

Petrographic evidence of the past occurrence of gas hydrates in the Tertiary Piedmont Basin (NW Italy)

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Abstract Methane-derived rocks in Monferrato and the Tertiary Piedmont Basin (NW Italy) consist of seep carbonates, formed by gas seepage at the seafloor, and macroconcretions resulting from the cementation of buried sediments crossed by gas-rich fluids. These rocks are characterized by both negative $\delta^{13}\text{C}$ values and a marked enrichment in $\delta^{18}\text{O}$. Petrographic features not commonly described and that point to enigmatic depositional and diagenetic conditions have been observed in both types of rocks: inhomogeneous distribution of cements within cavities; dolomite crystals floating within cavity-filling calcite spar; non-gravitational fabrics of internal sediments plastering cavity walls; open framework within microbial crusts. These features suggest the former presence of gas hydrates in sediments. During their dissociation, new space was formed and filled with authigenic carbonates or injected sediments. Analogous mechanisms of clathrate freeze-and-thaw processes have been inferred for the genesis of zebra and stromatactis structures and particular kinds of carbonate breccias. The term melt-seal structure is proposed for this kind of diagenetic structure. The fabrics of gas hydrates and the geochemical conditions of sediments, in turn depending on the relative rates of supply of methane-rich fluids and normal seawater, conditioned the final aspect of the rocks.

Introduction

Gas hydrates are ice-like crystalline compounds of water and gas, their stability depending on temperature, pressure and the availability of gas and water (e.g. Kvenvolden 1998; Beauchamp 2004). Variations of these parameters, due to different processes such as sea-level decline, tectonic uplift and temperature changes, can induce the destabilization of hydrates. In the last decade, much research has been made on methane hydrates for three main reasons: gas hydrates are an important potential energy resource (e.g. Collett 2002; Milkov 2004); methane is an effective greenhouse gas (e.g. Dickens 2003); the sudden release of huge amounts of gas, delivered by gas hydrate dissociation, may trigger large-scale landslides on continental margins (e.g. Haq 1993; Paull et al. 1996; Mienert et al. 1998, 2005).

Gas hydrates have been directly observed or even sampled on present-day seafloors and are clearly imaged on seismic profiles as bottom simulating reflectors (e.g. Sain et al. 2000; Pecher et al. 2001). Much less, however, is known about the past occurrence of gas hydrates in stratigraphic successions exposed on land (e.g. Pierre et al. 2002).

Anaerobic oxidation of methane (AOM), accomplished by consortia of methane-oxidizing archaea and sulphate-reducing bacteria, is a well-known process leading to abundant calcite, aragonite and/or dolomite precipitation (e.g. Boetius et al. 2000; Meister et al. 2007, 2008); authigenic carbonates have actually been described to form within or in proximity to gas hydrates (e.g. Greinert et al. 2001; Teichert et al. 2005; Mazzini et al. 2006) and have been named clathrites (Bohrmann et al. 2002). Because of the isotope fractionation inherent in gas hydrate formation, the $\delta^{18}\text{O}$ signature of these carbonates allows to relate them to gas hydrate. In particular, negative $\delta^{18}\text{O}$ values may be associated to gas hydrate formation, whereas positive values are related to dissociation

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events (e.g. Aloisi et al. 2000; Pierre and Rouchy 2004; Clari et al. 2004). Therefore, the O isotope signature of fossil CH₄-derived carbonates is the only means so far available to infer a possible role of gas hydrates in their genesis, even though other mechanisms, such as illitization of smectite, can also be called upon to explain the ¹⁸O fractionation (Dählmann and de Lange 2003). Clathrites have been described only macroscopically, however, and to date detailed microscopic observations have not been published and illustrated.

CH₄-derived rocks have been known for a long time in Northern Italy (e.g. Clari et al. 1988, 1994; Taviani 1994; Ricci Lucchi and Vai 1994; Terzi et al. 1994). In the Tertiary Piedmont Basin, they occur in several places scattered over a very wide area (Fig. 1), as carbonate-rich masses of various sizes (dm³ to hm³) at different stratigraphic levels. Given the richness of examples, these rocks have been recently reanalysed, in the light of the current state of knowledge concerning seeps and gas hydrates along modern continental margins. In particular, it has been pointed out that gas hydrates are not always massive but may show porous fabrics (e.g. Bohrmann and Torres 2006), that the gas hydrate stability zone is not an impermeable barrier but can be crossed by gas-charged fluids, and that gas hydrate dissociation may proceed at the same level side by side with gas hydrate formation (e.g. Liu and Flemings 2006). In such settings, AOM can trigger the precipitation of authigenic carbonates within the primary pores of gas

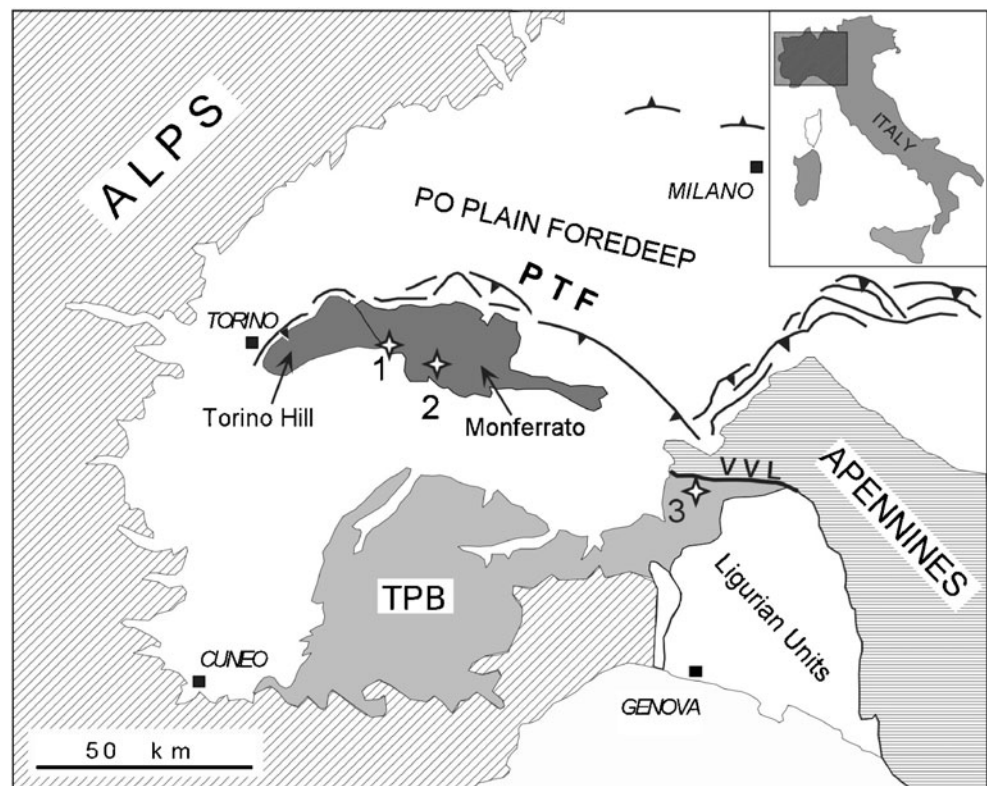
hydrates and/or in new pores that are progressively generated by gas hydrate dissociation. It may be envisioned that these carbonate cements precipitating along with hydrate dissociation should be characterized by geometries and distributions that contrast with those commonly seen in cements growing in pores filled only with pore-water. The purpose of this paper is to search for unusual petrographic features that could be referred to this process. Such structures have only scantily been reported in the literature, and would represent novel direct evidence of a fossil gas hydrate stability zone in ancient sedimentary successions.

Materials and methods

The studied methane-derived carbonate-rich rocks have been first observed and described in outcrop, with particular attention to the geometry of the lithified bodies and to the relationships with the host sediments. Hundreds of samples have been collected through the years and several tens of thin sections prepared from selected specimens.

Petrographic studies were carried out by plane and cross polarized light microscopy and with the aid of cathodoluminescence using CITL 8220MK3 equipment (working conditions: about 17 kV and 400 μA). Carbonate (calcite, dolomite, aragonite) and non-carbonate phases (pyrite,

Fig. 1 Structural sketch map of NW Italy (modified from Bigi et al. 1990) and location of the studied sections: 1 Marmorito, 2 Alfiano Natta, 3 Ripa dello Zolfo. TPB Tertiary Piedmont Basin, PTF Padane Thrust Front, VVL Villalvernia–Varzi Line



silicates) were identified by means of an EDS microprobe Link System connected to a scanning electron microscope (Cambridge S-360). SEM morphological observations were performed on both broken chips and slightly etched polished surfaces. Thin sections were analysed further for their UV-fluorescence, to reveal the occurrence and distribution of organic matter, by using ultraviolet light (illumination source 450–490 nm) under a Nikon microscope with a UV-2A filter block.

