



Clathritic microfabrics, fossilized giant bacteria, and tube worms provide new clues on radiometrically dated late Miocene seepage in the Romagna Apennines (Italy)

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Abstract

The late Miocene in the Mediterranean area was a period of drastic geological and climatic transformations that occurred in combination with widespread hydrocarbon emissions. This study aims to characterize seep carbonates from San Vernicio (Romagna, Italy), describing newly reported microfabrics using a combined petrographic-geochemical approach to get new insights on hydrocarbon seepage and its sedimentary products during the late Miocene in the studied area. Features herein reported include limpid spar-filled micro-domains (interpreted as a newly discovered gas hydrate-derived texture), spar-filled spheres representing giant sulphide-oxidising bacteria, dissolution cavities, botryoidal cements, and former organic-walled tube worms. In situ U-Pb dating of seep-related calcite cements within a former conduit yielded a lower intercept age of 6.8 ± 0.9 Ma (Tortonian – Messinian). This radiometric age, representing a late stage of seepage, postdates the deposition of the hosting sediments (<ca. 10.5 Ma, based on biostratigraphic proxies) by at least ca. 2.8 Ma. These findings add a useful piece to the complex puzzle picturing seepage activity in the Mediterranean area during the late Miocene.

Keywords Cold seeps · Gas hydrates · Geochronology · LA-ICP-MS · Raman microspectroscopy · U-Pb dating

Introduction

Cold seeps are subaqueous sites where methane or heavier hydrocarbons migrate through sediments towards the seafloor (Suess 2018). These environments have been

described from shallow to deep marine and even lacustrine environments, and from both ancient and modern settings (Van Rensbergen et al. 2002; Campbell 2006; Hryniewicz 2022a). Hydrocarbon emissions in cold seeps are responsible for the development of diverse ecological communities

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and seep carbonates (Kaim et al. 2022; Jakubowicz et al. 2025). The biological diversity in cold seeps includes chemosymbiotic taxa that rely on reduced compounds to perform metabolic processes, often acting in mutual benefit with one another (Sahling et al. 2002; Sassen et al. 2004). Seep carbonates result from anaerobic oxidation of methane (AOM, Cochran et al. 2022), a microbial process that leads to carbonate precipitation under high-alkaline conditions (Boetius et al. 2000; Peckmann and Thiel 2004). Seep carbonates are volumetrically insignificant compared to the overall sedimentary budget, but they represent valuable material for understanding key geo-biological issues such as ecology and evolution of non-photosynthetic fauna, and the reconstruction of depositional environments with important ramifications in climate studies and even astrobiology (Shapiro 2004; Teichert and Luppold 2013; Jakubowicz et al. 2017; Kaim et al. 2022; Akam et al. 2023). The complexity of seep-related deposits calls for a multidisciplinary

approach on a case-by-case basis (Jakubowicz et al. 2025). In fact, fabrics, carbonate cements, isotopic composition, and faunal assemblages can be very different from one site to another (or even within individual ones), so that it is not straightforward to establish common features across spatially and temporally separated cold seeps (Campbell 2006; Shapiro and Ingalls 2024). Being the physical expression of hydrocarbon migration, seep carbonates can be used to track the time of seepage activity in sedimentary basins (Miyajima et al. 2023; Himmler et al. 2024).

Late Miocene cold seeps have been reported all over the Mediterranean area (Pierre et al. 2002; Pierre and Rouchy 2004; Clari et al. 2009; Panieri et al. 2009; Ziegenbalg et al. 2012; Iadanza et al. 2013, 2015; Natalicchio et al. 2012, 2013; Grillenzoni et al. 2017; Conti et al. 2021, 2024a). Many of these seep-related deposits are hosted in the Tortonian and Messinian sediments deposited prior to the Messinian Salinity Crisis (e.g. Pierre et al. 2002; Conti et al. 2021). However, the age of seep carbonates can be considerably younger than that of the enclosing sediments (Giunti et al. 2025). This fact makes absolute radiometric dating of seep carbonates fundamental to understand the effects of hydrocarbon emission on the climate and ecology of the Mediterranean area at the end of the Miocene. This study aims to characterize in detail seep carbonates from San Vernicio (Romagna, Italy), describing their microfabrics, fauna, and geochemistry to better understand the seepage dynamics that led to their formation.

Geological setting

The northern Apennines are a fold-and-thrust belt formed as a result of the convergence and consequent collision of the European and Africa plates, as well as of the interposed Adria and Corsica-Sardinia microplates. Starting from the late Oligocene, the internal oceanic units (Ligurian Units) were thrust over the continental units deposited on the Adria microplate (Tuscan and Umbro-Romagna-Marchean units; Barchi et al. 2012; Malusà et al. 2016). During the north-eastern migration of the accretionary prism, sedimentation occurred both in wedge-top basins (Epiligurian units) and in the foredeep (Marnoso-arenacea Fm) (Fig. 1a). The Verghereto Marls sedimented laterally to the foredeep over a structural high at the frontal slope of the migrating orogenic wedge and represent a closure phase of the inner stage of the Marnoso-arenacea Fm (Fig. 1b). The basal part of the Verghereto Marls is composed of fine-grained turbidites alternated with pelitic hemipelagites, whilst the top is dominated by laminated pelites (Fig. 2). This latter upper part of the Verghereto Marls hosts numerous seep carbonate deposits (Conti et al. 2024b), including the ones described

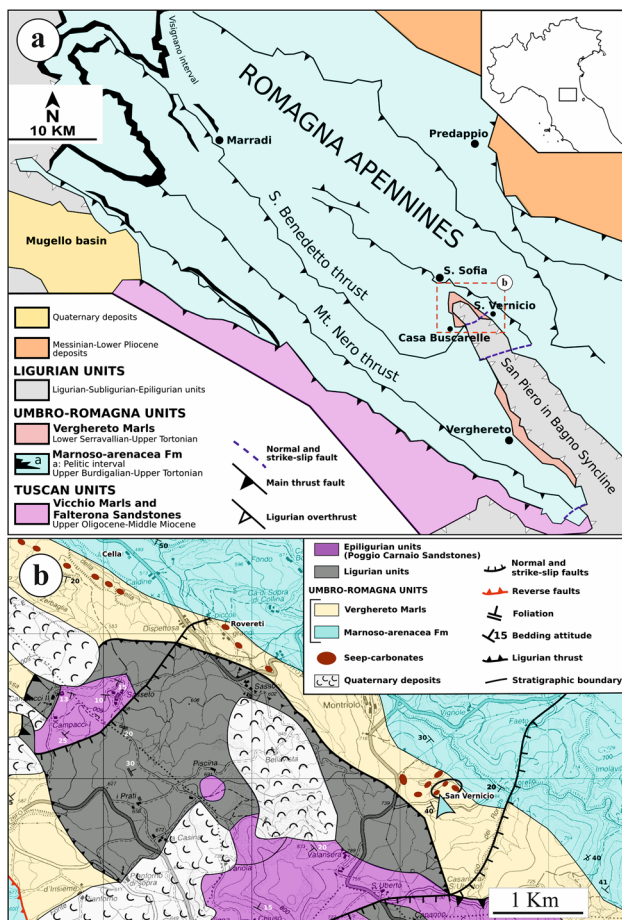


Fig. 1 (a) Simplified geological map of the Romagna Apennines (modified from Roveri et al. 2003). Red dashed area indicates the location of the studied area in (b) (slightly enlarged for clarity). (b) Detailed geological map of the area around San Vernicio. Black circle indicates the location of the carbonate blocks and mound described in this study (the latter indicated by a light blue arrowhead) (modified from Conti et al. 2024b)

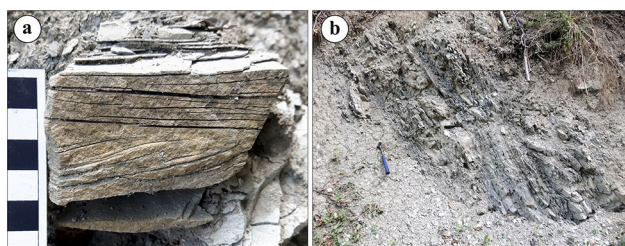


Fig. 2 Field photographs of the Verghereto Marls. **(a)** Basal part of the Verghereto Marls composed of fine-grained turbidites. **(b)** Top part of the Verghereto Marls dominated by laminated pelites. Hammer on the left-hand side is ca. 35 cm long for scale

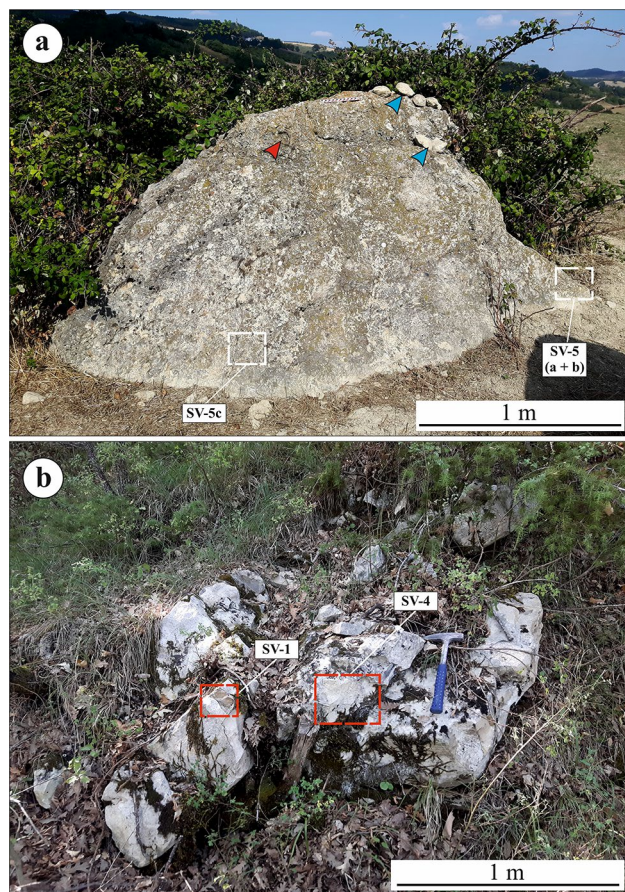


Fig. 3 **(a)** Field view of the top of the carbonate mound in San Vernicio (facing North). Note the general mottled texture. Bivalve moulds extracted or found lying in close proximity to the mound are gathered in the upper right (light blue arrowheads). Red arrowhead indicates the position of a cast previously occupied by a bivalve mould. White dashed rectangle indicates the location of specimens SV-5 (a and b) and SV-5c. **(b)** Field photograph of one of the carbonate blocks with location of the sampling position of specimens SV-1 and SV-4

in the present study. The age of the upper part of the Verghereto Marls hosting seep carbonates has been determined on micropaleontological basis to be late Serravallian – early Tortonian (biozones MNN 7 and 8) by Conti et al. (2024b).

