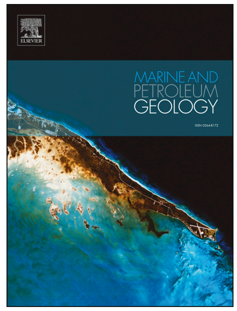

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PII: S0264-8172(15)00141-5
DOI: 10.1016/j.marpetgeo.2015.04.013
Reference: JMPG 2220

To appear in: *Marine and Petroleum Geology*

Received Date: 28 November 2014
Revised Date: 9 April 2015
Accepted Date: 15 April 2015

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 Villalvernia-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 paroxistic 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 sediment s 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 diametre 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 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 charactarized by negative $\delta^{13}C$ 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 expresses in ‰ PDB.

The $\delta^{18}O$ 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 $\delta^{13}C$ 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 $\delta^{18}O$ 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 $\delta^{13}C$ 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 $\delta^{13}C$ values ranging from –10 to –52 ‰ PDB and $\delta^{18}O$ 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 CH_4-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 ovepressured 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 $\delta^{18}O$ 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 cementformed 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.

ACKNOWLEDGEMENTS

The authors thank the Guest Editor Alessandra Negri, Daniela Fontana and an anonymous reviewer for useful comments and suggestions. This research was funded by PROactive Management of GEOlogical Heritagein the PIEMONTE Region project (co-founded by the University of Torino - Compagnia di San Paolo Bank, Project Id:

ORTO11Y7HR, P.I. M. Giardino), and University of Torino 2013 funds (ex 60% grant to F. Dela Pierre, Project Id: DELFRILO13).

References

Aiello, I.W., 2005. Fossil seep structures of the Monterey Bay region and tectonic/ structural controls on fluid flow in an active transform margin. Palaeogeography Palaeoclimatology Palaeoecology 227, 124–142.

Aiello, I.W., Garrison, R.E., Moore, J.C., Kastner, M., Stakes, D.S., 2001. Anatomy and origin of carbonate structures in a Miocene cold-seep field. Geology 29, 1111–1114.

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

Baker, P.A. Kastner, M., 1981. Constrains on the formation of sedimentary dolomite. Science 213 (4504), 214–216.

Barber, T., and Brown, K., 1988, Mud diapirism: The origin of mélanges in accretionary complexes?: Geology Today 4, 89–94.

Bayon, G., Dupré, S., Ponzevera, E., Etoubleau, J., Chéron, S., Pierre, C., Mascle, J., Boetius, A. De Lange, G.J., 2013. Formation of carbonate chimneys in the Mediterranean Sea linked to deep-water oxygen depletion. Nature Geoscience 6, 755–760.

Bertotti, G., Mosca, P., 2009. Late orogenic vertical movements within the arc of the SW Alps and Ligurian Alps. Tectonophysics 475 117–127.

Bigi, G., Cosentino, D., Parotto, M., Sartori, R., Scandone, P., 1990. Structural Model of Italy: Geodinamic Project: Consiglio Nazionale delle Ricerche, S.EL.CA, scale 1:500,000, sheet 1.

Boetius, A., Ravenschlag, K., Schubert, C.J., Rickert, D., Widdel, F., Gieseke, A., Amann, R., Jørgensen, B.B., Witte, U. Pfannkuche, O. 2000. A marine microbial consortium apparently mediating anaerobic oxidation of methane. Nature 5, 407 (6804), 623–626.

Borowski, W.S., Paull, C.K., Ussler, W., 1996. Marine pore-water sulfate profiles indicate in situ methane flux from underlying gas hydrate. Geology 24, 655–658.

Borowski, W.S., Paull, C.K., Ussler, W., 1999. Global and local variations of interstitial sulphate gradients in deep water, continental margin sediments: sensitivity to underlying methane and gas hydrates. Marine Geology 159, 131–154.

Campbell, K.A., 2006. Hydrocarbon seep and hydrothermal vent paleoenvironments and paleontology: past developments and future research directions. Palaeogeography Palaeoclimatology Palaeoecology 232, 362–407.

Campbell, K.A., Francis, D.A., Collins, M., Gregory, M.R., Nelson, C.S., Greinert, J Aharon, P. 2008. Hydrocarbon-seep carbonates of a Miocene forearc (East Coast Basin), North Island, New Zealand. Sedimentary Geology 204, 83–105.

Clari, P., Martire, L., 2000. Cold seep carbonates in the Tertiary of Northwestern Italy: evidence of bacterial degradation of methane. In: Riding, R.E., Awramik, S.M. (Eds.), Microbial sediments. Springer-Verlag, Heidelberg, 261–269.

Clari, P., Gagliardi, C., Governa, M.E., Ricci, B., Zuppi, G.M., 1988. I Calcari di Marmorito: una testimonianza di processi diagenetici in presenza di metano: Museo Regionale Scienze Naturali Torino, Bollettino 5, 197–216.

Clari, P., Fornara, L., Ricci, B., Zuppi, G.M., 1994. Methane-derived carbonates and chemosymbiotic communities of Piedmont (Miocene, northern Italy) — An update: Geo-Marine Letters 14, 201–209.

Clari, P., Dela Pierre, F., Novaretti, A., Timpanelli, M., 1995. Late Oligocene–Miocene sedimentary evolution of the critical Alps/Apennines junction — the Monferrato area, Northwestern Italy. Terra Nova 7, 144–152.

