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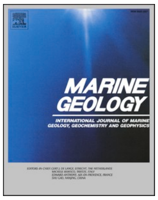

Research Article

The role of methane seepage in the formation of the Northern Adriatic Sea geosites

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ABSTRACT

The northern Adriatic Sea hosts patches of rock formations that have given rise to large biodiversity not otherwise found on the predominantly sandy and flat seabed. Various hypotheses have been invoked concerning the origin of these features, which are widespread in the northern Adriatic Sea and have been intensively studied since the eighteenth century. Here, we provide a significant advancement of knowledge in the lithification process associated with these peculiar rock formations. This study is based on geological, geophysical and mineralogical analyses performed on 45 rock outcrops identified in the study area. A key result of our analysis is the reconciliation of the different models related to the genesis of the northern Adriatic Sea outcrops, i.e., Holocene beach rocks that typically formed in the intertidal zone; cementation of paleo-channel systems, implying a groundwater influence; and methane-derived carbonates. Regardless of the depositional environment, we highlight the relationship between sediments and the processes that led to their evolution into the sandstone formation. We suggest that a common cementation process occurred in the various sedimentary deposits that are representative of different environments of the northern Adriatic Sea and was related to the post depositional precipitation of methane-derived carbonates. Our findings highlight the potential key role of widespread methane seepage from very shallow marine environments into the water column and then, eventually, into the atmosphere as a potential source of an increasing greenhouse gas.

1. Introduction

The most peculiar features of the northern Adriatic Sea are hundreds of submarine rock outcrops (Fig. 1), irregularly distributed and known by various dialectal names, e.g., tegnùe, trezze and grèbeni, which partly reflect their discovery. In fact, the location of these features has been identified over time by fishermen attracted by their value for fishing, but also because they represent a potential threat to bottom trawling. These rocky formations lie at varying water depths (between approximately −8 and − 22 m) and distances from the coast (between 2 and 17 km), rise up to several meters above the unconsolidated sandy-silty sea floor and host massive bio-concretion buildups, which are excellent hard substrates for a variety of calcareous benthic constituents, including bryozoans, mollusks, serpulid polychaetes, scleractinia, and calcareous algae that have contributed to the several-meter increase in elevation and width (Gordini et al., 2012; Tosi et al., 2017). The northern Adriatic Sea outcrops are unique geosites that have allowed the development of a rich flora and fauna community and thus represent a unique hotspot of biodiversity, attracting a global scientific interest, as testified by several international initiatives (i.e., TRECORALA-2012-2014, TRETAMARA 2020–2022, ADRIREEF 2018–2021, and the recent most TRECap 2023–2025 EU funded projects) devoted to valorizing them and promoting their sustainable management (e.g., Minelli et al., 2021). In fact, the coralline biogenic concretions that characterize these reefs play fundamental roles as habitats for the reproduction and nursery of demersal and pelagic species. The valuable benthic community hosted by the rock outcrops is very sensitive to human impacts, especially to unsustainable fishing activities, as testified by the widespread fragmentation of *Callista chione* Linnaeus, 1758, and *Venus verrucosa* Linnaeus, 1758.

The northern Adriatic Sea rock outcrops were first studied in the late 18th century by Abbot G. Olivi (1792), who reported “elevazione di qualche masso calcareo nudo durissimo, il quale sorge isolato dal fondo molle. Tali eminenze, dette volgarmente Tegnùe, conosciute ed aborrite

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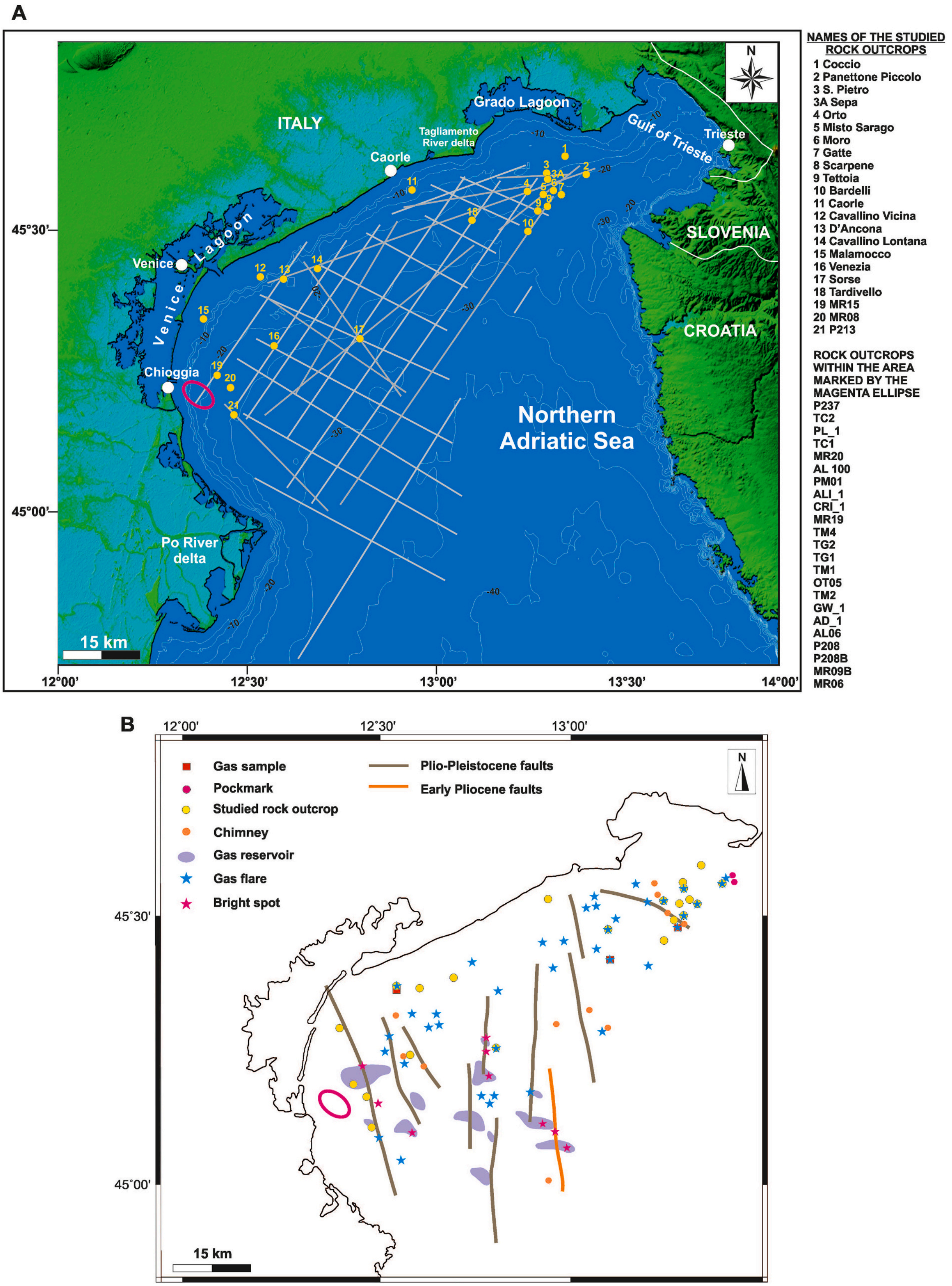

Fig. 1. A. Location map of the rock outcrops analyzed in this study (modified from Donda et al., 2015); gray lines indicate the position of the OGS - multichannel and CHIRP data; B. structural map (modified from Brancolini et al., 2019) and the gas-related features identified in the study area (modified from Donda et al., 2019).

dai nostri pescatori……esistono dirimpetto a Maran, a Carole, ai Tre Porti,…. …..soprattutto dirimpetto a Malamocco ed a Chioggia, e dal volgo sono creduti residui di due antiche Città sprofondate per una impetuosa inondazione dal mare…..." (trad."elevation of some very hard bare limestone boulders, which rises from the soft sea floor…they exist in front of Maran, Caorle, Tre Porti….mostly in front of Malamocco and Chioggia; the common people believe that they are remnants of two ancient cities, sunk by an impetuous sea flood…"). In the following two centuries, they were almost forgotten. Highly focused and multidisciplinary studies began around the 1960s, when several geophysical and geomorphological surveys were carried out (e.g., Stefanon, 1966, 1967, 1970; Braga and Stefanon, 1969; Stefanon and Mozzi, 1972; Newton and Stefanon, 1975, 1982; Colantoni and Taviani, 1980; Colantoni et al., 1997a, 1997b, 1998; Gabbianelli et al., 1997; Caressa et al., 2001; Franceschini et al., 2002; Giovanardi et al., 2003; Gordini et al., 2003; Gordini et al., 2004).

Since the last century, several hypotheses have been put forward about the origin of these lithified deposits and the main process at the base of sediment lithification originating these rock outcrops. These features have been interpreted as Holocene beach rocks (Braga and Stefanon, 1969), i.e., rocks formed along a shoreline by the cementation of predominantly calcareous sediments, further colonized by calcareous algae with secondary madreporaria and associated bryozoa and serpulidae, which formed at a very early stage of postglacial transgression (Stefanon, 1969; Stefanon, 1984; Newton and Stefanon, 1975; Newton and Stefanon, 1982). They were thus interpreted as the outcropping of older sedimentary horizons, rather than associated with siltation of fluviatile inputs (Braga and Stefanon, 1969), highlighting the role of strong sediment erosion along the Northern Adriatic shelf (Stefanon, 1984). Based on this model, the rock outcrops in the study area thus represent remnants of lithified shorelines, which could then be used to define the past shoreline locations and their migration over time (Newton and Stefanon, 1982).

Further data and studies documented the occurrence of gas-charged sediments and gas seeps (Stefanon, 1980) in the study area, and a relationship with the formation of these deposits was suggested (Conti et al., 2002a; Panieri, 2006; Capozzi et al., 2012).

A genetic model was then developed for a group of rock outcrops named "Tegnue di Chioggia" (Tosi et al., 2017; see the magenta ellipse in Fig. 1). Based on this model, the "Tegnue di Chioggia" are interpreted as morphologies inherited from fluvial systems that developed on the Last Glacial Maximum (LGM) alluvial plain and reactivated as tidal channels in a protected lagoonal environment during the post-Last Glacial Maximum transgression. The cementation of such deposits, which are suggested to be associated with the interaction between marine and fresher fluids, favored the growth of coralligenous buildups (Tosi et al., 2017).