Materials and methods

Sampling and petrography

A total of seven carbonate specimens were collected from a carbonate mound (SV-5a, SV-5b, and SV-5c, Fig. 3a) and from two isolated and reworked blocks (SV-1, SV-2a, SV-2b, and SV-4, Fig. 3b) in the San Vernicio locality (GPS coordinates 43°91'44.89" N; 11°96'63.83" E). The blocks (up to 1.5 m high and 2 m long) are surrounded by vegetation, not in situ, and were found downhill with respect to the carbonate mound. Due to lack of other outcrops of seep carbonates (apart from the carbonate mound), sampling was performed on such reworked blocks. Five standard thin sections (from SV-2a, SV-2b, and SV-4, two from SV-5a) were studied at the Institute of Geological Sciences of the Polish Academy of Sciences (IGS PAS), Warsaw, in transmitted and reflected light using a Nikon Eclipse LV100POL polarising microscope, whereas cold cathode microscopy (CL) was performed using a Nikon Eclipse 80i Y-IDP microscope equipped with a CITL Mk-2 unit (Cambridge Image Technology, Cambridge, UK) operated at 0.003 mBar, 300 μ A, 17.0 kV. The photomicrographs were acquired with a NIS-Elements BR 3.2 software (Nikon, Japan). Back scattered electron (BSE) images of the investigated textures were acquired with scanning electron microscopy (SEM) on thin sections and rock chips (both HCl-etched and not etched) at the Faculty of Geology, University of Warsaw (FG UW), using a FE-SEM ZEISS Sigma VP (Zeiss AG, Oberkochen, Germany) operated at 20 kV acceleration voltage and 120 μ m aperture. Phase identification was carried out using two Bruker XFlash 6|10 EDS (Bruker Corporation, Billerica, MA, U.S.A.) silicon drift detectors with internal FET (iFet SDD), 5 mm² active area, 10⁶ cps maximum count rate, >123 eV energy resolution, and 0.5 wt% detection limit. Elemental composition was measured using a Cameca SXFiveFE electron probe microanalyzer (EPMA) equipped with five WDS spectrometers at FG UW. Analyses were conducted using an acceleration voltage of 15 kV, a current of 10 nA, and a beam diameter of 15 μ m. The following standards were used for EPMA: albite (Na), MgO (Mg), orthoclase (Al, K), wollastonite (Si, Ca), SrSO₄ (S, Sr), rhodonite (Mn), Fe₂O₃ (Fe), PrPO₄ (P), BaSO₄ (Ba), CePO₄ (Ce). The analytical crystals and X-ray lines (in brackets) were as follows: TAP (Na K α , Mg K α , Al K α , Sr L α), LPET (Ca K α , S K α , K K α , P K α , Ba L α , Si K α), and LLIF (Fe K α , Mn K α , Ce L α) were used as analytical crystals (X-ray lines in brackets). For additional information, see Appendix A – EPMA.

Stable C and O isotope analysis

Seventeen subsamples (13 from SV-5a and 4 from SV-4) were hand-drilled to analyse the carbon and oxygen stable isotope composition ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) (see Tab. SII in the Supplementary Information). Nine of these were analysed at the Stable Isotope Laboratory of IGS PAS in Warsaw using a Thermo KIEL IV Carbonate Device coupled to a Finnigan Delta Plus isotope ratio mass spectrometer in Dual Inlet system. Extraction of CO_2 from the carbonates was done after the method of McCrea (1950). A minimum of 20 μg of powder reacted with anhydrous orthophosphoric acid at 70 °C for at least 2 h, after which the isotopic composition of released CO_2 was measured. The results were calibrated using three international standards NBS-18, IAEA-CO8 and IAEA-603. Eight subsamples were reacted with 100% phosphoric acid at 70 °C using a Gasbench II connected to a ThermoFisher Delta V Plus mass spectrometer (Thermo Fisher Scientific, Bremen, Germany) at the GeoZentrum Nordbayern in Erlangen, Germany. Reproducibility and accuracy were monitored by replicate analyses of laboratory standards calibrated by assigning a $\delta^{13}\text{C}$ of +1.95‰ to NBS-19 and −47.3‰ to IAEA-CO9 and a $\delta^{18}\text{O}$ of −2.20‰ to NBS-19 and −23.2‰ to NBS-18. International standard IAEA-603 was additionally analysed as quality control. Analytical precision (1 σ) and reproducibility were better than 0.1‰ for both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. The inter-laboratory bias from the two laboratories was reported by Wielgosz-Rondolino et al. (2020) to be less than 0.2‰ for $\delta^{13}\text{C}$ and 0.6‰ for $\delta^{18}\text{O}$. All isotopic results are reported in per mil (‰) relative to the Vienna PeeDee Belemnite (V-PDB) standard.

Raman microspectroscopy

Raman microspectroscopy was applied across various textural micro-domains using a Thermo Scientific Apreo 2 S Raman SEM at FG UW. A 532 nm excitation laser was used at 7–10 mW power with a Leica objective (x8/0.25 NA) and a CCD (−70 °C) detector. Single spot analyses were conducted at room temperature with an acquisition time of 3 s and 100 accumulations. Focus was set ca. 5 μm below the sample surface to avoid structural damage from polishing (Beyssac et al. 2003). The Raman spectra (0.3 cm^{-1} FWHM resolution) were background corrected using in-house software. Deconvolution was done using Omnic 9 with the Gaussian/Lorentzian procedure. The inLux SEM interface allows BSE imaging and EDX measurements coupled with reflected light images and Raman microanalyses. The SEM was set to a current of 26 nA and an acceleration voltage of 15 keV. For additional information, see Supplementary Information and Appendix B – Raman.

LA-ICP-MS U-Pb geochronology

U-Pb dating was performed at the University of Portsmouth, UK, using an ASI RESOLUTION© 193 nm ArF excimer (Australian Scientific Instruments, Fyshwick, Australia) laser coupled to an Agilent 8900 Triple Quadrupole Inductively Coupled Plasma Mass Spectrometry instrument (ICP-QQQ-MS, Agilent). Calcite was analysed using 80 μm spot size following 100 μm pre-ablation cleaning of 3 pulses, using a laser fluence of $\sim 3.5 \text{ J/cm}^2$, and a repetition rate of 8 Hz. Primary reference materials were SRM-614 glass (NIST-614; 0.82 ppb U and 2.3 Pb) and WC-1 carbonate ($254.4 \pm 6.4 \text{ Ma}$; Roberts et al. 2017), while Duff Brown Limestone ($64 \pm 2 \text{ Ma}$; Hill et al. 2016) and RA-138 ($321.99 \pm 0.65 \text{ Ma}$; Guillong et al. 2024) served as secondary reference material to test long-term reproducibility. Analyses of Duff Brown yielded a $^{206}\text{Pb}/^{238}\text{U}$ lower intercept age of $62.2 \pm 1.1 \text{ Ma}$ (MSWD=0.5; 3% from reported age), whilst RA-138 yielded a $^{206}\text{Pb}/^{238}\text{U}$ lower intercept age of $312.0 \pm 6.4 \text{ Ma}$ (MSWD=0.8; 1.0% from reported age). U-Pb data are presented on Tera-Wasserburg plots using IsoplotR (Vermeesch 2018) and are uncorrected for common Pb. Quoted 2 σ uncertainties include fully propagated analytical uncertainties, including an additional 3% to account for the long-term reproducibility of the secondary reference materials (see Figs. SI 1–5 in the Supplementary Information and Appendix C – U-Pb for full details). Full analytical methods can be also found in Parrish et al. (2018) and Mottram et al. (2020).

Results

Carbonate mound

The exposed part of the mound (ca. 5 m $\times$ 3 m), shows sharp contacts with the surrounding marly sediments, and is located on top of a hill (Fig. 3a). Bivalve moulds are abundant, but none of the shells are preserved. The mound is composed predominantly of beige or brown micrite and irregular cavities (up to 5 cm long) filled with grey-greenish carbonate material. This resulted in a heterogeneous and mottled texture (Figs. 3, 4 and 5). Microscopically, the brown micrite is dense whilst the beige micrite is cemented by microspar and locally clotted (Fig. 4a). Both show moderate to bright orange CL colour. Silt-sized quartz and micas are scarce in the micrite, as are foraminifera tests (Fig. 4a). The cavities are filled with cloudy elongated crystals, up to 500 μm in length and up to 150 μm in diameter, showing a sheaf-like morphology and a pseudo-hexagonal cross section (Fig. 4b). These crystals are homogeneous bright orange in CL (Fig. 4ac) and surrounded by abundant platy

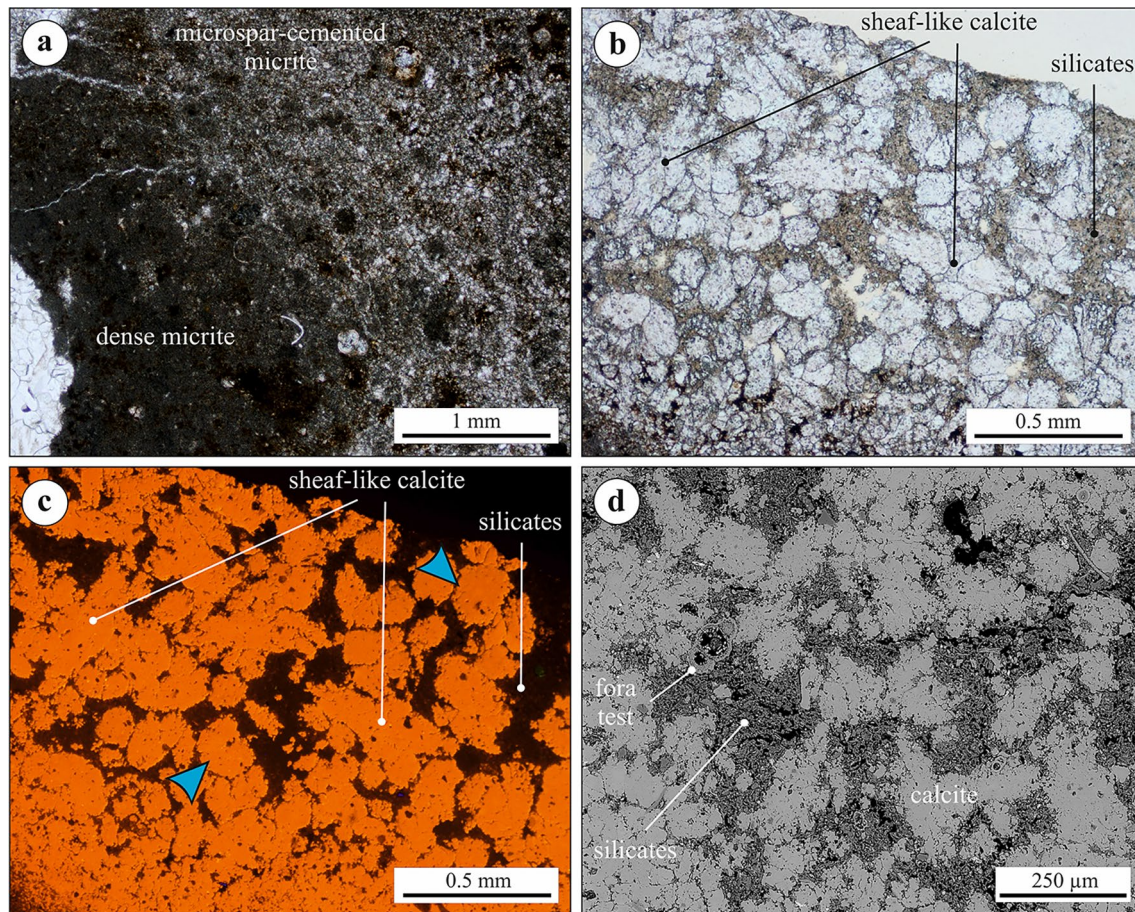


Fig. 4 Microfacies of the carbonate mound (from specimen SV-5a). **(a)** Photomicrograph of the dense micrite (left hand side) and microspar-cemented micrite (upper right corner) in the carbonate mound. **(b–c)** Paired plane polarized light **(b)** and CL **(c)** photomicrographs of the

sheaf-like calcite crystals associated with silicates within the cavities of the carbonate mound. Note the hexagonal cross sections of the crystals (light blue arrowheads in **c**). See also Fig. 14d. **(d)** BSE image of the sheaf-like crystals and silicate minerals in the cavities

silicate minerals and siliciclastic silt, with rare foraminifera tests (Fig. 4d). The micrite and the sheaf-like crystals in the cavities are composed of calcium carbonate with low Mg content (<3.5 and <2.8 mol%, respectively) (Appendix A). Two micrite subsamples show negative $\delta^{13}\text{C}$ values (−39.2‰ in the beige micrite and −15.4‰ in the brown one) and positive $\delta^{18}\text{O}$ values (+2.8‰ and +2.2‰, respectively) (Fig. 5a). The sheaf-like crystals in the cavities shows negative $\delta^{13}\text{C}$ (−27.3‰ to −25.9‰) and $\delta^{18}\text{O}$ values (−5.4‰ to −3.5‰) (Fig. 5a).

