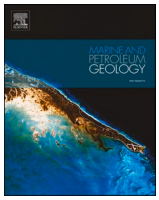
Marine and Petroleum Geology 170 (2024) 107121

Contents lists available at ScienceDirect

Marine and Petroleum Geology

journal homepage: www.elsevier.com/locate/marpetgeo



# Paleo-redox conditions during the demise of a carbonate platform in the Tethyan ocean: Evidence from phosphatized and metals (Mn and Fe) rich hardgrounds

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ARTICLE INFO

*Keywords:*
Cretaceous carbonate platform
Drowning unconformity
Fe-Mn hardground
Paleo redox conditions
C and O isotopes
Raman spectroscopy
Climate change
Synsedimentary tectonic
Sicily

ABSTRACT

Phosphatized Mn and Fe rich hardgrounds and condensed pelagic deposits in carbonate platform successions are precious archives of abrupt climate and environmental changes (redox conditions and phosphorous availability) in the past shallow-water marine environment. While numerous examples have been documented in the Cretaceous successions of the Northern Tethys, the scarcity of similar descriptions from the southern margins suggests differences in sedimentary processes or preservation conditions.

In this work we study three phosphatized Mn and Fe rich hardgrounds and pelagic condensed deposits that mark the repetitive demise of the Panormide carbonate platform developed in the Southern Tethyan margin during the Cretaceous. The integration of SEM-EDS, PXRD, and Micro-Raman spectroscopy data shows that these hardgrounds consist of fine-grained Fe (goethite and hematite) and Mn (birnessite and/or vernadite) oxides dispersed in a calcite and apatite matrix. Micro-Raman spectroscopy shows the presence of oxidized Mn species: $Mn^{3+}$ and $Mn^{4+}$. The oxidation of $Mn^{2+} \rightarrow Mn^{3+/4+}$ and/or $Fe^{2+} \rightarrow Fe^{3+}$ occurred at the sediment-seawater interface under oxic conditions (where both Mn and Fe oxidize) or suboxic conditions (where only Fe oxidizes). The paleoenvironmental perturbations that triggered the formation of both hardgrounds and condensed pelagic deposits were likely related to $pCO_2$ cycle, upwelling of P-Mn-Fe-rich water masses, eutrophication and phosphatization related to the Cretaceous climate oscillations during the main Oceanic Anoxic Events. These perturbations were likely enhanced by tectonic activity. Moreover, we show that the formation of the phosphatized metals-rich hardgrounds and the recovery of shallow-water sedimentation occurred after long-term periods (6–12 Ma). Thus, the Panormide serves as a remarkable example of resilience amidst significant climatic changes.

## 1. Introduction

Marine ferromanganese crusts consist of Mn and Fe oxyhydroxides precipitating directly from ocean water over hard rock substrates (Hein and Koschinsky, 2014). They form on the flanks and summits of seamounts, ridges, and plateaus where the currents have kept the rocks swept clean of sediments (Segl et al., 1984; De Carlo, 1991). These mineralizations represent the most important polymetallic deposits on seamounts in the central and western Pacific Ocean – notable examples are those of guyots of the Mid-Pacific Mountains (De Carlo, 1991; Wen et al., 1997) –, Rio Grande Rise in South Atlantic (Benites et al., 2020; 2023), Mid-Atlantic ridge (Mills et al., 2001), Canary Islands (Kfouri et al., 2021), Lion seamount (Koschinsky et al., 1996) and Cadiz Contourite Channel (González et al., 2012) in the NE Atlantic Ocean.

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https://doi.org/10.1016/j.marpetgeo.2024.107121
Received 23 July 2024; Received in revised form 16 September 2024; Accepted 17 September 2024
Available online 19 September 2024

A fundamental geochemical property of Mn and Fe (the most common metals on Earth) is their high sensitivity to redox conditions. For instance, the solubility of Mn is much higher than that of Fe when the pH ranges from 6 to 8, except at high oxidation/reduction potential (Eh > 600 mV) (Hem, 1963, 1972). Therefore, the geochemical separation between these metals can be used to identify different redox environments and to investigate the evolution of the seawater chemistry over geological time (Berner, 1981; Maynard, 2010; Kfouri et al., 2021). Moreover, in the crystal structures of oxide minerals, Mn may occur under different oxidation states ($Mn^{2+}$, $Mn^{3+}$, and $Mn^{4+}$) depending on the (bio)geochemical conditions existing during mineral formation (*e.g.,* Bernardini et al., 2021a). Marine Fe-Mn deposits are thus precious archives of regional and global oceanic and climatic conditions (Hein and Koschinsky, 2014; Koschinsky and Hein, 2017; Benites et al., 2020; Sutherland et al., 2020; Cornaggia et al., 2020).

Phosphorus is an essential nutrient for life and a limiting element for ocean productivity; thus, its availability can strongly influence the marine carbon cycle and the sequestration of atmospheric $CO_2$ (Paytan and McLaughlin, 2007). The formation of phosphatized hardgrounds in shallow-marine environments can be related to both continental weathering and/or upwelling of P-rich deep waters. For instance, at seamounts/plateaus, the formation of phosphates (*e.g.,* carbonate fluorapatite) in the sediments/rocks commonly occurs at depths where the seafloor intersects the oxygen minimum zone (OMZ) which is a source of reactive P and metals (Kraal et al., 2012; Benites et al., 2021, 2022). Phosphogenesis may be thus accompanied by the precipitation of Fe and Mn oxyhydroxides, depending on the redox condition of seawaters (Baturin, 1989; Benninger and Hein, 2000).

The demise and drowning of carbonate platform are commonly associated with the formation of Fe and Mn rich levels, phosphatized hardgrounds, pelagic condensed deposits, and changes in the ecology of carbonate-producing organisms. These events thus record the paleoclimate changes (Föllmi et al., 1994; Peter and Simo, 1997; Godet, 2013), as well as the tectonic subsidence and sea-level rises (Schlager, 2005; Nieto et al., 2014; Basilone, 2020) that triggered changes of shallow-water carbonate productivity.

In the Mesozoic Tethyan geological record, Fe-Mn rich levels and drowning unconformities widely occur in different chronostratigraphic intervals. For example, Fe-Mn rich layers and condensed sedimentation (*i.e.,* Rosso Ammonitico), related to the paleoclimatic and paleoenvironmental changes occurring during the Tethyan rifting (Jurassic, *e.g.*, Critelli, 2018; Critelli et al., 2018), have been described from Subbetic (Nieto et al., 2014; Reolid and Abad, 2019), Alpine (Cronan et al., 1991; Vörös, 2012; Godet, 2013), Apennine (Santantonio, 1993; Clari et al., 1995) and western Sicily (Mallarino et al., 2002; Wendt, 2017; Basilone, 2011). Paleoenvironmental perturbations during the Cretaceous produced Fe-Mn levels, pelagite intercalations, facies changes in shallow-water successions and drowning of Northern Tethyan carbonate platforms (Peter and Simo, 1997; Wissler et al., 2003) and Southern Tethyan margin (Immenhauser et al., 2005; Perrone et al., 2006; Parente et al., 2007; Graziano, 2013; Basilone, 2021a, 2021b). These events are related to the climatic changes producing the Oceanic Anoxic Events (OAE) and biotic extinctions (Larson and Erba, 1999), as demonstrated by the several geochemical, biostratigraphic, and sedimentological analyses of worldwide pelagic successions (Arthur et al., 1990; Menegatti et al., 1998). They record periods of global warming (greenhouse conditions) genetically linked with changes of the $pCO_2$ of the hydrosphere-atmosphere system, the latter related the tectonic and volcanic processes acting at a global scale (Vogt, 1989; Tarduno et al., 1991; Weissert and Erba, 2004; Tejada et al., 2009; Méahy et al., 2009; Critelli et al., 2023).

Although these mineralizations are precious archives of the environmental perturbations characterizing the stage of demise and drowning of carbonate platforms, they still remain poorly studied. The lack of data is mainly due to the challenging characterization of fine-grained mixtures of poorly-crystalline Mn and Fe compounds, carbonates, silicates, and phosphates by standard X-ray diffraction methods. Raman spectroscopy provides a valuable tool for characterizing Mn- and Fe-bearing mixtures (Bernardini et al., 2019), being sensitive to short-range cation-anion arrangements. Moreover, the laser spot on the sample can be reduced to ~1 $\mu m^2$ allowing for high spatial resolution chemical analysis (Bernardini et al., 2021a; Kfouri et al., 2021). Beside the mineral identification, Raman spectroscopy provides a quick and reliable determination of the oxidation state of Mn down to the microscale (Bernardini et al., 2021b) thus allowing the use of these minerals for paleoenvironmental reconstructions (Bernardini et al., 2021a; Kfouri et al., 2021).

In this paper we provide a detailed sedimentological, stratigraphical and mineralogical description of three phosphatized MnFe-rich hardgrounds associated with discontinuous and condensed sediments, firstly recognized in the Cretaceous shallow-water carbonates of the Panormide Southern Tethyan domain (NW Sicily, Fig. 1a). These hardgrounds were studied by combining Optical Microscopy (OM), Scanning Electron Microscopy coupled with an X-ray Energy Dispersive System (SEM-EDS), Powder X-Ray Diffraction (PXRD), and Micro-Raman spectroscopy (RS). The aim of this work is at providing insights into the paleoclimate changes of a shallow-water marine environment triggering the repetitive demise of a carbonate platform in the Southern Tethyan margin.

## 2. Geological setting

Sicily is a segment of the Alpine orogen (inset in Fig. 1a) whose upbuild refers to both the convergence between Africa and a complex "European" crust (Bonardi et al., 2001) and to the coeval roll-back of the subduction hinge of the Adriatic Ionian-African lithosphere (Chiarabba et al., 2008; Critelli and Martín-Martín, 2022, 2024). The Sicily chain is a S- and SE-verging, up to 15 km thick, fold and thrust belt (FTB) involving Meso-Cenozoic carbonate and siliciclastic units, overthrusting the Iblean foreland (Finetti, 2005; Catalano et al., 2013a; Henriquet et al., 2020). Its formation was associated with the counter-clockwise rotation of Corsica and Sardinia and the Calabrian/Peloritani Kabylian units, during the late Neogene (Channell et al., 1990; Critelli, 2018; Critelli and Martín-Martín, 2022, 2024). Thrust-top basins grew above the deforming units during the Late Miocene, when clastics and Messinian evaporites were deposited, sealing unconformably the deformed units (Gasparo Morticelli et al., 2015). A thick-skinned thrusting in the frontal area of the Sicilian FTB as well as the crystalline basement in the inner and deeper sector of the chain involve Plio-Pleistocene deposits (Sulli et al., 2021). Quaternary deposits, outcropping in thin and patchy exposed successions mostly along the coastal belt (Fig. 1a–Agate et al., 2017) and made up of continental (aeolian, debrites, alluvium) and shallow-water carbonate marine deposits, are bounded by unconformity surfaces with regional extension (Di Maggio et al., 2009).

The Palermo Mountains, representing the north-westernmost sector of the outcropping Sicilian FTB, result from the piling-up of shallow-water and deep-water carbonate tectonic units (Fig. 1a, Servizio Geologico d'Italia, 2011a, 2011b), deriving from the deformation of the Panormide carbonate platform and Imerese basin respectively, which developed during the Meso-Cenozoic along the Southern Tethyan stretched continental margin (Catalano et al., 1996). The carbonate platform tectonic units, 800-1200 m-thick and 3–8 $km^2$ wide, are progressively superimposed along N-S and NW-SE trending thrusts, with ramp and flat geometry (Fig. 1b). The tectonic units are separated by the Oligo-Miocene Numidian flysch deposits that postdate the tectonic emplacement (Catalano et al., 2013b, 2013c). Recent extensional and transtensional tectonic dissects, with E-W oriented and N to S dipping faults, the previously formed structures, being responsible for the present-day morpho-structural setting (Fig. 1a and Basilone and Di Maggio, 2016; Di Maggio et al., 2017).