Tens of samples have also been prepared for C and O stable isotope analyses: the carbonate fraction was analysed following the classical method of McCrea (1950), according to which carbonate powder reacts under vacuum conditions with 99% orthophosphoric acid at 25°C (time of reaction: 4 h for calcite and 7 h for dolomite). The $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ ratios of the CO_2 obtained were analysed by means of a Finnigan MAT 250 mass spectrometer. The isotopic ratios are expressed as $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ per mil relative to the PDB standard; the analytical error is $\pm 0.5\%$ and $\pm 0.1\%$ for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ respectively.

Geological setting

The Tertiary Piedmont Basin is composed of upper Eocene to Messinian sediments deposited unconformably after the mesoalpine collisional event in both alpine metamorphic rocks and Apennine Ligurian units (e.g. Gelati and Gnaccolini 1988; Castellarin 1994; Mutti et al. 1995; Roure et al. 1996). Deposition of these sediments was strongly influenced by synsedimentary compressional tectonics related to the building of the Apennine thrust belt. As a consequence, several tectono-sedimentary domains (the Tertiary Piedmont Basin to the south and the Monferrato and Torino Hill to the north), resting on different crustal blocks and characterized by different sedimentary features, developed during the Cainozoic (Piana and Polino 1995; Clari et al. 1995). Although the relationships among these domains are masked by Pliocene to Quaternary deposits (Fig. 1), seismic profiles show that their boundaries correspond to long-lived, major tectonic structures (e.g. Biella et al. 1997).

Both the Tertiary Piedmont Basin and the Monferrato–Torino Hill are overthrust to the north onto the Po Plain foredeep along the Late Neogene to Quaternary Padane thrust fronts (Fig. 1), presently buried below the Quaternary Po plain deposits (Dalla et al. 1992; Castellarin 1994; Falletti et al. 1995).

The studied samples have been collected both in Monferrato and in the eastern sector of the Tertiary Piedmont Basin, in the Ripa dello Zolfo area. The stratigraphic setting of these two sectors is briefly illustrated below (for more details, see Clari et al. 2009; Dela Pierre et al. 2009).

Monferrato

The Monferrato stratigraphic succession ranges in age from Late Eocene to Late Miocene (Messinian) and consists mainly of terrigenous sediments that unconformably overlie Mesozoic mélanges (Ligurian units) originating from the Alpine accretionary prism (e.g. Pini 1999). Deposition of Oligocene and lower Miocene sediments was controlled by a complex seafloor topography produced by NW–SE-trending transpressive faults (Piana and Polino 1995; Clari et al. 1995; Piana 2000). The thickest successions consist of fine-grained deep water facies deposited in fault-bounded subbasins. On intervening structural highs (e.g. the Marmorito and Villadeati–Alfiano Natta palaeohighs, where the studied samples were collected), coarse fan delta sediments were deposited. These sites are also characterized by the occurrence of erosional unconformities and extensive hiatuses e.g. the Oligocene–Messinian boundary of the Villadeati–Alfiano Natta palaeo-high (Clari et al. 1995; Dela Pierre et al. 2003). Middle to upper Miocene sediments consist of outer shelf to slope fine-grained sediments of Langhian–Tortonian age that are unconformably overlain by an upper Messinian mélange (Valle Versa Chaotic Complex; Dela Pierre et al. 2002, 2003) comprising blocks of different nature (Ca sulphates and a wide range of carbonate facies) floating in a fine-grained matrix.

Ripa dello Zolfo

The Ripa dello Zolfo area is located in the eastern part of the Tertiary Piedmont Basin (Fig. 1), south of the Villalvernia–Varzi Line, an E–W-striking strike-slip fault that was considered as the Alps–Apennine boundary (Elter and Pertusati 1973).

The stratigraphic succession exposed here ranges in age from Oligocene to Messinian and unconformably overlies Ligurian Cretaceous turbidites (Ghibaudo et al. 1985). It starts with coarse-grained Oligocene shallow water sediments, followed by upper Oligocene to middle Miocene deep water facies.

The upper Miocene part of the succession consists of Tortonian–lower Messinian fine-grained outer shelf to slope sediments (Sant’Agata Fossili Marls) that are unconformably overlain by the Valle Versa Chaotic Complex (upper Messinian). The latter is followed by brackish water deposits known as Conglomerati di Cassano Spinola (upper Messinian).

The Sant’Agata Fossili Marls, which host the studied samples, consist of two members (Clari and Ghibaudo 1979):

- the lower member (Tortonian), about 180 m thick, consists of outer shelf sandstones and muddy siltstones (Ghibaudo et al. 1985). At its top occur several

- multiple intraformational discordances, corresponding to slump scars (Clari and Ghibaudo 1979);
- the upper member (lower Messinian) is about 80 m thick and consists of homogeneous blue grey silty marls with thin bedded turbidites, indicative of a slope depositional environment (Ghibaudo et al. 1985).

This vertical evolution is related to the deepening of the basin, interpreted to be of tectonic origin, as suggested by the occurrence of slump scars resulting from oversteepening of a gentle slope and consequent downslope sliding of variably thick sediment packages (Ghibaudo et al. 1985).

The Tertiary Piedmont Basin clathrites

The present research was focussed on three selected outcrops, two in Monferrato (Marmorito and Alfiano Natta) and one in the eastern sector of the Tertiary Piedmont Basin (Ripa dello Zolfo; Fig. 1). Monferrato is one of the first places in the world where the fossil products of CH₄-rich fluid seepage were identified (Clari et al. 1988). Recent developments of research in this area and the discovery of new outcrops in the eastern sector of the Tertiary Piedmont Basin allowed to distinguish two types of methane-derived rocks: (1) macroconcretions, generated by localized precipitation of carbonate cements within the pores of buried sediments located at variable depths below the seafloor, and along the upward flow path of gas-rich fluids, and (2) seep carbonates, formed by the expulsion of gas-rich fluids at the seafloor (Clari et al. 2009). Both these types of rocks are characterized by negative $\delta^{13}\text{C}$ values (up to -52% PDB) and, especially in the macroconcretions, systematically positive $\delta^{18}\text{O}$ values (up to $+7\%$ PDB; for summary of isotopic data, see Clari et al. 2009).

Monferrato

At Alfiano Natta and Marmorito, macroconcretions form variably large indurated masses, up to 100,000 s of m³. They have developed within fan delta deposits consisting of interbedded conglomerates, sandstones and mudrocks of Oligocene and Aquitanian age respectively. At Marmorito, they grade upwards to lower Burdigalian diatomites, in turn followed by poorly exposed thin Messinian siltites. At Alfiano Natta, by contrast, they are overlain unconformably by upper Messinian chaotic deposits (Valle Versa Chaotic Complex; Dela Pierre et al. 2002, 2007). The strong induration of macroconcretions is due to the presence of an abundant intergranular dolomite cement. A striking feature of the macroconcretions is the occurrence of a pervasive network of mainly subvertical clastic dykes and veins. Dykes vary from millimetres to some decimetres in

width and are filled with a variety of sediments ranging from mudstones to sandstones; brecciated textures result from polyphase opening of the same fracture. Veins show complex carbonate cement infillings with a variety of mineralogies (aragonite, calcite, dolomite) and morphologies (fibrous, sparry, peloidal). These macroconcretions have been inferred to have developed during Messinian deformation and massive fluid expulsion through older sediments (Clari et al. 2009).

In the surroundings of Marmorito, typical seep carbonates (*Lucina* Limestone), consisting of cream-coloured marly limestones and characterized by a variably dense packing of chemosynthetic bivalves (*Lucina* sp.), have also been reported (Clari et al. 1988, 1994). They are commonly found as ex situ blocks scattered at the base of present-day slopes. The recent finding of an in situ seep carbonate mass within silty outer shelf marls allows to date this seepage event (less widespread and effective than the Messinian one) to the Langhian (Clari et al. 2009).

Ripa dello Zolfo

Different methane-derived carbonate-rich rocks, including *Lucina* limestones and concretions, occur at Ripa dello Zolfo in the eastern sector of the Tertiary Piedmont Basin, within the upper member of the Sant'Agata Fossili marls (lower Messinian) that consists of silty slope marls (Ghibaudo et al. 1985; Dela Pierre et al. 2009). A large variety of concretions have been observed, among which bed-parallel ones up to 50 cm thick and with a lateral extent of some tens of metres. In these concretions, no remains of chemosynthetic organisms (such as lucinoid bivalves and tubeworms) or evidence of seafloor exposure occur. A Messinian phase of gas-rich fluid expulsion has been inferred also for these concretions (Dela Pierre et al. 2009).

Microstructures

In all methane-derived rocks of Monferrato and Ripa dello Zolfo, there is ample evidence of enigmatic features that cannot be explained with common knowledge of sedimentary petrology—in our opinion, they suggest the former presence of gas hydrates. Selected examples are described below and an interpretation proposed.