Additionally, two distinct types of tubular structures were recognised in the micritic matrix of the carbonate mound. The most abundant type (type I) is represented by short tubes, typically 2 to 7.5 cm-long, straight or slightly curved, and 0.5 to 1 cm in diameter (Fig. 5). Their diameter is mostly constant throughout their length and they only rarely appear to taper (see Fig. SI6). These tubes are filled with concentric millimetric laminae beige to dark brown in colour with common limpid calcite in their centre (Figs. 5 and 6). There is a sharp contact between the tubes and the

hosting micritic sediment (Fig. 6a). Microscopically, a sequence of carbonate phases makes up the different concentric laminae (Fig. 6a). Usually, the outermost lamina is also the thickest, and it is composed of a mixture of microspar-cemented micrite (Fig. 6a, e), moderate orange luminescent in CL, with a relatively high amount of silt-size detrital material, mostly quartz and micas. Towards the centre, a dense-clotted micrite lamina typically follows, mostly free of detrital material. This lamina exhibits moderate to bright orange luminescence in CL and is locally disrupted and discontinuous (Fig. 6b–d). The central part of the structures is then cemented by microspar and blocky calcite, which are homogeneously bright orange in CL (Fig. 6d, e). Spherical structures (50 to 200 μm in diameter) are surrounded by a dark rim and occur in both the external lamina and in the intermediate micritic lamina in some of these tubular structures (Fig. 6f). These spheres are filled with limpid spar, and coalesce in clusters of two to four.

Isotopic transects performed across two of these type I tubular structures indicate consistently negative $\delta^{13}\text{C}$ values

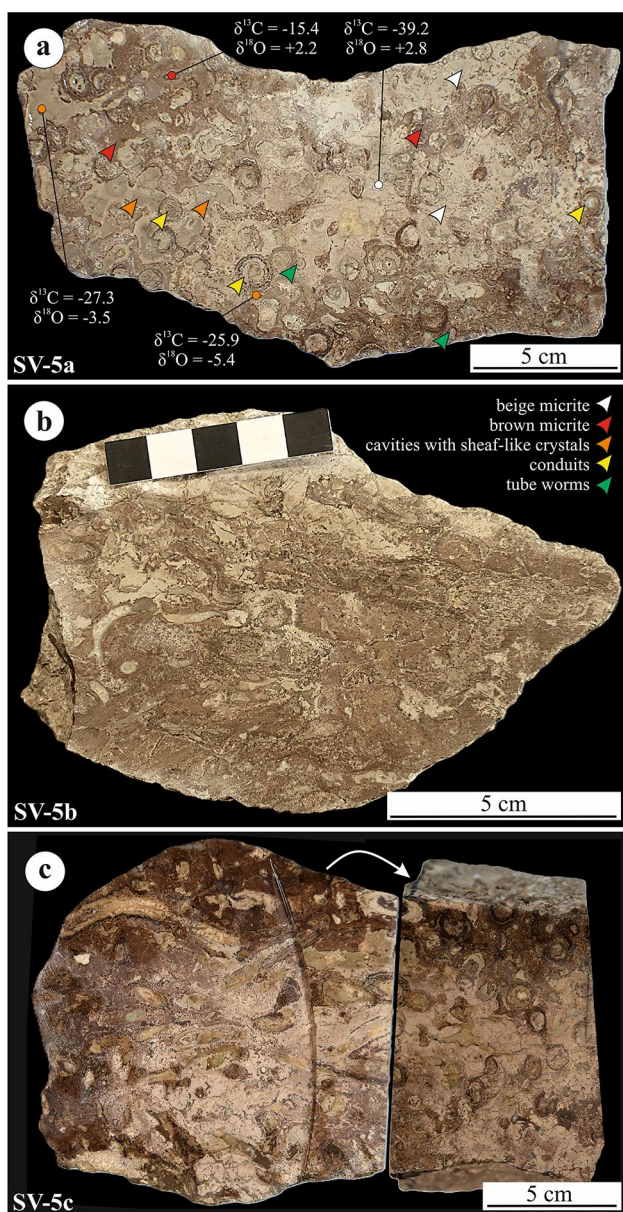


Fig. 5 Polished slabs of the specimens collected from the carbonate mound. **(a)** Slab of SV-5a showing numerous cross sections of conduits and tube worms. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are in per mill. **(b)** Polished slab of the carbonate mound with some curved and elongated tubular structures (centre left side). **(c)** Polished slab (SV-5c) showing longitudinal (left) and perpendicular (right) sections of the tubular structures

(ranging from -38.8‰ to -22.7‰), and negative $\delta^{18}\text{O}$ values (ranging from -5.2‰ to -0.6‰) (Fig. 7). U-Pb dating of the microspar in the centre of one of these structures yielded a $^{208}\text{Pb}_{\text{common}}/^{206}\text{Pb}$ Tera-Wasserburg (86T-W) intercept age of 6.8 ± 0.9 Ma (MSWD=1.1; $n=37$; $^{206}\text{Pb}_{\text{common}}/^{208}\text{Pb}=0.4839 \pm 0.0053$) (Fig. 8a). U-Pb dating of the other concentric laminae and the surrounding micrite yield an imprecise $^{208}\text{Pb}_{\text{common}}/^{206}\text{Pb}$ Tera-Wasserburg (86T-W) intercept age of 5.9 ± 3.8 Ma (MSWD=1.3; $n=89$; $^{206}\text{Pb}_{\text{common}}/^{208}\text{Pb}=0.$

4853 ± 0.002) due to the high relative content of common Pb and short spread along the intercept (see Fig. SI5).

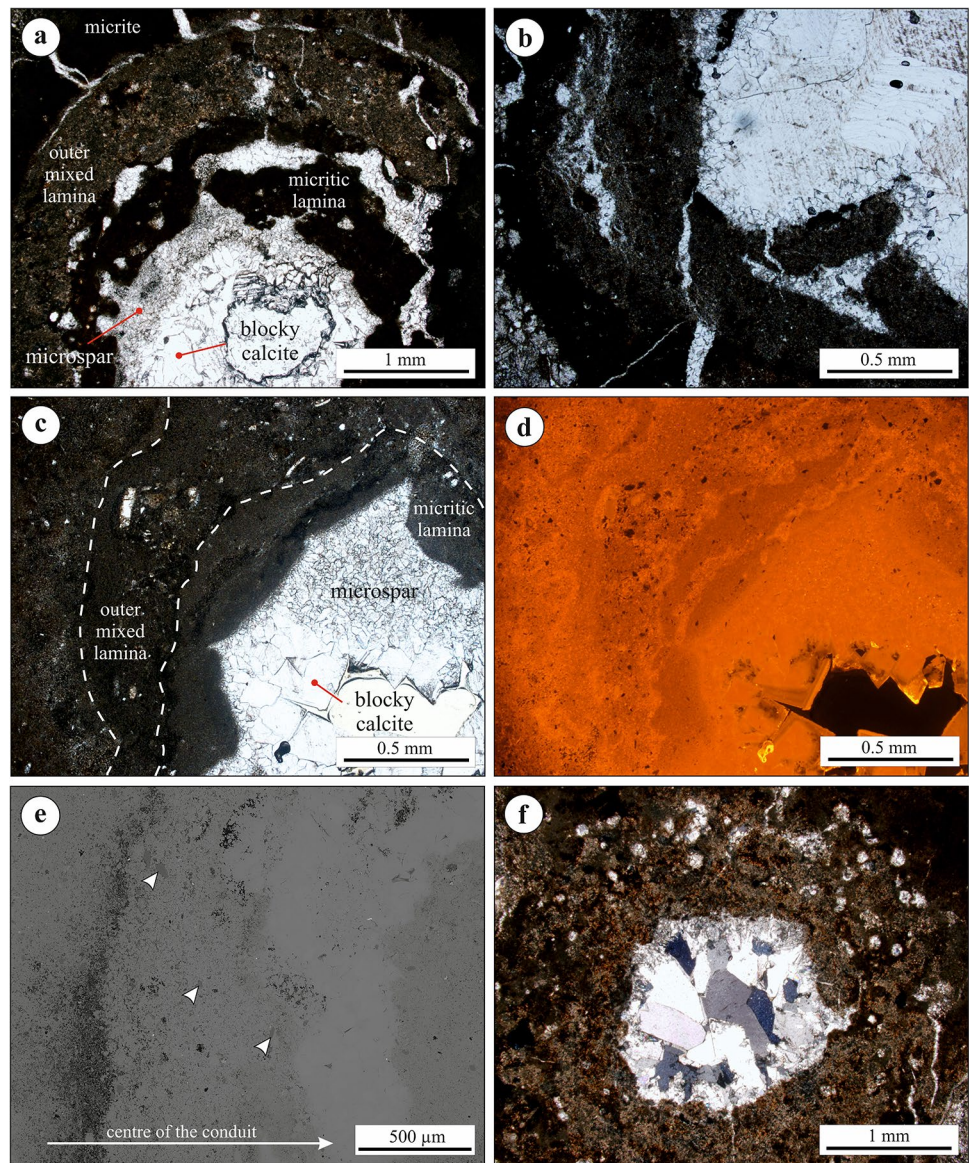
A transect of Raman spots from the micrite surrounding one of these type I tubular structures to the blocky calcite at its centre displays characteristic changes of the Raman signals, particularly at higher Raman shift ($>1100 \text{ cm}^{-1}$). The highest signal to noise ratio is observed in spectra of the micrite outside of the tubular structure (Spectra 8, 9; Fig. 8b). The background noise increases significantly in the outermost mixed carbonate-siliciclastic lamina and in the micritic lamina (Spectra 10–13). The signal to noise ratio then increases again towards the centre of the structure (Spectra 14–16). Even though increasing oscillatory background noise partially obstruct clear identification of bands at a Raman shift $>1100 \text{ cm}^{-1}$, organic bands $\text{D}_1\text{--D}_6$ (D_1 : 1345 cm^{-1} ; D_2 : 1650 cm^{-1} ; D_4 : 1236 cm^{-1} ; D_5/D_6 : 1428 cm^{-1}) are visible in the blocky calcite in the centre of the structure (Spectra 16). The presence of a D_2 band ($1630\text{--}1639 \text{ cm}^{-1}$) and an overtone ($1736\text{--}1744 \text{ cm}^{-1}$), which is caused by the bending mode of the IR active CO_3^{2-} mode at 874.5 cm^{-1} (Gillet et al. 1996; De La Pierre et al. 2014), may be present in the outer mixed lamina and the micritic lamina, as well as one spectrum in the microspar (Spectra 11–13, 15). The calculated full width at half maximum values (FWHM) of the ν_1 symmetric stretching band are lower in the outer region of the tubular structure ($6.1\text{--}6.3 \text{ cm}^{-1}$, Spectra 8–10, Fig. 8c) and slightly increase further inside the tube ($6.2\text{--}7.4 \text{ cm}^{-1}$, Spectra 11–16; Fig. 8c). Primary Raman features of all measured textures fit to signals of the calcite structure (Scheetz and White 1977; Wehrmeister et al. 2010), with visible T modes (ca. $144\text{--}157 \text{ cm}^{-1}$), L modes ($280\text{--}283 \text{ cm}^{-1}$), and the prominent ν_1 symmetric stretching band ($1086\text{--}1087 \text{ cm}^{-1}$; Fig. 8b).