Clari, P., Cavagna, S., Martire, L., Hunziker, J., 2004. A Miocene mud volcano and its plumbing system: A chaotic complex revisited (Monferrato, NW Italy): Journal of Sedimentary Research 74, 662–676.

Clari P., Dela Pierre F., Martire L. Cavagna S., 2009. The Cenozoic CH4-derived carbonates of Monferrato (NW Italy): A solid evidence of fluid circulation in the sedimentary column. Marine Geology 265, 167–184.

Craig J., Campbell, K.A., Torres M.E., Martin, R.A., Pohlman, J.W., Riedel M., Rose, K., 2013. Methane-derived authigenic carbonates from modern and paleoseeps on the Cascadia margin: Mechanisms of formation and diagenetic signals. Palaeogeography, Palaeoclimatology, Palaeoecology 390, 52–67.

De Boever, E., Swennen, R., Dimitrov, L. 2006. Lower Eocene carbonate cemented chimneys (Varna, NE Bulgaria): Formation mechanisms and the (a)biological mediation of chimney growth? Sedimentary Geology 185, 159–173.

Dela Pierre F., Piana F., Fioraso G., Boano P., Bicchi E., Forno MG., Violanti D., Balestro G., Clari P., D'atri A., De Luca D., Morelli M., Ruffini R., 2003. Note Illustrative della Carta geologica d'Italia alla scala 1: 50.000; Foglio 157 Trino. APAT and Dipartimento di Difesa del Suolo, Litografia Geda, Nichelino, 147 pp.

Dela Pierre F., Clari P., Bernardi E., Natalicchio M., Costa E., Cavagna S., Lozar F., Lugli S., Manzi V., Roveri M., Violanti D., 2012. Messinian carbonate-rich beds of the Tertiary Piedmont Basin (NW Italy): Microbially-mediated products straddling the onset of the salinity crisis. Palaeogeography Palaeoclimatology Palaeoecology 344–345, 78 –93.

Dela Pierre F., Bernardi E., Cavagna S., Clari P., Gennari R., Irace A., Lozar F., Lugli S., Manzi V., Natalicchio M., Roveri M., Violanti D., 2011. The record of the Messinian salinity crisis in the Tertiary Piedmont Basin (NW Italy): The Alba section revisited. Palaeogeography Palaeoclimatology Palaeoecology 310, 238–255.

Dela Pierre F., Clari P., Natalicchio M., Ferrando S., Giustetto R. and Lozar F., 2014. Flocculent layers and bacterial mats in the mudstone interbeds of the Primary Lower Gypsum unit (Tertiary Piedmont Basin, NW Italy): archives of palaeoenvironmental changes during the Messinian salinity crisis. Marine Geology 355, 71–87.

Dela Pierre F., Festa A, Irace A., 2007. Interaction of tectonic, sedimentary and diapiric processes in the origin of chaotic sediments: an example from the Messinian of the Torino Hill (Tertiary Piedmont Basin, NW Italy). Geological Society of America Bulletin 119, 1107–1119.

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? Geological Society of America Bulletin 122, 994–1010.

Diaz-del-Rio, V., Somoza, L., Martin-Frias, J., Mata, M.P., Delgado, A., Hernandez-Molina, F.J., Lunar, R., Martin-Rubi, J.A., Maestro, A., Fernadez-Puga, M.C., Leon, R., Llave, E., Medialdea, T., Vazquez, J.T., 2003. Vast fields of hydrocarbon-derived carbonate chimneys related to the accretionary wedge/olistostrome of the Gulf of Cadiz. Marine Geology 195, 177–200.

D'Hondt, S., Rutherford, S., Spivack, A.J., 2002. Metabolic activity of subsurface life in deep-sea sediments. Science 295, 2067–2070.

Elter, P., Pertusati, P. 1973. Considerazioni sul limite Alpi-Appennino e sulle relazioni con l’arco delle Alpi Occidentali. Memorie della Società Geologica Italiana 12, 359–373.

Fontana, D., Conti, S. ,Grillenzoni, C., Mecozzi, S., Petrucci, F., Turco, E. 2013. Evidence of climatic control on hydrocarbon seepage in the Miocene of the northern Apennines: The case study of the Vicchio Marls. Marine and Petroleum Geology 48, 90–99.

Fontana, D., Lucente, C.C., Pini, G.A. 2014. Relationships between seep-carbonates, mud volcanism and basin geometry in the Late Miocene of the northern Apennines of Italy: The Montardone mélange. International Journal of Earth Sciences 103, 281–295.

Ghibaudo, G., Clari, P., Perello, M., 1985. Litostratigrafia, sedimentologia ed evoluzione tettonico sedimentaria dei depositi miocenici del margine Sud-Orientale del Bacino Terziario Ligure-Piemontese (Valli Borbera, Scrivia e Lemme). Bollettino della Società Geologica Italiana 104, 349–397.

Hovland, M., Talbot, M.R., Qvale, H., Olaussen, S. Aasberg, L., 1987. Methane-related carbonate cements in pockmarks of the North-Sea. Journal of Sedimentary Petrology 57, 881–892.

Levin L.A., 2005. Ecology of cold seep sediments: interaction of fauna with flow, chemistry and microbes. Oceanography and Marine Biology. An Annual Review 43, 1–46.

