New ESR ages for Piano San Nicola site, Gulf of Taranto, Italy

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ABSTRACT At Piano San Nicola site (Basilicata region, southern Italy) four samples of Glycimeris sp. shells were collected from the uppermost fossiliferous stratigraphic level of one of the main Quaternary marine terraces of the Taranto Gulf, which extends across the external sector of the southern Apennines fold-and-thrust belt, the Bradano Foredeep and the Apulian Foreland. These samples were analysed using the Electron Spin Resonance (ESR) technique, applied for the first time to this area. The obtained new chronological results provided reliable absolute ages ranging between 40.4 ± 7.7 ka and 64.0 ± 11.2 ka, which are in good agreement with the datings known in literature and obtained by different chronological methods as well as palaeontological inferences. The absolute ages achieved by our study represent fresh evidence supporting the chronological correlation between the marine terrace where Piano San Nicola site is located (Policoro Terrace) and the Marine Isotope Substage (MIS) 3.3.

Key words: marine terraces, Pleistocene, sea-level changes, regional uplift, ESR dating.

1. Introduction

Piano San Nicola is a site well known among the geologists working on the morphotectonics of the Taranto Gulf, southern Italy, and particularly on the Late Quaternary coastal evolution of the region which represents a bridge between the external sector of the southern Apennines fold-and-thrust belt, the Bradano Foredeep and the Apulian Foreland (Fig. 1a). The Piano San Nicola site is indeed located on the top of one of the major marine terraces, which characterize the whole area with their classical staircase geometry (Vezzani, 1967; Boenzi et al., 1976; Brückner, 1980, 1982; Parea, 1986; Amato et al., 1997; Caputo et al., 2010).

Piano San Nicola is located about 6 km ESE from Nova Siri (Calabria) and consists of a flat slope gently degrading seawards (Fig. 1b). This wide surface represents a portion of a 70-km long marine terrace which was entirely mapped all along its length (Caputo et al., 2010). At this locality, the inner edge of the Policoro Terrace [as defined in Caputo et al., (2010)] is at an elevation of ca 85 m a.s.l.
Beyond these palaeontological constraints, the first numerical chronological information was provided by Dai Pra and Hearty (1992) who used the Amino-Acid Racemization (AAR) method for dating 6 samples of Glycymeris sp. collected at 43 m a.s.l. in a coarse-grained sandy layer belonging to the terrace deposits. Their laboratory analyses provided a mean D/L ratio of 0.29 ±0.02, which they associate with the so-called Aminogroup C. In this sector of the Mediterranean, Hearty et al. (1986) attribute the Aminogroup C to the marine isotope substage (MIS) 5.1 (80-85 ka) though the associated APK-ages (apparent parabolic kinetics; Mitterer and Kriausakul, 1989) are generally younger (52 and 74 ka; Hearty and Dai Pra, 1992). Similarly, based on the systematic comparison between D/L ratios and U-Th absolute ages obtained from several samples collected in a contiguous area (eastern Gulf of Taranto), Belluomini et al. (2002) propose an empirical relationship between D/L ratio and age, whose validity is tested for the period between 40 and 140 ka, therefore including the possible ages of the above samples. Accordingly, the application of the Belluomini et al. (2002) empirical relationship to the results of Dai Pra and Hearty (1992) from the Piano San Nicola site provides an absolute age of 54.2 ±6.5 ka, in any case, Caldara et al. (2003), associate D/L ratios between 0.20 and 0.31 to MIS 3. The latter ages obtained for the Piano San Nicola site are also in good agreement with those proposed from another site (La Petrulla), located ca 30 km to the north and belonging to the same marine terrace as documented by a detailed morphological mapping of the broader area (Fig. 1a; Caputo et al., 2010). It is worth mentioning that at La Petrulla site, ages have been obtained with different techniques. The first one was carried out by Brückner (1980) and based on U-Th isotopic analyses of Mollusc shells. The provided absolute age was 63.0 ±3.0 ka. More recently, Zander et al. (2006) analysed several samples from fine-grained sands using the OSL-IRSL method. They analysed samples at different stratigraphic positions, while the samples closest to the terrace surface yielded feldspar ages of 55.5 ±4.0 ka and 55.2 ±4.6 ka with the SAR (Single Aliquot Regeneration) and the MAA (Multiple Aliquot Additive) techniques, respectively.

