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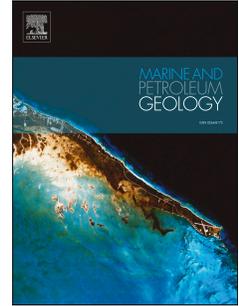
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(Article begins on next page)

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Sluggish and steady focussed flows through fine-grained sediments: the methane-derived cylindrical concretions of the Tertiary Piedmont Basin (NW Italy)

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Abstract

In the Cenozoic succession of the Tertiary Piedmont Basin (NW Italy) a wide array of methane-derived carbonate rocks including both seafloor and sub-seafloor products have been reported in the last decades. The most intriguing features are cylindrical concretions, more than 1 metre long and around 10 centimetres across, that were found within fine-grained sediments of Messinian age in their original stratigraphic position, crossing the bedding planes at high angles. These concretions result from cementation of the host muddy sediments by intergranular dolomite microcrystals, and lack any evidence of exposure at the sea floor. Their C and O stable isotope signature suggests that dolomite

precipitation was induced by anaerobic oxidation of methane, possibly sourced by gas hydrate destabilisation. Such cylindrical morphologies are interpreted as the result of carbonate precipitation and cementation of the sediments around fluid conduits and record a relatively long period of steady, sluggish flux of methane-rich fluids that opened their way rising up through fine-grained unconsolidated sediments. They formed immediately below the sea floor, in a narrow horizon bracketed between the sulphate-methane interface and the oxic/anoxic interface. Cylindrical concretions represent only the highest part of pipes through which methane-rich fluids flowed up. The deeper part of the conduits, conversely, left no trace in the stratigraphic record because of the lack of chemical/microbiological conditions favourable for carbonate precipitation.

Keywords

cylindrical concretions, methane-derived carbonates, fluid conduits, microbial dolomite, gas hydrates, Tertiary Piedmont Basin, NW Italy.

1. Introduction

Seep sites have been documented worldwide in various geodynamic settings and in sediments of different ages (Paull et al., 1992; Aloisi et al., 2000; Peckmann et al., 2001; Levin, 2005; Campbell, 2006). Studies of present-day active systems have been focussed on the seafloor morphological features, rather than on the subseafloor products which form as the results of the upward rise of methane-rich fluids through the sedimentary column. A common product of subseafloor seepage are cylindrical carbonate concretions, which have been generally interpreted as a direct evidence of a channelized fluid flow in the subsurface. Their study thus provides important clues on the types of fluid flow and the architecture of the seepage system (De Boever et al., 2006; Takeuchi et al., 2007;

Campbell et al., 2008; Mazzini et al., 2008; Nyman et al., 2010; Magalhães et al., 2012; Bayon et al., 2013; Craig et al., 2013).

The Tertiary Piedmont Basin (NW Italy) is one of the first places in the world where methane-derived rocks interpreted as fossil counterparts of modern seepage sites have been reported in literature (Clari et al., 1988, 1994). These methane-derived rocks include a wide array of products showing diverse sizes, geometries, petrographic features, including cylindrical concretions, and referable to variable styles of fluid flows and different position with respect to the seafloor (Clari et al. 2009). Fossil methane-derived rocks in fact provide the third dimension in the subsurface and show us the result of processes taking place over a time interval rather than a snapshot as it is imaged in present-day settings surveys.

Here we present a review of some cylindrical concretions found within Cenozoic sediments in different sectors of the Tertiary Piedmont Basin (Clari et al., 2004, 2009; Dela Pierre et al., 2010). They will be compared with the other products of methane-rich fluid flows with the aim of shedding light on some uninvestigated aspects of cylindrical concretions such as their precise position in the flow system, their random occurrence, and the flow regime responsible for their growth.

In this paper the term cylindrical concretion will be used to refer to the carbonate rocks with a pipe-like or cylindrical-like morphology. The term fluid conduit or pipe is here employed to mean the tube or the conduit, i.e. an open space of cylindrical shape, through which a fluid migrates. The term chimney, sometimes informally used in literature, is avoided because it implies a genesis of these structures above the sea floor whereas the cylindrical concretions below described developed within the sedimentary column.

2. Geological setting

The Tertiary Piedmont Basin (TPB) is located on the inner side of the Western Alps (Fig. 1), and is filled with Upper Eocene to Messinian sediments that unconformably overlie a complex tectonic wedge of Alpine, Adria and Ligurian basement units, juxtaposed during the mesoalpine collision event between the European and Africa plates (e.g. Mutti et al., 1995; Roure et al., 1996; Mosca et al., 2010; Bertotti and Mosca, 2009).

Fig. 1. Simplified structural map of NW Italy, showing the location of the studied sites (modified from Bigi et al., 1990). RF: Rio Freddo fault zone; VF: Villadeati fault zone; VVL: Villavernia-Varzi Line; ANM: Alfiano Natta macroconcretion.

The TPB is separated from the Northern Apennine by the Villavernia-Varzi fault zone. This is an E-W–striking regional structural feature, considered as the Alps-Apennine boundary (Elter and Pertusati, 1973). Its main activity took place during the Oligocene–early Miocene interval and was characterized by left-lateral transpressive movements (Schumacher and Laubscher, 1996).

The TPB Cenozoic sediments are presently exposed in the southern (TPB s.s.) and northern (Monferrato and Torino Hill arc) sector of the basin. The relationships between the two outcropping sectors are masked by Pliocene and Quaternary sediments of the Savigliano and Alessandria basins, but are well imaged by seismic data (Mosca et al., 2010). Outcrop and seismic data show that the early Oligocene sediments consist of continental and shallow marine terrigenous facies, deposited in fault-bounded sub-basins, followed by lower Miocene turbidites (Rossi et al., 2009). Since the late Burdigalian, a more regular physiography was established, and the TPB behaved as a single wedge top basin bounded to the north by the uplifted Monferrato arc (Rossi et al., 2009). The structural setting of this last sector is complicated by NW-SE transpressive faults, the most important of which are the Rio Freddo and the Villadeati fault zones (Clari et al., 1994;

Piana and Polino, 1995; Piana, 2000). These structures affected the deposition of the Cenozoic succession, which was deposited in fault-bounded sub-basins separated by intervening structural highs (Dela Pierre et al., 2003).

During the late Miocene, the north-verging Apennine tectonics involved the Torino Hill area. The N-S crustal shortening was accommodated by the establishment of two major subsiding depocentres (Savigliano and Alessandria basins) bordered by the Torino Hill-Monferrato tectonic arc (Rossi et al. 2009). Outer shelf to slope muddy sediments (Sant'Agata Fossili Marls, Tortonian to lower Messinian) were deposited in the whole TPB, followed by Messinian evaporites recording the effects of the Messinian salinity crisis (Dela Pierre et al., 2011; 2012; 2014. Natalicchio et al., 2013; 2014). These evaporites include both primary facies (Primary Lower Gypsum unit) and chaotic and resedimented deposits (Valle Versa Chaotic Complex) emplaced by large scale mass wasting events triggered by Intra-Messinian tectonics (Dela Pierre et al., 2007; Clari et al., 2009). The Monferrato-Torino Hill area was eventually overthrust to the north onto the Po Plain foredeep along the Late Neogene to Quaternary Padane thrust front that corresponds to the westward prolongation of the more external Apennine thrusts (Roure et al., 1996).