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

Martire L., Natalicchio M., Petrea C., Cavagna S., Clari P., Dela Pierre F., 2010. Petrographic evidence of the past occurrence of gas hydrates in the Tertiary Piedmont Basin (NW Italy). Geo Marine Letters 30, 461–476.

Mastalerz, V., de Lange, G.J., Dählmann, A., Feseker, T., 2007. Active venting at the Isis mud volcano, offshore Egypt: origin and migration of hydrocarbons. Chemical Geology 246, 87–106.

Mazzini, A., Ivanov, M.K., Nermoen, A., Bahr, A., Bohrmann, G., Svensen, H., Planke, S. 2008. Complex plumbing system in the near subsurface: Geometries of authigenic carbonates from Dolgovskoy Mound (Black Sea) constrained by analogue experiments. Marine and Petroleum Geology 25, 457–472.

Meister, P., McKenzie, J.A., Vasconcelos, C., Bernasconi, S., Frank, M., Gutjahr, M., Schrag, D.P., 2007. Dolomite formation in the dynamic deep biosphere: results from the Peru Margin. Sedimentology 54, 1007-1031.

Mörz, T., Karlik, E.A., Kreiter, S., Kopf, A. 2007. An experimental setup for fluid venting in unconsolidated sediments: New insights to fluid mechanics and structures. Sedimentary Geology 196, 251–267.

Mosca, P., Polino, R., Rogledi, S., Rossi, M., 2010. New data for the kinematic interpretation of the Alps–Apennines junction (Northwestern Italy). International Journal of Earth Sciences 99, 833–849.

Mutti, E., Papani, L., Di Biase, D., Davoli, G., Segadelli, S., Tinterri, R., 1995. Il Bacino Terziario Epimesoalpino e le sue implicazioni sui rapporti Alpi - Appennino. Memorie di Scienze Geologiche 47, 217–244.

Natalicchio M., Birgel D., Dela Pierre F., Martire L., Clari P., Spötl C., Peckmann J., 2012. Polyphasic carbonate precipitation in the shallow subsurface: Insights from microbially-formed authigenic carbonate beds in upper Miocene sediments of the Tertiary Piedmont Basin (NW Italy). Palaeogeography, Palaeoclimatology, Palaeoecology 329–330, 158–172.

Natalicchio M., Dela Pierre F., Clari P., Birgel D., Cavagna S., Martire L., Peckmann J., 2013. Hydrocarbon seepage during the Messinian salinity crisis in the Tertiary

Piedmont Basin (NW Italy) Palaeogeography Palaeoclimatology Palaeoecology 390, 68–80.

Natalicchio M., Dela Pierre F., Lugli S., Lowenstein T.K., Feiner S.J., Ferrando S., Manzi V., Roveri M., Clari P., 2014. Did Late Miocene (Messinian) gypsum precipitate from evaporated marine brines? Insights from the Piedmont Basin (Italy). Geology 42, 179–182.

Nyman, S.L., Nelson, C.S., Campbell, K.A., 2010. Miocene tubular Concretions in East Coast Basin, New Zealand: analogue for the subsurface plumbing of cold seeps. Marine Geology 272, 319–336.

O'Hara, S.C.M., Dando, P.R., Schuster, U., Bennis, A., Boyle, J.D., Chui, F.T.W., Hatherell, T.V. J., Niven, S.J., Taylor, L.J., 1995. Gas seep induced interstitial water circulation: observations and environmental implications. Continental Shelf Research 15, 931–948.

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 Apennine (Italy). In: R. Capozzi, A. Negri, J. Reithner, M. Taviani (eds) Carbonate conduits linked to hydrocarbon-enriched fluid escape. Special Issue of Marine and Petroleum Geology, doi 10.1016/j.marpetgeo.2015.03.002.

Orpin A.R., 1997. Dolomite chimneys as possible evidence of coastal fluid expulsion, uppermost Otago continenental slope, southern New Zealand. Marine Geology 138, 51–67.

Paull, C.K., Chanton, J.P., Neumann, A.C., Coston, J.A., Martens, C.S., 1992. Indicators of methane-derived carbonates and chemosynthetic organic carbon deposits: examples from the Florida Escarpment. Palaios 7, 361– 375.

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. Marine Geology 177, 129–150.

Piana, F., 2000. Structural setting of western Monferrato (Alps-Apennines Junction Zone, NW Italy). Tectonics 19, 943–960.

Piana, F. and Polino, R., 1995. Tertiary structural relationships between Alps and Apennines: the critical Torino Hill and Monferrato area, Northwestern Italy. Terra Nova 7, 138–143.

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. Chemical Geology 205, 469–484.

Pierre C., Blanc-Valleron M.M., Demange J., Boudouma O., Foucher J.P., Pape T., Himmler T., Fekete N., Spiess V., 2012. Authigenic carbonates from active methane seeps offshore southwest Africa. Geo-Marine Letters 32, 501–513.

Ritger, S., Carson, B., Suess, E., 1987. Methane-derived authigenic carbonates formed by subduction-induced pore-water expulsion along the Oregon/Washington margin. Geological Society of America Bulletin 98, 147–156.

Rossi, M., Mosca, P., Polino, R., Rogledi, S., Biffi, U., 2009. New outcrop and subsurface data in the Tertiary Piedmont Basin (NW-Italy): unconformity-bounded stratigraphic units and their relationships with basin-modification phases. Rivista Italiana Paleontologia Stratigrafica 115, 305–335.