In summary, different chronological approaches as well as palaeontological constraints independently support the correlation between the Policoro Terrace and the MIS 3.3 (Caputo et al., 2010). On the other hand, this correlation is also supported by other chronological and stratigraphic constraints available for both higher (see San Teodoro I, San Teodoro II and La Maddalena sites in Fig. 1) and lower terraces (see Fosso Marzoccolo site in Fig. 1a) belonging to the entire terrace suite developed across this coastal sector of the Taranto Gulf.

In this note, we provide and discuss the results of new absolute chronologies obtained from the analysis of Bivalve shells (Glycymeris sp.) collected at Piano San Nicola site and based on a different technique: the Electron Spin Resonance (ESR) spectroscopy.

2. ESR dating

2.1. Background

ESR spectroscopy is a technique that directly detects paramagnetic species, i.e., chemical species with unpaired electrons. The method has been widely used to date geological Mollusc shells that act as radiation dosimeters. Indeed, ESR dating is based on the measurement of radiation-induced paramagnetic centres in the shell carbonate crystal lattice by means of natural radiation. The ESR age is calculated by the ratio (Ikeya, 1993):

Chronological information for this site was provided by different authors. Moncharmont-Zei (1957) probably was the first to document a rich “banal” fossil fauna completely lacking any Senegalese affinity, the latter commonly used by many researchers as the principal proxy to attribute a (Eu)Tyrhenian age (e.g., Bordoni and Valensise, 1998; Cucci and Cinti, 1998; Ferranti et al., 2006).
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where $D_E$ is the equivalent dose representing the total accumulated dose in the shell from its formation up to the time of measurement, while the annual dose ($d$) is the rate at which this dose was absorbed by the shell. The former parameter is measured in gray [Gy], the latter in gray/annum [Gy/a]. The irradiation comes from the disintegration of uranium, thorium and potassium and their decay products contained in the shell itself and in the surrounding environment, plus cosmic radiation.

### 2.2. Sample preparation and ESR measurements

The analysed shells were firstly separated from the sediments used to calculate the external dose rate. Before performing the ESR measurements, the outer layer of each side (about 0.5 mm), which has absorbed the external alpha particle dosage, was carefully removed with a dentist drill. The shells were subsequently gently crushed and sieved to 100-200 μm. Finally, eleven aliquots of about 100 mg were prepared for each sample. Ten aliquots out of eleven were irradiated by a $^{60}$Co calibrated source at the Ente per le Nuove Tecnologie, l’Energia e l’Ambiente (ENEA Casaccia, Rome) using the following doses: 32, 63, 100, 132, 200, 320, 630, 1000, 1320, 1600 Gy. After irradiation the samples were transferred to ESR quartz tubes and spectra were recorded at PH3DRA Laboratories of University of Catania at room temperature with a X-band Jeol ESR spectrometer (Series JES FA-100). The spectrometer parameters are: central field 337.5 mT, scan width 8 mT, modulation amplitude 0.5 mT, modulation frequency 100 kHz, time constant 0.1 s and microwave power 2 mW.

### 2.3. Equivalent dose ($D_E$)

The equivalent dose $D_E$ values were estimated using the additive dose method (Ikeya, 1993) from the ESR peak at $g = 2.0007$. For each sample, ESR signal growth curve was obtained recording spectra of the 11 aliquots. All the ESR intensities were measured from peak-to-peak amplitudes of the selected signal and normalized by the aliquots weights. A Single Saturating Exponential (SSE) function was fitted to the experimental data points in order to get the $D_E$ value (Apers et al., 1981):

$$
I_{ESR} = I_s \left(1 - e^{-\left(D_s D_e\right)/D_s}\right)
$$

where $I_{ESR}$ is the measured ESR signal intensity, $D$ the laboratory added dose, $I_s$ the saturation level and $D_s$ the dose at 63% of the saturation value. $D_E$ was calculated by extrapolating the SSE function to the zero ordinate.

### 2.4. Annual dose rate ($d$) determination

In order to estimate the external and the internal dose rate, the concentrations of U, Th and K in the sediments as well as in the shells themselves were respectively determined by ICP-MS analyses carried out at the Ferrara University. The dose rate was then evaluated using the conversion factors of Adamiec and Aitken (1998) for α, β and γ radiations assuming secular equilibrium. The cosmic dose rate was calculated from the equation of Prescott and Hutton (1988). In calculating the internal dose rate, we neglected the internal γ-ray contribution since the shell is too thin to absorb the γ radiation emitted from the inside. For external dose rate...
determination, α-particles contribution was not considered since we removed the outer part of shells. Because the range of β particles is comparable with the thickness of the removed outer layer, a β attenuation correction factor has been used for estimating also the external contribution (Engin et al., 2006) and therefore calculating more correct ages.

