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Carbonate platform record of the end-Triassic mass extinction

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Abstract

The main aim of this PhD research project is to investigate the response of tropical carbonate platforms to global perturbations of the carbon cycle during the end-Triassic mass extinction. We have studied three southern-Tethyan sections that show persistent shallow-water carbonate sedimentation across the Triassic/Jurassic boundary: Mt. Messapion (Pelagonian Domain, Greece); Valle Agricola (Southern Apennines, Italy); Mt. Sparagio (Sicily, Italy).

The sedimentological and micropaleontological analysis of Mt. Messapion and Valle Agricola sections allowed us to describe the record of biotic changes across the TJB and discuss how some carbonate platforms were able to keep growing in the shallow-water tropics despite the sudden extinction of the massive biocalcifiers during the end-Triassic mass extinction.

Integrating biostratigraphy and carbon-isotope stratigraphy in the three studied sections permits us to build a high-resolution correlation framework across the Triassic/Jurassic boundary interval that can be reliably used for correlations of Tethyan tropical shallow-water records. Moreover, based on a reappraisal of the $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ records of well-dated sections of the Northern Calcareous Alps, Transdanubian Range and Lombardy Basin, we propose a correlation between Tethyan carbonate platforms and reference sections that has important implications for worldwide correlations and provides new insights into the timing and causes of the end-Triassic mass extinction in Tethyan tropical neritic ecosystems.

Finally, we present the record of Hg concentration across the Triassic/Jurassic boundary interval in the Mt. Messapion section. The correlation with the Hg concentration records of reference sections suggests that the mercury anomaly at Mt. Messapion is not directly related to the volcanic activity of the Central Atlantic Magmatic Province.

1. Introduction

The geological archive of marine and continental organic matter and of marine carbonates, is characterized by some large and geologically short (10s to 10^2 kyr) negative carbon isotope excursions (CIE) that have been interpreted as episodes of short-term massive injection of CO_2 in the ocean-atmosphere system. A wealth of geochemical and palaeontological data indicates that these global perturbations of the carbon cycle are invariably associated with abrupt climate changes and severe palaeoenvironmental crises (e.g., Jenkyns, 2003). These episodes of global change in the geological past were caused by natural phenomena, such as paroxysmal phases of volcanic activity. They are of great interest inasmuch as they can serve to test models and predictions of anthropogenic CO_2-induced global change. In particular, the geological archive of ancient carbonate platforms holds precious information on extreme paleoclimatic and paleoceanographic events. About one third of the CO_2 released into the atmosphere from anthropogenic sources is transferred into the oceans where it reacts to form carbonic acid (Sabine et al., 2004). As a result, the pH and the carbonate saturation of the ocean decrease in a process called ocean acidification (Doney et al., 2009; Raven et al. 2005). Detrimental effects on extant calcifying organisms, which use carbonate minerals to build their protective shells and skeletons, have been documented (Fabry et al., 2008; Hall-Spencer et al., 2008). However, due to the spatio-temporal limits of laboratory manipulations and field observations of living marine communities, the long-term impact on marine ecosystems and the adaptative potential of marine fauna and flora are best investigated by looking at the geological record of past episodes of ocean acidification (Hönisch et al., 2012; Zeebe, 2012). Much of what we know about these events comes from the pelagic and hemipelagic successions deposited in relatively deep basins. Comparatively much less is known about shallow-water carbonate platforms. Carbonate production and biocalcification in shallow-water environments are particularly sensitive to several environmental factors that are strongly influenced by changes in atmospheric pCO_2, such as the concentration of nutrients, temperature, pH, and carbonate saturation. Many studies have revealed a pattern of carbonate platform drowning during episodes of perturbation of the global carbon cycle, because one of the main effects of a CO_2-triggered paleoenvironmental crisis is to destabilize the communities of calcium carbonate producers. However, some carbonate platforms were able to escape drowning and continued to accumulate shallow-water carbonate sediments across the crisis events. These resilient carbonate platforms are the focus of my PhD research project, which aims at investigating the response of tropical carbonate platforms to the global perturbation of the carbon cycle during the end-Triassic extinction (ETE). The end of Triassic was characterized by three global events: 1) the emplacement of the Central Atlantic Magmatic province (CAMP), which represent the most aerially extensive continental Large Igneous Province (LIP) known on Earth; 2) the end-Triassic mass extinction, described as one of the "Big Five" mass extinctions of the Phanerozoic; 3) a severe perturbation of the carbon cycle (Raup and Sepkoski, 1982; Marzoli et al., 2004; Schoene et al., 2010; Blackburn et al., 2013; Bond & Wignall, 2014). This latter is evidenced by three sharp negative carbon isotope excursions (CIEs) in organic matter and marine carbonate, suggesting a massive input into the oceans and atmosphere of large quantities of ^{13}C-depleted CO_2 (Hesselbo et al., 2002; Ruhl et al., 2011; Dal Corso et al., 2014). Given the age overlap, the emplacement of the CAMP seems to be the most likely cause of the negative CIEs (Marzoli et al., 2004; Cirilli et al., 2009; Davies et al., 2017). In the marine realm, ocean acidification greatly influenced carbonate-secreting organisms (Hautmann, 2004; van de Schootbrugge et al., 2007; Kiessling et al., 2009). A significant drop in carbonate production has been recorded in the pelagic realm and in some carbonate platforms (Greene et al., 2012). The pattern of extinction in the subtropical carbonate platforms, affecting selectively the massive hypercalcifiers, has been proposed as evidence of ocean acidification, caused by the massive emission of carbon dioxide in the ocean-atmosphere system (Hallam, 2002; Hautmann, 2004; Martindale et al., 2012; Kiessling and Simpson 2011; Hönisch et al., 2012; Greene et al., 2012).