The second type of tubular structures (type II) is commonly curved in longitudinal sections and ranges from 1 to 3 mm in diameter and from 2 to 4 cm in length (Fig. 5). These structures are formed by a $10\text{--}50 \text{ }\mu\text{m}$ -thick outer rim composed of microcrystalline calcite (Fig. 9a, b). A ca. $20 \text{ }\mu\text{m}$ -thick, porous wall follows towards the centre and is composed of radially arranged fibrous crystals and often detached from the outer rim (Fig. 9c–f). EDS spectra of these fibrous crystals revealed a CaCO_3 composition (Fig. 9g–h). The innermost part of these structures is occupied by cloudy microspar and/or limpid spar showing homogeneous bright orange luminescence in CL (Fig. 9e, f, see also Fig. SI8).

Carbonate blocks

Two carbonate blocks were found about 30 and 50 m northwards and downhill respect to the carbonate mound (Figs. 1b and 3b). They mostly show a massive facies, locally faintly laminated or brecciated (Figs. 10 and 11). Burrows filled

Fig. 6 Photomicrographs of the conduits in specimen SV-5a. **(a)** Plane polarized light image of a conduit formed by different concentric laminae, including the mixed outermost one composed of microspar-cemented micrite and detrital material (mostly quartz and micas), followed by a dense micritic one, microspar and blocky calcite in the centre. See also Fig. 14a, c. **(b)** Disrupted laminae in a conduit (plane polarized light image). **(c–d)** Paired plane polarized light **(c)** and CL **(d)** images of a conduit. Note the abundant clastic material in the outer mixed lamina. **(e)** BSE image of the concentric laminae forming the conduits. Note the abundant silt-size detrital material (white arrowheads). **(f)** Cross-Nichols photomicrograph of a conduit with numerous spar-filled and rimmed spheres in its outer laminae



with internal sediment and/or blocky calcite are visible (Fig. 10). Microscopically, they are composed of micrite, subordinate detrital quartz and mica, with sparse foraminifera tests (see Fig. SI8). This micrite recorded two strongly ^{13}C -depleted values (-39.8 and -40.0‰) and positive $\delta^{18}\text{O}$ values ($+4.8$ and $+4.4\text{‰}$, Figs. 7 and 10b). Inside the burrows, the internal sediment yielded $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of -19.9 and -2.3‰ , whilst the blocky calcite yielded $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of -6.7 and $+1.7\text{‰}$, respectively (Fig. 10b). The brecciated facies shows angular clasts arranged in a jigsaw-puzzle fabric and carbonate-filled veins (Fig. 11). The clasts are composed of dense micrite with abundant silt, mostly quartz (Fig. 11b). The space between the micritic angular clasts is filled by calcite cement, mostly microspar either alone (Fig. 11b) or, more commonly, mixed with fine sand-sized detrital material with numerous foraminifera tests and

bivalve shell fragments (Fig. 11c). Detritus-free, carbonate-filled cavities are present in the mixed carbonate-clastic matrix (Figs. 11c and 12). These cavities have irregular and rounded outlines, locally smoothing the angular shape of the clasts (Fig. 12a–b). They are filled with various calcite cements, including a homogeneous, microcrystalline groundmass and botryoids of fibrous crystals (Fig. 12a–d). The fibrous calcite crystals are non-luminescent in CL and show signs of neomorphism as the fibrous morphology is obliterated by neomorphic blocky calcite crystals (Fig. 12e–f). EDS spectra performed on such fibrous crystals reveal Sr peaks (see Fig. SI8). Additionally, these cavities contain rounded and irregular-shaped micro-domains filled with limpid spar and partially covered by a thin rim of micrite (Fig. 12a–d). The micrite rim does not continue into the clasts. These micro-domains are isolated one from each

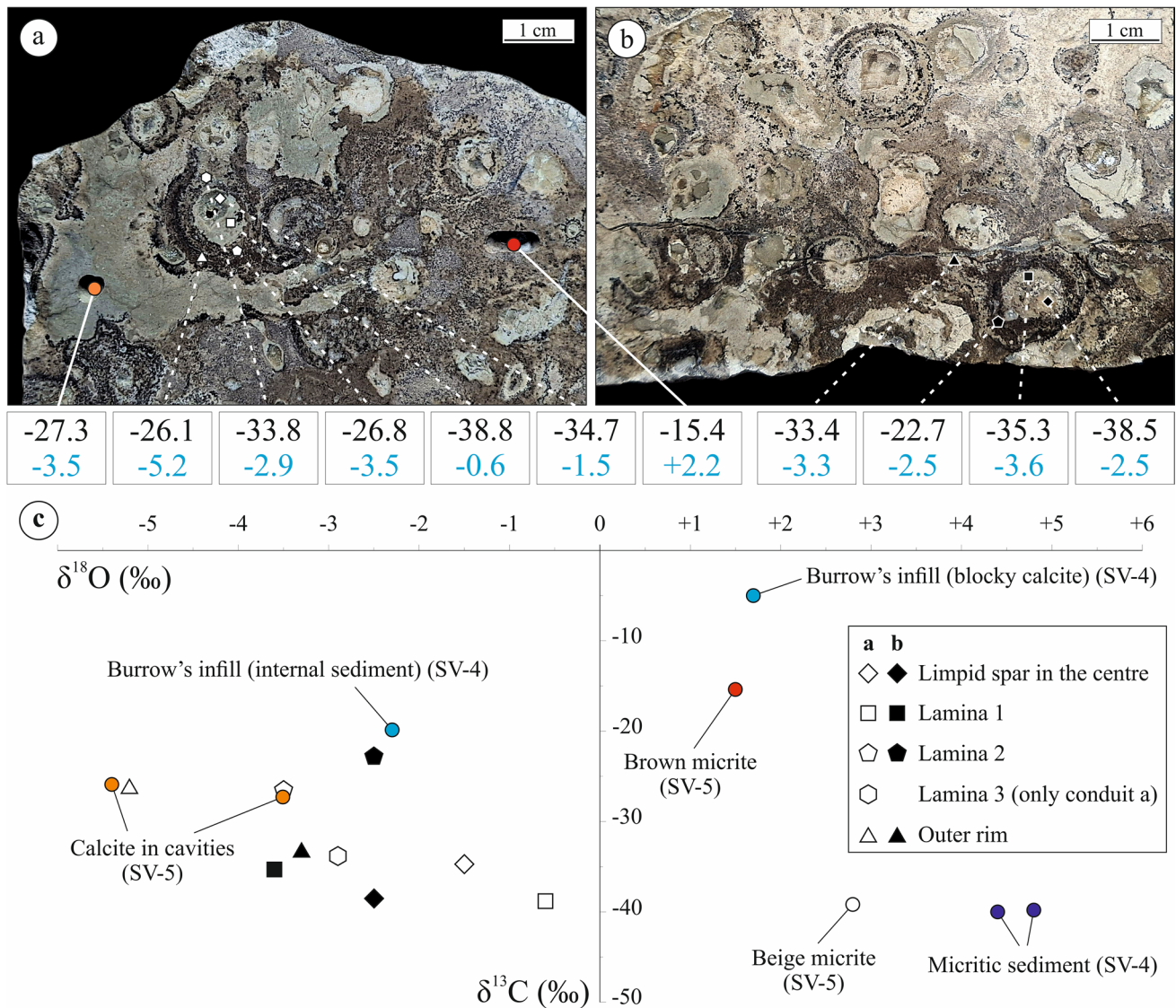


Fig. 7 (a–b) $\delta^{13}\text{C}$ (black) and $\delta^{18}\text{O}$ (light blue) values of different carbonate phases in sample SV-5a (in per mill). Dashed lines are values of two transects across the concentric laminae composing the conduits. Orange and red spots indicate the values of a cavity filled

with sheaf-like calcite crystals in the cavities and of the brown micrite, respectively. (c) $\delta^{13}\text{C}$ – $\delta^{18}\text{O}$ plot of the of different carbonate phases in samples SV-4 and SV-5a

other and are up to ca. 3 mm long, either confined within the cavities (Fig. 12a–b) or in contact with the clasts (Fig. 12a–c–d). Millimetric-thick veins cross-cut the micritic clasts, as well as the matrix and the cavities within it (Figs. 11a and 13a and b). These veins are filled with various carbonate cements, with a minor presence of silt-sized detrital quartz. The cements filling the veins include cloudy microsparite, usually organised in thin laminae parallel to the walls, followed by dark micritic laminae towards the vein's middle plane (Fig. 13a, b). Within the veins, radial fibrous crystals truncate these laminae abruptly (Fig. 13b). Spheres similar to the ones observed in the tubular structures of the mound are visible in these veins, ranging from 50 to 150 μm in diameter and clustering in groups up to three (Fig. 13c).

These spheres are surrounded by a dark rim, locally with signs of possible indentation (Fig. 13d). This rim can be either formed by micritic carbonate (Fig. 13c, d) or made of a mixture of silt-size quartz and platy silicates and micrite (Fig. 13e, f).