Roure, F., Bergerat, F., Damotte, B., Mugnier, J.L., Polino, R., 1996. The Ecors-Crop Alpine seismic traverse. Bulletin Societé Géologique de France 170, 1–113.

Schumacher, M.E., Laubscher, H.P., 1996. 3D crustal architecture of the Alps-Apennines join – A new view on seismic data. Tectonophysics 260, 349–363.

Takeuchi, R., Matsumoto, R., Ogihara, S., Machiyama, H., 2007. Methane-induced dolomite “chimneys” on the Kuroshima Knoll, Ryukyu islands, Japan. Journal of Geochemical Exploration 95, 16–28.

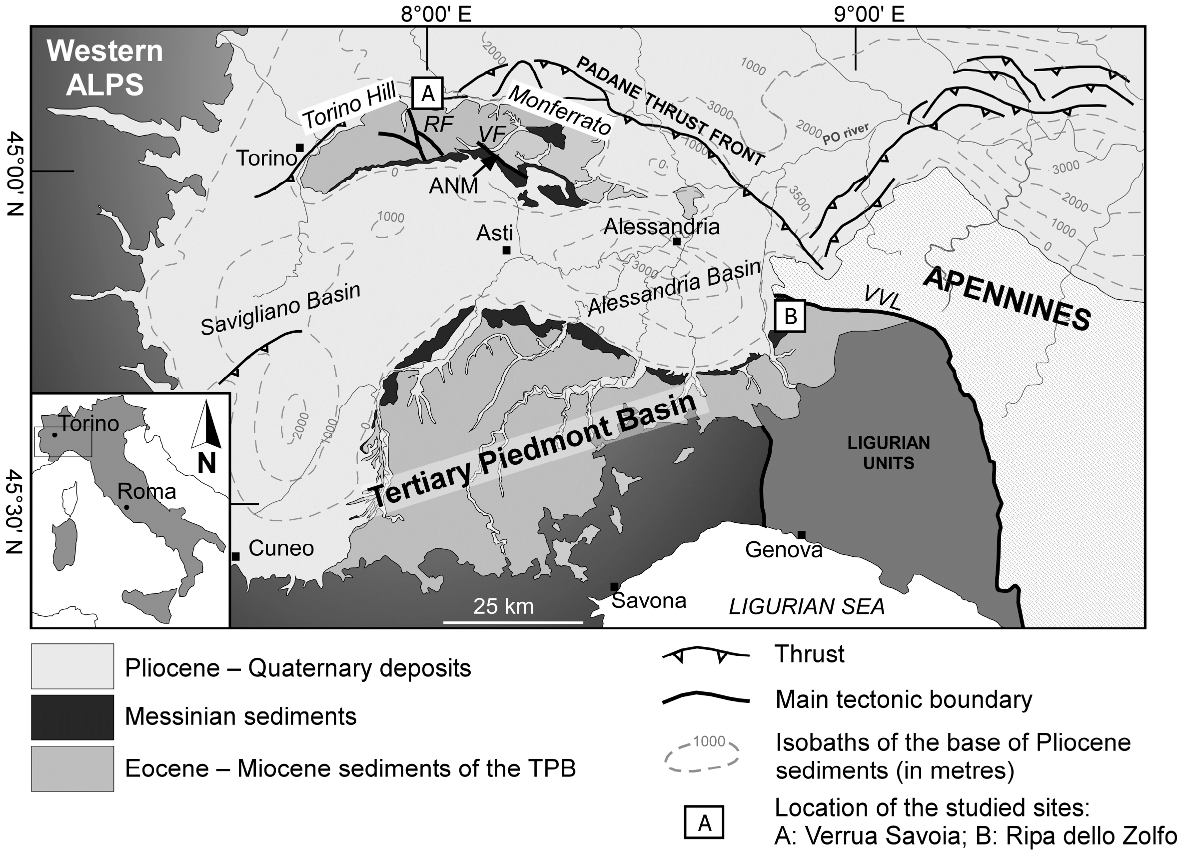
Ussler III,W., Paull, C.K., 2001. Ion exclusion associated with marine gas hydrate deposits. In: Paull, C.K. and Dillon, W.P. eds., Natural Gas Hydrates: Occurrence, Distribution and Detection. American Geophysical Monograph 124, 41-51.

Ussler III,W., Paull, C.K., 2008. Rates of anaerobic oxidation of methane and authigenic carbonate mineralization in methane-rich deep-sea sediments inferred from models and geochemical profiles. Earth and Planetary Science Letters 266, 271–278.