Pinch outs of fringing cements

These structures have been observed in typical seep *Lucina* limestones at Marmorito in Monferrato, which show $\delta^{13}\text{C}$ values of -25 to -35% PDB and $\delta^{18}\text{O}$ values of $+0.1$ to $+0.9\%$ PDB. A common feature is the presence of irregular cavities with rounded edges and up to 2 cm wide, filled with cements (Fig. 2). These cavities are interpreted as fluid

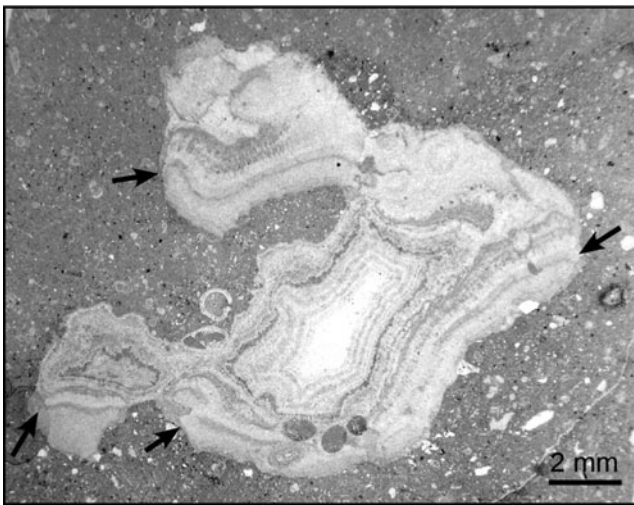


Fig. 2 Marmorito, *Lucina* Limestone. Cross section of a fluid conduit likely developed on a burrow. Except for a few faecal pellets in the centre bottom, it is completely filled with cements. The first generations do not encrust all the cavity walls but stop abruptly against them (arrows). Thin section

conduits, most probably following former burrows, developed within semilithified fine-grained sediments in close proximity to the sea bottom (Clari and Martire 2000). Some grains, such as faecal pellets, may also be present on the cavity floor. The filling cements are mainly aragonite and inclusion-rich calcite, but microsparitic and coarse limpid sparry calcite also occur. Even though a typical centripetal growth of consecutive cement layers predominates, notable exceptions are common that are due to marked differences in the distribution of the first cement generations that coat only a part of the cavity and abruptly stop against the cavity walls (Fig. 2). By contrast, the following generations centripetally and isopachously fill the remaining void.

An even clearer example of this fabric has been observed in the bed-parallel concretions at Ripa dello Zolfo, in the eastern sector of the Tertiary Piedmont Basin (for more details, see Dela Pierre et al. 2009). These concretions are indurated due to a very finely crystalline intergranular dolomite cement ($\delta^{13}\text{C}$ -25 to -34% PDB; $\delta^{18}\text{O}$ $+6.0$ to $+7.0\%$ PDB) forming a more or less complex network of mainly bed-parallel fractures, commonly wedge-shaped and mm- to some cm-wide; from the core of the concretion, these gradually thin outwards, giving rise to features that strongly recall septarian cracks. Syneresis seems the most probable cause of fissure opening. This process is considered responsible for the opening of contractional cracks in muddy sediments, especially where it is enhanced by the decay of bacterial extracellular polymeric substances (e.g. Dewhurst et al. 1999; Hendry et al. 2006). Some of these wedge-shaped fractures are empty; others are filled with either internal sediments or carbonate cements. The latter consist of sparry dolomite and calcite ($\delta^{13}\text{C}$ -28 to -43%

PDB; $\delta^{18}\text{O}$ -5.0 to $+6.0\%$ PDB) and show a banding defined by alternating turbid and limpid layers (Fig. 3a). Cathodoluminescence helps to highlight the high complexity in the distribution of these cements (Fig. 3b). A first thin rim of dull to bright yellow dolomite fringes the crack walls isopachously (cement 1 in Fig. 3c). It is followed by a dull brown to moderate orange zoned calcite cement that does not overgrow uniformly the first dolomite rim. In particular, the first dull brown zone (cement 2 in Fig. 3c) shows marked variations in thickness and even tapers out completely. Consequently the next, orange luminescing cement zone in some portions of the fracture walls directly overlies the first isopachous dolomite rim (cement 3 in Fig. 3c). Because of this strongly inhomogeneous distribution of cement zones, adjacent fractures may show markedly different fillings, the one being almost fully plugged with the dull brown zone that, by contrast, is nearly absent in another (Fig. 3b). By analogy with the terminology used in lithostratigraphy for bed terminations, this feature will be hereafter referred to as *cement pinch out*.

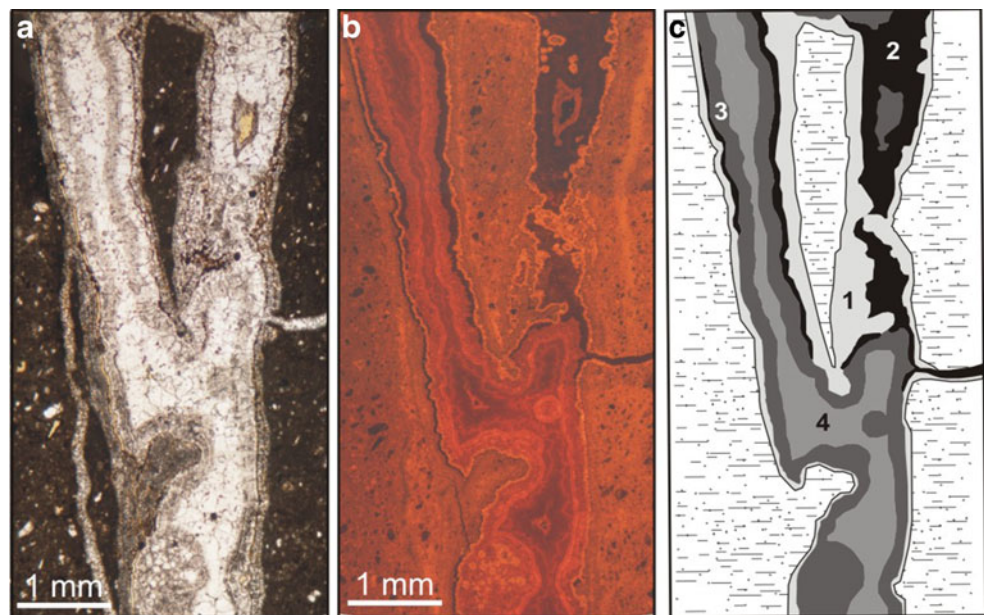
Non-gravitational fabrics in cavity fills

In the *Lucina* limestones of Marmorito, other cavities, even larger than those described above, are filled mainly with fine-grained carbonates (Fig. 4a). These internal sediments range from micrite to silt-sized pelssparites that show a loose packing and also include scattered planktonic foraminifer tests and siliciclastic grains (Fig. 4b). They are locally further characterized by an irregular lamination defined by alternation of finer and coarser laminae (Fig. 4c). Three enigmatic features characterize such sediments: some pelssparitic laminae are separated from adjacent laminae by calcite sparry cement; sediments not only cover the cavity floor but also are plastered on the lateral walls and the ceiling of the cavity, so that single laminae may be traced all around the cavity edges (Fig. 4c); where the distribution of internal sediments is discontinuous, the same sediment is observed to occur on the bottom or “stuck” to a vertical wall, and sediment and sparry cement patches are very irregularly juxtaposed (Fig. 4a). These fabrics represent incongruent geopetal structures within a single cavity and document infilling mechanisms not governed by gravity.

Dolomite crystals floating in void-filling coarse calcite spar

The Marmorito macroconcretion is crossed by a network of mainly subvertical sediment-filled dykes and cement-filled veins (Fig. 5a). Some of these are some centimetres large and show particularly complex infillings. The walls of the veins, occurring within dolomite-cemented sandstones, are rimmed by a finely crystalline to microcrystalline luminescent dolomite organized in fine laminae that follow the shape of the

Fig. 3 Ripa dello Zolfo, Marne di S. Agata Fossili. **a** Transmitted light and **b** cathodoluminescence image of a bed-parallel cement-filled fissure. **c** Simplified line drawing evidencing the main generations of cements (1–4: oldest to youngest) and their inhomogeneous thickness and distribution. Thin section



fracture walls. This rim, about 0.5 mm thick, is overlain basically by a non-drusy mosaic of equant coarse sparry calcite cement with an undulous extinction ($\delta^{13}\text{C}$ -27 to -28‰ PDB; $\delta^{18}\text{O}$ $+3.4$ to $+3.5\text{‰}$ PDB). It is moderate orange in cathodoluminescence (CL) and shows a complex sectorial zoning. Poikilotopically engulfed by this coarse calcite spar, zoned dolomite is easily recognized due to its greenish yellow to brown luminescence (Fig. 5b–d). It occurs as euhedral rhombic crystals and as sphaerulites up to 200 μm across, scattered or mainly clustered in patches up to a few mm across ($\delta^{13}\text{C}$ -35 to -40‰ PDB; $\delta^{18}\text{O}$ $+3.0$ to $+4.7\text{‰}$ PDB). Sphaerulites commonly have hollow cores that may show dumbbell shapes. Although the latter have also been obtained abiotically (Fernandez Diaz et al. 1996; Tracy et al. 1998; Warren et al. 2001), dumbbell shapes are commonly reported in bacterially induced carbonate precipitates (e.g. Buczynski and Chafetz 1991; Chekroun et al. 2004; Brehm et al. 2006). A marked greenish yellow fluorescence, which contrasts with the very weak signature of the surrounding calcite spar (Fig. 5e), shows the presence of organic matter within the authigenic carbonate and, thus, supports a microbial origin proposed previously (Cavagna et al. 1999; Clari and Martire 2000). The central part of many dolomite rhombs and sphaerulites is irregularly occupied by the orange calcite spar.