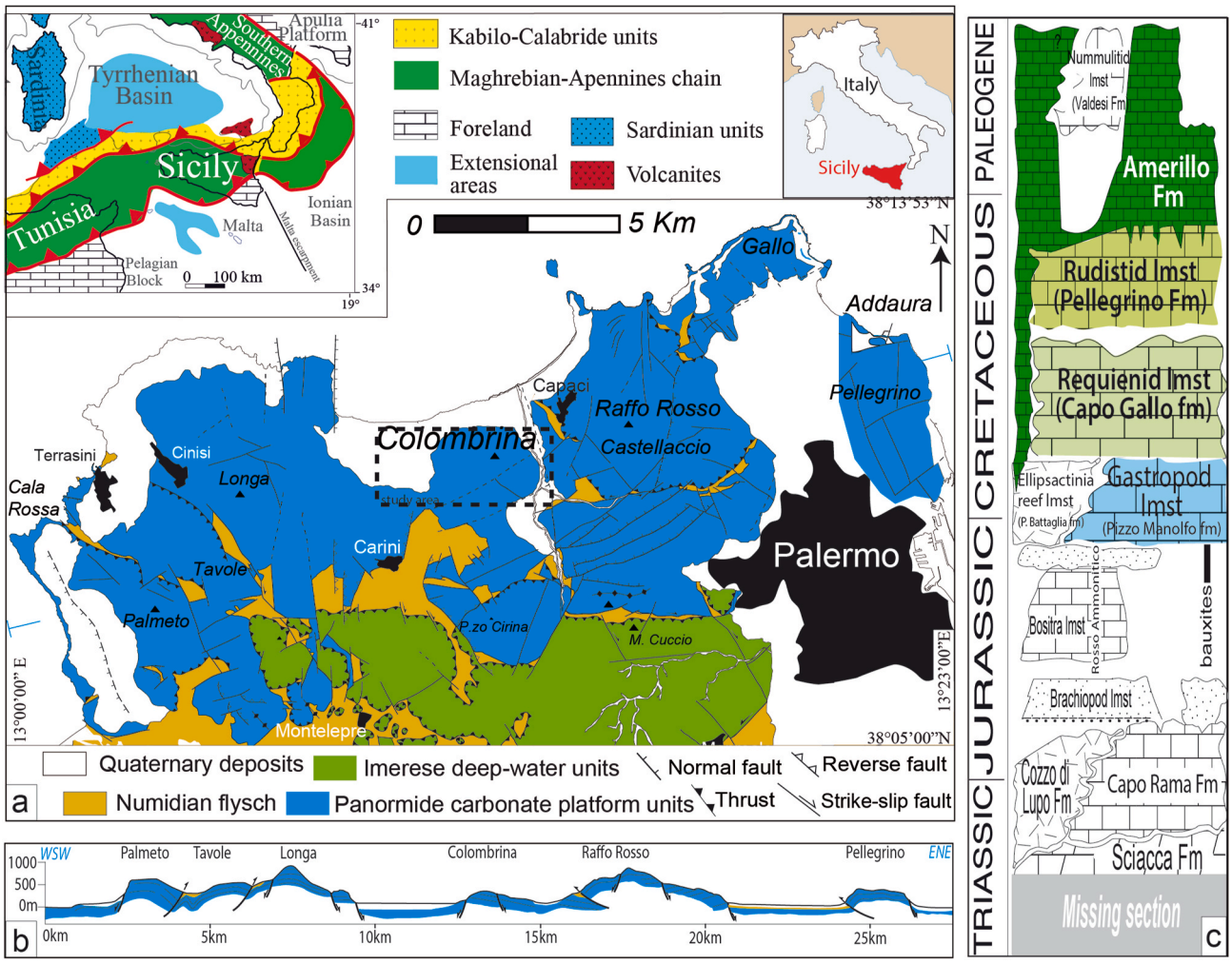


**Fig. 1.** a) Geologic map of the Palermo Mountains and location of the study area (after Servizio Geologico d'Italia, 2011a; 2011b); inset, tectonic map of central Mediterranean area (after Catalano et al., 2013a); b) simplified geological cross-section showing the ramp and flat geometry of the Panormide tectonic units with the interposition of the Numidian flysch deposits; c) Upper Triassic–Eocene lithostratigraphy of the Panormide succession outcropping in the Palermo Mountains (after Basilone, 2018). The Cretaceous study units are highlighted.

### *2.1. Main stratigraphy and paleogeography of the Panormide carbonate platform*

The Panormide succession outcropping in the Palermo Mountains consists of Upper Triassic-Eocene carbonates, mostly characterized by neritic facies with rimmed margin (Late Triassic and Late Jurassic: Catalano et al., 2013b, 2013c; Basilone and Sulli, 2016) and open platform with ramp geometries (Cretaceous and Eocene: Di Stefano and Ruberti, 2000; Basilone and Di Maggio, 2016). Common fossils include corals, sponges, hydrozoans, rudists and large benthic foraminifera. Several formations, recently revised and amended (Catalano et al., 2013b, 2013c; Basilone, 2018), compose the lithostratigraphic column reconstructed for the study area (Fig. 1c). The Upper Jurassic-Upper Cretaceous deposits, outcropping in the study section, consist of shallow-water carbonates belonging to different lithostratigraphic units (Fig. 1c, see Basilone, 2021a, 2021b for further details): the Calcari di Pizzo Manolfo Fm consisting of peritidal limestone with diceratids and nerineids and cm-thick graded oolitic (Table 1) encompasses the Late Tithonian-Berriasian time interval (Fig. 2); the Calcari di Capo Gallo Fm (Fig. 1c), consisting of peritidal limestone with algae and Requienids alternated to oolitic packstone-grainstone are assigned on the basis of the fossil content (Table 1) to the Barremian-lower Aptian (Fig. 2); the Pellegrino Fm (Fig. 1c) features shallowing upward cycles of thick-bedded massive floatstone-wackestone and boundstone with rudistids, corals and benthic foraminifera, along with graded packstone-grainstone and darkish oolitic grainstone (Table 1). The fossil evidence dates these deposits to the upper Albian-Cenomanian (Fig. 2). Upwards, the pelagic carbonates with planktonic foraminifera (globotruncanids and globorotalids), radiolarians, and *Apthycus* sp. of the Amerillo Fm (Fig. 1c–Table 1), encompassing the latest Cretaceous-Eocene (Fig. 2), close the succession.

Paleoenvironmental reconstruction refers the deposits of the Panormide to a Bahamian-type carbonate platform flanked northwards (present-day) by deep-water basins (Catalano et al., 1996). At the Sinemurian-Pliensbachian boundary, the latest stage of rifting, the Triassic-Lower Jurassic wide carbonate platform was tectonically dismembered and consequently drowned (Jenkyns, 1970). During the Jurassic and the Cretaceous the paleophysiography of the Sicilian margin was characterized by shelf areas alternated with several small intraplatform basins (Catalano et al., 2000; Basilone, 2020), frequently associated with strike-slip movements (Basilone et al., 2016; Basilone, 2022) and emerged areas with continental deposits (*i.e.,* subaerial exposure: Catalano et al., 2013b; Basilone et al., 2017).

## 3. Methodologies

Several thin sections have been studied by OM for the analysis of fossil content and textural features, applying microfacies Dunham

**Table 1**
Facies and lithostratigraphic characteristics of the studied shallow-water carbonates.

| Units | Texture and lithology | thick (m) | Fossil content | Lower boundary | Environment | Age | Main references |
|---|---|---|---|---|---|---|---|
| Amerillo Fm | red and white planktonic foraminifera bearing-wackestone and marly limestone with intercalation of resedimented bioclastic packstone/grainstone | 1–10 | Globotruncana ex gr. lapparenti, Globotruncana ventricosa | onlap infilling | pelagic | Campanian-Paleogene | |
| Drowning unconformity 3 (DU3) | | | | | | | |
| Rudistid Limestone | floatstone-to-wackestone with rudistid shells and large Nerinea sp., corals, corallinaceous algae, encrusting organisms (microbialites), microproblematics and crinoid fragments alternated to oolitic packstone-grainstone | 100–150 | caprinids (Caprina schiosensis Boehm, Caprina carinata Boehm) caprotinids (Polyconites verneuilli Bayle), hippuritids, large radiolitids (Sauvagesia sp., Radiolites sauvagesi D'ombres-Firmas), benthic foraminifera (Orbitolina (Conicorbitolina) conica D'Archiac), microproblematics, algae, corals | downlap | open shelf with patch reefs | Upper Albian-Cenomanian | Montanari (1965); Camoin (1983) |
| Drowning unconformity 2 (DU2) | | | | | | | |
| Requienid Limestone | thick bedded floatstone-rudstone with requienids and large Nerinea sp., corals, coated grains, benthic foraminifera, algae and microproblematics alternated to dm-thick graded darkish oolitic grainstone and coral boundstone (patch reefs). | 20–100 | requienids (Offneria sp.), algae (Clypeina solkani Sokac, Epimastopora cekici Radoičić, Salpingoporella hasi Conrad, Radoicic & Rey, Triploporella cf. decastroi Barattolo), benthic foraminifera (Palorbitolina lenticularis (Blumenbach), P. praecursor (Montanari), Rectodyctioconus giganteus Schroeder), Bacinella irregularis Radoicic, Lithocodium aggregatum Elliot | onlap | open shelf and sand bar | Barremian-Lower Aptian | Montanari (1965); Camoin (1983) |
| Drowning unconformity 1 (DU1) | | | | | | | |
| Gastropod Limestone | thick bedded graded rudstone-floatstone with gastropods, colonial corals (patch reef) and chetetids, bioclastic wackestone with algae, oncoids and coated grains, graded oolitic and bioclastic packstone-grainstone | 100–150 | Nerinea sp., algae (Cayeuxia sp., Clypeina jurassica Favre & Richard, Campbeliella striata Carozzi, Epimastopora cekici Radoičić), benthic foraminifera (Protopeneroplis striata Weynschenk, Trocholina cfr. elongata Leupold), microproblematics (Lithocodium aggregatum, Bacinella irregularis), echinoids, crinoids bryozoans | onlap | lagoon and landward marine sand belt | Upper Tithonian-Lower Valanginian | Basilone and Sulli (2016) |

classification (Dunham, 1962). The resulting lithofacies were calibrated by using biostratigraphic data, mostly based on algae and benthic foraminifera biozonations (Fig. 2), coming from studies on Sicilian (Montanari, 1965; Camoin, 1983), Southern Apennine (De Castro, 1991; Chiocchini et al., 2008), and Adriatic (Husinec and Sokač, 2006; Velić, 2007) successions. Pelagic intercalations were age-calibrated by using calpionellid (Allemann et al., 1971; Remane, 1998) and planktonic foraminifera (Caron, 1985) biozonations. The numerical age of the sedimentary bodies refers to the official chronostratigraphic scale (Cohen et al., 2013).

SEM-EDS data were collected at DAFNE-L (Istituto Nazionale di Fisica Nucleare, INFN) in Frascati (Rome, Italy) using a SNE3200M microscope, equipped with a high-resolution energy-dispersive (EDS) Bruker detector (XFLASH Detector 410 M) and the ESPRIT 1.9 software.