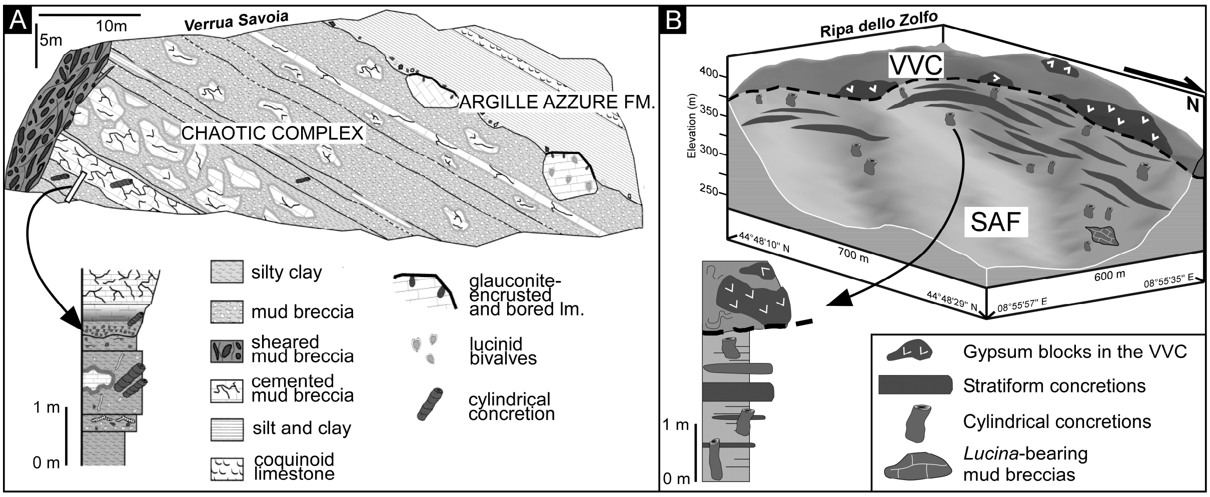
Whiticar, M.J., 1999. Carbon and Hydrogen isotope systematics of bacterial formation and oxidation of methane. Chemical Geology 161, 291–314.