Open framework structures in microbial mats

The Alfiano Natta macroconcretion is crossed by a network of fractures that are larger, denser and more complex than those of Marmorito. The complete description of their filling is beyond the scope of this paper and here we rather focus our attention on a striking feature that is locally observed. Some fractures, about 10 cm large, show

encrustation by authigenic carbonates on the walls and injected sediment infill in the centre. The authigenic carbonates show a wide variety of mineralogies and growth morphologies and also include thin microcrystalline laminated crusts (Fig. 6a). The laminae (about 30 μm thick) tightly overlie each other and follow the micromorphology of the substrate they coat (Fig. 6b). The overall “stromatolitic” aspect of these crusts recalls calcified bacterial mats, and the bright epifluorescence of the single laminae confirm the fundamental contribution of microbial communities in their genesis (Fig. 6c). Commonly, however, the laminae divert and are widely spaced, giving rise to an irregular fenestral fabric, with fenestrae up to a few millimetres large. Some fenestrae are very smooth and ellipsoidal; others are quite irregular and show some evidence of internal subdivision due to the inward branching of single microcrystalline laminae that surround them (Fig. 6a). The fenestrae are filled with a dolomite and calcite crystal mosaic zoned in CL (Fig. 6d, e). These cements are partly turbid and partly limpid; the turbid parts occur both as discontinuous rims and as isolated patches, and commonly preserve “ghosts” of a fibrous fabric clearly caused by aragonite recrystallization (Fig. 6f). All these carbonates show negative C isotopes and rather positive O isotopes ($\delta^{13}\text{C}$ -17.0 to -21.9‰ PDB; $\delta^{18}\text{O}$ $+1.9$ to $+5.9\text{‰}$ PDB).

Geopetal fill of mouldic cavities of former clasts

In the Alfiano Natta macroconcretion, some dykes consist of grain-supported coarse muddy sandstones in which no cement-filled pores are recognizable because of the abundance of the muddy matrix (Fig. 7a). The rock is lithified by a finely crystalline dolomite grown in the pores of the matrix ($\delta^{13}\text{C}$ -16.2 to -22.3‰ PDB; $\delta^{18}\text{O}$ $+5.0$ to $+6.0\text{‰}$

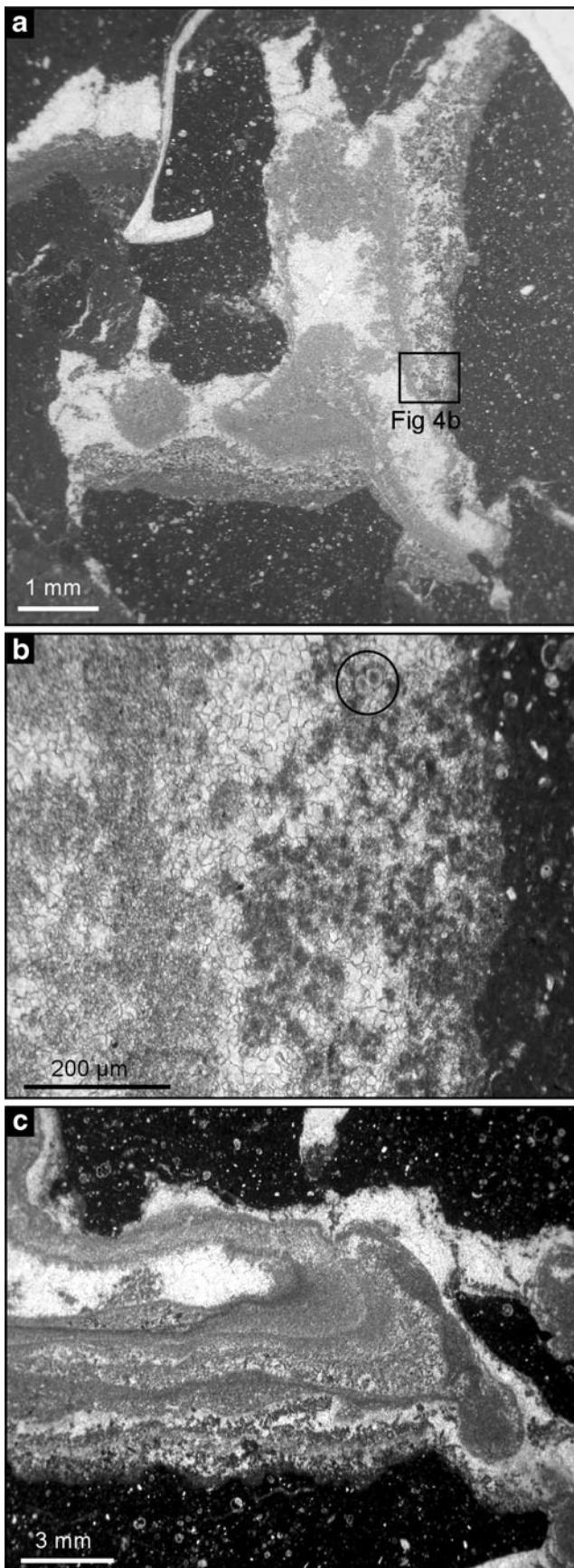


Fig. 4 Marmorito, *Lucina* Limestone. **a** Sediment- and cement-filled cavity. Note the distribution of sediments and cements at the bottom of the cavity and to the *right*, which give rise to two incongruent geopetal structures in the same cavity. **b** Close up of **a**. Note the loose packing of peloids and the presence of scattered clastic grains (foraminifer test encircled). Thin section. **c** Laminated, peloidal to micritic sediments partially infilling a cavity. Note that some laminae may be followed from the floor to the ceiling of the cavity. Thin section

PDB). In cathodoluminescence, this dolomite is zoned and ranges from orange to brown. Clastic grains of the sandstone comprise serpentinite, quartz, K feldspars, plagioclase and lithic fragments of Mesozoic micritic limestones. In addition, other carbonate grains occur, angular to subrounded in shape and 0.5–1.0 mm across. Some show evidence of internal complexity due to the presence both of fine-grained sediment, also containing framboidal pyrite and cemented by finely crystalline dolomite (crystals 10–30 µm), and of limpid coarser sparry dolomite (crystals up to 400 µm), locally showing a drusy fabric (Fig. 7b–d); commonly, a hollow core is also present. The finely crystalline dolomite systematically occurs in the lower part and the coarse dolomite in the upper part, giving rise to typical geopetal structures. Cathodoluminescence shows that a first generation of brightly luminescing dolomite nucleated as scattered crystals in the sediment and formed a thin rim growing inwards from the outer edge (Fig. 7c). It is overgrown by a moderately luminescing brown zone (II), and a very dull brown zone (III) that occurs only in the limpid coarse dolomite. These features indicate that these are not primary clastic grains but mouldic secondary pores generated by dissolution and later filled in a rather complex way.

Other carbonate grains also occur that are completely composed of the finely crystalline dolomite mosaic, identical in size and CL zoning to the lower part of the geopetally filled mouldic pores (Fig. 7e, f).

