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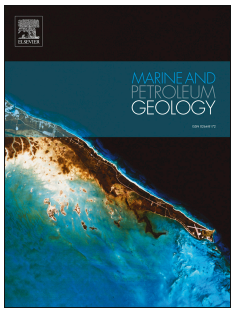

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ACCEPTED MANUSCRIPT

Fluid sources and stable isotope signatures in Authigenic Carbonates from the Northern Apennines, Italy

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Abstract

Authigenic carbonates are frequently associated with methane cold-seep systems, which extensively occur in various geologic settings worldwide. Of interest is the relation between the fluids involved in their formation and the isotopic signals recorded in the carbonate cements. Along the Northern Apennines foothills (Italy), hydrocarbons and connate waters still seeping nowadays are believed to be the primary sources for the formation of fossil authigenic carbonate found in Plio-Pleistocene marine sediments. Four selected outcrops of dolomitic authigenic carbonates were analysed to compare signature of seeping fluids with fractionation of stable carbon and oxygen isotopes recorded in the carbonate.

Along the foothills, deep methane-rich fluids spontaneously rise to the surface through mud volcanoes or are exploited in wells drilled nearby to the fossil Plio-Pleistocene authigenic carbonates. The plumbing system providing fluids to present-day cold seeps was structurally achieved in Late Miocene and Plio-Pleistocene. $\delta^{13}C$ values of methane, which vary from -51.9 to -43.0‰ VPDB, indicate that gas composition from the deep hydrocarbon reservoirs is relatively uniform along the foothills. On the contrary, $\delta^{13}C$ in fossil authigenic carbonates strongly varies among different areas and also within the same outcrop.

The different carbon sources that fed the investigated carbonates were identified and include: thermogenic methane from the deep Miocene reservoirs, ^{13}C-enriched CO_2 derived from secondary

methanogenesis and microbial methane from Pliocene successions buried in the Po Plain. The $\delta^{13}C$ variability documented among samples from a single outcrop testifies that the authigenic carbonates might represent a record of varying biogeochemical processes in the hydrocarbon reservoirs. The sources of stable oxygen isotopes in authigenic carbonates are often ascribed to marine water. Oxygen isotopic fractionation in the dolomite cements indicates that marine pore water couldn't be the sole source of oxygen. $\delta^{18}O$ values provide a preliminary evidence that connate waters had a role in the carbonates precipitation. The concomitant occurrence of active cold seepages and fossil record of former plumbing systems suggests that generation and migration of hydrocarbons are long-lasting and very effective processes along the Northern Apennines foothills.

Keywords

Authigenic Carbonates; Cold seep; Oxygen and Carbon stable isotopes; Petroleum system; Methane migration; Connate water.

1 Introduction

Seafloor fluid seepages represent widespread and highly dynamic environments. Their physical and chemical characteristics reflect their fluid sources, fluid flow intensities, tectonic setting, and properties of the hosting sediment (e.g. Judd et al., 2002; Judd and Hovland, 2007; Nyman and Nelson, 2011; Magalhães et al., 2012; Hensen et al., 2015). The various processes of formation, migration and alteration of hydrocarbons represent key factors to define the natural fluid seepage settings. The role of microbial consortia promoting the Anaerobic Oxidation of Methane (AOM), and coupled Sulphate Reduction (SR), was stressed to represent the major diagenetic processes occurring at cold seeps (e.g., Peckmann et al., 1999; Boetius et al., 2000). The formation of Methane-Derived Authigenic Carbonate (MDAC) represents the main by-product of the AOM-SR process in marine environment (e.g. Peckmann et al., 2001; Reitner et al., 2005), and could preserve the geochemical imprint of the fluids involved in their formation. The correlation between

authigenic carbonates (AC) and hydrocarbon source in present-day cold seeps is often facilitated by associated gas leakage from the seafloor, which can be sampled and analysed. Otherwise, in fossil systems this correlation can be more challenging due to scarce knowledge of the associated petroleum system. Mineralogy, oxygen and carbon stable isotopes, and biomarkers (e.g., Peckmann and Thiel, 2004; Magalhães et al., 2012; Pierre et al., 2014; Reitner et al., 2015; Taviani et al., 2015) are commonly used to describe the processes and fluids involved during methane-derived authigenic carbonate precipitation. Carbon stable isotopes are useful to identify the carbon sources, whereas oxygen isotopes provide information on the ambient water and temperature during carbonate formation. However, the isotopic composition might be influenced by mixing of hydrocarbon with waters from different sources and by recrystallization processes, which mask the original signal and hinder a correct interpretation. Despite to define a direct correlation between authigenic carbonates and fluid sources might be difficult, it is clear that they are a fossil record of changes in both the biogeochemical processes active within the fluid reservoirs and in the flux intensity during the fluid leakage. Therefore, the methane-derived authigenic carbonates can provide elements useful during hydrocarbon exploration and insights on the contributions of methane seepage in the marine environments and, possibly, the atmosphere.

The main objective of this work is to assess a possible direct correlation between the fluids that were present during fossil authigenic carbonate formation and those occurring in the present-day active fluid seepage sites along the Northern Apennine foothills. This research would contribute to shed light on the Northern Apennines seepage history, with the aim to better interpreting modern and fossil occurrences worldwide, both offshore and onshore, and to identify the processes resulting in different isotopic signature and geochemistry of authigenic carbonates. In particular, we evaluate the geological and geochemical constraints that could have influenced the oxygen and carbon isotopic compositions during the precipitation of fossil authigenic carbonates in four representative outcrops: Stirone River, Secchia River, Enza River and Nirano mud volcano field (NMVF) (Fig. 1). Present-day seeps and deep wells along the foothills are used to define the geochemical

characteristics of the fluids contained in the reservoirs that are part of the Northern Apennines petroleum system.

Fig. 1: Geological map of the investigated sector of the Northern Apennines with the location of the analysed authigenic carbonate outcrops. Salsomaggiore and Salvarola Terme wells location is shown. The traces of cross sections of figures 2, 4 and 5 are indicated.

2 Geological setting

The Northern Apennines formed in consequence of complex interactions between Adria and European plates. The Oligo-Miocene collision between Adria and the Corsica-Sardinia block rearranged the Jurassic-Eocene units belonging to the Ligurian deformed oceanic wedge, which progressively thrust over the foredeep successions of Miocene age, forming the Ligurian Nappe (Zattin et al., 2002). In the Po Plain side of the Northern Apennines, the Ligurian Nappe shows a wedge-shaped closure along the foothills with a gravitational reworking at its tip. The underlying foredeep deposits have been progressively incorporated into the orogenic belt, and the fold-and-thrust belt formed during Miocene and Pliocene provided the structural traps for hydrocarbon accumulation in the subsurface of Northern Apennines and Po Plain (e.g. Oppo et al., 2013 and references therein). Folds and thrusts in the foredeep succession formed during and after the tectonic and gravitational emplacement of the Ligurian Nappe, which acted as seal for the fluid reservoirs. The Epiligurian Units filled numerous satellite basins occurring above the Ligurian Nappe. Late orogenic extensional tectonics, crosscutting the sedimentary cover down to the Miocene units, is responsible for the formation of high-angle normal faults (Picotti and Pazzaglia, 2008; Picotti et al., 2009), which provide the main fluid migration pathways for numerous present-day spontaneous seepages (Picotti et al., 2009; Capozzi and Picotti, 2010; Oppo et al., 2013). The mountain range is characterized by Plio-Pleistocene uplift and exhumation (Balestrieri et al., 2003; Bartolini, 2003), with a consequent transition from exclusively marine to continental environments (e.g. Ghielmi et al., 2009; Gunderson et al., 2014).

2.1 Salsomaggiore and the Stirone authigenic carbonate field

The Salsomaggiore anticline is the westernmost structure considered in this study (Fig. 1). It is formed by a Burdigalian-Serravallian succession of turbiditic sandstones and marls. It was deformed since Langhian through Tortonian as an intrabasinal structure, verging northeast, which was ultimately exposed and eroded at the thrust-top (Fig. 2). After a subsidence pulse during Messinian, the structure was covered and sealed by an olistostrome detached from the Ligurian nappe. A large wave-length folding and erosion phase in Plio-Pleistocene led to refolding of the upper thrust sheet with a northwest vergence.

Fig. 2: Strike cross-section of Salsomaggiore anticline and Stirone authigenic carbonate field along the Northern Apennines foothills (Vertical exaggeration 2:1). In this area, Burdigalian to Serravallian reservoir outcrops after Plio-Pleistocene northwestward reactivation of a lateral ramp and erosion of sealing units. The fluids migrated up-dip along the sedimentary layers into the anticline culmination.

Synsedimentary deformation and tectono-thermal evolution governed the migration of fluids in the anticline flanks since Serravallian, and caused various episodes of hydrocarbon venting on the seafloor, marked by several seep-related carbonate concretions and chemoherms (e.g., Ricci Lucchi and Vai, 1994; Terzi et al., 1994; Taviani, 2001; Conti et al., 2007; Cau et al., 2015).

Authigenic carbonates occurring in the Pliocene hemipelagic succession that overlies the northwestern flank of Salsomaggiore structure outcrop along the Stirone River. The authigenic carbonates investigated in this study are located in a ca. 50 meters-long outcrop formed of hemipelagic clays and silty clays pertaining to the Argille Azzurre Fm., and deposited at the transition between Zanclean and Piacenzian (Cau et al., 2015). The authigenic carbonates form pipe-like conduits and slabs (Fig.3a). Moving up-section, various brecciated micritic limestones, Lucinid mudstones and chemosymbiotic organisms occur interspersed within organic-rich (sapropel) horizons (e.g., Cau et al., 2015), deposited during Piacenzian and controlled by precession cycles (e.g., Capozzi et al., 2006).

2.2 Enza River authigenic carbonate field

Authigenic carbonates outcropping along the Enza riverbanks (Blumenberg et al., 2015; Oppo et al., 2015; Viola et al., 2015) (Figs. 1 and 3b) develop at the Northern Apennines foothills in a well-preserved Early Pleistocene succession that marks the change from shallow marine to coastal sedimentary environment (Gunderson et al., 2014).

Southwards of the authigenic carbonate outcrop, the Quattro Castella ramp anticline locally delineates the present-day mountain front, which was generated by the formation of a detachment within the Ligurian Nappe during Plio-Pleistocene (Gunderson et al., 2014) (Fig. 4). A further E-W trending fold located in more external position was also actively growing in the Po Plain subsurface (Fig. 4; Oppo et al., 2015).

Fig. 3: Authigenic carbonate outcrops in the studied areas. a) Stirone chimney ca. 1m wide with the conduit filled by cemented sediments (white arrow); b) Chimneys and irregular carbonate concretions outcropping along the Enza riverbanks. Arrows indicate chimneys perpendicular to the stratification of the hosting sediment (strata marked by dashed lines). Note the chimney emerging from the water in foreground; c) Bulbous, slab-like authigenic carbonate concretions in Secchia riverbanks. Arrows point to main concretions. The concretions are roughly aligned to sediment stratification, which is exposed in the lower-right corner of the image.

Fig. 4: Cross-section in the Enza authigenic carbonate field along dip of Northern Apennines foothills. Deformation of the named Ghiardo Plateau fold can be observed on NNE; the erosional truncation of Tortonian units and following onlap of Messinian sediments are evidenced. Southwards to Enza authigenic carbonate field, a thrust detachment plane, related with the deformation of the Quattro Castella anticline, is located within the Ligurian Units. The source rocks in marine Pliocene sediments generated biogenic methane, which progressively migrated up-dip along the deformed sediments on the Ligurian Nappe forelimb. The horizon marking the base of the Enza River section (1.7 Ma) is shown.