3. The cylindrical concretions

Cylindrical concretions have been found in two different outcrops: Verrua Savoia and Ripa dello Zolfo (Fig. 1). Verrua Savoia is located in Monferrato close to the Rio Freddo fault zone (Clari et al., 2004); Ripa dello Zolfo is located in the eastern part of the TPB to the south of the Villalvernia-Varzi fault zone (Dela Pierre et al., 2010).

3.1 Outcrop data

3.1.1 Verrua Savoia

In this outcrop, cylindrical concretions were found in a chaotic unit belonging to the Valle Versa Chaotic Complex (Clari et al., 2004; Dela Pierre et al., 2007) (Fig. 2A).

Fig. 2. A) Schematic cross section of the chaotic succession (Valle Versa Chaotic Complex) exposed in the Verrua Savoia quarry (after Clari et al., 2004). B) Block diagram and stratigraphic log showing the location of the Ripa dello Zolfo methane-derived rocks (after Dela Pierre et al., 2010). SAF: Sant'Agata Fossili Marls; VVC: Valle Versa Chaotic Complex).

This chaotic succession, which is overlain by outer shelf Pliocene mudrocks (Argille Azzurre Fm.), has been interpreted as the geological record of a Messinian mud volcano on the basis of comparison with present-day examples (Clari et al., 2004). The chaotic succession is mostly made up of grey, soft, mud-supported breccias. They represent the product of mud flows along the flanks of the volcano generated during short paroxysmic phases. Locally, the mud breccias display a remarkable sheared texture which is interpreted as the result of the injection of plastic overpressured fine-grained sediments. At places, they are strongly lithified and form dm- to m-sized masses containing clusters of valves of the chemosymbiotic taxon *Lucina* sp. (Fig. 2A). These cemented rocks testify long periods of quiescence that led to the local cementation of the mud breccias and their colonization by chemosymbiotic bivalves (Clari et al., 2004) (see below).

The cylindrical concretions were found in their original stratigraphic position, within poorly lithified mud breccias and interlayered silty clays, crossing the bedding planes at high angle (40° to 80°). The boundary with host sediments is sharp. Most common concretions are 8 to 15 centimetres in diameter and more than 1 metre long (Figs 3A, 4 A, B).

Fig. 3. Outcrop view of cylindrical concretions (arrows) from the Verrua Savoia quarry (A) and Ripa dello Zolfo (B). The dashed line in A) indicates bedding.

The bulk of the concretion is made up of yellowish silty or sandy clays, generally homogeneous, locally burrowed and laminated. The intergranular cement is made of dolomite (Fig. 4C); SEM observations reveal that dolomite occurs as euhedral crystal less than 10 μm in size and thus hardly recognizable in thin section (Fig. 4D). Opaque pyrite grains surrounded by red oxidation haloes are present within the sediment. No trace of exposure at the sea floor such as authigenic mineral coating, biogenic encrustation, or borings have been observed. An axial central portion clearly distinguishable from the main body and generally less than 3 cm in diameter is generally present (Figs. 4A, B). In some concretions it is completely filled with sediment. This generally consists of a darker grey cemented mud showing a sharp boundary with the concretion body. In thin section, this fill is a homogeneous silty mud with a lesser amount of silt and sand grains (Fig. 4E). Differently coloured, sub angular to sub rounded scattered clasts up to 5 mm also occur. They consist mainly of fragments of the encasing sediment. In other cases the axial portion is empty (Fig. 4B), the walls are very irregular, mainly because of the presence of axial prismatic fractures wedging out in a few centimetres towards the periphery. When seen on transversal cuts, this fracture system shows a septarian morphology.

Fig. 4. Axial (A) and transversal (B) polished slabs of cylindrical concretions from the Verrua Savoia quarry. Note that the axial portion is filled with sediments (A) or is empty (B). C) Cathodoluminescence photomicrograph of the dolomite intergranular cement within the concretion body. D) SEM image of broken chip from the concretion body: note the euhedral dolomite crystals. E) Photomicrograph of the sharp boundary between the mud-filled axial portion and the sandy mud concretion body. Location is shown by the white box in Fig. 4A.

3.1.2 Ripa dello Zolfo

In the Ripa dello Zolfo outcrop (Dela Pierre et al., 2010; Natalicchio et al., 2012, 2013) the cylindrical concretions, up to 1 m long and 3-70 cm across, were found in lower Messinian slope marls (Ghibaudo et al., 1985) (Figs. 2B, 3B). The concretions are commonly very straight and show an equal diameter throughout their length, with long axes perpendicular to bedding. The intergranular cement consists of euhedral microcrystals of dolomite less than 10 μm in size; rusty grains, resulting from oxidation of pyrite, are a common feature. In the largest concretions, a central axis has been observed; it is about 2 cm across, and can be empty or, more commonly, filled with a dark muddy sediment. The boundary between this portion and the walls of the concretions is uneven. Uncompacted burrows can be observed within most of the concretion bodies, suggesting that these features originated from early cementation of sediments deposited under oxygenated conditions. No boring or other traces of exposure at the sea floor were observed. Locally, cylindrical concretions are vertically embedded within a tabular cemented bed (Fig. 5).

Fig. 5. Ripa dello Zolfo cylindrical concretions (outlined by dashed yellow lines) embedded within a stratiform concretion. Pencil for scale is 14 cm long.

3.2 Stable Isotopes

The results of carbon and oxygen stable isotope analyses performed on the Piedmont cylindrical concretions are characterized by negative $\delta^{13}\text{C}$ values, spanning from -34.3 to -9.7 ‰ PDB with an average value of -16.6 ‰ PDB (Fig. 6).

Fig. 6. C and O stable isotope values of the Verrua Savoia and Ripa dello Zolfo cylindrical concretions. Values are expressed in ‰ PDB.

The $\delta^{18}\text{O}$ values are invariably positive and range from +4 to +8 ‰ PDB, with an average value of +7.1 ‰ PDB. No trends in isotope composition have been detected from the edge to the core in every concretion. The most negative $\delta^{13}\text{C}$ values document carbonate precipitation related to anaerobic oxidation of methane (Clari et al., 2004; Dela Pierre et al., 2010). Interpretation of less negative values is not equally straightforward because the mixing of several carbon sources, such as sediment organic matter, heavier hydrocarbons, seawater dissolved inorganic carbon, biogenic carbonate, may affect the final isotopic signature of authigenic carbonate minerals (e.g. Pierre et al., 2012). Moreover, also methane may show different isotope compositions depending on its biogenic or thermogenic origin, resulting in more or less ^{13}C -depleted values, respectively (e.g. Whitecar, 1999). However, the strict analogy of shape, size, occurrence, and petrographic features of all the cylindrical concretions in both localities suggest that anaerobic oxidation of methane played the pivotal role in carbonate precipitation in these rocks. The variability of C isotope values would thus reflect the mixing in variable proportions of the different C sources cited above.

