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(Article begins on next page)

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From biogenic silica and organic matter to authigenic clays and dolomite: Insights from Messinian (upper Miocene) sediments of the Northern Mediterranean

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ABSTRACT

The biogeochemical cycles of carbon and silicon are tightly coupled in modern marine environments due to the pivotal role of planktonic diatoms. Once diatoms are sedimented, the fate of organic matter and biogenic silica is initially governed by bottom water oxygen levels and bacterial communities involved in remineralization processes. The early diagenesis of biosiliceous sediments may result in drastic changes in composition, sometimes hampering palaeoenvironmental reconstruction. Sedimentary successions deposited in the Mediterranean region during the Messinian salinity crisis (5.97 – 5.33 Ma) allow to explore the early diagenetic transformation of organic matter and biogenic silica in a restricted basin experiencing a severe palaeoceanographic turnover. Sedimentological and petrographic observations coupled to elemental, mineralogical,

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inorganic and organic geochemical analyses were carried out on biosiliceous (diatomaceous shales and diatom-bearing mudstones) and associated clay-rich and dolomite-rich sediments (dolomitic mudstones) interbedded with primary gypsum layers in the Piedmont Basin (north-west Italy). The state of preservation of biogenic silica was governed by different pathways of organic matter remineralization, depending on bottom and pore water redox conditions, which were controlled by the structure of the water column. Aerobic respiration of organic matter in a mixed water column and an oxygenated seafloor promoted biogenic silica preservation. In contrast, bottom water anoxia induced by permanent stratification of the water column favoured the concomitant formation of dolomite and authigenic clays. In particular, organic matter degradation through bacterial sulphate reduction increased pore water alkalinity, promoting the precipitation of dolomite. At the same time, the rise in pH promoted the dissolution of biogenic silica which, reacting with pore water cations, ultimately caused the formation of authigenic clays. This study suggests that the apparent annihilation of Mediterranean marine biota during the Messinian salinity crisis partially reflects an early diagenetic bias produced by interactions of the carbon, silicon and sulphur biogeochemical cycles in a restricted basin.

Key-words: authigenic clays, biogenic silica, dolomite; early diagenesis, lipid biomarkers, Messinian salinity crisis, organic matter.

INTRODUCTION

In modern oceans silica-secreting microorganisms play a fundamental role in the biogeochemical cycles of carbon (C) and silicon (Si) (Tréguer *et al.*, 2018, 2021). Notably, planktonic diatoms account for approximately 40% of marine primary production and dominate the pelagic production of biogenic silica, exporting around 0.1 to 0.2 Gt C and 3.1 Gt Si from surface waters each year (Pierella Karlusich *et al.*, 2021; Tréguer *et al.*, 2021). Both C and Si are subjected

to various degrees of diagenetic transformation immediately after deposition at ambient conditions (e.g. Michalopoulos & Aller, 2004), and during burial following significant temperature change depending on depth and local geothermal gradient (e.g. van der Lingen, 1977). Addressing diagenetic processes is therefore pivotal for constraining the biogeochemical cycles of C and Si since diagenetic alteration may compromise the reconstruction of palaeoenvironments and the study of evolutionary trajectories of siliceous microorganisms – both potentially biased by the sequential loss of biomineralized remains in the sedimentary record (e.g. Cermeño, 2016; Westacott *et al.*, 2021). Several studies have demonstrated a fundamental contribution of diatoms and other siliceous organisms to the accumulation of organic matter in sediments, even in cases where biogenic silica is scarce or no longer preserved (e.g. Sinninghe Damsté *et al.*, 1995; Schulz *et al.*, 1996; Dickman & Glenwright, 1997; Kemp *et al.*, 1998, 1999; Pearce *et al.*, 1998; Schwark *et al.*, 2009; McKirdy *et al.*, 2013; Isaji *et al.*, 2019; Elling *et al.*, 2021).

While burial diagenesis of biosiliceous sediments has already been studied extensively (e.g. van der Lingen, 1977; Hein *et al.*, 1978; Pisciotto, 1981; Behl & Garrison, 1994; Thyberg *et al.*, 1999; Davies & Cartwright, 2002; Abu-Mahfouz *et al.*, 2020; Varkouhi *et al.*, 2021), the early diagenetic transformation and degradation pathways involving biogenic silica and organic matter at the sediment–water interface and in the topmost part of the sedimentary column are less well constrained (e.g. Michalopoulos & Aller, 1995, 2004). Organic matter associated with cells of siliceous microorganisms can be degraded aerobically (e.g. Holstein & Hensen, 2009; Jørgensen *et al.*, 2022), leaving no direct mineralogical evidence in the rock record if diatom frustules are dissolved. In contrast, bottom water anoxia favours bacterial organoclastic sulphate reduction (i.e. sulphate reduction with organic matter as electron donor). Sulphate reduction commonly causes the formation of authigenic carbonate – especially dolomite – and iron sulphide (pyrite) minerals by the generation of alkalinity and more reducing conditions (e.g. Vasconcelos *et al.*, 1995; Wilkin *et al.*, 1996; Wright, 1999; Mazzullo, 2000; Warren, 2000; Shoonen, 2004; Wright & Wacey, 2005; Bontognali *et al.*, 2010, 2013; Zhang *et al.*, 2012; Petrash *et al.*, 2017; Lu *et al.*, 2018; Duverger *et*

al., 2020; Li *et al.*, 2021; Tribovillard *et al.*, 2022). Such microbially-produced mineral phases provide evidence of formerly high contents of organic matter in the sediments, even if organic matter is no longer preserved.

The early diagenesis of biogenic silica in modern sediments has been addressed mainly by numerical model calculations based on the chemical analysis of pore water (e.g. Tréguer *et al.*, 2021), with few studies focusing on mineralogical aspects of this process (e.g. Michalopoulos & Aller, 1995, 2004). Interestingly, biogenic silica alteration in combination with free cation-rich pore waters promotes authigenic clay formation (a reaction known as reverse weathering), which is a fast process potentially representing an underestimated sink of Si (e.g. Badaut & Risacher, 1983; Noël & Rouchy, 1986; Michalopoulos and Aller, 1995, 2004; Presti & Michalopoulos, 2008; Rahman, 2019). Several studies demonstrated that authigenic clay formation can be microbially-mediated, highlighting the close interplay of the C and Si biogeochemical cycles during early diagenesis (e.g. Konhauser & Urrutia, 1999; Kim *et al.*, 2004, 2019; Liu *et al.*, 2012; Bontognali *et al.*, 2014; Burne *et al.*, 2014; Kremer *et al.*, 2018, 2019; del Buey *et al.*, 2021).

This paper presents the results of a combined sedimentological, petrographic, mineralogical and geochemical study of biogenic silica-rich, dolomite-rich and clay-rich deposits formed during the so-called Messinian salinity crisis (MSC), a major palaeoceanographic event that affected the Mediterranean in the late Neogene, between 5.97 and 5.33 Ma (Ryan, 1973; Selli, 1973; Hsü *et al.*, 1973; Cita *et al.*, 1978; Krijgsman *et al.*, 1999; Rouchy & Caruso, 2006; Roveri *et al.*, 2014). This event was associated with the formation of more than 1 million km³ of evaporites (carbonate minerals, gypsum and halite; Haq *et al.*, 2020) in both peripheral marginal basins and deep basinal areas. Many evaporites are rhythmically interbedded with clay-rich and dolomite-rich layers. The lithologies consisting of non-evaporite minerals have received much less attention than the evaporites themselves, although their study can provide valuable insights for palaeoenvironmental reconstructions (e.g. Dela Pierre *et al.*, 2014). This study focuses on a sedimentary succession deposited during the first stage of the MSC in the Piedmont Basin, at the northernmost offshoot of

the Mediterranean (cf. Dela Pierre *et al.*, 2011). This succession comprises an alternation of gypsum beds, dolomitic mudstones and diatomaceous layers (Fourtanier *et al.*, 1991), allowing a detailed reconstruction of the early diagenetic transformation of biogenic silica-rich and organic matter-rich sediments deposited in a restricted basin during a palaeoenvironmental crisis.

GEOLOGICAL AND STRATIGRAPHIC SETTING

Overview of Messinian salinity crisis events in the Mediterranean

Following the restriction of the connection with the Atlantic Ocean along the Rifian and Betic gateways, which started at approximately 7.2 Ma (Kouwenhoven & van der Zwaan, 2006), the Mediterranean turned into the youngest salt giant in Earth history during the MSC. Recent studies have highlighted that the MSC evolved through three main stages (e.g. Roveri *et al.*, 2014). During the first stage (5.97–5.60 Ma), sulphate evaporites referred to as the Primary Lower Gypsum unit (PLG) were deposited in the peripheral basins of the Mediterranean. The PLG unit consists of the rhythmic alternation of shales, mudstones and primary, *in situ* gypsum beds. The lithological cyclicity is interpreted to reflect precession-driven climate change, with shales and mudstones associated with humid climate at precession minima (insolation maxima) and gypsum coinciding with arid climate at precession maxima (insolation minima). Shales and mudstones are commonly characterized by high contents of dolomite and smectite, traditionally interpreted as reflecting a sabkha-like palaeoenvironment and the erosion of seasonally arid peri-Mediterranean palaeosoils, respectively (e.g. Chamley *et al.*, 1977; Friedman, 1973). During the second stage (5.60–5.55 Ma), the PLG unit was uplifted and eroded. The products of erosion were transferred downslope by various types of gravity flows (Manzi *et al.*, 2005), forming the Resedimented Lower Gypsum (RLG) unit, which consists of clastic gypsum deposits mixed with shales (Manzi *et al.*, 2021) that interfinger, at least in Sicily, with halite and potassium/magnesium salts. During the third stage

(5.55–5.33 Ma), a new evaporitic unit (Upper Gypsum) was deposited in the Southern and Eastern Mediterranean, whereas clastic sediments are found in the western and northern sectors of the basin. Both units are typified, in the upper part, by brackish water sediments associated with the so-called Lago Mare phase, whose origin is still being debated (e.g. Caruso *et al.*, 2020; Andreetto *et al.*, 2021; Carnevale & Schwarzahans, 2022).

Messinian salinity crisis record in the Piedmont Basin

The Piedmont Basin (**Fig. 1**) is a large wedge top basin filled with Eocene to upper Miocene sediments overlying a complex tectonic wedge of Alpine, Ligurian and Adria basement units juxtaposed during the meso-Alpine collisional event (e.g. Mosca *et al.*, 2010; Rossi & Craig, 2016; Rossi, 2017). The MSC sedimentary record consists of the PLG unit at the basin margins passing laterally into organic-rich and dolomite-rich shales towards the basin depocentre (e.g. Lozar *et al.*, 2018; Sabino *et al.*, 2021; Natalicchio *et al.*, 2021). The PLG unit consists of up to 15 lithological cycles made up of shale/mudstone and gypsum couplets (e.g. Natalicchio *et al.*, 2021). The sixth gypsum bed corresponds to a distinct marker bed (Sturani Key Bed; see Dela Pierre *et al.*, 2011), recording the appearance of two gypsum lithofacies not observed in the underlying beds that consist of vertically oriented selenite crystals: laminar gypsum (balatino, *sensu* Ogniben, 1957) and branching selenite, i.e. metre-sized flattened cones composed of horizontally oriented millimetre to centimetre-sized crystals (e.g. Natalicchio *et al.*, 2021). The lateral distribution of the gypsum lithofacies reflects the progressive deepening of the basin from south-west to north-east, whereas the vertical stacking pattern indicates basin shallowing. Interestingly, the non-evaporitic component of the PLG unit (i.e. the shale and mudstone interbeds that are the object of this study) is typified by high contents of dolomite, interpreted to be of microbial origin (e.g. Dela Pierre *et al.*, 2014). Isolated diatom moulds (Dela Pierre *et al.*, 2014) and thin layers of diatomaceous sediments have also been reported (Fourtanier *et al.*, 1991; Irace *et al.*, 2005), the latter exposed in the Bric

Cenciurio and Cascina Botto sections investigated in this study. The PLG unit is overlain by chaotic and clastic gypsum deposits of the Valle Versa Chaotic complex, corresponding to the local equivalent of the RLG unit, and by the Cassano Spinola Conglomerates, consisting of fluvial, lacustrine and marine sediments deposited during the third stage of the MSC (Dela Pierre *et al.*, 2011; Andreetto *et al.*, 2022).

MATERIAL AND METHODS

Sampling sites

Two sections exposing the PLG unit were studied (**Fig. 1**): the Bric Cenciurio section (44°45'45.0"N; 8°03'07.9"E) and the Cascina Botto section (44°44'59.6"N; 8°23'05.1"E). In both sections, gypsum layers are interbedded with dolomite-rich and diatomaceous sediments (Fourtanier *et al.*, 1991; Irace *et al.*, 2005). In the field, weathered surfaces on rocks were thoroughly removed and fourteen samples (thirteen from the Bric Cenciurio section and one from the Cascina Botto section, for the sake of comparison) were collected. Samples from the Bric Cenciurio section were wrapped in aluminium foil and stored at −20°C until further treatment.

Sedimentological and petrographic study

The lithology and sedimentological features of the non-evaporitic intervals of the PLG unit were documented. Fifteen petrographic, polished thin sections (thirteen perpendicular and two parallel to the bedding plane) were produced after epoxy impregnation of the samples from the Bric Cenciurio section (**Fig. 2**), and more than 100 chips of unconsolidated samples were studied using transmitted, reflected and UV light microscopy using a Leica DM 2770 P microscopy equipped with a digital photcamera (Leica Microsystems, Wetzlar, Germany). Scanning electron

microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analyses were performed on thin sections (backscattered electron imaging, BSEI) and sediment chips (secondary electron imaging, SEI) after carbon coating, using a JSM IT300LV (Department of Earth Sciences of the University of Torino; JEOL Limited, Tokyo, Japan) and a Tescan S9000G, (Department of Chemistry of the University of Torino; Tescan, Brno, Czechia). For the diatom-bearing samples of the Bric Cenciurio section, only the dominant or more recurrent taxa observed on freshly broken subsamples are reported (for a comprehensive taxonomic list see Fourtanier *et al.*, 1991). Freshly-broken sediment chips from the Cascina Botto section were studied with SEM-EDS.

