The Biotic-Abiotic Control of Si Burial in Marine Carbonate Systems of the Pre-Eocene Si Cycle

Agata Jurkowska

1AGH University of Science and Technology in Kraków, Faculty of Geology, Geophysics and Environmental Protection, Kraków, Poland

Abstract The silicon (Si) cycle in the modern ocean might still be representative of some of the processes that occurred in the Si-depleted post-Eocene oceans resulting after the expansion of diatoms. However, silicon-rich pre-Eocene seas, where sponges and radiolarians were major Si users before the emergence of diatoms, were radically different from modern ocean scenarios. The spatial and temporal evolution of Si cycling in Earth history is recorded in geological deposits and could be reconstructed by petrographic and mineralogical analyses. The thick successions of carbonate siliceous rocks deposited in marine environments during the Paleozoic and Mesozoic indicate the significant role of Si outflow from the Si cycle via burial in sediments. The aim of this study is to fill an important gap in knowledge concerning the functioning of the main silicon sink in the oceans: burial in sediments. Si outflow from the marine biogeochemical Si cycle occurs via early diagenetic silica crystallization within seabed mud. The mechanisms leading to Si binding in silica minerals are a complex process controlled by abiotic global events, biological activity of silicifiers and geochemical conditions mediated by microbes. This study concentrates on reconstructions of the mechanisms of Si outflow from the Si cycle by silica polymorph crystallization below the seabed surface and was realized through mineralogical and microtextural analyses of the main components of Upper Cretaceous carbonate–siliceous rocks.

Plain Language Summary I would like to present a manuscript, which highlights the mechanism of the Si burial in marine environment of carbonate sedimentation in pre-Eocene Si geochemical cycle. The Si outflow from the cycle via diagenetic silica polymorphs crystallization is an unrecognized stage of Si biogeochemical cycle. Due to fact that the diagenetic alternations cannot be traced in modern deposits I used an geological record of Late Cretaceous succession of European Basin to reconstruct the Si burial. The conducted studies of the geological record of marine deposits enable to reconstruct the interplay between biotic, abiotic and biologically mediated processes which led to silica crystallization. Moreover the data derived from the study allowed for the critical discussion about the role of siliceous sponges in pre-Eocene Si cycle and for the overview of estimated for the Late Cretaceous seas seawater Si concentrations. The goals of the studies has been realized through detailed mineralogical analysis of the carbonate-siliceous Upper Cretaceous facies in combination with microtextural studies of mineralogical components as well as identified silica polymorphs.

1. Introduction

Silicon (Si) is the second most abundant element on Earth, and its cycle is one of the most important biogeochemical processes. The Si cycle not only affects the biological evolution of organisms but also has an impact on rock formation (Jurkowska & Świerczewska-Gładysz, 2020a; Maliva et al., 1989; Racki & Cordey, 2000). Si occurs in seawater in the dissolved form (=DSi), orthosilicic acid (H₄SiO₄). DSi enters seawater from varying sources (as a substrate of terrestrial/submarine weathering, volcanic eruptions and hydrothermal fluids), circulates in the water column under biological controls and flows out via burial by diagenetic precipitation of authigenic minerals within seabed mud (Siever, 1991; Tréguer et al., 2021). The evolution of Si cycling in Earth history within the marine environment is an interplay between the biological world and abiotic global processes, which mutually control the seawater concentration of dissolved silicon. The Si cycle has changed throughout Earth history due to the biological evolution of silicifiers, paleogeographic reconfigurations and paleoenvironmental events that control the abiotic sources of DSi (Conley et al., 2017; Kidder & Erwin, 2000; Racki & Cordey, 2000). The present Si cycle is representative of post-Eocene DSi-depleted marine environments, which correlates with the expansion of diatoms, which are the most effective organisms consuming DSi from seawater (Conley et al., 2017; Maldonado et al., 2011). The effects of these DSi decreases are still evident in the silicification behavior of sponges...
The diatoms responsible for Si circulation in the water column, in post-Eocene times, fixed that part of the cycle within the planktonic zone, which decreased the overall DSi outflow (Conley et al., 2017; Tréguer et al., 2021). The situation was different in pre-Eocene times when the overall DSi seawater concentrations were higher (Conley et al., 2017; Siever, 1991), siliceous sponges were the main controllers of the Si cycle, and Si burial was significantly higher than today (Jurkowska & Świerczewska-Gładysz, 2020a; Racki & Cordey, 2000). Most studies devoted to the evolution of pre-Eocene Si cycling have concentrated on determining the primary source of DSI and evaluating the role of silicifiers in the Si cycle (e.g., Gao et al., 2020; Jurkowska & Świerczewska-Gładysz, 2020a; Kidder & Tomescu, 2016; Maldonado et al., 2017; Racki & Cordey, 2000; Siever, 1991), while little attention has been given to reconstruction of the mechanisms of DSI outflow by its crystallization within seabed mud. These primary mechanisms connecting biological (dissolution of siliceous skeletons) and abiotic (silica crystallization) processes with biologically mediated (bacterial decomposition of organic matter) activity have a crucial role in controlling the DSI concentration not only in porewaters of seabed mud but also in the overall DSI concentration in seawater (Jurkowska & Świerczewska-Gładysz, 2020a). The aim of this study is to reconstruct the biotic, biologically mediated and abiotic interactions within the marine environment, which govern Si outflow from the cycle via early diagenetic silica crystallization in seabed mud in the pre-Eocene Si cycle.

The Upper Cretaceous (∼100-66 Ma) carbonate-siliceous marine deposits of the European Basin containing abundant fossil siliceous sponges enables for the reconstruction of the Si sink by burial in sediments. The main goal of this research included the identification of the mechanisms of generating DSI concentrations sufficient for silica crystallization within porewaters, in addition to the determination of the role of abiotic DSI sources and the recognition of the biologically mediated geochemical conditions essential for silica crystallization in carbonate seabed mud.

This approach was carried out through mineralogical and microtextural analysis of Upper Cretaceous (Campanian-lower Maastrichtian) opoka (carbonate-siliceous rock) deposited in the marine environment in the European Basin. This study included a large number of samples to verify whether the precipitation of a certain type of silica polymorph was a regional-scale process or represented a general trend developed in the Late Cretaceous European Basin. Information derived from petrographic analyses was used to propose a model of Si burial via early diagenetic silica polymorph crystallization in Upper Cretaceous carbonate-siliceous rocks of the European Basin.

This study fills an important gap in knowledge concerning the mechanisms of Si burial within the marine environment and the influence of silica diagenesis on other authigenic minerals (calcite, clays) and rock fabrics. Increased knowledge of the mechanisms of DSI crystallization in carbonate seabed mud is essential for recognition of biogeochemical Si cycling and reconstructing the diagenesis of carbonate-siliceous rocks. The collected data facilitate further discussion about the role of siliceous sponges in the pre-Eocene Si cycle, as well as a critical review of the estimated high level of DSI concentration in Late Cretaceous seawater.

### 2. Geological Setting

The Late Cretaceous was characterized by extremely high sea level, greenhouse climate and intensive spreading of the ocean floor. During that time, most European territory was covered by a relatively shallow epicontinental shelf basin in which carbonate and pelagic sedimentation dominated. The Late Cretaceous Sea was also characterized by an overall elevated DSI concentration (∼40 ppm; which was four times higher than in present seas; Conley et al., 2017; Racki & Cordey, 2000; Siever, 1991) and domination of siliceous sponges among the silicifiers. This was also the last period before the major evolutionary turnover among silicifiers and the domination by diatoms (Conley et al., 2017; Siever, 1991).