PXRD data were collected at CORE-Laboratory (University of São Paulo, Brazil) using a Siemens D5000 powder diffractometer under CuKα radiation filtered by a monochromator graphite crystal in the 5–70° 2θ range, with a step size of 0.02° 2θ, and a counting time of 4 s/step.

Raman measurements were performed at the Raman Spectra Lab, Department of Science, Roma Tre University, at room temperature using an inVia Renishaw spectrometer equipped with a diode laser (532 nm, output power 100 mW), an edge filter, 1800 lines per mm diffraction grating and a Peltier cooled 1024 × 256 pixel CCD detector. Samples were mounted on the manual stage of a Leica DM2700 M confocal microscope. Focusing of the laser beam and collection of Raman scatterings was realised by a 50X long-working distance objective. The spectra were collected using a laser power of 0.5 mW (three accumulations, 30 s each) in order to avoid any laser-induced degradation of the sample (Bernardini et al., 2020, 2023). The Raman spectrometer was calibrated prior to the measurements using a Si wafer. Spectra acquisition and data analyses were accomplished using WiRE™ and OriginPro software. The measured spectra were baseline-corrected and fitted with pseudo-Voigt functions to derive the phonon wavenumber. The peak positions are estimated to be accurate to at least ±2 $cm^{-1}$.

Stable isotopes (C and O) analyses of the micritic component collected from the polished slabs with a micro drill were carried out at the Stable Isotope Laboratory of the INGV (Palermo), using Analytical Precision AP 2003 and FinniganMAT Delta Plus IRMS devices. The results were calibrated to the VPDB standard, with a precision better than 0.1‰ for both C and O isotope compositions.

## 4. Results

The 250-500 m-thick Upper Jurassic-Upper Cretaceous studied section (Fig. 3), consists of shallow-water carbonates, divided into three lithostratigraphic units (Figs. 1c and 2; Table 1): (1) the Calcari di Pizzo Manolfo (hereafter Gastropod Limestone), (2) the Calcari di Capo Gallo (Requienid Limestone) and (3) the Pellegrino Fm (Rudistid Limestone). Upwards, the serie ends with pelagic carbonates belonging to the Amerillo Fm that lie with onlap and infilling geometry above the older unit.

The cited shallow-water units are separated by unconformities (DUs in Fig. 3) associated with dm-thick condensed sections (CSs in Fig. 3). The unconformities are submarine erosional surfaces (Fig. 4a, c and 4e). The condensed sections are made up of blackish/reddish hardgrounds (HGs in Fig. 3), which directly overlie the previously eroded shallow-water deposits, and by a package of condensed pelagites (CPs in Fig. 3). Mineralization also fills neptunian dykes along orthogonal fractures and stratabounds (Fig. 4b).

### *4.1. 1. Unconformities and associated condensed deposits*

The lowermost condensed section (CS1 in Fig. 3) marks the boundary between the Gastropod Limestone and the Requienid Limestone (Fig. 4a). The CS1 thick-bedded package (30-80 cm-thick) consists of

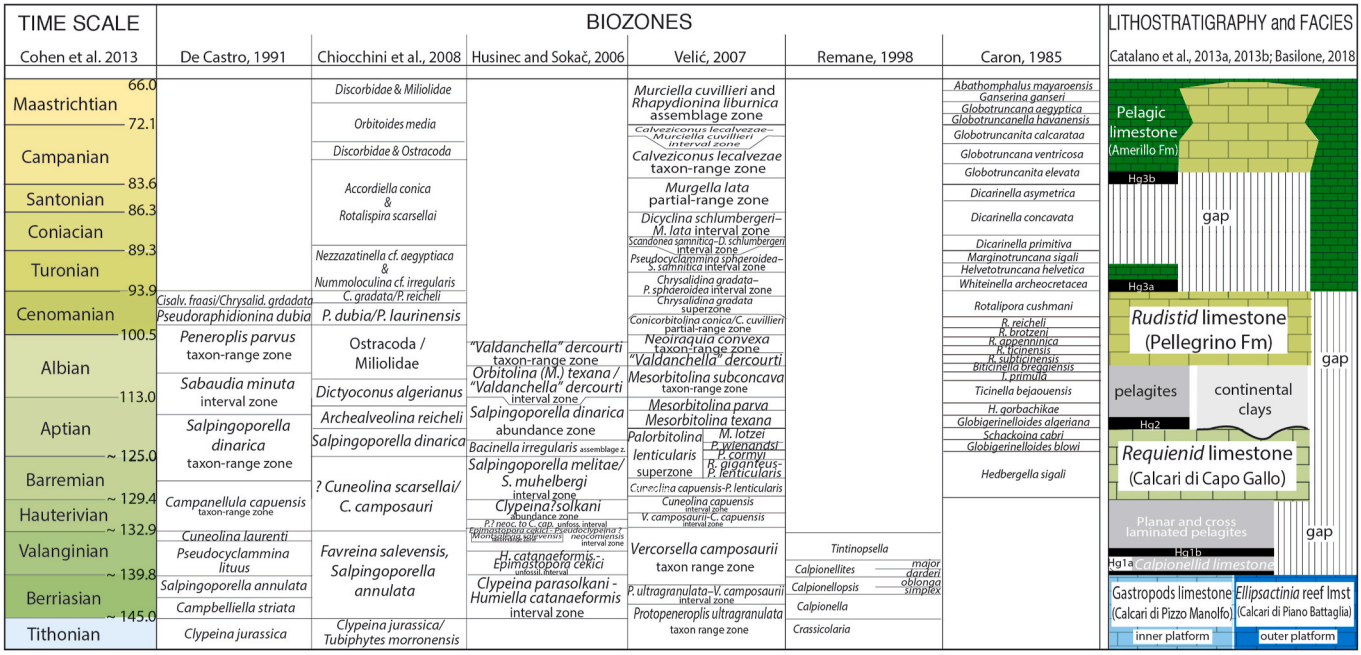


**Fig. 2.** Cretaceous biostratigraphy of carbonate platform and deep-water deposits of central–southern Tethyan, constraining the lithostratigraphic units of the Panormide outcropping in the Palermo Mountains.

two hardgrounds (HG1a and HG1b in Figs. 3 and 4a) alternating with condensed pelagites (CP1 in Fig. 3 and layers a-f in Fig. 4a). HG1a is a 2-6 cm-thick blackish massive crust draping the top of the shallow-water deposits (*i.e.*, the Gastropods limestone, GAS in Fig. 4a). HG1b is an 8-10 cm-thick brick red laminated crust (Fig. 4a). The condensed pelagites comprise graded and planar laminated bioclastic grainstone-to-packstone with reworked shallow-water intraclasts, recrystallized thick-shelled mollusc fragments, crinoids and echinoids (layer a in Figs. 4a and 5a) and red to grey massive wackestone-mudstone (layers b-c in Fig. 4a) with thin-shelled molluscs (filaments), *Protopeneroplis trochangulata* Septfontaine, *Salpingoporella* sp., sponge spiculae, calcitized radiolarians, and *Calpionellites darderi* Colom (Fig. 5b). White and greyish reverse graded and planar-to oblique-laminated wackestone with thin-shelled bivalve and gastropod fragments (layers d-e-f in Fig. 4a) rests on the HG1b. On the basis of the fossil content and stratigraphic constraints we can refer the CS1 to the Valanginian-Hauterivian time interval (8–10 Ma). In detail, the unconformity surface formed at the Berriasian/Valanginian boundary (DU1 in Fig. 3). The immediately overlying hardground (HG1a) and the pelagites with calpionellids (layers a-c in Fig. 4a) belong to the lower Valanginian, based on the *Calpionellites darderi* biozone (Fig. 2). The upper laminated pelagites (layers d-f in Fig. 4a), lacking calpionellids due to their extinction at the early/late Valanginian boundary (Allemann et al., 1971; Remane, 1998), were deposited in the late Valanginian-Hauterivian time interval, capped by the Barremian Requienid Limestone (REQ in Fig. 4a). Consequently, the hardground HG1b, interlayered between the two pelagic horizons, can be assigned to the lower to upper Valanginian boundary.

The intermediate condensed section (CS2 in Fig. 3) marks the boundary between the Requienid Limestone (Barremian-lower Aptian) and the Rudistid Limestone (Upper Albian-Cenomanian). It consists of a 10-20 cm-thick massive reddish hardground (HG2 in Figs. 3 and 4c), draping the Requienid Limestone along an irregular bio-eroded surface (DU2 in Fig. 3), with infilling geometries, and 5-20 cm-thick of red to yellowish pelagic carbonates (CP2 in Figs. 3 and 4c). The pelagites include bioclastic and intraclastic laminated wackestone with aligned thin-shelled bivalve fragments, sponge spiculae, radiolarians and strongly recrystallized planktonic foraminifera (Fig. 5c). Upwards, a sharp surface marks the boundary with the younger Rudistid Limestone (RUD in Fig. 4c). Since the DU2 unconformity marks the top of the Barremian-lower Aptian carbonate platform, the hardground (HG2) and the overlying condensed pelagites (CP2) are stratigraphically assigned to the upper Aptian-lower Albian time interval (10–12 Ma).

The uppermost condensed section (CS3 in Fig. 3) consists of two thin reddish hardgrounds (HG3a and HG3b in Figs. 3 and 4e) interlayered with condensed pelagites (CP3 in Figs. 3 and 4e). HG3a, marking the upper boundary of the Cenomanian Rudistid limestone (RUD in Fig. 4e), is a mm-thick oxide encrustation, developing over irregular dissolution surface (Fig. 5d). The condensed pelagites are made up by dm-thick wackestone with abundant thin-shelled bivalves and planktonic foraminifera (*Hedbergella* sp., rotalipods). The latter show planar and oblique lamination (Fig. 5f) and laterally drape the RUD with infilling geometry. Upwards, the HG3b is a cm-thick hardground that lies immediately below the white and reddish Late Cretaceous (Campanian, due to the occurrence of the markers of the *Globotruncana ventricosa* biozone, see Catalano et al., 2013b)-Eocene planktonic foraminifera-bearing wackestone of the Amerillo Fm (AMM in Fig. 4e). Assuming the unconformity (DU3 in Fig. 3) formed at the Cenomanian/Turonian boundary (Fig. 2), the CS3 can be assigned to the Turonian-early Campanian time (ca. 10 Ma).

### 4.2. *Synsedimentary tectonic*

A common feature characterizing the topmost portion of the three shallow-water units is the occurrence of synsedimentary normal faults and of a metre-scale dense network of neptunian dykes and enlarged fractures (Fig. 4b). The synsedimentary faults, NNE-SSW oriented and variously dipping (ENE and WSW), cut the top of the shallow-water units with small downthrown; they are sealed by the hardgrounds (HGs) and the pelagites (CPs) that, locally, display onlap and buttress unconformity relationships (Fig. 4a). The neptunian dykes, both bed-parallel and vertical to the bedding, and large (some decimetres wide) to small dissolution cavities (Fig. 4d) are also filled by the hardgrounds and pelagites (Fig. 4b).