Geological and geophysical data collected throughout the northern Adriatic Sea unveiled the key role of gas migration through the marine sediments, causing the precipitation of methane-derived calcium carbonate as cement (Hovland et al., 1987a; Jorgensen, 1992; Peckmann et al., 2001; Mazzini et al., 2004), in the formation of the rock outcrops in the study area, thus leading to the interpretation of these deposits as methane-derived authigenic carbonates (MDACs; Stefanon and Molinaroli, 1995; Conti et al., 2002b; Panieri, 2006; Gordini, 2009; Gordini et al., 2012; Donda et al., 2008, 2013, 2015 and Donda et al., 2019; Gordini and Donda, 2020). MDACs are deposits formed as a result of anaerobic methane oxidation by a microbial consortia, and are therefore directly associated with natural methane seepage (Boetius et al., 2000 and references therein). MDACs occur globally from coastal areas to the deep ocean, in a variety of geological and oceanographic settings (Judd and Hovland, 2007). They are commonly colonized by dense biological communities, resulting in "oases of life" on an otherwise barren seabed (Dando, 2010; Noble-James et al., 2019 and references therein). One of the Europe's largest areas of MDACs (approximately 116 km^2) is the Croker Carbonate Slabs SAC (Irish Sea), located in water depths ranging from approximately 65 to 110 m. These sites are part of the European MDAC structures and their biological communities are listed as 'habitats of Community importance' under Annex I of the EC Habitats Directive (European Commission, 2013), with a network of 'Natura 2000' Marine Protected Areas designated for their management (James et al., 2019 and references therein).

Similar features have also been identified in the central Adriatic Sea, where both geophysical and geological records reveal that carbonate concretions occur directly above active gas seeps (Capozzi et al., 2012). Here, gas occurrences in the shallow sedimentary succession have been known since the 1980s (e.g., Colantoni et al., 1979; Stefanon, 1980; Curzi and Veggiani, 1985). Fluid vents are characterized by gas bubbling, carbonate crusts and pockmarks (Hovland and Curzi, 1989; Conti et al., 2002b; Judd and Hovland, 2007), the latter ranging from 60 to 350 m in diameter and approximately 6 m deep (Central Adriatic Sea), with the most famous associated with the Bonaccia gas field (Curzi et al., 1998).

Gas seeps in the northern Adriatic Sea were first reported by Morgante (1940), who identified bubbling on the sea surface off Rovinj (Croatia). Evidence of gas-related features have then been provided by García-García et al. (2007), Colantoni et al. (1998) and Conti et al. (1998), whose isotopic analyses of rock samples collected in the study area reveal their methane-related origin. Some rock outcrops are located above deep gas reservoirs and at tectonic lines that promote the upward migration and seepage of gas from the seafloor (Donda et al., 2015; Donda et al., 2019).

The aim of this study is to provide a conceptual model that reconciles all previous hypotheses concerning the genesis of the Northern Adriatic geosites. This aim is achieved on the basis of both a review of the existing data and the analysis of new geophysical and geomorphological datasets recently collected as part of the INTERREG Italia-Slovenia TRETAMARA project (https://www.ita-slo.eu/en/tretamara). The outcomes of our study reconcile all the genetic models that have been previously proposed for the northern Adriatic Sea rock outcrops, by highlighting the methane -related origin of most of them, and thus the key role of methane in their genesis. This study represents a significant advance in the knowledge of the northern Adriatic Sea outcrops, while raising new scientific questions that will hopefully be answered by future scientific investigations.

2. Regional setting

The Adriatic Sea is an epicontinental basin about 800 km long and 150–200 km wide, extending from the Gulf of Trieste to the Strait of Otranto, which connects the Adriatic and Ionian seas (Artegiani et al., 1997).

The northern Adriatic Sea is a shallow-water sedimentary basin (mean water depth: 25 m) that is part of the Padano-Adriatic foreland-foredeep domain and characterized by deep basins with clastic sequences up to 8 km thick (Royden et al., 1987; Fantoni and Franciosi, 2010; Ghielmi et al., 2010).

The sedimentary succession in the study area is characterized by Mesozoic to early Cenozoic carbonates overlain by Eocene to Miocene, southward-prograding marl-rich sediments, fed by erosion of the uplifting Southern Alpine chain (Massari et al., 1986; Barbieri et al., 2007). The Eocene to Miocene unit is truncated by a prominent unconformity, the Messinian Erosion Surface (Cita and Ryan, 1978), resulting from the high-magnitude relative sea-level fall that occurred during the Messinian salinity crisis (Ghielmi et al., 2013, 2010; Tosi et al., 2012; Zecchin and Tosi, 2014). The Plio-Quaternary succession is composed of deep-marine turbidites and shallow-marine deposits (Ghielmi et al., 2013; Zecchin and Tosi, 2014; Zecchin et al., 2017; Zecchin et al., 2022) and is composed of alternating of sand, clay, and silt (Donda et al., 2013; Zecchin et al., 2017; Zecchin et al., 2022), which also characterize the surficial sediments (Brambati et al., 1988).

The oceanographic setting of the study area is characterized by a microtidal regime dominated by a cyclonic circulation driven by thermohaline currents (Malanotte Rizzoli and Bergamasco, 1983; Bondesan et al., 1995). The mean basin circulation is counterclockwise.

In the Venice area, the monthly distribution of high tides recorded between 1872 and 2017 shows peaks in winter with variations on the order of 100 cm, but peaks of 140–150 cm also occur (Previsioni delle altezze di marea per il bacino San Marco e delle velocità di corrente per il Canal Porto di Lido - Laguna di Venezia), especially in autumn and winter, when a rise in sea level caused by south-easterly winds coincides with low atmospheric pressure (Gačić et al., 2004, and references therein).

The mean annual significant wave height is <0.5 m, while the highest offshore wave height, generated by the Bora- and Sirocco-storms, is approximately 5 m (Cavaleri et al., 1996). The mean basin circulation is counterclockwise.

The general circulation of the northern Adriatic Sea is also modulated by the Po River runoff, which sometimes produces typical gyres and mushroom-like mesoscale gyres. Large-amplitude storm surges can be triggered by SE Sirocco winds blowing along the main axis of the Adriatic Sea: the excited free oscillations of the basin with a period close to 24 h have an impact on the well-known flooding events in the city of Venice and on the northwestern Adriatic coast.

Relevant effects on basin oceanographic characteristics are the Bora wind episodes in winter: when strong north-easterly winds blow on the northern Adriatic, the rapid cooling of the surface waters leads to a loss of upwelling and the formation of a denser water mass (NADW) that flows southward along the isobaths of the Italian continental shelf and slope at depths of 50–150 m (Artegiani et al., 1989). The winter process also has important effects in the northern Adriatic: the ventilation of the water column leads to complete vertical mixing, disruption of the seasonal thermocline and the revitalization of the bottom water, i.e., the habitat of the rock outcrops. The water temperature at the seafloor varies throughout the year between 6 and 7 °C in January–February and 25 °C in July, while the salinity varies from 36 to 37 °C to >38 °C depending on the season and river discharges (Bergamasco and Gacic, 1996; Bergamasco et al., 1999).

3. Materials and methods

Geophysical, geological and mineralogical data presented and discussed in this paper have been collected by the Istituto Nazionale di Oceanografia e di Geofisica Sperimentale (OGS), the Istituto di Geoscienze e Georisorse (IGG) and the Istituto di Scienze Marine (ISMAR) of the Consiglio Nazionale delle Ricerche (CNR), and the University of Trieste, within the framework of several projects since the 1990s.

Part of the dataset shown and discussed in this study, both at the local, i.e., outcrop scale, and at the regional scale, i.e., in the whole northern Adriatic Sea, has already been published (see Table A1- supplementary Material). Information on data collection and processing can be found in the cited papers.

Below, we provide details on unpublished data at the local scale, most of which collected in the framework of the TRETAMARA Project. Regarding data already used in the framework of previous, published studies, we refer to their descriptive in-depth information in the references given.

3.1. Geophysical data

Various geophysical data have been collected from several of the studied outcrops on board the Castorino II vessel: 1. Swath morpho-bathymetry data (Reson Seabat 8125 multibeam), (2) Side-scan sonar data (Edgetech DF-1000/DCI, 100–500 kHz); and (3) CHIRP profiles (CHIRP Edgetech 3200XS).

In particular, side-scan sonar surveys were carried out in two phases; the first one provided an overview mapping of areas that measured approximately 3.0 × 2.0 km in size; parallel routes were then undertaken 160 m apart with a 100 m wide swath (overlap of 20%). Subsequently, more detailed surveys were carried out at each rock outcrop identified in the abovementioned area, along routes spaced 80 m apart with a 50 m wide swath to provide a comprehensive morphological characterization. The area surveyed at each outcrop was approximately 500 × 500 m.

Both multibeam and single beam surveys were carried out at 16 outcrops, and CHIRP profiles were collected across 9 outcrops.

For the area named “Tegnùe di Chioggia”, which was investigated by Tosi et al. (2007), Zecchin et al. (2008) and Tosi et al. (2017), CHIRP and BOOMER sub-bottom profiles were recorded for a total length of about 140 line-kilometeres off the coast of Chioggia on board of the R/V URANIA and LITUS (CNR). Multibeam and side-scan sonar maps are also available from Regione Veneto (Giovanardi et al., 2003).

3.2. In situ sampling and laboratory data analysis

Rock, unconsolidated sediment and gas samples were collected at each of the studied outcrops and their surroundings. Specifically, 20 new rock samples were collected from 14 outcrops using push cores and with the support of a ‘Prometeo’ Remote Operating Vehicle (ROV) equipped with a digital video camera that guided both rock/sediment and gas sample collection. Additional rock samples collected by scuba divers at three outcrops offshore Chioggia (Tosi et al., 2017; Franchi et al., 2018) were used along with the new samples to complement the existing dataset. Gas sampling was performed at 5 seepage sites, identified and selected based on their acoustic signature in the CHIRP data and numerous scuba dives. Details of the gas sampling procedure and of gas analysis are provided in Donda et al. (2019).

Sedimentological, mineralogical, SEM-EDX electron microscope determinations, X-ray diffractometries, and radiocarbon ^{14}C dating were carried out on bulk sediments and rock samples (e.g., detrital granules, shell fragments, authigenic carbonates) collected from most of the studied outcrops (Table A1-Supplementary Material).

The 20 rock samples were used to produce thin slices, which allowed us to provide the initial mineralogical characterization. Some rock samples from the Bardelli, Caorle, D’Ancona and Venezia outcrops were analyzed using a JEOL 840A Scanning Electron microscope, coupled with an Energy Dispersion microanalysis system SEM-EDX (Energy Dispersive X-ray) Oxford ISIS 300, at Eni S.p.A., Divisione Exploration & Production. Two diffractometers, i.e., a PANalytical CubiX PRO X-ray diffractometer (Eni S.p.A laboratories, Exploration & Production Division) and a STOE D 500 X-ray were used to determine the bulk composition of eight rock samples and the carbonate cement that was sampled under a microscope, respectively (see Gordini, 2009 and Donda et al., 2015 for further details).