Monotonous pelagic sedimentation led to the formation of the thick Campanian-lower Maastrichtian succession, which comprised two main lithofacies: chalk-almost pure carbonates and opoka carbonates with silica (Jurkowska & Świerczewska-Gładysz, 2020a; Jurkowska et al., 2019; Figure 1a). This facies diversity was controlled by the global biogeochemical Si cycle, which led to the formation of siliceous rocks in a part of the basin characterized by elevated DSI concentrations, while carbonate facies dominated in the remaining part of the offshore zones, where the DSI concentration was much lower (Jurkowska & Świerczewska-Gładysz, 2020a). Carbonate...
sedimentation was interrupted by the formation of horizons of siliceous nodules (flints and cherts), which have been abundantly documented in the Campanian-lower Maastrichtian European successions.

The presence of carbonate-siliceous facies represented by opoka, gaize and horizons of cherts is one of the most distinctive features of the Late Cretaceous epicontinental European Basin (Clayton, 1986; Jurkowska & Świerczewska-Gładysz, 2020b; Jurkowska et al., 2019; Maliva et al., 1989; Pożaryska, 1952; Sujkowski, 1931). Silica occurs in the form of an authigenic (precipitated in situ) polymorph represented by opal-CT (hydrated, paracrystalline form of silica with disordered structure-opaline silica; Fröhlich, 2020; Jeans, 1978; Jurkowska & Świerczewska-Gładysz, 2020a, 2020b; Pożaryska, 1952; Sujkowski, 1931). Opal-CT is characterized by a disordered structure composed of interlayered α-cristobalite and α-trydymite stacking units (Flörke, 1955; Jones & Segnit, 1971). In the literature, it has also been termed fibrous lussatite, crystobalite-trydyme porcellanite and opaline silica (Jones & Segnit, 1971; Mallard, 1890). The other distinctive feature of opoka facies is the presence of abundant siliceous sponge fossils, which occur as preserved body specimens (Hurcewicz, 1966, 1968; Świerczewska-Gładysz, 2006, 2012) and voids left after the dissolution of spicules (Jurkowska & Świerczewska-Gładysz, 2020a; Sujkowski, 1931).

2.1. Study Sections

Two Polish areas, the Miechów Synclinorium (MS) and Middle Vistula River valley (MVR), which are typical regions of opoka occurrence, were chosen for this study (Jurkowska et al., 2019; Pożaryska, 1952; Sujkowski, 1931; Figure 1b). In the MS and MVR, thick (up to several hundred meters) Campanian-Maastrichtian opoka deposits occur in abundant quarries and natural outcrops (Błaszkiewicz, 1980; Peryt & Dubicka, 2015; Remin, 2012; Sujkowski, 1931; Walaszczyk, 2004). The MS Campanian succession is monotonous and composed of opoka with horizons of chert nodules and marly intercalations in the lower section (Jurkowska & Świerczewska-Gładysz, 2020b; Jurkowska et al., 2019), which are overlain by marls and sandy opoka in the upper section (Jurkowska, 2016; Rutkowski, 1965). The Maastrichtian is represented by sandy opoka and gaize (carbonate rock with a significant amount of detrital quartz; Cayeux, 1929; Sujkowski, 1931). In the MVR, the middle Campanian-lower Maastrichtian facies is composed of poorly bedded opoka with abundant fossils (Jurkowska & Świerczewska-Gładysz, 2020a; Marcinowski & Radwański, 1983; Walaszczyk, 2012). Recently, published data (Jurkowska & Świerczewska-Gładysz, 2020a, 2020b; Jurkowska et al., 2019) have been supplemented by new analyses performed in both regions. The newly studied sections, along with sections from which data have been used in the aforementioned previous studies, are summarized in Table 1.
3. Materials and Methods

The laboratory methods allowed the mineralogical characterization of opoka and mineralogical identification and microtextural analysis of silica polymorphs, carbonates and clays (Figure 2). The analysis enabled the authigenic minerals (formed during diagenesis) to be distinguished, and the order of their crystallization to be established. This also allowed the type of authigenic silica polymorphs in which Si was bound to be identified. The identification of the type of silica polymorph, which forms the rock framework (Jurkowska et al., 2019) and are found in fossils of siliceous sponges (spicules and rigid skeletons), is essential for planning further geochemical analyses. The presence of secondary, authigenic minerals (e.g., opal-CT) that are found in the fossil skeletons of siliceous sponges limits the wide use of modern siliceous sponge methods, such as δ³⁰Si, to estimate seawater DSI concentrations (e.g., Fontorbe et al., 2016). Moreover, the recognition of the type of silica polymorph, in combination with its microtexture, is useful in estimating DSI porewater concentration and the geochemical parameters during precipitation (e.g., pH) (Gao et al., 2020; Jurkowska & Świerczewska-Gładysz, 2020a; Kastner et al., 1977; Lindgreen & Jakobsen, 2012; Maldonado et al., 2019; Siever, 1991; Figure 2). Comparative analyses of mineralogical composition, as well as that of silica polymorph microtexture, of different types of rock within Campanian-Maastrichtian carbonate-siliceous facies enabled the influence of variable minerals (e.g., clays) on silica polymorph microtexture to be distinguished.

This research was performed to collect a large dataset comprising mineralogical composition and microtextural data of Upper Cretaceous carbonate-siliceous facies (Figure 2). The fieldwork studies comprised the collection of samples from the 19 Campanian-Lower Maastrichtian sections in the MVR and MS (Jurkowska & Świerczewska-Gładysz, 2020a; Table 1). During this study, new sections in the MS (Strzęków 1, Strzęków 2 Mierzawa, Wola...
Chroberska, Michałów, Muniakowice, and Antolka 2; Table 1) were sampled. The new sections are abandoned quarries representing 8–15 m of opoka/gaize; a detailed description and inoceramid stratigraphy of which was described in previous studies (Jurkowka, 2016). The rock samples were collected per 1 m (Strzeżów 1, Strzeżów 2, Wola Chroberska, Muniakowice, Mierzawa, Michałów, Antolka 2, Dorotka, Ciszyca Górna, Pawłowice Cemetery, Raj, Raj North, and Dziurków), while those sections in which lithological variability was noted (Bonarka, Biała Wielka, Wierzbica, Jeżówka 2, Wierzchowisko, and Rzeżuśnia), one sample from each lithological horizon was collected. Additional samples were also collected from sections that were described in terms of petrography/mineralogy in previous articles (Jurkowska & Świerczewska-Gładysz, 2020a, 2020b; Jurkowska et al., 2019; Table 2). The presented database comprised 111 samples, from which 50 samples were newly studied (Table 2).

Due to the existence of terminological inconsistency in naming carbonate-siliceous rock, the first stage of this study was to establish the quantitative and qualitative mineralogical composition of the rocks forming the Campanian-lower Maastrichtian succession (opoka, gaize, and marls; Table 2), This stage of study was important to reconstruct the generalized model of Si outflow via early diagenetic crystallization, which should also be valid for all carbonate-siliceous rocks within the study succession. Moreover, the recognition of the mineralogical composition of the whole succession of carbonate-siliceous Campanian-Maastrichtian rocks enables the verification of the impact of other mineralogical components (e.g., clays) on mechanisms of silica polymorph crystallization and microtexture. The mineralogical composition analysis enabled the distinction of three types of rocks: opoka, gaize and marls. The next stage included the analysis of opal-CT microtexture in all types of rocks (opoka, gaize and marls) to recognize whether differences in opal-CT microtexture reflect different mechanisms of DSi outflow generated by variable mineralogical rock composition.