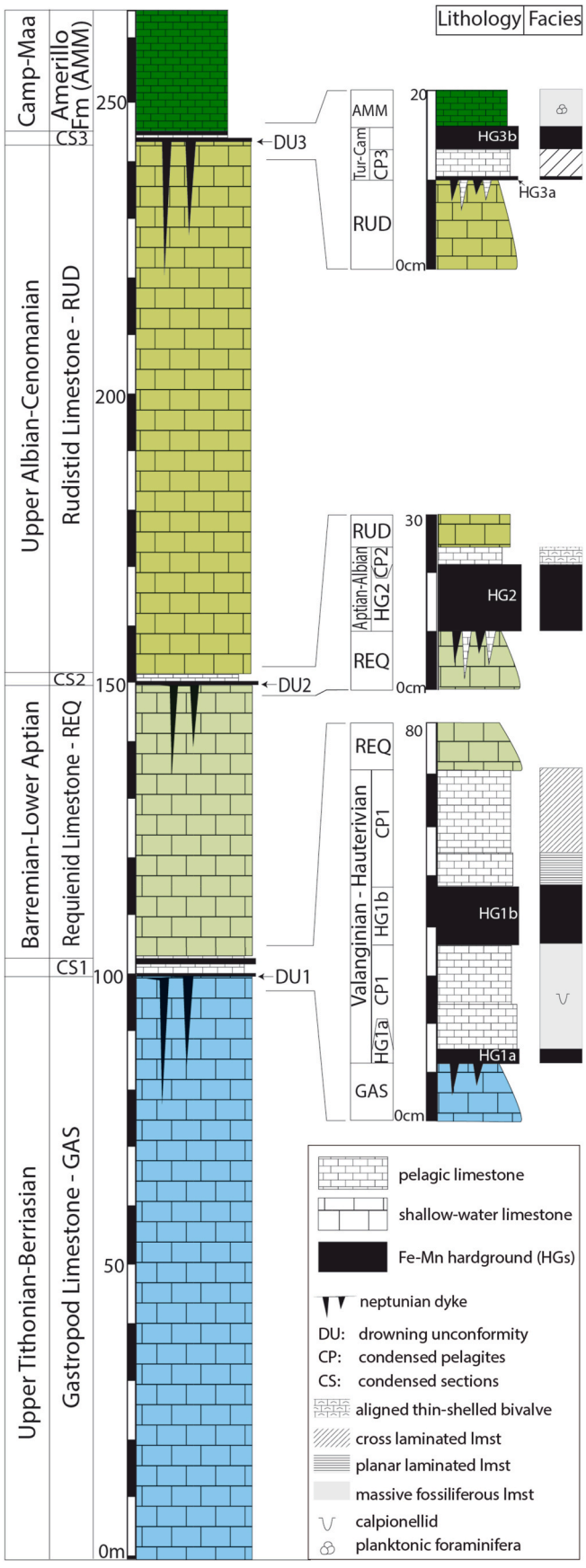


**Fig. 3.** Synthetic stratigraphic Colombrina section. Each one of the condensed sections (CSs) is draught to more detail, highlighting facies of the hardground levels (HGs) and condensed pelagic horizons (CPs).

### 4.3. Mineralogy of the phosphatized FeMn-rich hardgrounds

Preliminary OM examination of the hardgrounds shows that they consist of blackish-to-reddish grains (with a size of few microns) finely dispersed within a calcite-rich matrix (Fig. 5d) or encrusting fractures/fissures, dissolution cavities, and stylolite surfaces (Fig. 5e–f).

SEM-EDS chemical maps collected from samples of all hardgrounds show that the μm-sized blackish-to-reddish grains in the calcite matrix are rich of Fe (red grains in Fig. 6a). Notably, in the HG1a and HG1b levels the Fe-grains are finely intermixed with Mn-rich grains (Fig. 6b). Single point EDS spectra collected from the Mn-grains show the occurrence of other metals: Co, Ni, and Cu (Fig. 6c).

PXRD data collected from the three hardgrounds yielded sharp Bragg peaks of calcite and carbonate fluoro-apatite (Ca and CFA in Fig. 7, respectively). Notably, the uppermost hardgrounds (HG3a and HG3b) show the highest content of CFA (see the strong reflection at ~ 32° 2θ, Fig. 7). Additional weak and broad peaks of poorly-crystalline goethite [FeOOH] have been identified in the patterns collected from the samples HG1a, HG1b, and HG2 (see the weak reflection at ~ 21° 2θ in Fig. 7).

Raman spectra show the presence of different Fe compounds in all hardgrounds: hematite [$Fe_2O_3$] characterized by peaks at ~ 223, 293, 407, 655 and 1315 $cm^{-1}$ (spectrum S1 in Fig. 8), goethite (S2 in Fig. 8) with peaks at ~300, 394, 480, 553 $cm^{-1}$ (de Faria and Lopes, 2007); finally, a band at ~ 685 $cm^{-1}$ in spectrum S2 suggests the possible presence of magnetite [$Fe_3O_4$] (de Faria and Lopes, 2007). Mn oxide(s) have been identified in samples from HG1a-b hardgrounds by bands at ~ 399, 500, 580, 630, and 735 $cm^{-1}$ (S3 in Fig. 8). These spectral features are consistent with the mineral birnessite [a Mn oxide with a layer structure and ideal formula (Na, Ca, K)($Mn^{4+}$, $Mn^{3+}$)$_2O_4$·1.5$H_2O$] or vernadite (Bernardini et al., 2019; Julien et al., 2003), a z-disordered variety of birnessite. Based on the data of Bernardini et al. (2021b), in these compounds Mn occurs as $Mn^{3+}$ (strong scattering ~ 580 $cm^{-1}$) and $Mn^{4+}$ (scattering at ~ 630 $cm^{-1}$, see Fig. 8).

A summary of the mineralogical results is provided in Table 2.

### 4.4. Carbon and Oxygen isotope analysis

The evolution of carbon and oxygen isotopic composition along the three condensed sections (CSs in Fig. 3) comprising the hardgrounds and the condensed pelagites is given in Fig. 9.

In the lower condensed section (CS1), the $\delta^{13}C$ curve (average value 0.35 ‰) is characterised by a sharp negative shift (from ~1.5 ‰ to −3.49 ‰) approaching the HG1b hardground (Fig. 9). A subsequent positive shift towards ~2.7 ‰ is observed in the uppermost CP1 pelagic horizon (Fig. 9). The $\delta^{18}O$ (average value −2.32 ‰) shows a similar trend: it reaches its minimum value in the HG1b hardground (−4.49 ‰, Fig. 9) and increases up to −0.12 ‰ in the upper CP1 horizon (Fig. 9). No clear perturbation of $\delta^{13}C$ and $\delta^{18}O$ is observed in the HG1a hardground (Fig. 9).

A similar variation is observed in the intermediate condensed section (CS2 in Fig. 9); the $\delta^{13}C$ record shows values between 2.44 ‰ and −3.97 ‰ (average value 0.23 ‰), reaching the minimum values (−3.97 ‰) in the HG2 hardground (Fig. 9). A subsequent positive shift to 1.93 ‰ is observed toward the CP2 horizon (Fig. 9). In this interval, the $\delta^{18}O$ isotope data range from −4.84 to −1.47 ‰ (average value −2.66 ‰), reaching its minimum value in the HG2 hardground (Fig. 9) and increasing in the upper pelagic horizon (CP2 in Fig. 9).

In the uppermost condensed section (CS3 in Fig. 9) the $\delta^{13}C$ record shows values between 2.70 ‰ and −1.84 ‰ (average value 1.37 ‰). In the lowermost part of the section (*i.e.,* the top of the shallow-water Rudistid Limestone, RUD in Fig. 9), $\delta^{13}C$ values range between 0.86 ‰ and 2.15 ‰ (Fig. 9) and then decrease in the lowest phosphatized HG3a hardground (Fig. 9). The $\delta^{13}C$ reach the maximum value (2.70 ‰) in the following thin pelagic horizon (CP3, Fig. 9) and then shift to −1.84 ‰ in the HG3b hardground (Fig. 9). Finally, the $\delta^{13}C$ increases up to 2.52 ‰ in the planktonic foraminifera-bearing wackestone of the