Elemental, mineralogical and dolomite C and O stable isotope analyses

Selected polished thin sections and freshly-broken sediment chips of a single sample of diatomaceous shales, a single sample of diatom-bearing mudstones and two samples of dolomitic mudstones from the Bric Cenciurio section (samples 10, 13, 3 and 2; see **Fig. 2**) have been semi-quantitatively analyzed by means of electron dispersive X-ray spectroscopy (EDS Oxford INCA Energy 200 equipped with INCA detector X-act SDD thin window; Oxford Instruments, Abingdon, UK), combining automated maps and manual check of single spots using the software AZtec® and INCA® (Oxford Instruments). The percentages of aluminium (Al), iron (Fe), potassium (K), magnesium (Mg) and Si obtained from 150 spots (50 for each analyzed lithology) were plotted on ternary diagrams following Konhauser & Urrutia (1999).

Bulk mineralogy of the same samples was characterized with X-ray powder diffraction (XRPD). Clay minerals *sensu lato* were characterized with the standard sequential characterization procedure (e.g. Brindley & Brown, 1961) on the silt-sized and clay-sized fraction (<20 µm) obtained by gravimetric separation. This fraction was saturated with Mg by continuous stirring overnight using a 1 M magnesium chloride (MgCl₂) solution. After Mg saturation, the excess MgCl₂ was removed by washing the sample in ultrapure water 18 MOhm and shaking it with an

elliptical shaker for two hours. The washing routine was repeated three times for each sample to avoid $MgCl_2$ precipitation during drying. The fraction was collected each time by centrifugation at 4000 RPM for 60 minutes. After the last rinse, the samples were deposited on glass slides and dried at room temperature to obtain oriented clay samples for further treatments. Swelling clay minerals were determined by vapour saturation of the oriented clay samples in glycol ethylene at 70°C for three hours. Thermally sensitive mineral phases were determined by heating the oriented clay samples at 300°C and 550°C for two hours, respectively. After each treatment, oriented clay samples were characterized with a Rigaku MiniFlex 600 benchtop X-ray diffractometer (Rigaku, Tokyo, Japan), Bragg-Brentano geometry, $CuK\alpha$ radiation, X-ray source operating at 40 kV and 15 mA; D/teX Ultra2 silicon strip detector; $2^\circ < 2\theta < 50^\circ$, step width 0.005° , scan speed $0.3^\circ/\text{min}$. XRPD patterns after each treatment were decomposed using the Fityk free curve fitting and data analysis software (Wojdyr, 2010) and analyzed to determine the clay minerals in the fine-grained fraction of each sample. Interlayered structures were simulated using the PyXRD free software (Dumon & Van Rast, 2016) to model X-ray diffraction patterns of disordered lamellar structures.

The bulk mineralogical characterization of the samples and quantitative analysis were performed using a Rigaku SmartLab XE X-ray diffractometer with Bragg-Brentano geometry, $CuK\alpha$ radiation, X-ray source operating at 40 kV, 30 mA; D/teX Ultra 250 HE silicon strip detector; $5^\circ < 2\theta < 80^\circ$, step width 0.01° , scan speed $1^\circ/\text{min}$. Data were analyzed using the Match! (Crystal Impact) phase analysis software. Quantitative analysis was performed using the Reference Intensity Ratio method with silicon as the internal reference standard.

Carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) stable isotope analyses were conducted at the Department of Earth Sciences of the University of Milano (Italy) on six samples of dolomitic mudstones from the Bric Cenciurio section (samples 2, 3, 4, 5, 6 and 8; see **Fig. 2**). Analyses were performed using an automated carbonate preparation device (Gasbench II) and a Thermo Fisher Scientific Delta V Advantage continuous flow mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). The powders of dolomitic samples were reacted with >99% orthophosphoric acid at 70°C for 8

hours. The carbon and oxygen isotope compositions are expressed in the conventional delta notation calibrated to the Vienna Pee-Dee Belemnite (V-PDB) scale by the international standards IAEA 603 and NBS-18. Most samples were analyzed twice and the average values are provided.

Analytical reproducibility for the analyses was better than $\pm 0.1\%$ for both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. Corrections for different reaction times and fractionation for dolomite were carried out using the protocol of Kim *et al.* (2015).

Total organic carbon and biomarkers

Total organic carbon (TOC) quantification and lipid biomarker analyses were performed at the Institute for Geology of the University of Hamburg (Germany) on two samples of diatomaceous shales, one sample of diatom-bearing mudstones and three samples of dolomitic mudstones from the Bric Cenciurio section (samples 10, 12, 13, 8, 3 and 2; see **Fig. 2**). For carbon content analyses, the samples were powdered and split in two aliquots. The first aliquot was heated to 1350°C to measure the total carbon (TC) content using a LECO SC-144DR Carbon Analyzer equipped with an infrared detector (Leco Corporation, St. Joseph, MI, USA). The second aliquot was first heated to 550°C for 5 hours to remove the TOC and subsequently heated to 1350°C to measure total inorganic carbon (TIC). The TOC content was then calculated using the formula $\text{TOC} = \text{TC} - \text{TIC}$. Prior to the measurements, a standard (Synthetic Carbon Leco 501-034; 1.01 ± 0.02 carbon%) was analyzed for reference.

For lipid biomarker analyses, aliquots of the six samples above were dried overnight in an oven (45°C) and subsequently cleaned by removing a few millimetres of sediment from the external surfaces with a chisel. A homogenous powder was then produced for each sample using mortar and pestle. The samples were saponified with 6% potassium hydroxide in methanol (2 h, 80°C) and subsequently extracted manually via repeated ultrasonication, using a mixture of dichloromethane (DCM) and methanol (3:1), until the extracts became colourless. The combined extracts were

cleaned by washing with MilliQ water, and carboxylic acid salts in the aqueous phase were transferred to the organic phase by adding 10% hydrochloric acid (HCl) until the pH was approximately 2. After extraction, the previously extracted powder of the three dolomite-rich samples was decalcified with 10% HCl according to the procedure described by Birgel *et al.* (2014) and subsequently saponified and extracted a second time according to the procedure described above; the second extract tends to yield the molecular signature preserved within the carbonate mineral matrix. The total lipid extracts obtained after the two extractions (before and after decalcification) were separated into maltene (*n*-hexane-soluble) and asphaltene (DCM-soluble) fractions (see Natalicchio *et al.*, 2019, for further details). Maltene fractions were further separated into four different fractions of increasing polarity using aminopropyl-bonded silica gel column chromatography (Supelco glass cartridge: 6 ml, 500 mg, DSC-NH2) and a sequence of organic solvents: (i) hydrocarbons using *n*-hexane; (ii) ketones using *n*-hexane:DCM (3:1); (iii) alcohols using DCM:acetone (9:1); and (iv) carboxylic acids using 2% formic acid in DCM:formic acid. Compounds in the alcohol fraction were derivatized by adding a mixture of pyridine and (N,O)-*bis*(trimethylsilyl)trifluoroacetamide (BSTFA) to measure the alcohols as their TMS-derivatives. For hydrocarbons, alcohols and carboxylic acids, internal standards were added prior to extraction (5 α -cholestane, 1-nonadecanol, 2-me-C₁₈ fatty acid, and the dialkyl glycerol diether *n*-C₁₈/*n*-C₁₈). Compounds were identified using a gas chromatography–mass spectrometer (GC–MS) system, a Thermo Scientific Trace GC Ultra coupled to a Thermo Scientific DSQ II mass spectrometer. Compound assignment was based on relative retention times and published mass spectral data. In this study, a detailed quantification of lipids is only provided for the alcohol fraction, which revealed a high abundance and a good preservation of compounds produced by algae, bacteria and archaea (see below).

RESULTS

Field observations

The Bric Cenciurio section consists of an alternation of decimetre to metre-thick dolomitic mudstone and gypsum beds, the latter displaying different lithofacies (**Fig. 2**). The first two layers consist of clastic gypsum (gypsum-rudites grading into gypsum-arenites), whereas the overlying beds are made up of primary gypsum. In particular, the third bed contains decimetre-sized bottom-grown twinned selenite crystals, forming metre-sized cones in the upper part, separated by dolomitic mudstones (**Fig. 2**). The third gypsum bed, *ca* 3 m-thick, records the appearance of the branching selenite lithofacies and corresponds to the so-called Sturani Key Bed (**Fig. 2**; see Natalicchio *et al.*, 2021, for details). The Sturani Key Bed allows physical correlation with other Messinian sections of the Piedmont Basin (Dela Pierre *et al.*, 2011). Branching selenite is observed also in the upper two beds, *ca* 2 and 1 m thick, respectively. Above the Sturani Key Bed, a *ca* 20 cm-thick, whitish to pale brown diatomaceous shale layer is observed below a decimetre-thick slumped bed. In the upper part of the section, a prominent carbonate bed is found, containing diagenetic gypsum nodules and cavities derived from the dissolution of gypsum crystals. Above, a whitish to pale brown diatomaceous shale layer, *ca* 50 cm thick, underlies a decimetre-thick slumped layer. A *ca* 20 cm thick, faintly pinkish diatom-bearing mudstone layer is situated below the fourth gypsum bed (**Fig. 2**).

The Cascina Botto section starts with the alternation of homogeneous marls and laminated mudstones belonging to the Sant'Agata Fossili Marls (upper Tortonian–lower Messinian). The lower boundary of the PLG unit was traced at the base of sandy and clayey beds interrupted by diagenetic carbonate masses and dolomitic mudstones; a decimetre-thick diatomaceous layer was also recognized (Irace *et al.*, 2005, for details).

Sedimentology and petrography

Three lithofacies can be distinguished in the non-evaporitic interbeds of the PLG unit exposed in the Bric Cenciurio and Cascina Botto sections on the basis of the content and preservation of biogenic silica: (i) diatomaceous shales, typified by very high contents of pristine diatom valves; (ii) diatom-bearing mudstones, with common and poorly-preserved biosiliceous remains; and (iii) dolomitic mudstones, typified by traces of biogenic silica represented by close to completely dissolved diatom valves and etched sponge spicules.

Diatomaceous shales

The diatomaceous shales are characterized by fine lamination generated by the alternation of submillimetre-thick, white and dark (greyish, reddish to pale-brown) laminae (**Fig. 3A and B**).

Clear laminae enclose only minor clay-sized and silt-sized grains within an opal matrix (**Fig. 3C**).

Locally, gypsum rosettes displace single laminae or bundles of laminae (**Fig. 3D**). Contacts between laminae are sharp and most of the opal-rich laminae are laterally continuous (**Fig. 3E and F**); the latter are composed of closely stacked diatom valves and subordinate lensoidal pockets of clay-sized and silt-sized grains (**Fig. 3G**). In contrast, the laminae appearing dark in reflected light have a higher clay-sized and silt-sized grain content (**Fig. 3C**), with diatom valves and sponge spicules as accessory components (**Fig. 3H**). Dolomite and pyrite framboids are rare.

Opal-rich laminae are formed by dense mats of marine planktonic diatoms, notably well preserved specimens of Thalassionemataceae (*Thalassionema* spp. and *Thalassiothrix longissima*; **Fig. 4A and B**) and fragmented remains of Rhizosoleniaceae (**Fig. 4C and D**). Scattered specimens of other planktonic (for example, *Asterolampra* spp., *Bacteriastrum* sp., *Coscinodiscus* spp., *Chaetoceros* resting spores, *Nitzschia* spp., *Thalassiosira* spp.) and benthic (for example, *Cymatosira* spp.) diatoms, as well as chrysophyte cysts and silicoflagellates (*Stephanocha speculum*, commonly represented by aberrant specimens) occur in both opal-rich and clayey-silty laminae.

Diatom-bearing mudstones

The diatom-bearing mudstones are characterized by the alternation of submillimetre-thick, pale and brownish-reddish laminae, irregularly enriched in lensoidal, rhombohedral or roundish silt-sized gypsum grains and locally interrupted by greyish, massive layers (**Fig. 5A**). Close observation reveals compositional contrast between individual laminae, caused by minor fluctuation in the content of silt-sized grains (**Fig. 5B to D**). The brownish-reddish laminae contain abundant pyrite framboids and unidentified micron-sized grains, possibly corresponding to framboid microcrystallites (**Fig. 5B and E to G**); the laminae have high Fe and Si contents. The diatom assemblage comprises both planktonic marine (*Actinocyclus* cf. *octonarius* var. *tenellus*; Thalassionemataceae; **Fig. 5H to J**) and benthic, marine to brackish taxa (biddulphoids, naviculoids, *Surirella* spp.; **Fig. 5K to M**). The diatom remains are affected by dissolution, and are commonly coated with flocky lumps of clay minerals (**Fig. 5I to L**). Locally, thin threads occur at the interface between diatom valves and surrounding clays (**Fig. 5N**). Sponge spicules are better preserved than diatom valves, but also show etching pits (**Fig. 5O**).

Dolomitic mudstones

Dolomitic mudstones are characterized by closely to widely-spaced lamination defined by submillimetre to millimetre-thick, whitish to pale brown and reddish laminae (**Fig. 6A to C**); packets of laminae are locally disrupted by brownish to greyish millimetre to centimetre-thick massive to graded layers (**Fig. 6B**). Reddish laminae contain abundant pyrite framboids similar to the reddish diatom-bearing mudstones. Silt-sized terrigenous grains (quartz, feldspars and micas) are common and often surrounded by a reddish halo and pyrite framboids; the edges of terrigenous grains are commonly corroded (**Fig. 6D and E**). Blackish, lensoidal amorphous aggregates (**Fig.**

6F) and partially corroded gypsum crystals are present (Fig. 6F to H). All components are embedded in a finely crystalline matrix composed of spheroidal dolomite microcrystals, some of which exhibit a hollow core, and clay minerals. Dolomite microcrystals are a few microns in diameter and show a globular to cauliflower-like morphology (Fig. 7A to D). Locally, aggregations of framboids occur (Fig. 7E and F). Poorly preserved sponge spicules (Fig. 8A to D) and benthic diatom remains (Fig. 8E and F) are rare.

Elemental composition, mineralogy and dolomite C and O stable isotopes

The diatomaceous shales are typified by high Si contents caused by diatom valves (Fig. 9A); some spots of this lithology are characterized by high Al and Fe contents (Fig. 9B). Elements other than Si are mostly present in the laminae enriched in silt-sized and clay-sized terrigenous grains (Fig. 9C). In contrast, altered diatom remains are enriched in Al, Fe, K and Mg in the diatom-bearing mudstones (Fig. 9D and E). Interestingly, the elemental composition of these remains is similar to the composition of the finely crystalline clay minerals associated with spheroidal dolomite of the dolomitic mudstones (Fig. 9F and G). A trend of progressive enrichment in Fe, K and Mg from the pristine biosiliceous remains in diatomaceous shales over altered biosiliceous remains in the diatom-bearing mudstones to clay minerals in dolomitic mudstones is nicely illustrated by ternary diagrams (Fig. 10).