3. Analytical results

Four samples of Glycimeris sp. shells were collected from the uppermost fossiliferous stratigraphic position and analysed following the above described procedure (see Fig. 1 and Table 1 for their location). The spectra corresponding to laboratory doses of 0 (Nat) and 1000 Gy are reported in Fig. 2. All samples show similar ESR spectra where it was possible to identify the following signals: h1 (Yokoyama et al., 1981, 1985), centred at g = 2.0057, linked to the presence of SO2 radicals (Barabas, 1992), B centred at g = 2.0031 related to SO1 radicals (Ikeya, 1993) and h3 centred at g = 2.0007 (Yokoyama et al., 1981, 1985), associated with CO2 radicals (Barabas et al., 1992). The latter signal was preferred for dating because it is radiation-sensitive and stable over geological times. On the contrary, the h1-peak is not sensitive to radiation, while the B signal quickly saturates. As an example, in Fig. 3 the peak-to-peak amplitudes (at g = 2.0007) vs. dose are reported for the SNC-1 sample. By extrapolating the regression line to zero ESR intensities the Dk values were determined. Table 2 presents the equivalent dose, the dose rate and the age values obtained for each analyzed sample.

Table 1 - Characteristics of the sampling sites at Piano San Nicola.

<table>
<thead>
<tr>
<th>sample label</th>
<th>latitude (N)</th>
<th>longitude (E)</th>
<th>depth below terrace top</th>
<th>lithology</th>
</tr>
</thead>
<tbody>
<tr>
<td>SNC-1</td>
<td>40°07’27&quot;</td>
<td>16°36’56&quot;</td>
<td>5 m</td>
<td>fine-grained sand and silt alternating with clay lenses</td>
</tr>
<tr>
<td>SNC-3</td>
<td>40°07’26&quot;</td>
<td>16°36’57&quot;</td>
<td>4 m</td>
<td>coarse grained sand-gravels</td>
</tr>
<tr>
<td>SNC-6a</td>
<td>40°07’37&quot;</td>
<td>16°36’52&quot;</td>
<td>8 m</td>
<td>silt-fine-grained sand</td>
</tr>
<tr>
<td>SNC-6b</td>
<td>40°07’37&quot;</td>
<td>16°36’52&quot;</td>
<td>9 m</td>
<td>silt-fine-grained sand</td>
</tr>
</tbody>
</table>

4. Discussion and conclusions

The new chronological results based on the ESR technique and presented in this note suggest an age of the Piano San Nicola site ranging between 40.4 ±7.7 ka and 64.0 ±11.2 ka. Considering that these deposits have been accumulated during a highstand sea level period, the real age should correspond in principle to a specific peak as provided by the mean sea level curves reconstructed for the Late Pleistocene (Fig. 4). Although a detailed analysis of several published curves sometimes shows important differences i) in the number of highstand peaks, ii) on their absolute age as well as iii) on the corresponding elevation/depth of the sea level [see discussion in Caputo, (2007)], the best time window constrained by our results (40-64 ka; graphically emphasized by the dark gray vertical band in Fig. 4) entirely falls within the last
Table 2 - ESR results for shells from Piano San Nicola.

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>DE (Gy)</th>
<th>d (Gy/ka)</th>
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<tbody>
<tr>
<td>SNC-1</td>
<td>125.1 ± 10.2</td>
<td>2.5 ± 0.3</td>
<td>51.1 ± 8.2</td>
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<tr>
<td>SNC-3</td>
<td>73.6 ± 6.0</td>
<td>1.8 ± 0.3</td>
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</tr>
<tr>
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<td>SNC-6b</td>
<td>99.9 ± 8.3</td>
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<td>46.1 ± 7.9</td>
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Firstly, the detailed mapping of the marine terraces exposed within the broader coastal sector including the investigated site shows the occurrence of three lower (i.e., younger) terraces (Fig. 1). Accordingly, (at least) three younger highstand sea level peaks should exist to justify and explain the occurrence of these morphological features. As a consequence, assuming a correlation of Piano San Nicola site, and hence the Policoro Terrace, with MIS 3.1 would pose a major chronological problem due to the lack of a sufficient number of younger highstand sea levels. In principle, the ‘lack’ of one (or more) terraces in a coastal sector could be due to a highly variable uplift rate characterized by accelerations and decelerations of the process, but this would be not justified in the frame of this tectonic and geodynamic setting (Ferranti et al., 2009; Santoro et al., 2009).