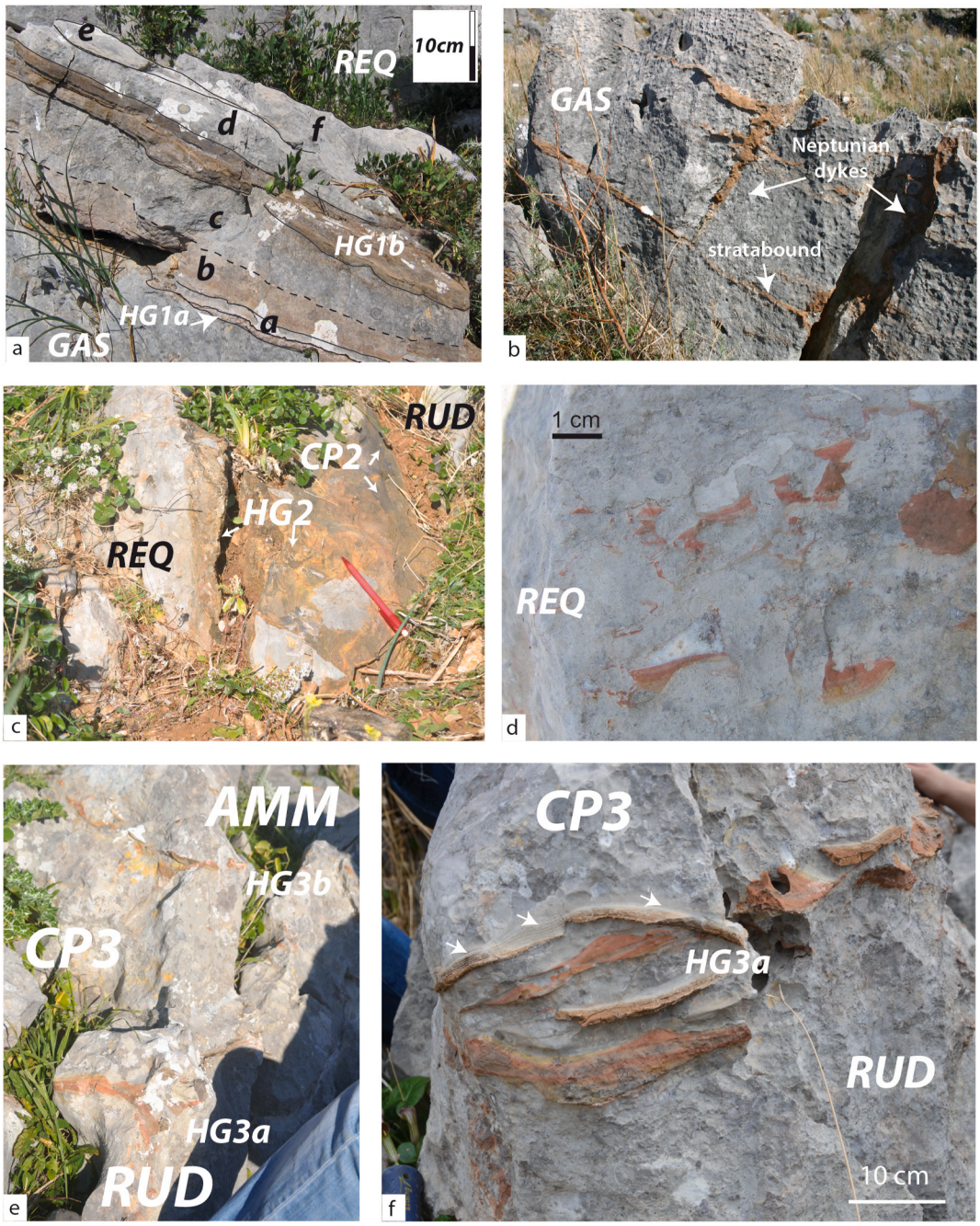


**Fig. 4.** a) Detailed view of the lowermost condensed section (CS1 in Fig. 3) and relative unconformity (DU1 in Fig. 3). The massive reddish HG1a hardground rests with laterally thinning above the Upper Tithonian-Berriasian Gastropod Limestone (GAS). The brick-red to blackish laminated HG1b hardground is interlayered in the thick condensed pelagites (CP1 in Fig. 3). The latter consists of: i) thin grey bioclastic grainstone-to-packstone (layer a) that rests above the HG1a and onlap the GAS; ii) massive red and grey lumachella wackestone (layers b and c), onlapping the shallow-water limestone (GAS); iii) grey pelagic mudstone and planar laminated to graded packstone-grainstone intercalations with reworked shallow-water fragments (layer d); iv) planar, oblique and cross-laminated grey and whitish wackestone-packstone (layer e); v) brown-to-yellow phosphatized packstone with thin-shelled bivalve fragments (layer f). Follow upward the Barremian-Lower Aptian Requienid Limestone (REQ); b) vertical to bed-parallel (stratabound) neptunian dykes, cutting the uppermost beds of the Gastropod Limestone (GAS) and filled by mineralized material; c) intermediate condensed section (CS2 in Fig. 3). The unconformity surface (DU2 in Fig. 3), cutting the Barremian-lower Aptian Requienid limestone (REQ), is marked by the HG2 hardground and condensed pelagites (CP2); follow upward the Rudistid limestone (RUD); d) dissolution cavities, occurring in the topmost beds of the REQ, filled by reddish pelagites and occluded by whitish calcite cements, highlighting geopetal structures; e) uppermost condensed section (CS3 in Fig. 3); it consists of a thin hardground (HG3a), marking the unconformity surface (DU3 in Fig. 3) at the top of the Rudistid limestone (RUD), a package of condensed pelagites (CP3), and by another hardground (HG3b) followed upward by the Upper Cretaceous-Paleogene pelagites of the Amerillo Fm (AMM); f) detailed view of the HG3a hardground locally characterized by lamination (arrows).

Amerillo Fm (Fig. 9). The $\delta^{18}O$ record range from −0.50 to −3.98 ‰ (average value −1.94 ‰). The $\delta^{18}O$ increases from −3.11 to −0.50 ‰ approaching the lower phosphatized HG3a hardground (Fig. 9), where it decreases to −2.04 ‰ (Fig. 9). The $\delta^{18}O$ increases up to −0.50 ‰ in the upper pelagic (CP3) horizon (Fig. 9) and decreases to −3.98 ‰ within the HG3b hardground (Fig. 9). Similarly to what observed for the $\delta^{13}C$ curve, the $\delta^{18}O$ shows a gradual increasing trend towards positive values in the pelagites of the Amerillo Fm (Fig. 9).

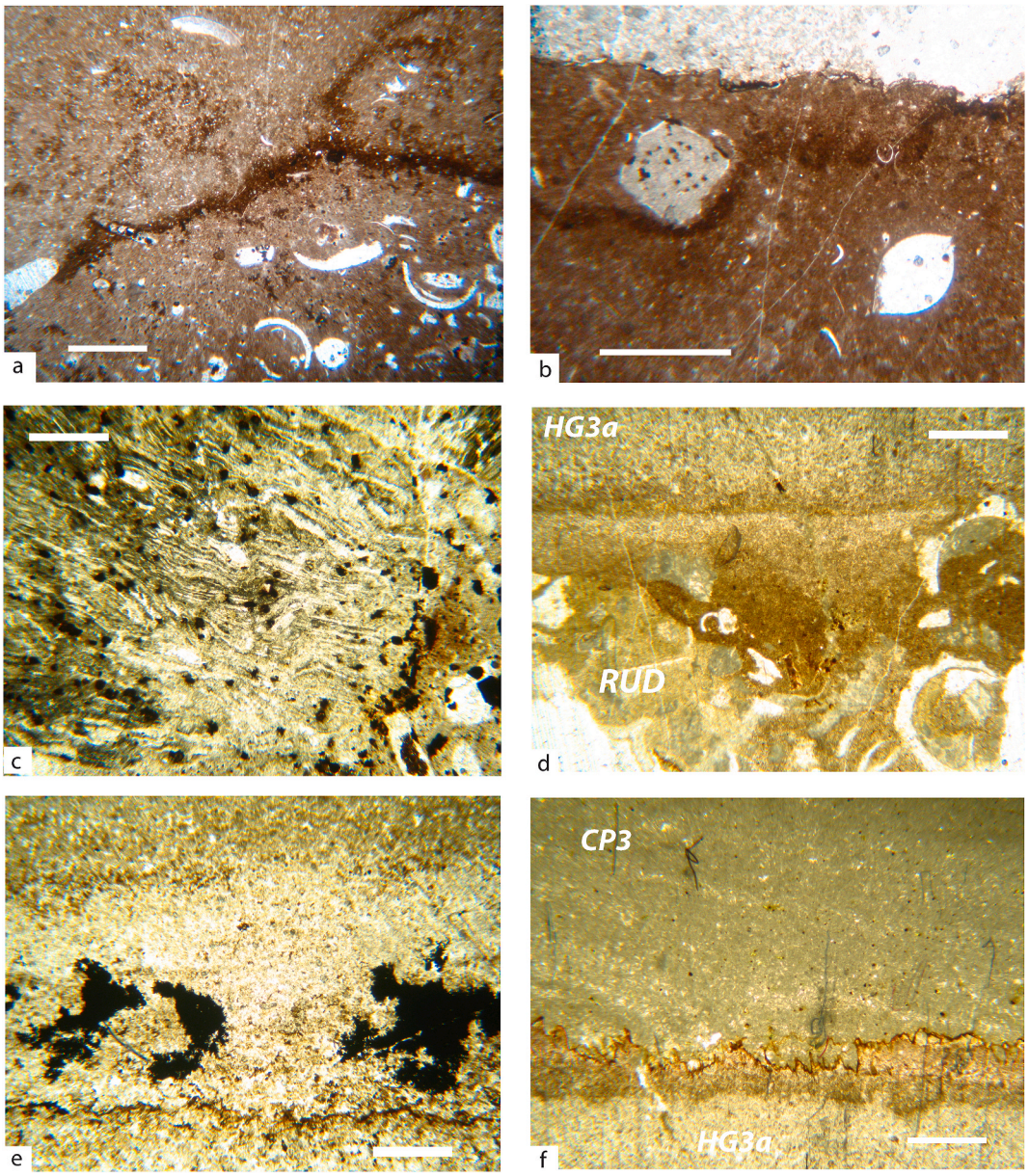


**Fig. 5.** Microfacies of the HGs hardgrounds and condensed pelagites (scale bar 1 mm for all images): a) red pelagites consisting of packstone and wackestone with thick-shelled molluscs, intraclasts, crinoids, echinoids (layer a in Fig. 4a); b) red wackestone with *Protopeneroplis* sp., *Calpionellites darderi*, recrystallized radiolarians, mollusc fragments and intraclasts (layer b in Fig. 4a) passing to grey wackestone (layer c in Fig. 4a) through a stylolite surface impregnated by darkish Fe-Mn oxides; c) aligned thin-shelled molluscs, d) uppermost unconformity surface (DU3 in Fig. 3) represented by an irregular dissolution surface cutting the Rudistid limestone (RUD) and covered by the HG3a hardground. The reddish mineralized material impregnates the top of the RUD; e) darkish Fe-Mn oxides filling cavities and stylolites in the hardground layers; f) planar and oblique laminated condensed pelagites covering the phosphatized HG3a hardground, through a strongly mineralized stylolite surface.

## 5. Discussion

### 5.1. Stratigraphy of the condensed intervals of the Panormide Cretaceous succession

Three phosphatized metal-rich hardgrounds (HGs in Fig. 3) associated with unconformity surfaces and condensed pelagic deposits (DUs and CPs in Fig. 3) mark repetitive episodes of shallow-water carbonate production shutdown in the Tethyan Ocean during the Cretaceous.

Mineralogical and textural features and fossil assemblages in the condensed pelagic deposits overlying each carbonate platform unit (Figs. 3–5) record strong environmental changes with the development of open-sea conditions that are the typical characteristics of drowning unconformities (*e.g.*, Schlager, 1981; Godet, 2013). The strong environmental perturbations during the three demise events are represented by the occurrence of authigenic minerals' hardgrounds, producing negative shifts in the $\delta^{13}C$ and $\delta^{18}O$ curves (Fig. 9) due to the different types of carbonate minerals respect to the rest of the succession along the studied section (biogenic *vs*. authigenic carbonates). These features highlight abrupt episodes of demise and recovery of the carbonate platform (*e.g.,* Reolid and Abad, 2019; Danisch et al., 2021).

The lowermost demise event (DU1/CP1 in Figs. 3 and 10) encompasses a long-time period: from the demise of the carbonate platform at Berriasian/Valanginian boundary to its recovery since the Barremian. This event is coeval with other demise and drowning events recorded along many Tethyan carbonate platforms that prelude the onset of the "Weissert Event" (Fig. 10, Simo et al., 1993; Van de Schootbrugge et al., 2003; Grădinaru et al., 2016).

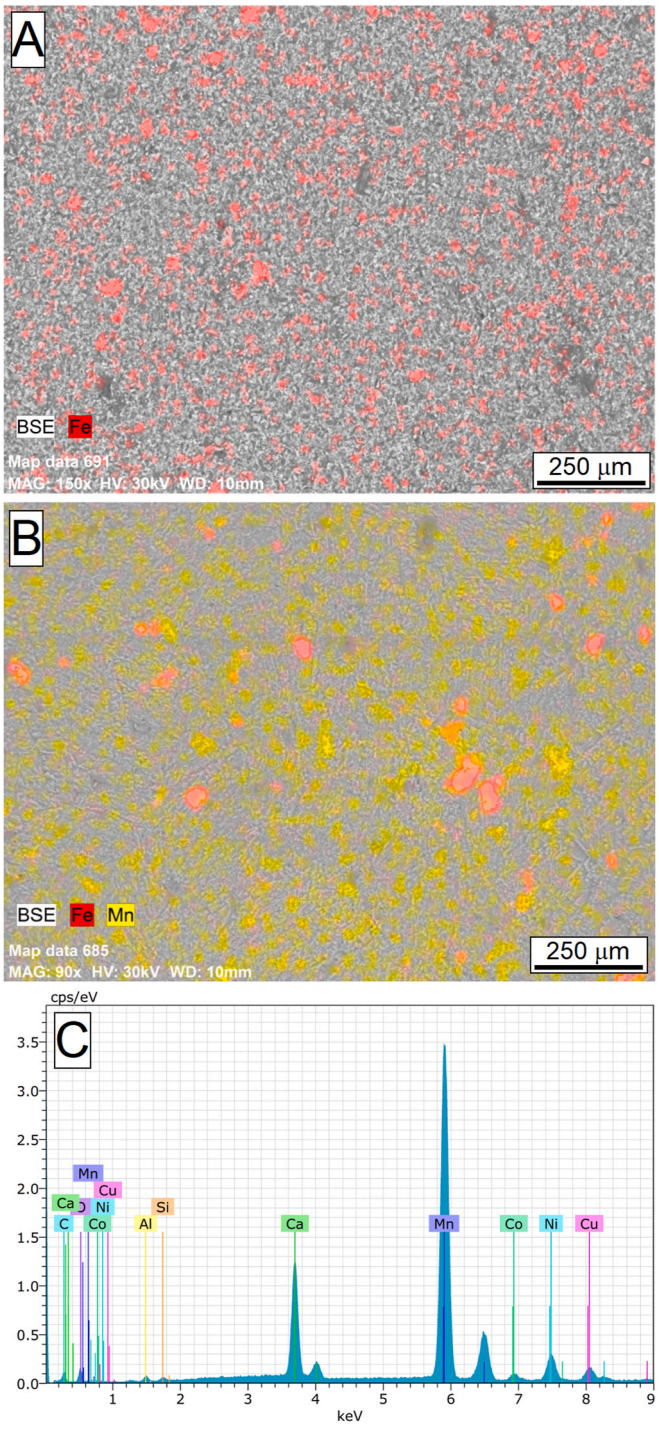


**Fig. 6.** EDS mapping of Mn and Fe (highly redox-sensitive metals) collected from HG2 and HG3 hardgrounds (A) and from the HG1 hardground (B). Single point EDS spectrum collected from a Mn-rich grain in the HG1 showing the occurrence of Co, Ni, and Cu (C). Fe (red) have been identified in all the HGs while Mn (yellow) occurs only in the HG1 hardground.