Fifty out of the 111 samples available were utilized for further petrographic analysis during this study. Quantitative and qualitative mineralogical analyses were performed by the Clay Minerals Research Group of the Polish Academy of Science in Kraków (XRD quantitative and qualitative mineralogical composition analysis) and at AGH Faculty Laboratories (XRD qualitative mineralogical composition analysis). The mineralogy of selected samples was determined on randomly oriented (side-loaded) powder specimens by XRD analysis using a Thermo ARL X'tra diffractometer equipped with a Cu lamp. The samples were mildly ground and then milled in a McCrone micronizing mill for 5 min. Diffractograms were recorded in a range of 3–65° 2 theta with a step of 0.02° (5 s/step). QMin software was used for quantitative analysis. The program utilized the mineral intensity factor method in conjunction with a collection of pure standards (Omotoso et al., 2006; Śródoń et al., 2001). Determination of mineral composition was achieved by matching the sum of the diffraction patterns of mineral standards to the experimental pattern. The accuracy of this approach was proven by the high finishing positions of laboratories using this methodology in the Reynolds Cup, which is a biennial round-robin competition for quantitative mineralogical analysis on clay-bearing type samples (Raven & Self, 2017). For the qualitative...
## Table 2
The Quantitative and Qualitative Mineralogical Composition of the Studied Rocks: Opoka, Marls and Gaize

| Area                     | Source          | Sample  | Quartz | Calcite | Opal-CT | Clays | Clinoptilolite | Lithology        |
|--------------------------|-----------------|---------|--------|---------|--------|-------|----------------|------------------|
| Miechów Synclinorium     |                  |         |        |         |        |       |                |                  |
|                          | Jurkowska et al., 2019 | Wierzbica 1.1 | 1.8    | 88      | 5.4    | 4.8   | 0              |                  |
|                          | Jurkowska et al., 2019 | Wierzbica 1.2 | 1.2    | 90.5    | 6.1    | 2.2   | 0              |                  |
|                          | Jurkowska et al., 2019 | Wierzbica 1.3 | 2      | 89      | 5      | 4     | 0              |                  |
|                          | Jurkowska et al., 2019 | Wierzbica 1.4 | 1.8    | 82.4    | 10     | 7.6   | 0              |                  |
|                          | Jurkowska et al., 2019 | Wierzbica 1.5 | 1.8    | 95      | 2      | 1.2   | 0              |                  |
|                          | Jurkowska et al., 2019 | Wierzbica 1.6 | 1.2    | 92.3    | 4      | 2.5   | 0              |                  |
|                          | Jurkowska et al., 2019 | Wierzbica 1.7 | 0.8    | 94.4    | 3      | 1.8   | 0              |                  |
|                          | Jurkowska et al., 2019 | Wierzbica 1.8 | 1.8    | 87      | 5.9    | 5.3   | 0              |                  |
|                          | Jurkowska et al., 2019 | Wierzbica 1.9 | 0.5    | 96      | 2.2    | 1.3   | 0              |                  |
|                          | Jurkowska et al., 2019 | Wierzbica 1.10 | 1.1    | 90.8    | 4.3    | 3.8   | 0              |                  |
|                          | Jurkowska et al., 2019 | Wierzbica 1.11 | 0.8    | 92.8    | 3.5    | 2.9   | 0              |                  |
|                          | Jurkowska et al., 2019 | Wierzbica 1.13 | 1.2    | 91.6    | 3.8    | 3.4   | 0              |                  |
|                          | Jurkowska et al., 2019 | Wierzbica 1.14 | 0      | 95      | 4      | 1     | 0              |                  |
|                          | Jurkowska et al., 2019 | Wierzbica 1.15 | 1.8    | 93.7    | 2      | 2.5   | 0              |                  |
|                          | Jurkowska et al., 2019 | Wierzbica 1.16 | 1.6    | 90.7    | 4      | 3.7   | 0              |                  |
|                          | Jurkowska et al., 2019 | Wierzbica 1.17 | 1      | 94.9    | 2.3    | 1.8   | 0              |                  |
|                          | Jurkowska et al., 2019 | Wierzbica 1.18 | 1.8    | 87      | 6      | 5.2   | 0              |                  |
|                          | Jurkowska et al., 2019 | Wierzbica 1.19 | 1.1    | 92.3    | 4      | 2.6   | 0              |                  |
|                          | Jurkowska et al., 2019 | Jeżówka 2.1  | 5      | 69      | 9.6    | 16.4  | 0              |                  |
|                          | Jurkowska et al., 2019 | Jeżówka 2.2  | 3.2    | 84.5    | 6.7    | 5.6   | 0              |                  |
|                          | Jurkowska et al., 2019 | Jeżówka 2.3  | 1.4    | 93.4    | 4.3    | 0.9   | 0              |                  |
|                          | Jurkowska et al., 2019 | Jeżówka 2.4  | 4      | 74.2    | 8.8    | 13    | 0              |                  |
|                          | Jurkowska et al., 2019 | Jeżówka 2.5  | 2.1    | 90.5    | 5.3    | 2.1   | 0              |                  |
|                          | Jurkowska et al., 2019 | Jeżówka 2.6  | 3      | 85.3    | 5.4    | 6.3   | 0              |                  |
|                          | Jurkowska et al., 2019 | Jeżówka 2.7  | 0.4    | 92.5    | 3.4    | 3.7   | 0              |                  |
|                          | This study        | Jeżowa 2.8  | 1.1    | 93      | 4.3    | 1.6   | 0              |                  |
|                          | This study        | Jeżowa 2.9  | 1.4    | 89.7    | 6      | 2.9   | 0              |                  |
|                          | This study        | Jeżowa 2.10 | 1.7    | 92.3    | 5      | 1     | 0              |                  |
|                          | Jurkowska et al., 2019 | Bonarka 1.1 | 1.2    | 90.4    | 2      | 5.3   | 1.1            |                  |
|                          | Jurkowska et al., 2019 | Bonarka 1.2 | 3.5    | 89.7    | 4.1    | 0.6   | 2.1            |                  |
|                          | Jurkowska et al., 2019 | Bonarka 1.4 | 1.3    | 91.2    | 2.7    | 3.1   | 1.7            |                  |
|                          | Jurkowska et al., 2019 | Bonarka 1.5 | 2.1    | 89.8    | 3.9    | 4.2   | 1.8            |                  |
|                          | This study        | Bonarka 1.6 | 3      | 92      | 3.1    | 1.9   | 0              |                  |
|                          | Average          |          | 1.75   | 89.72   | 4.61   | 3.82  | 0.22           |                  |

**Average**

| Area                     | Source          | Sample  | Quartz | Calcite | Opal-CT | Clays | Clinoptilolite | Lithology        |
|--------------------------|-----------------|---------|--------|---------|--------|-------|----------------|------------------|
| Miechów Synclinorium     |                  |         |        |         |        |       |                |                  |
|                          | Jurkowska and ŠG, 2020a | Białe Wlk 1.1 | 5.2    | 53.8    | 26.3   | 14.7 | 0              |                  |
|                          | Jurkowska and ŠG, 2020a | Białe Wlk 1.4 | 4.5    | 60      | 29     | 6.5   | 0              |                  |
|                          | Jurkowska and ŠG, 2020a | Białe Wlk 1.7 | 7.2    | 51.7    | 27.6   | 13.5 | 0              |                  |
|                          | Jurkowska and ŠG, 2020a | Białe Wlk 1.9 | 5.2    | 59.2    | 27     | 8.6   | 0              |                  |
|                          | Jurkowska and ŠG, 2020a | Białe Wlk 1.10 | 3.7    | 50.7    | 29.3   | 16.3 | 0              |                  |