Eight mineralogical determinations were made by X-ray diffractometry on bulk samples (approximately 10 g) of rock outcrops.

In the Chioggia outcrop samples, radiocarbon 14C dating was carried out on well-preserved and whole shells extracted from cemented sand (Franchi et al., 2018).

The methods adopted for the morphological characterization, chemical composition and carbonate cement analyses of samples from the Chioggia area are reported in Franchi et al. (2018).

4. Results

4.1. Morpho-bathymetric and acoustic analysis

The rock outcrops occurring in the northern Adriatic Sea have very different characteristics from several points of view, e.g., their size, shape, distance from the coast and distribution (Figs. 2, 3, 4 and 5; Table A2-Supplementary Material; further information is provided in Table A3, Supplementary Material). However, the height of the outcrops is within a limited range of 1 to 2.8 m (including the bioconcretioned part above the cemented sandy layer), except for AL06 (within the

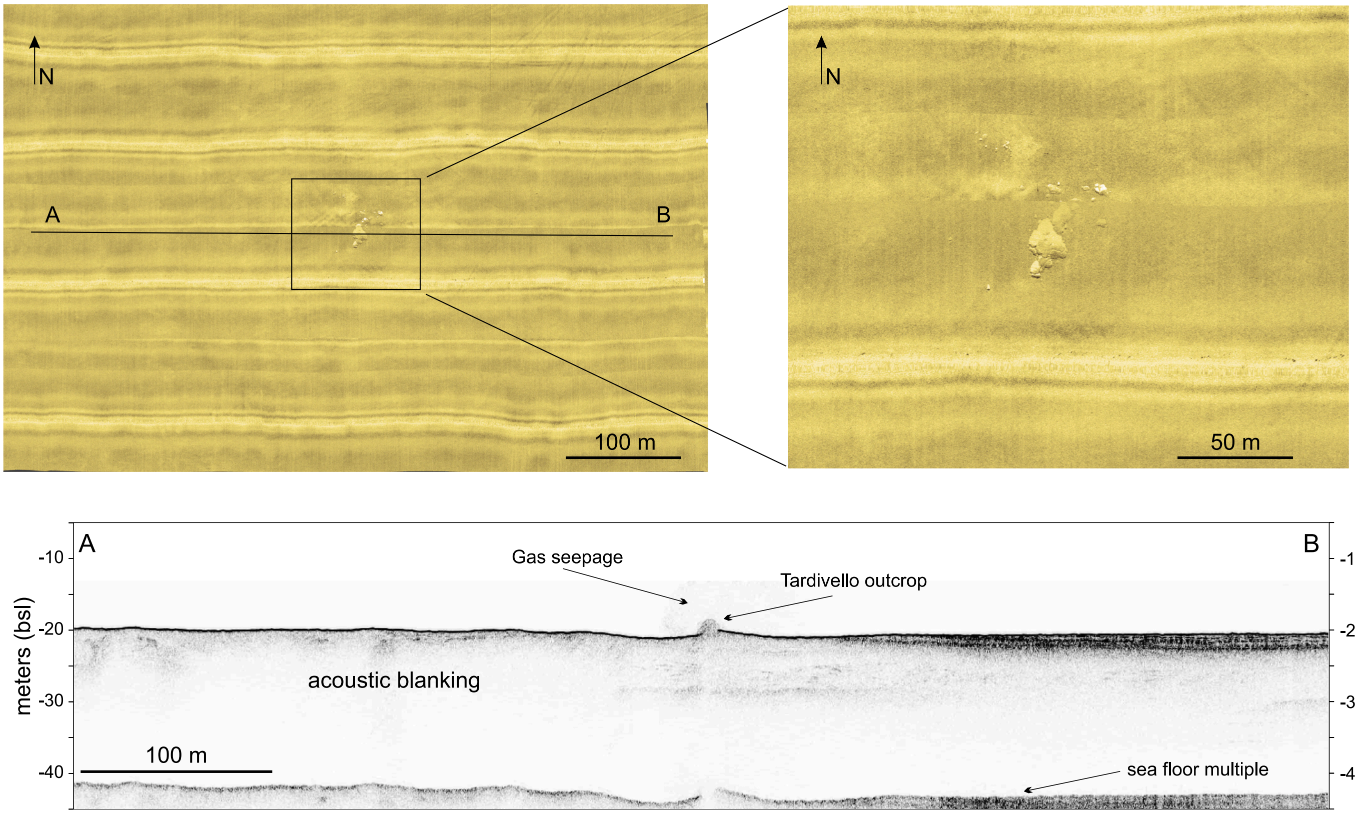

Fig. 2. Tardivello outcrop (“18” in Fig. 1); above left: regional scale side-scan sonar mosaic collected across the outcrop. Above right: zoom on side-scan sonar collected across the outcrop. Below: CHIRP profile collected across the outcrop; acoustic blanking indicates the widespread occurrence of gas, which seeps at the sea floor and is also recognizable in the water column.

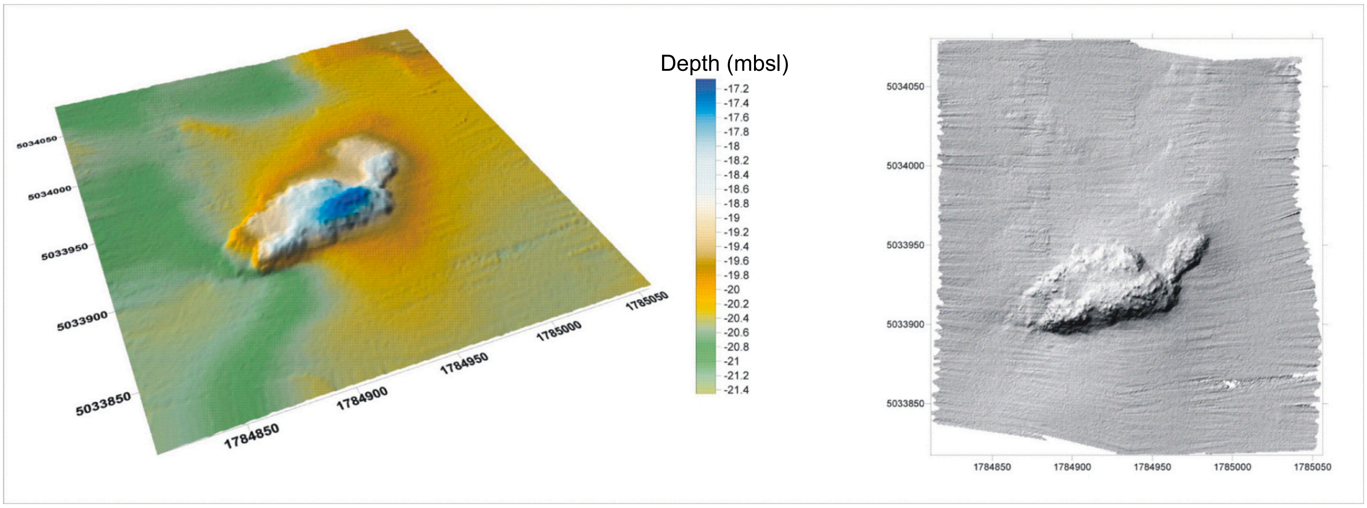

Fig. 3. Multibeam data collected at the Cavallino Lontana outcrop (“14”in Fig. 1).

magenta ellipse in Fig. 1), which is 4.4 m high (Table 2A- Supplementary Material). Notably, the areal extent of the rock outcrops located in the Gulf of Venice is greater than those identified in the Gulf of Trieste. Moreover, some of the studied outcrops show a preferential orientation. This is the case of the Gulf of Trieste and of the area located offshore Venice, where most of the rock outcrops have a NE-SW and NW-SE elongated shape, respectively (e.g., Fig. 5).

Although a straightforward correlation with the structural setting is still unclear, these preferential orientations seem to be mostly consistent with the tectonic features identified in the study area (Donda et al., 2015; Brancolini et al., 2019). During inspections by divers, it was noted that the cemented sand layer at the base of the coralligenous buildups is not always horizontal, as is the seafloor, but is often inclined, and therefore reasonably associated with local geomorphologic structures that are currently partially exposed.

Rock outcrops are clearly recognizable on morpho-bathymetric datasets. On side-scan sonar data, they are represented by high backscatter features, usually consisting of 2 to 4 main groups of rock blocks (Fig. 2), except for the Caorle outcrop, which consists of 15 rock blocks (Table A2-Supplementary Material).

