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# Looking for the oldest diatoms

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ABSTRACT

Paleontological observations of ancient flora and fauna provide powerful insights into past diversity and relationship dynamics between organisms and their environments. Diatoms are globally distributed protists that influence major biogeochemical cycles and sustain oceanic food webs. The fossil diatom record extends 120 million years back to the Early Cretaceous where rare deposits were discovered worldwide and are occasionally represented by diverse communities. However scarce, the taxonomic richness and geographical spread of these diatom communities suggest prior evolutionary events and therefore earlier deposits. To complement the existing fossil information and to discover diatom deposits predating 120 Ma, we examined 33 study sites from cores and outcrops across oceans and continents. These efforts did not generate new fossil discoveries, however. Our assessment suggests biogenic silica that comprises the cell wall of diatoms was likely dissolved from Mesozoic sediments through diagenetic processes. Altogether, the search for the oldest diatoms must continue but should target sediments that experienced shallow burial and concretions.

## 1. Introduction

The fossil record documents the history of life and provides a unique long-term perspective on ancient life and its relationships with past environments. Based on the fossil record we can explore evolutionary relationships and the origin of modern floras and faunas. Diatoms are globally distributed photosynthetic protists that influence major biogeochemical cycles and sustain oceanic food webs (Armbrust, 2009). Diatoms found in the sedimentary archives are valuable for various inferences regarding early evolution, past diversity, biogeography, ecology, the role of diatoms in ancient ecosystems, and their impact on elemental cycles (Davies et al., 2009; Renaudie, 2016; Conley et al., 2017; Bryłka et al., 2024). The deep fossil record of diatoms is limited, which restricts our understanding of the early evolution and diversification of the lineage. The lack of direct evidence is often explored by extrapolations through modelling (Naidoo-Bagwell et al., 2023) and phylogenetics (Nakov et al., 2018).

To study the fossil record of diatoms, scientists have collected sediments from the Earth's surface and explored oceanic sediments through drilling. Due to dissolution of the siliceous cell walls (frustules) of diatoms and diagenetic processes, an estimated 3% of living assemblages is preserved in sediments, thus leaving limited traces of the past (Tréguer et al., 1995). The earliest, moderately preserved diatoms have been recorded in the Aptian (Lower Cretaceous, 120 Ma) in Queensland, Australia, and were represented by diverse communities of 38 species in 13 genera (Nikolaev et al., 2001a). Records of earlier Jurassic diatoms from Liassic shales in Boll, Germany, are unsubstantiated (Bryłka et al., 2023). The oldest well-preserved diatoms were recorded from the Lower Cretaceous (113–100 Ma) of the Weddell Sea and are represented by 35 species in 20 genera (Gersonde and Harwood, 1990). Several deposits of Lower Cretaceous diatoms (120–100 Ma) have been described worldwide, but only from narrow and isolated niches representing shallow epicontinental seas and near-shore environments (Forti and Schultz, 1932; Jousé, 1949; Geroch, 1978; Strel'nikova and Martirosjan, 1981; Foucault et al., 1986). Most of the records from this period are represented by a few poorly preserved or diagenetically altered diatom frustules, where pyrite crystals substitute the original opal (e.g., Geroch, 1978). Towards the Late Cretaceous, there is a substantial increase in the number of deposits found that contain well-preserved, diverse, and abundant diatom assemblages (Hajós and Stradner, 1975; Harwood, 1988; Nikolaev et al., 2001b; Tapia and Harwood, 2002; Harwood et al., 2007; Witkowski et al., 2011). Regardless of the many records published on diatoms, the Cretaceous period remains understudied, and during the past decade, only a handful of records have been published describing diatoms (Davies and Kemp, 2016; Shimada et al., 2022). Although the Lower Cretaceous record is limited, the global distribution of study sites

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and the diversity of the oldest diatoms point towards earlier dispersal and diversification events. Indirect evidence for the earlier evolution is also provided through molecular clocks, which suggest an origin near the Triassic-Jurassic boundary, 200–190 Ma (Nakov et al., 2018).

Considering the global importance of diatoms in the contemporary ocean and the broad use of fossil information across scientific disciplines, it would be valuable to complement the existing record and extend the record back through time. Of particular interest for this study is the time surrounding the oldest fossils found in the Lower Cretaceous and the time predating those fossils, i.e., the Jurassic. Through the careful analysis of the current distribution of diatoms and their past occurrences, together with lithology and paleoenvironmental reconstructions, we chose 33 study sites to search for diatom fossils. These efforts did not generate new fossil discoveries, however. In this paper, we address the challenges in recovering diatoms from the Mesozoic sediments.

## 2. Materials and Methods

### 2.1. Worldwide Search for Mesozoic diatoms. Where to look?

To find diatom fossils of Lower Cretaceous and Jurassic age we surveyed the literature in search of promising locations and lithologies. In this process we accounted for the following: (1) environments that have high diatom abundance in the modern ocean, (2) regions with described Cretaceous diatoms, (3) lithologies known to have high preservation potential, (4) lithologies from which Cretaceous diatoms were previously described, and (5) accessibility of the material.