According to XRPD analysis (see **Supporting Information**), dolomite content varies from 61% in the dolomitic mudstones to 9.7% in the diatom-bearing mudstones and 1.8% in the diatomaceous shales (Table 1). The poorly crystalline clay fraction of all lithologies can mostly be attributed to illite–smectite (I-S) interlayers and vermiculite. An associated, more crystalline fraction, most likely of detrital origin, is composed of chlorite, plagioclase and quartz (Fig. 11). In the dolomitic mudstones, at least two families of interlayered structures with swelling properties have been recognized in the poorly crystalline fraction: a smectite–smectite (SS) interlayer,

represented by a double population with slightly different values of d_{001} and same 0 (random) *reichweite ordering*, and illite–chlorite–smectite (ICS) mixed-layers with higher ordering (*reichweite ordering 2*). The poorly crystalline fractions of the diatom-bearing mudstones and the diatomaceous shales show similar composition.

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the samples of dolomitic mudstones range from -5.4 to -0.6% and from $+3.4$ to $+6.8\%$, respectively (**Table 2**).

Total organic carbon and biomarkers

The TOC contents of the studied lithologies range from 0.3 to 2.3% (**Table 3**). The dolomitic mudstones (samples 2, 3 and 8) show rather constant TOC contents, 2% on average, whereas the diatomaceous deposits are characterized by lower TOC contents, ranging from 0.3% (diatom-bearing mudstones, sample 13) to 0.7% (diatomaceous shales, sample 10).

Lipid biomarkers of the alcohol fraction are generally well preserved (**Fig. 12**; see **Supporting Information**), although overall contents vary from high in the diatomaceous shales (up to 530 $\mu\text{g/g}$ TOC in sample 10), over intermediate in the diatom-bearing mudstones (average *ca* 281 $\mu\text{g/g}$ TOC in sample 13), to low in the dolomitic mudstones (samples 2, 3, 8; *ca* 14 $\mu\text{g/g}$ TOC on average; **Fig. 12A**, **Table 3**; see **Supporting Information**).

An even-over-odd carbon number predominance of *n*-alcohols (ranging from *n*-C₁₆ to *n*-C₃₄) is present in the studied lithologies with the highest contents in the diatomaceous shales (up to *ca* 180 $\mu\text{g/g}$ TOC) and diatom-bearing mudstones (*ca* 166 $\mu\text{g/g}$ TOC), while the dolomitic mudstones revealed lower contents (up to *ca* 14 $\mu\text{g/g}$ TOC; **Table 3**). Long-chain *n*-alcohols from *n*-C₂₆ to *n*-C₃₂, sourced from plant waxes (e.g. Rommerskirchen *et al.*, 2006; Hemingway *et al.*, 2016), are abundant in all samples and the dominant compounds in the diatom-bearing mudstones and dolomitic mudstones (**Table 3**; **Fig. 12A**).

Phytoplankton-derived lipid biomarkers are prominent in the diatomaceous shales. Among them, long-chain 1,X diols (C₂₆–C₃₂) are very abundant, corresponding to up to 67% of all alcohols (**Fig. 12A and B**). In particular, the 1,X-C₂₈₋₃₀ diol homologues account for 24 (sample 12) to 54% (sample 10) of all alcohols for the diatomaceous shales and represent 26% in case of the diatom-bearing mudstones (see **Supporting Information**). The X indicates the position of a hydroxyl group either at carbon 12, 13, 14 or 15. Among them, 1,14-C₂₈ and 1,14-C₃₀ diols are the most abundant, comprising up to 85% of 1,X-C₂₈ diols and between 91 to 97% of 1,X-C₃₀ diols, respectively (see **Supporting information**). Minor keto-ols comprising C₃₀₋₃₄ carbons are present in the diatomaceous shales, accounting for less than 9% of all alcohols. Keto-ols probably derive from the oxidation of the corresponding diols (e.g. Versteegh *et al.*, 1997; Ferreira *et al.*, 2001), agreeing with a phytoplankton source. Several phytoplankton-derived sterols are also present in the diatomaceous shales, including high amounts of brassicasterol (up to 19 µg/g TOC in sample 10) and 24-methylenecholesterol (up to 5 µg/g TOC in sample 12), common biomarkers of various diatoms (cf. Rampen *et al.*, 2010) and dinosterol (up to 11 µg/g TOC in sample 12), typically sourced by dinoflagellates and diatoms (Volkman *et al.*, 1993). β-sitosterol and its degradation product stigmastanol are also abundant, representing 3 to 4% of all alcohols in diatomaceous shales and diatom-bearing mudstones. These compounds are chiefly produced by eustigmatophytes, land plants and in minor amount by diatoms (cf. Rampen *et al.*, 2010). However, their strict association with pristine diatom valves suggests that they were mostly sourced by diatoms. Short-chain *n*-alcohols *n*-C₁₆ to *n*-C₂₅ also contribute to the pool of probable phytoplankton-derived lipids, but represent less than 4% of all lipids in the alcohol fraction (**Table 3, Fig. 12A**).

A different relative proportion between the algal-sourced lipids, sterols, diols and keto-ols is observed for the dolomitic mudstones (**Fig. 12B**). In this lithology, C₂₈₋₃₂ diols exhibit significantly lower contents (less than 1.1 µg/g TOC) in samples 2 and 3, and are absent in sample 8, whereas the algal derived C₂₄₋₃₆ keto-ols predominate with contents as high as 2.7 µg/g TOC, representing up to 33% of total alcohols in sample 8 (**Table 3**). Contents of algal sterols are also lower than in the

diatomaceous shales and diatom-bearing mudstones (<7% of the total alcohols), with stigmastanol, dinosterol and dinostanol predominating. Similarly, contents of the short-chain *n*-alcohols *n*-C₁₆ to *n*-C₂₆ are also lower (as high as 3.8 µg/g TOC in sample 3), yet their relative proportion is higher than in the diatomaceous shales and diatom-bearing mudstones, making up to the 20% of the measured alcohols (Fig. 12A).

The decalcification procedure applied for the dolomitic mudstones (see *Material and methods* section) released an additional lipid assemblage (Fig. 12C; see **Supporting Information**). For sample 8, the majority of lipid biomarkers was only released after the second extraction following decalcification (see **Supporting Information** for details). In particular, C₂₀₋₂₀ archaeol, phytanol and *sn*2-, *sn*3-phytanylglycerol monoethers (ph-monoethers), which are common lipids of archaea (e.g. De Rosa & Gambacorta, 1988; Hoffmann-Sell *et al.*, 2011; Birgel *et al.*, 2014), were found in all samples with highest contents in sample 8. Accessory C₁₆ monoalkyl glycerol monoether (MAGE *n*-C_{16:0}), a biomarker of various bacteria including sulphate-reducing bacteria (Grossi *et al.*, 2015), was detected in samples 2 and 3. This major MAGE, already apparent in the total ion current, is accompanied by other MAGEs ranging from 14 to 20 carbons; the latter compounds were recognized when scanning for the diagnostic *m/z* 205 on the GC-MS, and include terminally-branched MAGEs with 15 to 17 carbons (see Fig. 12C). The pentacyclic triterpenoid tetrahymanol (Sinninghe Damsté *et al.*, 1995; Natalicchio *et al.*, 2017) was also only detected in the extracts after decalcification.

DISCUSSION

Evidence of primary productivity by diatoms during the Messinian salinity crisis

Petrographic and organic geochemical data (Table 4) suggest that marine productivity dominated by planktonic diatoms, generating organic matter and biogenic silica, persisted during

the early stage of the MSC (cf. Fourtanier *et al.*, 1991; Pellegrino *et al.*, 2021). The well-preserved diatom valves in the diatomaceous shales (**Fig. 4**) and the altered remains of diatoms in the diatom-bearing mudstones (**Fig. 5I to N**) represent the most obvious evidence of high biosiliceous productivity in a marine environment. The high abundance of rhizosolenioid diatoms and Thalassionemataceae in the diatomaceous shales of the Bric Cenciurio section (**Fig. 4**) is in line with a scenario typified by the intermittent alternation of water column stratification (associated with surface oligotrophy) and water column mixing (associated with surface eutrophic conditions). Stratified waters during warm periods may have favoured the build-up of rhizosolenioid-dominated mats at the nutricline-thermocline and a deep chlorophyll maximum (e.g. Kemp *et al.*, 2000). Subsequent vertical mixing during cool and dry periods destabilized the mats, promoting their fast deposition ('fall dump') on the seafloor (cf. Kemp *et al.*, 2000). In contrast, the Thalassionemataceae probably thrived in the upper layer of the water column, following a nutrient pulse provided by riverine input in accord with the scattered occurrence of reworked chrysophycean cysts and benthic diatoms (cf. Pellegrino *et al.*, 2020a) or water column mixing, forming large aggregates. Once nutrients were exhausted, diatom aggregates rapidly sank toward the seafloor. High terrestrial input is evident from the high content of long-chain *n*-alcohols (e.g. Natalicchio *et al.*, 2019; **Fig. 12A**). Elevated biosiliceous productivity is also reflected by the high content of algal-derived lipid biomarkers in the diatomaceous shales (**Fig. 12B and C**), including the 1,14-C₂₈₋₃₀ diols and the C₂₇₋₂₉ sterols (i.e. brassicasterol, β -sitosterol, 24-methylenecholesterol) (Volkman *et al.*, 1999; Rampen *et al.*, 2010, 2022). In particular, C₂₈ and C₃₀ 1,14 diols are common constituents of modern rhizosolenioid diatoms (i.e. *Proboscia*; Sinninghe Damsté *et al.*, 2003; Rampen *et al.*, 2022), whereas 24-methylenecholesterol has been found as the most common sterol in the Thalassiosirales, *Coscinodiscus* sp. and *Chaetoceros* sp. (Volkman & Hallegraeff, 1988; Rampen *et al.*, 2010). The molecular fossil inventory is therefore consistent with the microfossil content.

In contrast, the close to total absence of biosiliceous remains in the dolomitic mudstones would suggest that biosiliceous productivity was temporarily interrupted. Nevertheless, the

occurrence of etched sponge spicules and altered benthic diatom remains in these sediments (**Fig. 8**) suggest that this was not the case. These features, along with the presence of corroded siliciclastic grains (**Fig. 6D and E**), point to a severe alteration of both biogenic and lithogenic silica pools. The absence of planktonic diatom remains in these sediments probably reflects their higher susceptibility to dissolution. Actually, planktonic diatoms are on average less silicified than benthic diatoms (e.g. Conley *et al.*, 1990). Furthermore, phytoplankton-derived lipids archived in dolomitic mudstones (**Fig. 12**) are a compelling evidence of persistent biosiliceous productivity. The lipid biomarker inventory of dolomitic mudstones includes dinosterol and dinostanol and accessory 1,X-C₂₈₋₃₀ diols, representing the most abundant phytoplankton-derived lipids found in the diatomaceous shales. In the absence of microfossil remains supporting the diatomaceous origin of the diols, other sources of these compounds cannot be excluded, including eustigmatophyte microalgae (e.g. Volkman *et al.*, 1999; Rampen *et al.*, 2022). However, keto-ols are typically considered as degradation product of diols (e.g. Versteegh *et al.*, 1997; Ferreira *et al.*, 2001). Therefore, the near to complete absence of siliceous microfossils and the dominance of long-chain keto-ols in the dolomitic mudstones over long-chain diols probably reflects bottom water or surface sediment conditions unfavourable for the preservation of biogenic silica.

Bottom water conditions

Petrographic, mineralogical and geochemical evidence (**Figs 6 and 7; Tables 1 and 2**) suggests that the dolomitic mudstones formed in an anoxic environment possibly below a stratified water column (cf. Sabino *et al.*, 2021). First, the TOC content is high (from 2.04 to 2.32%; see **Table 3**), which agrees with oxygen-depleted bottom water conditions, favouring the preservation of organic carbon. Second, the sediments are composed of dolomite (>47%; see also **Table 1**). Dolomite is a common component of the Messinian sedimentary successions of the Mediterranean (e.g. Kelts & McKenzie, 1984; Bellanca *et al.*, 1986; Pierre *et al.*, 2002), and its origin had first

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been related to hypersaline conditions in very shallow, sabkha-like environments (e.g. Friedman, 1973; Di Bella *et al.*, 2020), chiefly explained by positive $\delta^{18}\text{O}$ values indicative of evaporated seawater. However, dolomite also commonly forms in organic-rich, strongly reducing and sulphidic sediments after pronounced bacterial sulphate reduction (e.g. Kelts and McKenzie, 1984; de Lange & Krijgsman, 2010; Dela Pierre *et al.*, 2012; Lu *et al.*, 2018; Natalicchio *et al.*, 2021; Sabino *et al.*, 2021). Bacterial sulphate reduction tends to increase alkalinity, favouring the precipitation of ^{13}C -depleted carbonate minerals including dolomite (e.g. Vasconcelos *et al.*, 1995; Sanz-Montero *et al.*, 2009; Bontognali *et al.*, 2010). At high sulphide levels, the kinetic inhibition of dolomite formation under surface conditions is overcome, and dolomite forms by sulphide catalysis and subsequent ordering during early diagenesis (Zhang *et al.*, 2012; Lu *et al.*, 2021). The hydrogen sulphide released by bacterial sulphate reduction also reacts with iron to form pyrite, a mineral common in the studied lithologies (e.g. Berner, 1984). Since sulphate-reducing bacteria are mostly obligate anaerobes (e.g. Londry & Des Marais, 2003; Dolla *et al.*, 2006), the presence of microbially-formed dolomite is an indicator of anoxic conditions in pore waters (e.g. Petrash *et al.*, 2017; Li *et al.*, 2021). In the studied samples, the spheroidal and cauliflower-like morphology of the dolomite crystals, the hollow core and negative $\delta^{13}\text{C}$ values (from -5.4 to -0.6% ; see **Table 2**) agree with a microbial origin (cf. Vasconcelos *et al.*, 1995; Bontognali *et al.*, 2010; Lindtke *et al.*, 2011). The absence of evidence of compaction suggests that dolomite was formed in porous sediments at shallow depth below the sediment–water interface. A bacterially-induced formation of dolomite is corroborated by the characteristic MAGE patterns and, particularly, the circumstance that MAGEs are only released after decalcification of the dolomite crystal lattice. The obtained MAGE patterns resemble compound inventories of sulphate-reducing bacteria from cultures, sediments and authigenic minerals (cf. Hinrichs *et al.*, 2000; Rütters *et al.*, 2001; Heindel *et al.*, 2012; Guido *et al.*, 2013; Grossi *et al.*, 2015; Vinçon-Laugier *et al.*, 2016). These biomarkers of sulphate-reducing bacteria, in accord with low $\delta^{13}\text{C}_{\text{dolomite}}$ values, therefore suggest a tight connection between metabolism (i.e. sulphate reduction) and dolomite formation.