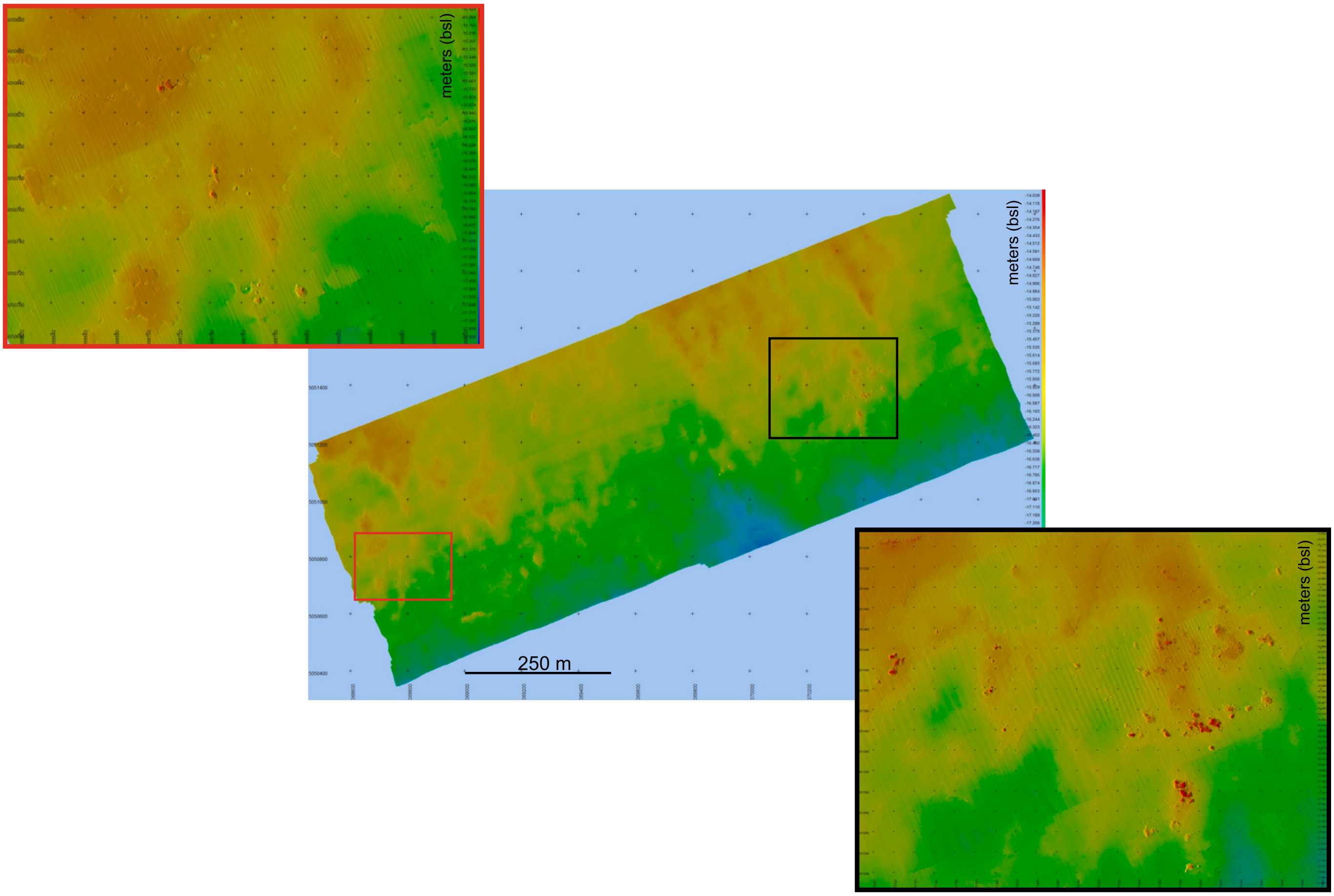

Fig. 4. Multibeam data collected in the northern sector of the study area. The red features within the right side of the black rectangle represent the San Pietro outcrop ("3" in Fig. 1), whereas those delimited by the red rectangle are newly discovered, still unnamed outcrops. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

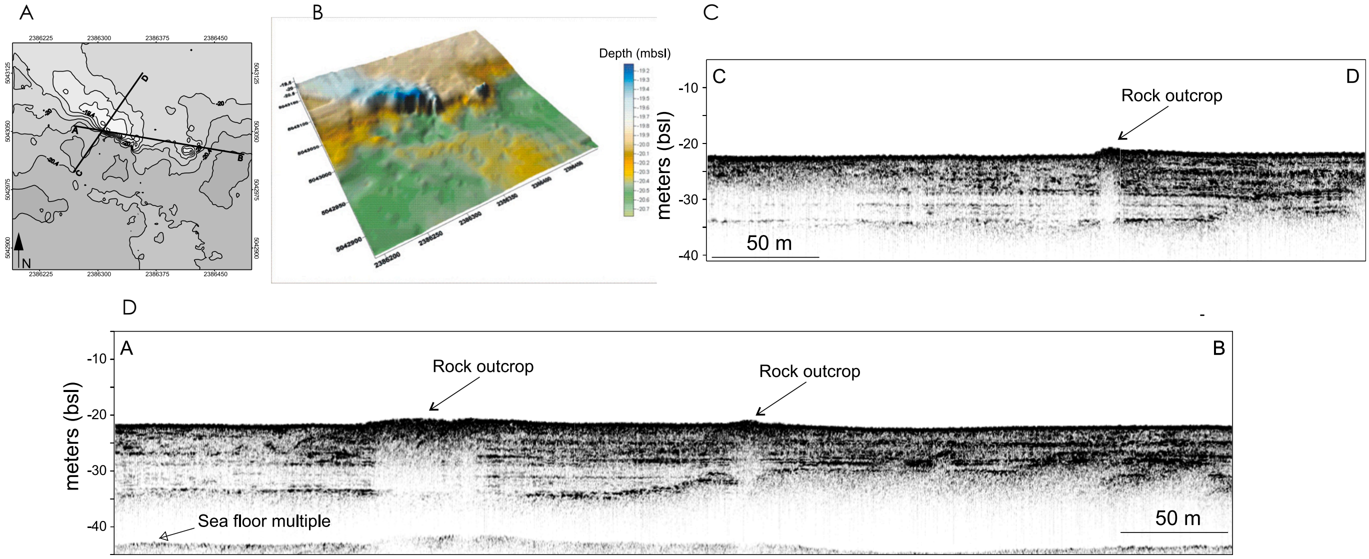

Fig. 5. Tettoia outcrop ("9" in Fig. 1). A and B: contour map and 3D map of contours from single beam data, showing the predominant NW-SE orientation of the outcrop; C and D: CHIRP profiles collected across the outcrop.

In singlebeam and multibeam data, rock outcrops commonly appear to be characterized by a tabular, elongated shape, although pinnacle morphologies were also found (Figs. 3, 4 and 5; see also Gordini et al., 2012). In some places, the tabular outcrops have vertical fractures that are about 0.2 m wide.

Both very high-resolution subbottom CHIRP data and multichannel seismic data were collected across several of the studied outcrops. In the CHIRP data, the rock outcrops appear as semi-transparent facies embedded in the sedimentary sequence up to several meters from the seafloor (Figs. 2 and 5; see also Gordini et al., 2012). Here, they are represented by a rough morphology associated with highly reflective facies, which is clearly recognizable on the commonly flat sea floor.

In the multichannel seismic profiles, the rock outcrops are not easily identifiable due to the lower resolution of this type of dataset. In fact, their occurrence in the seismic data was mainly determined by correlation with the coincident CHIRP profile. However, in some places, the rock outcrops have a peculiar seismic signature, represented by a couple of high-amplitude reflectors (see, e.g., Fig. 2 of Donda et al., 2015).

High-resolution seismic profiles collected on the Tegnùe di Chioggia clearly show the rough morphology associated with highly reflective signals. The rock outcrops are developed on the seafloor near the outcrop that marks the Pleistocene-Holocene boundary, where the wedge of Holocene deposits tapers until it closes. Sub-outcropping channelized systems are cut in the Pleistocene deposits near the Tegnùe di Chioggia; rarely the seismic signal allows the identification of significant reflectors directly beneath the rock formation (Tosi et al., 2017).

4.2. Thin slice, SEM and X-Ray diffractometer analyses

Thin slices of sandstone rock samples, commonly dark gray in colour with some light gray and light brown halos at the sample margin, are interpreted to be the result of chemical and mechanical activities of lithodomes. The strata geometries within the sandstone layers reveal the occurrence of lenticular planes bounded by both curved and planar surfaces. Internally, each layer consists of groups of mostly oblique laminae. Vertical and lateral grain size variations, as well as the occurrence of dark gray laminae, make the stratification clearly recognizable. The boundary between sandstone and pelitic layers is marked by an irregular stratigraphic unconformity.

Thin slice analyses revealed that all the sampled rocks are characterized by a grainstone texture (Dunham, 1962), with local intercalations of packstone. The terrigenous detrital grains are ungraded, polygenic, angular to sub rounded and characterized by a low sphericity. The primary porosity is interparticle porosity (Choquette and Pray, 1970), and the thickening is low to moderate.

XRD analyses were carried out on eight bulk outcrops samples, which are described below.

Caorle outcrop (“11” in Fig. 1): XRD analysis revealed highly variable contents of the three carbonate components. The sandstone sample with rare shell fragments consists of 35.5%calcite, 35.1% dolomite and 0,0% aragonite. On the other hand, the bioclastic-rich sample (coquina) has lower calcite and dolomite contents (16.0 e 15.8%, respectively) and a higher aragonite content (35.8%). Both samples are also composed by quartz (10.0–10.1%), albite (0.0–6.5%), micas (muscovite and biotite) and kaolinite-rich clays (15.9–19.3%).

D’Ancona outcrop (“13” in Fig. 1): Similar to the Caorle outcrop, the XRD analyses revealed the presence of calcite, dolomite and aragonite, with contents of 9.3–11.8%; 5.5–7.6% and 52.5–53.9%, respectively. The sample also shows the occurrence of quartz (10 0.2–11.0%), microcline (2.5%), albite (2.7–3.9%), micas (muscovite and biotite) and kaolinite-rich clays (13.0–13.6%).

Venezia outcrop (“16” in Fig. 1): An analysis of the bulk sandstone sample revealed the presence of calcite (2.8–25.1%), dolomite (24.2–74.4%), quartz (6.4–18.0%), micas (muscovite and biotite) and kaolinite-rich clays (11.9–13.9%), albite (5.0–11.3%), and microcline (2.0–5.9%). Only a small amount of aragonite is present here (0–1.6%) (Fig. 6).

Bardelli outcrop (“10” in Fig. 1): Different from the Venezia outcrop, the sample collected from this outcrop reveals a higher calcite (41.1%), lower dolomite (13.1%) and a high aragonite (21.5%) content. Quartz (12.5%), microcline (0.9%), albite (2.7%), micas (muscovite and biotite) and kaolinite-rich clays (8.2%) are also present (Fig. 7).

San Pietro outcrop (“3”in Fig. 1): In this outcrop, the sample was collected only from the sandstone component. It has the highest calcite and the lowest aragonite contents of 49.2% and 0.0% respectively. The dolomite content is 13.5%. Quartz (19.5%), microcline (1.9%), albite (5.6%), micas (muscovite and biotite) and kaolinite-rich clays (10%) are also present.

The rock samples from Tegnùe di Chioggia (within the magenta ellipse in Fig. 1) analyzed for petrographic characterization, are predominantly allochemical sandstone, sandy allochemical limestone, and algal boundstone (Franchi et al., 2018). The sandstone consists of detrital carbonate with abundant siliciclastic material (mainly quartz and phyllosilicates) and minor amounts of Fe-oxyhydroxides. EDS analyses show that the detrital carbonates are mainly low-Mg calcite and dolomite, while the cements are mainly high-Mg calcite, with variable amounts of low-Mg calcite. XRD analyses confirm the presence of both detrital calcite and dolomite.

P204 Tegnùa Sub Mestre outcrop: This outcrop consists mainly of bioclastic carbonate, i. e. Rudstone (Fig. 1a) and Boundstone (Fig. 1b), encrusted by serpulids, red algae and bryozoans. The samples show traces of bioerosion and burrows containing loose marly sediments. Thin sections show that the samples consist of biosomes (bivalve shells) and bioclasts (mainly red algae). The bioclasts are cemented by micrite, more rarely by microsparite with a high-Fe content; there are numerous pores and cavities (void ratio up to 25%). The mineralogical composition consists of calcite, aragonite and subordinate quartz. The bulk of the sample consists of high-Mg calcite (ca. 12–15 mol% MgCO3) (Franchi et al., 2018).