The authigenic carbonate field is located on the Quattro Castella anticline forelimb, which deforms a fine-grained succession belonging to the Lower Pleistocene Argille Azzurre Fm. and that

represents part of the marine intervals before the transition to continental deposits (Gunderson et al., 2014). The authigenic carbonates occur as slabs and pipe-like bodies (chimneys, similar to those described in Magalhães et al., 2012) within a 35 meters-thick section formed of continuous inner shelf silty clays, with intercalations of cm-thick sandy layers progressively more frequent towards the top of the section. This latter, dated at 1.4 Ma, is marked by a significant angular unconformity and by a layer containing chimney fragments and reworked coarse siliciclastics. This layer is pervaded by dark grey micritic carbonate concretions and colonized by a corallinaceous assemblage (Oppo et al., 2015).

Southwards to Enza field, a weakly-cemented body ca. 10 meters high (Enza Hills in Sec. 3.1) occurs within sand layers. These latter sediments pertain to the upper Argille Azzurre Fm., deposited after the pelitic succession hosting authigenic carbonates along the Enza riverbanks (Gunderson et al., 2014). This body was likely formed close to the seafloor due to its richness in benthic fauna and bioturbation.

2.3 The Secchia River authigenic carbonate field and Nirano mud volcanoes area

The stripe of Northern Apennines foothills comprised between Secchia River and Nirano shows several features that testify present-day fluid emission, such as the Nirano Mud Volcano Field (NMVF) and saline waters (exploited in spa activities at Salvarola) mixed with hydrocarbons (Fig. 1). In this area, thrusts deforming the Miocene foredeep units create structural traps for the fluids: Their growth proceeded during the Late Miocene and Pliocene, with minor deformation also in the Quaternary (Oppo et al., 2013) (Fig. 5). Later high-angle normal faults along the foothills are likely providing the main pathways for fluids migration and present-day fluids emission at surface (e.g. Oppo et al., 2013).

Fig. 5: Cross-section through Nirano Mud Volcano Field along dip of the Northern Apennines foothills. Present-day fluid emissions are associated with ramp anticlines along the foothills. Normal faults likely allow upwards migration of saline water and thermogenic hydrocarbons, connecting Miocene reservoirs to the surface.

Various authigenic carbonate concretions outcrop along Secchia riverbanks (Fig. 3c) within the Lower Pleistocene (1.7 Ma) succession of Argille Azzurre Fm. Carbonates mostly form meter-size bulbous and slab-like concretions, with a minor occurrence of smaller chimneys. Slab-like concretions are interlayered within the succession, whereas bulbous concretions and chimneys crosscut the stratification. Small normal faults, dipping northeast, are documented along the riverbanks close to the concretions.

North-eastwards of Secchia River, the NMVF develops over an area of ca. 75,000 m^2 into Plio-Pleistocene Argille Azzurre Fm., and at the bottom of a caldera-like structure that is likely resulting from a collapse within the pelitic succession following strong and prolonged events of fluid expulsion. The ramp-anticline forming the fluid trap in Miocene foredeep sediments, and also deforming the Ligurian Nappe sealing units, is overlaid by outcropping Argille Azzurre Fm (Fig. 5) (Oppo et al., 2013). Mud cones and pools at NMVF are active with constant emission of saline waters and methane, together with small amounts of oil and condensates migrating from the Miocene reservoir (Oppo et al. 2013). Along a small creek to the west of NMVF, a few carbonate chimney concretions were recovered within the Argille Azzurre Fm.

3 Materials and Methods

3.1 Analysed samples

Samples from four authigenic carbonate outcrops were considered in this study. A total number of 45 subsamples, representing various carbonate morphologies, were selected and analysed. A total number of 21 subsamples from Enza River field were analysed, belonging to two chimneys, En5 and En10 (Figs.6a and 6b), one tabular slab, Cr2 (Fig. 6c) and one concretion within the upper

horizon colonized by the corallinaceous assemblage, Cr3 (Fig. 6d). Chimney En10 shows an open central conduit, is 170 cm long and 20 cm in diameter. The top and the bottom of the chimney were analysed. The top was divided in external (E) and internal (I) portions (Fig. 6b), whereas only the internal area of the bottom has been analysed. En5 chimney is 63 cm long and 20 cm in diameter. (Fig 6a). It was divided in 8 sections from bottom (1) to top (8), to investigate possible geochemical variations along the chimney. Each section, excluding 1 and 8, was longitudinally separated in internal (I), middle (M) and external (E) parts (Fig. 6a). In this paper, selected subsamples from sections 1, 3, 4, 6 and 8 are presented. Cr3 sample is a concretion at the top of the Enza section; the dark-grey portion of sample (Cr3A) was analysed and compared with the light-grey adjacent areas (Cr3B) (Fig. 6d). Cr2 slab is located stratigraphically below the corallinaceous assemblage layer and shows a general grey colour (Cr2A) with a light-grey area (Cr2B) (Fig. 6c). One sample from the semi-consolidated carbonate concretions cementing the sandy intervals at Enza Hills was also analysed (ENCO 1) (Fig. 6i).

Five samples were collected from globular slab-like concretions of Secchia river (SCH1 to SCH5) (Figs. 6e and 6f), with weak cementation and meter-size dimensions. Subsamples were collected for the external (E) and internal (I) areas of each concretion. One chimney (SCH6) with high degree of cementation was subsampled: a light-grey layer in the more external area (E), a darker interval forming the bulk of the concretion (M), and the yellowish-grey poorly consolidated infilling of the conduit (I) (Fig. 6g).

Eastward to NMVF, a single chimney ca. 20 cm in diameter and 30 cm long was recovered. Two subsamples of internal (I) and one of external (E) areas were analysed (Fig. 6h). Two cylindrical concretions collected at Stirone River (STN1B and STN2) are ca. 50 cm in diameter and 1 m long, contain abundant detrital fraction cemented by authigenic carbonate. The concretions are identified as chimneys where the central conduit is filled with carbonate cement and sediment arranged in a rose-like morphology. Both chimneys were subsampled in the external (E), middle (M) and internal (I) areas (Fig. 6j).

The authigenic carbonate formation can be related to deep fluids generated by the Northern Apennines petroleum system. This is supported by the geologic evolution and tectono-thermal history of the reservoirs (Capozzi and Picotti, 2010; Oppo et al., 2013). Therefore, gas samples collected in the four sites were used to constrain the gas isotopic signature recorded in carbonates. Three fluid samples have been collected in deep wells drilled in the Salsomaggiore anticline (Salsomaggiore 7 and 93, and Salsominore 16). Two samples represent fluids emitted by NMVF, one of which is related to a strong emission event. Methane gas has been also collected from Salvarola Terme wells, which were drilled in the same sedimentary succession occurring at Secchia authigenic carbonate field. One gas sample has been recovered from a small seepage occurring in the Enza riverbed stratigraphically at the top of the carbonate occurrences.

Fig. 6: Carbonate samples representative of the concretions considered in this study. a) En5 chimney from Enza River, was divided in 8 sections bottom (1) to top (8); subsamples: external (E), middle (M) and internal (I); b) En10 chimney's top from Enza River, divided in external (1E) and internal (1I) portions; c) The Cr2 slab from Enza river divided in two subsamples according to colour variation: grey (2A) and light-grey (2B); d) Cr3 concretion from Enza River divided in two subsamples according to colour variation: dark-grey (3A) and light-grey matrix (3B); e-f) Two globular concretions at Secchia River, SCH3 (e) and SCH5 (f). Each sample was divided in external (E) and internal (I) areas; g) SCH6 chimney from Secchia River, three subsamples from external (E), internal(I) and middle(M) portions were analysed; h) Nirano chimney was divided in three subsamples: two internal (1a-I and 1b-I) and one external (1-E); i) Enza Hill sample; j) STN1 chimney from Stirone River. The three analysed subsamples belong to external (E), internal (I) and middle (M) portions.

3.2 Methods

Subsamples of carbonate concretions were collected by micro-drilling, and homogenized in agate mortar for analysis of mineralogy. X-ray diffractometry (XRD) was performed using a Philips PW 1130 (Cu Ka radiation Ni filtered) in the Laboratory of BiGeA Department, University of Bologna. Powders were pressed into alumina holders in order to avoid preferential orientation of sheet-silicates. Estimates of the relative minerals abundance were determined using MacDiff software

packages and carbonate mineral composition according to Goldsmith and Graf (1958) and Lumsden (1979).

Carbon and oxygen isotopic analyses of the Enza carbonates were performed at CNR-Institute for Geosciences and Georesources (CNR-IGG) of Pisa, while the Enza hills, Stirone and Secchia rivers, and Nirano samples were analysed at the Swiss Federal Institute of Technology in Zurich (ETHz) . At CRN-IGG, powdered sub-samples (100 and 200 μg) were treated for 10 min at 90°C with 100% phosphoric acid on an automated carbonate device connected to a VG-PRISM mass spectrometer calibrated with NBS18, NBS19 and NBS20 standards. The results are reported in conventional δ‰ notation with reference to VPDB (Vienna Pee-Dee Belemnite). For samples with more than 20% of dolomite, $\delta^{18}O$ values were calculated with the Rosenbaum and Sheppard fractionation factor (Rosenbaum and Sheppard, 1986). Analytical reproducibility of the method, based on repeated analysis of standards, is better than ±0.1‰ for both carbon and oxygen (Rosenbaum, 1994; Rosenbaum and Sheppard, 1986). At ETHz, $\delta^{13}C$ and $\delta^{18}O$ values of carbonates were measured using Thermo Fisher DELTA Plus XP Gas Bench mass spectrometer. Between 90 and 140μg of powder were inserted in flasks then sealed and flushed by 99.99% helium gas. After the atmospheric air was swept out, 100% phosphoric acid was injected to react with the samples. Released CO_2 was purified and analysed. $\delta^{13}C$ and $\delta^{18}O$ values reported relative to the Vienna Pee-Dee Belemnite (VPDB) were corrected using IsolabB and MS1 standards, resulting in a precision of ±0.1‰.

The gas from present-day seeping fluids and drilled wells was analysed by GC-MS to determine hydrocarbon composition and carbon isotopes of methane, ethane and CO_2 at ENI laboratories and at CNR- Institute for Geosciences and Georesources in Pisa, Italy.

4 Results

4.1 Hydrocarbon geochemistry

Analyses of gas from the sampled areas indicate that it is mainly composed of methane (up to 99.86%, Salvarola Terme), with only Nirano paroxysmal sample showing a lower concentration due to an increase in CO_2 content. Ethane was detected in all samples, and shows clear abundances dissimilarity in the four areas: Salsomaggiore and Salsominore wells content is 0.577 % to 1.392%, Salvarola Terme 0.123% to 0.241%, Nirano 0.041% to 0.065%. The total content of higher hydrocarbon fractions is less than 2% (Tab. 1). Carbon dioxide occurs in measurable amount only in 4 samples and varies between 0.14% (Salsomaggiore 93) and 1.7% (Nirano Parox).

Tab. 1: Chemical and isotopic composition of sampled gases.

$\delta^{13}C$ of methane varies in the different sites and is comprised between -51.9‰ VPDB (Salsomaggiore 7) and -43.0‰ VPDB (Salsomaggiore 93). The gas sample collected along the Enza riverbed has significantly lower $\delta^{13}C$ value (-72‰ VPDB), which differentiates from all other areas. The carbon isotopic composition of CO_2 is generally enriched in ^{13}C, with the most positive $\delta^{13}C$ registered at Nirano (+19.9‰ VPDB), and lowest value in Salsomaggiore 93 (-20.9‰ VPDB).

4.2 Mineralogy and stable isotopes of authigenic carbonates

Authigenic carbonates from the sampling sites show similar mineralogy and petrography (Table 2; Fig. 7). Total carbonate fraction in bulk samples varies between 42 wt% and 81 wt%. Exception is the sandy concretion from Enza Hills that shows lower carbonate amounts, up to 37 wt%, due to elevated content of siliciclastic fraction. Carbonates are mainly composed of dolomite (up to 81wt%, En10 2A) (Table 2). Calcite is absent in concretions from Stirone and Secchia rivers, whereas it occurs in variable amount in Enza and Nirano. Viola et al. (2015) observed the preferential occurrence of calcite in external areas of chimneys along the Enza River, as in En5 4E and En5 3E samples from this study.