Interpretation and discussion

Evidence of hydrocarbon seepage

The ^{13}C -depleted signature recorded by the different carbonate phases (with $\delta^{13}\text{C}$ values as low as -38.8‰) indicates hydrocarbons as the main source of inorganic carbon

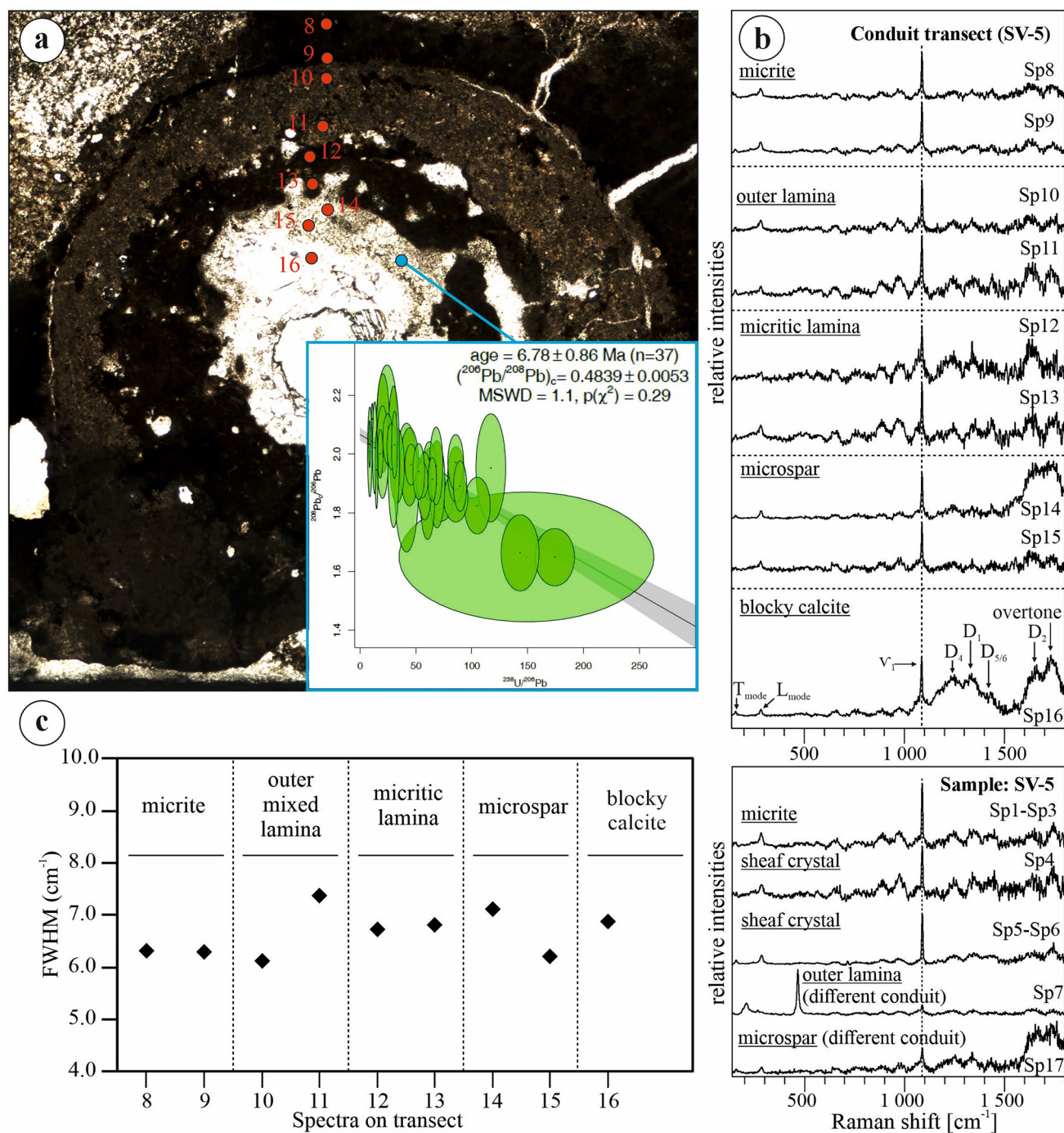


Fig. 8 (a) Plane polarized scan of a conduit's cross section (same as Fig. 6a, rotated 90° clockwise) with location of the Raman spots. Inset displays the Tera-Wasserburg (86T-W; Parrish et al. 2018) plot obtained from the ablated spots located in the microspar towards the

centre of the conduit. (b) Raman spectra of the different laminae composing the conduit in (a) (Sp8 to 16, upper part). Spectra of other components are shown in the lower part (Sp. 1 to 7, and 17). (c) FWHM values plotted across the transect shown in (a)

(Whiticar 1999; Peckmann and Thiel 2004; Campbell 2006; Cochran et al. 2022). Higher $\delta^{13}\text{C}$ values (e.g. -15.4‰ of brown micrite in the carbonate mound) are likely due to mixing with ^{13}C -richer sources of dissolved inorganic carbon (DIC), such as seawater or methanogenesis (see Natalicchio et al. 2012; Bojanowski et al. 2015). Hydrocarbon migration

and carbonate precipitation in cold seeps are linked by anaerobic oxidation of methane (AOM), a microbial process that oxidises hydrocarbons (especially methane) using sulphate as electron acceptor producing bicarbonate anions that eventually are bound to Ca (and Mg) cations to form carbonate minerals (Ritger et al. 1987; Boetius et al. 2000).

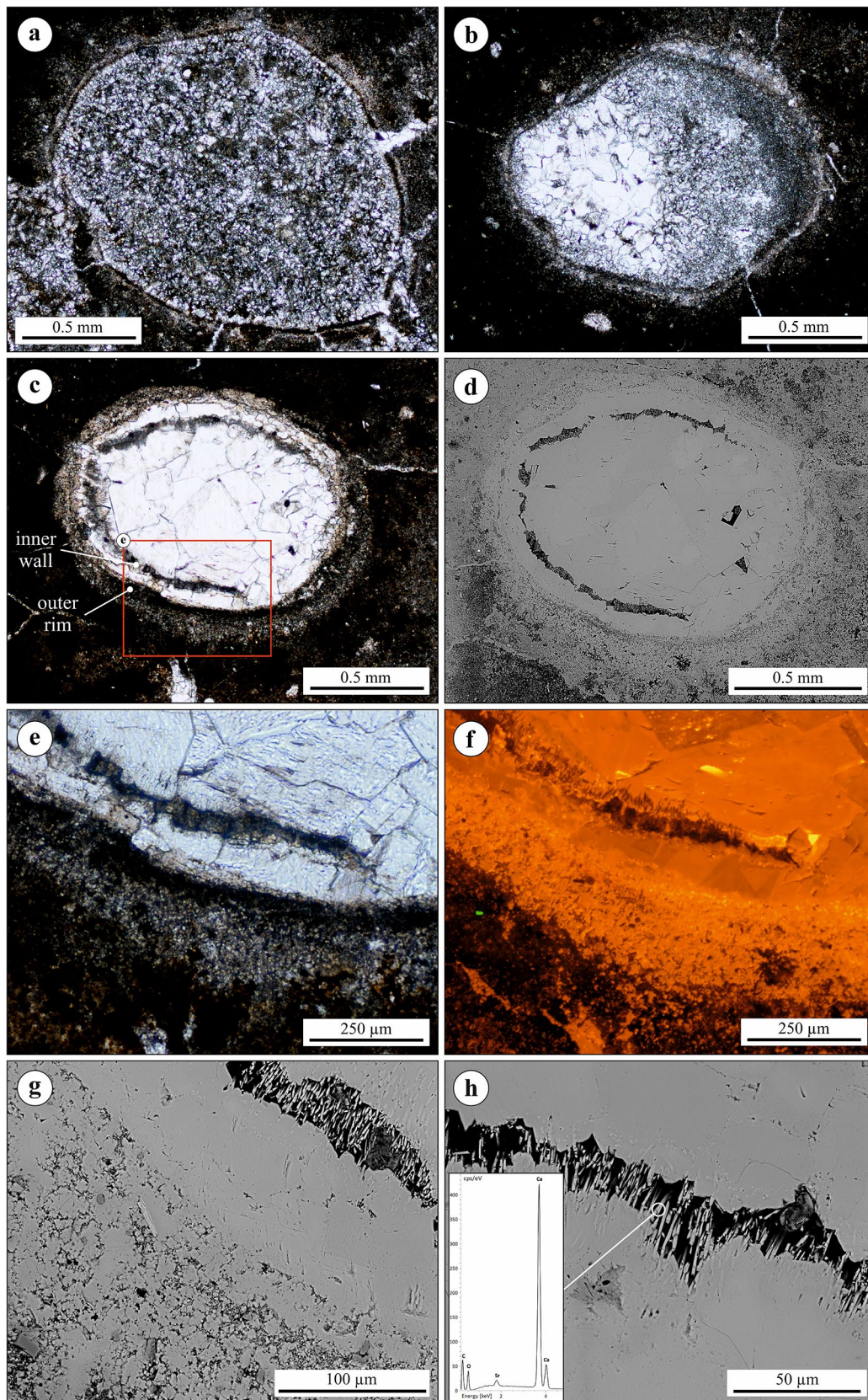


Fig. 9 Photomicrographs of the tube worms. **(a)** Interior of the tube filled with cloudy microspar. Note the disrupted outer micritic rim in the lower right corner. Plane polarized light. **(b)** Tube worm filled with spar showing different crystal size. Plane polarized light. **(c-d)** Plane polarized light **(c)** and BSE **(d)** images of a tube worm filled with limpid coarse spar. Note the outer rim and the discontinuous inner wall. **(e-f)** Plane polarized light **(e)** and CL **(f)** images of the inner wall (same as **c**). Note the fibrous morphology and the non-luminescence of the crystals composing the wall. **(g)** BSE image of the outermost rim of the tube worm (lower left corner) followed by spar and by the porous inner wall. **(h)** Zoom in on the wall of the tube worm. Note the porous structure and the presence of needle-like crystals with BSE spectra indicating their CaCO_3 composition

Alternatively, AOM can also be performed via microbial pathways that use different electron acceptors instead of sulphate, such as manganese or iron oxides (Cochran et al. 2022; and references therein). Hydrocarbon seepage in the studied area is also supported by facies and petrographic features typical of Apennine cold seeps (Conti et al. 2021). Carbonate mounds with chemoautotrophic macrofauna (and other organisms able to tolerate reduced and sulphide-rich environments) such as (possible) lucinid bivalves and tube worms (see below), are also often reported from ancient and modern cold seeps (Aharon and Sen Gupta 1994; Taviani 1994; Sassen et al. 2004). Brecciated facies resulted from in situ hydraulic fragmentation by over-pressured fluids followed by several stages of hydrocarbon-derived carbonate cementation are analogous to other paleoseeps (Jenkins et al. 2008; Iadanza et al. 2013; Giunti and Bojanowski 2025). Such complex sequences of carbonate cements are typical for seep carbonates (Peckmann et al. 2003; Hryniewicz 2022b; Jakubowicz et al. 2025). A specific microfabric is represented by the spherical structures preserved in the veins cross-cutting the brecciated facies and within some of the concentric laminae of the more abundant tubular structures (type I) (Figs. 6f and 13c-f). Since these features are embedded in seep-related cements and within the external (i.e. early-formed) concentric laminae of the tubes, these CaCO_3 -spheres probably represent early-diagenetic features. These spherical structures have the same diameter and show similar features to those reported from the Holland Mound seep deposit in Morocco ('carbonate with spheres'; Peckmann et al. 1999; 2005). Originally interpreted as former hydrocarbon droplets as a consequence of carbonate precipitation following microbial degradation of petroleum, these spheres have been recently re-interpreted as representing fossilized giant sulphide-oxidising bacteria (Smrzka et al. 2024).

