 70$	$383 + 28$	
$IM-08$	$904 + 80$	$977 + 150$	$1136 + 140$	$88 + 12$	
$IM-09$	$5904 + 380$	$5299 + 380$	$4972 + 370$	$4710 + 300$	

The residual TL process or UV bleaching effect on quartz grains is somewhat complex. Laboratory UV and solar UV light produce different glow curves. This is probably due to the fact that the UV-C component is much stronger in the laboratory lamp source, while the UV-A and UV-B components are stronger in sunlight. The UV-C acts on the low temperature peaks, so that in the laboratory UV bleached sample the residual TL of high temperature peak is smaller. UV-A and UV-B components act on low temperature peaks, hence in a sun-bleached sample these peaks are eliminated, but not in sample bleached in laboratory UV light. This result shows the limitation of using laboratory lamp source for residual TL determination. The residual TL measurement using laboratory UV source is far simpler. An attempt is underway to find an appropriate optical filter in the 200 nm region to simulate at least partly the solar UV light spectrum.

The solar bleaching carried out on three of the samples collected from Ilha do Mel has shown that the residual TL always diminished the age values. To determine whether the results obtained here would be observed in other sediment samples, future measurements will be conducted on sediments collected from different sites.

All the sediment samples from Ilha do Mel investigated here presented ages within the Quaternary after residual TL correction (Table 3), with sediment ages from 2200 years to 10,300 years. Each sediment has a different origin and, furthermore, it was exposed to solar radiation as indicated by the age found in the dating.

Two hypothesis have been made in the present study concerning the geological samples. The first hypothesis is that all 12 samples originated from the same kind of geological sediment. Each one was exposed to sunlight for different times due to varying weather conditions, leading to different ages. The second hypothesis is that some samples have originated from a different kind of geological material.

Chemical analysis has been carried out to find the main chemical elements that compose the samples using an ICP-mass spectrometer (Fig. 13). IM01 and IM02 were not included for technical reasons. Fe is found only in IM04, IM06, IM07, IM10, IM11 and IM12. IM04 contains large concentrations of Ca, Mg, Al and K. IM06 is very rich in Fe and Ti. IM03 and IM09 have similar compositions. This result seems to indicate that the materials from which these samples originated differ. In this context, it is necessary to extend analysis at Paranagua Bay in order to determine the nature of the location from which samples were collected.



Fig. 13. Concentration of some of the chemical elements as determined by ICP-MS mass spectrometer: (a) In w % and (b) In ppm.

#### <span id="page-7-0"></span>5. Discussion

[McKeever \(1985\)](#page-8-0) comments that, "undoubtedly the most innovative of the recent developments in the thermoluminescent age determination have centered upon the dating of sediments". Huntley and Johnson (1976) first observed that the natural thermoluminescence from the deep sea sediments increased with core depth. Since then many authors investigated and used the method for dating sediments. On the other hand as Aitken (1998) states in his book, "the prime motivation that led to the initial trial of optical dating (Huntley et al., 1985) was to achieve a better method of dating sediment than was possible with thermoluminescence". Optical dating based on OSL is in many senses preferred to TL dating. In OSL, dating quartz grains as well as feldspar grains is basic to the process, but in TL dating quartz predominates although feldspar can also be used. Therefore, zeroing the geological clock in the case of quartz grains should be based on the bleaching susceptibility of the quartz grains and the thermoluminescent behavior of the quartz grains with solar light. A typical glow curve of quartz has peaks at 110, 220, 325 and 375 $\degree$ C. The two last peaks at high temperatures very often appear superposed, and they are the ones of importance in dating. As [McKeever \(1985\)](#page-8-0) and Aitken (1998) pointed out and as shown by [Wintle and Huntley \(1980\),](#page-8-0) there is always a residual signal (denoted  $TL<sub>r</sub>$ ) even though the bleaching by sunlight is initially very rapid. Several authors, including Aitken (1998), have shown that the 325 °C TL peak is easy to bleach while the 375  $\degree$ C peak is hard to bleach. Therefore under solar or other light bleaching, a residual TL is expected, due mainly to the second peak.