Secondly, if the Policoro Terrace would be correlated with MIS 3.1.3 (Fig. 4), the corresponding late Quaternary uplift-rate would be geologically unreasonable. Indeed, taking into account i) a sea level ranging between -50 and -80 m (Fig. 4), ii) an inner-edge of the terrace locally standing at ca 85 m a.s.l. and iii) an age of 45-35 ka (Fig. 4), the estimated uplift rate would range between 3.0 and 4.7 mm/a. No such values have been ever proposed in the literature of the region.

Moreover, as already recalled and discussed, the Policoro Terrace, where Piano San Nicola site stands on, has been also dated at La Petrulla site, ca 30 km NE. The available ages at that site provided by different and independent methodological approaches (amino-acid racemization, U-Th isotopic analyses and OSL-IRSL method) range between 54 and 63 ka, therefore in better agreement with the MIS 3.3 (Caputo et al., 2010). These ages are reported for reference in Fig. 4.

Further support to the proposed chronology of the Policoro Terrace comes from more general geodynamic considerations and particularly from the long-term uplift rate of this coastal sector of the Taranto Gulf. Indeed, by associating the Policoro Terrace with MIS 3.3, and taking into account the present-day altitude of the higher and lower inner-edges and the corresponding sea level depth at the time of the terrace formation (Fig. 4), the mean uplift rate during at least the last 100 ka remains roughly constant. This is graphically emphasized in Fig. 4 by the uniform slope of the long inclined arrows connecting the altitude value of the inner-edges (ordinate axis) with the corresponding MIS (Caputo et al., 2010). Using the graphical clinometer it is possible to measure a value of about 2.0 mm/a for the Policoro Terrace as well as a slight and regular increase from ca 1.7-1.8 mm/a (San Teodoro-3 Terrace, MIS 5.3.1) to ca 2.0-2.2 mm/a (Metaponto Terrace, MIS 1.1). As above mentioned, associating the Policoro Terrace to another MIS (e.g., 3.1.3) would force the assumption of an unreasonably variable uplift rate. Considering that the regional uplift is a consequence of large-scale tectonic and geodynamic processes (Caputo and Bianca, 2004; Ferranti et al., 2009; Santoro et al., 2009; Caputo et al., 2010), no such abrupt variations could be explained in the time span of few thousands of years.

By taking also into account the 1σ uncertainties associated with our chronological results (Table 2; light gray vertical band in Fig. 4), a possible correlation with MIS 3.1 could be not rigorously disregarded from a statistical point of view. However, this younger chronological correlation is unlikely on the basis of the following arguments.

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Fig. 2 - ESR spectra of sample SNC-1 for natural (gain = 300) and 1000 Gy γ-irradiated sample (gain = 120) showing the obtained peaks. See text for discussion.

Fig. 3 - Example of graph showing the distribution of ESR intensity vs. dose for g = 2.0007 signal for SNC-1 sample. By extrapolating the regression curve to zero ESR intensities the $D_E$ value is determined. These values are reported in Table 2.

major glacial period (i.e., MIS 5.5 to Present) and it mainly overlaps with the MIS 3.3 (Fig. 4).

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The inclination of the correlating arrows gives a measure of the long-term uplift rate. The chronological constraint for La Petrulla site located on the same terrace and references therein. The dark gray vertical band represents the best ages obtained in this work for Piano San Nicola site, while the light gray band includes the 1σ uncertainties (see Table 2). Numbers on top of the curves refer to the principal marine isotope substages (MIS). The chronological constraint for La Petrulla site located on the same terrace ca 30 km NE, is also reported for reference. The present-day altitude of the higher and lower inner edges mapped in this sector of Taranto Gulf (Caputo et al., 2010) is represented by short horizontal arrows along the ordinate axis, while the suggested chronological correlation is marked by a couple of inclined arrows [for including age and sea level depth uncertainties; (Caputo, 2007)]. The inclination of the correlating arrows gives a measure of the long-term uplift rate (see graphical clinometer for reference).
In conclusion, the results presented in this note based on the ESR technique, applied for the first time to this area, perfectly fit the datings previously provided by different chronological approaches as well as palaeontological inferences, therefore supporting the most likely correlation between the Policoro Terrace and the MIS 3.3 (Caputo et al., 2010).

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