Discussion

Despite marked differences, all the diagenetic fabrics described above share a common feature, i.e. they all deviate from basic rules in sedimentary petrology. In some cases, what should be there is not found—for example, irregular layers of pinching out cements (Fig. 3) occurring on the walls of cavities indicate that something hindered formation of what should form in a water-filled void, i.e. uniform rims of isopachous cements. In other cases, what should not be there is found—dolomite crystals grown in the middle of a cavity subsequently plugged by calcite spar, i.e. in the apparent absence of a substrate (Fig. 5); laminated sediments plastering cavity walls, rather than gravitationally accumulating on the bottom (Fig. 4). The

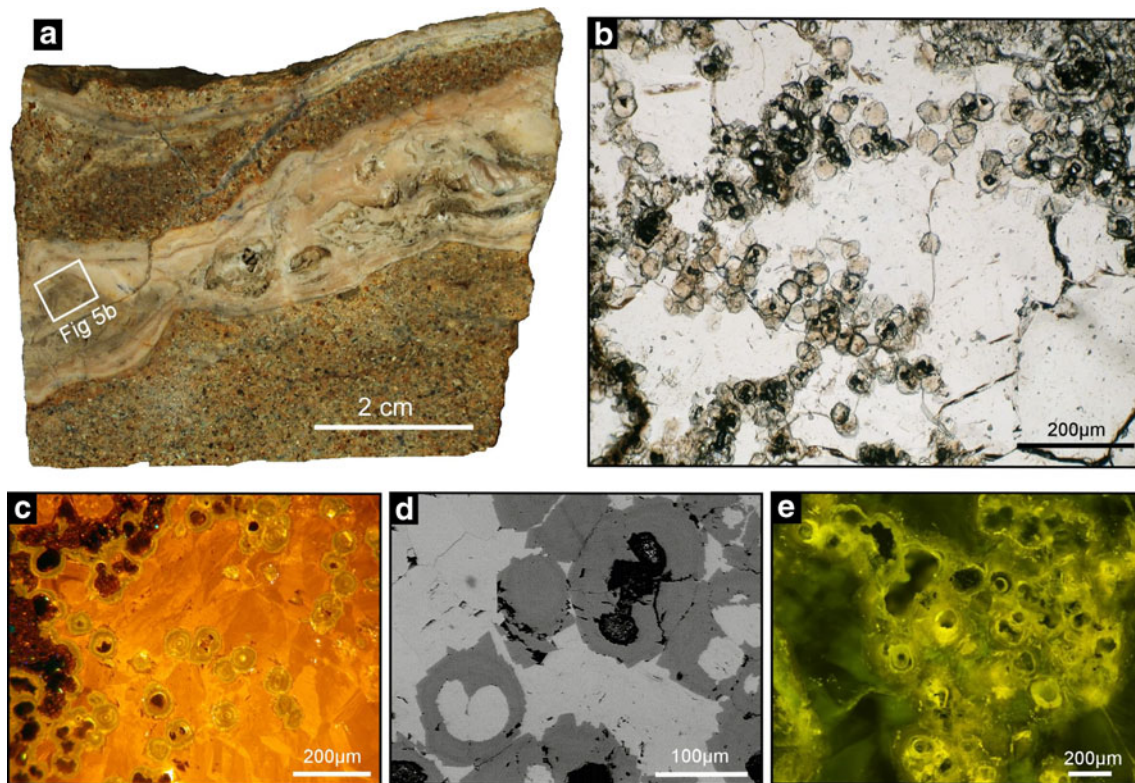


Fig. 5 Marmorito macroconcretion. **a** Polished slab of a sample of Marmorito Sandstone crossed by a vein with a complex cement infilling. **b** Dolomite sphaerulites “floating” in a coarse calcite spar. Note that most show hollow cores locally with a dumbbell shape (arrows). Thin section. **c** Cathodoluminescence image showing the contrast between the finely zoned, greenish yellow dolomite and the

orange yellow calcite spar. Thin section. **d** Backscattered electron image of the dolomite sphaerulites (dark grey). Note that the cores, locally dumbbell-shaped, may be hollow (black) or filled with calcite (light grey). Polished thin section. **e** UV epifluorescence image showing the bright colour of the dolomite sphaerulites contrasting with the weak fluorescence of the surrounding calcite spar. Thin section

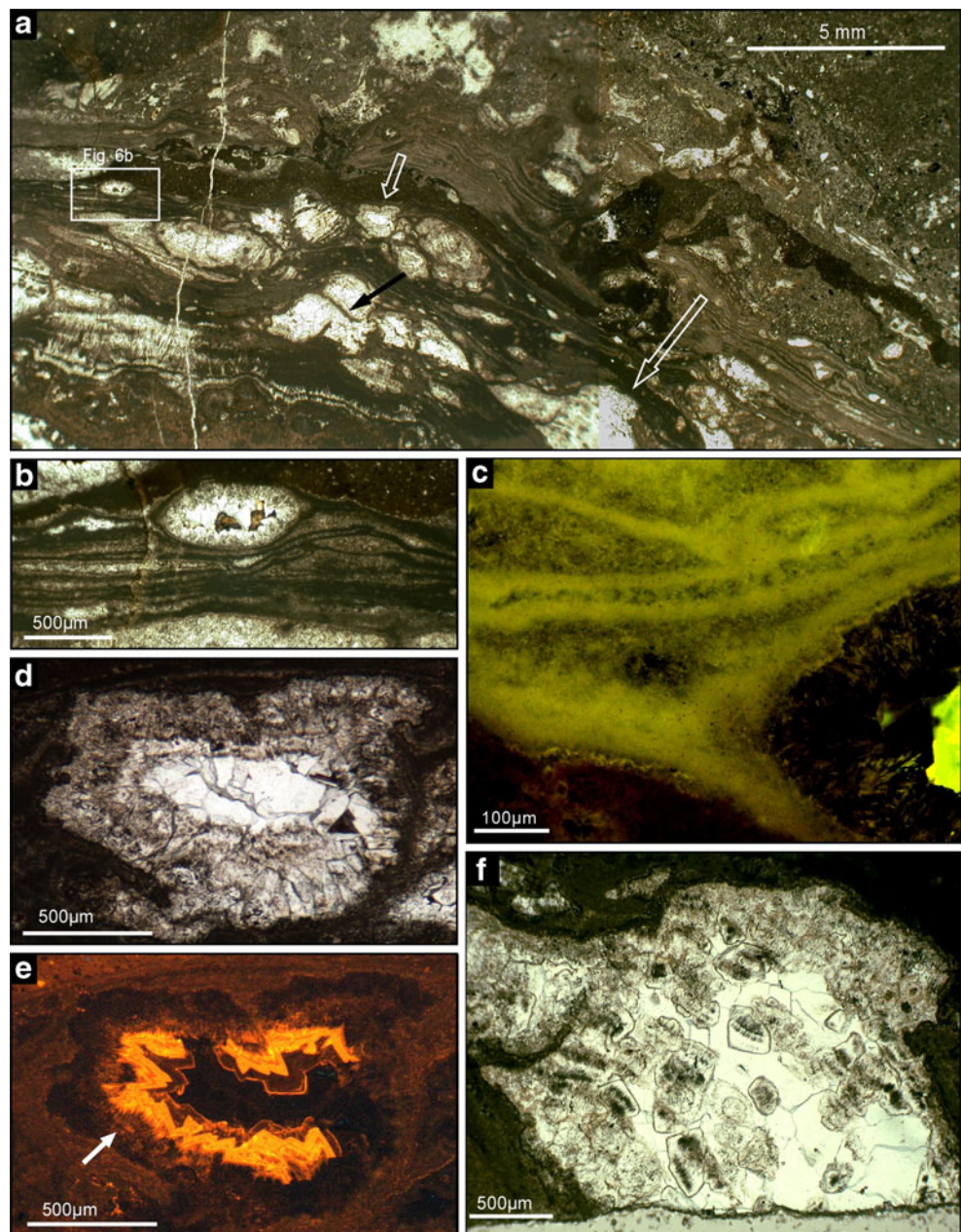
most likely process that could explain all these fabrics, as well as the geopetal fill of mouldic cavities in sandstone dykes, is dissolution of a metastable phase that fully or partly occupied the cavities; this phase would represent a solid substrate that could have been coated by microbial communities or encrusted by authigenic carbonates, and that then dissolved, leaving voids of various sizes and shapes. The geometry of these voids is not consistent with any of the growth morphologies of easily dissolvable carbonates such as aragonite or Mg-calcite. Considering that, on the basis of the isotope data presented, the carbonate fraction of the rocks in which these fabrics are found is all methane-derived, we hypothesize that the metastable phase could correspond to gas hydrate. The systematically positive or strongly positive $\delta^{18}\text{O}$ values of the authigenic carbonates contribute to supporting this hypothesis.

In this light, each of the described features may be explained in a relatively simple way by calling upon the same basic process related to the formation and dissociation of gas hydrates.