The intermediate demise event (DU2/CP2 in Fig. 3) occurred at end of the lower Aptian Requienid Limestone sedimentation. The condensed pelagites (CP2) and phosphatized Fe-rich hardground (HG2) are capped by the uppermost Albian-Cenomanian Rudistid Limestone (Fig. 3). This condensed interval is coeval with the drowning events, widely recognized in the peri-Tethyan carbonate platforms (Simo et al., 1993; Föllmi and Gainon, 2008; Graziano, 2013; Westermann et al., 2013; Huck et al., 2013) that prelude the onset of the OAEs, among them the so called

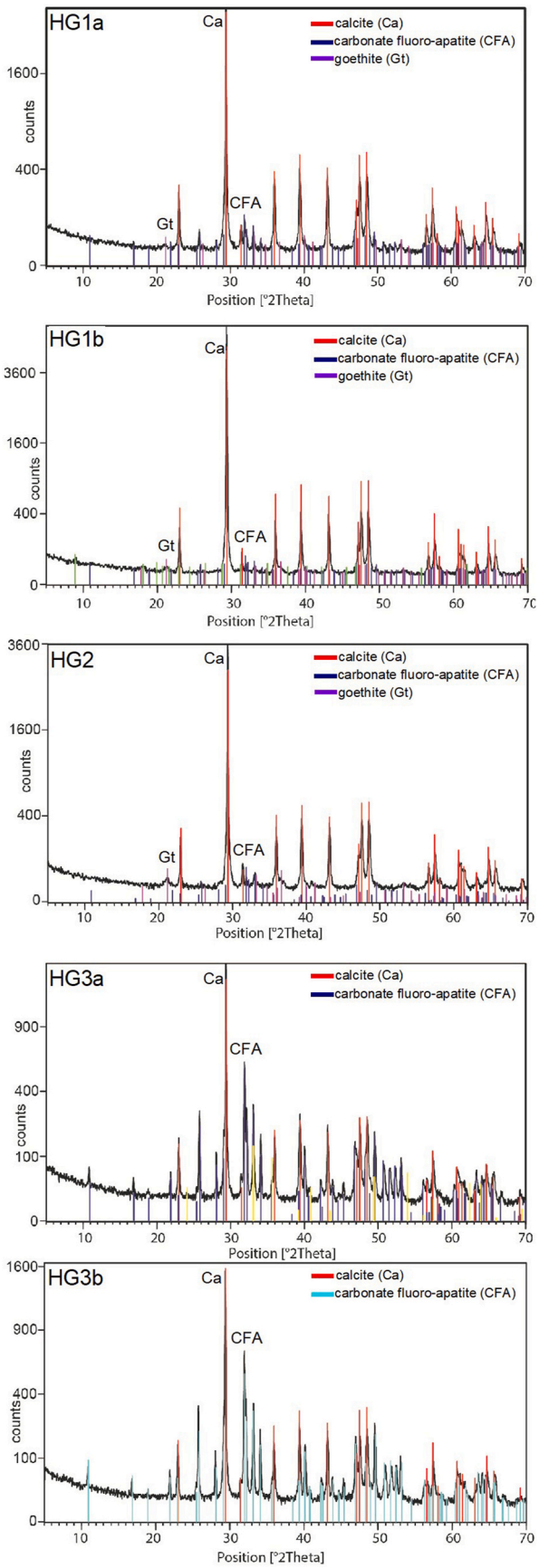


**Fig. 7.** PXRD patterns of the HGs hardgrounds from the Colombrina section. Ca: calcite, Gt: goethite, CFA: carbonate fluoro-apatite.

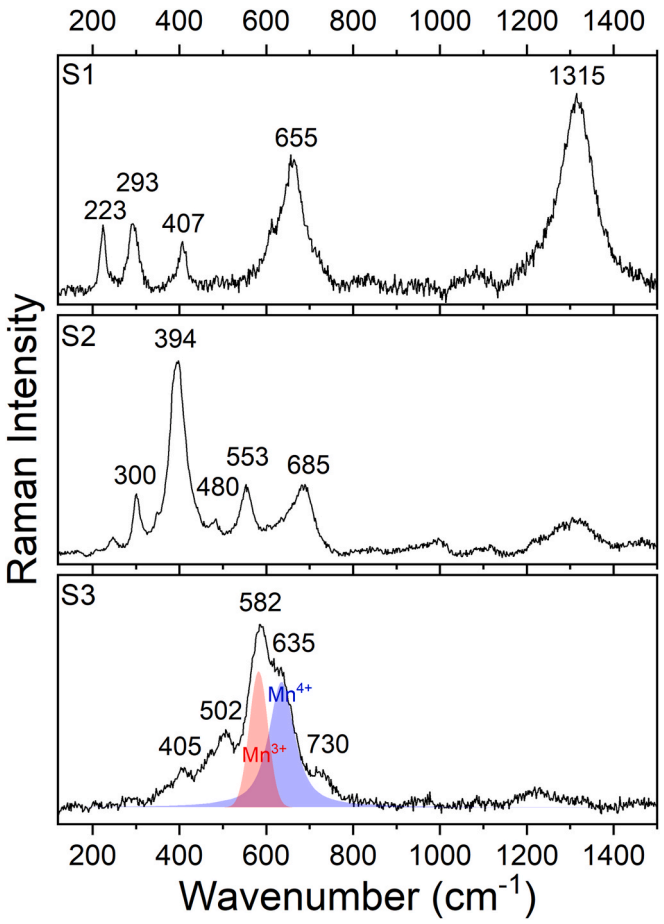


**Fig. 8.** Raman spectra collected from the HGs hardgrounds. S1: hematite, S2: goethite, S3: birnessite and/or vernadite. Raman spectra of Fe oxides (S1 and S2) have been collected from all the HGs while that of Mn oxides (birnessite/vernadite) only from the Mn-rich HG1 hardgrounds (see Table 2). The peaks of $Mn^{3+}$ (red) and $Mn^{4+}$ (blue) in the spectrum S3 are assigned according to Bernardini et al. (2021).

"Selli level" (Fig. 10, Menegatti et al., 1998; Jenkyns, 2018). This is the time interval of the very peculiar paleoceanographic conditions of the mid-Cretaceous: the so called "undecided ocean" (Wortmann et al., 1999) or "unstable ocean" (Giorgioni et al., 2012, 2015), which contrasts with the "chalk ocean" of the Upper Cretaceous that starts in the late Albian.

The uppermost drowning event (DU3/CP3 in Fig. 3) occurs at the end of the Cenomanian shallow-water sedimentation. The overlying pelagites and the phosphatized Fe-rich hardground (CP3 and HG3b in Fig. 3) are capped by the upper Campanian-Paleogene pelagic limestone (AMM), which reveals the definitively drowning of the whole Panormide carbonate platform. This event coincides with the drowning and/or long-term uplifting events described from Sicily, Southern Apennines and Apulia carbonate platforms (Fig. 10; Mindszenty et al., 1995; Carannante et al., 2008; Basilone and Sulli, 2018), some of which were related with the onset of the OAE2 "Bonarelli level" (Fig. 10; Parente et al., 2007).

Among the several mechanisms proposed to explain the demise of carbonate platforms and the generation of a drowning unconformity, rapid tectonic collapse of the platform, sea-level rise, upwelling of anoxic deep-ocean waters, and/or climate changes are the most accepted (*e.g.,* Dromart et al., 2003; Mutti and Bernoulli, 2003; Brandano et al., 2016a). The occurrence, just below of each unconformity, of enlarged fractures, normal faults, open spaces, collapse phenomena, and neptunian dykes (Fig. 4b–d) suggests fracturing in an overall tensional regime (Bourrouilh et al., 1998; Wendt, 2017) and dislocation of an already hardened substrate (James and Choquette, 1983) in faulted-platform blocks (see Santantonio, 1993; Bosence, 2005; Nieto et al., 2014; Basilone, 2020).

**Table 2**
Sample description and summary of the minerals identified in the HGs hardgrounds integrating OM, SEM-EDS, PXRD, and RS results. Ca: calcite, CFA: carbonate fluoro-apatite, Gt: goethite, He: hematite, Bi/Ve: birnessite and/or vernadite.

| Sample | Lithology and texture | Thick. (cm) | Stratigraphy | Major minerals | Minor minerals |
|---|---|---|---|---|---|
| HG1a | Brick-red to blackish massive and infilling fractures and sedimentary dykes | 6 to 8 | top of *Gastropods* limestone | Ca | CFA, Gt, He, Bi/Ve |
| HG1b | laminated black | 8 to 12 | interlayered in the CS1 | Ca | CFA, Gt, He, Bi/Ve |
| HG2 | brick-red to blackish massive, with infilling materials in neptunian dykes | 10 to 20 | top of *Requienid* limestone | Ca | CFA, Gt, He, Bi/Ve |
| HG3a | reddish to brick-red crust alternated with planktonic foraminifers-bearing grainstone and infilling neptunian dykes and dissolution cavities | 4 to 6 | top of *Rudistid* limestone | Ca, CFA | Gt, He |
| HG3b | reddish encrustations | 1 to 3 | top of CS3 | Ca, CFA | Gt, He |

The abundant CFA identified by PXRD and SEM-EDS in the metal-rich hardgrounds (*i.e.,* mostly in the HG3a-b, see Figs. 6 and 7) in the Colombrina section suggests that the demise events occurred during high nutrients supply. Under high phosphate levels, nutrient conditions became eutrophic and the platform ecosystem stop producing carbonate, leading to platform demise (*e.g.,* N Tethyan margin; Fo;llmi and Godet, 2013; Chatalov et al., 2015). Phosphorus is primarily delivered to marine surface waters *via* continental weathering (riverine influx) and upwelling of deep waters (Paytan and McLaughlin, 2007). Notably, episodic upwelling of cold and nutrient-rich waters has been related to development of phosphatized hardgrounds on several Miocene carbonate platforms (Mutti and Bernoulli, 2003; Brandano et al., 2016b). Therefore, the repetitive demise of the Panormide carbonate platform can be linked with episodic enrichment of phosphorous resulting from increased continental weathering and/or upwelling of deep-water masses; the latter likely favoured by the tectonic setting of the study area, characterized by structural high and structural low (Basilone, 2020, 2021b).

### 5.2. Redox conditions and paleoenvironmental implications

In the scenario depicted above, the episodic perturbations in the redox conditions during the demise events and the repetitive phosphatization of the platform seafloor may have been recorded by the redox-sensitive (Mn and Fe) metals. Notably, our SEM-EDS, PXRD and RS data show the separation between Mn and Fe in the different phosphatized hardgrounds (HGs).