**Average**
| Area                  | Source                  | Sample       | Quartz | Calcite | Opal-CT | Clays | Clinoptilolite | Lithology       |
|-----------------------|-------------------------|--------------|--------|---------|---------|-------|----------------|----------------|
| MVRS                  | Jurkowska and ŠG, 2020a | Biała Wilk 1.1 | 5.9    | 59.4    | 25.1    | 9.6   | 0              |                |
|                       | Jurkowska and ŠG, 2020a | Biała Wilk 1.15 | 5.8    | 57.9    | 30.5    | 5.8   | 0              |                |
|                       | Jurkowska and ŠG, 2020a | Biała Wilk 1.18 | 6.2    | 59.5    | 25.6    | 8.7   | 0              |                |
|                       | Jurkowska and ŠG, 2020a | Ciszyca G. 1.1 | 6.7    | 57.1    | 27.5    | 8.7   | 0              |                |
|                       | Jurkowska and ŠG, 2020a | Ciszyca G. 1.2 | 6.7    | 57.1    | 27.5    | 8.7   | 0              |                |
|                       | Jurkowska and ŠG, 2020a | Dorotka 1.1   | 5.9    | 60.1    | 20.0    | 14.0  | 0              |                |
|                      | This study              | Dorotka 1.2   | 6.1    | 65.2    | 22.4    | 6.3   | 0              |                |
|                      | This study              | Dorotka 1.3   | 5.9    | 60.1    | 20.0    | 14.0  | 0              |                |
|                      | This study              | Dorotka 1.8   | 4.7    | 58.4    | 22.9    | 14.0  | 0              |                |
|                      | This study              | Dorotka 1/9   | 4.9    | 63.1    | 25.6    | 6.4   | 0              |                |
|                      | Jurkowska and ŠG, 2020a | Dzjurkow 1.4  | 4.5    | 58.6    | 26.6    | 10.3  | 0              |                |
|                      | Jurkowska and ŠG, 2020a | Raj 1.1       | 6.7    | 47      | 31.6    | 14.7  | 0              |                |
|                      | This study              | Raj 1.2       | 7.8    | 49.2    | 28.6    | 14.4  | 0              |                |
|                      | This study              | Raj 1.3       | 8.1    | 46.2    | 33.7    | 12.0  | 0              |                |
|                      | Jurkowska and ŠG, 2020a | Raj 1.4       | 6.9    | 56.8    | 25.9    | 10.4  | 0              |                |
|                      | Jurkowska and ŠG, 2020a | Pawłowice Cm. 1.1 | 5.7    | 56.1    | 32.8    | 5.4   | 0              |                |
|                      | This study              | Pawłowice Cm. 1.2 | 5.2    | 55.6    | 30.3    | 8.9   | 0              |                |
|                      | Jurkowska and ŠG, 2020a | Pawłowice Cm. 1.4 | 5     | 54.7    | 32      | 8.3   | 0              |                |
|                      | This study              | Pawłowice Cm. 1.5 | 6.2    | 57.8    | 31.9    | 4.1   | 0              |                |
|                      | Jurkowska and ŠG, 2020a | Pawłowice Cm. 1.10 | 5.8   | 56.9    | 29.8    | 7.5   | 0              |                |
|                      | **Average**             | **6.35**      | **56.93** | **26.76** | **9.97** | 0     |                |                |

| Area                  | Source                  | Sample       | Quartz | Calcite | Opal-CT | Clays | Clinoptilolite | Lithology       |
|-----------------------|-------------------------|--------------|--------|---------|---------|-------|----------------|----------------|
| MVRS                  | This study              | Michałów 1.1 | 6.6    | 36.6    | 48      | 8.8   | 0              |                |
|                      | This study              | Michałów 1.2 | 6.6    | 36.6    | 48      | 8.8   | 0              |                |
|                      | This study              | Michałów 1.3 | 5.9    | 38.4    | 48.2    | 7.5   | 0              |                |
|                      | This study              | Michałów 1.4 | 5.5    | 42.3    | 45.6    | 6.6   | 0              |                |
|                      | This study              | Michałów 1.5 | 5.1    | 39.2    | 47.6    | 8.1   | 0              |                |
|                      | Jurkowska and ŠG, 2020a | Raj N 1.1    | 7.6    | 35.7    | 48.2    | 8.5   | 0              |                |
|                      | Jurkowska and ŠG, 2020a | Raj N 1.3    | 6.4    | 39.7    | 45.6    | 8.3   | 0              |                |
|                      | Jurkowska and ŠG, 2020a | Raj N 1.6    | 7.8    | 35.2    | 48.3    | 8.7   | 0              |                |
|                      | This study              | Raj N 1.7    | 8.2    | 35.7    | 45.1    | 11.5  | 0              |                |
|                      | **Average**             | **6.57**      | **38.26** | **45.65** | **9**    | 0     |                |                |

| Area                  | Source                  | Sample       | Quartz | Calcite | Opal-CT | Clays | Clinoptilolite | Lithology       |
|-----------------------|-------------------------|--------------|--------|---------|---------|-------|----------------|----------------|
| MS                    | This study              | Rzeźnińia 1.3 | 3.9    | 77.20   | 10.9    | 8     | 0              |                |
|                      | This study              | Rzeźnińia 1.5 | 4.1    | 77.1    | 12.5    | 6.3   | 0              |                |
|                      | This study              | Rzeźnińia 1.7 | 2.7    | 78.6    | 10.7    | 8     | 0              |                |
|                      | This study              | Rzeźnińia 1.8 | 3.4    | 76.8    | 11.3    | 8.5   | 0              |                |
|                      | Jurkowska and ŠG, 2020b | Rzeźnińia 1.10 | 3.8   | 74      | 10.9    | 11.3  | 0              |                |
|                      | This study              | Rzeźnińia 1.11 | 4.2   | 75.1    | 12.3    | 8.4   | 0              |                |
|                      | This study              | Rzeźnińia 1.12 | 4.3    | 73.2    | 10.9    | 1.1   | 0              |                |
|                      | This study              | Rzeźnińia 1.13 | 2.7    | 78.6    | 10.7    | 8     | 0              |                |
|                      | **Average**             | **3.25**      | **75.23** | **11.2** | **7.2**  | 0     |                |                |
Identification of opal-CT in the samples, an additional method, FWHM (full width at half maximum intensity) of the distinctive 4 Å diffraction band measurements, was applied (Lee, 2007; Lynne et al., 2005, 2007). This method, which is used as an indication of silica phase order/disorder, has been widely applied during the identification of silica polymorphs, with narrower FWHM values indicative of a greater degree of ordering (Elzea, et al., 1994; Graetsh, 1994).