In the modern ocean, diatoms are the most abundant in upwelling zones and high latitudes (Malviya et al., 2016), and therefore, examining past upwelling zones has the highest potential for fossil preservation. We also mapped study sites containing Cretaceous diatoms on paleogeographical maps to identify areas of past diatom occurrences (Fig. 1). Most study sites are located at higher latitudes, with scarce representation in equatorial regions. In terms of lithology, it is estimated that a large fraction of the current export of diatoms to sediment is through aggregates (particulate organic matter with inclusions of bacteria and phytoplankton) and fecal pellets (Ploug et al., 2008). Aggregates often terminate the diatom bloom and result in a large number of cells sinking together (Alldredge and Gotschalk, 1989). Fecal pellets and coprolites of the Cretaceous age were described to contain diatoms (Chin et al., 2008), hence, analysis of Mesozoic coprolites may contain undiscovered fossil communities. Previous studies suggest that diatom preservation is elevated under anoxic conditions (McMinn, 1995). Soft tissues of invertebrates buried under anoxic conditions were found in sediments as old as 380 Ma (Melendez et al., 2013). Therefore, analysis of Mesozoic sediments deposited under oxygen-depleted conditions such as black shales (Sinha et al., 2021) may also preserve diatoms. These environments may also cause pyritization, however (Berner, 1984). Some of the oldest (120–100 Ma) diatom fossils were described from phosphatic and calcareous nodules (Forti and Schultz, 1932; Nikolaev et al., 2001a). Preservation of fossils in concretions is excellent in many localities, conserving soft tissues, bones, and delicate structures (Brun, 1894; Arena, 2008; Gaines et al., 2012; Mccoy et al., 2015). Accordingly, concretions have a high potential to preserve diatom fossils. Lastly, we surveyed the literature for study sites with described opaline microfossils such as radiolarians and sponge spicules of Jurassic and Early Cretaceous ages. The extraction of these microfossils generally used sieving techniques that might have excluded smaller diatoms. Through the above assessment, we chose 33 study sites to search for fossil diatoms. Samples were ordered from the Deep Sea Drilling Project (DSDP)/Ocean Drilling Project (ODP) repositories, collected in the field, or received from collaborators and various museum collections (Table 1).

### 2.2. Laboratory methods

#### 2.2.1. Chemical digestions

All the samples except cherts were cleaned following common chemical digestions for diatom extraction (Trobajo and Mann, 2019). First, the sample, of weight between 10 g and 1 kg, was crushed with a hammer to increase the reactive surface and placed in a 300 ml glass

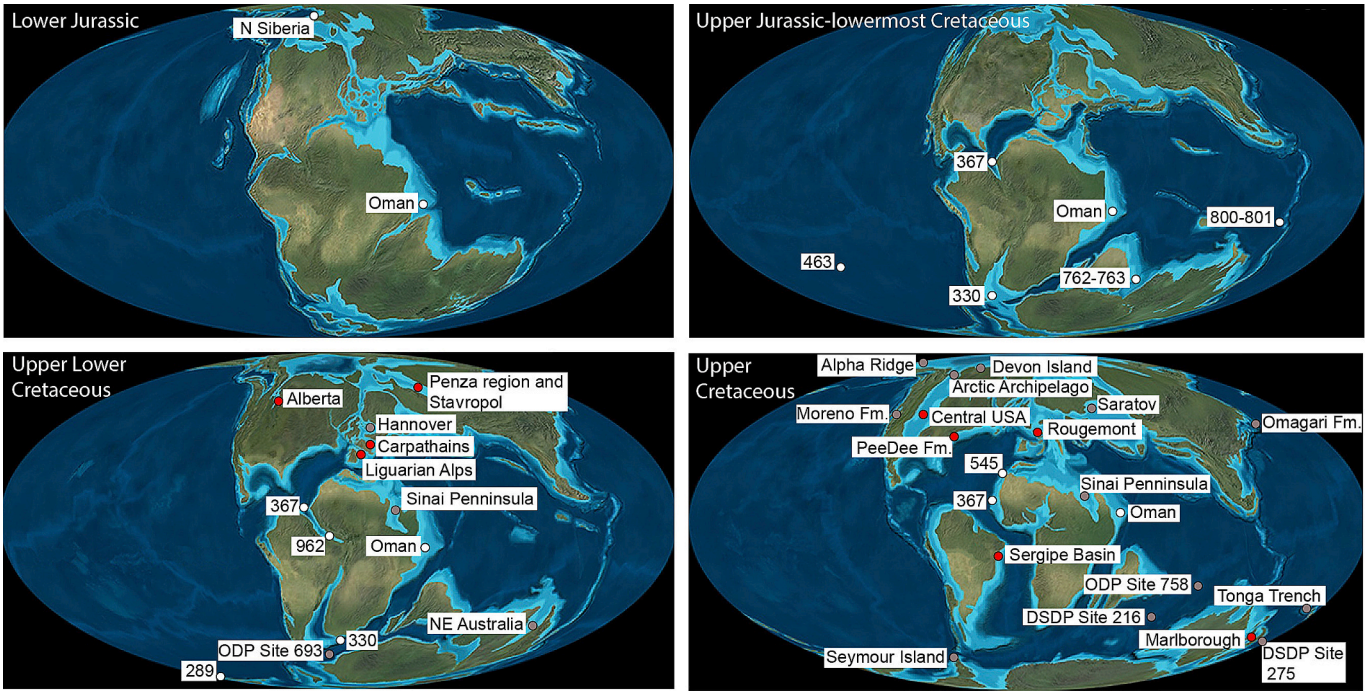


**Fig. 1.** Location of investigated study sites (Table 1; white dots) and Cretaceous study sites (summarized in Supplementary Table 1) that record Cretaceous diatoms (gray dots-opaline preservation, red dots-pyritized fossils) on the paleogeographical world map. Modified from ©Deep Time Maps™ 2020. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Table 1**
Compilation table of relevant information on study sites examined during the search for Mesozoic diatoms.