Pinching out cements grew in cavities during the dissociation of gas hydrates that previously fully occupied them. Dissociation started from the walls of the voids and

proceeded centripetally at relatively slow rates (Fig. 8). This allowed carbonate precipitation to take place concomitantly with gas hydrate dissociation, at every step filling the newly generated free spaces that extended from the cavity walls and the external surface of the still stable gas hydrate mass. Slightly changing geochemical conditions are recorded by different cathodoluminescence colours of the authigenic carbonates. A possible alternative for the genesis of the Ripa dello Zolfo pinching out cements could be cementation during progressive opening of tectonic cracks. This hypothesis has been ruled out for two main reasons: (1) tectonic features, not ubiquitously recognizable, are represented by dm-spaced cleavages that cross all the beds and show a typical rheologically controlled refraction, from subvertical in more cemented layers to more gently sloping in the marls; thus, these are clearly distinguishable from the irregular but mainly subhorizontal, wedge-shaped, septarian-like cracks hosting the pinch out cements; (2) the cracks are lined by the isopachous rim of brightly luminescing cement 1; should the cracks have opened by successive steps, the first cement crust would have been broken and the fragments would have fallen to the floor of the fissure. Moreover, a tectonic origin cannot be applied

Fig. 6 Alfiano Natta macroconcretion. **a** Photomosaic of part of the infill of a cm-large fracture (centre of the fracture to the top). Note the finely laminated fabric with stromatolite-like wavy geometry of the laminae, and the occurrence of irregularly shaped or ellipsoidal cement-filled fenestrae. Arrow points to branching microbial laminae. The short and long open arrows point to the locations of **d** and **f** respectively. Thin section. **b** Close up of an ellipsoidal fenestra “wrapped” in regular, micritic microbial laminae. Thin section. **c** UV epifluorescence image of the left-hand part of **b** evidencing the marked fluorescence contrast of the laminae (bright) and the crystalline cement (black). **d** Transmitted light and **e** cathodoluminescence (CL) images of an irregularly shaped fenestra. Note the turbid rim of the walls, dull in CL, with preserved “ghosts” of pristine fibrous aragonite (arrow); the cavity is plugged with bright orange to brown calcite and very dull, limpid dolomite. Thin section. **f** Close up of the fenestra indicated with a long arrow in **a**. Note portions of recrystallized aragonite fans rimming the cavity and scattered within calcite spar. Thin section



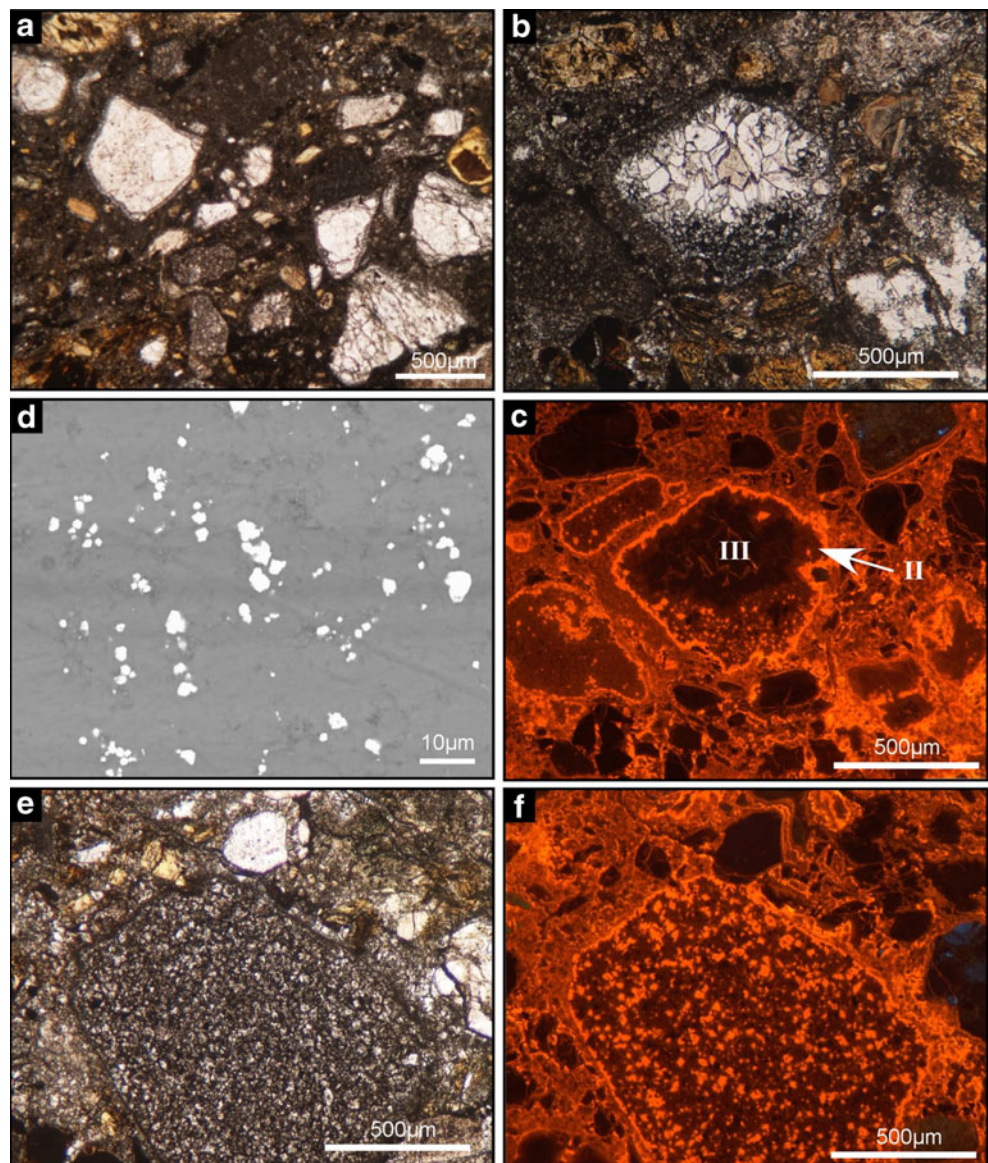
for the Monferrato pinching out cements that grow within small, rounded cavities interpreted as fluid conduits.

Non-gravitational fabrics, displayed by internal sediments partially filling cavities, record the disappearance of gas hydrates plugging fluid conduits, each step of progressive dissociation being followed by the reactivation of flow of fluids entraining fine-grained sediments and triggering carbonate precipitation both as microbially induced microcrystalline calcite or dolomite at the hydrate surface or even within it, and as intergranular sparry cement (Fig. 9). Different patterns of dissociation, i.e. random and more or less regularly centripetal, resulted in non-continuous patches of internal sediments and relatively continuous laminated sediments parallel to cavity walls respectively.

For the *dolomite crystals floating in calcite spar*, the following points can be made:

- Dolomite rhombs and sphaerulites, limpid and subtly zoned in CL, clearly precede the coarse calcite spar in which they are poikilotopically engulfed.
- Dolomite rhombs and sphaerulites, especially at the first stages of growth, did not form a self-supporting framework and, thus, could not have developed and “floated” in an empty cavity in the absence of a solid substrate.
- No relics or ghosts of a carbonate precursor are observable in the orange luminescing, limpid calcite spar, even if aragonite precipitation and subsequent dissolution are frequently observed in Monferrato CH₄-derived

Fig. 7 Alfiano Natta macroconcretion. **a** General aspect of a sandstone dyke. Note the abundance of muddy matrix among sand grains and the absence of intergranular pores. Thin section. **b** Transmitted light (TL) and **c** cathodoluminescence (CL) images of a geopetally filled mouldic cavity. Note the brightly luminescing, finely crystalline dolomite growing within the sediment at the *bottom* and forming a rim at the outer edge, and the dull, limpid sparry dolomite (II + III) filling the upper part of the void. Thin section. **d** Backscattered electron image of the sediment in the lower part of the mouldic cavity in **b**. The *white spots* are framboidal pyrite. **e** TL and **f** CL images of a mud clast cemented by finely crystalline dolomite. Note that crystal size and CL zoning are the same as in the lower part of the geopetally filled mouldic pores in **b**, **c**



carbonates (Clari and Martire 1995; Clari et al. 2009). This allows to rule out that the solid substrate necessary to sustain the rhombs and spherulites could be a former aragonite cement subsequently dissolved.

On the basis of these considerations, the following evolution may be sketched (Fig. 10). Fractures opened within dolomite-cemented sandstones and were at first lined by microbial mats that promoted the precipitation of microcrystalline laminated carbonates. Gas hydrates, locally characterized by a fine bubble fabric, plugged the open spaces. When they started to dissociate, dolomite precipitated around coccoidal microbial colonies within the hydrate pores. Coarse calcite spar eventually precipitated in all the open spaces after the complete disappearance of gas hydrates. The scarcity of CL concentric zoning of these cements could suggest a rather rapid precipitation, i.e. under relatively stable geochemical conditions.

Open framework structures, similar to those described above, have also been reported in the literature as primary voids within microbial carbonates. They are related mainly to light-dependant cyanobacteria both inferred in ancient submarine environments affected by methane seepage and stromatolite-like growth (Gomez-Perez 2003), and observed in modern travertines found at thermal springs (Arp et al. 1998; Pache et al. 2001). In the latter, dehydration and shrinkage of the organic mucus (extracellular polymeric substance) of the microbial mats and the development of gas bubbles resulted in the formation of irregular and lenticular voids. Even though the role of this mechanism cannot be ruled out, the general context (fractures occurring within lithified sediments at a certain depth below the seafloor) and the positive $\delta^{18}\text{O}$ values of the authigenic carbonates lead to consider another mechanism.