The positive $\delta^{18}\text{O}$ values, and in particular the samples with +7 to +8 ‰ PDB values, point to authigenic carbonate precipitation from fluids enriched in ^{18}O . The association of these positive values with negative $\delta^{13}\text{C}$ ones suggests that methane fluxes were possibly sourced from destabilisation of gas hydrates trapped within the sedimentary column (Dela Pierre et al., 2010; Martire et al., 2010; Natalicchio et al., 2012). This mechanism was responsible for the production of fluids that at the same time were enriched in ^{18}O and depleted in ^{13}C (e.g. Aloisi et al., 2000; Ussler and Paul, 2001; Pierre and Rouchy, 2004).

4. Other types of methane-derived rocks in the TPB

In addition to the cylindrical concretions, other types of carbonate-rich rocks interpreted as methane-derived rocks were found in the TPB (Clari et al. 1994; 2004; 2009; Martire et al., 2010; Natalicchio et al., 2012, 2013). The main features of these rocks will be briefly summarized in the following in order to better constrain the setting in which cylindrical concretions developed. All the TPB methane-derived rocks are characterized by $\delta^{13}\text{C}$ values ranging from -10 to -52 ‰ PDB and $\delta^{18}\text{O}$ values comprised between 0 and $+7$ ‰ PDB. They may be distinguished in three main types (Tab. 1; Fig. 7):

Table 1. Comparison between the main characteristics of the methane-derived carbonates of the Tertiary Piedmont Basin.

1) *Lucina* limestones, consisting of lenticular m-sized masses embedded in unlithified fine-grained sediments and characterized by remains of chemosymbiotic bivalves (*Lucina* sp.) (Fig. 7A). These sediments are interpreted as by-products of methane-rich fluid seepage at the seafloor in analogy with comparable carbonate masses found at modern CH_4 seep sites where rich assemblages of chemosynthetic and chemosymbiotic organisms thrive thanks to the emission of gas-rich fluids (H_2S , CH_4) (e.g. Paull et al., 1992).

Fig. 7. A) Lucina limestones from the Verrua Savoia quarry. Pencil for scale is 14 cm long. B) Alfiano Natta macroconcretions: strongly indurated conglomerates crosscut by cm-wide sediment filled dykes are recognisable. Coin for scale is 1.9 cm in diameter. C) Photomicrograph of an aragonite-filled vein crosscutting a coarse cemented sandstone (Alfiano Natta). D) A stratiform concretion at Ripa dello Zolfo. Note the sharp boundary with underlying unconsolidated sediments. Hammer for scale is 32 cm long. E) Polished slab of the stratiform concretion shown in D). Note the complex network of vertical and horizontal sediment- and cement-filled fractures.

2) Macroconcretions, consisting of metre- to hundreds of metre-sized masses of strongly indurated coarse-to fine- grained terrigenous sediments (conglomerates, sandstones and siltstones) (Fig. 7B) devoid of chemosymbiotic organism remains (Clari et al. 2009; Clari and Martire, 2000). These rocks occur in Monferrato, within Oligocene fan delta deposits and are beautifully exposed at Alfiano Natta (Fig. 1). The hardness is due to the presence of an abundant intergranular dolomite cement which is clearly recognizable in thin section within sandstone beds but is also very abundant in original muddy sediments that at present macroscopically appear as fine-grained dolostones. Pyrite is commonly abundant, appears as finely disseminated framboids or as larger grains, and is responsible for the dark colour of the rock. Several generations of subvertical sedimentary dykes and carbonate-filled veins occur within the macroconcretions (Fig. 7C). Most of them can be followed vertically for tens of metres. Dykes are a few millimetres to several decimetres thick and are filled with lithified mudstones or coarse sandstones. Veins are a few millimetres to 10 cm thick and are plugged by carbonate cements (Fig. 7C) showing a great complexity for both mineralogy (calcite, dolomite, aragonite) and growth morphologies (peloidal, inclusion-rich fibrous rims, splays, limpid blocky spar). Complex crosscutting relationships show that fracturing, cement precipitation within open fractures, sediment injection, and even dissolution of cements alternated during the formation of the macroconcretions. Locally in conglomerate beds, veins crosscut the pebbles documenting that the whole rock was fully lithified at the time of veining.

Macroconcretions have no present-day analogue so their interpretation is not so straightforward as that of *Lucina* Limestones. However the lack of any trace of formation close to the sea floor indicates authigenic carbonate precipitation in the pores of shallow buried clastic sediments (Clari et al., 2009). The dense network of dykes and veins, on the other hand, documents overpressured conditions of uprising fluids resulting in fracturation

of the previously lithified macroconcretions, fluidized sediment injection, and cavity-filling cementation.

3) Stratiform concretions devoid of chemosymbiotic fossil and cemented by dolomite (Fig. 7D); these rocks, observed at Ripa dello Zolfo associated with cylindrical concretions, result from three microbially-driven processes consisting of sulphate reduction, methanogenesis and finally anaerobic oxidation of methane (Natalicchio et al., 2012). Some of the stratiform concretions show an intricate network of septarian-like cracks filled with both injected sediments and polyphasic carbonate cements (dolomite and calcite) (Fig. 7E). The latter displays unusual growth geometries, referred to as “pinch-out structures” which have been interpreted to reflect the past occurrence of gas hydrates within the cracks (Dela Pierre et al., 2010; Martire et al., 2010). The bed-parallel geometry of stratiform concretions suggests that carbonate precipitation took place at a geochemical interface parallel to the sea floor and located within the sedimentary column, where anaerobic oxidation of methane could take place concomitantly with sulphate reduction. The prolonged permanence of these interfaces at discrete subbottom stratigraphic levels, probably due to minor discontinuities in sedimentation, allowed conspicuous amounts of cement to precipitate. The occurrence of melt-seal structures (Martire et al., 2010) point to the fact that these rocks formed in close proximity to the gas hydrate stability zone and that gas hydrate formation and dissociation played a role in the migration of methane-rich fluids (Dela Pierre et al., 2010; Natalicchio et al., 2012).

In the following paragraph, we will focus on the cylindrical concretions; in particular, they will be compared with the three types of methane-derived carbonates above described (*Lucina* limestones, macroconcretions, and stratiform concretions) in order to underline the different flow regime and the portion of the flow system in which they formed.