| Location | Age Ma | #samples | Lithology | Depositional environment | Microfossils | Map denoted | Credit | reference |
|---|---|---|---|---|---|---|---|---|
| Al Aridh formation | 201–89 | 14 | chert | pelagic | radiolarians; sponge spicules | Oman | Goričan Š | Goričan et al., 2013 |
| Leg 36 Site 330 | 164–110 | 4 | chert, claystone | pelagic | – | 330 | DSDP | Barker et al., 2007 |
| Leg 122 Site 762C, 763 B,C | 143–83 | 20 | chalk, claystone | prodelta to pelagic | – | 762–763 | ODP | Haq et al., 1990 |
| Leg 41 Site 367Z, 368Z | 125–72 | 8 | black shales | pelagic | – | 367 | DSDP | Gardner and Herring, 1975 |
| Leg 79 Site 545H | 113–107 | 5 | black shales | pelagic | sponge spicules | 545 | DSDP | Hinz et al., 1984 |
| Leg 159 Site 962B | 100.5 | 6 | chert | pelagic | Radiolarians, rare pieces of diatoms | 962 | ODP | Mascle et al., 1996 |
| Leg 41 Site 367Z | 157–139 | 3 | porcellanite | pelagic | – | 367 | DSDP | Gardner and Herring, 1975 |
| Leg 30 Site 289 | 125–113 | 1 | chert | pelagic | – | 289 | DSDP | Andrews et al., 1975 |
| Leg 62 Site 463 | 145–139 | 2 | chert | pelagic | – | 463 | DSDP | Thiede et al., 1981 |
| Leg 129 Site 800 A, 801B | 145 | 2 | chert | pelagic | – | 800–801 | ODP | Lancelot et al., 1990 |
| Schandelah | 190–174 | 40 | black shale, phosphatic concretions | hemipelagic | – | Schandelah | B. van de Schootbrugge | Van de Schootbrugge et al., 2019 |
| Arnager | 100–93 | 1 | phosphorite | outer shelf | sponge spicules | Arnager | J. Witkowski | Vajda-Santivanez and Solakius, 1999 |
| Scharrel 10 | 139–129 | 5 | mudstone | distal basin setting | – | Scharrel | A. Bornemann | Thöle et al., 2020 |
| Bächental | 182 | 4 | black shales | distal slope/basin | sponge spicules | Bächental | S. Neumeister | Neumeister et al., 2016 |
| N Slovakia | 182 | 2 | black shales | basin | – | N Slovakia | G. Suan | Suan et al., 2018 |
| N Siberia | 182 | 4 | black shales | shallow sea, intermediate and deep continental shelf | – | N Siberia | | Suan et al., 2011 |
| La Voult | 165–161 | 8 | limestones, marls | slope basin transition | sponge spicules | La Voulte | Field collected | Charbonnier et al., 2007 |
| Trept[1] | 165–161 | 8 | limestones, marls | shallow platform | – | French Jura | Field collected | Gaillard, 1971 |
| Löruns | 199–192 | 3 | hemipelagic limestones | outer shelf | – | Löruns | Field collected | Föllmi et al., 2007 |
| Bülls[2] | 139 | 5 | limestones and marls | distal platform | – | Bülls | Field collected | Föllmi et al., 2007 |
| Götzis[2] | 125–113 | 5 | marls and carbonate sediments | inner-outer shelf | – | Götzis | Field collected | Follmi and Ouwehand, 1987 |
| Vitznau[2] | 139–140 | 14 | marls and limestones | outer shelf to basin | | Vitznau | Field collected | Föllmi et al., 2007 |
| Palfris | 143–140 | 4 | shales, marls, marly limestones | outer shelf to basin | – | Palfris | Field collected | Föllmi et al., 2007 |
| Carrière Vicat Monlalieu Isère | 157 | 2 | calcified siliceous sponges | shelf environments | silicified foraminiferas | French Jura | Lyon Museum Collection | Gaillard, 1971 |
| General Jurassic Collection - Lyon (GJC) | 168–152 | 5 | calcified siliceous sponges | diverse shelf environments | sponge spicules | 3 samples French Jura; 2 samples La Voulte; one sample Bourgogne not marked | Lyon Museum Collection | |
| Université Grenoble Alpes (UG) | 170–83 | 17 | siliceous sponges | diverse shelf environments | sponge spicules | 3 samples St. Cyr<br>3 samples Catalonia<br>4 samples French Jura 2 samples Drôme<br>1 sample Normandy<br>3 samples La Voult | Université Grenoble Alpes | |
| Aselfingen[3] | 183–181 | 4 | black shales | basin | – | Asselfingen | Field collected | Gwinner and Geyer, 1984 |