Tetrahymanol is commonly considered as an indicator of water column stratification (e.g. Sinninghe Damsté *et al.*, 1995; Natalicchio *et al.*, 2017). However, since tetrahymanol was only detected in extracts after decalcification, a benthic source organism is more likely. Tetrahymanol is produced by many organisms (anoxygenic phototrophs, ciliates, aerobic methanotrophic bacteria and many others), but the majority of the known producers thrive in the water column. Two possible benthic source organisms are aerobic methanotrophic bacteria (e.g. Cordova-Gonzalez *et al.*, 2020, and references therein), and sediment-thriving, heterotrophic ciliates (Werne *et al.*, 2002, and references therein). The absence of other lipids of methanotrophic bacteria and of evidence of methane oxidation makes these bacteria an unlikely source. Therefore, benthic ciliates are the most likely producers of tetrahymanol. Interestingly, marine ciliates preferably live in porous, loose, organic-rich sediments, and can tolerate anoxic conditions (Werne *et al.*, 2002).

Unlike for the dolomitic mudstones, dolomite and pyrite framboids are very scarce in diatomaceous shales. Similarly, lipids of sulphate-reducing bacteria have not been detected in diatomaceous shales, suggesting that bacterial sulphate reduction was apparently less pronounced, probably suppressed by temporary oxygenated conditions at the seafloor and in the upper part of the sedimentary column. The diatom assemblages in the studied samples point to the intermittent mixing of the water column favouring bottom water oxygenation (e.g. Alfken *et al.*, 2021; see above). Similarly, low TOC contents of the diatomaceous shales in spite of high biosiliceous productivity agree with the notion that organic matter was mostly degraded aerobically, as hypothesized for other Neogene Mediterranean (e.g. Pérez-Folgado *et al.*, 2003; Pellegrino *et al.*, 2020a,b) and global (e.g. White *et al.*, 1992; Koizumi & Yamamoto, 2018) diatomaceous deposits. Such a scenario is in contrast with the laminated fabric of diatomaceous shales (**Fig. 3E and F**), which suggests the absence of bioturbation, and with the well-preserved algal lipids suggesting limited biodegradation. However, lamination cannot be considered *per se* as evidence for anoxic conditions since rapid deposition of diatom mats, such as those observed in the studied diatomaceous shales, may produce laminated sediments even under oxygenated bottom water

conditions. It has been shown that tensile-strength deriving from the close entanglement of diatom valves (**Fig. 4**) is able to inhibit benthic bioturbation (Kemp & Baldauf, 1993; Bodén & Backmann, 1996; Pike & Kemp, 1999; Shimada *et al.*, 2008; Pellegrino *et al.*, 2020b).

Lamination of diatomaceous shales is only deformed by symsedimentary growth of gypsum rosettes. The absence of palaeontological evidence of shallow and hypersaline depositional conditions (i.e. presence of halophilic benthic diatoms and lipids of halophilic archaea) suggests that gypsum was not formed by evaporation. In fact, similar features have been observed in open ocean organic-rich and methane-rich sediments, where gypsum forms from the oxidation of dissolved sulphide and sulphide minerals resulting from bacterial sulphate reduction (e.g. Muza & Sherwood, 1983; Lin *et al.*, 2016). Therefore, it is suggested that the Castagnito gypsum rosettes are the product of sulphide oxidation, even though additional geochemical data will be needed to confirm this hypothesis.

Fate of biogenic silica and organic matter

Dolomitic mudstones record persistent water column stratification and bottom water anoxia (cf. Sabino *et al.*, 2021). In this lithology, biogenic silica is scattered and poorly preserved. Such a feature is surprising since biogenic silica preservation is supposed to be favoured by oxygen depletion (e.g. Sturani & Sampò, 1973; Birnbaum & Wireman, 1985; Hüsing *et al.*, 2009; Zachariasse *et al.*, 2021) because of: (i) limited bioturbation reworking biogenic silica; (ii) the assumed inefficiency of anaerobic bacteria to consume the organic layer protecting diatom frustules from dissolution; and (iii) supposed establishment of acidic conditions favouring silica preservation; silica preferentially dissolves at higher pH (e.g. Ehrlich *et al.*, 2010; Smrzka *et al.*, 2015). However, growing evidence from both modern and ancient sedimentary environments suggests that organic-rich and oxygen-poor conditions can be detrimental for the preservation of biogenic silica and even

lithogenic silica, casting doubt on the general attribution of diatomaceous deposits to the establishment of anoxia (e.g. Hiebert & Bennett, 1992; Spagnoli & Bergamini, 1997; Souchu *et al.*, 1998; Belias *et al.*, 2007; Villnäss *et al.*, 2012; Abe *et al.*, 2014; Ekeroth *et al.*, 2016; Lehtimäki *et al.*, 2016; Siipola *et al.*, 2016; Huggett *et al.*, 2017; Petranich *et al.*, 2018; Dale *et al.*, 2020). In particular, under anoxic conditions, bacterially-mediated anaerobic degradation of organic matter plays a critical role in modulating the pH of pore waters, a fundamental parameter for biogenic silica preservation (e.g. Ehrlich *et al.*, 2010). For example, dissimilatory iron reduction – a proton-consuming process (e.g. Howell *et al.*, 1998) – and bacterial sulphate reduction – though depending on the electron donors involved (for example, formate, hydrogen) – promote the rise of pore water pH (e.g. Mazzullo 2000, Gallagher *et al.*, 2012, 2014; Han *et al.*, 2016), favouring silica dissolution (e.g. White *et al.*, 1992; Jurkowska *et al.*, 2019; Neumeister *et al.*, 2020).

Besides dolomite and a clay-sized and silt-sized terrigenous chlorite, plagioclase and quartz (**Figs 6D, 6E and 11**), dolomitic mudstones are typified by poorly crystalline clay minerals mostly consisting of I-S interlayers (**Figs 7A to D and 11**). The fact that their composition overlaps with the composition of the clay coating diatom remains found in the diatom-bearing mudstone, and in rare cases also in the dolomitic mudstones (**Fig. 10**), suggests that these poorly crystalline clays derive from an original biosiliceous source and are authigenic. In addition, the close association of clays and dolomite microcrystals (**Fig. 7A to D**) indicates that authigenic clay formation was penecontemporaneous with the precipitation of microbial dolomite. Interestingly, the clay minerals interpreted as authigenic display a flaky habit, which suggest that they precipitated onto a former organic template such as extracellular polymeric substances (EPS) produced both by bacteria and diatoms (cf. Bhaskar & Bhosle, 2005). Actually, the threads closely associated with diatom remains (**Fig. 5N**) could represent mineralized EPS structures.

Neoformation of clay minerals requires availability of alkalinity (HCO_3^-), free cations (Al^{3+} , Fe^{2+} , K^+ , Mg^{2+}) and dissolved silica (Michalopoulos & Aller, 1995; Rahman, 2019). Such conditions were probably favoured by anaerobic bacterial communities, and in particular by

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sulphate reducers thriving on the organic matter mostly provided by siliceous primary producers. Bacterial sulphate reduction therefore probably triggered concomitant precipitation of authigenic dolomite and dissolution of biogenic silica through an increase of pore water pH (**Fig. 13A**). In the case of the studied Piedmont Basin lithologies, biogenic silica dissolution and consequent release of dissolved silica are illustrated by: (i) rare, yet corroded remains of sponge spicules, which are more silicified and therefore more resistant to dissolution than diatom frustules; and (ii) partially dissolved diatom remains in the dolomitic mudstones from the Bric Cenciurio and Cascina Botto sections (**Fig. 8**). Such close to complete absence of biogenic silica is in line with the greater susceptibility to dissolution of amorphous biogenic silica compared to crystalline lithogenic silica (Ehrlich *et al.*, 2010). However, the reddish halo around corroded margins of silt-sized grains (**Fig. 6D and E**) is taken as evidence of the alteration of lithogenic material (cf. Sanz-Montero *et al.*, 2009). This process apparently provided an additional source of dissolved silica and pore water cations (**Fig. 13A**), enhancing clay neoformation. A biotic contribution to the corrosion of lithogenic material is possible since bacterial biofilms may attach to the surface of silicate grains for scavenging nutrients (e.g. Hiebert & Bennet, 1992; Ullman *et al.*, 1996).

Interestingly, neoformed clays consists of I-S interlayers (**Fig. 11**), which are intermediate products of the transformation of smectite into illite. Such progressive transformation is considered a late diagenetic, abiotic process affecting smectite-rich sediments (e.g. Pollastro, 1990; Compton, 1991; Wilson *et al.*, 2016). The progressive ordering (from *reichweite* 0 to 3) of the I-S interlayers, reflects the percentage of illite, which is correlated to burial depth and thermal gradient (e.g. Wilson *et al.*, 2016). However, recent studies have highlighted the role of microbial communities in catalyzing smectite to illite transformation, resulting in a very fast conversion at ambient conditions in the order of weeks (e.g. Kim *et al.*, 2004, 2019; Liu *et al.*, 2012). In organic-rich sediments, iron-reducing and sulphate-reducing bacteria can promote illitization of smectite, coupling organic matter oxidation and metal, notably iron, reduction (e.g. Kim *et al.*, 2004, 2019; Liu *et al.*, 2012). In case of the Piedmont Basin, geological reconstructions (e.g. Dela Pierre *et al.*, 1995) and

petrographic and sedimentological observations (for example, absence of significant compaction and anhydrite after gypsum, Dela Pierre *et al.*, 2011) rule out burial diagenesis as a trigger of the conversion of smectite to illite. Therefore, it is suggested that this process was mediated by bacteria, in particular sulphate reducing bacteria (cf. Liu *et al.*, 2012). Interestingly, smectite to illite transformation tends to alter the oxygen isotopic composition of pore waters. Smectite-dominated clay progressively loses its interlayer water that is enriched in ^{18}O (e.g. Dählmann & de Lange, 2003). Carbonate minerals precipitating from such fluid will consequently show positive $\delta^{18}\text{O}$ values (e.g. Dählmann & de Lange, 2003). Interestingly, many Messinian dolomite-rich beds of the Mediterranean, including those studied here, show positive $\delta^{18}\text{O}$ values, which has been interpreted to reflect evaporated seawater and hypersaline conditions (e.g. McKenzie *et al.*, 1979; Bellanca *et al.*, 2001; Caruso *et al.*, 2015; Tzevahirtzian *et al.*, 2022). Alternatively, some of the ^{18}O enrichment may result from smectite-to-illite transformation, rather than seawater evaporation.

In contrast to dolomitic mudstones, the Piedmont Basin diatomaceous shales formed when the water column was intermittently mixed and stratified and bottom waters were more oxygenated, favouring the excellent preservation of biogenic silica. More molecular oxygen leads to more aerobic remineralization of organic matter and more carbon dioxide produced, lowering pore water pH (e.g. Silburn *et al.*, 2017), thereby inhibiting biogenic silica dissolution (**Fig. 13B**). The diatomaceous mudstones represent an intermediate lithology between dolomitic mudstones and diatomaceous shales. While their dolomite content is lower than that of dolomitic mudstones (9.7% versus 46.9–61.1%, respectively; see **Table 1**), diatomaceous mudstones commonly contain altered diatom remains coated by authigenic clay. In this case, siliceous microfossils were only partially dissolved, probably because of a low rate of bacterial sulphate reduction (low dolomite contents and absence of molecular fossils of sulphate-reducing bacteria) resulting from redox conditions intermediate between those prevailing during dolomitic mudstone (oxygen-depleted) and diatomaceous shale (oxygen-replete) deposition.

Decline of biosiliceous productivity during the Messinian salinity crisis: fact or fiction?

The Messinian sedimentary succession of the Mediterranean is typified by pre-MSC diatomaceous deposits (e.g. Pellegrino *et al.*, 2018) that are overlain by thick layers of evaporites deposited during the MSC (e.g. Roveri *et al.*, 2014). Such vertical facies transition has been traditionally regarded as the product of a sharp rise of salinity in the water column, with the consequent establishment of environmental conditions unsuitable for most marine life including biosiliceous microorganisms (e.g. Selli, 1954; Cita, 1976). However, the scattered presence of biosiliceous fossils in the MSC sedimentary record (e.g. Fourtanier *et al.*, 1991; Carnevale *et al.*, 2019; Meilijson *et al.*, 2019; Pellegrino *et al.*, 2021) suggests that biosiliceous biota persisted during the MSC. Such an interpretation is consistent with the late Miocene to early Pliocene ‘biogenic bloom’ event and the associated dramatic intensification of deposition of biogenic silica centred between 7.0 Ma and 4.5 Ma (e.g. Farrell *et al.*, 1995; Dickens & Barron, 1997; Filippelli, 1997; Dickens & Owen, 1999; Hermoyan & Owen, 2001; Cortese *et al.*, 2004; Diester-Haass *et al.*, 2002, 2004, 2005, 2006; Herbert *et al.*, 2016; Steinthorsdottir *et al.*, 2021). The hypothesis that dissolution of biogenic silica promoted the formation of authigenic clay implies that much of the MSC sedimentary record is taphonomically biased (e.g. Mancini *et al.*, 2022), preserving only a small share of the original communities of biosiliceous primary producers. In addition, the taphonomic bias hypothesis provides an alternative explanation for the anomalous abundance of smectite in the Mediterranean Messinian successions (e.g. Chamley *et al.*, 1977, 1978; Chamley & Robert, 1980; de Visser, 1991; Martínez-Ruiz *et al.*, 1999). The enrichment in smectite has been attributed to the erosion of poorly drained peri-Mediterranean soils within a semiarid Messinian climate (e.g. Chamley *et al.*, 1977; de Visser, 1991; Cosentino *et al.*, 2005), but may actually be the product of authigenic clay formation (cf. Martínez-Ruiz *et al.*, 2014) promoted by the coupling of biosiliceous productivity and intensification of water column stratification in response to the progressive isolation of the basin (e.g. Natalicchio *et al.*, 2019). Therefore, caution is advised when

interpreting the absence of skeletal remains of marine microorganisms in the sedimentary record of the MSC as evidence of their decline caused by purportedly harsh environmental conditions.