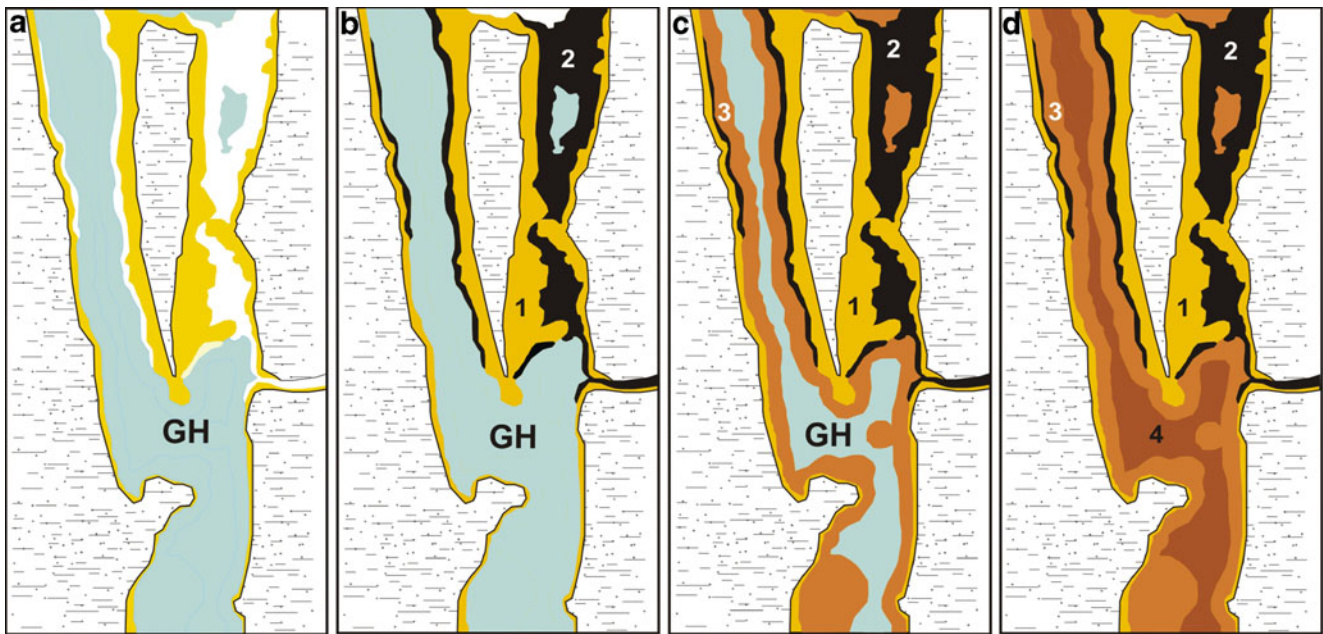
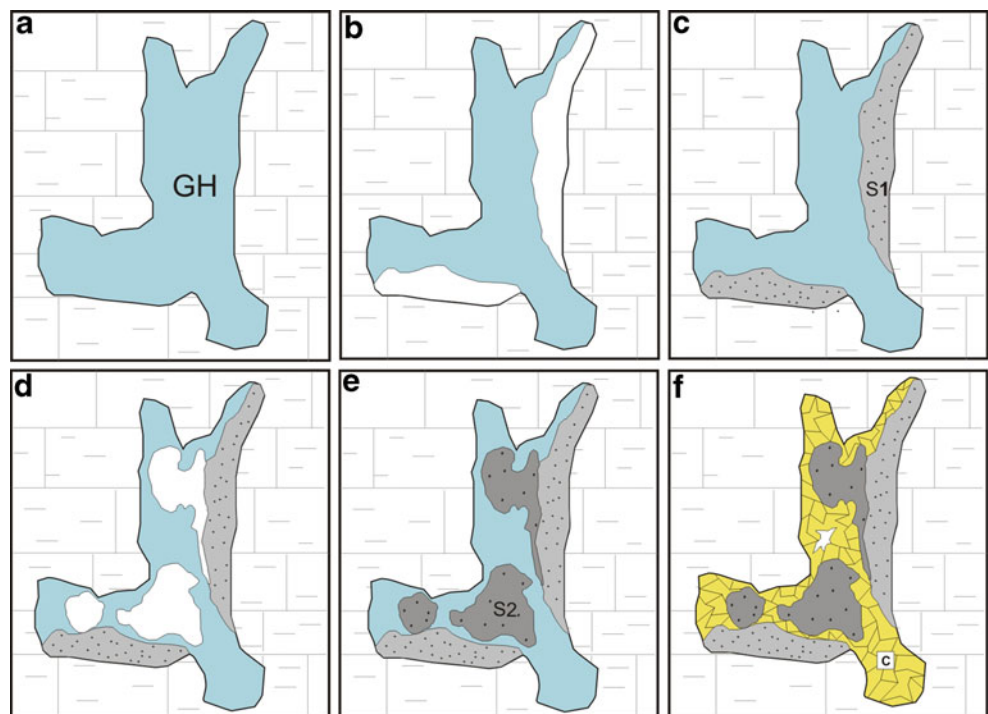


Fig. 8 Simplified sketch of the step-by-step evolution of pinch out cements (for details, see text)

The geometry of the fenestral fabrics in microbial mats strongly and directly recalls the vacuolar structure displayed by some gas hydrates recovered from present-day continental margins (Bohrmann et al. 1998; Bohrmann and Torres 2006; Mazzini et al. 2006). It is thus possible to envisage that gas hydrates, grown in a fracture, at least locally showed a vacuolar fabric that could allow gas-rich fluids to flow through it (Fig. 11). The hollows were then filled with

aragonite. Dissociation of gas hydrates then started and proceeded at a slow rate. Concomitantly, authigenic carbonates precipitated, as microcrystalline crusts, at the gas hydrate retreating surface and around the aragonite-filled former vacuoles, replacing their delicate walls and permanently recording the 3D framework. Aragonite was then partially dissolved, the relics recrystallized to calcite or dolomite preserving ghosts of the pristine fibrous habit, and the voids

Fig. 9 Simplified sketch of the step-by-step evolution of non-gravitational structures (cf. Fig. 4a; for details, see text). *s1, s2* Internal sediments, *white area* open space, *GH* gas hydrates, *c* sparry calcite



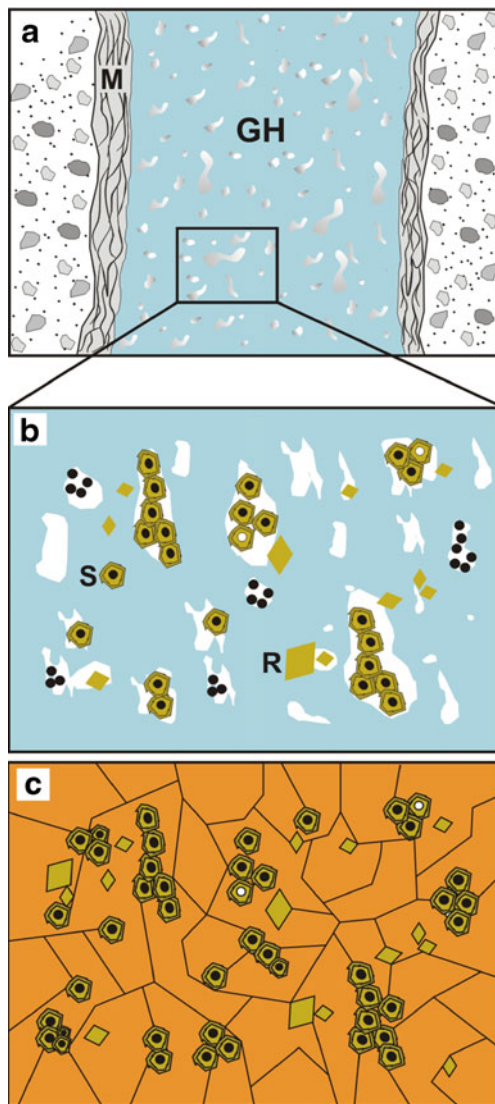


Fig. 10 Simplified sketch of the step-by-step evolution of dolomite crystals floating in calcite spar (for details, see text). *Black dots* Microbial colonies, *S* dolomite sphaerulites, *R* dolomite rhombs, *GH* gas hydrates, *M* microbial mat

filled with zoned sparry calcite and dolomite. The result is a complex crust with irregularly laminated microcrystalline carbonate replacing gas hydrate, and sparry calcite and dolomite forming moulds of hydrate vacuoles.