(*continued on next page*)

**Table 1** (*continued*)

| Location | Age Ma | #samples | Lithology | Depositional environment | Microfossils | Map denoted | Credit | reference |
|---|---|---|---|---|---|---|---|---|
| Holzmaden[3] | 183–181 | 7 | black shales | basin | – | Holzmaden | Field collected (5) J. Lindgren (2) | Sinha et al., 2021 |
| Boll[3] | 183–181 | 4 | black shales | basin | – | Boll | Field collected | Gwinner and Geyer, 1984 |
| Dotternhausen[3] | 183–181 | 6 | black shales | basin | – | Dotternhausen | Field collected | Röhl et al., 2001 |
| Nusplingen | 155–152 | 4 | coprolites, limestone samples | shallow lagoon | radiolarians | Nusplingen | Guenter Schweigert, Stuttgart Museum | Dietl and Schweigert, 2004 |
| Motorway construction Aichelberg and Gruibingen[3] | 163 | 1 | ammonite in phosphatic nodule | shallow platform | – | Gruibingen | G. Schweigert, Stuttgart Museum | Dimter and Smelror, 1990 |
| Plettenberg | 160–157 | 10 | calcareous sponges, limestone | deep-shelf | – | Dotternhausen (due to proximity) | Field collected | Olivier et al., 2004 |
| Bohemian Basin | 100.5–94 | 300 g | phosphatic concretions | shallow epicontinental sea | very rare diatom pieces | Bohemian Basin | Petra Zahajská | Košťák et al., 2018 |

[1] On Supplementary Fig. 2 marked as French Jura.
[2] On Supplementary Fig. 2 marked as Helvetic Alps.
[3] On Supplementary Fig. 2 marked as Posidonia shale.

beaker or multiple beakers when necessary. Next, 10% hydrochloric acid (HCl) was added and left at room temperature to remove calcium salts. HCl was replenished daily until the structure of the sample was destroyed (depending on the sample, this time varied between 1 day and 2 weeks). Samples were then cleaned from HCl using a triple rinse in Milli-Q® water (18.2 MΩ *cm). Samples were further treated with 35% nitric acid ($HNO_3$) on a 100 °C hotplate to remove organic matter. $HNO_3$ was replenished daily until the color of the sample brightened, indicating removal of organic matter (depending on the sample, this time varied between 1 and 4 weeks). Samples were then cleaned from $HNO_3$ by triple rinsing in Milli-Q® water. In the last step of chemical digestion, samples were treated with hydrogen peroxide ($H_2O_2$) on the hotplate at 100 °C to continue organic matter oxidation. Samples remained in $H_2O_2$ until the color of the samples was light gray to white/beige (depending on the sample, this step lasted from 1 to 6 weeks). Chemical treatment finished with a triple rinse in Milli-Q® water. Residual sediments were transferred to 50 ml sterile plastic tubes, frozen, and freeze-dried. Dried sediments were then mixed with a sodium polytungstate heavy liquid solution (SPT) of a density of 2.15 g $cm^{-3}$ to extract siliceous parts (diatom frustule density = 2.1 g $cm^{-3}$) and centrifuged for 15 min at 2850 RPM. The floating fraction was collected with a Pasteur pipette and filtered through a 0.45 μm cellulose nitrate membrane filter to remove SPT. Sediment collected on the filter was further transferred to a clean plastic tube and suspended in Milli-Q® water for later examination.

Cherts were dissolved using the hydrochloric acid protocol (HF) described in (De Wever et al., 2002) and modified by Bryłka et al. (2023). The protocol was tested on diatomite to ensure lack of frustule dissolution in 10% HF. First, 10–20 g of chert was crushed and placed in a 100 ml plastic beaker. Next, 20–40 ml of 10% HF was added to the beaker until the chert pieces were covered. After 30 min, the acid was poured from the beaker to the plastic filtering container. The remaining pieces of chert in the beaker were rinsed with Milli-Q® water to remove residual acid and dissolved sediment attached to the chert surface. Milli-Q® water used for the rinse was also poured into the plastic filtering container. The liquid collected in the container was filtered through a 0.45 μm polycarbonate filter, and sediment collected on the filter was transferred to the 50 ml sterile plastic tube. The remaining pieces of chert were submerged in HF again for further dissolution. All the activities above were repeated after 1 h, 1.5 h, and 2 h. In the end, residue from each chert sample was collected in 5 tubes: after 0.5 h, 1 h, 1.5 h, 2 h, and a "final wash" containing the remaining pieces of chert. Samples were used for further examination, except for the residue collected after 0.5 h, which was considered a wash run.

### 2.2.2. *Microscope analysis*

Slides for light microscope (LM) evaluation were prepared from the sample residue remaining after chemical digestion. The number of slides prepared depended on the initial weight of the sample used for digestion and varied between 10 and 60 slides per sample. First, 2 ml of the sample solution was poured on a glass coverslip placed on the hotplate set to 60 °C. A dried coverslip was fixed to the microscopic slide using Norland Optical Adhesive 61 (NOA 61) and placed in the UV box for 20 min to solidify the adhesive. Prepared slides were scanned for siliceous microfossils using an Olympus BX53 light microscope equipped with a digital camera at magnification x1000.