Gas hydrate-derived fabrics

The presence of cavities with rounded outlines now filled with carbonate cements in the mound and the breccias could be the result of carbonate dissolution, a process often

observed in seep carbonates (Himmler et al. 2011; Jakubowicz et al. 2015, 2025; Hryniewicz 2022b). The absence of preserved bivalve shells in the carbonate mound could also support dissolution in these seep carbonates. In this scenario, the dissolution that produced the cavities in the breccias would have been followed by precipitation of the botryoids of fibrous crystals and micritic-microsparitic cements. The neomorphosed fibrous crystals were probably originally aragonitic, as botryoidal aragonite has much more commonly been reported than calcite in modern cold seeps (Peckmann et al. 2001; Naehr et al. 2007). A localized dissolution could theoretically explain the irregular micro-domains filled with limpid spar within these cavities and veins (Figs. 12a-d and 13b). However, such scenario fails to explain either why other carbonate phases inside these irregular cavities were not corroded nor why these micro-domains are scattered and separated from one another. A more likely explanation is that these micro-domains were originally occupied by a solid substance, while carbonate precipitation occurred around them. This compound was apparently not stable and open pores/cavities formed when it dissolved. In cold seeps, such a metastable solid compound is commonly represented by gas hydrate, an ice-like substance formed by water molecules encaging methane and other low-weight hydrocarbons (Greinert et al. 2001; Bohrmann and Torres 2006). Gas hydrate is stable at low temperature and moderate-to-high pressure, and it decomposes quickly outside its stability field (Bohrmann and Torres 2006). Yet, when gas hydrate destabilization proceeds slowly enough and carbonate precipitation simultaneously takes place, the original shape of gas hydrate particles can be preserved as cavities filled with carbonate cements precipitating simultaneously to gas hydrate decomposition. Such fabrics have been observed in modern cold seeps with gas hydrate filling voids in seep carbonates composed of micrite and botryoidal aragonite (Bohrmann et al. 1998; Greinert et al. 2001; Sassen et al. 2004; Teichert et al. 2005). Hydrate-derived cements and microfabrics have also been reported in ancient seep carbonates (Dela Pierre et al. 2010; Martire et al. 2010; Bojanowski et al. 2015). This interpretation could explain the irregular shape of these micro-domains due to a non-homogeneous destabilization of gas hydrate, their isolated position within the cavities, and the void-filling limpid spar within them. Additionally, it is difficult to reconcile the thin micritic rim around these micro-domains with a local dissolution. The presence of the micritic rim could be related to carbonate precipitation mediated by microbial communities living in direct contact with gas hydrate (Sassen et al. 1998, 2004; Lanoil et al. 2001; Knittel et al. 2005). Therefore, it is proposed that these spar-filled micro-domains could represent a new clathritic microfabric (*sensu* Bojanowski et al.

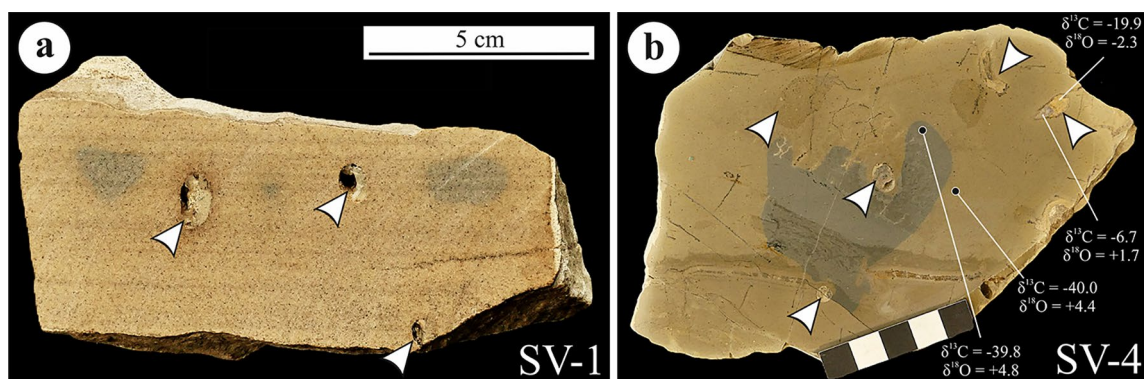


Fig. 10 Polished slabs of specimens SV-1 (a) and SV-4 (b). White arrowheads indicate sections of burrows. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values expressed in per mill

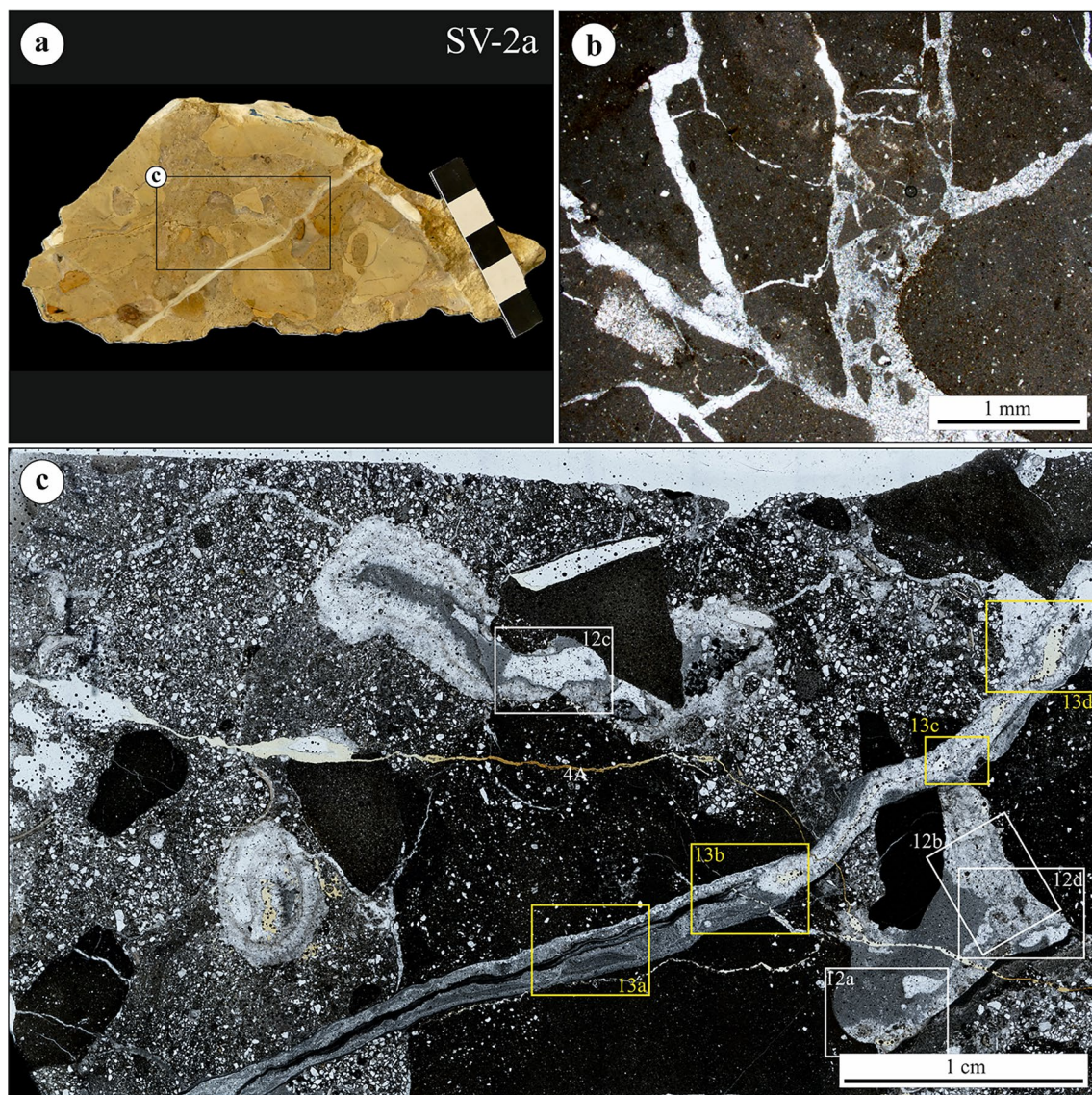


Fig. 11 (a) Polished slab of specimen SV-2a. (b) Jigsaw-puzzle fabric preserved in the brecciated facies, with microspar cementing the spaces among the micritic angular clasts (from SV-2b). (c) Thin section scan of specimen SV-2a (location in the black rectangle area in (a))