The detrital fraction includes mainly quartz and feldspars, with minor amounts of clays, micas, gypsum and oxides. Worth to note is the strong enrichment in sulphur (32,000 ppm) of Cr3B (Enza River), which accordingly shows high content of pyrite and arsenopyrite (5wt%).

The carbon isotopic compositions of carbonates display a high degree of variation among the different areas (Fig. 9). The Enza Hills sample has the lowest $\delta^{13}C$ value (-53.0‰ VPDB). The Enza River concretions have negative $\delta^{13}C$ values, with a large scattering comprised between -40.1‰ VPDB (Cr3A-2) and -8.2‰ VPDB (En5 4C) (Tab. 2). Internal subsamples of Enza chimneys have generally more negative $\delta^{13}C$ than middle and external subsamples.

Fig. 7: Photomicrographs of authigenic carbonates thin sections. A) Enza River: chimney concretion EN5 is formed by detrital grains, mainly quartz, within microcristalline dolomite cement and peloidal fabric (modified after Viola et al., 2015). B) Enza Hill concretion (image in crossed nicols): the sample shows elevated contents of siliciclastics sand-sized clasts and dense microcrystalline cement (sometimes clotted micrite). C) Stirone River: central part of chimney wall. Sparse siliciclastic grains cemented by micritic carbonate (modified after Cau et al., 2015). D) Secchia River: dense, clotted cement, sulphides (black spots), and sparse fine siliciclastic grains.

Fig. 8: Scanning Electron Microscope (SEM) photomicrographs and relative EDX spectrum of analysed carbonate cements. The spectrum was obtained at 15keV accelerating voltage. Arrows indicate areas and carbonate crystals selected for EDX analysis. A) Rhombohedral dolomite crystals forming microcrystalline cement in Enza River carbonates (images after Viola et al., 2015). B) Stirone River SEM photomicrograph of microcrystalline dolomite (image after Cau et al., 2015). C) Carbonate cement in Secchia River samples formed by dolomite crystals. D) Enza Hill dolomite cementing detrital rounded grains. E) Nirano SEM photomicrograph of dolomite with relative EDX spectrum. A calcitic coccolith is also visible.

Fig. 9: $\delta^{13}C$ vs. $\delta^{18}O$ diagram for authigenic carbonate samples considered in this study.

Stirone and Secchia chimneys have moderately negative $\delta^{13}C$, between -12.3‰ VPDB (SCH6 E) and -5.6‰ VPDB (STN1B M). In SCH6 chimney, $\delta^{13}C$ progressively increases from internal to

external areas. Slab-like concretions of Secchia River have positive $\delta^{13}C$, from +6.4‰ VPDB (SCH2 E) to +11.9‰ VPDB (SCH5 M), and a general increase of $\delta^{13}C$ values is observed from the base (SCH1) to the top (SCH5) of the section. Carbonate from Nirano chimney has the highest $\delta^{13}C$ value (up to +17.7‰ VPDB) among all the considered samples.

Differently from the carbon stable isotopes, the $\delta^{18}O$ values show a moderate variability, comprised between +3.4‰ VPDB (En5 4E) and +6.5‰ VPDB (NIR1a I) (Tab. 2). The Enza chimneys and the SCH6 chimney generally show higher $\delta^{18}O$ values in their inner parts.

Tab. 2: Mineralogy and stable isotopes in the analysed authigenic carbonates.

5 Discussion

5.1 Methane generation and petroleum system

To better define origin and characteristics of concretions is crucial to reconstruct the methane origin and its migration pathways towards the seafloor. In Salsomaggiore, NMVF and Salvarola Terme, the analysis of C_1 to C_3 gas fraction shows its thermogenic origin by oil cracking at temperatures exceeding 150°C (Oppo et al., 2013). The exact source rock responsible for generating these thermogenic hydrocarbons is still unknown, but it is likely located in the Upper Mesozoic successions involved in the Northern Apennine fold-and-thrust belt (Oppo et al., 2013). Carbon isotopic compositions of methane vs. ethane indicate that the gases are mixtures of thermogenic and biogenic methane contained in reservoirs of the deformed Miocene foredeep sequences (Fig. 10).

Fig. 10: Characterization of hydrocarbon gases by means of $\delta^{13}C$ in C_1 and C_2 fractions (Modified from Schoell, 1983). The diagram shows that mixing between biogenic and thermogenic components forms all considered gas samples. M, mixing of thermogenic and biogenic gas; T, thermogenic gas; TT, non-associated deep dry gases from humic (h) and marine (m) sources.

Generation of primary biogenic methane is not considered as a major source for the total gas budget in the Miocene reservoirs (Oppo et al, 2013). Otherwise, the generation of secondary biogenic gas related to biodegradation of liquid hydrocarbons can be relevant. Anaerobic microbial activity, responsible for altering the hydrocarbon geochemistry, was ascertained in connate waters from both deep wells and mud volcanoes (Heller et al., 2011; Oppo et al., 2013, Kokoschka et al., 2015). The secondary methanogenesis follows the CO_2 reduction pathway and produces ^{13}C-rich CO_2 at NMVF, Salvarola Terme and Salsomaggiore 7 (Tab. 1, Fig. 11). Differently, Salsomaggiore 93 and Salsominore 16 have CO_2 with negative $\delta^{13}C$ values that can be linked to a present-day very low microbial degradation activity; however, the data suggest that a secondary biogenic methane component cannot be completely ruled out.

Fig. 11: Plot of $\delta^{13}C$ in CO_2 vs. $\delta^{13}C$ in CH_4. Lines and values represent constant isotope fractionation. The samples show different contributions of secondary biogenic methane to the total gas budget, except Salsomaggiore 93 where this process is thought to be inactive during sampling.

Biodegradation of the migrating hydrocarbons can vary in time and space, even within a single area (Etiope et al. 2009). Therefore, the observed $\delta^{13}C$ values likely indicate that the generation of secondary biogenic methane was not relevant during the sampling, but could be active in other periods. This conclusion is supported by the calculated thermogenic methane end-member ($\delta^{13}C$ -39.3‰ V-PDB), which indicates that the measured $\delta^{13}C$ values of methane are due to mixing with biogenic methane; this latter accounts for up to 41.5% of the total gas budget in the Northern-Apennines sites (Oppo et al., 2013).

The hydrocarbons contained in the Miocene reservoirs along the foothills migrate since Miocene (e.g. Barbieri and Cavalazzi, 2005; Conti et al., 2007; Capozzi and Picotti, 2010; Oppo et al., 2013) and still feed the present-day cold seeps. Diffusion of methane towards the seafloor within Plio-Pleistocene sediments resulted in the formation of authigenic carbonate fields.

On the other hand, methane presently seeping along the Enza riverbed has a clear biogenic signature ($\delta^{13}C$= -72‰ VPDB), suggesting that thermogenic-generated hydrocarbons might be absent within the Pleistocene sediments of this section. This biogenic methane generated both from sapropel-bearing successions, such as the Piacenzian sapropel cluster observed in the Stirone River (Cau et al., 2015), and from the thick Pliocene turbidites buried under the Po plain (Mattavelli et al., 1993; Fantoni and Franciosi, 2010). This biogenic gas reached the Enza site migrating towards the forelimb of Quattro Castella Anticline along up-dip carrier beds (Oppo et al., 2015) (Fig. 4).

5.2 Isotopic signature of authigenic carbonates

Authigenic carbonates generally show substantial ^{13}C depletion, which indicates that the main dissolved inorganic carbon (DIC) source is methane oxidised during AOM. Possible contributions of other DIC sources, such as oxidation of organic matter and residual CO_2 from methanogenesis, can also occur (Formolo et al., 2004).

Possible kinetic effects have to be considered to fully understand the final isotopic signal in carbonates. The processes are related to incomplete and unidirectional processes like evaporation, dissociation reactions and diffusion (Hoefs, 2015 and reference therein). Isotope measurements taken during unidirectional chemical reactions always show a preferential enrichment of the lighter isotope in the reaction products. This enrichment, is detectable in carbonates thanks to a co-variation of $\delta^{13}C$ and $\delta^{18}O$ (Hoefs, 2015 and references therein). In our samples this co-variation is not detectable, thus excluding the kinetic effect influence on the recorded isotopic signatures. A further process that could influence the final stable isotope ratios is the recrystallization, which can alter the minerals formation and their structure. This process can lead to an enrichment in the new crystalline structure with respect to $\delta^{13}C$ and $\delta^{18}O$ (Hoefs, 2015 and reference therein; Swart, 2015). In the samples analysed this effect can be excluded due to the presence, observed at SEM-EDX, of preserved tests of calcite (Viola et al., 2017, in press).

Despite the relative homogeneity of $\delta^{13}C$ in gases of the Northern Apennines and the mineral similarity of all authigenic carbonates, $\delta^{13}C$ in these carbonates shows important variations among the different areas. This observation strongly suggests that carbon fractionation is linked to further DIC sources in addition to methane gas.

The characteristics of the petroleum system and fluids migration pathways at Stirone, Secchia and NMVF rule out significant contributions of biogenic methane during the formation of authigenic carbonates in these sites. Therefore, thermogenic methane migrating from Miocene reservoirs can be identified as the main gas source associated with these authigenic carbonates. A further DIC source can be related to the occurrence of ^{13}C-rich CO_2, which is consistent with the important input of secondary methane production in the total gas budget still observed in Northern Apennines. Examples of $\delta^{13}C$ higher than +5‰ are reported in various fossil authigenic carbonate systems worldwide, indicating methane generation during carbonate precipitation (e.g., Peckmann and Thiel, 2004; Naehr et al., 2007; Gieskes et al., 2005; Loyd et al., 2016). This contribution can be proposed to explain the positive $\delta^{13}C$ of the NMVF chimney and in the nearby Secchia River globular concretions, which point towards the presence of ^{13}C-rich DIC in ambient fluids. Moderately negative $\delta^{13}C$ in the Stirone River samples evidences that migrating thermogenic methane represents the main source of DIC during carbonates precipitation and a contribution from marine DIC and/or CO_2 from secondary biogenesis cannot be clearly recognized.

A different situation can be described for Enza River authigenic carbonates. Methane concentration in natural gas occurring in the Pliocene foredeep successions of Northern Apennines reaches over 90%, and is characterized by average carbon and hydrogen isotopic compositions of $\delta^{13}C$= -75‰ VPDB and δD= -171‰ VSMOW (Oppo et al., 2013), indicating that it was generated via CO_2 reduction (Whiticar, 1999). The very low $\delta^{13}C$ values in Enza authigenic chimneys, if compared to those of the other areas, evidence the biogenic origin of methane responsible for their formation. Enza Hills has the lowest value, which might be linked to increased gas flux intensity and its

diffusion within highly permeable sediments saturated by marine pore water near the seafloor. In this site, the main process leading to carbonate formation can be attributed to AOM (e.g. Oppo et al. 2015).