I have studied three southern-Tethyan sections that show persistent shallow-water carbonate sedimentation across the Triassic/Jurassic boundary: Mt. Messapion (Pelagonian Domain, Greece); Valle Agricola (Southern Apennines, Italy); Mt. Sparagio (Sicily, Italy). For each studied section, I have integrated facies analysis, biostratigraphy, and carbon-isotope stratigraphy. Moreover, the interval across the TJB has been analyzed for the concentration of Hg, which has been repeatedly used during the last two decades as a proxy of global volcanism.

This PhD research project is part of a wider project funded by the Italian Ministry of Research (PRIN 2017) entitled: *"Biota Resilience to global change: biomineralization of planktic and benthic calcifiers in the past, present and future"*, coordinated by Prof. Elisabetta Erba (University of Milan).
The main aim is to cover all the geological events starting from the Permian-Triassic boundary (about 250 million years ago), studying all the oceanic anoxic events of the Mesozoic, the Triassic/Jurassic boundary, and other events of paleoenvironmental perturbation during the Cenozoic.

Thesis outline.

This thesis is organized in seven chapters. Chapter 1 gives the aim of the thesis and a brief introduction on the ETE; chapters 2 and 3 briefly summarize the materials and methods and the stratigraphic sections studied, respectively. Chapter 4, 5 and 6 reproduces three manuscripts in preparation. Chapter 7 outlines the conclusion of this PhD research project.

2. Materials and methods

For each successions studied, a sedimentological-stratigraphic study was implemented based on the integration of the following dataset: facies and microfacies analysis, cyclostratigraphy and sequence stratigraphy, biostratigraphy, and carbon-isotope stratigraphy. The research activity was structured into two main activities: fieldwork and laboratory.

2.1 Fieldwork activity

The fieldwork activity consisted of 1) stratimetric measurement and sedimentological and biostratigraphic analysis, at decimetric to metric scales, of stratigraphic succession of Upper Triassic-Lower Jurassic age; 2) sampling at metric to sub-metric scale. In addition to rock samples analyzed for sedimentological and micropaleontological observations in thin sections, a hammer-drill was used to obtain samples of carbonate powder for geochemical analyses directly in the field. After removing the surface of altered rock, sampling was carried out by drilling with a 10 to 18 mm diameter tungsten carbide drill bit, producing 15-20 grams of powder per sample. The sampling step was from 30 cm to 2 m, depending on the quality of the outcrop in terms of stratigraphic continuity and the importance of the stratigraphic interval (higher sampling across the ETE).