CONCLUSIONS

A multiproxy analysis of Messinian diatomaceous deposits and associated clay and dolomite-rich layers interbedded with primary gypsum deposits (Primary Lower Gypsum unit) elucidates the role of biogenic silica in authigenic clay formation during the initial stage of the Messinian salinity crisis. Anoxic bottom water conditions, induced by intensification of water column stratification, triggered silica dissolution and concomitant formation of authigenic clays and dolomite, resulting in the dolomitic mudstones of the Piedmont Basin. Organic matter remineralization was driven to a large extent by bacterial sulphate reduction. An associated increase of alkalinity induced the early diagenetic formation of dolomite, whereas the rise of pH in pore waters promoted dissolution of biogenic silica. Such biologically-induced leaching of lithogenic material under anoxic conditions promoted the partial dissolution of silicate minerals. The resultant availability of dissolved silica and reactive cations promoted the formation of authigenic clay minerals, represented by illite/smectite interlayers deriving from a smectite precursor. Absence of significant burial in the studied succession of the Piedmont Basin suggests that illitization of smectite occurred at ambient temperature and was possibly mediated by microorganisms. In contrast to periods of deposition of the dolomitic mudstones, prevailing oxygenated bottom water conditions, caused by intermittent mixing of the water column, promoted the preservation of biosiliceous remains in the diatomaceous shales. This study reinforces the hypothesis that the apparent annihilation of Mediterranean marine biota during the MSC partly reflects a taphonomic bias produced by interactions between the biogeochemical cycles of carbon, silicon and sulphur in a restricted basin rather than the establishment of adverse hypersaline conditions in the Mediterranean water mass.

FIGURE CAPTIONS

Figure 1. Geological sketch of north-west Italy. Stars highlight the two locations of the studied stratigraphic sections. TH: Torino Hill; MO: Monferrato; AM: Alto Monferrato; BG: Borbera Grue sector; SVZ: Sestri-Voltaggio zone; VVL: Villalvernia-Varzi line; IL: Insubric Line. Dashed lines indicate the isobaths of Pliocene deposits (in km). Modified from Bigi *et al.* (1990).

Figure 2. The Bric Cenciurio section. Stratigraphic log. The numbers on the left side of the stratigraphic column refer to the gypsum layers. The black arrows and numbers indicate studied samples. SKB: Sturani Key Bed.

Figure 3. Photomicrographs of diatomaceous shales from Bric Cenciurio section (samples 10 and 12; see Fig. 2). (A) Scraped surface of a hand specimen, showing the alternation of whitish, greyish, reddish and pale brown laminae; arrowheads point to gypsum aggregates. (B) Hand specimen broken parallel to the bedding plane, showing whitish, closely-stacked laminae. (C) Polished thin section, showing the alternation of opal-rich laminae (clear with n//; dark with nx) and clayey-silty laminae (dark with n//; highly birefringent with nx). (D) Partially dissolved gypsum rosettes displacing opal-rich laminae. (E) Polished thin section photomosaic; note the lateral continuity of the opal-rich laminae (darker in BSEI) and the gypsum rosettes (mostly pseudomorphs) displacing the laminated packets (arrowheads). (F) Detail of the alternation of opal-rich (dark, due to a low backscattering coefficient) and clayey-silty laminae (pale, due to high backscattering coefficient); note the excellent preservation of lamina boundary of the opal-rich laminae. (G) Detail of an opal-rich lamina, enclosing lensoidal pockets (arrowhead). (H) Detail of a clayey-silty lamina; note the diatom remains (d) and a sponge spicule (s). (A) and (B): reflected light photomicrographs; (C) and

(D): transmitted light photomicrographs (n// = parallel nicols; nx = crossed nicols); (E) to (H): BSEI photomicrographs.

Figure 4. Diatomaceous shales from Bric Cenciurio section (sample 10; see Fig. 2). Dense accumulation of: (A) and (B) Thalassionemataceae; and (C) and (D) rhizosoleniid diatoms observed along the surface of opal-rich laminae. (A) to (D): SEI photomicrographs of freshly broken chips parallel to bedding plane.

Figure 5. Diatom-bearing mudstones from Bric Cenciurio section (sample 13; see Fig. 2). (A) Scraped surface of a hand specimen showing a slight lamination; note the greyish massive layer in the lower part; white arrowheads point to gypsum crystals, pristine or partially dissolved. (B) Alternation of poorly defined, pale and reddish laminae. (C) Polished thin section photomosaic; the apparent lamination observed in reflected and transmitted light is less well-expressed, but still recognizable; arrowhead points to a gypsum grain. (D) Close-up of silt-rich laminae alternated to very thin, silt-poor laminae; arrowhead points to a pyrite framboids. (E) and (F) Details on pyrite framboids. (G) Cluster of pyrite framboid microcrystallites. (H) and (I) Centric planktonic diatoms (*Actinocyclus* cf. *octonarius* var. *tenellus*) observed in polished thin section and on a freshly broken chip cut along the bedding plane, respectively. (J) Strongly altered remain of a pennate planktonic diatom (Thalassionemataceae). (K) to (M) Remains of benthic diatoms, showing different degrees of dissolution and clay-coating; arrowhead in (L) points to the only recognizable features attributable to the diatom, otherwise almost completely clay-coated. (N) Diatom remain (left) embedded in a clayey matrix (right); note the thin thread-like structure (arrowheads). (O) Etching pits on a sponge spicule.

(A): reflected light photomicrograph; (B): transmitted light photomicrograph (n// = parallel nicols); (C) to (O): BSEI/SEI photomicrographs.

Figure 6. Dolomitic mudstones from Bric Cenciurio (samples 2, 4 and 6, see Fig. 2) and Cascina Botto sections. (A) Scraped surface of a hand specimen from Bric Cenciurio section, showing the alternation of widely- and closely-spaced laminated packets of pale and reddish laminae. (B) Scraped surface of a hand specimen from Cascina Botto section, showing well-laminated and poorly-laminated to massive packets. (C) Reddish lamina enriched in pyrite framboids (arrowheads) from Bric Cenciurio section. (D) and (E) Detail of silt-sized grains showing corroded margins and coated by a reddish halo from Bric Cenciurio section. (F) Blackish aggregate of residual organic matter (?) embedded in a dolomite-rich matrix from Bric Cenciurio section. (G) and (H) Interspersed gypsum crystals from Bric Cenciurio section. (A) and (B): reflected light photomicrograph; (C) to (H): transmitted light photomicrograph (n// = parallel nicols; nx = crossed nicols).

Figure 7. Dolomitic mudstones from Bric Cenciurio section (samples 2 and 3, see Fig. 2). (A) to (D) Finely crystalline clays closely associated with spheroidal dolomite, some of which exhibit a hollow core, observed in polished thin section and on freshly-broken chips; in D, two zoned crystals can be observed. (E) and (F) Pyrite framboids, observed in polished thin section and on freshly broken chips, respectively. (A) to (F): BSEI/SEI photomicrographs of polished thin sections and freshly-broken chips parallel to bedding plane.

Figure 8. Dolomitic mudstones from Bric Cenciurio (sample 2, see Fig. 2) and Cascina Botto sections. (A) and (B) Sponge spicule from Bric Cenciurio section (squared area is enlarged in B); note in (B) the desquamated surface of sponge spicule. (C) and (D) Sponge spicule from Cascina Botto section (squared area enlarged in D); note in (D) the etching pits on the surface of sponge spicule. (E) and (F) Almost completely dissolved benthic diatom from the Cascina Botto section. BSEI/SEI photomicrographs of freshly-broken chips parallel to bedding plane.

Figure 9. Electron dispersive X-ray spectroscopy (EDS) data points and maps of diatomaceous shales (sample 10), diatom-bearing mudstones (sample 13) and dolomitic mudstones (sample 2) from Bric Cenciurio section (see Fig. 2). Diatomaceous shales: (A) EDS data points of an opal-rich lamina of diatomaceous shale. Note the pure siliceous composition of the diatom valve. (B) and (C) Element distribution along the surface of an opal-rich lamina and a polished thin section. In the EDS maps of the polished thin section, black–blue–green–yellow–orange–red–white represent, in this order, the increasing content of each element. Diatom-bearing mudstones: (D) EDS data points of diatom valve on freshly broken chips parallel to the bedding plane. Note that diatom valves are enriched in Al, K, Fe and Mg. (E) Element distribution in a freshly broken chip cut parallel to the bedding plane. Note the enrichment in elements other than Si, in particular Al. Dolomitic mudstones: (F) EDS data points of flaky clays around dolomite crystals on freshly broken chips cut parallel to the bedding plane. (G) Element distribution along the surface of a freshly broken chip parallel to the bedding plane.

Figure 10. Al-Fe/K/Mg-Si ternary diagrams obtained from EDS analyses of diatomaceous shales (sample 10), diatom-bearing mudstones (sample 13) and dolomitic mudstones (samples 2 and 3) from Bric Cenciurio section (see Fig. 2).

Figure 11. X-ray powder diffraction (XRPD) patterns of diatomaceous shales (sample 10), diatom-bearing mudstones (sample 13) and dolomitic mudstones (sample 2 on the left, sample 3 on the right) from Bric Cenciurio section (see Fig. 2). Chl = chlorite; Dol = dolomite; Ill = illite; MxL = mixed layer clay (illite-smectite); Ox = metal oxides; Pl = plagioclase; Qz = quartz; Ver = vermiculite.

Figure 12. (A) Relative percentages of the major groups of compounds of the alcohol fraction from the diatomaceous shales, diatom-bearing and dolomitic mudstones. Samples 2, 3 and 8 are pooled

results of two extracts (see *Material and methods*). See Table 2 for the content of the major groups of compounds and Supporting Information for detailed information and contents of all measured compounds. (B) Relative percentages of the algal-derived group of compounds (sterols, diols and ketols). See Fig. 2 for the stratigraphic distribution of the samples. (C) Partial chromatogram (retention time 32–40 minutes) of the alcohol fraction after decalcification of a dolomitic mudstone (sample 2; selected mass m/z 205). MAGE: monoalkyl glycerol monoether. Note the major peak of MAGE n -C_{16:0}, which is accompanied by smaller peaks of other MAGEs ranging from 14 to 20 carbons.

Figure 13. Scenario of the water column conditions and diagenetic pathways during the deposition of dolomitic mudstones (A) and diatomaceous shales (B). The size of square and circles reflects the abundance of authigenic clays (AC), biogenic silica (BSi), dolomite (D), lithogenic material (LM), organic matter (OM) and pore water cations (PWC); bitten squares in panel (A) represent altered BSi, OM and LM. The narrow grey triangle on the left indicates oxygen penetration depth, under which bacterial sulphate reduction (BSR) is active; other biogeochemical processes like nitrate reduction, manganese reduction and iron reduction, which typically occur between the zones of aerobic respiration (above) and sulphate reduction (below) are not considered in this simplified concept. The grey arrows indicate the transport of aggregates of BSi-OM and LM from the upper water column to the sediment-water interface (SWI); white arrows in panel (B) indicate water column mixing. See text for details. The grey shade in panel A indicates progressively more oxygen-depleted waters. In panel (B), the dotted lines below the sediment-water interface indicate that the diagenetic processes involving the diatomaceous shales were less effective.

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Sample	Lithology	% Dolomite
13	Diatom-bearing mudstone	9.7
10	Diatomaceous shale	1.8
3	Dolomitic mudstone	61.1
2	Dolomitic mudstone	46.9

Table 1. Relative percentage of dolomite in the three lithologies. See Fig. 2 for details.

Sample	Lithology	$\delta^{13}\text{C}$	SD $\delta^{13}\text{C}$	$\delta^{18}\text{O}$	SD $\delta^{18}\text{O}$
8	Dolomitic mudstone	-4.8	0.02	+4.8	0.04
6	Dolomitic mudstone	-3.5	0.04	+3.4	0.03
5	Dolomitic mudstone	-5.4	0.03	+6.2	0.04
4	Dolomitic mudstone	-1.6	0.03	+5.7	0.04
3	Dolomitic mudstone	-0.9	0.03	+6.8	0.04
2	Dolomitic mudstone	-0.6	0.02	+4.6	0.03
Average value		-2.8		+4.4	

Table 2. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of dolomitic mudstones; SD = standard deviation. See Fig. 2 for details.

Lithology	Diatomaceous shale		Diatom-bearing mudstone	Dolomitic mudstone		
	Sample	10		12	13	8
% TOC	0.7	0.4	0.3	2.2	2.3	2.0
SC <i>n</i> -alcohols (C ₁₆₋₂₅)	5.9 (1.1)	12 (2.6)	9.4 (3.7)	0.9 (11.4)	3.8 (19.8)	2.0 (13.8)
LC <i>n</i> -alcohols (C ₂₆₋₃₄)	59.3 (11.6)	167.8 (35.8)	156.8 (61.9)	2.9 (35.1)	10.7 (55.4)	8.2 (56.5)
Sum <i>n</i> -alcohols (C ₁₆₋₃₄)	65.2 (12.7)	179.8 (38.4)	166.2 (65.6)	3.9 (46.4)	14.5 (75.3)	10.2 (70.3)
Archaeal lipids	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	1.3 (16.0)	0.6 (2.9)	0.3 (1.9)
Tetrahymanol	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.1 (0.5)	0.0 (0.3)
Sterols	73.2 (14.2)	81.8 (17.4)	15.4 (6.1)	0.4 (4.6)	1.2 (6.5)	0.6 (4.0)
1,X-diols	345.5 (67.2)	167.1 (35.6)	71.9 (28.3)	0.0 (0.0)	0.3 (1.4)	1.1 (7.8)
1,X-keto-ols	29.9 (5.8)	40.2 (8.6)	traces (0.0)	2.7 (33.0)	2.5 (13.1)	2.3 (15.5)
MAGE <i>n</i> -C _{16:0}	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.1 (0.5)	0.0 (0.2)
Sum lipid alcohol fraction	513.8	468.9	253.5	8.3	19.3	14.6

Table 3. Content of total organic carbon (TOC) and main biomarkers in the three lithologies studied. Lipid content is given in $\mu\text{g/g}$ TOC; percentage of a compound in the alcohol fraction provided in brackets; SC = short-chain; LC = long-chain; MAGE = monoalkyl glycerol ether. See Fig. 2 for details.