SEM–EDS analysis of the microtexture of mineralogical components of the studied rocks was performed using an FEI QUANTA 200 scanning electron microscope in three modes: SE (secondary electrons), backscattered electrons (BSE) and mix (mix of both previous modes). Observations were conducted on all 111 samples and consisted of the documentation of rock chips and insoluble residue, which was prepared following a protocol described by Jurkowska et al. (2019).

| Area                      | Sample        | Quartz | Calcite | Opal CT | Clays | Clinoptilolite | Microcline |
|---------------------------|---------------|--------|---------|---------|-------|----------------|------------|
| Miechów Synclinorium      | Antolka 2.1   | 20.5   | 47.3    | 22.9    | 9.3   | 0              | 0.9        |
|                           | Antolka 2.2   | 21.2   | 46.8    | 31.2    | 0     | 0              | 0.8        |
|                           | Antolka 2.3   | 20.5   | 49.6    | 15.9    | 12.9  | 0              | 1.1        |
|                           | Antolka 2.4   | 19.7   | 48.6    | 23.7    | 6.1   | 0              | 1.9        |
|                           | Strzełów 2.1  | 16.8   | 40      | 28.3    | 11.9  | 2              | 1          |
|                           | Strzełów 2.5  | 18.4   | 40      | 26.6    | 11.5  | 2.3            | 1.2        |
|                           | Strzełów 2.6  | 20.7   | 41.2    | 25.4    | 10.9  | 1.8            | 0          |
|                           | Strzełów 1.1  | 17.9   | 32.1    | 40.6    | 13.4  | 2              | 1.8        |
|                           | Strzełów 1.2  | 18.9   | 47.6    | 14.6    | 17.3  | 3.7            | 0          |
|                           | **Average**   | **19.40** | **43.69** | **25.47** | **10.37** | **1.31** | **0.86** |
|                           | Bonarka 1.3 m  | 8.2    | 65.7    | 4.1     | 22    | 0              | 0          |
| Jurkowska and ŠG, 2020b   | Bonarka 1.7 m  | 7.4    | 66.7    | 3.9     | 22    | 0              | 0          |
| Jurkowska and ŠG, 2020b   | Jezówka 2.4 m  | 5.5    | 69.9    | 5       | 19.6  | 0              | 0          |
|                           | Jezówka 2.5 m  | 4.8    | 67.5    | 6.7     | 21    | 0              | 0          |
| Jurkowska and ŠG, 2020b   | Jezówka 2.7 m  | 4.6    | 64.6    | 13.7    | 17.1  | 0              | 0          |
| Jurkowska and ŠG, 2020b   | Jezówka 2.12 m | 4.2    | 73.8    | 4.8     | 17.2  | 0              | 0          |
|                           | Jezówka 2.14 m | 5.5    | 69.9    | 5       | 19.6  | 0              | 0          |
|                           | Biala Wielka 1.1 m | 6.9 | 69.2    | 5       | 18.7  | 0              | 0          |
| Jurkowska and ŠG, 2020b   | Biala Wielka 1.4 m | 6.7 | 68      | 4.9     | 20.4  | 0              | 0          |
| Jurkowska and ŠG, 2020b   | Biala Wielka 1.7 m | 7.1 | 67.1    | 3.3     | 22.5  | 0              | 0          |
| Jurkowska and ŠG, 2020b   | Biala Wielka 1.9 m | 11.1  | 67.3    | 3.1     | 18.5  | 0              | 0          |
|                           | **Average**   | **5.81** | **68.63** | **5.53** | **19.97** | **0**    | **0**   |

Table 2
Continued
4. Results

4.1. Quantitative Mineralogical Composition of the Studied Rocks

The mineralogical analysis presented here (Table 2) reveals 3 types of rocks: opoka, gaize and marls. Among them, a special consideration is given to the opoka, a carbonate siliceous rock whose petrographic definition is still under debate (Jurkowska et al., 2019; Pożaryska, 1952; Sujkowski, 1931). The database presented here, which is the largest of its kind, facilitates the formulation of the mineralogical definition of opoka. Opoka is a carbonate rock composed of calcite (38%–90%) and an insoluble residue (10%–62%), whose main component is authigenic opal-CT (4%–46%). The subordinate components of insoluble residue include clays (<10%), detrital quartz (<10%) and zeolites (clinooptilolite <5%). The characteristic feature of opoka is the insignificant (<10%) content of terrigenous material comprising detrital quartz and clays (Sujkowski, 1931). The quantitative mineralogical composition of opoka varies widely, and a single sample can contain slightly increased/decreased amounts of a certain mineralogical component relative to the average (e.g., intermediate opoka- Table 2), but opal-CT is always the dominant constituent of the insoluble residue. In comparison to chalk, opoka is characterized by smaller amounts of calcite (<90% vs. 98%–100% in chalk; Hjuler & Fabricius, 2009) and by the presence of opal-CT in insoluble residue (up to 45% vs. 0% in chalk; Faÿ-Gomord et al., 2016). Opoka differs from gaize (Cayeux, 1929; Sujkowski, 1931; Table 2) by the lower content of detrital quartz grains (<10% vs. 19% in gaize). Opoka is distinguished from marls by a lower content of clays (<10% vs. 20%; Table 2) and from cherts by a lower content of opal-CT (<50%; Jurkowska & Świerczewska-Gładysz, 2020b). After digestion of the opoka rock chips in HCl, according to a procedure described by Jurkowska et al. (2019), opoka does not disintegrate completely like chalk, but fragments composed of opal-CT lepispheres (spheres of blades, Wise & Kelts, 1972) are still preserved (Jurkowska & Świerczewska-Gładysz, 2020a).

The samples of opoka are grouped considering their similarity in quantitative mineralogical composition (Table 2). Group 1 consists of opoka characterized by the highest content of calcium carbonate (average of 89%), lowest content of opal-CT (average: 4.6%), and 1.7% detrital quartz and 3.8% clays (mixed layer of illite/smectite). In this group, rare zeolites of clinoptilolite (up to 2%) are found (only in one section). Group 2 differs from the previous group by the lower content of calcium carbonate (average: 56.9%) and higher content of opal-CT –26.7% and detrital components (quartz – 6.35% and mixed layer clays of illite/smectite (phylosilicates) – 9.9%). Group 3 is characterized by the lowest calcite content (38.2%) and highest amount of opal-CT (45.6%), while the content of detrital quartz is 6.5% and the mixed layer illite/smectite is 9%. Some samples represent intermediate values between these distinguished groups (e.g., Rzeżuśnia, which represents a mineralogical content between Groups 1 and 2).

The analyses confirm the definition of gaize given by Cayeux (1929), according to which, in addition to the presence of opaline silica (i.e., opal-CT), the rock is characterized by a significant amount of detrital quartz, which can be used to recognize this type of rock. Gaize, in comparison to opoka, contains more detrital quartz (19%,4%), while the contents of calcite (43.69%) and opal-CT (25.47%) are similar to those of opoka Group 2 (Table 2). The quantitative composition of marl is characterized by a significant amount of clays composed of phyllosilicates: a mixed layer of illite/smectite, dioctahedral smectite (19.97%), an average calcite content (68.63%) and almost equal contents of quartz (5.81%) and opal-CT (5.53%). The mineralogical composition of the chert nodules was documented in a previous study (Jurkowska & Świerczewska-Gładysz, 2020b); its main component is opal-CT (57.2%) with subordinate calcite (31.9%), authigenic nano-α quartz (10.2%) and clays (0.62%; Table 2).

4.2. Qualitative Mineralogical Composition and Microtextures

The microtextural recognition of the main mineralogical component of the studied rocks is crucial for the reconstruction of the diagenetic transformations that triggered the precipitation of silica polymorphs and removed the DSi from the cycle. The analysis also includes subordinate mineralogical components (quartz, clays) because their texture was also affected during diagenesis and records the primary geochemical signals of the microenvironment.