Scanning electron microscope (SEM) samples were prepared from 0.5 ml of the sample residue remaining after chemical digestion. Samples were coated with 5 nm Platinum-Palladium (Pt—Pd) powder in a Cressington sputter coater. Samples were then examined on the variable pressure Tescan Mira3 High-Resolution Schottky FE-SEM equipped with an Oxford EDS detector housed at the Department of Geology, Lund University, Sweden. Samples were photographed at 2 kV and elemental mapping was performed at 15 kV.

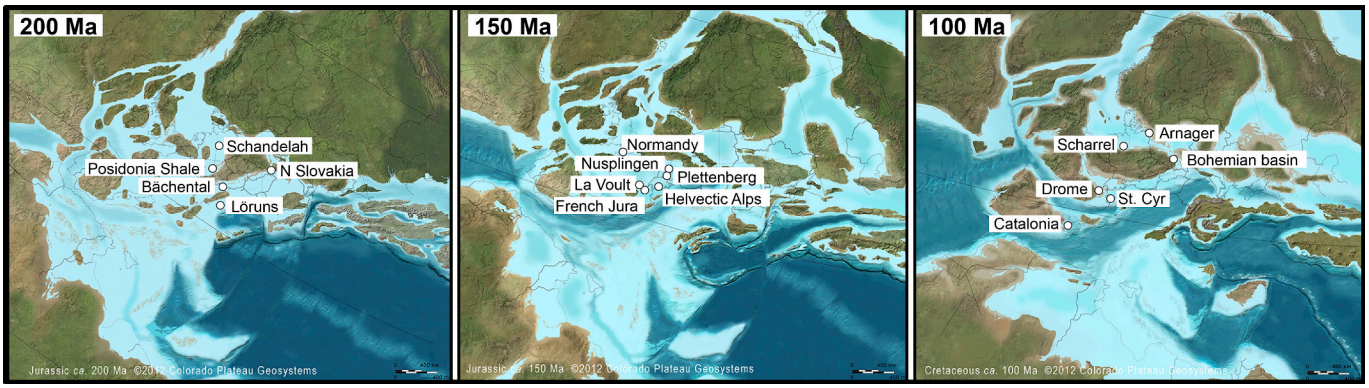


**Fig. 2.** Location of the investigated study sites (Table 1) on the paleogeographic map of Europe. Modified from ©Deep Time Maps™ 2020.