Lithology	Sedimentology and petrography	Mineralogical and element composition	Stable isotopes	TOC and biomarkers
Diatomaceous shale	<i>Finely laminated fabric</i> Abundant and well-preserved biosiliceous remains confined in biogenic laminae typified	Almost pure siliceous composition of diatom valves Low dolomite content (<i>ca</i> 2%)	–	TOC 0.4–0.7% Predominance of well-preserved algal-derived lipids

	by diatoms of the families Thalassionemataceae and Rhizosoleniaceae			
Diatom-bearing mudstone	<i>Laminated to massive fabric</i> Common and poorly-preserved biosiliceous remains closely associated with flaky clays	Diatom valves enriched in Al, Fe, K and Mg, mimicking the composition of flaky clays closely associated with dolomite crystals in the dolomitic mudstone More abundant dolomite content (<i>ca</i> 10%)	–	TOC 0.3% Predominance of well-preserved algal-derived lipids
Dolomitic mudstone	<i>Laminated to massive fabric</i> Rare and very poorly-preserved biosiliceous remains interspersed in a dolomite-rich and flaky clay-rich matrix Cauliflower to globular hollow dolomite crystals Pyrite framboids	Flaky clays closely associated with dolomite crystals are enriched in Fe, K and Mg Abundant dolomite content (up to <i>ca</i> 60%)	$\delta^{13}\text{C}$ average value: -2.8 $\delta^{18}\text{O}$ average value: +4.4	TOC 2.0–2.3% Occurrence of degraded algal lipids Tetrahymanol MAGEs

Table 4. Overview of main features of the three lithologies; TOC = total organic carbon.

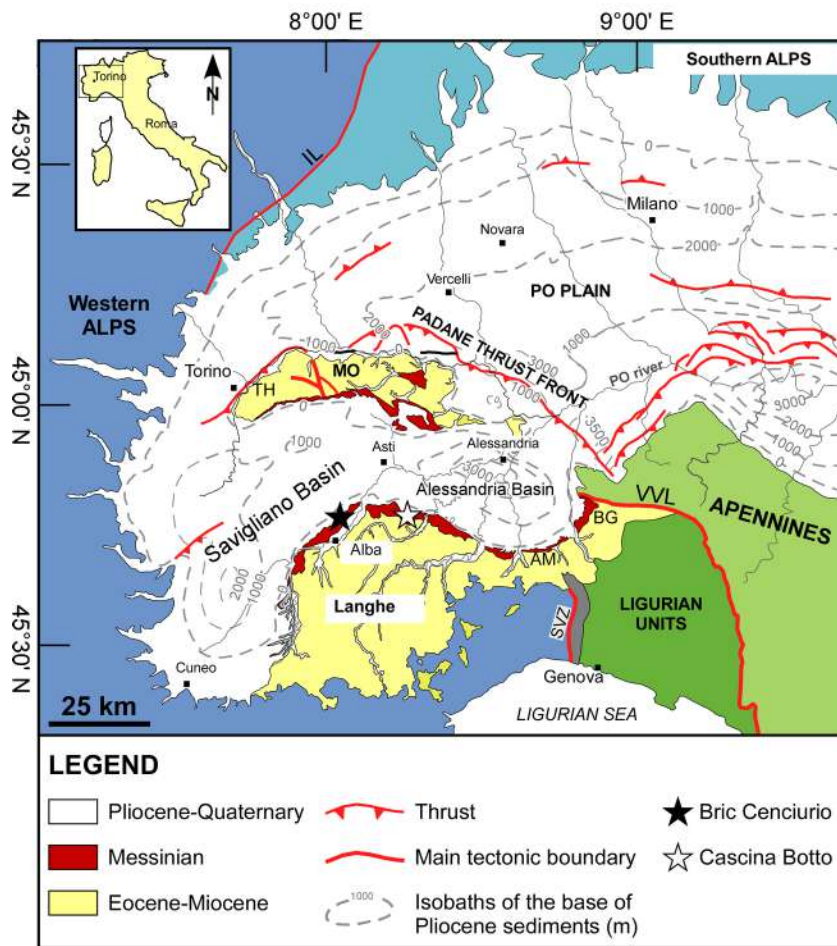


Fig. 1 - Two thirds page width

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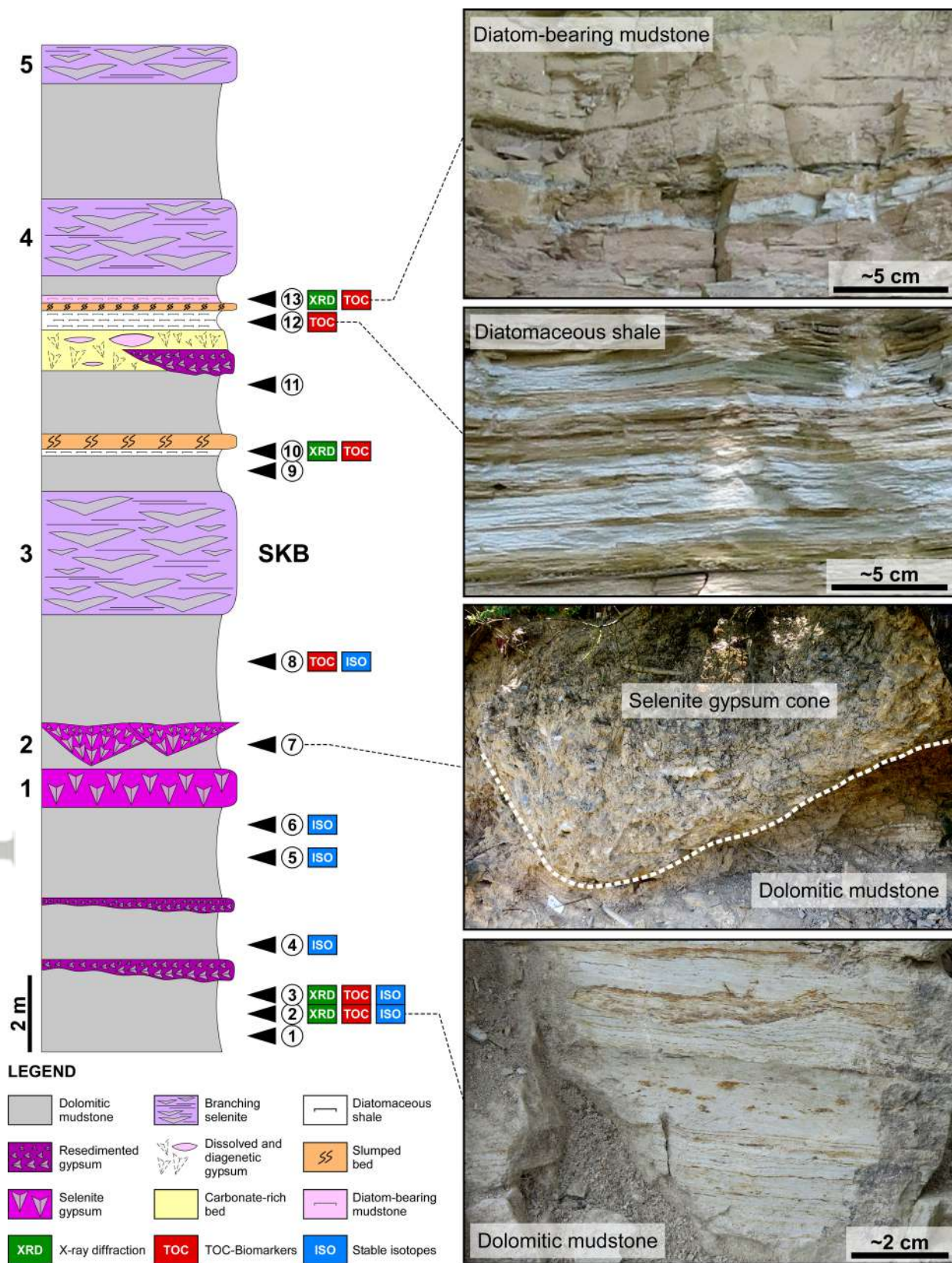


Fig. 2 - 1 page width

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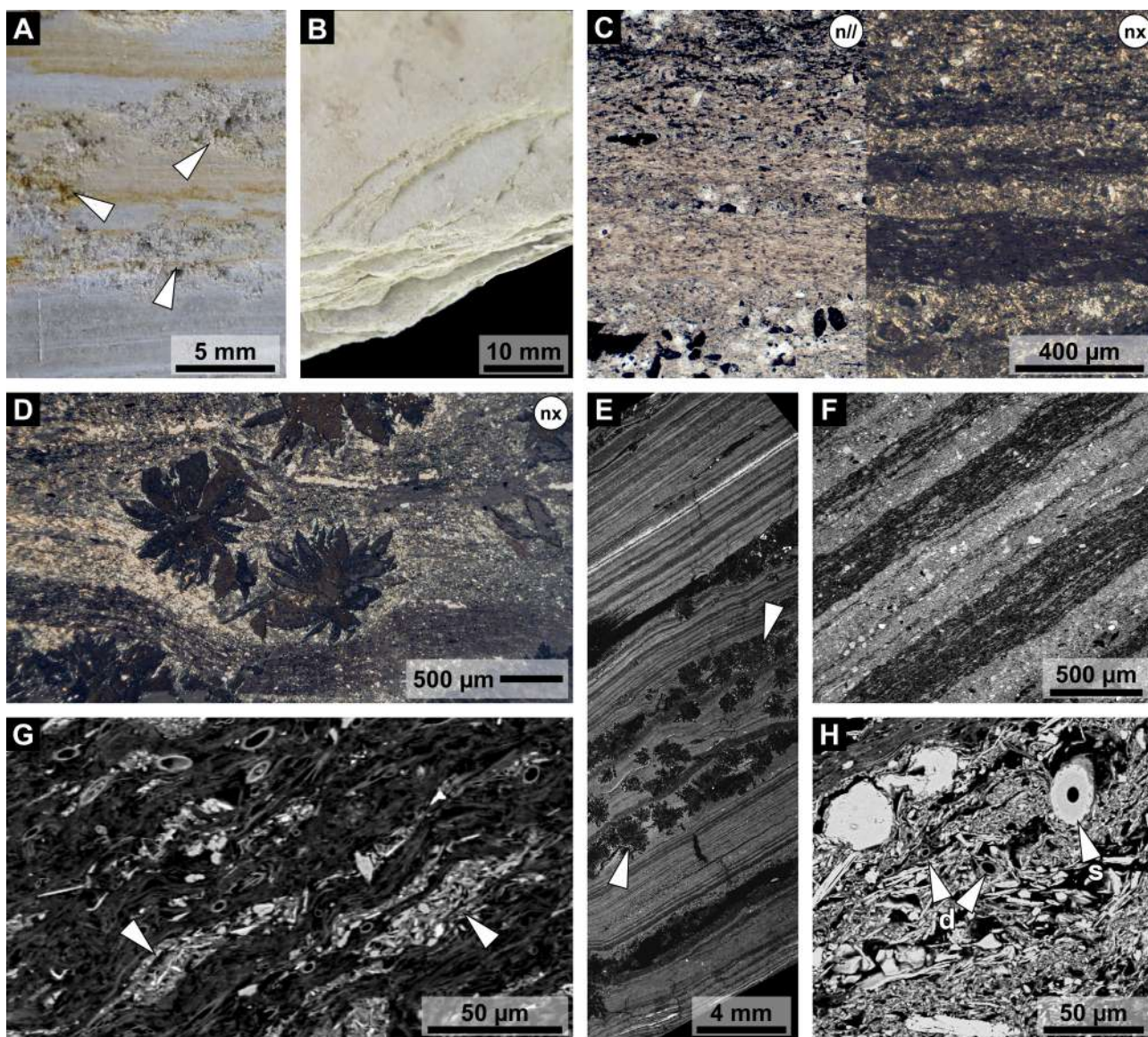


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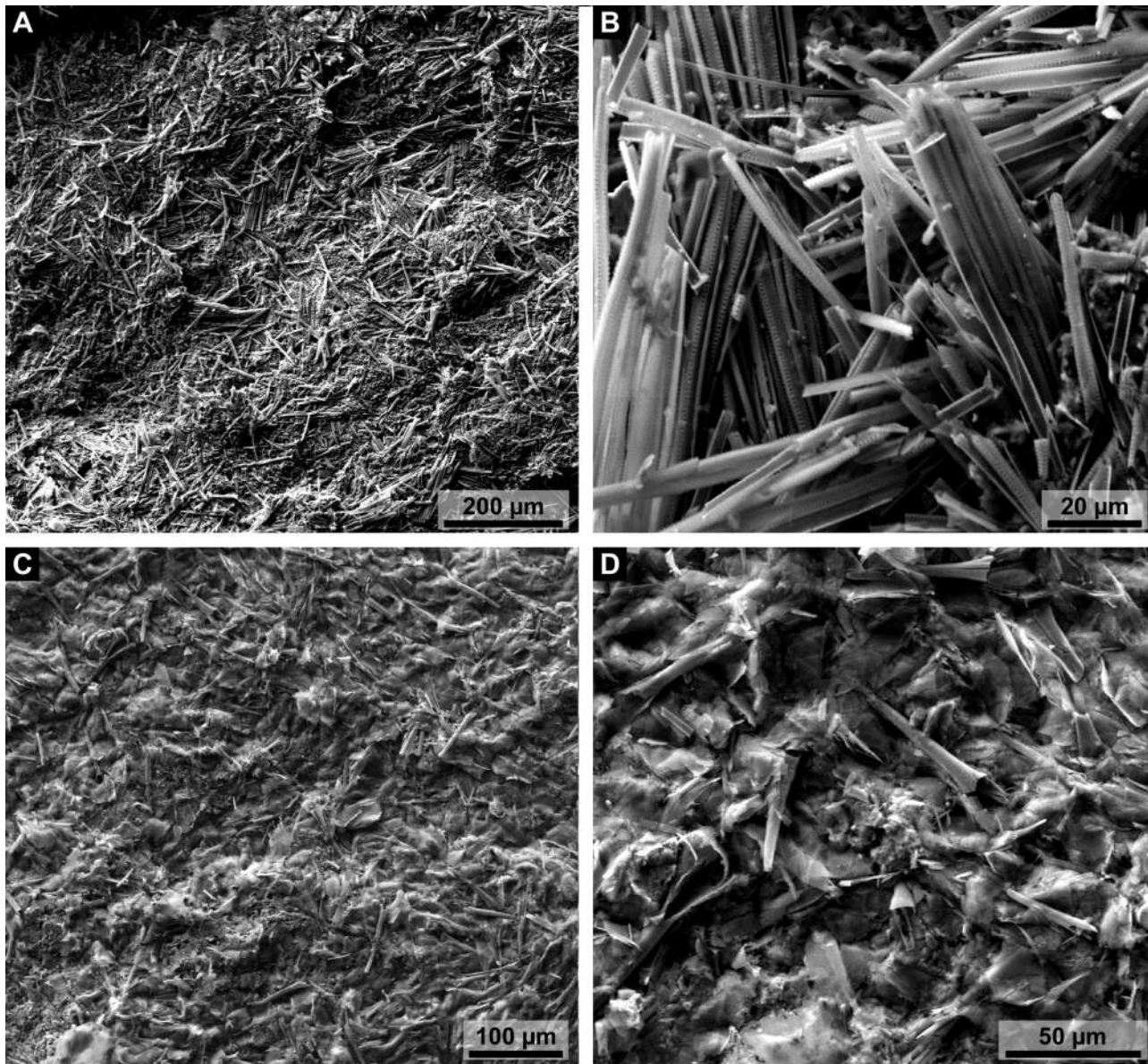