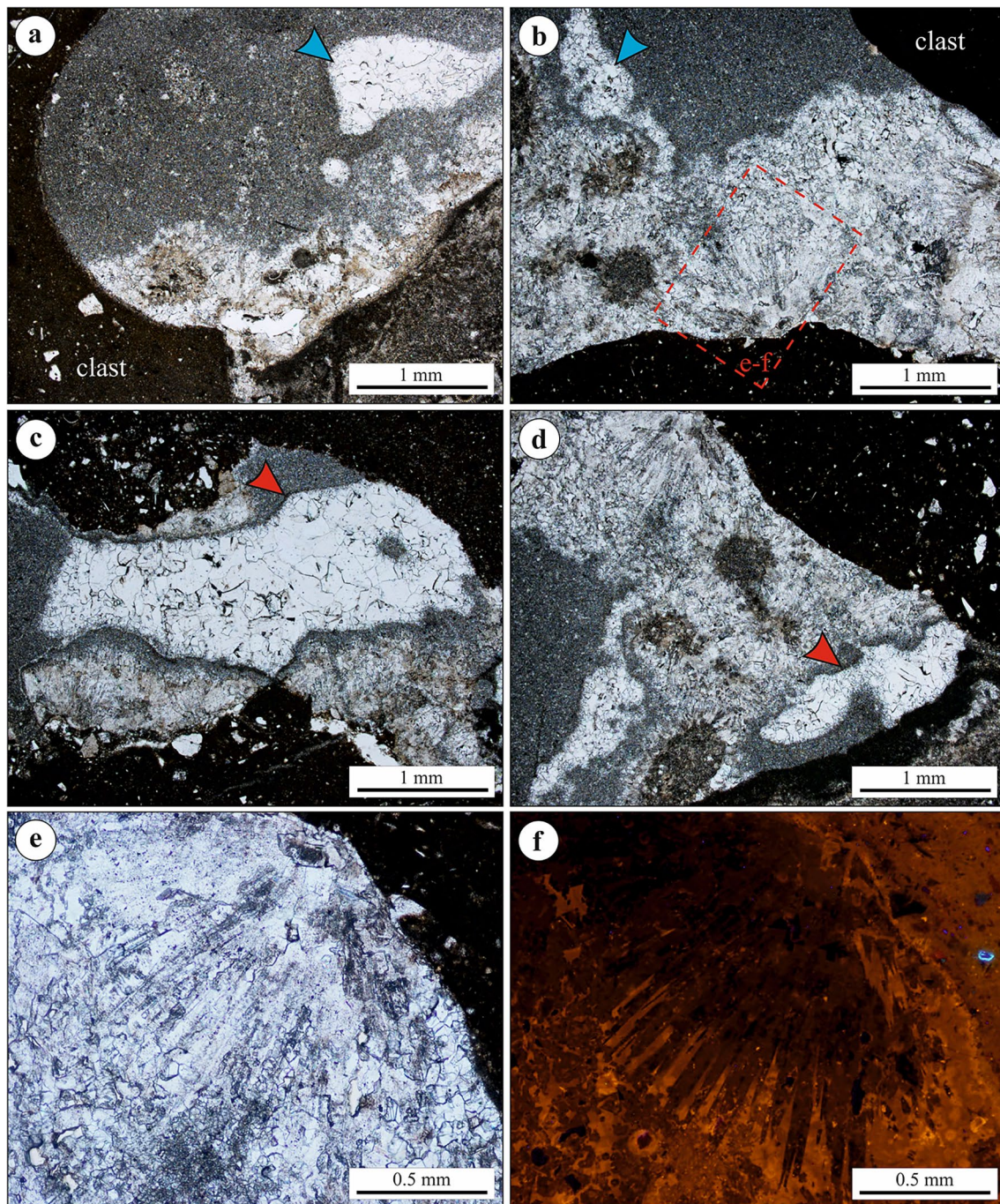


Fig. 12 Plane polarized photomicrographs (except **f**, in CL) of the different carbonate cements in the cavities of the brecciated facies. Sample SV-2a, see location in Fig. 11c. **(a)** Microsparitic cement coupled with fibrous crystals (lower part), and irregular-shaped, spar-filled irregular micro-domain (light blue arrowhead). Note the rounded but sharp contact with the surrounding micrite of the clasts. **(b)** Fibrous crystals (bottom) coupled with microsparitic cement, and spar-filled irregular micro-domain (light blue arrowhead) **(c)** Limpid spar-filled

micro-domain within a cavity. Note the thin micritic rim (red arrowhead) and the botryoids of fibrous crystals at the bottom. See also Fig. 14a, b. **(d)** Botryoids of fibrous crystals (upper left) and irregular-shaped, spar-filled micro-domains (lower right) surrounded by a micritic rim (red arrowhead). **(e-f)** Paired plane polarized light and CL images of the fibrous crystals forming a botryoid. Note the contrasting non-luminescence of the botryoid in comparison to the surrounding cement. Location in the red dashed rectangle in **(b)**

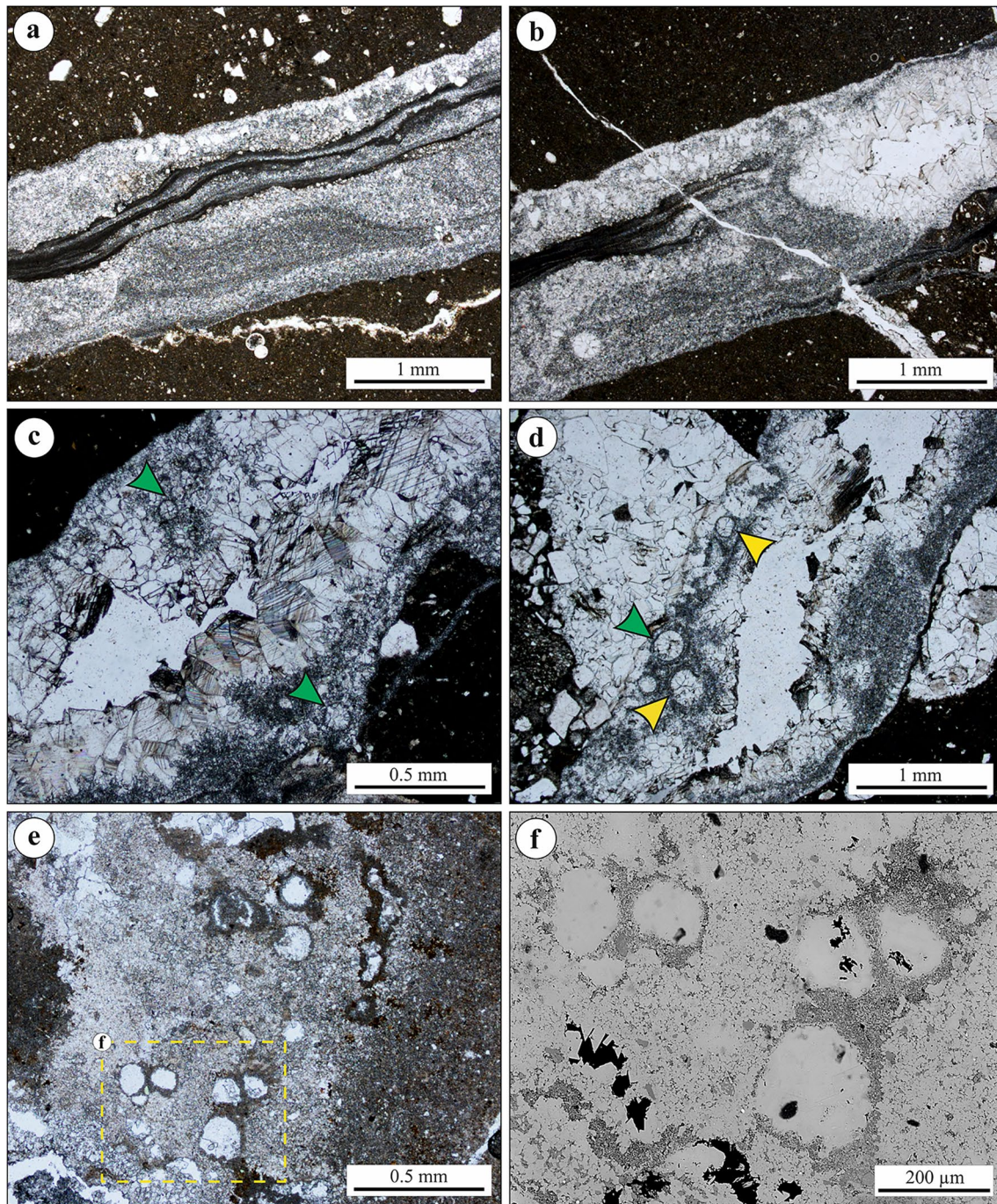


Fig. 13 (a) Micritic and microsparitic laminae within the veins cross cutting the brecciated facies. (b) Micritic laminae abruptly terminated at the margin of a rounded and carbonate-filled cavity. (c) Detail of the crystals filling the same cavity as in (b). (c) Spar-filled spheres within the veins (green arrowheads). Note the dark rim around them. (d) Clustered and isolated spheres (arrowheads) with possible indenta-

tions of the rim (yellow arrowheads). (e) Clustered spheres with a thick rim. (f) BSE image of the clustered spheres (location in the yellow rectangle in e). Note the detrital material present in the rim surrounding them. Plane polarized light except f (BSE). Panels a to d: sample SV-2a; panels e and f: sample SV-2b

2026), potentially useful for identification of past occurrences of gas hydrate in marine environments.

Evidence of benthic activity

The two types of tubular structures reported from the carbonate mound differ in both dimension and internal organization. The more abundant type (type I) is larger and formed by multiple concentric laminae and occluded by blocky calcite in the centre. The strongly negative $\delta^{13}\text{C}$ values of the laminae and the blocky calcite (as low as -38.8‰) may suggest that these structures acted as conduits for the migration of hydrocarbons (Figs. 6 and 7). Their parallel orientation, high density and uniform diameter, collectively suggest burrows. It is therefore proposed that these tubular structures were originated by the action of burrowing fauna and subsequently served as conduits for hydrocarbon-charged fluids (Minisini and Schwartz 2007; Wiese et al. 2015; Blouet et al. 2021; Wetzel and Blouet 2023; Bojanowski and Wetzel 2026), as reported also from modern environments (Tamboirino et al. 2019; and references therein). The outermost lamina of type I structures is composed of mixed carbonate and silt-sized detrital material. In this case, the detrital material in the outermost lamina would represent sediment particles transported into a burrow and stabilized on the walls (e.g. through mucus secretion), and eventually by carbonate cementation, possibly in response to microbial degradation of mucus, analogously to the scenario suggested by Bojanowski and Wetzel (2026). Carbonate precipitation in some of the conduits could have been also induced by the presence of sulphide-oxidising bacteria (Smrzka et al. 2024), whose bacterial cells were entombed in the process and preserved as spar-filled spheres (Fig. 6f). Formation of the following lamina composed of clotted micrite, typical for cold seeps, was probably also induced by microbial activity, but related to AOM or sulphide oxidation (Peckmann and Thiel 2004; Smrzka et al. 2024). Formation of the final microspar/blocky cement was probably related to AOM as well, which eventually clogged or strongly reduced the fluid flow. A similar case has been reported from the Late Cretaceous Tepee Buttes in Colorado, USA, where former methane expelling conduits are lined with particles of siliclastic material accumulated in response to ascending fluids, particularly adhering to gas bubbles (Krause et al. 2009). The different fine-crystalline laminae and the spar/blocky calcite in tube centre, all precipitated due to AOM, would have then progressively occluded these conduits (Krause et al. 2009). Alternatively, the outer lamina of these tubular structures could be indicative of agglutinated tube worms (Hryniewicz et al. 2020; Georgieva and Little 2022) or even agglutinated tubes produced by other organisms, such as crustaceans (Klompaker et al. 2022). The spar-filled

spheres occasionally found inside these structures could be a feature inherited from the porous structure of a tube worm (Gómez-Pérez 2003). Spherical features have also been reported on the outer surface of cold seep tube worms from the Rocky Knob in New Zealand, although with a bigger diameter (Georgieva et al. 2019).

The less-abundant and smaller tubular structures (type II) are possibly fossilised tube worms (Fig. 9). The inner layer composed of fibrous crystals could in fact represent the mineralisation process by which aragonite replaces the originally-organic posterior wall of vestimentiferans (Goedert et al. 2000; Haas et al. 2009; Georgieva and Little 2022). Disrupted and delaminated tube layers (Fig. 9a) have been reported from the geological record (Peckmann et al. 2005; Haas et al. 2009; Georgieva et al. 2019; Hryniewicz et al. 2020) and are the consequence of the progressive degradation of the chitin-protein secretions forming the original organic tube wall of vestimentiferans (Shillito et al. 1995; Peckmann et al. 2005). If this hypothesis is correct, this would be the first report of non-calcareous tube worm preserved in the Northern Apennines, useful for future ecological considerations (Vinn 2022). Tube worms have been reported from the northern Apennines, although belonging to the calcareous-walled family Serpulidae (Barbieri and Cavalazzi 2005; Vinn et al. 2012, 2013; Kiel et al. 2018).