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

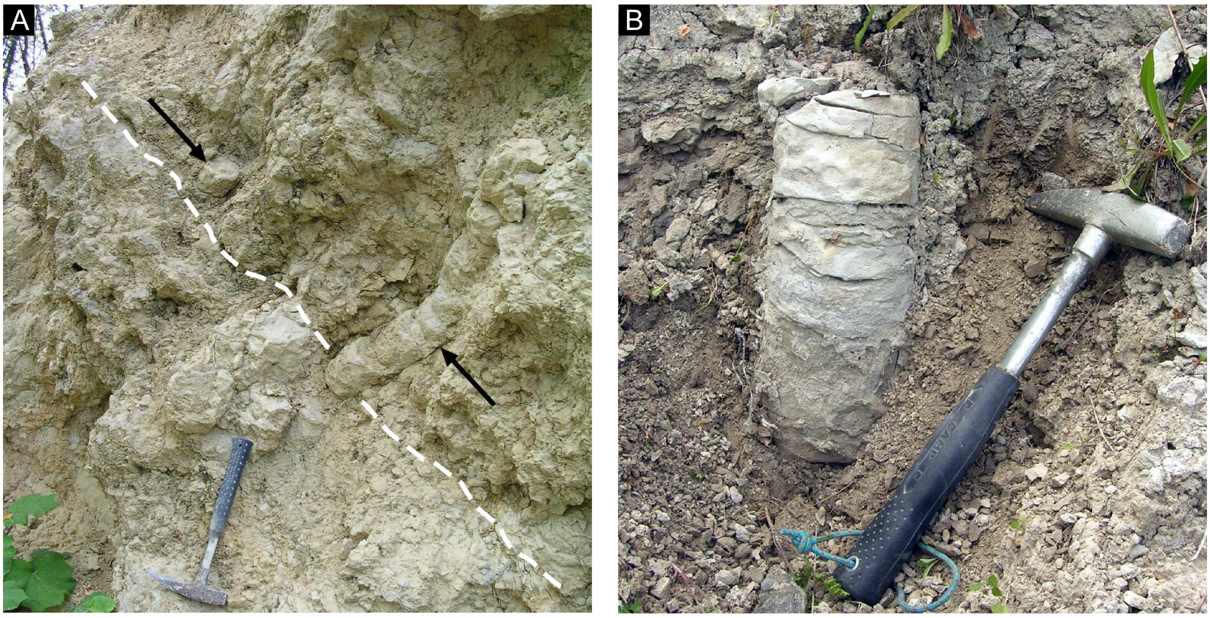
Cavagna et al., Table 1



Cavagna et al. Fig.1



Cavagna et al. Fig. 2



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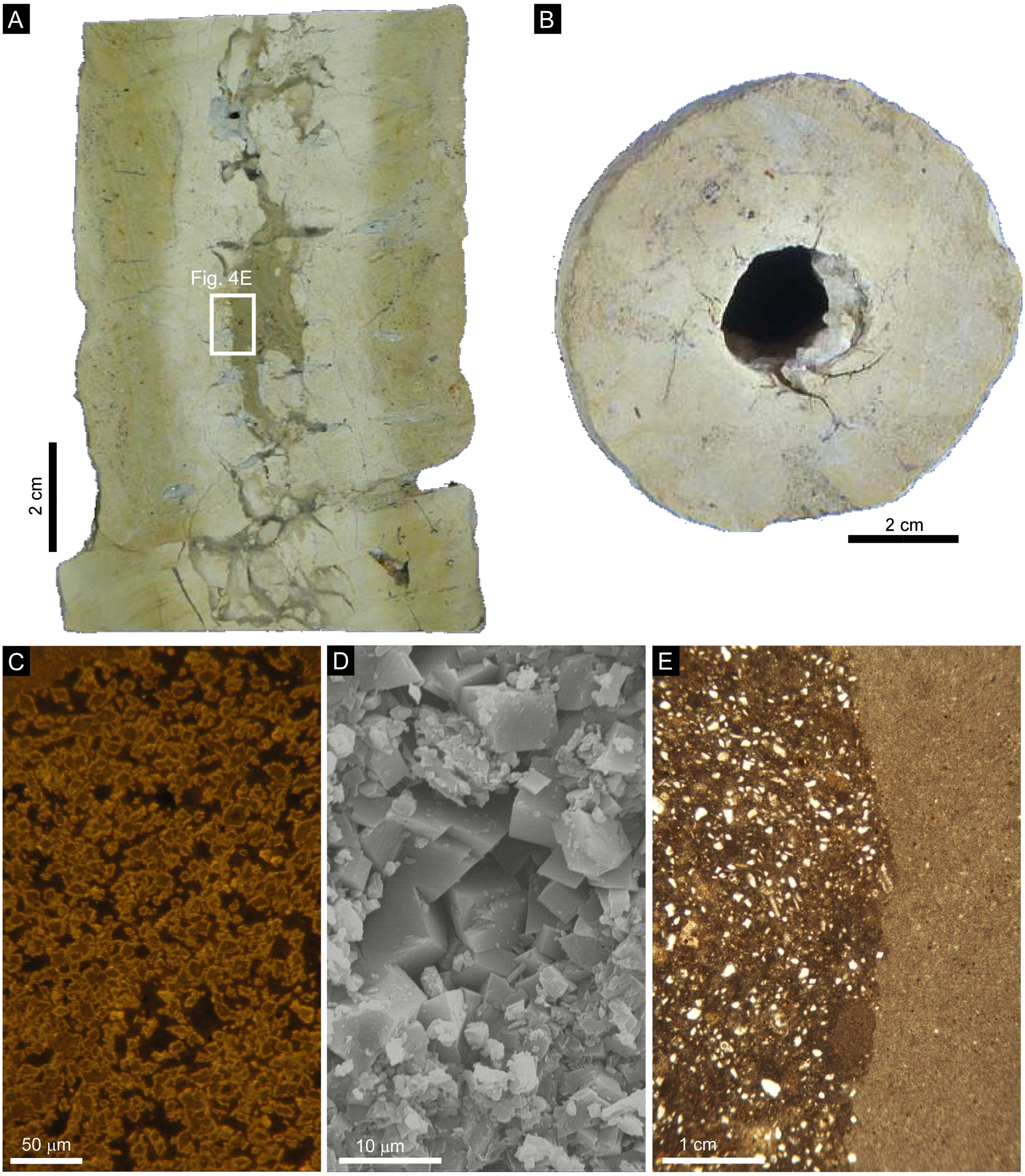

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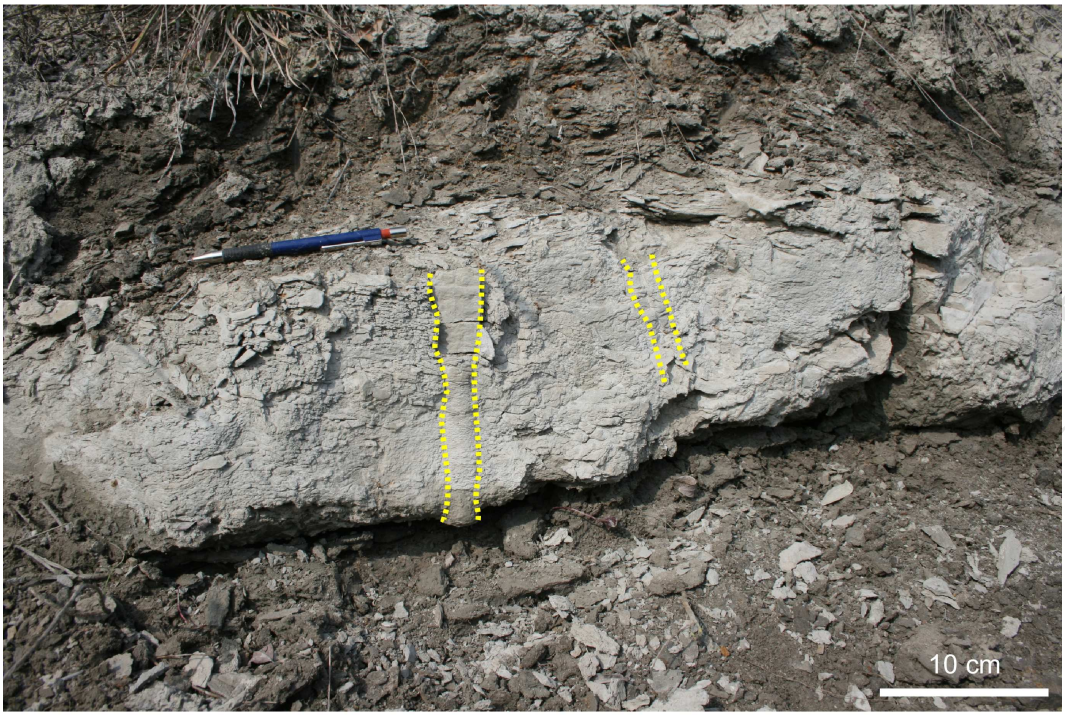