The $\delta^{18}O$ value of a carbonate depends on both temperature and $\delta^{18}O$ value of pore water where the carbonate precipitates. Water forming methane hydrates is enriched by about 3‰ in ^{18}O relative to hydrate-unaffected pore water (e.g. Hesse and Harrison 1981; Ussler and Paull 1995; Greinert et al., 2001). As consequence, relatively high $\delta^{18}O$ value of authigenic carbonates in several occurrences have been ascribed to the dissolution of methane hydrates (e.g. Aloisi et al., 2000; Pierre and Rouchy, 2004; De la Pierre et al., 2010). However, this process cannot be considered active in the Plio-Pleistocene successions of the study area, as they were deposited at a depth that did never reach the gas hydrates stability zone, even during cold periods. $\delta^{18}O$ values of authigenic carbonates in this study (Tab. 2) are related at first to their dolomitic mineral phase; dolomite usually shows oxygen isotope values of +2 - +4‰ (Budd, 1997). The dolomite cement increases towards the interior of the samples in all the analysed sites. Its formation can be attributed to the mediation of microbial mats, which act as carbonate nucleation and magnesium incorporation site at low temperature (Douglas, 2005; Bontognali et al., 2014). Furthermore, it has been documented that low or null amounts of sulphate ions in the pore water usually favour the precipitation of dolomite respect to calcite (Douglas, 2005; Magalhães et al.; Nielsen et al., 2016). The occurrence of this process can be inferred by the presence of authigenic sulphides (pyrite and arsenopyrite), which also indicates that the sulphate concentration in the water was low during the carbonates precipitation.

Oxygen stable isotopes can be useful to deduce information on paleo-temperature and water chemistry occurring during authigenic carbonate precipitation. A first attempt to estimate mineral precipitation temperature is assuming equilibrium crystallization for authigenic dolomite and marine bottom waters (Naehr et al., 2007).

The temperature of bottom waters in the enclosed sea at the uplifting Apennine border during the Plio-Pleistocene is unknown. To overcome this problem, present-day bottom water sampled at 100m water depths in central Adriatic Sea was used as analogue for the paleo marine environment object of this study. The Adriatic Sea water analysed for this work has $\delta^{18}O$ 0.99‰ V-SMOW, associated to 13-14°C temperature measured by Lipizer et al. (2014) for bottom water during winter. The calculated temperatures listed in Tab. 3 are determined using the fractionation factor of Vasconcelos et al., (2005). The resulting very low temperatures clearly attest isotopic disequilibrium or conditions (temperature and pore water $\delta^{18}O$ compositions) that significantly differ from the ones considered here as probable to occur.

The $\delta^{18}O$ of connate waters varies among the different sites (Tab. 3) and depends on diagenetic history of reservoirs and on migration processes (Capozzi and Picotti, 2010). They can be considered as the sole source of oxygen in the system to obtain a further estimation of paleo-temperature and to evaluate their possible contribution during carbonates precipitation (Tab. 3). To assess this relation, the $\delta^{18}O$ fractionation factor for dolomite precipitated under the seafloor was calculated, using the equations reported in Vaconcelos et al. (2005) and Zheng (1999), which are applicable for different temperature ranges. The connate waters in the area of NMVF and Salvarola belong to the same Late Miocene reservoir and the analysis carried out shows that their $\delta^{18}O$ varies from 4.62‰ and 5.16‰ VSMOW. The obtained higher paleo-temperatures could provide a preliminary indication that the final oxygen signature in the carbonates derives from the mixing with connate waters migrating from depth, and thus characterised by a higher temperature.

The very positive $\delta^{18}O$ end-member of the connate waters is documented at Salsomaggiore. This signature (+9.5 and +13.45‰ VSMOW) depends on the diagenetic process active when the original marine pore water was gradually mixed with water derived by progressive clay dehydration during recrystallization of smectite to illite during burial (Oppo et al., 2013). The calculated paleo-temperatures for carbonate precipitation are very high, from 46° to 69°C (23°C mean thermal gradient), and are unrealistic as the carbonates could not be precipitated at depths of ca. 2km below

the surface. Therefore, a contribution of deep connate waters on the observed $\delta^{18}O$ values in the chimneys of Stirone River can be inferred. To clear this question, further dedicated investigations using strontium isotope signatures are presented in Viola et al. (2017).

Tab. 3: Calculated pore water temperatures occurring during authigenic carbonates precipitation.

The Pleistocene age Enza site shows higher scatter of the calculated temperatures when compared with the other areas, which can be related to the location of this depositional environment close to coast and influenced by important freshwater inputs and, thus, varying salinity. When considering the $\delta^{18}O$ measured in connate waters sampled in Plio-Pleistocene reservoirs (0.65‰ VSMOW), the resulting temperatures are higher and more realistic.

6 Conclusions

Geological and geochemical analyses showed that authigenic carbonates in Stirone, Secchia and NMVF outcrops were generated due to methane and CO_2 migrating from the Northern Apennines Miocene reservoirs. The gas contained in these reservoirs is mainly a mix of biogenic and thermogenic methane, with minor condensates and oil. Thermogenic methane was generated both within the oil window and by thermal cracking of oils. The biogenic methane component was mostly formed by biodegradation of oils. Secondary biogenic methane concentrations up to 41.5% of the total gas budget indicate that microbial degradation is an important process in the reservoirs of this region.

The methane $\delta^{13}C$ in the reservoirs slightly varies around the average value of -46‰ VPDB; otherwise, $\delta^{13}C$ of authigenic carbonates shows significant variations indicating contribution of different DIC sources during their precipitation. Moderately negative $\delta^{13}C$ in Stirone samples indicates that those are partly derived from AOM, while positive $\delta^{13}C$ in NMVF and Secchia carbonates points towards a contribution from ^{13}C-rich CO_2, linked to the generation of secondary biogenic methane. Wide variations of $\delta^{13}C$ in Secchia concretions also testify that authigenic

carbonates provide a fossil record of changes in the biogeochemical processes, suggesting they can provide clues on varying condition within the reservoirs or during hydrocarbon migration.

The genesis of the carbonates in the Enza River area during the Pleistocene is linked to anaerobic oxidation of primary microbial methane that originated within the Pliocene sediments and migrated up-dip southwards from the sedimentary successions buried in the Po Plain. The observed decrease of $\delta^{13}C$ in progressively younger samples is possibly due to increased gas diffusion and flux to the seafloor, within more permeable sediments containing marine pore water. Intense gas migration led to increased efficiency of AOM process and to the escape of fluids into the water column, and in turn to a more negative $\delta^{13}C$ record in authigenic carbonates.

Estimates of $\delta^{18}O$ in the dolomite cements stress the presence of a temperature disequilibrium, which would indicate that marine bottom waters cannot be the sole oxygen source.

The joint analysis of present-day seepages and fossil seepage-related carbonates can be considered a step forward a better identification and definition of fluid sources influencing authigenic carbonate precipitation. Information on history of fluid migration in the Northern Apennines testifies that the tertiary migration of hydrocarbon is a long-lasting phenomenon in this region, in the scale of million years. This can suggest the persistence of hydrocarbon generation and migration and a new perspective on the residual potential.

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References

Aloisi, G., Pierre, C., Rouchy, J.-M., Foucher, J.-P., Woodside, J., 2000. Methane-related authigenic carbonates of eastern Mediterranean Sea mud volcanoes and their possible relation to gas hydrate destabilisation. Earth Planet. Sci. Lett. 184, 321–338.

Balestrieri, M.L., Bernet, M., Brandon, M.T., Picotti, V., Reiners, P., Zattin, M., 2003. Pliocene and Pleistocene exhumation and uplift of two key areas of the Northern Apennines. Quat. Int. 101–102, 67–73.

Barbieri, R., Cavalazzi, B., 2005. Microbial fabrics from Neogene cold seep carbonates, Northern Apennine, Italy. Palaeogeogr. Palaeoclimatol. Palaeoecol. 227,143-155.

Bartolini, C., 2003. When did the Northern Apennine become a mountain chain? Quat. Int. 101–102, 75–80.

Blumenberg, M., Walliser, E.-O., Taviani, M., Seifert, R., Reitner, J., 2015. Authigenic carbonate formation and its impact on the biomarker inventory at hydrocarbon seeps – A case study from the Holocene Black Sea and the Plio-Pleistocene Northern Apennines (Italy). Mar. Pet. Geol. 66, 532–541.

Boetius, A., Ravenschlag, K., Schubert, C.J., Rickert, D., Widdel, F., Gieseke, A., Amann, R., Jùrgensen, B.B., Witte, U., Pfannkuche, O., 2000. A marine microbial consortium apparently mediating anaerobic oxidation of methane 407, 623–626.

Bontognali, T.R.R., McKenzie, J.A., Warthmann, R.J., Vasconcelos, C., 2014. Microbially influenced formation of Mg-calcite and Ca-dolomite in the presence of exopolymeric substances produced by sulfate-reducing bacteria. Terra Nova, 26, 72-77.

Capozzi, R., Dinelli, E., Negri, A., Picotti, V., 2006. Productivity-generated annual laminae in mid-Pliocene sapropels deposited during precessionally forced periods of warmer Mediterranean climate. Palaeogeogr. Palaeoclimatol. Palaeoecol. 235, 208–222.

Capozzi, R., Picotti, V., 2010. Spontaneous fluid emissions in the Northern Apennines: geochemistry, structures and implications for the petroleum system. Geol. Soc. London, Spec. Publ. 348, 115–135.

Cau, S., Franchi, F., Roveri, M., Taviani, M., 2015. The Pliocene-age Stirone River hydrocarbon chemoherm complex (Northern Apennines, Italy). Mar. Pet. Geol. 66, Part 3, 582–595.

Conti, S., Artoni, A., Piola, G., 2007. Seep-carbonates in a thrust-related anticline at the leading edge of an orogenic wedge: The case of the middle–late Miocene Salsomaggiore Ridge (Northern Apennines, Italy). Sediment. Geol. 199, 233–251.

Dela Pierre, F., Martire, L., Natalicchio, M., Clari, P., Petrea, C., 2010. Authigenic carbonates in upper miocene sediments of the tertiary piedmont basin (NW Italy): Vestiges of an ancient gas hydrate stability zone? Bull. Geol. Soc. Am. 122, 994–1010.

Díaz-del-Río, V., Somoza, L., Martínez-Frias, J., Mata, M.P., Delgado, a., Hernandez-Molina, F.J., Lunar, R., Martín-Rubí, J. a., Maestro, a., Fernández-Puga, M.C., León, R., Llave, E., Medialdea, T., Vázquez, J.T., 2003. Vast fields of hydrocarbon-derived carbonate chimneys related to the accretionary wedge/olistostrome of the Gulf of Cádiz. Mar. Geol. 195, 177–200.

Douglas, S., 2005. Mineralogical footprints of microbial life. Am. J. Sci. 305, 503-525.

Etiope, G., Feyzullayev, A., Baciu, C.L., 2009. Terrestrial methane seeps and mud volcanoes: A global perspective of gas origin. Mar. Pet. Geol. 26, 333–344.

Fantoni, R., Franciosi, R., 2010. Tectono-sedimentary setting of the Po Plain and Adriatic foreland. Rend. Lincei 21, 197–209.

Formolo, M.J., Lyonsa T.W., Zhangb, C., Kelleya, C., Sassenc, R., Horitad, J., Coled, D.R., 2004. Quantifying carbon sources in the formation of authigenic carbonates at gas hydrate sites in the Gulf of Mexico. Chemical Geology 205, 253-264

Ghielmi, M., Minervini, M., Nini, C., Rogledi, S., Rossi, M., Vignolo, A., 2009. Sedimentary and Tectonic Evolution in the Eastern Po Plain and Northern Adriatic Sea Area from Messinian

to Middle Pleistocene (Italy), in: Convegno Natura E Geodinamica Della Litosfera Nell'alto Adriatico. pp. 2–5.

Gieskes, J., Mahn, C., Day, S., Martin, J.B., Greinert, J., Rathburn, T., McAdoo, B., 2005. A study of the chemistry of pore fluids and authigenic carbonates in methane seep environments: Kodiak Trench, Hydrate Ridge, Monterey Bay, and Eel River Basin. Chem. Geol. 220, 329–345.

Goldsmith, J.R., Graf, D.L., 1958. Relation between lattice constants and composition of the Ca-Mg carbonates. Am. Mineral. 43, 84–101.