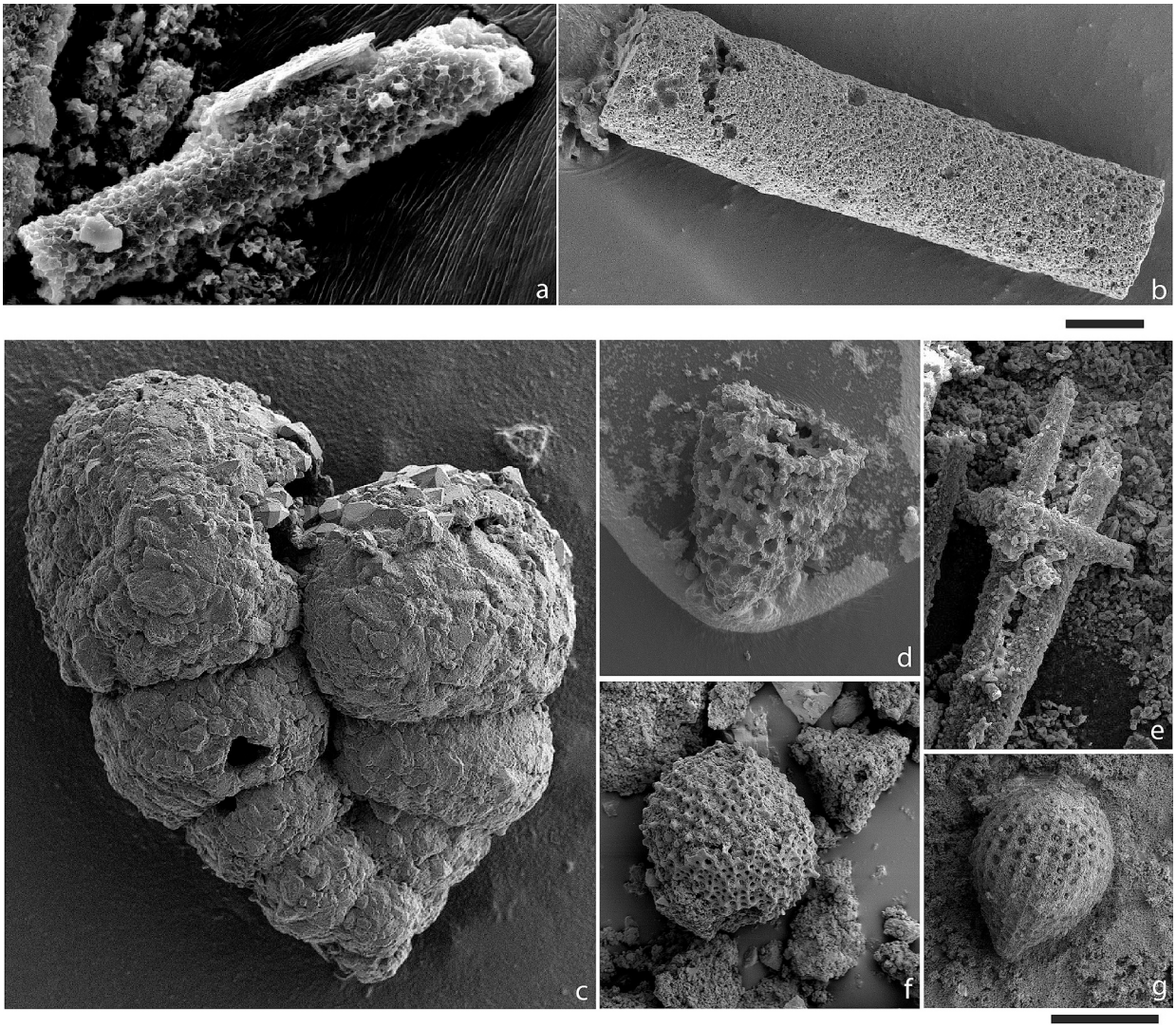


**Fig. 3.** SEM photographs of the microfossils observed at study sites. (a) sponge spicule – Arnager, (b) sponge spicule – Götzis, (c) silicified foraminifera – Carriére Vicat, (d) radiolaria – Nusplingen coprolite, (e) sponge spicules – la Voult, (f) radiolaria – ODP 159-962B-9H-5, 100–101 cm, (g) radiolaria – Oman. The top scale bar (5 μm) refers to pictures a-b, and the bottom scale bar (20 μm) refers to pictures c-g.

## 3. Results

### 3.1. Search for the Mesozoic diatoms

In the search for Mesozoic diatoms, 226 samples from 33 study sites (Table 1, Figs. 1, 2 and Supplementary Figs. 1 and 2) were chemically dissolved and evaluated with LM and SEM. Study sites ranged in age from the Earliest Jurassic to the Late Cretaceous (200–70 Ma) and represent a wide range of lithologies and environments. We collected samples representing: past open ocean pelagic environments, upwelling

zones, shallow epicontinental seas and their respective slopes, and various shelf and deltaic environments (Figs. 1, 2 and Table 1). Lithology-wise, we examined anoxic sediments, concretions, coprolites, sponge mummies, and cherts (Table 1). We also examined a range of limestones and marls, previously found to contain siliceous sponge spicules (Table 1).

Siliceous microfossils were observed at 11 study sites and consisted mainly of sponge spicules and radiolarians (Table 1, Fig. 3). In addition, we observed silicified foraminifera (Fig. 3d). All observed microfossils were present in low abundance (except for two calcareous sponges from La Voult, France, with abundant siliceous sponge spicules and Oman cherts with abundant radiolarians) and displayed a high degree of dissolution. Observed microfossils were extracted mainly from sponge mummies, cherts and black shales but also from one study site with coprolites (Nusplingen) and one study site with limestones (La Voult) (Table 1). Rare fragments likely derived from frustules of diatoms (radiolarians generally have large pores than diatom) were observed in Cenomanian phosphatic concretions from Bohemia and cherts from site 962.

## 4. Discussion

### 4.1. The search for diatoms

To extend the fossil record of diatoms in Mesozoic sediments and potentially discover diatoms older than so far described, we examined 33 study sites worldwide. However, all sites older than the Albian were barren in diatoms and contained mostly rare, poorly preserved sponge spicules and radiolarians. Since siliceous sponges and radiolarians have been reported in the fossil record as old as the Cambrian (ca. 540 Ma) (Kidder and Erwin, 2001), and all fossils we observed appeared dissolved and heavily altered, we suggest post-depositional diagenetic processes have effectively erased the early diatom fossil record at many sites. During post-depositional diagenesis, the amorphous phase of opal (opal-A) that comprises pristine diatom frustules, radiolarian tests, and sponge spicules is transformed by dissolution and reprecipitation into crystalline phases of opal such as opal-CT (cristobalite and tridymite) and quartz (Williams and Crerar, 1985). Indeed, all the fossils that we observed are preserved in the form of opal-CT and quartz (Supplementary Fig. 3), which further supports our hypothesis.

Post-depositional silica diagenesis is a complex process controlled by many factors including lithology, pH, temperature and pressure, elemental composition of the pore water in the sediment, and age of the sample (Kastner et al., 1977). Generally, temperature and pressure (which increases with depth) play a decisive role in converting opal-A to opal-CT and, eventually, to quartz (Lu et al., 2020). Conversion of opal-A to opal-CT in older sediments may occur even at temperatures of 10–20 °C (Williams and Crerar, 1985) and opal-CT to quartz at 60–80 °C (Worden et al., 2012). This conversion can occur at depths of several hundred meters. For example, diatom frustules recovered from ODP site 795 (Sea of Japan) dated at ca. 10–3 Ma exhibited opal-A to opal-CT conversion at a depth of ca. 315 m below the seafloor (5.1 Ma) and an opal-CT to quartz conversion occurred at ca. 365 m below the seafloor (5.9 Ma) (Yanchilina et al., 2020). In another sedimentary section of the comparable age located in the Bering Sea, opal-A to opal-CT transformation of diatom frustules occurred at 600 m below the seafloor (Hein et al., 1978). The depth for the opal-A to opal-CT and further to quartz is therefore not the same everywhere, and the temperature and pressure will have a large influence where in the sediment opal-A will be diagenetically altered.