2.2 Laboratory activity

The following activities were performed in the lab:

- Preparation of polished slabs and thin sections for optical microscope observations.
- Weighting and splitting of the powder samples into vials for the different geochemical analyses.
- Microsampling of micrite on the rock slabs using a hand-held microdrill avoiding sample areas where secondary carbonates are present, to check the reliability of bulk carbonate powders sampled in the field.
- Geochemical analyses, either in the DiSTAR laboratories or in collaboration with external laboratories:
    - $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ were analyzed at the University of Milan and the University of Ferrara (Italy).
    - minor and trace elements were analyzed with a portable XRF Bruker Tracer 5g at the University of Naples and at the Université de Liège (Belgium). A subset of samples was analyzed with an ICP-MS at Activation Laboratories LTD (Ancaster, Ontario, Canada)

- Hg content and Hg/TOC concentration were analyzed at the Université de Lausanne (Switzerland).

3. Studied sections

We studied three sections that record persistent shallow-water carbonate sedimentation at subtropical latitude in the south-western Tethyan Ocean during the Late Triassic-Early Jurassic time interval.

3.1 Mt. Messapion

The Mt. Messapion section (38°27'44.31"N, 23°28'43.08"E) is located in north-eastern Greece, 10 km west of the city of Halkida (or Chalkida). It was part of the Pelagonian Carbonate Platform, which was established in the early Middle Triassic and dismembered and drowned starting from the late Early Jurassic (Celet et al., 1988; Haas, 2010). The Upper Triassic-Lower Jurassic platform carbonates exposed in Mt. Messapion section display m-thick shallowing upward peritidal cycles, with subtidal facies capped by microbial laminites and paleosols. Facies, peritidal cyclicity and biostratigraphy of this section have been studied by Romano et al. (2008).

3.2 Valle Agricola

The Valle Agricola section is located near the village of Valle Agricola (Matese Mountains, Italy, 41°25'42.97"N, 14°14'39.22"E). It was part of the Apennine Carbonate Platform, which was established in the Late Triassic at the north-western margin of the Adria promontory and persisted, with only short interruptions, until the Late Cretaceous, when it was terminated by emersion (D'Argenio and Alvarez, 1980; Bernoulli, 2001; Bosellini, 2004; Parente et al., 2022). Shallow-water carbonate sedimentations resumed in limited areas during the Paleogene and early Miocene, to be finally terminated by drowning in the middle Miocene, followed by foredeep siliciclastics sedimentation and finally incorporation in the Apennine fold-and-thrust belt starting from the late Miocene (Vitale and Ciarcia, 2013; Sabbatino et al., 2021). The Valle Agricola section consists of Upper Triassic peritidal limestones with megalodontids and corals, followed by Lower Jurassic oolitic-oncolitic limestones. The section described in this paper corresponds to the lower part of the Costa dei Frascari section of Mancinelli et al. (2005).

3.3 Mt. Sparagio

The Mt. Sparagio section (38°3'47.36"N, 12°43'13.32"E) is located near the Village of Custonaci (north-western Sicily, Southern Italy), along the northern slope of Mt. Sparagio, in the southern part of the San Vito Lo Capo Peninsula. This section belongs to the Mt. Sparagio tectonic unit, an element of the Maghrebian fold and thrust belt in north-western Sicily (Todaro et al., 2018). The stratigraphy of this tectonic unit consists of 1000 m of peritidal limestone (Upper Triassic-Lower Jurassic) that are overlain by slope and pelagic carbonates (Middle Jurassic-Eocene) and sandstones and clays

(Oligocene-Miocene) (Abate et al., 1991, 1993). The Mt. Sparagio section was previously studied by Todaro et al. (2017, 2018, 2022). It consists of 400 meters of whitish to grey peritidal limestones of the Upper Triassic Sciacca formation overlain by 150 meters of Hettangian-Sinemurian limestones of the Inici formation. The Mt. Sparagio section records sedimentation in the inner part of a carbonate platform (Todaro et al., 2017) that was part of a wide shelf connecting Africa and Adria at the southwestern margin of the Tethyan ocean (Di Stefano et al., 2015).