Timing of hydrocarbon seepage

U-Pb carbonate dating method is an established approach for providing timing constraints for sedimentary processes (e.g. Rasbury and Cole 2009; Roberts et al. 2020); and has been successfully applied to seep carbonates, showing that their radiometric age can match the age assumed by biostratigraphic investigations (Miyajima et al. 2023) or detecting age discrepancies between seep-related carbonate precipitation and the sediments hosting the seep carbonates (Giunti et al. 2025). $^{234}\text{U}/^{238}\text{U}$ or ^{230}Th disequilibrium can occur in carbonates due to alpha recoil in the U-Pb system, or inheritance of detrital ^{230}Th (e.g. Roberts et al. 2020; Weij and Edwards 2025) and if uncorrected, can lead to over-estimation of $^{206}\text{Pb}/^{238}\text{U}$ ages (e.g. Vermeesch et al. 2025), or U-Th ages (for samples younger than $\sim 500,000$ years; Van Calsteren and Thomas 2006). ^{234}U was not measured in this study, so we cannot accurately assess any potential $^{234}\text{U}/^{238}\text{U}$ disequilibrium. However, as the data are imprecise ($\sim 12\%$ uncertainty), any potential over-estimation in ages would not impact the yielded age significantly within the uncertainty of the age estimation. For example, if we apply a correction based on an assumed initial $^{234}\text{U}/^{238}\text{U}$ of 2.25 (average for carbonates; Roberts et al. 2020), the yielded age reduces from ca. 6.8 to ca. 6.3 Ma, within the uncertainty of ± 0.9 Ma (see Fig. SI4). We therefore interpret

the radiometric age measured in the microspar at the centre of one of the conduit as reasonably well constrained, even though the associated error makes it spanning from the late Tortonian to the Messinian (6.8 ± 0.9 Ma). This age significantly postdates the late Serravallian – early Tortonian age (ca. 12.5–10.5 Ma) of the Verghereto Marls enclosing the studied seep carbonates (Conti et al. 2024b), and far out of range of any disequilibrium (ca. 0.5 Ma). The Verghereto Marls are bio-stratigraphically constrained to the biozones MNN7 and 8 (Conti et al. 2021, 2024b); the latter has as upper limit concomitant with the first appearance of *Discoaster hamatus*, placed at ca. 10.5 Ma (Raffi et al. 2003; Backman et al. 2012). Consequently, a significant amount of time passed (at least 2.8 Ma) since the deposition of the marls and the hydrocarbon seepage that led to the precipitation of the spar inside this conduit. However, this single radiometric age does not allow to determine exactly when the initial seepage started, as this cement represents only the latest carbonate phase observed. The presence of chemosynthesis-based fauna such as tube worms and possibly lucinids (even though the bivalve moulds observed lacked diagnostic features) suggests that the carbonate mound started to form during active hydrocarbon seepage at the sediment-water interface. Additionally, such age does not imply that the seepage was continuously active, as fluid emissions in cold seeps can be episodic and not steady over time (e.g. Taviani et al. 2013).

The U-Pb age obtained from the conduit predates the onset of the MSC (5.97–5.33 Ma; Roveri et al. 2016). The large number of cold paleoseeps dispersed in different sub-basins in upper Miocene sediments (Pierre et al. 2002; Pierre and Rouchy 2004; Clari et al. 2009; Argentino et al. 2019a, b; Conti et al. 2021) suggests that the Mediterranean basins experienced large-scale hydrocarbon emissions. In this context, the relationships between such emissions and the important paleogeographic changes of the Messinian, in particular the onset of the sea level drop (Bertoni et al. 2013), could benefit from the application of absolute dating techniques on seep carbonates across the Mediterranean.

Raman microspectroscopy

Marine cold seeps are sites where organic matter is often abundant (Suess 2018). The Raman spectra, collected in a transect through a representative conduit, display signals with varying intensities and shapes at the first-order region >1000 cm^{-1} , aside of the primary ν_1 symmetric stretching band at 1086–1087 cm^{-1} (Fig. 8b). Signals in the spectral region of 1000–1800 cm^{-1} belong to organic matter (OM) and may be used to identify its maturity and structural order (Allwood et al. 2006; Kouketsu et al. 2014; Henry et al. 2019). The low $\delta^{13}\text{C}$ values of the calcite in the conduits

imply AOM, and thus these Raman signals could represent the presence of hydrocarbons trapped in nano-scale inclusions or residual biomass preserved after AOM-related carbonate precipitation. The signals of the Raman spectra reported in the present work fit best to of the presence of amorphous, disordered OM due to the lack of a distinct G band at 1580 cm^{-1} and the presence of a predominant D2 band (ca. 1640 cm^{-1}) (Fig. 8b). In fact, the overall signals of crystalline OM separate into the prominent G band of graphite (ca. 1580 cm^{-1}) and a broad D band at 1340–1360 cm^{-1} (Henry et al. 2019). In disordered OM however, several D bands (D1: ca. 1340 cm^{-1} , D2: ca. 1610 cm^{-1} , D3: ca. 1500 cm^{-1} , D4: ca. 1200 cm^{-1} , D5: ca. 1260 cm^{-1} , D6: 1440 cm^{-1}) associated with structural defects and the presence of heteroatoms appear with increasing disorder (Henry et al. 2019). In the case of highly disordered OM, a debate regarding the correct nomenclature and number of the G and D bands is still ongoing (Henry et al. 2019; and references therein). According to Kouketsu et al. (2014), the G band disappears entirely in amorphous OM, and the band >1600 cm^{-1} represents the signal of the disordered graphite lattice at A_{1g} symmetry assigned to the D2 band becomes most prominent.

The broad signals of organic bands (D1, D2, D4, and D5/6), present in the blocky calcite, are indicative for disordered organic matter due to the lack of a distinct graphite G band (Beny-Bassez and Rouzaud 1985; Allwood et al. 2006; Romero-Sarmiento et al. 2014; Henry et al. 2019). In fact, Allwood et al. (2006) interpreted the band above 1600 cm^{-1} as a combination band of a D2+G band and up shift as a result of increasing disorder of carbonaceous material represented in disordered $^{2\text{sp}}$ carbons. The disordered OM present in the blocky spar may be explained by cementation of OM during filling of the conduit. The intensive distinct D2 band, which is present in the spar towards the centre of the conduit (Spectrum 14) and in the micritic lamina (Spectrum 12), may indicate sequential entrapment of OM during progressively filling of the conduit (Fig. 8b).

Conclusions

Seep carbonates from the San Vernicio area (northern Apennines, Italy) were studied with different techniques to characterize the hydrocarbon seepage that occurred during the late Miocene (Fig. 14a). Petrographic observations led to the recognition of numerous seep-related features, such as dissolution cavities, fossilized giant sulphide-oxidising bacteria, organic-walled tube worms and botryoids of aragonite neomorphosed into calcite, as well as to the discovery of a new potential gas hydrate-derived (clathritic) micro-fabric (Fig. 14b). Overall, the $\delta^{13}\text{C}$ values ($>38.8\text{‰}$ V-PDB)

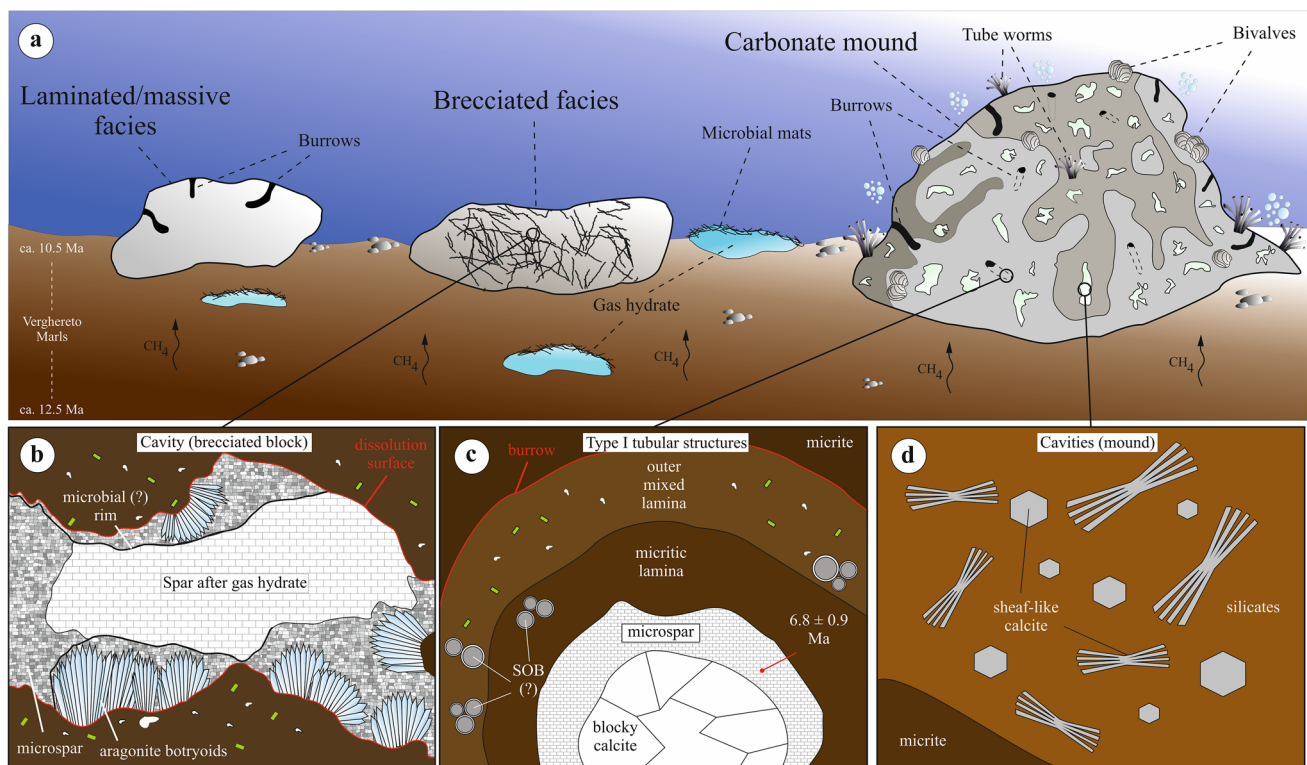


Fig. 14 (a) Simplified scenario of late Miocene seepage and its various products in the studied area (not to scale). (b) Schematic representation of cavities inside the brecciated carbonate facies. (c) Schematic sequence of laminae inside a former burrow now preserved as fluid

additionally imply that carbonate precipitation was related to hydrocarbon seepage. Tubular structures (up to 1 cm in diameter) are filled with concentric laminae and interpreted as remnants of conduits representing former burrows (Fig. 14c). These conduits facilitated focused fluid flow of ascending hydrocarbon-charged fluids, as testified by the consistently ¹³C-depleted composition of all the concentric laminae. The microspar in the central part of one of these conduits yielded a U-Pb age of 6.8 ± 0.9 Ma, indicating that the seepage responsible for the precipitation of this cement postdates the deposition of the enclosing marl deposits, which are biostratigraphically dated between ca. 12.5 and 10.5 Ma. The description of features previously unreported in this northern Apennines paleoseep, as well as a new gas hydrate-derived (clathritic) petrographic indicator, shed new light on the modalities of hydrocarbon emissions during the late Miocene, a period of drastic geological and climatic transformations in the Mediterranean area.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10347-026-00742-8>.

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conduit. SOB: sulphide-oxidising bacteria. (d) Sheaf-like calcite crystals (in longitudinal and hexagonal cross sections) and silicates inside a cavity of the carbonate mound

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