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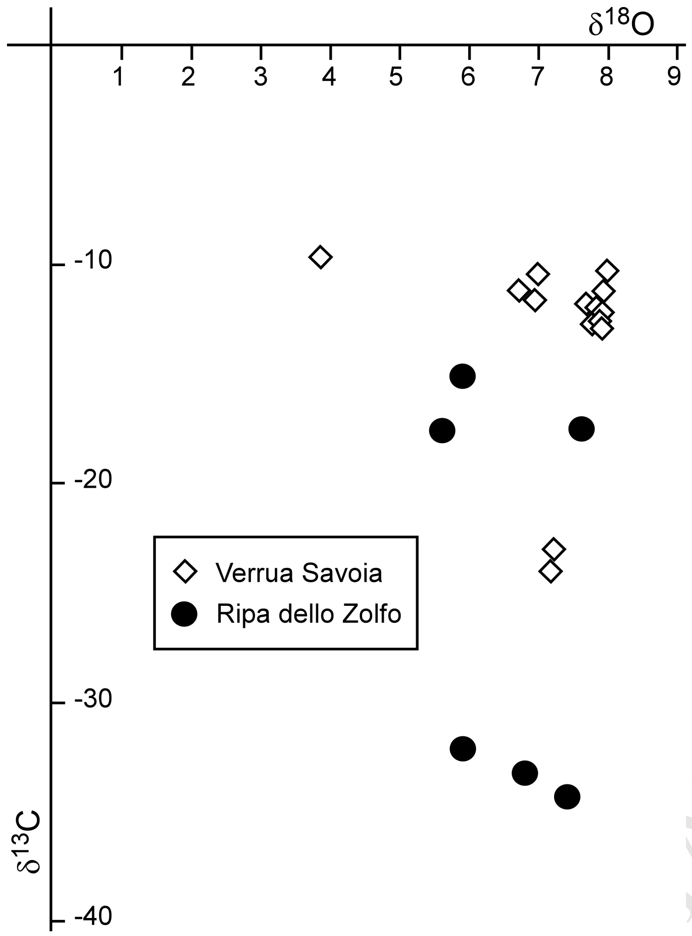
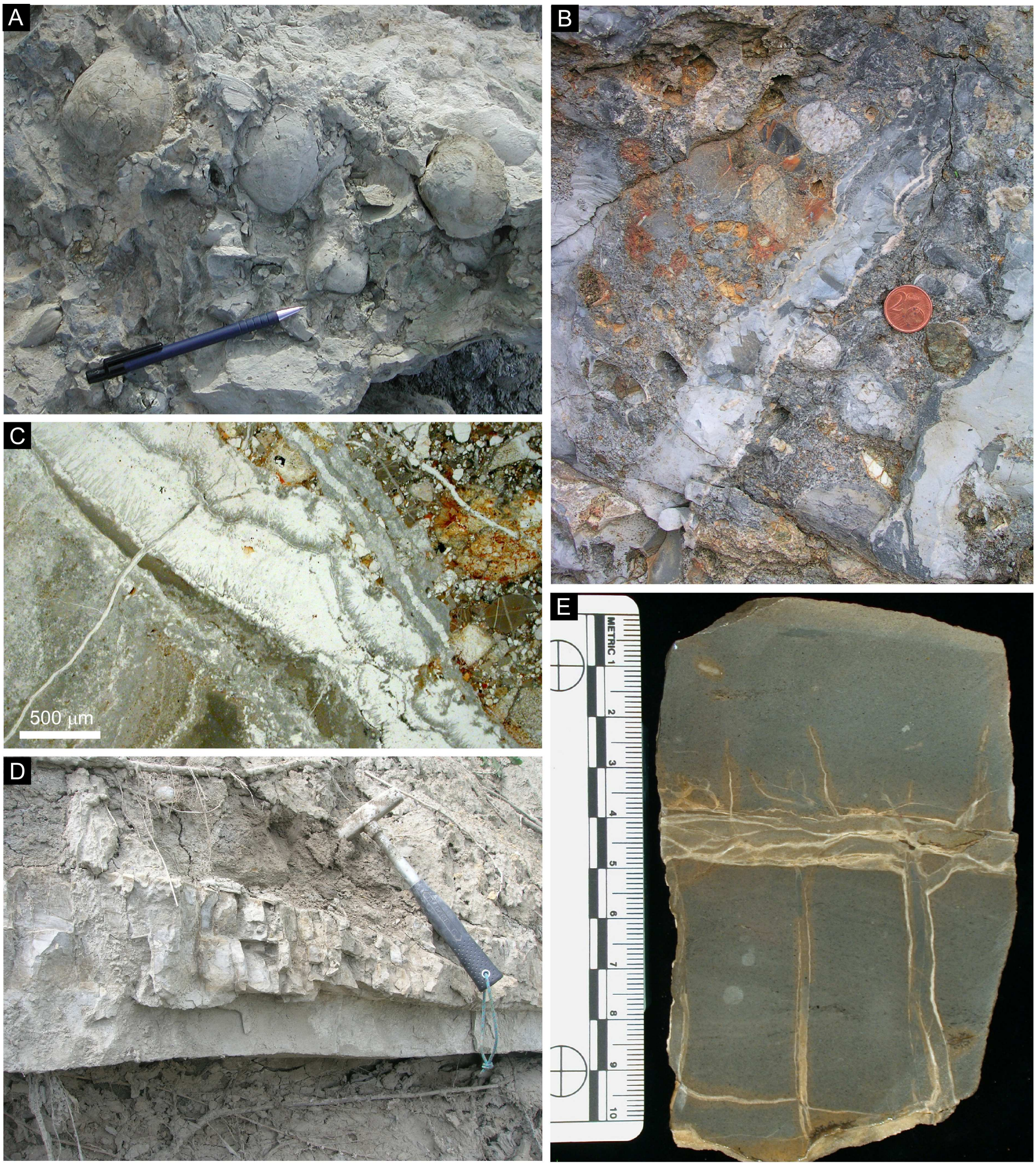