7. Conclusions

We have studied three different southern-Tethyan resilient shallow-water carbonate platform sections (Mt. Messapion, Pelagonian Domain, Greece; Valle Agricola, Matese Mountains, Southern Apennines, Italy; Mt. Sparagio, Sicily, Italy). The study of these resilient shallow-water sections allows us to add further new data to clarify some open questions about the TJB and the ETE.

A detailed biostratigraphic, facies analysis, and micropaleontological characterization of Mt. Messapion and Valle Agricola sections has enabled us to describe the record of biotic changes and the paleoenvironmental evolution across the TJB. Both sections are fossil-rich in the Upper Triassic interval and poorly fossiliferous in the Lower Jurassic and the ETE is marked by the disappearance of the Rhaetian fossils association. An inner platform depositional environment (at Mt. Messapion) and a more marginal setting (at Valle Agricola) are suggested by benthic foraminiferal assemblages. Both sections show a shallow-water peritidal cyclicity akin to that observed in Dachstein Limestone of NCA. Changes of cyclicity suggest a transition to a shallower depositional environment during the ETE, as is observed in other Southern Tethyan carbonate platforms, suggesting a common pattern at tropical and equatorial paleolatitudes. A different trend is observed in other carbonate platforms in Northern Tethys where carbonate productivity ceased at the TJB, and that could be due to different paleogeographic and palaeolatitudinal conditions.

New integrated bio- and carbon isotope stratigraphy data of the three studied sections were presented and correlated to the best-known reference sections at the TJB. A correlation with other Southern Tethyan resilient carbonate platform sections suggests a well-reproducible bio- and chemostratigraphic framework where the extinction of the Rhaetian taxa occurred in a positive excursion of carbon curve supporting the hypothesis that it could be a global pattern. In the well-studied reference sections of the TJB, the pattern is completely different, and the extinction of the Rhaetian taxa has been related to one of the three negative CIE. To clarify this incongruence, we have examined the bio- and chemostratigraphy of two reference sections (Tiefengraben and Csővár) where $\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$ records are available. The decoupling of the isotopic trends at Tiefengraben and the identification of four stratigraphic intervals based on the $\delta^{13}C_{carb}$ trend at Csővár have allowed the correlation between basinal and carbonate platform reference sections, which in turn have been related to resilient Southern Tethyan carbonate platform sections. The correlation shows that in the studied sections the extinction of the Rhaetian taxa is delayed compared to the TJB reference sections. This would constitute a third and latest phase of the extinction, following the two proposed by Wignall and Atkinson (2020), suggesting that the extinctions in all the other sections would show a pseudo extinction caused by the loss of the carbonate platform habitat.

We also attempted to measure mercury (Hg) content and TOC in the three studied sections, but only Mt. Messapion shows a record above the detection limit and a marked anomaly in Hg concentration, representing the first published mercury record of shallow-water carbonate platform section spanned across the TJB. Some reference Hg records at the TJB show a mercury anomaly at the Initial CIE (Kuhjoch, St. Audrie's Bay, New York Canyon), while other records show a mercury anomaly both at the Initial CIE and higher-up stratigraphically (Arroyo Malo, Csővár). Our bio- and chemostratigraphic correlations suggest that the mercury anomaly at Mt. Messapion is above the TJB. Therefore, it is not time-correlative with Kuhjoch, St. Audrie's Bay, and New York Canyon. Beyond that, an increase in the concentration of detrital elements (Aluminium, Iron, Potassium) and a decrease of Calcium content is observed in the interval of the anomaly, suggesting a terrigenous source as a possible cause of higher mercury concentration. This interpretation proves that the Hg anomaly at Mt. Messapion is not directly related to the volcanic activity of the Central Atlantic Magmatic Province.

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