TM1 Tegnùa Delfino Bianco-Tegnùa Free Diver outcrop: Well lithified gray sandstones with cross-stratifications were collected from this outcrop. The slabs are only partially encrusted by organisms. Some burrows filled with siliciclastic sand are present. The mineralogical composition consists of quartz, calcite, and dolomite. Sixty percent of the clasts are carbonates that are well rounded and subspherical. Approximately 30% of the clasts are composed of subangular quartz clasts. Ten percent of the clasts consist of other minerals (e.g., glauconite) and lithoclasts (e.g., siltstone with micritic cement). The sample has a high pore index. Carbonate cements, mainly microcrystalline and scalenohedral cements, form a thin rim around the clasts, creating a local meniscus structure. Cathodoluminescence analysis confirms the heterogeneity of the clasts making up the sample and the presence of two generations of carbonate cements around the clasts. EDS analyses also show a change in the composition of the carbonate cements, in particular, a decrease in the Mg content and an increase in Ca content in the second generation of cements (Franchi et al., 2018).

MR08 Tegnùa Sub Chioggia-Tegnùa Marina del Sole outcrop: various lithologies were sampled in this outcrop.

The bioclastic carbonate is bioclastic rudstone dominated by red algal fragments and cemented by micrite. The bioclasts show traces of corrosion with oxidized irregular rims and burrows filled with micritic cement. The pore index is very high (up to 25%). Some of the pores are filled with mesospathic carbonate cement.

The samples of biofouled sandstone show abundant traces of bioerosion: the upper part is covered with encrusting (living) red algae; the lower part is affected by burrows of lithodomes. They are allochemical sandstones cemented by isopachous crusts of carbonate cements and sandy allochemical limestone with biosomes. The well-rounded carbonate lithoclasts are brownish dolomite or less abundant clear spar; the quartz grains are subangular; at least 5% of the clasts are composed of other silicates (i.e., phyllosilicates). Cathodoluminescence analyses show the presence of a double generation of cements associated with different Fe and Mn contents. Cross-stratified sandstone samples are also present in this outcrop. These blocks are encrusted by serpulids and red algae, with burrows filled with siliceous sand. The mineralogical composition is given by quartz, calcite and dolomite. Thin sections show that the pores are partially filled with carbonate matrix and by meso- and microspathic carbonate cement. Some carbonate clasts are covered by two generations of cements: an isopaque and fibrous carbonate

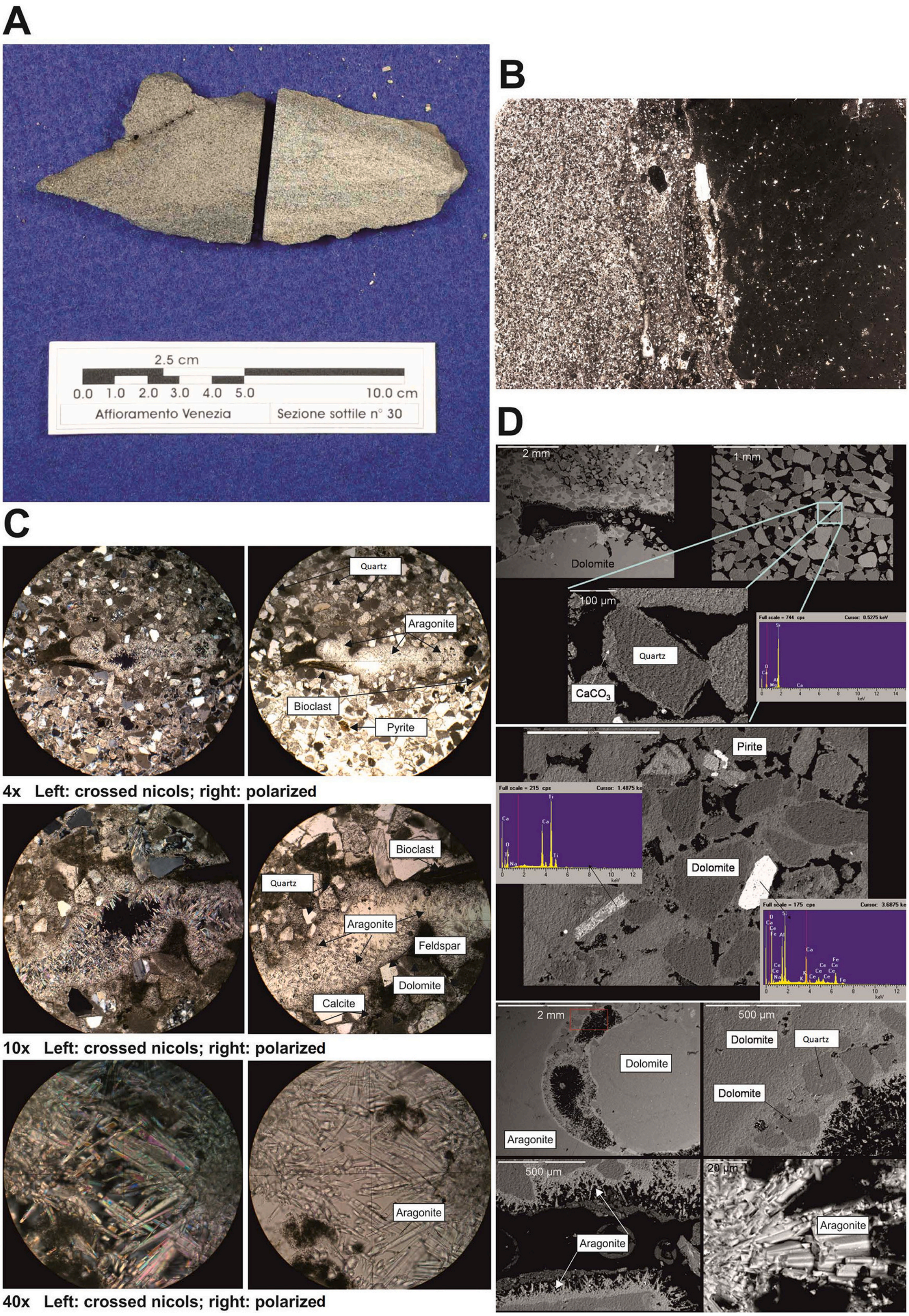

Fig. 6. Venezia outcrop ("16" in Fig. 1) A. Section of a rock sample; B. thin slice, in which the contact between different grain sizes is visible, i.e., sandy sediments on the right and fine sediments on the left. In the former, the presence of bioclasts and voids partially filled with acicular carbonate is recognizable; C. Thin section details at various levels of magnification (4×, 10×, and 40×), with crossed and polarized nicols. The predominant constituents of the rock (carbonate fragments, dolomite, quartz, feldspar, rare pyrite, etc.) and details of the voids filled with acicular aragonite are highlighted. D. SEM-EDX image, showing the measurements made and details of the carbonate surrounding the detrital clasts. In the lowermost panel, aragonite occurring on void walls is visible.

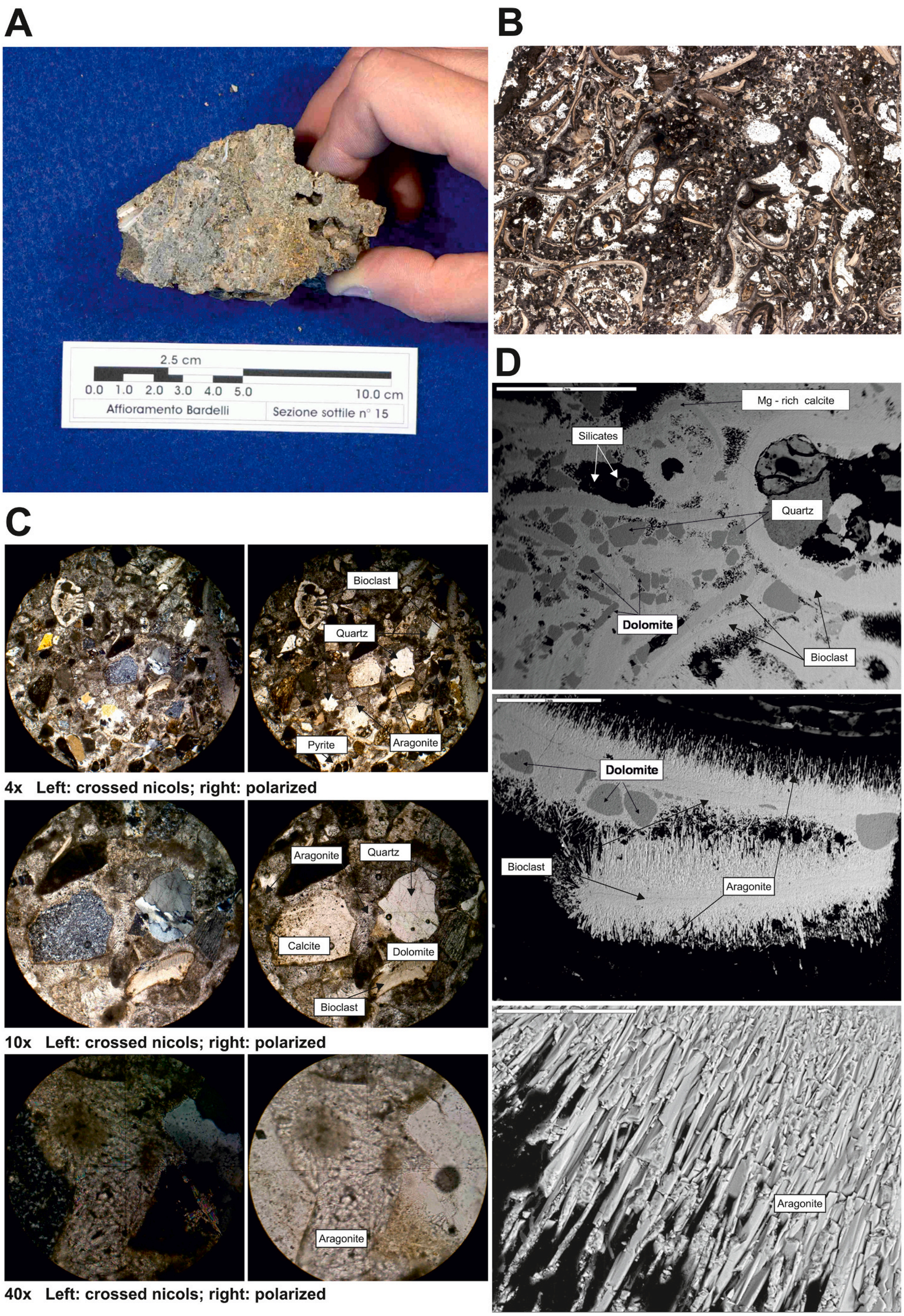

Fig. 7. Bardelli outcrop ("10"in Fig. 1). A. Section of a rock sample; B. thin slice. The sample consists mainly of sand and numerous bioclastic fragments (bivalves and gastropods). Voids that are partially filled with acicular carbonate are observed among the detrital granules bioclasts. C. Details of the thin section at various levels of magnification (4×, 10×, and 40×) with crossed and polarized nicols. The detrital component of the rock consists of carbonate fragments, dolomite, quartz, and feldspars. The voids among the granules and/or the bioclasts reveal the occurrence of abundant acicular aragonitic cement. D. SEM-EDX image, showing the occurrence of abundant dolomite, Mg-rich calcite, quartz, and abundant bioclasts. The aragonitic cement grains, orthogonal to the granule faces, are also recognizable, together with the bioclasts and voids.

cement followed by a microspathic cement.