Cavagna et al   FIG. 6



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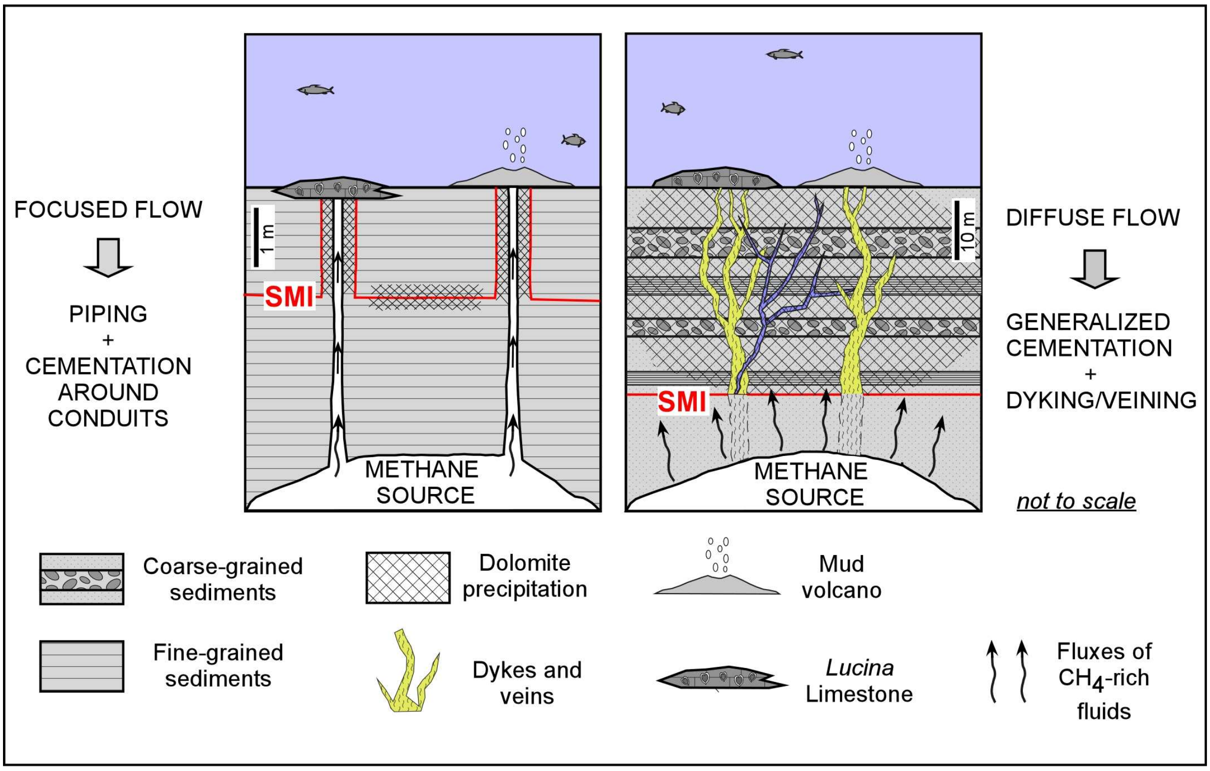

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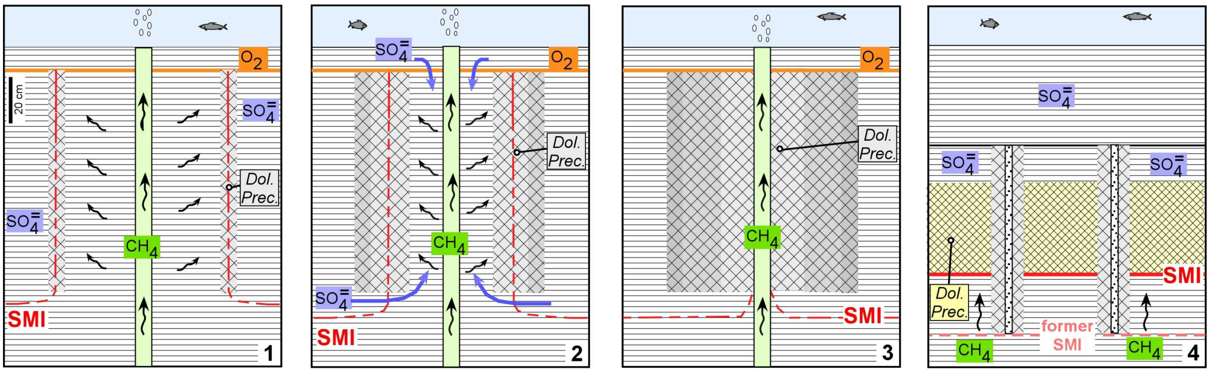

Cavagna et al. Fig. 9

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