A basic principle of diagenesis is that biogenic opal-A of siliceous microorganisms is dissolved and then either (1) reprecipitate and crystallize on the substrate in situ mimicking the original morphology (e.g., Fig. 3e), (2) reprecipitate into authigenic silicate which depends on the availability of ions (Riech and von Rad, 1979), or (3) diffuse into pore waters (Williams and Crerar, 1985). As a consequence, we either observe reprecipitated microfossils that lack part of the original structure, or the biogenic component is completely dissolved. The reprecipitated radiolarians and sponge spicules we observed retained some semblance of their original morphology, but detailed characters of radiolarians and sponge spicules were largely erased (Fig. 3d, f, g). In much more finely ornamented diatoms, the original micro- to nanoscale ultrastructural features would completely disappear, leaving behind shapes that resemble frustules but lack characteristics that would allow us to classify them unequivocally (Supplementary Fig. 4).

There are several other reasons why we observed radiolarians and sponge spicules but not diatoms. As previously mentioned only an estimated 3% of living diatom communities will be preserved in oceanic sediments (Tréguer et al., 1995), not only due to diagenesis but also biological and physical processes. In the water column live diatoms are subjected to extensive grazing, unlike radiolarians (Biard, 2022). Furthermore, diatoms have lower sinking rates than radiolarians; for example, 35 m $day^{-1}$ for a single diatom (Miklasz and Denny, 2010) and 70 m $day^{-1}$ for a single radiolarian (Takahashi and Honjo, 1983). Although the main export of diatoms in the contemporary ocean is through aggregates with sinking rates of 100 m $day^{-1}$ (Smetacek, 1985), this rate is restricted to diatom blooms. Blooms have not been recorded in sediments older than ca. 70 Ma (Davies and Kemp, 2016) and were likely rare or absent in warm, weakly stratified Mesozoic oceans (Behrenfeld et al., 2021). Lastly, as much as 50% of the biogenic silica dissolves in the upper 100 m of the water column (Nelson et al., 1995) where diatoms typically live, whilst radiolarians live at depths down to 400 m (Suzuki and Not, 2015). For these reasons, we argue that the smaller frustules of diatoms, which might have been infrequent in the Mesozoic oceans, had lower preservation potential than larger abundant radiolarians. As for the sponge spicules, siliceous sponges grow directly on the sea floor (Beaulieu, 2001), so spicules do not experience the same dissolution in the top 100 m of the photic zone and throughout the water column, which is a further advantage for preservation in the sediments. Laboratory experiments also show that diatom frustules dissolve faster than siliceous sponges (Maldonado et al., 2022) which may be attributed to structural order of the silica or differing atomic bonds (Farfan et al., 2023). Collectively, these are likely the reasons why we did not observe diatoms despite the presence of other siliceous microfossils.

The absence of diatoms in sediments predating 120 Ma has been also attributed to: (1) the naked-cell theory suggesting ancestral diatoms did not have a siliceous cell covering and were not preserved (Round and Crawford, 1981), (2) a paucity of Jurassic and older marine deposits due to ocean crust subduction (Harwood and Gersonde, 1990), and (3) early diatoms might have proliferated in specialized habitats, making the likelihood of discovering them low (Behrenfeld et al., 2021). All of the above will be addressed in the next section.

### 4.2. Other considerations regarding the Mesozoic diatoms

One may argue that the lack of fossil diatoms in the Jurassic and Lower Cretaceous simply reflects that diatoms originated no later than 120 Ma, but indirect evidence from existing fossil record suggests otherwise. The Early Cretaceous diversity consists of centric and multipolar diatoms belonging to several lineages (Forti and Schultz, 1932; Gersonde and Harwood, 1990; Nikolaev et al., 2001a). Moreover, each study site exhibits unique assemblages, with some shared and some distinctive species, which suggests the possibility of independent diversification events following dispersal. Although diversification can be accelerated early on in a lineage (Lee and Ho, 2016), which would create a large diversity in a short time, the contrary has also been shown (Bromham, 2003). Another currently untestable hypothesis is that the oldest diatoms had a different type of frustule. Diatoms are sister to Parmales, a group of marine picoplankton with cell coverings consisting of small siliceous plates (Ichinomiya et al., 2016), so the earliest diatoms were likely silicified as well. A diatom frustule is constructed across all diatom taxa of two valves that match together like a petri dish (Round

et al., 1990). Therefore, it seems unlikely and speculative that diatoms switched from one frustule type to another following the split from Parmales. Notably, the fossil record does not include an abundance of siliceous cell coverings that cannot be tied to known lineages. Despite these and other hypotheses that posit a fundamentally different cell wall architecture in the earliest diatoms, the most parsimonious explanation is that diatoms had a bipartite siliceous encasement from the very beginning of the lineage, but preservation issues like the ones described above make observing them difficult.