Greinert, J., Bohrmann, G., Suess, E., 2001. Gas hydrate-associated carbonates and methane-venting at Hydrate Ridge: classification, distribution and origin of authigenic lithologies. Geophys. Monogr. Am. Geophys. Union 124, 99–114.Gunderson, K.L., Pazzaglia, F.J., Picotti, V., Anastasio, D. a., Kodama, K.P., Rittenour, T., Frankel, K.F., Ponza, A., Berti, C., Negri, A., Sabbatini, A., 2014. Unraveling tectonic and climatic controls on synorogenic growth strata (Northern Apennines, Italy). Bull. Geol. Soc. Am. 126, 532–552.

Heller, C., Blumenberg, M., Kokoschka, S., Wrede, C., Hoppert, M., Taviani, M., Reitner, J., 2011. Geomicrobiology of Fluid Venting Structures at the Salse di Nirano Mud Volcano Area in the Northern Apennines (Italy), in: Advances in Stromatolite Geobiology SE - 14, Lecture Notes in Earth Sciences. Springer Berlin Heidelberg, pp. 209–220.

Hensen, C., Scholz, F., Nuzzo, M., Valadares, V., Gracia, E., Terrinha, P., Liebetrau, V., Kaul, N., Silva, S., Martinez-Loriente, S., Bartolome, R., Pinero, E., Magalhaes, V.H., Schmidt, M., Weise, S.M., Cunha, M., Hilario, a., Perea, H., Rovelli, L., Lackschewitz, K., 2015. Strike-slip faults mediate the rise of crustal-derived fluids and mud volcanism in the deep sea. Geology 43, 1–4.

Hesse, R., Harrison, W.E., 1981. Gas hydrates (clathrates) causing pore-water freshening and oxygen isotope fractionation in deep-water sedimentary sections of terrigenous continental margins. Earth Planet. Sci. Lett. 55, 453–462.

Hoefs, J., 2015. Stable isotope Geochemistry. 7th edition. Springer International Publishing.

Judd, A., Hovland, M., Dimitrov, L.I., Garcia Gil, S., Jukes, V., 2002. The geological methane budget at Continental Margins and its in uence on climate change. Geofluids 2, 109–126.

Judd, A.G., Hovland, M., 2007. Seabed Fluid Flow. Cambridge University Press, Cambridge.

Khélifi, N., Sarnthein, M., Frank, M., Andersen, N., Garbe-Schönberg, D., 2014. Late Pliocene variations of the Mediterranean outflow. Mar. Geol. 357, 182–194.

Kokoschka, S., Dreier, A., Romoth, K., Taviani, M., Schäfer, N., Reitner, J., Hoppert, M., 2015. Isolation of Anaerobic Bacteria from Terrestrial Mud Volcanoes (Salse di Nirano, Northern Apennines, Italy). Geomicrobiol. J. 32, 355–364.

Lipizer, M., Partescano, E., Rabitti, A., Giorgetti, A., Crise, A., 2014. Qualified temperature, salinity and dissolved oxygen climatologies in a changing Adriatic Sea. Oc. Sci. 10, 771–797.

Loyd, S.J., Sample, J., Tripati, R.E., Defliese, W.F., Brooks, K., Hovland, M., Torres, M., Marlow, J., Hancock, L.G., Martin, R., Lyons, T., Tripati, A.E., 2016. Methane seep carbonates yield clumped isotope signatures out of equilibrium with formation temperatures. Nat. Commun. 7:12274 doi: 10.1038/ncomms12274.

Lumsden, D., 1979. Discrepancy between thin-section and X-ray estimates of dolomite in limestone. J. Sediment. Res. 49, 429–436.

Magalhães, V.H., Pinheiro, L.M., Ivanov, M.K., Kozlova, E., Blinova, V., Kolganova, J., Vasconcelos, C., McKenzie, J.A., Bernasconi, S.M., Kopf, A.J., Díaz-del-Río, V., González, F.J., Somoza, L., 2012. Formation processes of methane-derived authigenic carbonates from the Gulf of Cadiz. Sediment. Geol. 243-244, 155–168.

Mattavelli, L., Pieri, M., Groppi, G., 1993. Petroleum exploration in Italy: a review. Mar. Pet. Geol. 10, 410–425.

Naehr, T.H., Eichhubl, P., Orphan, V.J., Hovland, M., Paull, C.K., Ussler III, W., Lorenson, T.D., Greene H.G., 2007. Authigenic carbonate formation at hydrocarbon seeps in continental margin sediments: A comparative study Deep-Sea Res., II, 54,1268–1291.

Nielsen, M. R., Sand, K. K., Rodriguez-Blanco, J. D., Bovet, N., Generosi, J., Dalby, K.N., Stipp, S.L.S., 2016. Inhibition of calcite growth: combined effect of Mg2+ and SO42- . American Chemical Society, 16, 6199-6207.

Nyman, S.L., Nelson, C.S., 2011. The place of tubular concretions in hydrocarbon cold seep systems: Late Miocene Urenui Formation, Taranaki Basin, New Zealand. Am. Assoc. Pet. Geol. Bull. 95, 1495–1524.

Oppo, D., Capozzi, R., Picotti, V., 2013. A new model of the petroleum system in the Northern Apennines, Italy. Mar. Pet. Geol. 48, 57–76.

Oppo, D., Capozzi, R., Picotti, V., Ponza, A., 2015. A genetic model of hydrocarbon-derived carbonate chimneys in shelfal fine-grained sediments: The Enza River field, Northern Apennines (Italy). Mar. Pet. Geol. 66, Part 3, 555–565.

Peckmann, J., Thiel, V., Michaelis, W., Clari, P., Gaillard, C., Martire, L., Reitner, J., 1999. Cold seep deposits of Beauvoisin (Oxfordian; southeastern France) and Marmorito (Miocene; northern Italy): Microbially induced authigenic carbonates. Int. J. Earth Sci. 88, 60–75.

Peckmann, J., Reimer, a., Luth, U., Luth, C., Hansen, B.T., Heinicke, C., Hoefs, J., Reitner, J., 2001. Methane-derived carbonates and authigenic pyrite from the northwestern Black Sea. Mar. Geol. 177, 129–150.

Peckmann, J., Thiel, V., 2004. Carbon cycling at ancient methane–seeps. Chem. Geol. 205, 443–467.

Picotti, V., Pazzaglia, F.J., 2008. A new active tectonic model for the construction of the Northern Apennines mountain front near Bologna (Italy). J. Geophys. Res. Solid Earth 113, 1–24.

Picotti, V., Ponza, A., Pazzaglia, F.J., 2009. Topographic expression of active faults in the foothills of the Northern Apennines. Tectonophysics 474, 285–294.

Pierre, C., Blanc-Valleron, M.M., Caquineau, S., März, C., Ravelo, a. C., Takahashi, K., Alvarez Zarikian, C., 2014. Mineralogical, geochemical and isotopic characterization of authigenic carbonates from the methane-bearing sediments of the Bering Sea continental margin (IODP Expedition 323, Sites U1343-U1345). Deep. Res. Part II Top. Stud. Oceanogr. 1–12.

Pierre, C., Rouchy, J.-M., 2004. Isotopic compositions of diagenetic dolomites in the Tortonian marls of the western Mediterranean margins: evidence of past gas hydrate formation and dissociation. Chem. Geol. 205, 469–484.

Reitner, J., Blumenberg, M., Walliser, E.-O., Schäfer, N., Duda, J.-P., 2015. Methane-derived carbonate conduits from the late Aptian of Salinac (Marne Bleues, Vocontian Basin, France): Petrology and biosignatures. Mar. Pet. Geol. 1–12.

Reitner, J., Peckmann, J., Reimer, A., Schumann, G., Thiel, V., 2005. Methane-derived carbonate build-ups and associated microbial communities at cold seeps on the lower Crimean shelf (Black Sea). Facies 51, 66–79.

Ricci Lucchi, F., Vai, G.B., 1994. A stratigraphic and tectonofacies framework of the “calcari aLucina” in the Apennine Chain, Italy. Geo-Marine Lett. 14, 210–218.

Rosenbaum, J., Sheppard, S.M.., 1986. An isotopic study of siderites, dolomites and ankerites at high temperatures. Geochim. Cosmochim. Acta 50, 1147–1150.

Rosenbaum, J.M., 1994. Stable-Isotope Fractionation between Carbon-Dioxide and Calcite at 900-Degrees-C. Geochim. Cosmochim. Acta 58, 3747–3753.

Schoell, M., 1983. Genetic Characterization of Natural Gases. Am. Assoc. Pet. Geol. Bull. 67, 2225–2238.

Smith, J.P., Coffin, R.B., 2014. Methane Flux and Authigenic Carbonate in Shallow Sediments Overlying Methane Hydrate Bearing Strata in Alaminos Canyon, Gulf of Mexico. Energies 7, 6118–6141.

Swart, P.K., 2015. The geochemistry of carbonate diagenesis: the past, present and future. Sedimentology 5, 1233-1304.

Taviani, M., 2001. Fluid venting and associated processes, in: Vai, G., Martini, I.P. (Eds.), Anatomy of an Orogen: The Apennines and Adjacent Mediterranean Basins SE - 20. Springer Netherlands, pp. 351–366.

Taviani, M., Franchi, F., Angeletti, L., Correggiari, A., Lopez Correa, M., Maselli, V., Mazzoli, C., Peckmann, J., 2015. Biodetrital carbonates on the Adriatic continental shelf imprinted by oxidation of seeping hydrocarbons. Marine and Petroleum Geology 66, 511-531.

Terzi, C., Lucchi, F., Vai, G., Aharon, P., 1994. Petrography and stable isotope aspects of cold-vent activity imprinted on Miocene-age “calcari aLucina” from Tuscan and Romagna Apennines, Italy. Geo-Marine Lett. 14, 177–184.

Ussler III, W., Paull, C.K., 1995. Effects of ion exclusion and isotopic fractionation on pore water geochemistry during gas hydrate formation and decomposition. Geo-Marine Lett. 15, 37–44.

Vasconcelos, C., McKenzie, J.A., Warthmann, R., Bernasconi, S.M., 2005. Calibration of the delta O-18 paleothermometer for dolomite precipitated in microbial cultures and natural environments. Geology 33, 317 - 320.

Viola, I., Capozzi, R., Bernasconi, S.M., Rickli, J., 2017. Carbon, oxygen and strontium isotopic constraints on fluid sources, temperature and biogeochemical processes during the formation of seep carbonates- Secchia River site, Northern Apennines. Sedimentary Geology, in press.

Viola, I., Oppo, D., Franchi, F., Capozzi, R., Dinelli, E., Liverani, B., Taviani, M., 2015. Mineralogy, geochemistry and petrography of methane-derived authigenic carbonates from Enza River, Northern Apennines (Italy). Mar. Pet. Geol. 66, 566–581.

Whiticar, M.J., 1999. Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. Chem. Geol. 161, 291–314.

Zachos, J.C., Pagani, M., Sloan, L., Thomas, E., Billups, K., 2001. Trends, rhythms, and aberrations in global climate 65 Ma to present. Science (80-.). 292, 686–693.

Zattin, M., Picotti, V., Zuffa, G., 2002. Fission-track reconstruction of the front of the Northern Apennine thrust wedge and overlying Ligurian unit. Am. J. Sci. 302, 346–379.

Zheng, Y.-F., 1999. Oxygen isotope fractionation in carbonate and sulfate minerals. Geochemical Journal 33, 109-126.

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Tab. 1: Chemical and isotopic composition of the considered gases.