5. Discussion

The cylindrical concretions here described show a remarkable similarity with the “chimneys” observed on present day sea bottoms, as far as size (diameter, length), presence of central axial conduit, texture of cemented sediment, isotopic signature, and dolomitic composition of cements are concerned (e.g. Orpin, 1997; Diaz del Rio et al., 2003; Takeuchi et al., 2007; Magalhães et al., 2012). These cylindrical concretions represent ancient fluid conduits related to the upward migration of CH₄-rich fluids through the sedimentary column. This interpretation, already proposed for the TPB (e.g. Clari et al., 2004; Dela Pierre et al., 2010) and other fossil examples (e.g. Aiello et al., 2001; Aiello, 2005; Campbell et al., 2008; Nyman et al., 2010) seems clearly supported by field, petrographic, and geochemical evidences. However, several questions still remain open and concern: i) the influence of the characteristics of the host sediments (porosity and permeability) in their genesis; ii) the depth in the sedimentary column at which these features are formed; iii) the intensity and mode of fluid flow generating conduits. The large available dataset about rocks derived from the flux of methane-rich fluids through the sediment column in the TPB allows to shed light on this aspects through the comparison of different types of rocks related to variable controlling factors.

5.1 Host sediment features

The comparison between the cylindrical concretions and the other products of cementation below the sea floor (i.e. macroconcretions) reveals the influence of the host sediment properties over the formation of the cylindrical concretions (Fig. 8).

Fig. 8. Sketch of comparison between the settings in which cylindrical concretions (left) and macroconcretions (right) are developed. Note that the size of the two products are different. Graphic scales however are only indicative. See text for details.

Macroconcretions are only developed within coarse grained and therefore permeable sediments which allow ascending methane-rich fluids to diffuse and permeate all the pore system (Clari et al., 2009). This results in a pervasive cementation widespread to the sediment volume crossed by the flow. The persistence of an upward flux of fluids generates local overpressures that cause fracturing of the overlying, rigid, cemented plug. The flux becomes channelized within laterally extensive, cm- to dm-sized fractures. Dykes and veins are the product of sediment plugging and cement precipitation within these fractures which continue to develop crosscutting each other until the demise of the overpressured conditions. Conversely, the cylindrical concretions developed in low-permeability, cohesive muddy sediments hampering a diffuse flow (Fig. 8). Any heterogeneity in the sediments, such as burrows, involving textural and hence permeability contrast, can favour the start of a localized, channelized flux that then opens its way vertically through the overlying sediments because of its buoyancy related to the high gas content (Mörz et al., 2007). Once the flux pierces all the overlying sediment cover and reaches the sea floor, a pipe-like fluid conduit is generated. This system remains active as long as a steady flux of methane-rich fluid is maintained. A figure of about 400 ky is provided on a biostratigraphic basis by Fontana et al. (2013) for the formation of comparable methane-derived carbonates in the northern Apennines. It is around these conduits that carbonate precipitation, induced by anaerobic oxidation of methane, takes place giving rise to the cylindrical concretions (see below).

5.2 *Fluid flow regime*

Given that the cylindrical concretions are the product of carbonate precipitation around fluid conduits within fine grained sediments, some important aspects concerning the flow regime can be discussed. Two scenarios can be envisaged:

- a) Intermittent and massive release of hydrocarbons-rich fluids originated at depth by thermogenic processes, related to tectonic squeezing of overpressured muddy

deposits. Such a scenario is more consistent with the development of large scale mud diapirs and/or mud volcanoes classically documented by chaotic deposits in the stratigraphic record (e.g. Barber and Brown, 1988; Fontana et al., 2014), rather than the metre-scale features under study.

- b) Steady and moderate fluxes of methane rich fluids of biogenic (e.g. Oppo et al., 2015) and/or thermogenic origin, possibly sourced by destabilization of gas hydrates.

The latter mechanism is the one that better fits with the shape, size, and composition of the cylindrical concretions which result from cementation of hosting sediments without important disruption of their primary features. Furthermore, the positive $\delta^{18}\text{O}$ values of all the studied concretions suggest that the involvement of gas hydrate destabilization is probable. The formation of cylindrical concretions likely takes place over quite short time intervals and may represent short-lived episodes in the life of a mud volcano documenting phases of slow degassing alternated with paroxistic eruptive phases as described in the Verrua Savoia outcrop (Clari et al., 2004).

5.3 *Depth in the sedimentary column*

The lack of any evidence of exposure at the sea floor documents that the cylindrical concretions formed within the sedimentary column. However, the dolomite composition of the intergranular cement and its methane-derived origin constrain to a shallow depth the loci of formation. In fact, dolomite is the typical product of methane oxidation in an anaerobic environment led by consortia of Archaea and sulphate-reducing bacteria (e.g. Boetius et al., 2000; Ussler and Paull, 2008; Magalhães et al., 2012). The anaerobic oxidation of methane (AOM), coupled with sulphate reduction contributes to high saturation in HCO_3^- , and consumption of seawater sulphate, causing a depletion in MgSO_4 . The concentration of free Mg ions consequently increases and dolomite is preferentially precipitated (Baker and Kastner, 1981). These conditions exist at the

Sulphate-Methane Interface (SMI) where methane generated in the underlying sediments, either biogenically or thermogenically, rises up and mixes with sulphate-rich, marine-derived, porewaters. The depth of the SMI in open marine environments, within fine-grained sediments, is in the order of a few tens of metres at most (e.g. Borowski et al., 1999; D'Hondt et al., 2002, Meister et al., 2007) but is much shallower where methane is diffusely seeping and its oxidation consumes sulphates (e.g. Borowski et al., 1996). Along focussed, sustained, flows of methane-rich fluids, i.e. within fluid conduits, the SMI is bent up and may even reach the sea floor at venting sites (Magalhães et al., 2012). AOM-related dolomite precipitation, thus, is limited downwards by the position of the SMI but it is also limited upwards by the oxic-anoxic interface boundary whose position is regulated by the downward penetration of oxygen-rich seawaters. Above this surface the activity of sulphate-reducing bacteria is inhibited, no methane is anaerobically oxidated and consequently no appreciable dolomite precipitation can take place. It can be concluded that the studied cylindrical concretions formed within a very narrow zone (up to a few metres) immediately below the seafloor. This hypothesis is supported by the great amount of authigenic carbonate implying that the cement formed within still porous sediments prior to significant compaction (see also Nyman et al., 2010).. This means that the cylindrical concretions represent the topmost part of the fluid conduits that crossed the sediment column (Fig. 8). Our scenario is also in agreement with present-day examples of cylindrical concretions which are often found as scattered bodies lying on the sea floor as a result of their exhumation by bottom current erosion (Takeuchi et al., 2007; Magalhães et al., 2012). This implies that they likely formed just below the sediment-water interface.

5.4 *Model of formation*

The formation of cylindrical concretions can be summarized in four steps (Fig. 9).

Fig. 9. Sketch showing the four step evolution of cylindrical concretions. Graphic scales are only indicative See text for details. Dol. prec.: dolomite precipitation.