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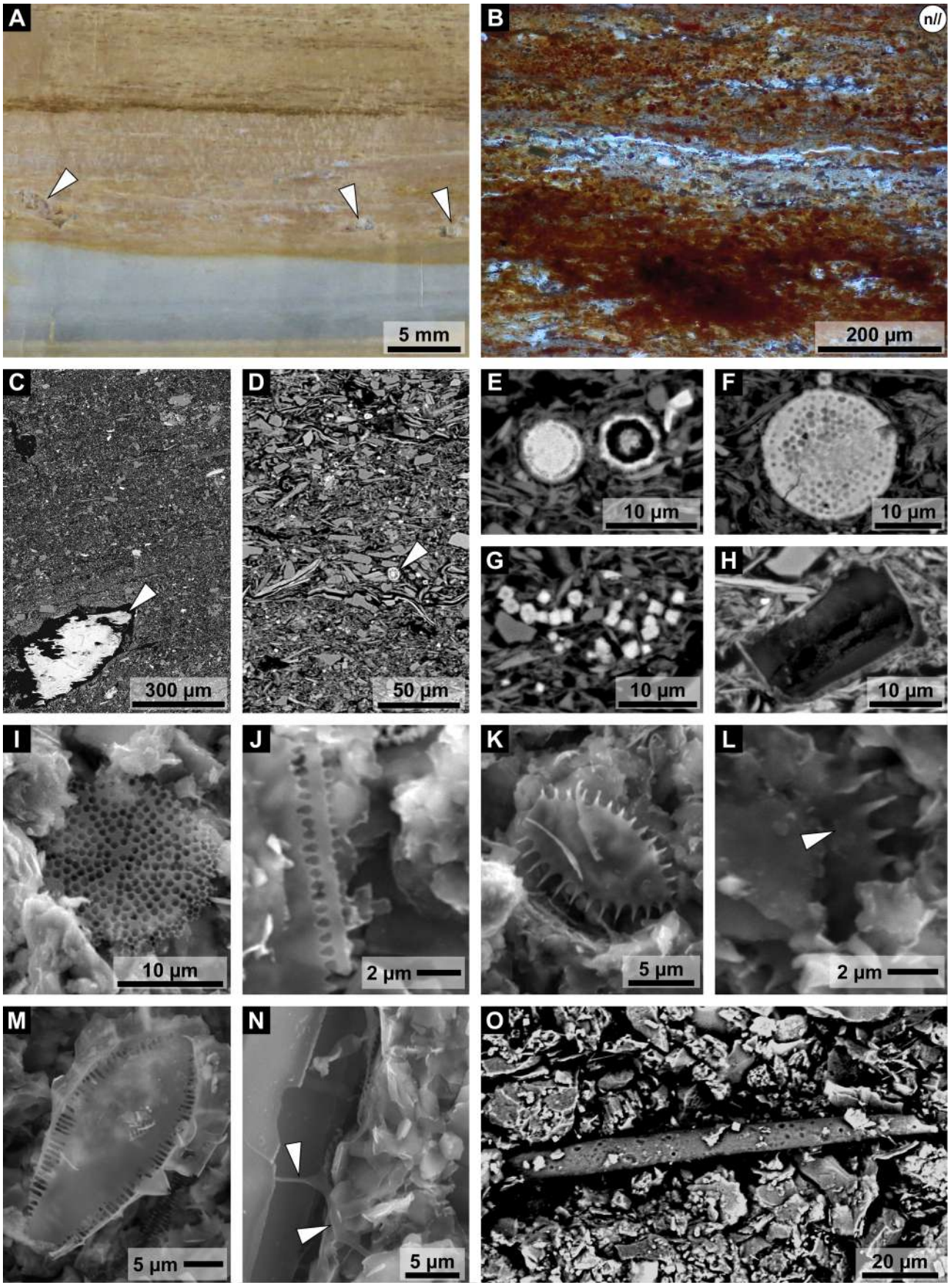


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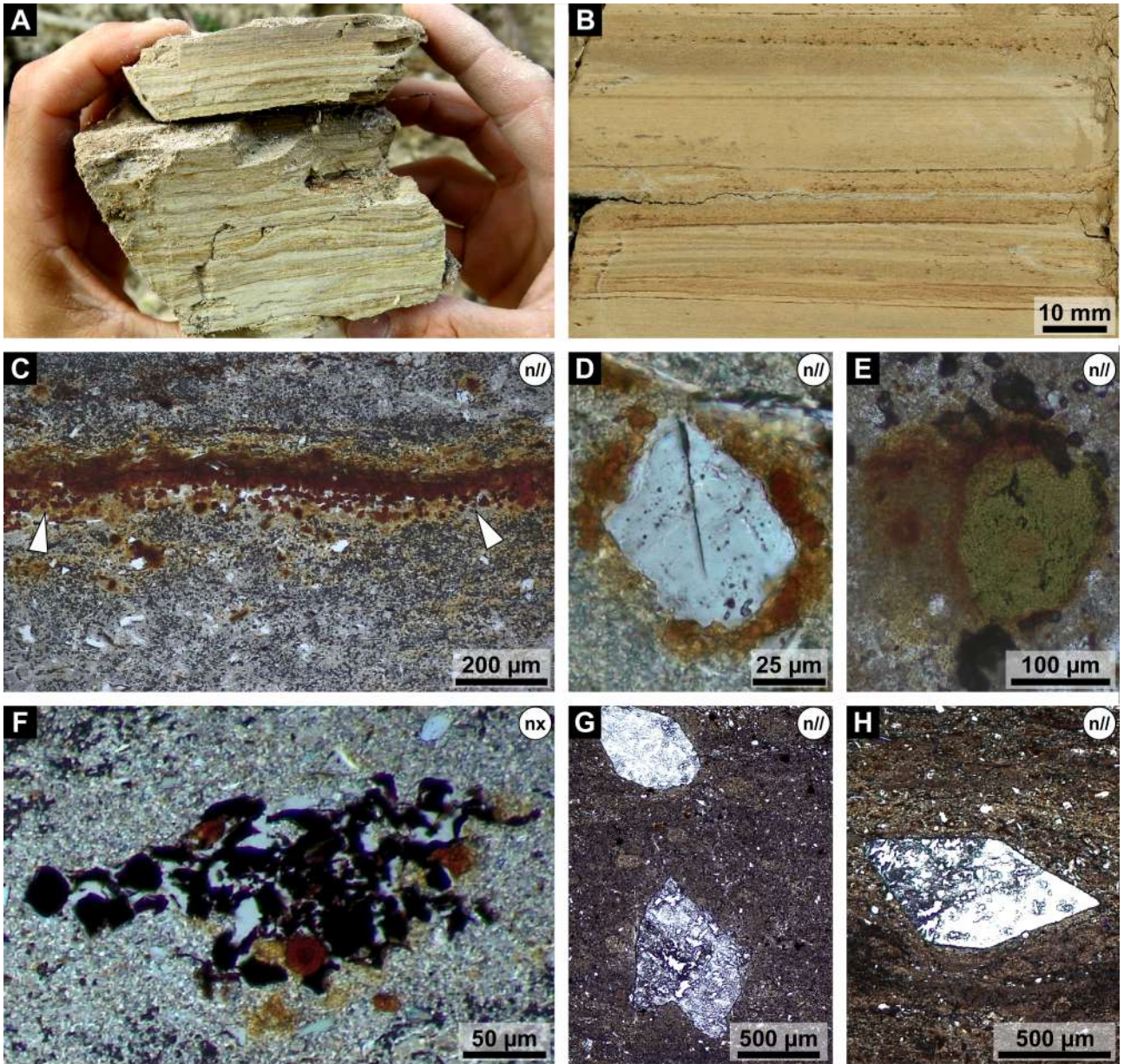


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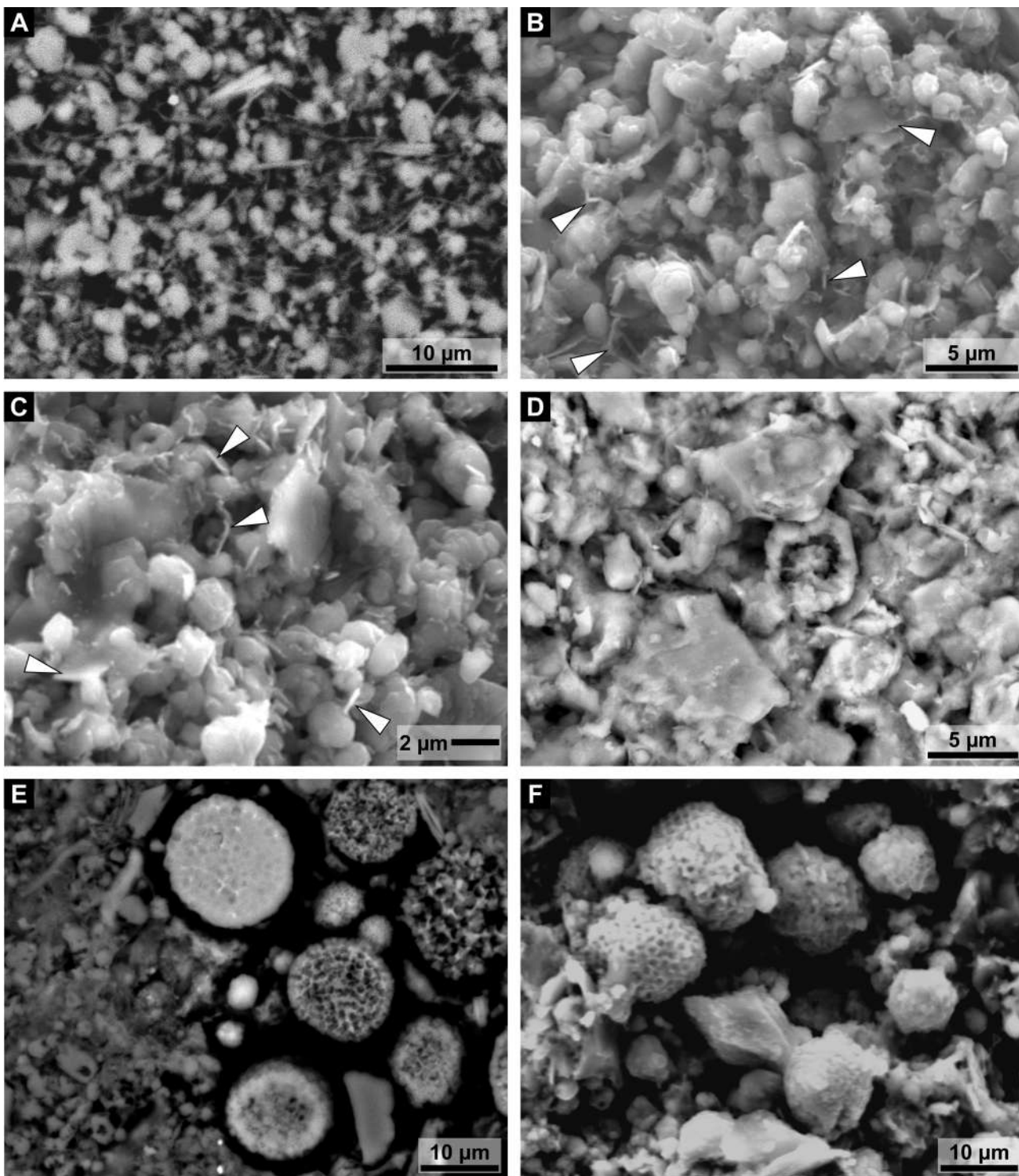


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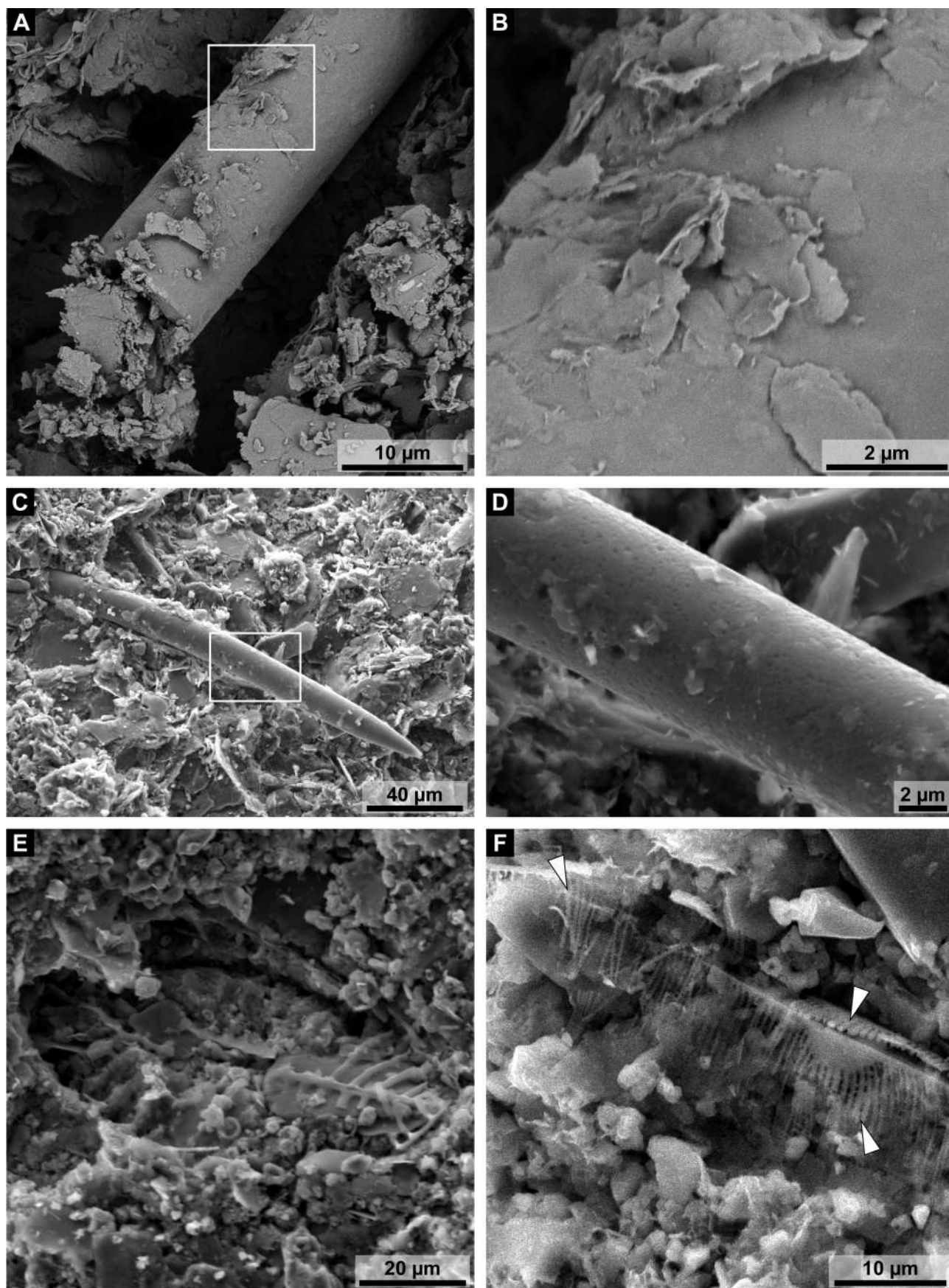