	Type	CH_4	C_2H_6	ΣC_2+	CO_2	$\delta\ ^{13}C_1$	$\delta\ ^{13}C_2$	$\delta\ ^{13}C\ CO_2$
		%	%	%	%	‰ VPDB	‰ VPDB	‰ VPDB
Salsomaggiore 7	Well	96.94	1.392	1.920	-	-51.87	-27.56	7.98
Salsomaggiore 93	Well	96.90	1.220	1.450	0.14	-42.99	-25.70	-20.91
Salsominore 16	Well	97.44	0.577	0.630	0.33	-44.87	-21.10	-0.73
Nirano	MV	98.00	0.065	0.068	0.65	-46.87	bdl	19.90
Nirano Parox	MV	70.10	0.041	0.044	1.70	-48.44	-22.99	12.36
Salvarola Terme	Well	99.76	0.241	0.241	bdl	-47.60	-23.75	4.64
	Well	99.86	0.123	0.135	bdl	-47.50	-25.28	5.37
	Well	99.78	0.220	0.220	bdl	-46.89	-28.23	4.43

bdl: below detection level; - not determined; MV Mud Volcano

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Tab. 2: Mineralogy and stable isotopes in the analysed MDACs.

		Type	Calcite	Dolomite	Others	$\delta^{13}C$	$\delta^{18}O$
			%wt	%wt	%wt	V-PDB	V-PDB
STIRONE	STN1B E	Chimney	0.0	54.9	48.1	-6.9	5.2
	STN1B I	Chimney	0.0	48.5	51.5	-6.5	5.2
	STN1B M	Chimney	0.0	51.2	48.8	-5.6	5.2
	STN2 E	Chimney	0.0	51.5	48.5	-8.0	5.2
	STN2 I	Chimney	0.0	53.3	46.7	-8.2	5.2
	STN2 M	Chimney	0.0	52.4	47.6	-9.1	5.3
ENZA	En10 1 I	Chimney	0.0	75.7	24.3	-28.3	5.7
	En10 1 E	Chimney	2.0	75.0	23.0	-23.4	4.8
	En10 2 I	Chimney	0.0	81.2	18.8	-24.1	5.2
	En5 8 I	Chimney	0.0	64.5	35.5	-20.1	5.9
	En5 8 M	Chimney	5.9	57.2	36.9	-19.5	5.5
	En5 6 I	Chimney	4.8	57.8	37.5	-19.3	6.2
	En5 6 M	Chimney	0.9	65.4	33.7	-19.0	6.1
	En5 4 I	Chimney	0.0	77.8	22.2	-18.4	5.6
	En5 4 M	Chimney	0.0	71.1	28.9	-18.4	5.6
	En5 4 E	Chimney	13.2	46.3	40.5	-8.2	3.4
	En5 3 I	Chimney	0.0	80.0	20.0	-18.6	6.2
	En5 3 E	Chimney	10.9	50.4	38.7	-8.6	4.4
	En5 1 M	Chimney	0.0	71.1	28.9	-17.1	5.6
	Cr2A	Slab	0.0	79.7	20.3	-28.5	5.6
	Cr2B	Slab	3.7	71.3	25.0	-27.7	3.8
	Cr3A-1	Concretion	0.0	64.9	35.1	-35.4	4.5
	Cr3A-2	Concretion	0.0	52.0	48.0	-40.1	4.4
	Cr3A -3	Concretion	0.0	42.0	58.0	-31.8	4.6
	Cr3B-1	Concretion	11.4	52.0	36.7	-35.1	5.7
	Cr3B-2	Concretion	-	-	-	-35.4	6.1
	Cr3B-4	Concretion	-	-	-	-30.9	5.4
ENZA HILLS	ENCO1	Concretion	1.0	36.0	63.0	-53.0	5.5
SECCHIA	SCH1 E	Slab	0.0	51.5	48.5	6.9	5.5
	SCH1 I	Slab	0.0	69.8	30.2	-9.4	5.4
	SCH2 E	Slab	0.0	51.9	48.1	6.4	5.3
	SCH2 I	Slab	0.0	51.3	48.7	7.5	5.5
	SCH3 E	Slab	0.0	46.8	53.0	6.5	5.2
	SCH3 I	Slab	0.0	55.7	44.0	9.7	5.1
	SCH4 E	Slab	0.0	59.1	40.9	10.6	5.1
	SCH4 I	Slab	0.0	47.5	52.5	10.7	5.1
	SCH5 E	Slab	0.0	50.1	49.9	11.9	5.7
	SCH5 I	Slab	0.0	57.1	42.9	11.8	5.7
	SCH6 E	Chimney	0.0	59.4	40.6	-12.3	5.1
	SCH6 M	Chimney	0.0	61.8	38.2	-9.3	5.2
	SCH6 I	Chimney	0.0	63.1	36.9	-8.3	5.2
NIRANO	NIR1-E	Chimney	4.0	41.0	55.0	17.7	6.4
	NIR1a-I	Chimney	4.0	41.0	55.0	16.7	6.5
	NIR1b-I	Chimney	4.0	41.0	55.0	16.6	6.3

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Pleistocene

Carbonate			Adriatic Sea 0.99‰		Connate water		
Area	Sample	$\delta^{18}O$ (V-PDB)	α dolomite-water (1)	T (°C)	$\delta^{18}O$ (V-SMOW)	α dolomite-water (1)	T (°C)
Enza River	En10 1 I	5.65	35.75	4	0.65‰	36.09	9
	En10 1 E	4.81	34.88	7	Po Plain Pleistocene	35.22	12
	En10 2 I	5.16	35.23	6		35.58	10
	En5 8 I	5.86	35.96	3		36.30	8
	En5 8 M	5.47	35.56	4		35.90	9
	En5 6 I	6.20	36.31	1		36.65	7
	En5 6 M	6.13	36.24	1		36.58	7
	En5 4 I	5.56	35.65	4		35.99	9
	En5 4 M	5.62	35.72	3		36.06	9
	En5 4 E	3.35	33.38	13		33.72	17
	En5 3 I	6.21	36.32	1		36.66	7
	En5 3 E	4.37	34.43	9		34.77	13
	En5 1 M	5.59	35.68	4		36.02	9
	Cr2A	5.63	35.72	3		36.06	9
	Cr2B	3.77	33.81	11		34.15	16
	Cr3A-1	4.49	34.55	8		34.89	13
	Cr3A-2	4.44	34.50	9		34.84	13
	Cr3A -3	4.65	34.71	8		35.05	12
	Cr3B-1	5.69	35.78	3		36.13	9
	Cr3B-2	6.13	36.24	1		36.58	7
	Cr3B-4	5.44	35.53	4		35.87	7
Enza Hill	ENCO1	5.47	35.56	4	0.65‰	35.90	3
Secchia River	SCH1E	5.49	35.59	4	5.16‰	31.41	22
	SCH1I	5.36	35.45	5	Salvarola terme	31.28	23
	SCH2E	5.34	35.44	5		31.26	23
	SCH2I	5.50	35.60	4		31.42	22
	SCH3E	5.18	35.27	5		31.09	24
	SCH3I	5.12	35.20	6		31.03	24
	SCH4E	5.06	35.14	6		30.97	24
	SCH4I	5.15	35.24	6		31.06	24
	SCH5E	5.73	35.84	3		31.66	21
	SCH5I	5.66	35.77	3		31.59	21

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	SCH6E	5.12	35.21	6		31.03	24
	SCH6M	5.20	35.29	5		31.11	24
	SCH6I	5.18	35.28	5		31.10	24
Nirano MVF	NIR1-E	6.41	36.53	4	4.62‰	32.90	15
	NIR1a-I	6.54	36.66	4	Nirano MVF	33.03	15
	NIR1b-I	6.32	36.44	5		32.81	16

Pliocene

Carbonate			**Adriatic Sea 0.99‰**		**Connate water**		
Area	Sample	$\delta^{18}O$ (V-PDB) ‰	$\alpha_{\text{dolomite-water (1)}}$	T (°C)	$\delta^{18}O$ (V-SMOW)	$\alpha_{\text{dolomite-water (2)}}$	T (°C)
Stirone River	STN1BI	5.17	35.25	6	9.5‰	26.77	46
	STN1BE	5.20	35.28	5	Salsomaggiore (well 93)	26.74	47
	STN1BM	5.18	35.26	6		26.75	46
	STN2I	5.19	35.27	6		26.76	46
	STN2E	5.19	35.27	6		26.76	46
	STN2M	5.27	35.36	5		26.85	46
Stirone River	STN1BI				13.45‰	22.83	68
	STN1BE				Salsominore	22.79	69
	STN1BM					22.81	68
	STN2I					22.81	68
	STN2E					22.82	68
	STN2M					22.90	68

(1) Vasconcelos et al., 2005; (2) Zheng ,1999

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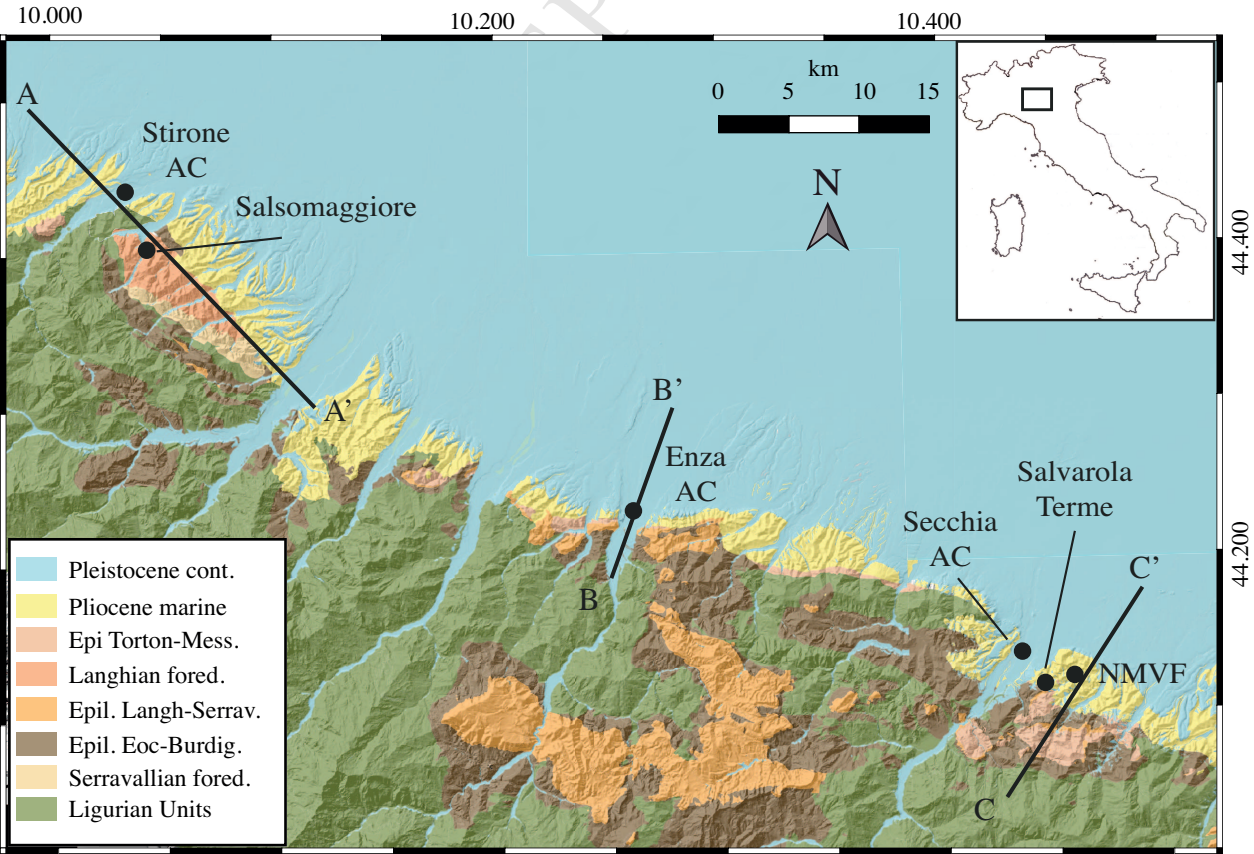