Although OSL has some advantages over TL dating, we decided to use TL technique for the present work for two reasons. Firstly, we wanted to study the behavior of the residual TL under different conditions, and secondly the TL dating technique is still a good dating technique once the residual TL effect is taken into account.

The main part of the Ilha do Mel coastal plain is Mid- to Late-Holocene (Angulo and Souza, 2005). Hundreds of <sup>14</sup>C dates of Holocene southern Brazilian coastal plains, including areas near Ilha do Mel yielded maximum Holocene ages of 8000-7000 BP (Angulo et al., 2006). Therefore, it is plausible to infer the occurrence of similar ages in the Ilha do Mel coastal plain. The corrected sediment ages, after taking into account residual TL left in the samples collected from Ilha do Mel Holocene coastal plain (IM01 to IM10), are compatible with the geologically expected ages, younger than 8000-7000 BP. The ages of the three pair of samples taken at the same place at different depths (IM-03-04, IM-05-06 and IM-07-08) were older at the base and younger at the top, which is in accordance with the depositional sequence.

The paleo-geographical evolution of the island proposed by Angulo and Souza (2005) suggests that the Holocene coastal plain becomes younger eastward ([Fig. 1\)](#page-1-0). However, the TL ages of the ten samples of the Holocene coastal plain do not conform to this expected distribution. Therefore, more geological and geochronological studies are necessary to elucidate if the differences are related to dating techniques or to a more complex geological coastal evolution.

The Pleistocene terrace that occurred at the southern part of the island is covered by aeolian fixed dunes [\(Fig. 1](#page-1-0)). The sand dune ridge morphology suggests that the ridge is a remnant of a larger dune field that was eroded by waves during the 5800-5000 BP Holocene sea-level maximum (Ângulo, 1993). The dune ridge was built prior to the sea-level maximum. TL ages around  $9000-11,000$  BP of samples taken from dune ridge agree with this scenario and suggest that the dune ridge was building when sea was rising. This is a common scenario in many places around the world where transgressive dune fields were formed during postglacial transgression (Hesp and Thom, 1990; Hesp and Short, 1999).

[Watanabe et al. \(1997\)](#page-8-0) dated six sediment samples collected from depths of 10, 25, 50, 75, 310 and 410 m of Cananeia Island on the State of São Paulo coast, about 330 km south of São Paulo City. After washing with a solution of HCl and distilled water, very white quartz grains remained, and these were sieved to retain  $0.080-$ 0.180 mm size grains only. The paleodose (or accumulated dose  $D_{ac}$ ) was determined by the additive method using TL. An annual dose rate,  $D_{an}$ , of about 1.40 mGy/y was determined by gammaspectroscopy. Ages of 17.00, 57.41, 68.55, 77.01, 96.77 and 110.23 ka in order of depth of samples were obtained. This result indicates that the island of Cananeia is of Pleistocene age, but was formed in the course of more than 100 ka.

[Tatumi et al. \(1998\)](#page-8-0) used TL to date 20 samples of sediments of aeolian dunes on the margin of São Francisco River, about 200 km from the coast of the state of Bahia. After the usual procedure to prepare samples for TL dating, ages varying from 0.9 to 14.4 ka were obtained, indicating that the sediments are Late Holocene to Early Pleistocene.

## 6. Conclusions

In any sediment dating, the residual TL correction is always necessary. The residual TL-value must be obtained using sunlight bleaching of the sample. Unfortunately, the laboratory UV light produces residual TL-value quite different from sunlight bleaching. Residual TL-values in 24 h sun-bleached IM07, IM08 and IM09 are found to be very large. The residual TL-values in these samples bleached in laboratory UV light are also relatively large. OSL dating of these three samples will be carried out for comparison.

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