4.2.1. Opal-CT

X-ray powder diffraction (XRD) is the principal technique used to determine silica phase mineralogy (Jones & Segnit, 1971) and to compare the degree of silica mineralogical maturation among samples (Lynne et al., 2007). In all studied lithologies, only one type of authigenic silica polymorph was detected and is represented by...
opal-CT. Its XRD patterns are characterized by two broad reflections: a broad strong (101) peak centered at 4.09 Å (=21.75°2θ) and a weaker peak at 4.32 Å and a subsidiary reflection at 2.50 Å (Elzea et al., 1994; Jones & Segnit, 1971; Lee, 2007; Lynne et al., 2005). The full width at half-maximum intensity (FWHM) of the ∼4 Å diffraction band is applied as a guide to the degree of lattice order/disorder within each silica phase, with narrower FWHM values indicative of a greater degree of ordering (Elzea et al., 1994; Graetsch, 1994). The highest FWHM values are noted for marls (2.7–2.3°2θ) and opoka in Groups 1 and 2 from MS (2.5–1.95°2θ) and indicates the presence of less mature (less degree of ordering) opal-CT phases. The opal-CT of opoka in Groups 2 and 3 from MVR and gaize from MS have FWHM values of 1.1–0.6°2θ and indicate mature phases of opaline silica. The lowest value (0.8–0.6°2θ) was noted in cherts (Jurkowska & Świerczewska-Gładysz, 2020b) and represents the best developed opal-CT microtextures (Lynne et al., 2005).

In all studied lithologies, opal-CT occurs in the form of authigenic lepispheres (spheres of blades; Wise & Kelts, 1972) of variable sizes and microtextures (Figures 3a–3c). The lepispheres form a network, which is visible in all lithologies after removing calcium carbonate (Figure 3d). The opal-CT networks (Figures 3a and 3b) occur even in the samples of opoka in Group 1, in which the content is the lowest (2%; Table 2). The lepispheres of the opal-CT network are of equal sizes and are densely packed adjacent to each other (Figure 3b). The lepispheres are

Figure 3. The opal-CT and calcite microtextures in opoka. (a) An rock network formed by the opal-CT lepispheres (black arrows) in opoka of gr 1. The lepispheres are visible between the calcite grains (black triangles) and in cavities in coccoliths skeletons (white arrow) and its shields. Sample: Jeżówka 1.1. (b) An opal-CT network visible after removing of calcium carbonate of opoka gr. 1. The detrital clays (white arrows) are visible between the lepispheres Sample: Wierzbica 1.15. Scale bar: 5 μm. (c) An network of medium-large opal-CT lepispheres (black arrows) with visible characteristic criss-cross structure of a blades of opoka gr. 2. The calcite is composed of rounded micrite grains (black triangles) and fragments of coccoliths skeletons (white triangles). The detrital clays (white arrows) are stacked between the calcite grains. Sample: Dziurków 1.4. (d) An insoluble residue left after opoka dissolution in HCl. Visible large fragments composed of opal-CT network. (e) Voids left after spicules dissolution infilled by the layer of opal-CT lepispheres (black arrows). Sample: Dziurków 1.4. (f) The layer of lepispheres of opal-CT infilling the voids after spicules dissolution. Sample: Dziurków 1.4.
the smallest (sizes of ∼1 μm) and are poorly developed in the samples of opoka in Group 1 (Figures 3a and 3b), while in samples in Groups 2 and 3, which have higher opal-CT contents, the lepispheres are larger (2–4 μm) and fully developed (Figure 3c). Moreover, in opoka in Group 2 from the MVR, the opal-CT lepispheres show a characteristic pattern in which they are composed of intersecting blades (called criss-cross pattern; Figure 3c), typical for the mature form of opals (Lynne et al., 2005, 2007).

In all opoka samples, the surface of voids left after sponge spicule dissolution (Figure 3e) are covered by a single layer composed of densely packed opal-CT lepispheres (Figure 3f). The differing opaline silica microtexture is visible in siliceous infillings of foraminifera chambers and includes one large lepispheres composed of aligned nanospheres (Figures 4a and 4b). This microtexture is characteristic of the early forms of opal-A/CT (Lynne et al., 2005). The large lepispheres usually do not infill the whole space within the chambers and leave a small (∼0.1 μm) empty area between the wall of the foraminifera skeleton and the lepispheres (Figure 4a). It is also necessary to mention that not all foraminifera chambers are infilled by opaline silica; in some of them, quartztic infillings were noted (Jurkowska & Świerczewska-Gładysz, 2020a). The opal-CT of different microtextures comprises rigid skeletons of siliceous sponges, which are composed of smooth silica representing early forms of opal-A/CT (Jurkowska & Świerczewska-Gładysz, 2020a). The observed microtextural variability of opal-CT within the opoka is controlled by the rate of maturity (degree of ordering) and includes well-developed/cryptocrystalline
lepispheres of opal-CT (Figures 3a–3f) and transitional, amorphous early forms of opal-A/CT composed of aligned nanospheres and smooth silica (Figures 4a and 4b; Jurkowska & Świerczewska-Gładysz, 2020a).

Within the chert nodules, opal-CT microtextures, consisting of networks composed of aggregates of large lepispheres (20–100 μm), are composed of sharply bladed bodies of opal-CT (Figure 4c), which in the same part of the samples are fused into homogeneous masses with visible relicts of primary rounded shapes (Jurkowska & Świerczewska-Gładysz, 2020b). The second microtexture visible in chert nodules consists of small opal-CT lepispheres (1–2 μm), which form a network (Jurkowska & Świerczewska-Gładysz, 2020b). This second chert microtexture is less porous than that observed in opoka and differs by containing denser packages of lepispheres.

In marls, the opal-CT network is composed of very small (<1 μm), densely packed lepispheres (Figure 4d). The lepispheres are not well developed with smooth blades, which makes them look fuzzy and they were described in the literature as immature, embryonic opal-CT (Kastner et al., 1977, Figures 2a and 2b; 4a and 4b). These phases are characterized by having a significant content of Mg (Minde et al., 2018), which was also confirmed in this study by EDS analysis. The embryonic opal-CT lepispheres are overgrown by authigenic clays with honeycomb morphologies (Figures 4d and 4e).

The opal-CT network also occurs in the gaizes and is composed of 1–3 μm lepispheres with sharply edged blades (Figure 4f). The lepispheres, which are densely packed and adjoined to each other, show a distinctive criss-cross pattern characteristic of mature forms of opal-CT.

Although in all lithologies (opoka, cherts, marls and gaizes), opal-CT forms a network of adjoining lepispheres, they differ in size, maturity and density of packing (Figures 3b; 4c, 4d, 4f). The largest and most densely packed lepispheres were documented in cherts (Figure 4e), and the smallest and less mature lepispheres were noted in marls (Figure 4d), while in opoka and gaize, a loosely arranged network and medium lepisphere size were observed (Figure 3b).

4.2.2. Carbonates and Clays

Calcium carbonate, which is a main component of opoka, marls, and gaize and a secondary component of cherts, is represented in all lithologies by primary grains composed of coccolith shields and authigenic grains of diagenetic origin (Figures 3a and 3c). The latter is composed of rounded micrite grains (<4 μm) and, more rarely, euhedral calcite crystals (microsparite; Figures 3a and 3c). Clays rarely occur in cherts, while in opoka and gaizes, they are commonly noted in small amounts. In those lithologies, the clays are detrital in origin, which could be recognized by their flaky morphologies (Figure 3c). In marls, in which the clays are most abundant, detrital and authigenic clays could be distinguished. The latter forms a typical rose-like/honeycomb texture characteristic of authigenic genesis (Figures 4d–4e).