The HG1a-b hardgrounds, formed during the lowermost demise event (Valanginian – Hauterivian, see Fig. 11a), are rich of Mn and Fe (see Fig. 6b) and consist of a very fine mixture of Mn oxides with a layer structure (birnessite and/or its disordered variety vernadite), Fe oxides

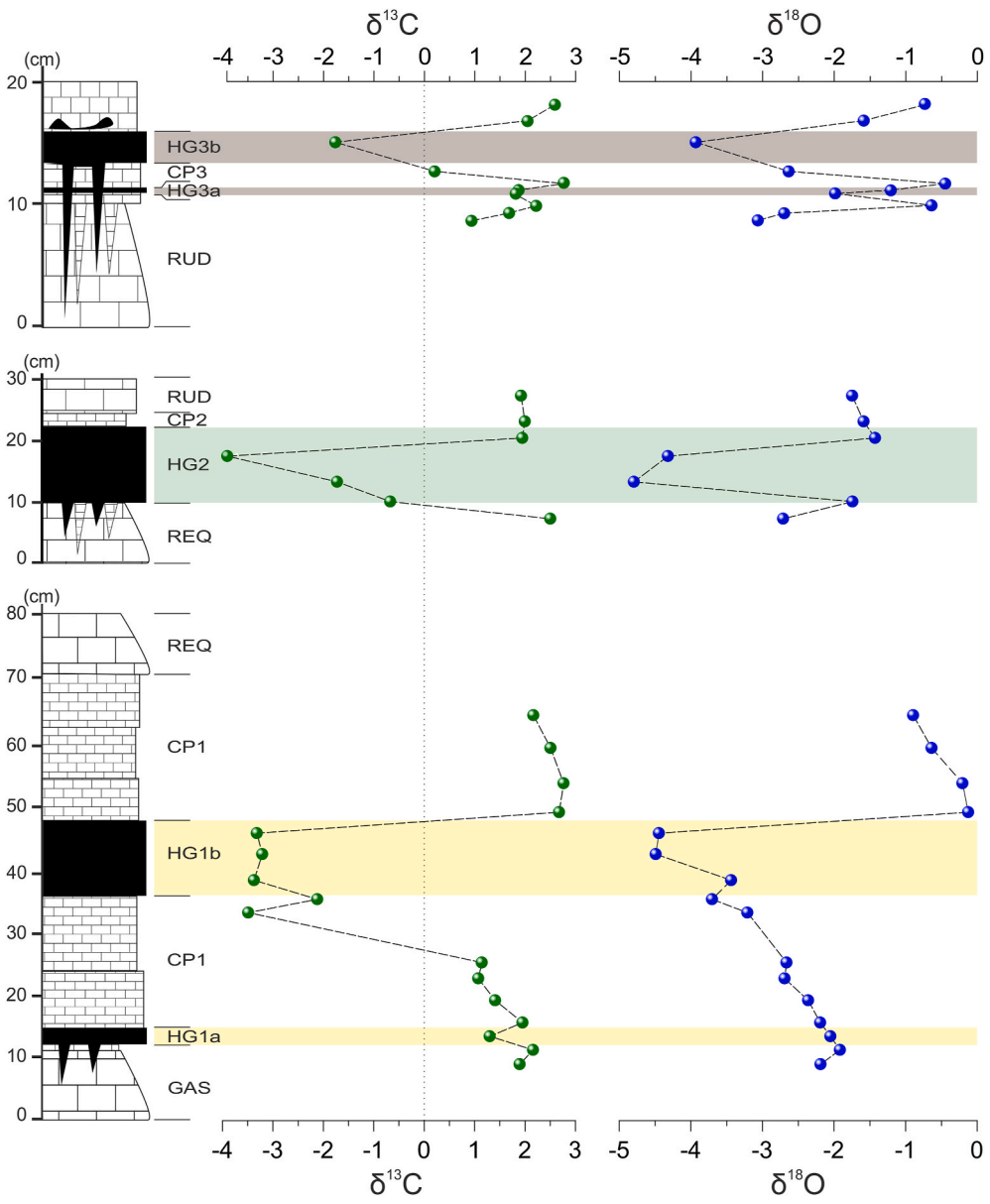


**Fig. 9.** Evolution of the stable isotope compositions ($\delta^{13}C$ and $\delta^{18}O$) along the condensed sections (CSs). Note the sharp negative shifts of both $\delta^{13}C$ and $\delta^{18}O$ during the formation of the HGs hardgrounds.

(goethite, hematite, and minor magnetite), calcite, and CFA (see Table 2). Notably, vernadite is a common mineral in marine ferromanganese deposits that typically precipitates under oxic conditions directly from ocean water (hydrogenesis) onto hard rock substrates (see Hein and Koschinsky, 2014 for a detailed explanation). This genetic process is also consistent with the identification of abundant goethite, a compound that can be interpreted as the final product of hydrogenetic $Fe^{2+}$ to $Fe^{3+}$ oxidation (Hein et al., 2000). In marine environment, Mn and Fe oxides concentrate different critical elements from seawater (*e.g.,* Co, Ti, Li, Pt, Zr, Nb, Te, Ni, V, Bi, Mo, W, among others), depending on the water (redox) conditions (Hein et al., 2000). For example, Co, Te, and Ce are the most characteristic metals of hydrogenetic precipitation (under oxic conditions) while Ni, Cu, Li, and Zn (which are produced by dissolution of redox-sensitive components in the sediment) are typical of diagenetic precipitation under suboxic conditions (Hein and Koschinsky, 2014). EDS data revealed that the birnessite/vernadite grains are rich of Cu, Ni, and Co (Fig. 6c). The identification of trace metals characteristic of both hydrogenetic (Co) and diagenetic (Cu and Ni) precipitation is consistent with the oxidation of Mn at the seawater-sediment interface (Fig. 11a). Moreover, analysis of the Raman spectra revealed the presence of oxidized Mn species: $Mn^{3+}$ and $Mn^{4+}$ (see Fig. 8). Altogether these results suggests that the oxidation of $Fe^{2+}$ to $Fe^{3+}$ and $Mn^{2+}$ to $Mn^{3+/4+}$ during the DU1/CP1 event occurred onto the seafloor under oxic seawater conditions (Fig. 11a).

A slightly different scenario can be proposed for the intermediate demise (Aptian-Albian) and uppermost drowning (Turonian-Campanian) events (DU2/CP2 and DU3/CP3 in Fig. 11b and c). Our data show that the HG2 and HG3a-b hardgrounds are free of Mn (see Fig. 6) and (similarly to the HG1a-b hardgrounds) consist of a fine mixture of goethite, hematite, magnetite, calcite, and CFA (Table 2). The important point here is that Mn has higher solubility than Fe when the pH is between 6 and 8, except at high Eh (above 600 mV) (Hem, 1963, 1972). Our results thus suggest that the formation of Fe oxides during these events (DU2/CP2 and DU3/CP3) occurred under suboxic conditions in which $Fe^{2+}$ oxidizes to $Fe^{3+}$ while Mn remains dissolved as $Mn^{2+}$ (Figs. 11b and c). Therefore, these hardgrounds likely formed under lower pH and/or Eh conditions than those characterizing the Valanginian – Hauterivian (DU1/CP1) event. Notably, the HG3a-b

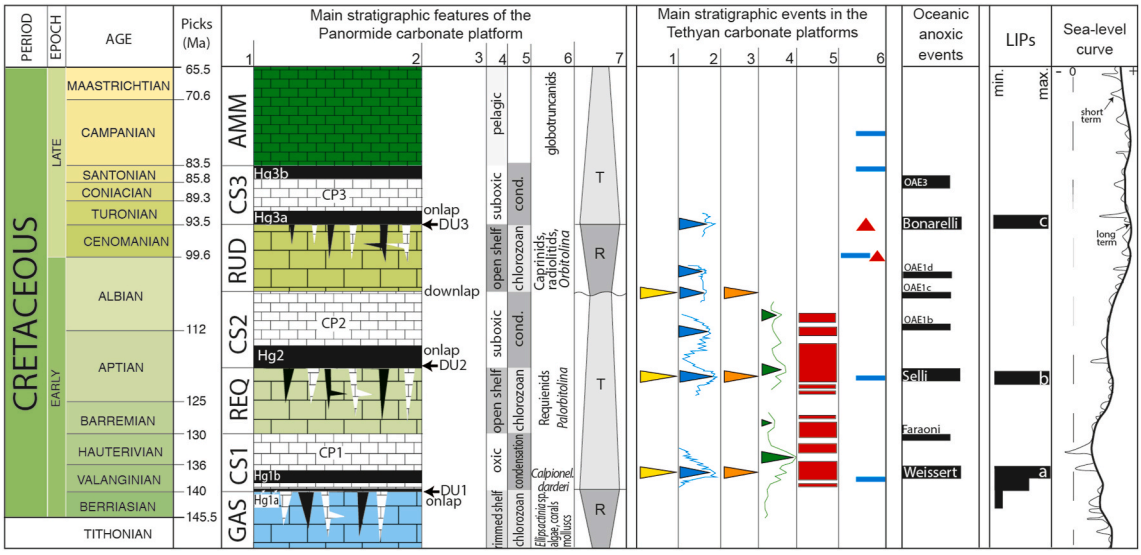


**Fig. 10.** Synthetic correlation of the stratigraphic features of the study Cretaceous Panormide carbonate platform, sampled at Colombrina section, with the main oceanographic and stratigraphic events recorded in the Tethyan realm. Main stratigraphic events in the Panormide carbonate platforms: 1. formation labels (GAS: Gastropod Limestone, REQ: Requienid Limestone, RUD: Rudistid Limestone, AMM: Amerillo Fm) and interlayered condensed section (CS1-3); 2. columnar section with indication of the different Fe-Mn hardgrounds considered in this study (HG1-3) and condensed pelagites (CP1-3); 3. Drowning unconformities (DU1-3) and stratigraphic relationships; 4. Depositional environments and geometric-types of carbonate platforms and redox conditions of the condensed sections; 5. skeletal grain associations; 6. main biota; 7. Major Transgressive (T)/Regressive (R) tectono-eustatic cycles of the Sicilian carbonate platform-basin system (after Basilone, 2009). Main stratigraphic events in the Tethyan carbonate platforms: 1. Main growth crises of the Tethyan carbonate platforms (after Simo et al., 1993); 2. Positives spikes of stable carbon isotopic curve (after Weissert and Erba, 2004); 3. Episodes of enhanced greenhouse condition (after Weissert et al., 1998); 4. Phosphorous accumulation rates (after Föllmi et al., 1994; Föllmi and Godet, 2013); 5. Phases of phosphogenesis, condensation and platform drowning in the Alpine carbonate platforms (after Föllmi and Godet, 2013); 6. Drowning unconformity (blue bold line) and uplift/bauxites sedimentation events (red triangle) in the Apulia and Southern Appennines carbonate platforms (after Mindszenty et al., 1995; Carannante et al., 2008). OAEs. Oceanic anoxic events (after Arthur et al., 1990). LIPs: Large Igneous Provinces, volcanic activity rates of the Paranà province (a, after Stewart et al., 1996), Ontong-Java Plateau1 (b), Ontog Java2 and Caribbean Plateau (c, after Tarduno et al., 1991; Tejada et al., 2009). Long- and short-term sea-level curve (Haq et al., 1987).

hardgrounds mark the transition to pelagic limestone deposition (Amerillo Fm, *i.e.*, the drowning of the Panormide platform) and, compared to the other hardgrounds, they are the most enriched in CFA (Fig. 7). This suggests elevated phosphorous concentrations at the top of the platform during the Turonian – Campanian likely related to the stage of descent of the platform toward the OMZ (Fig. 11c).