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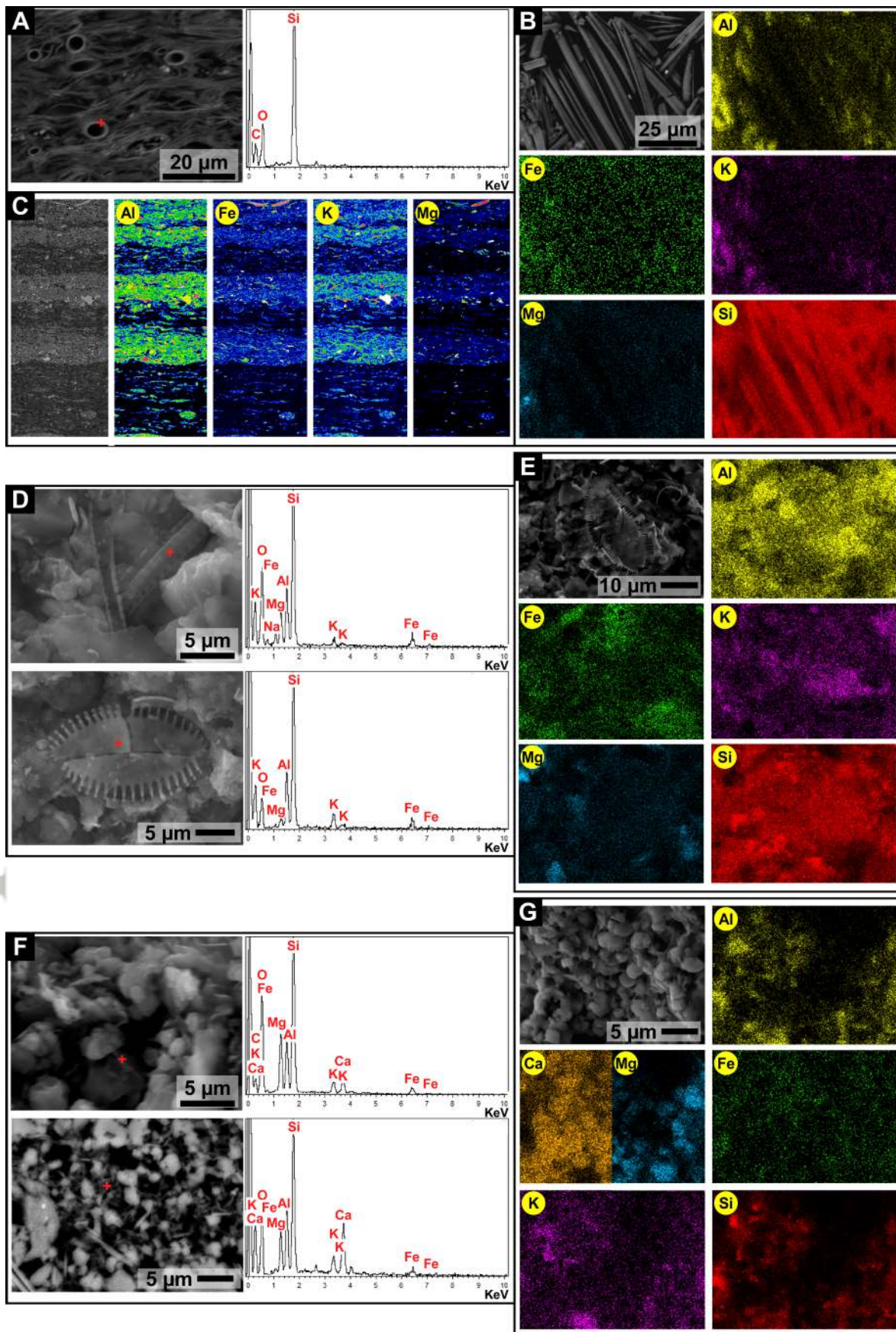


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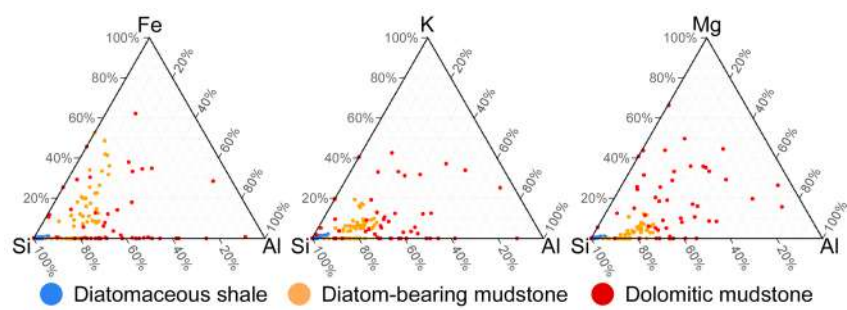


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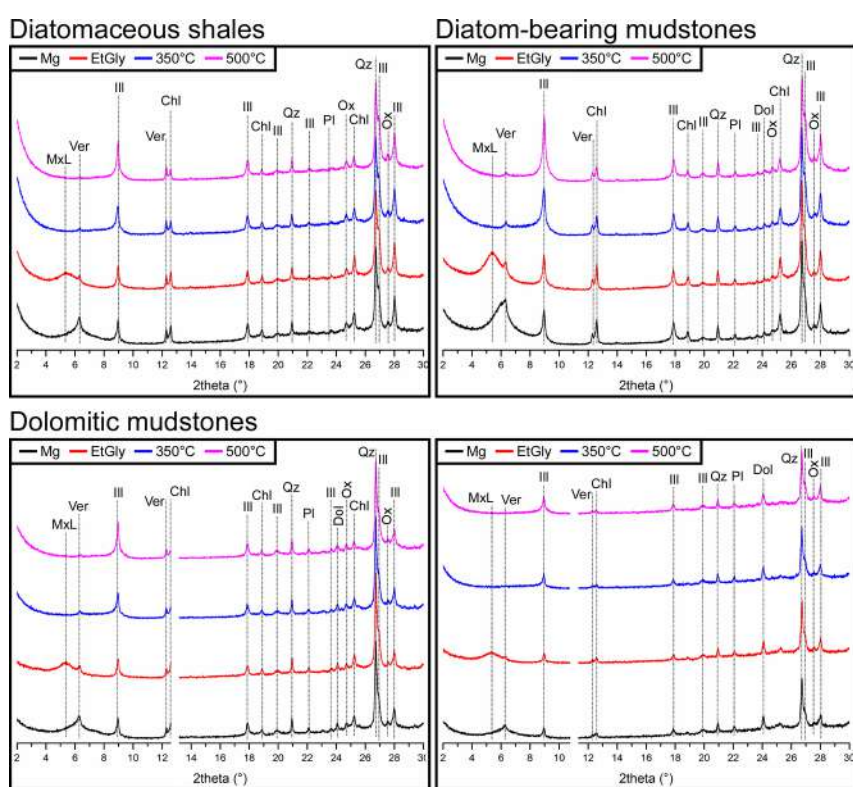


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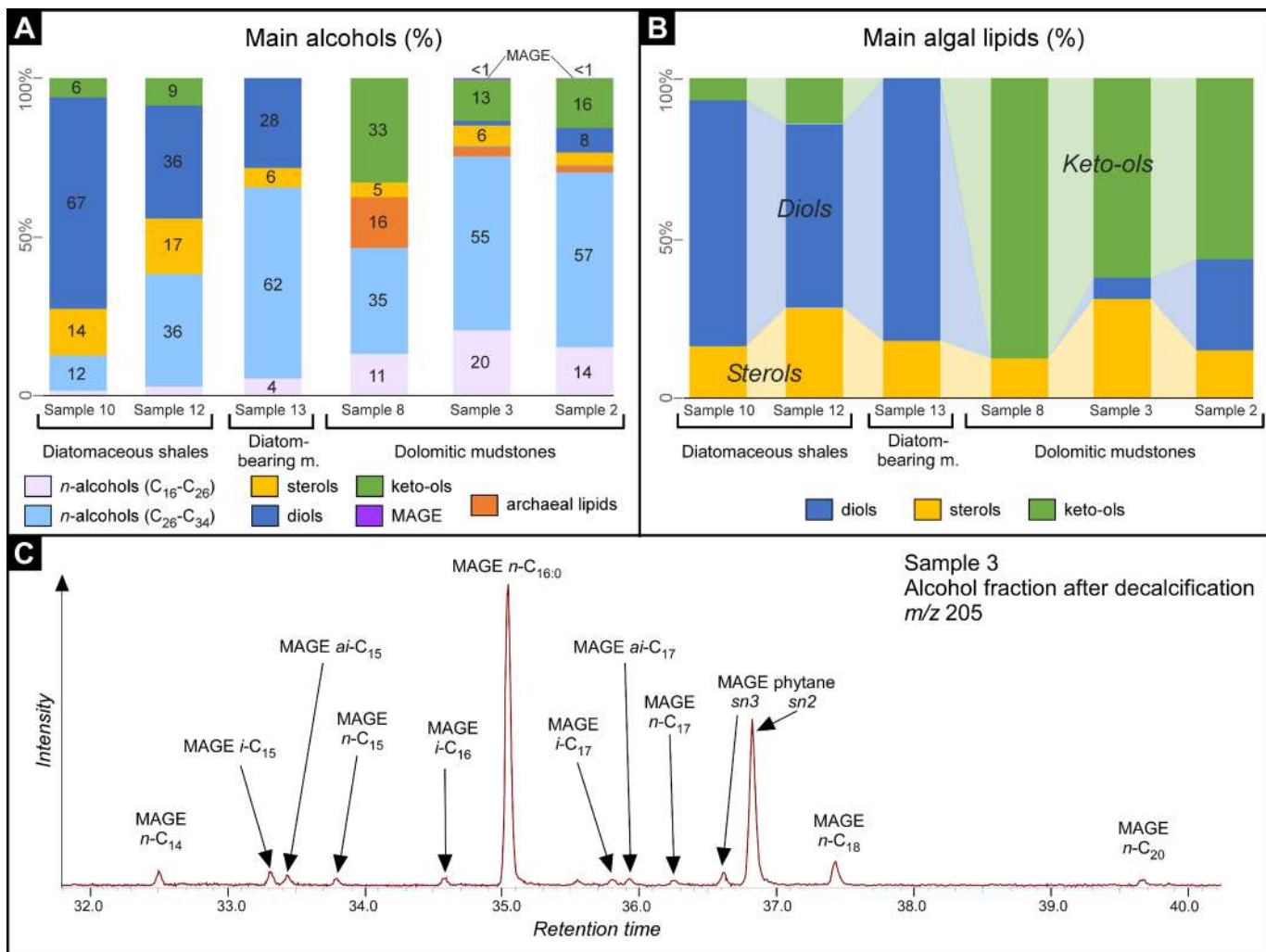


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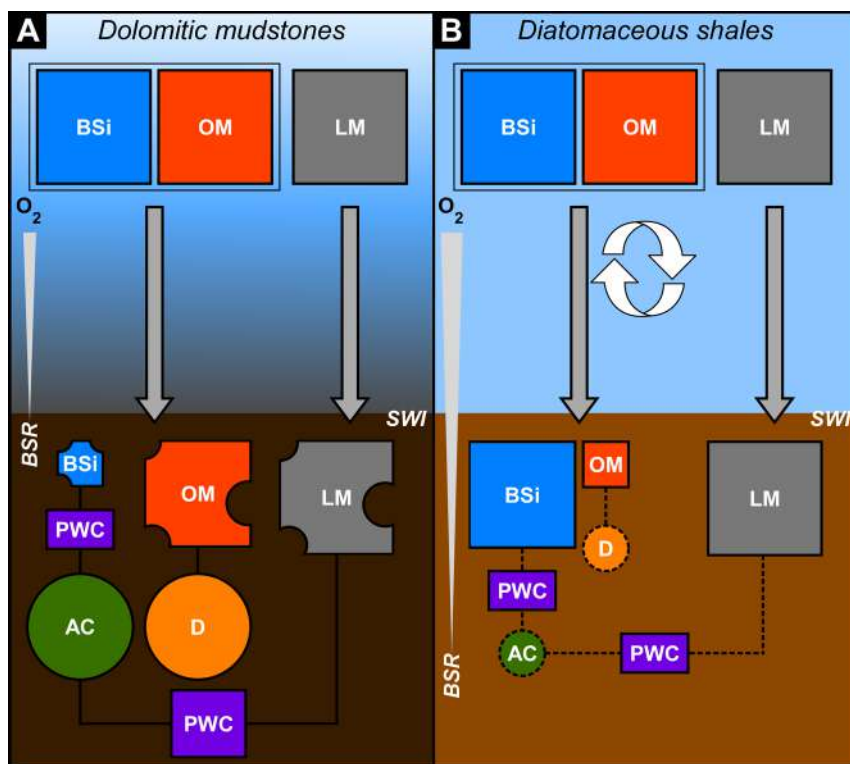


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