Another lithology that is present in this outcrop consists of rounded dark-colored lithoclasts contained in some sandstone blocks in association with biosomes. They consist of siltstone and silty limestone with fine to very fine texture. The clasts are mainly quartz and, to a lesser extent, carbonates, feldspar and mica. The cement consists of dark peloidal micrite and subordinate microsparite (Franchi et al., 2018).

4.3. Radiocarbon analysis results

Radiocarbon analyses carried out on samples collected from three rock outcrops revealed a wide age range. As an example, carbonate interpreted as cement supporting sandstone grains from the D'Ancona and Bardelli outcrops shows ages of 15,940 +/− 360 B.P. and 21,700 +/− 2265 B.P., respectively. On the other hand, the age of the bioclasts is 4990 +/− 45 for Caorle, 8200 +/− 55 for D'Ancona and 7150 +/− 60 for Bardelli (Table 1). These ^{14}C ages of acicular aragonite and microcrystalline carbonate do not reflect the timing of carbonate formation because the degree of mixing between methane-derived carbon and marine bicarbonate is unknown.

In the MR08-Tegnùa Sub Chioggia-Tegnùa Marina del Sole outcrop, some bioclasts and biosomes embedded in the sandstone were analyzed (Tosi et al., 2017). The bioclasts and biosomes result from organisms living in different environments, from brackish lagoon (e.g.,

Table 1
Conventional radiocarbon ages obtained from some of the studied outcrops.

Rock outcrop	Sample type	Depth (m)	Conventional age ^{14}C (yrs B.P.)	δ ^{13}C (‰)
Bardelli	Bivalve	−21	7150 +/− 60	−2.6
Bardelli	Cement	−21	21,700 +/− 2265	−49.8
Caorle	Bivalve	−10	4990 +/− 45	−1.8
D'Ancona	Cement	−18	15,940 +/− 360	−39.4
D'Ancona	Gastropode	−18	8200 +/− 55	−2.6
MR08 - Tegnùa Sub Chioggia; Tegnùa Marina del Sole - TE 1*	Bivalve *Chamelea gallina*	−20	8070 +/− 30	−0,9
MR08 - Tegnùa Sub Chioggia; Tegnùa Marina del Sole – TE 2*	Bivalve *Loripes lucinalis*	−20	6880 +/− 30	−0,3
MR08 - Tegnùa Sub Chioggia; Tegnùa Marina del Sole – TE 3*	Bivalve *Flexopecten glaber*	−20	7450 +/− 30	−1,1
MR08 - Tegnùa Sub Chioggia; Tegnùa Marina del Sole – TE 4*	Bivalve *Cerastoderma glaucum*	−20	8620 +/− 30	−4,3

Conventional radiocarbon age obtained from the analysis of five representative samples of the entire study area.

* From Tosi et al., 2017.

Cerastoderma glaucum, *Loripes lucinalis*) to shallow marine taxa (*Chamelea gallina*, Flexopecten glaber). Analyses carried out on a selection of these bivalves revealed ages ranging from 6880 +/− 30 to 8620 +/− 30 years B.P.

4.4. Gas occurrence within the sedimentary succession

Geological and geophysical data at different scales of resolution show that widespread gas occurrences are present throughout the whole study area within the sedimentary succession, at the sea floor and in the water column (Gordini, 2009; Gordini et al., 2012; Donda et al., 2013, 2015; Donda et al., 2019; Giustiniani et al., 2020; Ferrante et al., 2022).

The most evident signatures of gas occurrence both throughout the Plio-Quaternary sedimentary succession and in the uppermost Pleistocene-to-present sediment are revealed by multichannel seismic data and CHIRP profiles, respectively, and are represented by the following: a. bright spots, b. gas chimneys, c. pull down reflectors and pull up reflectors; wipe-out zones; and semitransparent acoustic facies (Fig. 8; Donda et al., 2015 and Donda et al., 2019; Giustiniani et al., 2020; Ferrante et al., 2022).

Overall, the gas occurrence in the sedimentary succession is represented by an acoustically opaque facies, whose internal configuration is almost completely masked. In multichannel seismic data, they appear both as subvertical chimney-like features up to 2–3 km wide (e.g., Figs. 6 and 7 of Donda et al., 2015) and as horizontally distributed features following the seismostratigraphic setting (Ferrante et al., 2022). The former represents preferential pathways for gas migration throughout the Plio-Quaternary sequence (Donda et al., 2015) that is possibly related to the main tectonic features (Brancolini et al., 2019). The data also image the upper termination of the gas chimney-like features, confirming that focused gas accumulations in subvertical pathways also affect the uppermost stratigraphic layers and, locally, the seafloor. Here, the gas can escape into the water column, as shown by numerous gas bubble streams (Gordini et al., 2012; Donda et al., 2015; Donda et al., 2019). A first estimate of the gas mean volumetric concentration was made using multichannel seismic data collected in the study area, which also quantitatively constrained the gas distribution from resistivity anomalies. This confirmed that the gas is both diffuse and concentrated in local accumulations, with gas contents ranging from 0.15 to 0.3% (Ferrante et al., 2022).

CHIRP data also clearly show gas occurrence as a diffuse acoustic blanking (Gordini et al., 2012; Donda et al., 2015 and Donda et al., 2019), which almost completely masks underlying reflections in the stratigraphic succession, with the gas front being represented by a high-amplitude reflector over the blanking zone (Donda et al., 2019).

Truncated reflections at the gas front indicate that the gas-trapping horizons are not continuous. A geophysical and geochemical study performed on some CHIRP data collected in the study area allowed us to quantitatively constrain the occurrence of uniformly distributed gas within the uppermost sedimentary succession and to date the shallow gas seeping at three leakage sites selected based on the aforementioned analyses. The seep gasses were found to be microbial and largely derived from relatively laterally persistent late Pleistocene peat layers (Donda et al., 2019).

Overall, the analyses confirmed that the gas is both diffuse and concentrated in local accumulations, both in the deep Plio-Quaternary succession and in the uppermost stratigraphic layers fed by both deeply rooted gas and Quaternary methane (Donda et al., 2019; Giustiniani et al., 2020; Ferrante et al., 2022).

4.5. Gas-related features on the sea floor

Gas seepage is widespread in the study area, as evidenced by several types of gas-related features on the sea floor and in the water column. The former are represented by the following: a. white microbial mats likely composed of chemosynthetic sulfide-oxidizing proteobacteria Archaea and Beggiatoa; b. small-scale mud volcanoes, about 2/3 cm high and 4/5 cm in diameter and are associated with gas leaking from a hole on top of them; these features are clearly recognizable because of their darker colour compared to the surrounding sediments (see also Fig. A1-Supplementary Material), indicating upward transport of deeper sediments deposited in a reducing environment; and c. pockmarks, up to 200 m in diameter and 1 m deep (Gordini, 2009; Gordini et al., 2012; Donda et al., 2015; Donda et al., 2019) (Fig. 8).

Numerous gas bubble streams have been identified in the water column both through direct observations during scuba diving and indirectly from the CHIRP data (Fig. 2). Almost all the rock outcrops presented in this study have gas bubble flows immediately above the outcrops or in their proximity (Fig. 8).

Gas samples collected from five seepage sites consist mainly of methane (ca. 53% to ca. 90%), and radiocarbon dating revealed an apparent age of the organic material source for the microbial gas that is between approximately 32,000 and 34,000 years B.P. (Donda et al., 2019). However, multichannel seismic data have revealed that gas chimneys are deeply rooted in the sedimentary succession, locally reaching the Messinian unconformity (Donda et al., 2015). Gas of deeper origin can locally migrate upward through the tectonic features identified in the area (Brancolini et al., 2019), suggesting that faults act as preferential conduits for the upward migration of gas. The distribution of all gas-related features identified in the study area, both within the sedimentary succession and on the sea floor, is shown in Fig. 1b.

5. Discussion

5.1. Genesis of the rock outcrops

The outcomes of all geological, geomorphological, geophysical, mineralogical analyses carried out on the studied rock outcrops, together with the analyses performed on gas seeping at the seafloor, allow us to conclude that most of them represent sandstones cemented by methane-derived authigenic carbonates.

The cementation process is a product of the archaea- and bacteria-driven anaerobic oxidation of methane and sulfate reduction, which takes place as the gas-rich fluids migrate to the seafloor (Hovland et al., 1987b; Greinert et al., 2001). Calcium carbonate precipitates are typically found as remnants of methane seepage (Greinert et al., 2001; Aloisi