Finally, the *geopetally filled mouldic cavities* cannot be due to the dissolution of labile grains such as feldspars, plagioclase and clastic carbonates that are perfectly preserved in these rocks; also aragonite clasts are excluded because the rounded edges cannot be reconciled with the fibrous habit of aragonite that would generate very irregular, spiky margins as observed in other dykes at Alfiano Natta. The geopetally filled mouldic cavities, by contrast, may be interpreted as small clasts of almost pure gas hydrates (Fig. 12). They were formed within clastic dykes, disrupted and transported upwards by a new phase of violent fluid and sediment

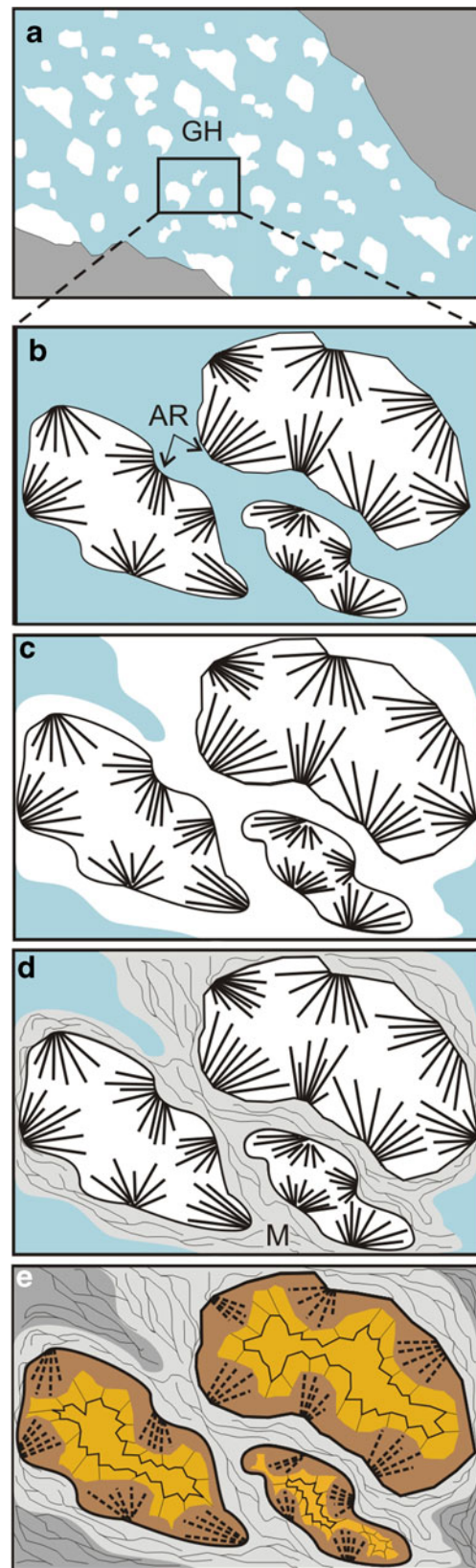
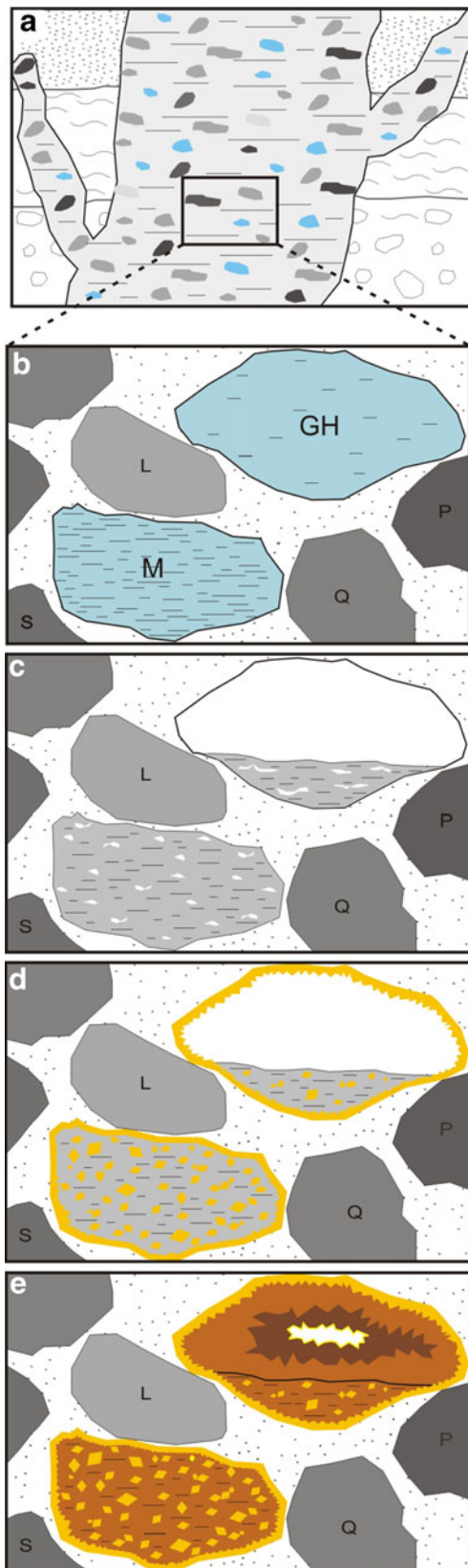


Fig. 11 Simplified sketch of the step-by-step evolution of microbial mats (for details, see text). *AR* Aragonite fans, *GH* gas hydrates, *M* microbial mat, *white area* open space, *orange yellow* sparry cements



◀ **Fig. 12** Simplified sketch of the step-by-step evolution of geopetally filled mouldic cavities and dolomite-cemented mud clasts (for details, see text). *Q* Quartz, *P* plagioclase, *S* serpentinite, *L* limestone clast, *GH* gas hydrates, *M* clathrate-cemented mud clast, yellow orange brown consecutive dolomite generations

injection. When gas hydrate started to dissociate, a void was essentially left: clay particles, previously floating in the clathrate, fell to the floor under the effect of gravity and gave rise to geopetal structures. Framboidal pyrite and brightly luminescing finely crystalline dolomite, both related to anaerobic oxidation of methane, formed within this sediment flooring the mouldic pore; luminescing dolomite also rimmed the cavity walls. Eventually, coarser sparry dolomite almost completely plugged the remaining void. The fine-grained dolomite clasts may rather be interpreted as small clasts of clathrate-cemented muds. Dissociation of gas hydrates left mud clasts with a high porosity within which the same brightly luminescing, finely crystalline dolomite occurring in the geopetal mouldic cavities could nucleate.

The described diagenetic fabrics could also allow to infer different pristine fabrics of gas hydrates. Pinching out cements and non-gravitational internal sediments likely formed within cavities plugged by massive gas hydrates, whereas open frameworks in microbial mats and floating dolomite spherulites record carbonate precipitation within gas hydrates characterized by a bubble fabric. Most of the described anomalous features result from the generation of cavities during gas hydrate dissociation and concomitant filling by carbonate cements of various aspects and mineralogies. Paraphrasing the polyphase mechanism of tectonic vein filling named crack-seal (Ramsay 1980), we propose to use the term *melt-seal* for this new kind of diagenetic sedimentary structure. Zebra and stromatactis structures, related to clathrate freeze-and-thaw processes by Krause (2001), and carbonate breccias, interpreted by Bojanowski (2007) as being due to cementation and then replacement of gas hydrate clasts, are further examples (not documented in the Tertiary Piedmont Basin) that fall perfectly within this category.

Conclusions

The described fabrics of methane-derived authigenic carbonates of the Tertiary Piedmont Basin are particularly complex and point to processes that cannot be unravelled in the light of common knowledge in sedimentary petrology. They are here interpreted as resulting from carbonate precipitation in the open spaces left by gas hydrate destabilization and, because of this, named melt-seal structures. The recognition of these features provides the only direct evidence so far available of the past occurrence of gas hydrates in ancient sediments and, hence, of a fossil gas hydrate stability zone.

Although the genetic process proposed is the same for all the described examples, i.e. the formation and dissociation of clathrates, markedly different structures result. This may be related to the interplay of some key factors: (1) the original fabric of gas hydrates, which can be massive or vacuolar; (2) rates and modes of dissociation of gas hydrates: rapid dissociation would generate open spaces subsequently filled by authigenic carbonates in a simple, non-diagnostic way (e.g. calcite spar engulfing dolomite sphaerulites), whereas a progressive dissociation proceeding along with carbonate precipitation would produce melt-seal diagnostic features (e.g. pinching out cements, discontinuous internal sediments); (3) biogeochemical conditions constraining mineralogy and growth morphologies of authigenic carbonates; in particular, the degree of supersaturation and the concentration of sulphates are considered to favour aragonite precipitation over that of Mg-bearing carbonates (e.g. Reitner et al. 2005). The chemistry of pore fluids within buried sediments, in turn, obviously strictly depends on the balance between the continuous downward supply of seawater, containing sulphate, and the upward flux of methane-rich fluids. The described Tertiary Piedmont Basin clathrites therefore document a relatively shallow gas hydrate stability zone, i.e. in the reach of a downward advection of normal seawater, as recently observed during periods of active seepage in present-day settings (Solomon et al. 2008).

A re-examination of sediments hosting methane-derived authigenic carbonates, carried out in the light of this working hypothesis, could on one hand widen the spectrum of melt-and-seal fabrics and, on the other hand, contribute to better understanding aspects—such as the behaviour and evolution of gas hydrates and their host sediments—that cannot be adequately addressed in a time perspective in current seafloor exploration.

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