### 5.3. *Sensitivity of carbonate platforms to major climatic perturbations in the cretaceous tethys*

Episodes of paleoenvironmental stress trigger reduction or halt in shallow-water carbonate production. Sea-surface water temperature directly drives the ecology and morphology of carbonate platforms (Lees and Buller, 1972; Pomar 2020). Thus, changes in sea-surface water temperatures (Jenkyns and Wilson, 1999) or in detrital fluxes and flooding of platforms by nutrient-rich waters frequently cause the eutrophication of the carbonate system and a drastic reduction of its growth potential (Föllmi, 2012). One of the most important factors causing changes of sea-surface ocean water chemistry is the increase of dissolved $CO_2$ contents in the hydrosphere/atmosphere system, which induces lower pH values, producing the so-called “ocean acidification” (Kleypas et al., 1999; Orr et al., 2005). Drowning events and phosphatized deposits observed in Northern Tethyan and North Atlantic carbonate platforms were related to flooding of carbonate platforms by nutrient-rich waters during enhanced burial of organic matter and acidification of the oceanic waters (Föllmi et al., 1994; Weissert et al., 1998; Föllmi and Gainon, 2008). Notably, excess of $CO_2$ can be related to intensive volcanism (Large Igneous Provinces, Fig. 10): Paraná-Etendeka (136-133 Ma), Ontong-Java Plateau-Manihiki Plateau (125-123 Ma), Kerguelen Plateau-Rajmahal Traps (118 Ma) and Caribbean-Colombian Province (90 Ma) (see Gale et al., 2020).

The Panormide carbonate platform exhibits unique characteristics in its recovery after climatic perturbations compared to other Cretaceous carbonate platforms of the Tethyan realm. While many of the latter have permanently drowning and failed to regenerate, the Panormide has shown the ability to recover despite severe environmental pressures and temporary collapse. Many periTethyan carbonate platforms, after their drowning, followed a path of sinking and formation of siliclastic or carbon-rich deposits, with no possibility of carbonate recovery. Examples are those of the Helvetic Alps (Van de Schootbrugge et al., 2003; Föllmi and Gainon, 2008), Basque-Cantabrian basin (Wilmsen, 2000) for the N and NW Tethyan margins and from Apulia (Graziano, 2013), Egypt (Mansour et al., 2024), Tunisia (Heldt et al., 2010), Turkey (Yılmaz et al., 2022) for the S and SE margins.

The low rates of tectonic subsidence for the Colombrina block during the examined intervals, as noted by Basilone (2021b), along with the rapid transition from the demise to the recovery of the carbonate platform, imply that the environmental perturbation was likely driven by nutrient excess or eutrophication in shallow waters. This nutrient enrichment could have led to significant biological changes, impacting carbonate production. Subsequently, this was followed by a deepening phase at shallow depths (*e.g.*, Mallarino et al., 2002; Brandano et al., 2016b), which contributed to the recovery of the carbonate platform.

The carbonate systems typically took hundreds of thousands of years to recover after climatic perturbations (*e.g.*, Föllmi et al., 2006). In contrast, the Panormide basin experienced a much longer period of starvation, lasting millions of years, before showing signs of recovery. This marked difference illustrates the varying responses of carbonate platforms to environmental stresses, with the Panormide basin struggling significantly longer before resuming carbonate production. The reasons behind this prolonged starvation in the Panormide may include factors like changes in sea level, nutrient availability, tectonics and sedimentary dynamics that inhibited recovery during crucial periods.

In summary, the Panormide stands out as an emblematic example of

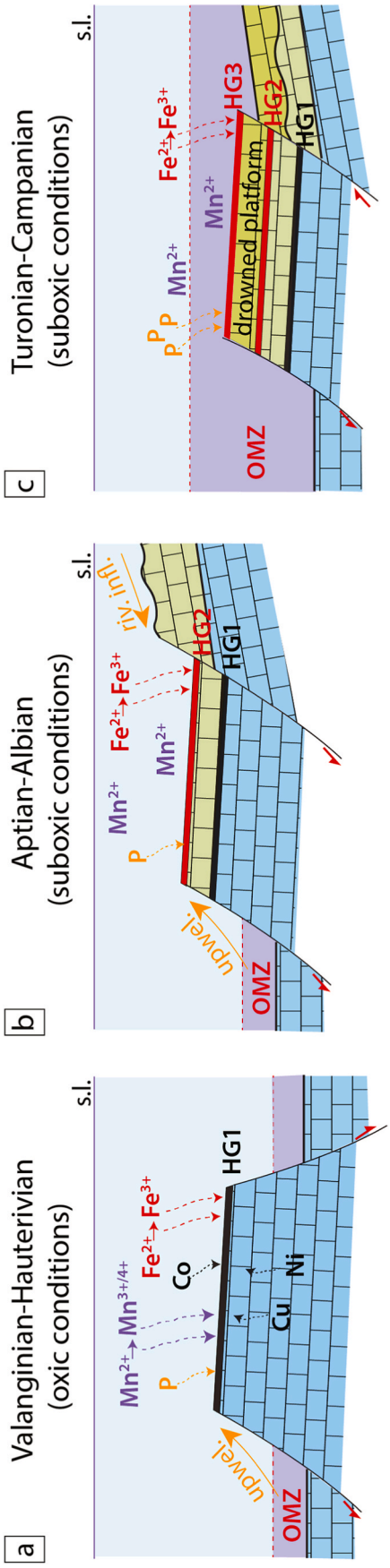


**Fig. 11.** Schematic redox models showing the formation of the phosphatized HGs hardgrounds during the repetitive demise (HG1 and HG2) and drowning (HG3) of the Panormide carbonate platform (Colombrina section). The metals typically enriched during hydrogenetic (Co) and diagenetic (Cu and Ni) growth are indicated. Phosphogenesis fuelled by upwelling of nutrients-rich water masses from the OMZ and/or riverine influx (a and b) or by the drowning of the platform (c) is accompanied by oxidation of $Fe^{2+}$ to $Fe^{3+}$ (*i.e.*, precipitation of goethite, hematite, and magnetite: red arrows) and of $Mn^{2+}$ to $Mn^{3+/4+}$ (*i.e.*, precipitation of birnessite/vernadite: purple arrows) depending on the redox conditions at the seawater-sediment interface. OMZ: oxygen minimum zone (the source of reactive phosphorous (P) and metals).

resilience in carbonate platforms in the face of drastic climate change.

Several studies highlight, from a paleoclimatic point of view, variations in the carbon cycle (Weissert and Erba, 2004) and cold pulses as interludes of the Cretaceous greenhouse mode (Price et al., 2000; Pucéat et al., 2003; McArthur et al., 2007; Cavalheiro et al., 2021), in relation to environmental stress events associated with OAEs. The rise in temperature, globally recorded during the Valanginian-Hauterivian (time of formation of HG1a-b), was accompanied by reduced storage capacity of $^{13}C$-enriched carbonate carbon, increased availability of nutrients, mostly by deep and cool water (*i.e.,* upwelling), despite oxic conditions being present at the sea floor (*e.g.,* Westermann et al., 2010). The latter condition is consistent with the oxidation of both Mn and Fe (under oxic conditions) at the top of the platform (see the schematic model given in Fig. 11a). In the case of the formation of the HG2 the warm and humid climate pulse was accompanied by enhanced continental weathering as that of coeval kaolinitic clays occurring in adjacent Panormide platform blocks, (Basilone et al., 2017), higher runoff and increased detrital input (Fig. 11b) resulted in the most intense water stratification and less efficient bottom-water renewal, with the establishment of suboxic conditions (*e.g.,* Gambacorta et al., 2023). These redox (suboxic) conditions triggered the separation between Mn and Fe and were likely related to the upwelling of phosphorous and nutrients rich water masses from the OMZ (Fig. 11b). Under these conditions, Mn remains as dissolved $Mn^{2+}$ while the oxidation of Fe produced the fine mixture of goethite and hematite (see the schematic model given in Fig. 11b).

## 6. Conclusions

Detailed stratigraphic study of the Cretaceous Panormide shallow-water limestone of the Colombrina section (Palermo Mts., NW Sicilian fold and thrust belt) allowed recognizing three main drowning unconformities marked by submarine phosphatized Fe-Mn rich hardgrounds and condensed pelagic carbonates. These events occurred in the Valanginian-Hauterivian, upper Aptian-Albian and Turonian-Early Campanian time intervals respectively, marked repeated long-term demise of the carbonate platform. Regional to global correlations highlight similarities, in terms of sedimentological features and time of formation, with the drowning features described both from the Northern and Southern Tethyan Cretaceous shallow-water carbonates in coincidence with the OAEs recorded world-wide in the Cretaceous pelagites (*e.g.,* Weissert, Selli and Bonarelli events).

PXRD, SEM-EDS and RS results suggest that the demise events are genetically related to episodic perturbations of the redox conditions at the platform seafloor. The phosphatized HG1 hardgrounds formed during the lowermost demise event consist of Mn and Fe oxides dispersed in a calcite matrix, suggesting oxic conditions at the sea floor. In strong contrast, the other phosphatized hardgrounds (HG2 and HG3) are free of Mn, suggesting suboxic conditions (due to the upwelling of water from the OMZ or the descend of the platform toward the OMZ, respectively) at the platform seafloor during these events.

The Panormide showcases an intriguing case in the Tethys Cretaceous margins, illustrating the resilience of carbonate platforms amidst environmental and climatic stresses. Key factors contributing to its recovery after demise include: (1) structural setting: variations in structural highs and lows enhance morphological complexity, influencing sediment distribution and biodiversity; (2) sedimentary dynamics: drowning conditions at shallow depths create favourable environments for carbonate deposition and preservation; (3) climate-oceanographic conditions: Favourable climatic and oceanographic factors support the growth and regeneration of marine ecosystems, facilitating recovery after crises. This resilience model provides valuable insights into the adaptability of carbonate platforms in the face of climate change over geological time.

## CRediT authorship contribution statement

**Luca Basilone:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Simone Bernardini:** Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization. **Fausto Grassa:** Formal analysis, Data curation. **Attilio Sulli:** Writing – original draft, Funding acquisition. **Luis M. Nieto:** Writing – original draft, Formal analysis. **Anas Abbassi:** Software, Methodology. **Luigi Jovane:** Writing – original draft, Supervision, Funding acquisition.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

the data are all reported in the manuscript and figures

## Acknowledgments

This research is supported by the Fundação de Amparo a Pesquisa do Estado de São Paulo (FAPESP 16/24946-9). The paper is an integral part of the Project: Magnetoestratigrafia e Cicloestratigrafia de alta resolução de seções Eocretáceas (Hauteriviano-Barremiano) das bacias da Margem Leste Brasileira (2018/00352-8), which is financially supported by Petróleo Brasileiro S.A.—Petrobras (FUSP 3687). Funding for research was provided by CARG Project (F_594-585 Partinico-Mondello fondi della Legge 305/89) (resp. Prof. A. Sulli). The Grant to Department of Science, Roma Tre University (MIUR-Italy Dipartimenti di Eccellenza, ARTICOLO 1, COMMI 314–337 LEGGE 232/2016) is gratefully acknowledged. L. M. Nieto: Research Group RNM200 (UJA-Junta de Andalucía) and Research Project 1380715 (FEDER-UJA). S. Critelli and an anonymous reviewer are acknowledged for their useful critical comments and suggestions in the revision of the manuscript. GeoLab laboratory (Palermo, Italy) is acknowledged for the initial analyses conducted on the hardground samples.

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