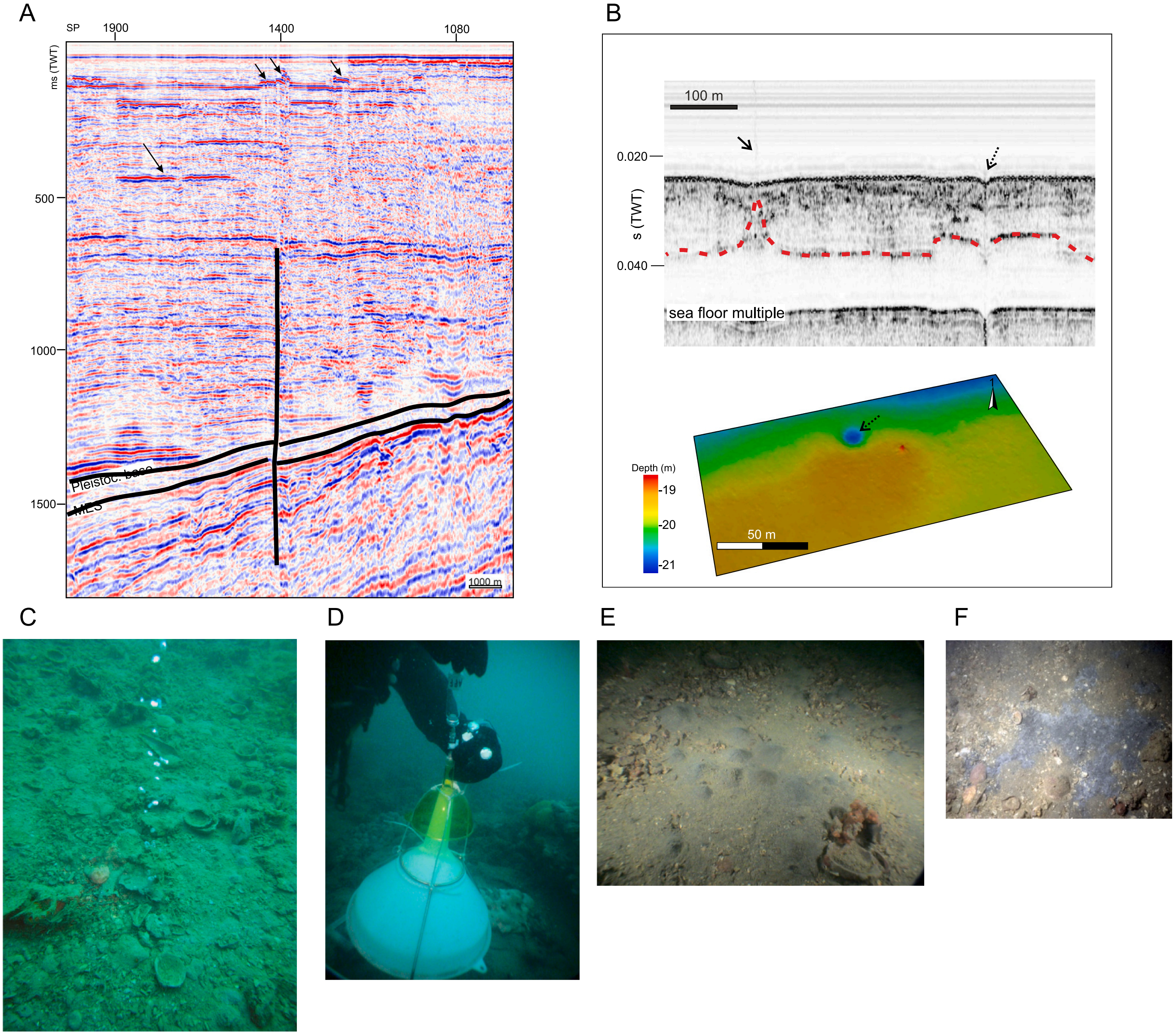

Fig. 8. Evidence of gas occurrence within the sedimentary succession, on the sea floor and in the water column. A. Part of the multichannel seismic profile revealing the occurrence of bright spots at various stratigraphic levels (from Donda et al., 2019); B. Part of the CHIRP profile (above) and of single beam data collected across a pockmark; arrows indicate gas flares in the water column, whereas the red dotted line highlights the gas front (from Donda et al., 2019); C. Photograph of bubbling gas (from Donda et al., 2015); D. gas collection procedure; E. Photograph of the sea floor, showing the occurrence of several small-scale mud volcanoes; F. Photograph of the sea floor, revealing the occurrence of chemosynthetic sulfide-oxidizing proteobacteria Beggiatoa (from Donda et al., 2015). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

et al., 2002; Campbell et al., 2002; Lein et al., 2002; Peckmann and Thiel, 2004). They mostly belong to two main groups. A first one deals with deposits formed below the water-sediments interface as porous plates of carbonate-cemented sediments, irregular crusts, smooth lenticular concretions, flat pancake-shaped deposits, and large metric-sized tabular constructions (Luth et al., 1999; Peckmann et al., 2001; Lein et al., 2002; Michaelis et al., 2002). A different situation is observed where carbonates can grow in the water column, forming high accumulations and, in some places, tower-like constructions that can reach several meters in height (Peckmann et al., 2001; Lein et al., 2002; Michaelis et al., 2002). In this context, microbial mats play an important role and are typically associated with methane-derived carbonates. It is widely recognized that methane-derived carbonates form preferentially in sediments (Paull et al., 1992; Gaillard et al., 1992). Methane is oxidized by a consortium of archaea and sulfate reducers (Hoehler et al., 1994), and this reaction is associated with an increase in alkalinity, which is responsible for carbonate formation (Ritger et al., 1987; Thiel et al., 1999, 2001). Because bottom waters of the northern Adriatic Sea are usually oxygenated, the formation of carbonates associated with anaerobic oxidation of methane is confined within the anoxic sediments. Therefore, seepage-associated carbonates with a positive relief at the seafloor should be an exception in the study area, and further studies are needed to investigate this aspect in detail.

In marine carbonates, the isotopic composition of carbon is a key signature for identifying the depositional environment, as it is closely related to chemical species dissolved in seawater. It can vary from +2/+3 ‰ for organogenic carbonates, to −80/−90‰, for carbonates precipitated or secreted in an environment influenced by methane emissions (e.g., Mazzini et al., 2004). Strongly negative 12C /13C values have already been recorded in the northern Adriatic Sea in the last century, when samples from some gas production wells yielded ratios of −73 ‰ to −38 ‰ PDB (Mattavelli et al., 1983 and Colantoni et al., 1997a and b).

In the study area, the aragonitic cement from some of the studied MDACs, i.e., the D'Ancona, Bardelli, Sorse and Orto sites, show δ^{13}C values ranging from −20.06‰ to −49.80‰, with the latter value being the most negative ever reported from the Northern Adriatic Sea methane-derived carbonates (Donda et al., 2015).

The ages of the analyzed cements range from 15,940 +/− 360 to 21,700 +/− 2265 B.P. (uncalibrated ages). These ages are always older than those of the bioclasts that form the skeleton of the rocks, which date 4990 +/− 45, 7150 +/− 60, and 8200 ±55 B.P. and appear to be progressively younger toward the coast (see Table 1). As for the age of the biogenic component of the outcrops, notice that the time spam of 8620 and 4990 years B.P defines the range at which the last phase of cementation took place, which followed that of the death of gastropods.

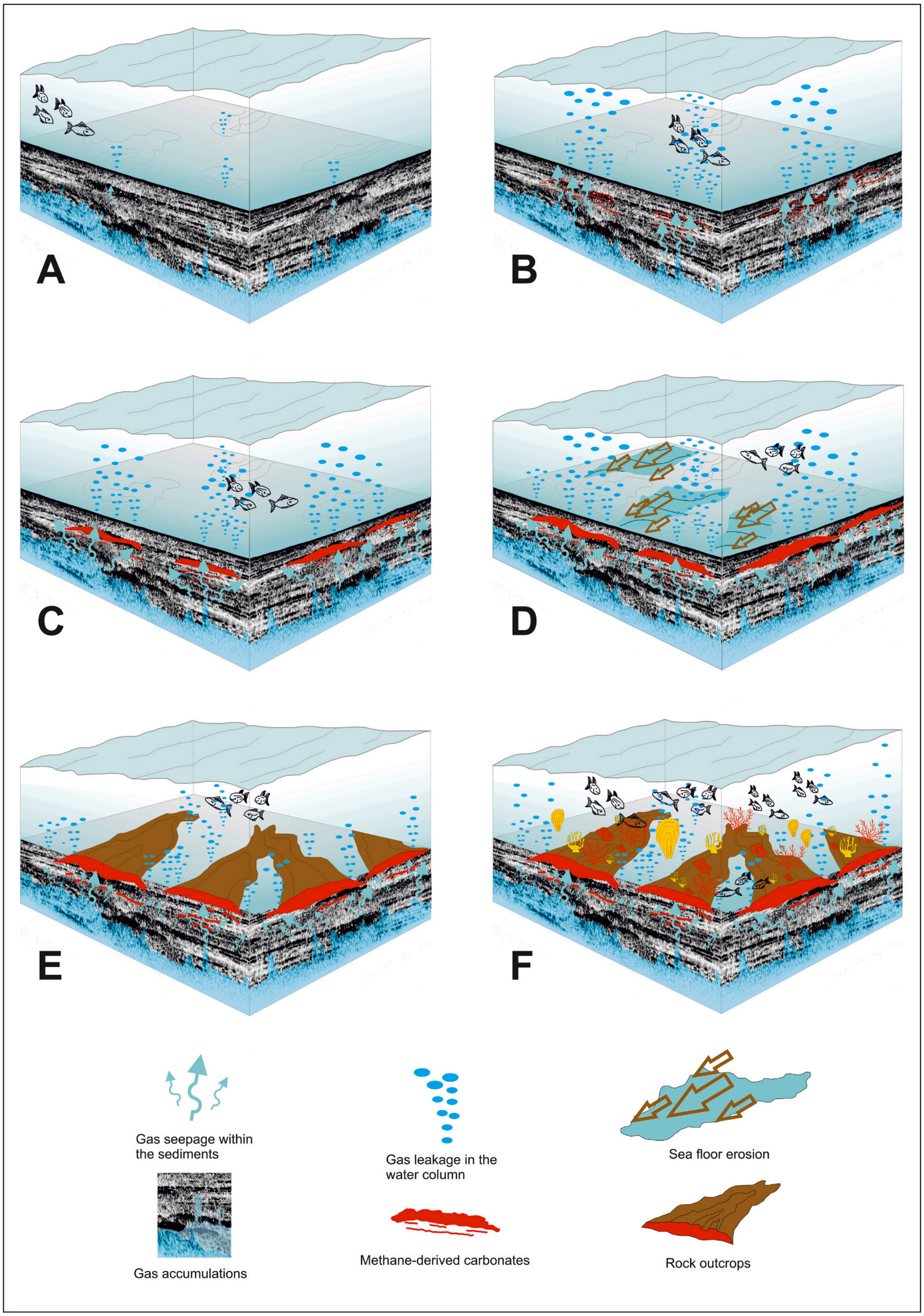

Fig. 9. Cartoon illustrating the genetic model of the northern Adriatic Sea rock outcrops.

As highlighted in the introduction major efforts have been made in recent decades to understand the main process at the base of the lithified sediment in the northern Adriatic Sea rocky outcrops. The data and analyses presented in this study reveal that the genetic models proposed in previous studies do not contradict each other and are united by the same methane-associated cementation process. We contend that the leading process of the lithification of these features is associated with hydrocarbon-enriched fluid seepage through porous sediment, as shown in Fig. 9.