The overall rock fabric is a record of the structural and geometric relationship between all components and includes autochthonous and authigenic mineralogical grains. The order of the formation of authigenic minerals can be recognized by the analysis of the structural relationship between the variable components. In the opoka, marls and gaizes, the opal-CT lepispheres infill the voids between coccoliths and cavities inside their skeletons (e.g., central area; Figures 3a and 3c), while the authigenic calcite grains cover the opal-CT lepispheres (Figures 3a and 3c). This order suggests that the authigenic micrite crystallized after opal-CT precipitation, which preferentially settled in voids between autochthonous calcite. In opoka and marls, the detrital clays, which are a primary component, are stacked between the calcite grains and are overgrown by authigenic opal-CT (Figures 3b and 3c). In marls, the authigenic clays cover the lepispheres and micrite grains (Figures 4d and 4e), suggesting that the clays precipitated as a final phase covering all other mineralogical components.

4.3. The Proposed Model of Si Outflow

Si outflow from marine systems occurs via early diagenetic crystallization of silica polymorphs (Gao et al., 2020; Tréguer et al., 2021) from DSI-saturated porewater trapped in pores of seabed mud. The early diagenetic precipitation of newly formed authigenic minerals is a very complex process and depends on the geochemical conditions of seawater, porewaters and mechanical properties of seabed mud. The type of authigenic minerals that form during early diagenesis are very useful in reconstructions of environmental conditions not only within seabed mud but also in seawater (Hjuler & Fabricius, 2009; Huggett et al., 2005; Jurkowska et al., 2019; Figure 2).

In the pre-Eocene Si cycle, the seawater DSI concentration was favorable for silica polymorph precipitation
(Racki & Cordey, 2000; Siver, 1991) and for siliceous sponge development (Conley et al., 2017). In the studied marine system of the Late Cretaceous shelf sea, carbonate mud deposited on the seabed, which included coccoliths (calcite fragments of the skeletons of single-celled algae), calcite fragments of echinoids and bivalves, and abundant spicles of siliceous sponges (Abdel-Gawad, 1986; Jurkowska, 2016; Jurkowska & Święczewska-Gładysz, 2020a), was favorable for long-term porewater retention due to its poor lithification.

The absence of secondary microtextures characteristic of the intermediate forms of silica polymorphs (e.g., opal-CT/C; see Lynne et al., 2007), as well as silica overgrowths or variable silica polymorphs in one sample, suggests that the silica precipitated straight from solution during the early stages of diagenesis (Jurkowska & Święczewska-Gładysz, 2020a, 2020b; Lancelot, 1973). The process of silica crystallization was a one-stage mechanism (without any precursors or intermediate forms), and the polymorphs were not transformed, for example, due to the maturation process to more mature phases of quartz (see discussion of Jurkowska & Święczewska-Gładysz, 2020b), during later stages of diagenesis.

4.3.1. Above the Seafloor Surface – Interplay of Biological and Abiotic Si Sources

Si occurs in seawater as a dissolved form of orthosilicic acid (H$_4$SiO$_4$). This is a weak acid, which, under certain geochemical conditions, condenses to silica. In the marine system of the Late Cretaceous European Basin, the primary sources of the DSi were located in the Atlantic and Tethys Oceans, where the DSi had been released into the seawater during volcanic and hydrothermal activity connected with subduction and rifting processes (Jurkowska & Święczewska-Gładysz, 2020a). The DSi from abiotic sources was transported to the epicontinental basin by oceanic currents, bringing the overall seawater concentration to a level of ~40 ppm (Racki & Cordey, 2000; Siever, 1991). Under such conditions, which were favorable for siliceous sponge development (Maldonado et al., 1999), DSi was removed from the seawater by these organisms (Święczewska-Gładysz, 2006, 2012) to build their skeletons (Figures 5a and 5b). Similar mechanisms of massive seawater DSi utilization are observed in the modern deep sea only in areas with abundant siliceous sponges (Maldonado et al., 2021).

The documented distinctive microtexture of the opal-CT network, which is composed of densely packed small lepispheres of equal sizes (in a sample from the same type of opoka) and without any secondary structures (overgrowths and intermediate forms; Figures 3b; 4days), indicates that during its crystallization, the porewater DSi concentration was sustained at the same level as that of opal-CT crystallization (Kastner et al., 1977). This could only have been achieved due to the biological control by siliceous sponges and was possible only under permanent and constant DSi transport to the seabed mud via continuous spicle deposition. If the precipitation of opal-CT lepispheres could have been inorganically controlled, for example, by direct DSi diffusion from seawater to porewater, then this would have been reflected in the microtexture of the silica polymorphs by secondary overgrowths and differing sizes of lepispheres. Such microtextures are observed only in chert nodules (Figure 4c), whose genesis is associated with abiotic silica precipitation (without sponge biological activity), triggered by the increased delivery of DSi by oceanic currents in a short period of time (Jurkowska & Święczewska-Gładysz, 2020b). This biological activity of siliceous sponges was the first stage in a complex mechanism of Si outflow from the cycle via early diagenetic silica polymorph crystallization.

The role of other silicifiers (radiolarians and diatoms) in removing Si from the cycle in Late Cretaceous epicontinental marine systems was subordinate in the European Basin (Jurkowska & Święczewska-Gładysz, 2020a). Most radiolarians, whose fossils are also present in the paleontological record within the Campanian-Maastrichtian deposits of the European Basin (Jurkowska et al., 2019), undergo dissolution before reaching the sea bottom surface (Jurkowska et al., 2019) but could have played a substantial role in Si cycling in other marine environments (e.g., oceans; Kidder & Erwin, 2000; Racki & Cordey, 2000).

4.3.2. Inside the Seabed Mud – Biologically Mediated Stage

The process of silica polymorph precipitation was preceded by a series of geochemical changes that started in the upper layer of seabed mud and were triggered by the bacterial decomposition of organic matter (Figures 5a and 5b). The existing geochemical zonation generated by the bacteria within the seafloor mud affected all mineralogical components of the rocks, leading to authigenic precipitation of newly formed silica phases. Based on geological records, it is very difficult to estimate the depth below the seabed surface at which geochemical zones were located, but the whole process of silica polymorph crystallization occurred 25–50 cm below the seabed surface (Madsen et al., 2010).
**Figure 5.** The model of opoka (a) and marls (b) formation. (a) The DSi from oceanic influx has been used by siliceous sponges to build its skeletons of BSi, what significantly diminishes DSi concentration in a zone above the seabed surface and below it. After its death and decomposition of organic membranes the BSi has been released to the porewater as DSi and saturated them. The bacterial decomposition of organic matter in the upper suboxic zone caused the lowering of the pH and triggered the aragonite and high-Mg calcite dissolution, what releases an additional amount of Mg$^{2+}$ ions to the porewater In the lower suboxic zone where the Mg$^{2+}$ ions and alkalinity (OH$^{-}$) was available, the magnesium hydroxide compound where formed and the opal-CT lepispheres started to precipitate in form of network and enhanced the aragonite dissolution. In the last stage of diagenesis in anoxic sulfate reduction zone the calcite start to precipitate as micrite rounded grains. (b) During the marls formation the similar processes as in opoka took place, but due to presence of significant amount of detrital clays the opal-CT precipitation in lower suboxic zone has been retarded and only small lepispheres were formed. On the last stage of diagenesis the authigenic clays covered the calcite grains and opal-CT lepispheres.
4.3.2.1. Below the Seabed Surface – Fe-Mn Reduction Zone