1. Start of channelized fluid flow and cementation at a distance around the fluid conduit where the SMI is located. Cementation is limited at the base by the SMI and upward by the oxic/anoxic interface within sediments.
2. Inward growth of the cemented pipe walls. Sulphate ions, requested for sustaining AOM, are replenished in the very shallow sub-seafloor from seawater and /or sucked upwards from sulphate-rich pore waters surrounding the pipe walls (e.g. O'Hara et al., 1995; Mastalerz et al., 2007). This interpretation, already proposed by Clari et al. (2004) and further confirmed for other fossil cylindrical concretions (e.g. Nyman et al., 2010; Oppo et al., 2015), is in agreement with the U-series datings provided by Bayon et al. (2013) on modern chimneys in the Mediterranean.
3. Completion of cementation of the cylindrical sediment volume surrounding the still active flow conduit.
4. Demise of flow. The pipe may be filled with sediments or remain empty depending on the nature of the last flow which could be made of fluidized dense muddy sediments or gas-rich waters, respectively. The accretion of the sea floor by sediment accumulation displaces upward the SMI, which may result locally in stratabound cementation with formation of a stratiform concretion embedding the cylindrical concretions previously formed (Fig. 5).

6. Conclusions

The main results of this paper may be summarized as follows:

- a) Methane-derived carbonate concretions characterized by a cylindrical shape record a relatively long period of steady, sluggish flux of methane-rich fluids through fine-

- grained unconsolidated sediments. These products contrast with macroconcretions i.e. large-scale volumes of sediment pervasively cemented by a diffuse flow of methane-rich fluids through coarse-grained sediments which, moreover, record the persistence of intermittent overpressured fluid flows as dense networks of dykes and veins.
- b) Cylindrical concretions represent the highest part of pipes through which methane-rich fluids, generated at depth in the sediment column, flowed up. The preservation of these flow paths is assured by precipitation of intergranular dolomite cement within the pores of terrigenous sediments due to microbially-driven anaerobic oxidation of methane between the SMI and the oxic/anoxic interface, immediately below the sea floor (few metres). Dolomite precipitation started at a distance of some centimetres around the uprising flow and proceeded progressively inward. The deeper part of the conduits, conversely, left no trace in the stratigraphic record because the lack of marine sulphate in the host sediment porewaters prevented AOM and consequent carbonate precipitation.
- c) A continuous flux of methane-rich fluids was likely related to dissociation of gas hydrates hosted in underlying sediments, as suggested by O isotope values of cylindrical concretions and petrographic features of carbonate concretions associated with them.

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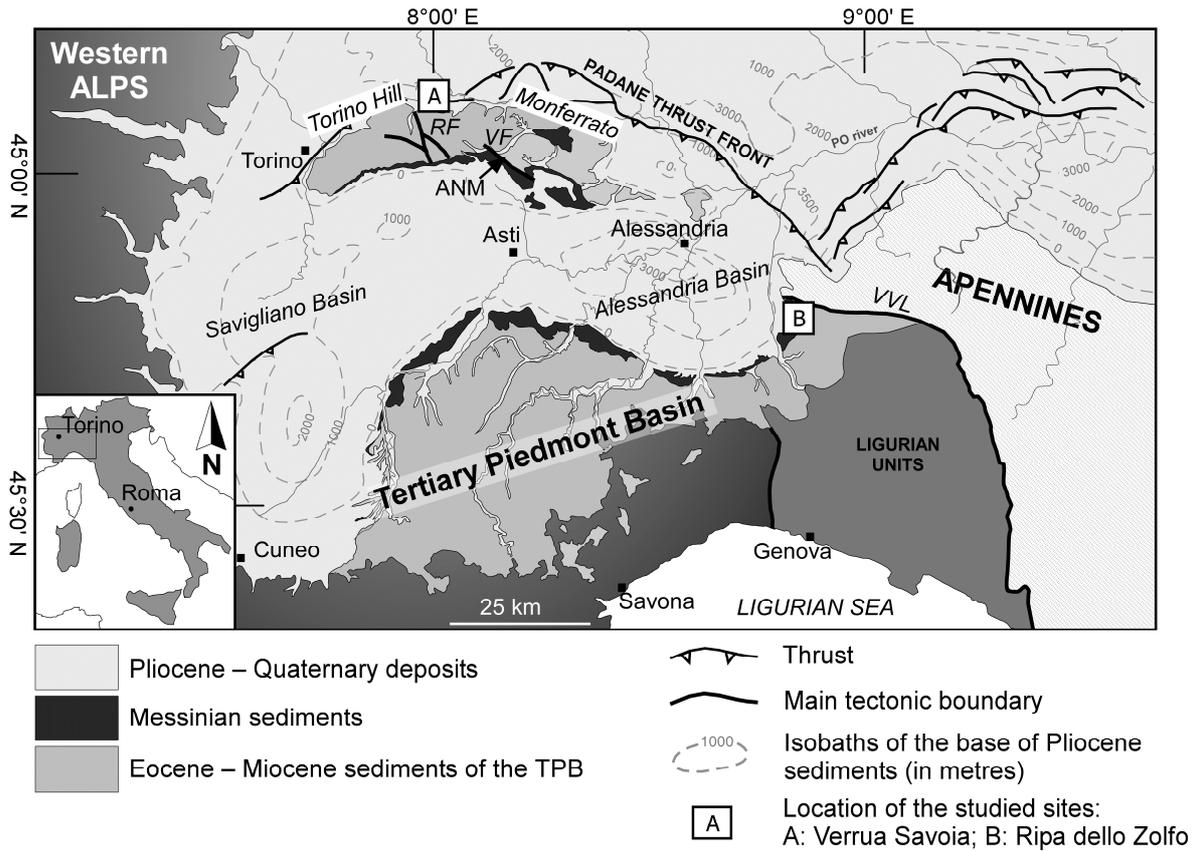
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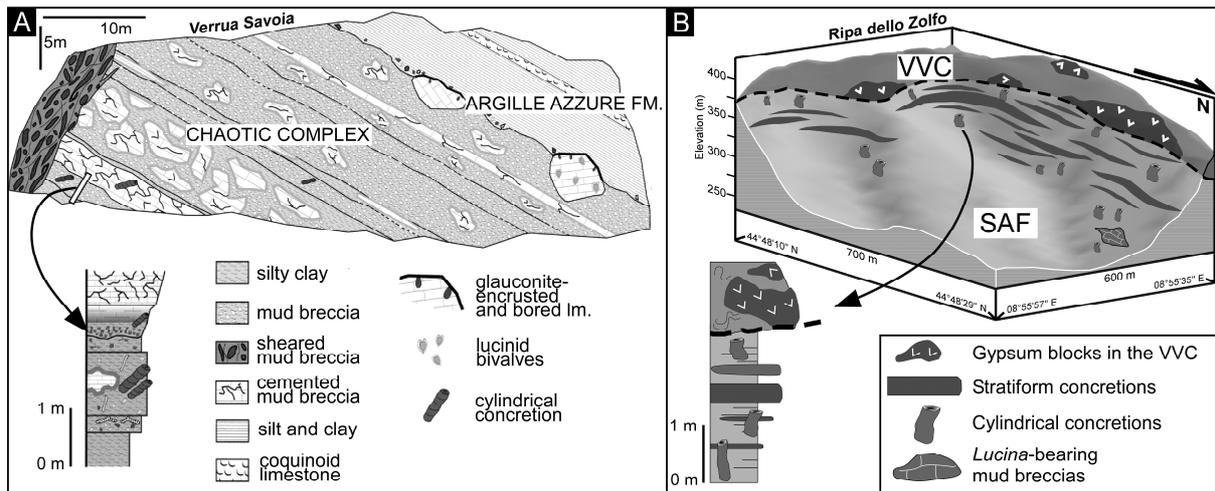
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Carbonate type	Size	Encasing sediments	Stable Isotopes (‰ PDB)	Number of analyses	Composition	Genesis
<i>Lucina</i> Limestones	m-sized	Marly limestones, mud breccias	$\delta^{13}\text{C}$: from -45 to -10 $\delta^{18}\text{O}$: from 0 to +8	38	Calcite, aragonite	Sea floor
Macroconcretions	100-m sized	Sandstones, conglomerates	$\delta^{13}\text{C}$: from -52 to -15 $\delta^{18}\text{O}$: from 0 to +6	42	Dolomite, calcite, aragonite	Within sedimentary column
Cylindrical concretions	m-sized	Marls	$\delta^{13}\text{C}$: from -34 to -10 $\delta^{18}\text{O}$: from +4 to +8	20	Dolomite	Within sedimentary column