In the early stages of development, gas formed as a consequence of alteration of organic matter occurring throughout the Plio-Quaternary sediments and accumulated below Impermeable strata in the uppermost stratigraphic layers. Locally, in association with areas of high porosity and/or with the increased pressure of its upward migration, gas seeps from the sea floor and propagates in the water column (Fig. 9A). The persistent upward gas migration, both from the deeper Plio-Quaternary sedimentary succession and from the upper peat layers, led to widespread accumulations of shallow gas, the onset of methanogenic bacterial processes and the consequent precipitation of small amounts of methane-derived calcium carbonates, leading to the lithification of sediments and the formation of thin cemented layers (Fig. 9B). The latter hinder the further upward flow of the gas, which is then forced to flow laterally to the cemented crusts. The horizontal spread of gas contributes to the progressive growth of the primeval cemented slabs, both in width and in thickness (Fig. 9C). Sea floor erosion exposes the shallowest sedimentary strata overlying the carbonate crusts and induces a further increase in the gas flow as a consequence of a decrease in the hydrostatic pressure and a further thickening of the cemented crusts (Fig. 9D). Strong sediment erosion has been evidenced in the Northern Adriatic sea since the last century, indeed. It is responsible for the removal of an about 10–15 m-thick sediment cover, so that the Holocene-to-Recent deposits are almost completely missing, except in areas proximal to the coast (Stefanon, 1984). Erosion also affected, and still affects, the rock outcrops (Stefanon, 1969), where a sedimentary cover is almost completely missing, and small-scale pinnacle features formed as a consequence of erosional processes (Newton and Stefanon, 1976; Newton and Stefanon, 1982). They are thought to have formed not only during the Last Glacial Maximum sea-level lowstand, but also during the subsequent Holocene transgression (Stefanon, 1984; Marocco, 1991). Ongoing sediment erosion has been mostly evidenced offshore of Venice and Caorle (Stefanon, 1984) and of the Tagliamento River, where Holocene sediments are <1 m thick or even absent (Trobec et al., 2018). It is suggested that sediment erosion is mostly related to the wave motion, and especially to Scirocco stormy waves (Stefanon, 1980; Cavaleri and Stefanon, 1980), which are able to re-suspend both coarse- and fine- grained sediments to depths of 100 m (Cavaleri and Malanotte-Rizzoli, 1981; Stefanon, 1984). The concurrent anti-clockwise circulation enhances such erosional processes and the prevailing southward transport of eroded sediments (Stefanon, 1984), which then allows MDACs outcrop (Fig. 9E). Pioneer marine species colonize the exposed rock substrates. Their tabular and elevated morphology with respect to the surrounding seafloor represents an ideal substratum for the growth of bioconstructive species, thus leading to the formation of an organogenic cap reef (Fig. 9F). Due to their high biodiversity, they have been defined as hot spots of underwater life and are included in protected marine areas (bio-geosites; https://www.ita-slo.eu/en/tretamara).

Isotopic signatures of the sampled gas indicate the formation of shallow methane in relatively laterally persistent, late Pleistocene peat layers that are widespread in the northern Adriatic Sea. However, multichannel seismic data have revealed that gas chimneys are deeply rooted in the sedimentary succession, locally reaching the Messinian unconformity (Donda et al., 2015). Based on the findings of thermogenic gas within the Paleogene sequences of the Central Adriatic Sea (Casero and Bigi, 2013), a possible mixing of biogenic and thermogenic gas feeding the gas accumulations in the study area has been hypothesized, i.e., gas originating within the Pliocene or within older sequences would mix with shallower methane that formed as a result of the decomposition of Quaternary peats (Donda et al., 2015). Methane formed within the Plio-Quaternary succession is microbial gas, occurring as multiple pools within thin sand beds at approximately 1200–1500 mbsf (Casero, 2004; Bertello et al., 2008; Casero and Bigi, 2013), which was exploited in the 1960s. Even the seeping and sampled gas is of microbial origin (Gordini, 2009; Gordini et al., 2012; Donda et al., 2019), thus suggesting that gas originating within the Pliocene strata or within older sequences would mix with shallower methane formed as a result of the decomposition of Quaternary peats (Donda et al., 2015). This gas of mixed origin permeates the shallow accumulations, which feed the studied methane-derived carbonates.

5.2. Spatial and temporal variability of gas emissions

Taking into account that the common denominator of the genesis of the studied rock outcrops is related to the occurrence and role of methane in the sedimentary succession of the northern Adriatic Sea, we discuss hereafter the potential oceanographic (i.e., in the water column) and hydro-geomorphological (i.e., in shallow coastal aquifers) interaction processes capable of modulating methane leakages. From an oceanographic perspective, the first physical factor that must be considered is the variation in the hydraulic head. In fine surface sediment, methane release is triggered by the drop in hydrostatic load that generates the gas-driven dilatation of microconduits and promotes bubble escape (Scandella et al., 2011). In particular, it has been shown that a hydrostatic pressure drops of 5 kPa (equivalent to approximately −0.5 m of water head, on the order of low tidal amplitudes) is sufficient to induce tensile strength failure of marine surface sediments with consequent gas release (Sultan et al., 2020). This confirms the hypothesis that intermittent degassing is modulated by tidal cycles (Donda et al., 2019), and is possibly influenced by meteo-climatic factors that control the average water head. In fact, tides have already been recognized as one of the main factors controlling gas emissions in shallow marine environments (Mikolaj and Ampaya, 1973; Boles and Clark, 2011).

Furthermore, the northern Adriatic basin is a well-known site for dense water-formation. Strong thermal and evaporative fluxes, which occur mainly during late autumn-winter seasons, induce complete overturning of the water column by mixing the surface and bottom layers (Bergamasco et al., 1999). Then, the cyclonic circulation of the northern semi-enclosed basin can reach high values of kinetic energy throughout the depth (Bergamasco and Gacic, 1996, Fig. 5). The bottom layer can experience a strong renewal due to the dense water leaving the site and the subsequent replacement of the water coming from the Croatian coast (Benetazzo et al., 2014). With a seabed of different roughness and with grain size varying from sand to clay depending on the depth, especially in front of the river mouths, the acting stress could have mobilized and displaced the surface sediment differentially and contributed to prevent long-term sedimentation on the cemented reliefs, favoring their biological colonization.

Finally, relevant vertical exchanges can be active between the seawater and the coastal aquifer that are able to modify the salinity and chemistry of the upper seabed layer under the mediation of the microbial component. Salinity can play a role in the coexistence and balance between sulfate-reducing and methanogenic bacterial communities, promoting a shift toward the production of CO2 instead of CH4 (Pattnaik et al., 2000; Sela-Adler et al., 2017). In the case of the northern Adriatic Sea, this implies that where a shallow unconfined and strongly salinized coastal aquifer does exist, such as south of Venice (Lovrinović et al., 2021; Tosi et al., 2022; Da Lio et al., 2015), the activity of sulfate-reducing bacteria could control and reduce the methane flux. The opposite could be true if the coastal aquifer is less exposed to saline intrusion, as is suspected in the northern coastal sector of the study area, where resurgence line generally extends only about 10 km inland (Zavagno, 2011); however, an offshore continuation of aquifers identified on land has been recently suggested (Giustiniani et al., 2022).

5.3. *Implications*

The key role of widespread methane seepage throughout the study area has potential and very practical outcomes. The first outcome concerns the impact of methane emissions on the water column and possibly the atmosphere. In fact, in very shallow environments, the potential transfer of methane-predominant gas from the sediments to the atmosphere could be significant (Sultan et al., 2020). Methane, despite its low occurrence in the atmosphere, is a potent greenhouse gas, with a 100-year warming potential that is ~23 times higher than that of carbon dioxide (Hartmann et al., 2013). Several uncertainties exist regarding the role of natural methane emissions, particularly geological seepage, in the global methane budget (Saunois et al., 2020). Seepage sites may be more widespread and numerous than expected (Etiope et al., 2019; Thornton et al., 2020), particularly in shallow-water marine environments (water depth of$<$30 m), where bubbles can rapidly reach the atmosphere (Borges et al., 2016). While the emissions from seeps should be considered natural sources in the global methane budget, further warming of surface waters could increase methane emissions and provide positive feedback to climate warming (Borges et al., 2016). This feedback is expected to be acute in shallow gassy areas, such as the northern Adriatic Sea.

This aspect is related to the second main finding of our study, i.e., the strong relationship between sea level and methane emissions, implying that degassing may not be detected in similar areas sampled at high tide, and gas-related features such as methane-derived carbonates may be misinterpreted, helping to cast non negligible doubt on the global budget of atmospheric methane (Sultan et al., 2020, and references therein).

6. Conclusions

This study represents a significant advance in the knowledge of the northern Adriatic Sea outcrops, especially with respect to the cementation processes that prompted the development of these coralligenous geosites. The comprehensive analysis of geological, geophysical and mineralogical data collected in the northern Adriatic Sea corroborates the hypothesis concerning the methane-related origin of most rock outcrops, which are characterized by a cementation process related to the precipitation of methane-derived carbonates.

A key result of our analysis is the relationship between the primeval sedimentary deposits and the processes that led to their evolution into the sandstone formation. The great morphological and lithological heterogeneity of the studied outcrops would induce us to believe that the different depositional environments in which they formed, i.e., paleo-fluvial channels, paleo-barrier lagoon systems, paleo-beaches, and alluvial plains, are associated with different cementation processes. Instead, our analyses led us to contend that they share the same cementation process that is related to the precipitation of methane-derived carbonates. We suggest that the concurrent presence of porous and permeable sandy layers and impermeable clay levels played a key role in gas accumulation and subsequent cementation processes. The primeval morphologies and related deposits thus represented the "skeleton" that was subsequently cemented by the methane-derived carbonates.

This conceptual model reconciles the conundrum of the different models related to the genesis of the northern Adriatic Sea outcrops by highlighting the key role of methane seepage in their formation. This outcome also highlights that since methane is one of the most powerful greenhouse gases, the study area is thus a unique natural laboratory for deciphering the dynamics of methane natural degassing, consumption, transport and subsequent, eventual emission to the atmosphere in shallow marine environments.

The outcomes of our study are an important step forward in the knowledge of the northern Adriatic Sea geosites, rising new outstanding scientific questions that deserve further investigation, such as: 1. How much seeping methane dissolves in the water column and how much of it is able to reach the atmosphere? 2. How has methane seepage changed in the past? 3. Does the precipitation of methane-derived carbonates still take place? 5. Which is the age of the Northern Adriatic MDACs? 4. Do other fluids, i.e., water, also seep from the rock outcrops of the northern Adriatic Sea?

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Emiliano Gordini reports financial support was provided by European Commission.

Data availability

Multichannel seismic data are stored and available at the "Seismic data Network Access Point (SNAP)" repository (https://snap.ogs.trieste.it/cache/index.jsp).

Bathymetry data of the studied rock outcrops are available through: Gordini, E., Saul, C., 2020. Bathymetry data (GeoTIFF grid format) of the Northern-most Adriatic area are as follows: Interreg Ita-Slo 2007-2013 TRECORALA Project. Integrated Earth Data Applications (IEDA). doi: 10.26022/IEDA/329903.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.margeo.2023.107081.

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