Altogether the distribution of diatom deposits in the Lower Cretaceous on both hemispheres, predominantly pyritized (Fig. 1), and the diversity of the oldest diatoms, suggests that the earliest diatoms are yet to be discovered. Diatoms likely had been diversifying before 120 Ma to evolve into separate lineages and dispersed, adapted, and prevailed in new environments where they further diversified. Eventually, only a small proportion of these communities were preserved in sediments whilst others were heavily affected by diagenetic processes such as pyritization in anoxic environments. We also must add that marine deposits of the pre-Cretaceous age that might have contained diatoms were eroded and/or consumed by subduction, altered by dissolution processes or deposited under conditions not conductive for fossilization (e.g., tidal zones) (Harwood and Nikolaev, 1995). Considering all the evidence collectively we suggest a further search for diatoms is promising, but must follow the guidelines proposed below.

### 4.3. *Where to look in the future?*

The best-preserved Cretaceous diatoms come from sediments that experienced shallow burial (Hanna, 1927; Gersonde and Harwood, 1990; Witkowski et al., 2011; Davies and Kemp, 2016) and, therefore, temperature and pressure likely did not create conditions for silica diagenetic processes. The estimated paleodepth of these study sites ranges from 50 to 1500 m and represents shallow to deeper outer shelves and open ocean settings of higher latitudes, i.e., a broad range of depositional environments (Chambers, 1997). These deposits were found on land. For example, Devon Island sediments were deposited in the coastal ocean and tectonically uplifted and therefore not buried (Witkowski et al., 2011). In addition, samples have been recovered from the oceanic seafloor through drilling, e.g., the Alpha Ridge sediments that experienced shallow burial (Davies and Kemp, 2016). As noted by Chambers (1997) many oceanic localities with preserved diatoms are associated with strong geographical features (e.g., submarine ridges such as Alpha Ridge and Tonga Trench) that could have driven local upwelling where bottom currents are forced upwards, providing nutrient-rich water to the surface.

Cretaceous diatoms were also preserved in concretions deposited in shallow seas (Forti and Schultz, 1932; Nikolaev et al., 2001a). Concretions are formed early in the diagenetic history of a rock, which impairs further diagenetic processes and consequently can prevent frustule dissolution (Barron, 1993), on occasion regardless of the burial depth of the host rock. For example, concretions preserving the oldest diatoms have been found at depths of 100 m but also as deep as 700 m in the sediment (Nikolaev et al., 2001a). Furthermore, diatoms from the continental sedimentary section of Seymour Island were preserved only in concretions even from the deepest parts of the section (>1400 m depth) (Harwood, 1988). Several Cretaceous study sites (e.g., Devon Island, Tonga Trench, and ODP site 785) are also associated with volcanic ash deposition, which is known to enhance preservation of siliceous fossils (Chambers, 1997).

The majority of siliceous microfossils we observed come from a range of structures, including phosphatic concretions, sponge mummies, and coprolites. Like concretions, sponge mummies and coprolites are likely connected to early cementation that impaired later diagenetic processes and preserved fossils we observed. It was shown that the conversion of biogenic opal to opal-CT is slightly accelerated in carbonate host rocks, whereas clayey facies retard the opal-CT to quartz transformation considerably (Kastner et al., 1977; Riech and von Rad, 1979). This could be the reason why the majority of carbonaceous sediments we examined yielded no fossils.

Considering all of the above, the further search for diatoms should target sediments that fulfil a combination of the aforementioned factors. Ideally, such sediments should be deposited in shallow epicontinental seas, shallow to deeper shelves and underwater ridges of higher latitudes. Lithology-wise, concretions, coprolites, sponge mummies and sediments in which preservation was enhanced by the influx of volcanic ash are most promising. Lastly, frustule preservation requires shallow burial and low-heat flow (Barron, 1993). A good place to start is in the vicinity of existing sites with preserved Cretaceous diatoms. We must note, however, that possibilities are seemingly endless, as exhibited by diatom fossils observed in amber (Saint Martin et al., 2015), gypsum (Pellegrino et al., 2021), and detected through molecular markers (Damsté et al., 2004).

## 5. Conclusions

Our assessment suggests that Lower Cretaceous and Jurassic diatom assemblages were likely dissolved from Mesozoic sediments by diagenetic processes. Our observation highlighted that lithified deeply buried sediments have little preservation potential and should be excluded from further searches. Most promising for future discoveries are shallow burial settings and concretions. Overall, we argue that earlier diatom records exist and are yet to be discovered.

## CRediT authorship contribution statement

**Karolina Bryłka:** Writing – review & editing, Writing – original draft, Visualization, Investigation, Formal analysis, Data curation, Conceptualization. **Sylvain Richoz:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Investigation, Conceptualization. **Andrew J. Alverson:** Writing – review & editing, Writing – original draft, Supervision, Funding acquisition, Conceptualization. **Daniel J. Conley:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Funding acquisition, Conceptualization.

## Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Daniel J. Conley reports financial support was provided by European Research Council. Daniel J. Conley reports financial support was provided by Knut and Alice Wallenberg Foundation. Andrew J. Alverson reports financial support was provided by National Science Foundation. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

No data was used for the research described in the article.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marmicro.2024.102371.

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