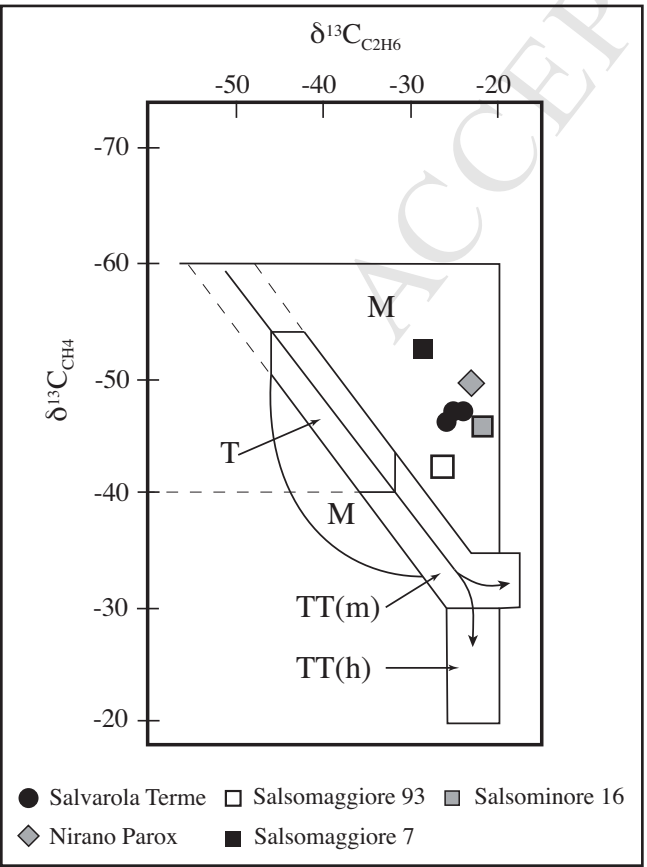

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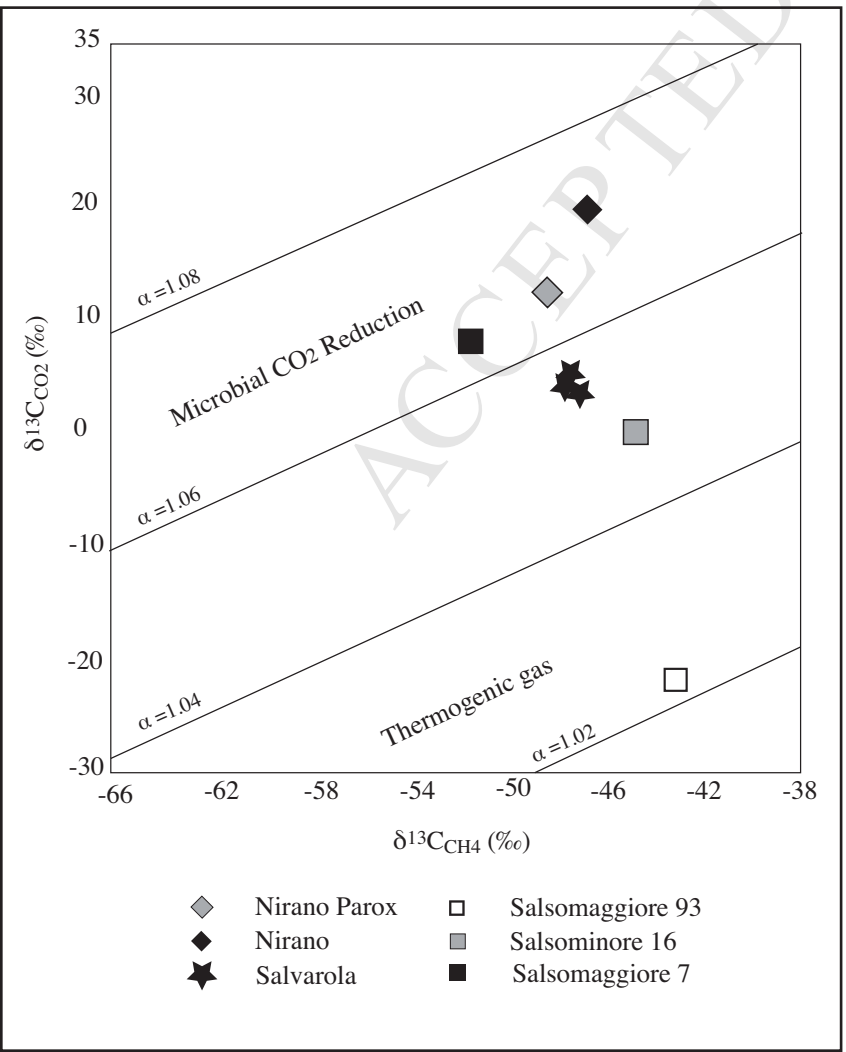

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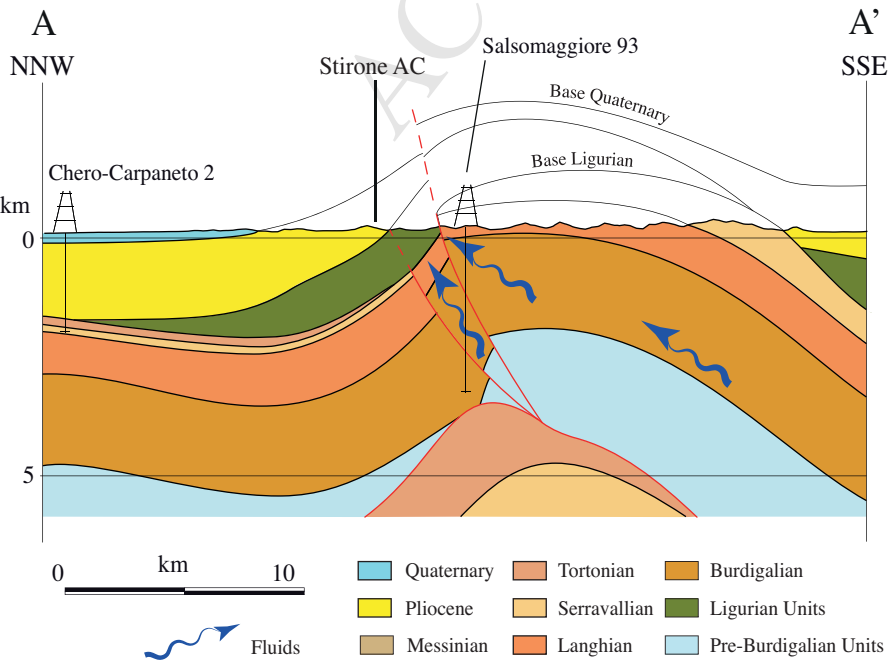

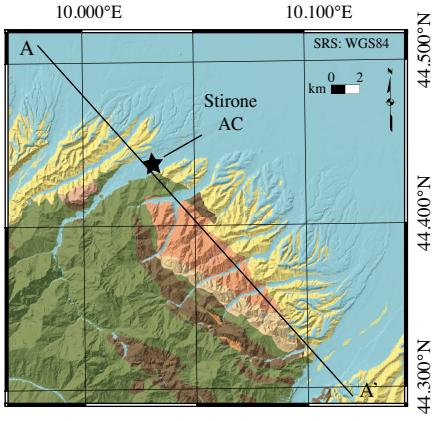

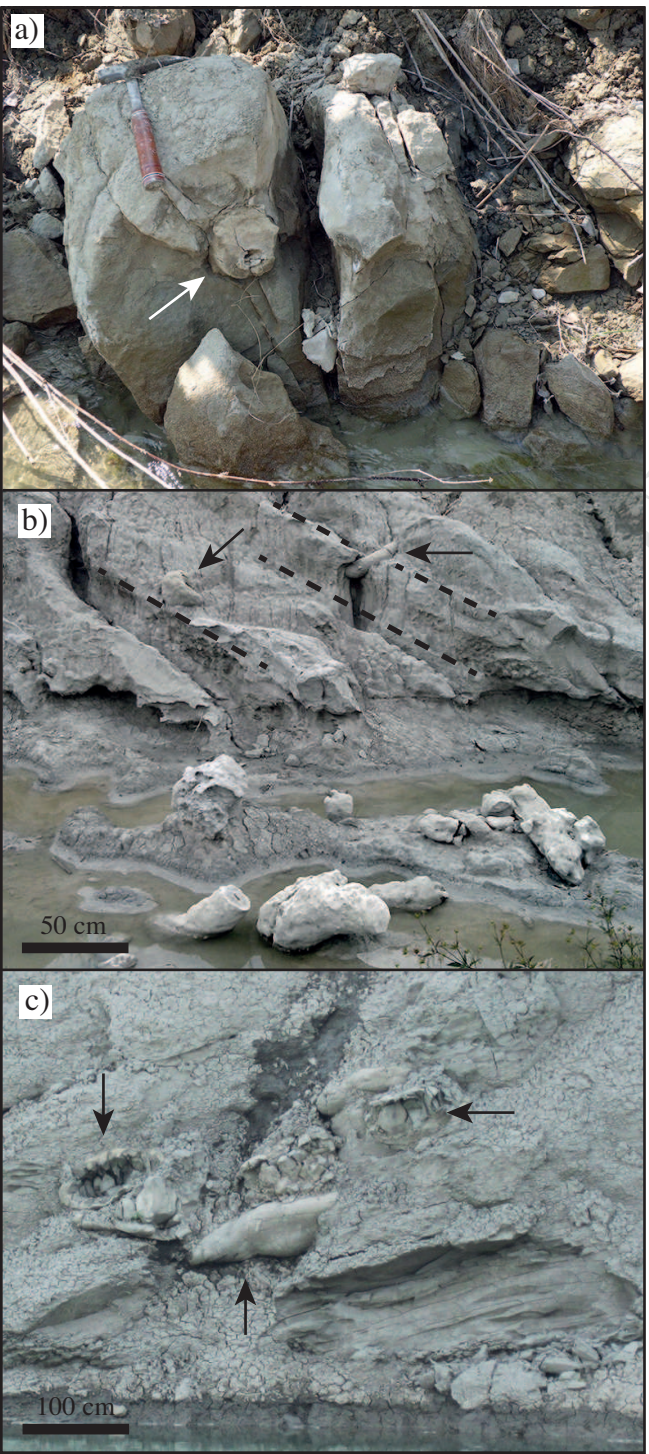

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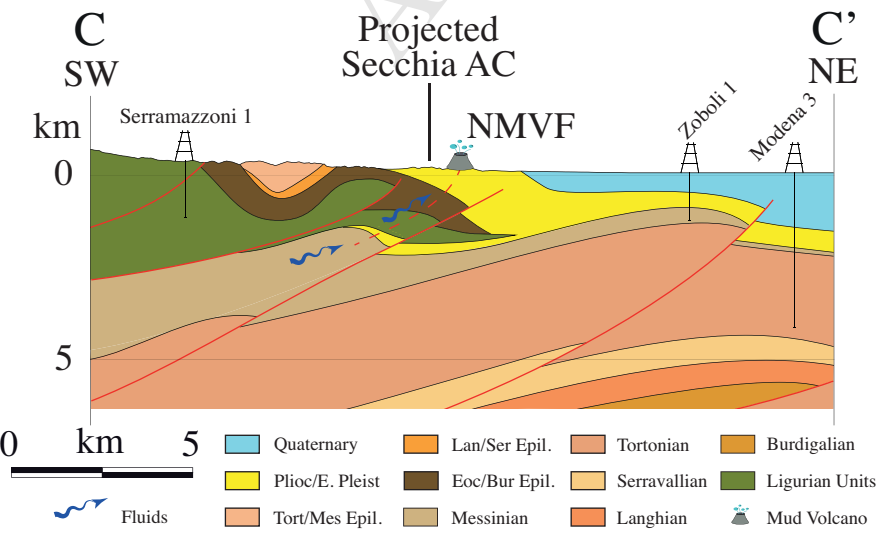