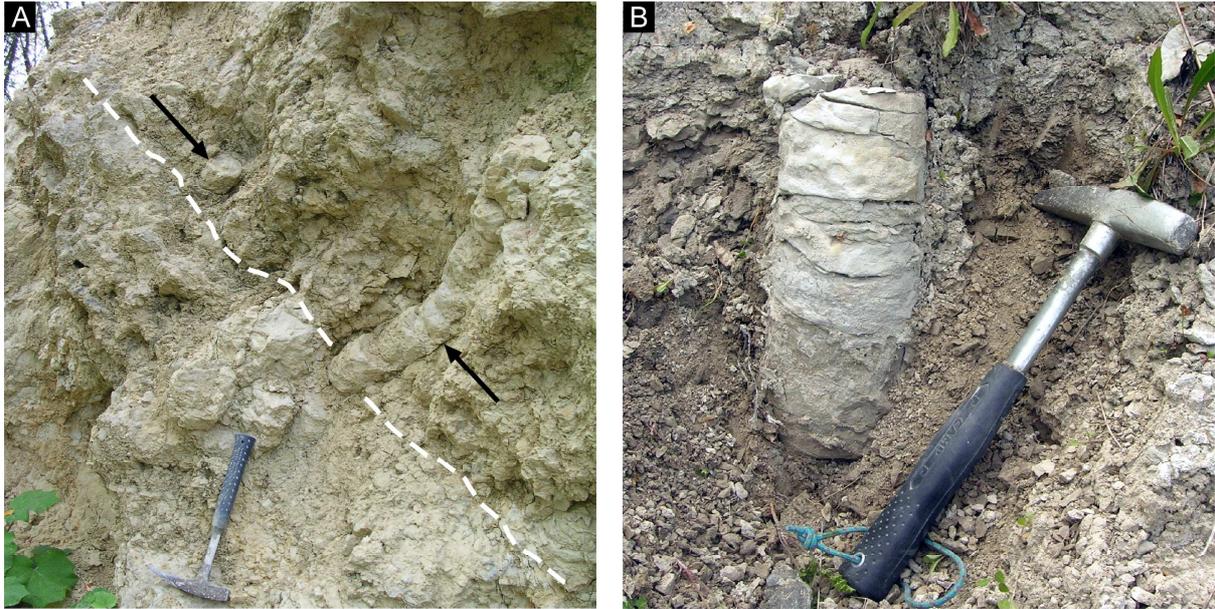
Cavagna et al., Table 1



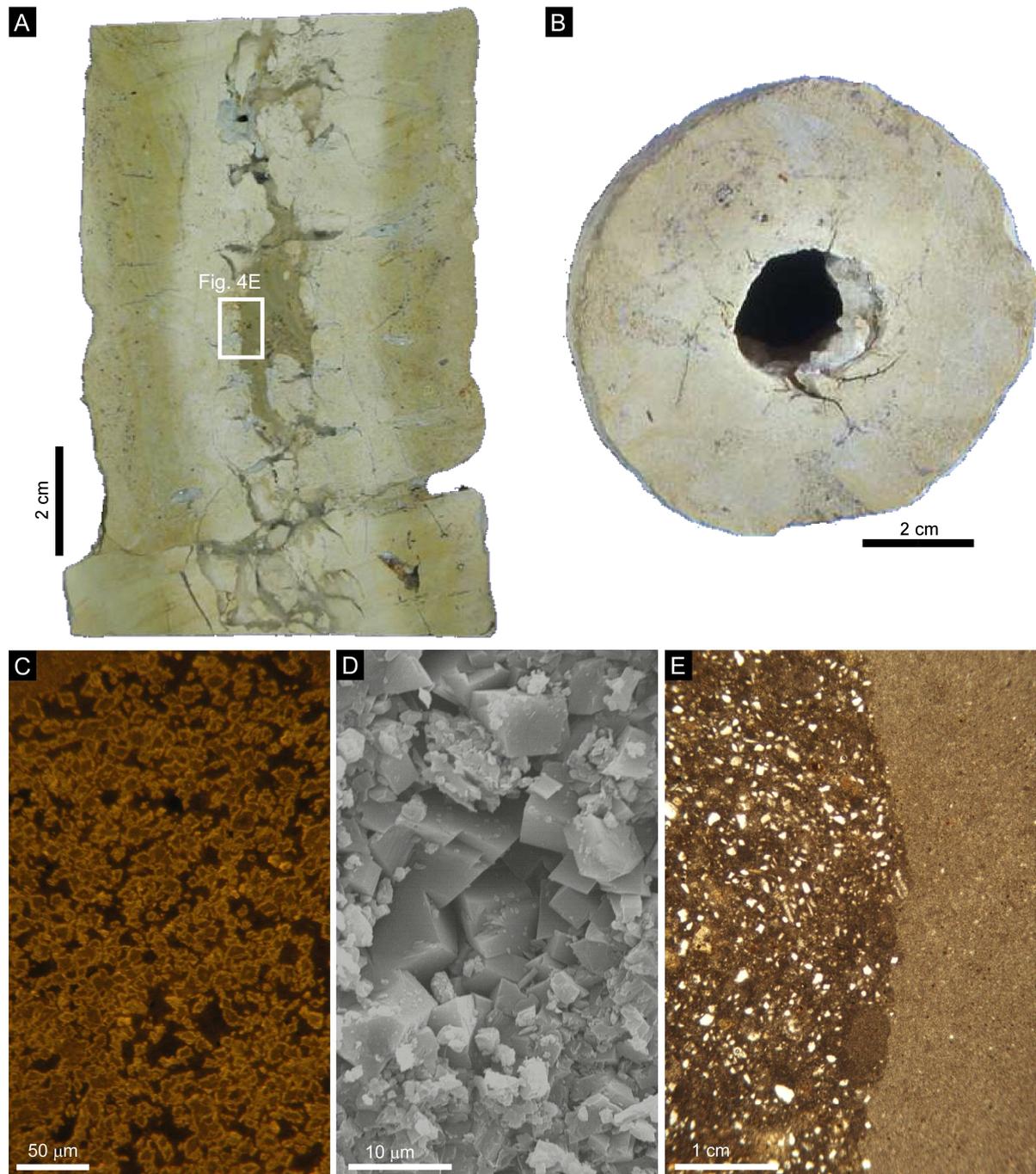
Cavagna et al. Fig.1



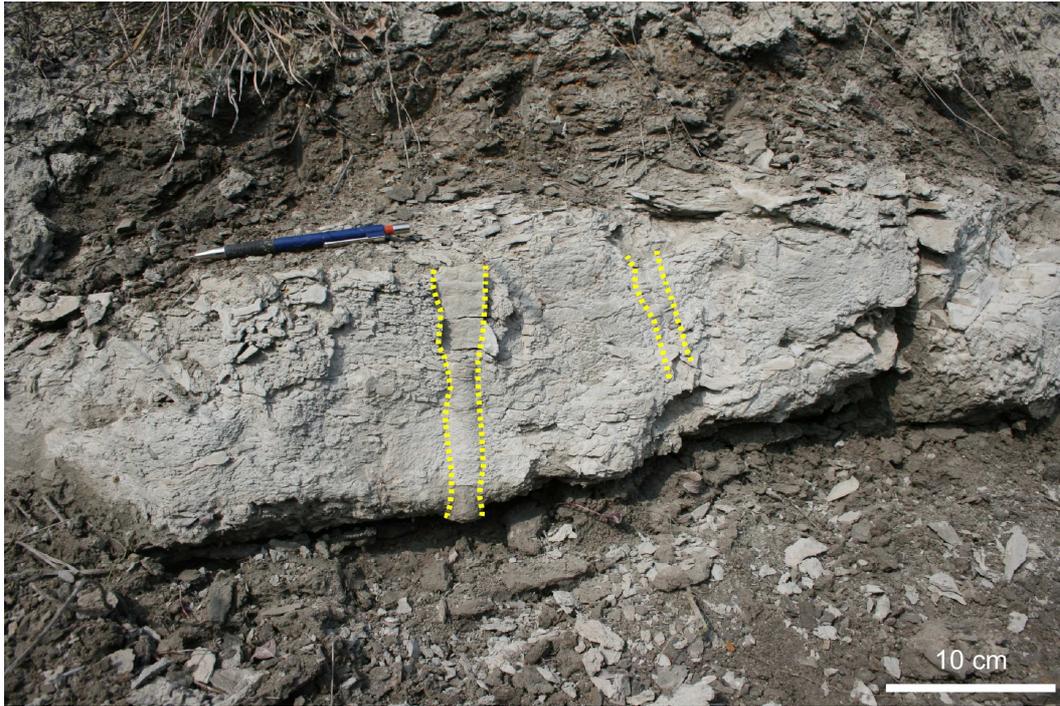
Cavagna et al. Fig. 2



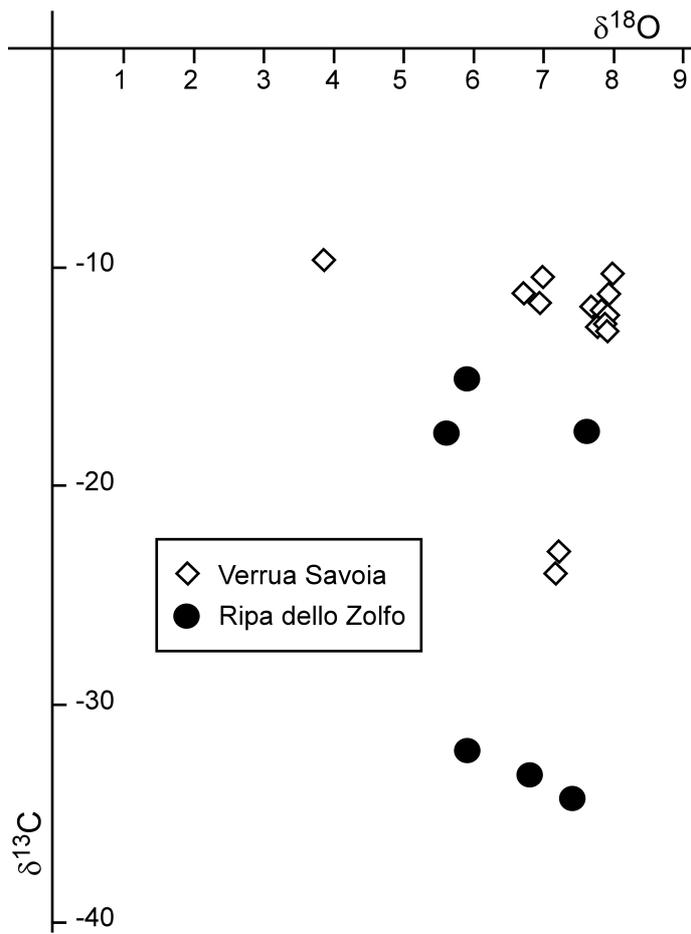
Cavagna et al. Fig. 3



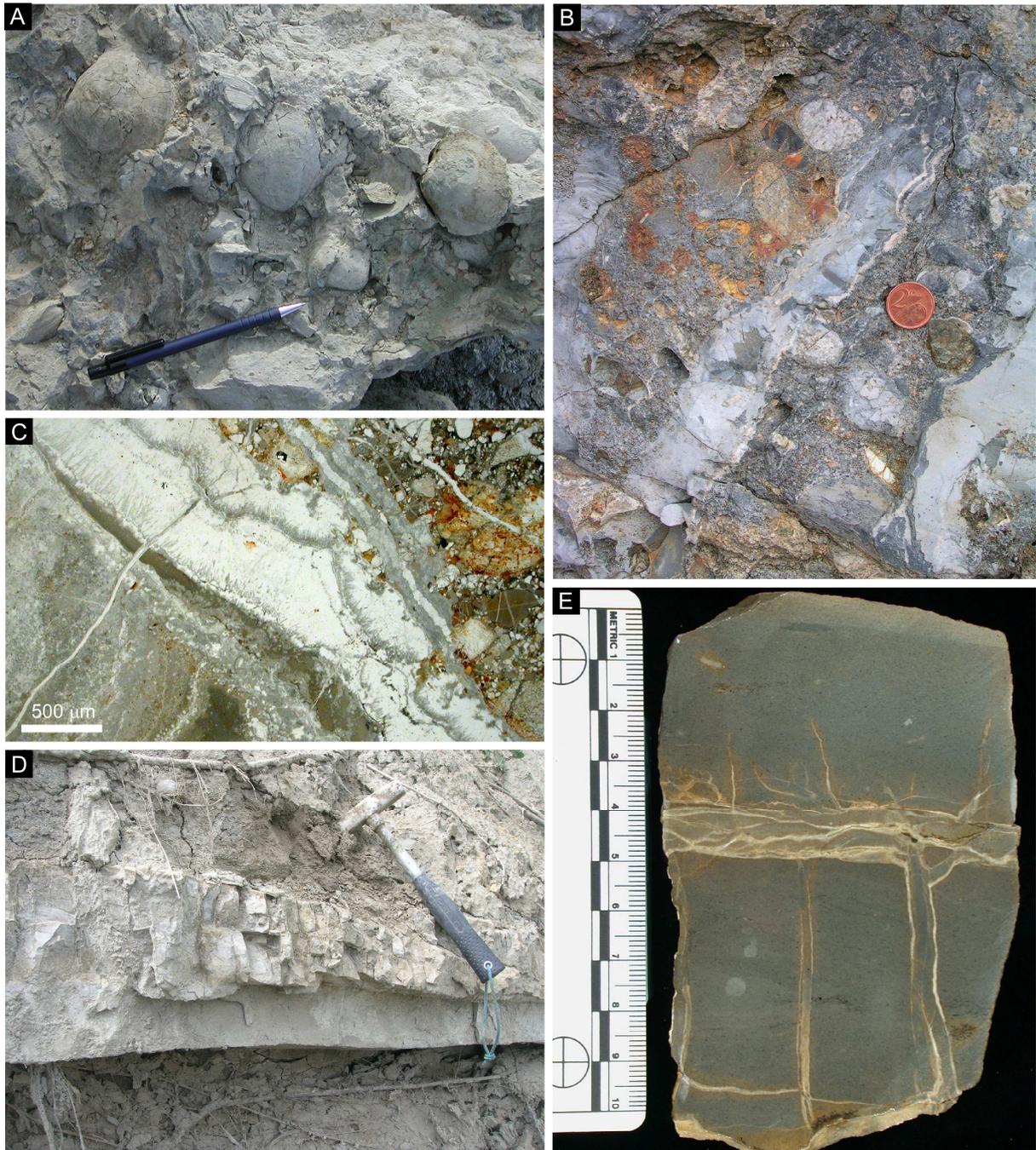
Cavagna et al. Fig. 4



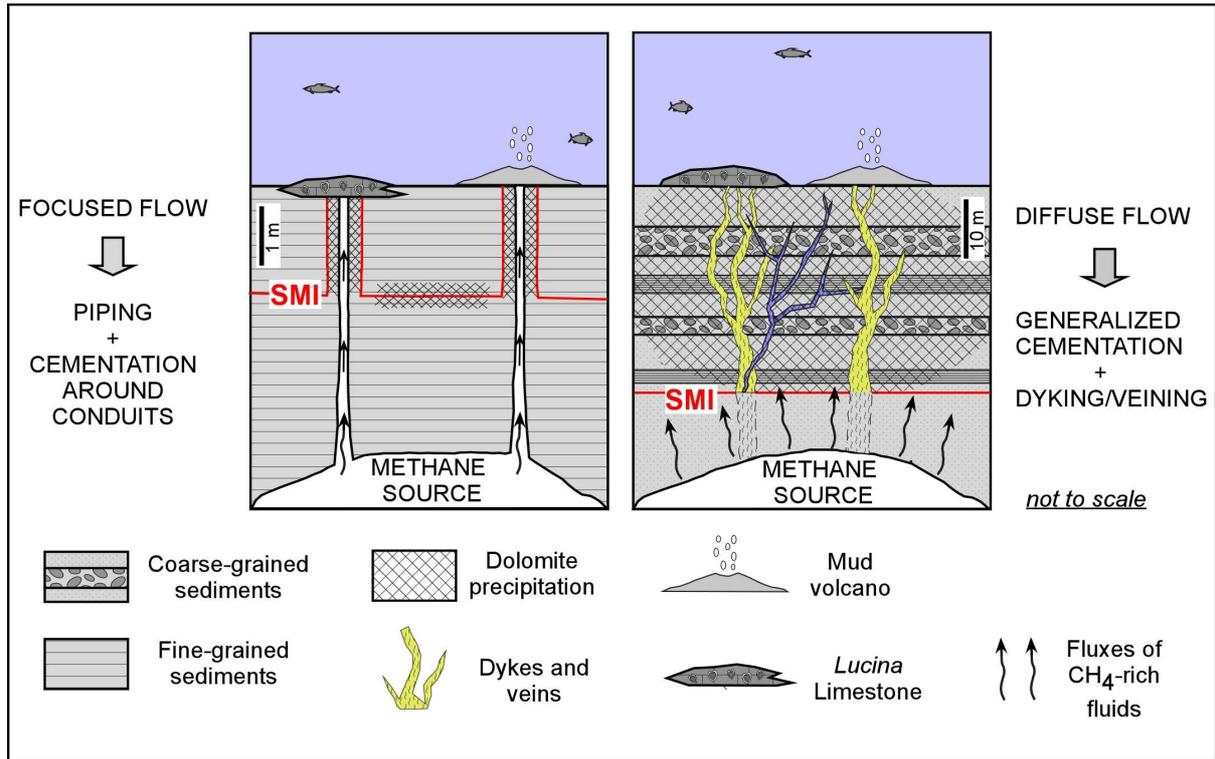
Cavagna et al. Fig. 5



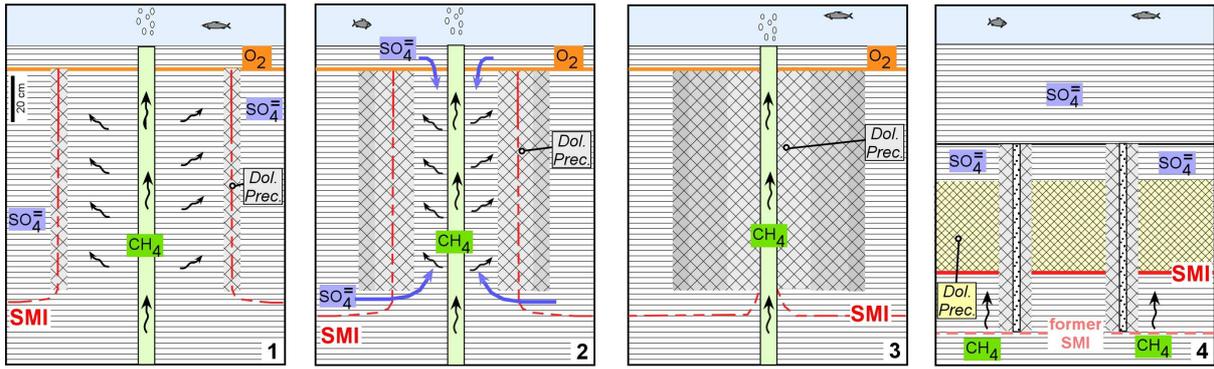
Cavagna et al FIG. 6



Cavagna et al. Fig. 7



Cavagna et al. Fig. 8



Cavagna et al. Fig. 9

HIGHLIGHTS

- cylindrical concretions developed around ancient fluid conduits
- they record steady, sluggish fluxes of methane-rich fluids through muddy sediments
- they result from microbially-induced dolomite precipitation
- they formed below the seafloor, between the SO_4/CH_4 and the oxic/anoxic interfaces
- they preserve only the highest part of fluid conduits