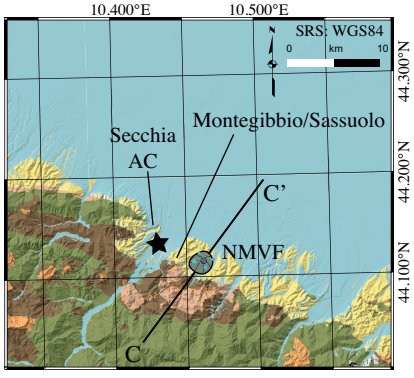

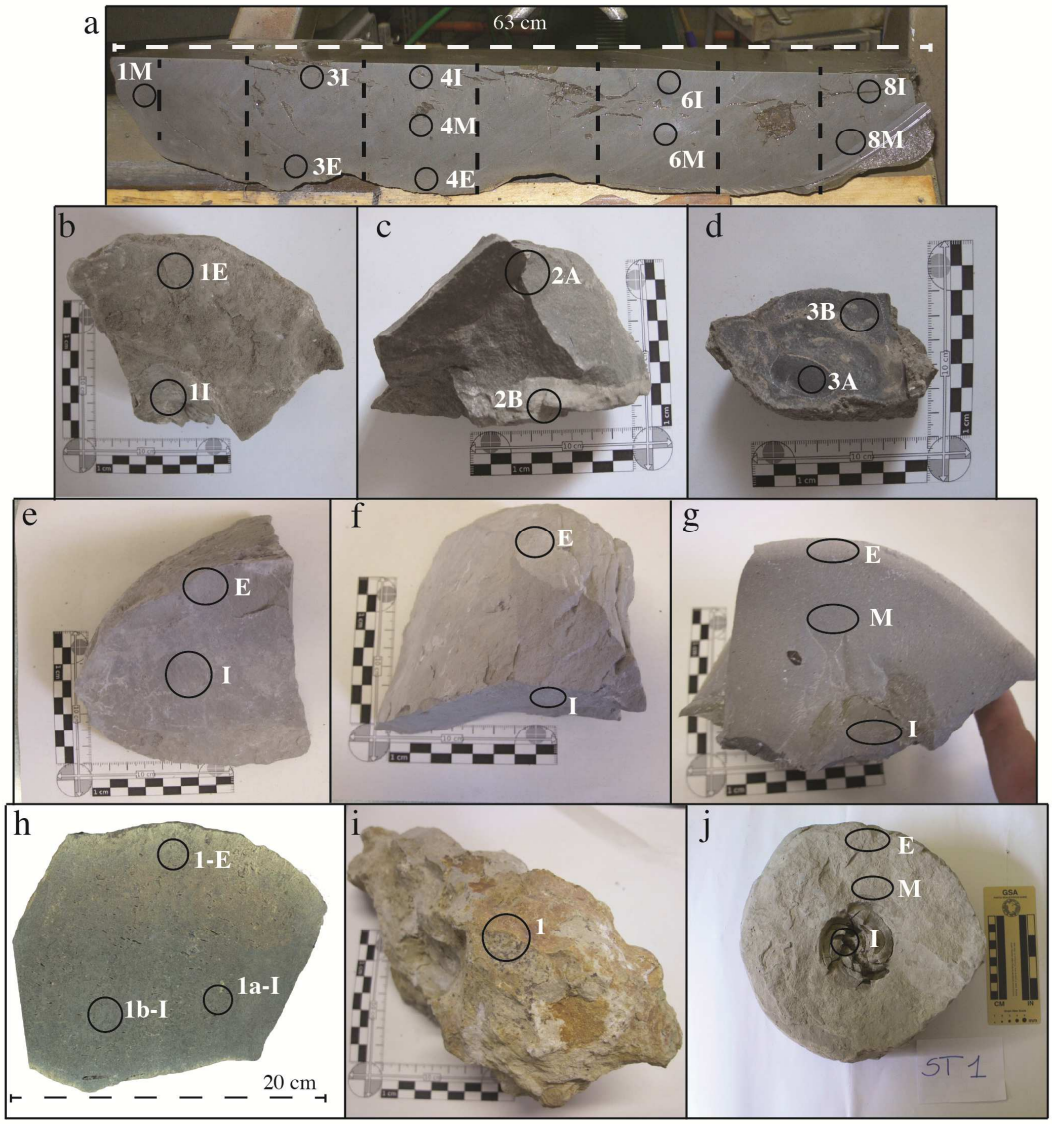
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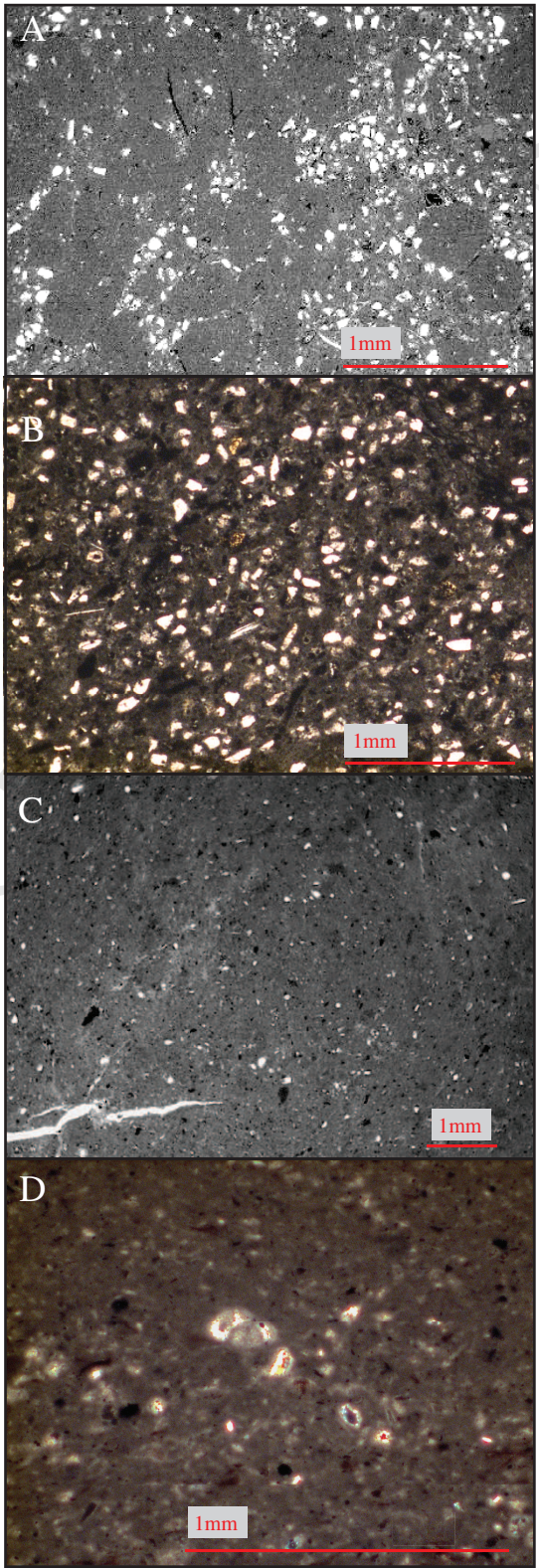
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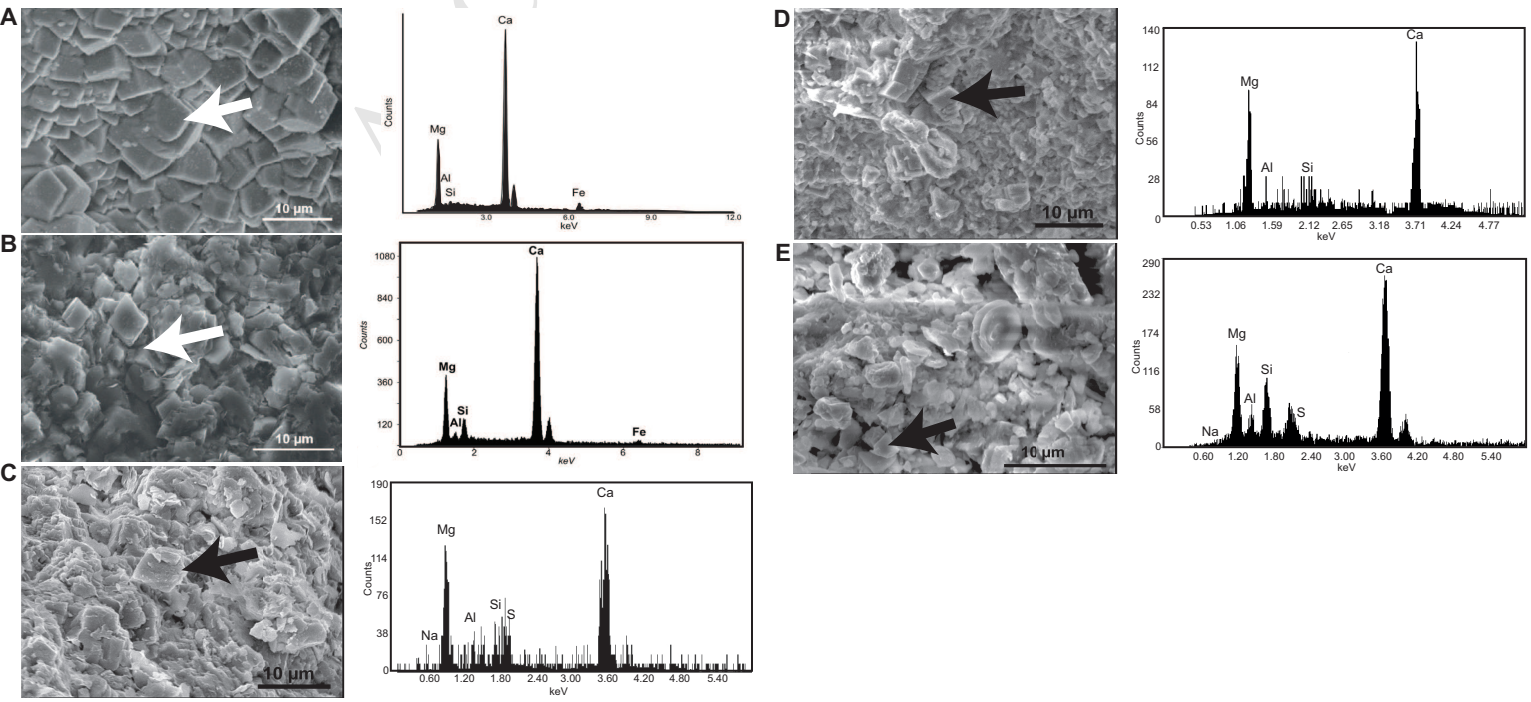

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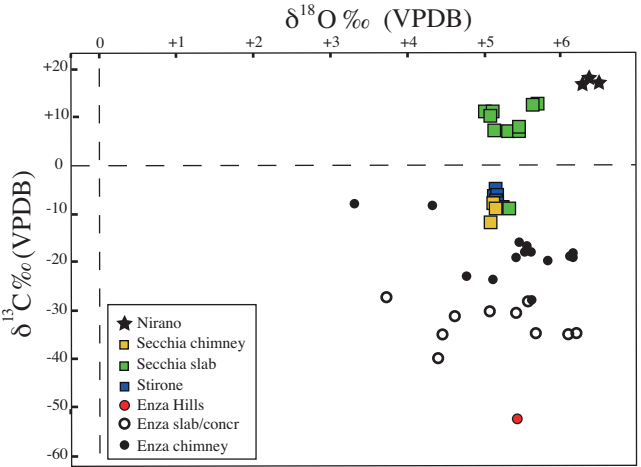

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- Authigenic carbonates in Northern Apennines foothills.
- Gas migrating from Miocene reservoirs through normal faults and updip along carrier beds.
- Carbon stable isotopes register the contribution of gas from Miocene reservoirs, CO_2 reduction and biogenic methane.
- Stable oxygen isotopes record the role of both marine and connate water during the concretions precipitation.
- Authigenic carbonates testify a long-lasting hydrocarbon migration during Tertiary, in the scale of million years.

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