Among the factors that are essential for opal-CT crystallization, the availability of Mg$^{2+}$ ions is a necessity (Hesse et al., 2011; Kastner & Gieskies, 1983; Kastner et al., 1977; Rodgers et al., 2004; Williams & Crerar, 1985; Zijlstra, 1987; Zijlstra, 1994). Based on geological records, it is impossible to estimate the amount of Mg$^{2+}$ ions that are indispensable to initiate opal-CT crystallization, but the concentration of Mg$^{2+}$ ions in Late Cretaceous seawater was sufficient to start this process (Jurkowska & Świerczewska-Gładysz, 2020a; Jurkowska et al., 2019; Kastner et al., 1977; Williams & Crerar, 1985). Moreover, the absence of aragonitic shells in the paleontological record in opoka successions (Jurkowska, 2016), as well as observed dissolution marks on high-Mg calcite shells of echinoids (Jurkowska, 2016), indicate that after their dissolution, they were acting as an additional source of Mg$^{2+}$ ions. The decreasing pH level, sufficient for aragonite and high-Mg calcite dissolution, was generated by the bacterial decomposition of organic matter in the upper suboxic Fe-Mn reduction zone (Figures 5a and 5b). The pH level was reduced only slightly and, therefore, only caused the dissolution of less resistant calcite polymorphs (Tynan & Opdyke, 2011), while the coccoliths, composed of low-Mg calcite, remained intact. The bacterial activity that occurred in this zone also caused the decomposition of organic membranes covering the skeletons of dead siliceous sponges (Jurkowska & Świerczewska-Gładysz, 2020a). Their skeletons, composed of biogenic opal-A (BSi), started to dissolve and saturated the porewater with respect to DSI levels, generating a concentration favorable for opal-CT precipitation. The BSi in the form of DSI migrated according to the Landmesser diffusion process (Landmesser, 1995) from the spicules of siliceous sponges without rigid skeletons, which were more prone to dissolution by the porewaters (Jurkowska & Świerczewska-Gładysz, 2020b). Landmesser diffusion is a process of solution transport of DSI governed by the different chemical potentials of two sites occupied by variable silica polymorph phases. In the studied situation, one site was represented by biogenic opal-A and acted as a source, while the sink was located in a different geochemical zone, where all factors enabling opal-CT crystallization were available. For opal-A to reach a lower chemical potential, it is kinetically easier to dissolve and diffuse to the site where opal-CT (of lower chemical potential) precipitates than to precipitate in the primary place (inside of the sponge spicule; Landmesser, 1995; Rodgers et al., 2004). The Landmesser diffusion (1995) mechanism triggered downward DSI migration, causing burial, instead of DSI recycling to the cycle. The records of this process are empty voids left after complete sponge spicule dissolution, which is abundantly documented in the opoka facies (Figures 3e and 3f). The dissolution of skeletons of other sponges (with rigid skeletons) was a much slower process than the dissolution of loose spicules incorporated within the seabed mud (Maldonado et al., 2021; Rützler & Macintyre, 1978). The sluggishness of DSI diffusion in more resistant to dissolution sponge skeletons led to crystallization of smooth silica as a secondary infilling in sponge skeletons (Jurkowska & Świerczewska-Gładysz, 2020a).

At this stage of Si outflow, which occurred a few centimeters (∼10–15 cm) below the seafloor surface due to bacterially mediated activity, Mg$^{2+}$ ions became available, and a DSI concentration sufficient for opal-CT crystallization due to dissolution of the siliceous sponge skeleton was generated.

4.3.2.2. Below the Seabed: Fe-Mn Reduction Zone/Sulphate Reduction Zone

The other factor necessary for lepisphere formation is high pH (the availability of OH$^-$ ions) (Hesse et al., 2011; Kastner & Gieskies, 1983; Kastner et al., 1977; Rodgers et al., 2004; Williams & Crerar, 1985; Zijlstra, 1987, 1994). Alkaline conditions increase during burial by bacterial decomposition of organic matter and in the sulphate reduction zone, the high pH is generated by the reduction of sulphate and methane oxidation (Coleman, 1993; Wetzel & Allia, 2000). OH$^-$ ions are essential for magnesium hydroxide (MgOH$_2$), which induces the formation of interparticle bonds between the silanol groups and triggers DSI crystallization to produce more ordered forms (Iler, 1979; Williams & Crerar, 1985; Zijlstra, 1987). The opal-CT precipitation started in the lower part of the Fe-Mn reduction zone and continued into the lower anoxic sulphate reduction zone (Figures 5a and 5b), where alkaline conditions were sustained due to the microbially induced reduction of sulphate and anaerobic methane oxidation.

As was experimentally demonstrated by Kastner et al. (1977), under the conditions of sufficient DSI concentration for opal-CT crystallization and availability of Mg$^{2+}$ ions depending on the availability of OH$^-$ ions, opal-CT forms lepispheres of different sizes. Under low availability of OH$^-$ ions, only the embryonic lepispheres of opal-CT precipitate, while under high alkalinity, the embryonic lepispheres grow in size over time and form large well-developed forms. The precipitation of the latter occurs in two stages: during the first stage, almost the whole source of OH$^-$ ions is consumed, and small embryonic opal-CT lepispheres form, while in the second stage, the lepispheres grow...
in size and consume the remainder of the OH\(^{-}\) ions. The presence of a significant amount of detrital clays within the seabed can affect these mechanisms due to competition for alkalinity and Mg\(^{2+}\) ions between clays and opal-CT (Kastner et al., 1977; Williams & Crerar, 1985). The significant amount of detrital clays inhibited the rate of silica polymorph formation in the studied marls, leading to the formation of only small embryonic opal-CT lepispheres (Figures 5a and 5b) and enabling the good preservation of rigid skeletons of siliceous sponges. When the alkalinity had been consumed and the DSI of the porewater dropped below the level of silica polymorph crystallization, the process of lepisphere precipitation stopped, and crystallization (Figures 5a and 5b) of calcium carbonate started. Rounded small grains of micrite precipitated and covered the opal-CT lepispheres (Figure 4a), while during the last stage of diagenesis in the sedimentation of the marls, the authigenic growth of clays was initiated (Figure 5b).

The precipitation of opal-CT lepispheres in bioclasts (voids after spicule dissolution and inside foraminifera chambers; Figures 3e and 3f; 4a and 4b) was induced by the specific geochemical conditions maintained in small microenvironments of the voids of sponge spicules or inside foraminifera chambers. The spicules of siliceous sponges, which acted as a site for DSI diffusion (Jurkowska & Świerczewska-Gładysz, 2020b), created a distinctive microenvironment in which the high concentration of DSI, in a close range to that of carbonate grains (source of alkalinity), was available inside the empty voids, enabling the precipitation of the opal-CT lepispheres in the form of a densely packed layer (Figure 3f). Similar conditions were maintained inside the foraminifera chambers, in which, due to the existence of pores, DSI diffused and probably reached a higher concentration in comparison to the surrounding porewater, while the necessary OH\(^{-}\) ions were available due to the dissolution of carbonate foraminifera shells.

5. Discussion
5.1. The Role of Siliceous Sponges in Si Burial

Considering that in the studied part of the Late Cretaceous epicontinental basin, the overall seawater DSI concentration reached ~40 ppm (Siever, 1991; Williams & Crerar, 1985), opal-CT could precipitate abiotically within sediment if only Mg\(^{2+}\) and high pH were reached. These two factors were available in the studied environment due to bacterial decomposition of organic matter within the sediment and could easily diffuse upward to the seabed surface by porewater-seawater diffusion. Previous studies have revealed that inorganic opal-CT precipitation is reflected by different opal-CT microtextures that do not occur in opoka, gaize and marly lithologies. Moreover, in opoka, which always contains opal-CT lepispheres, voids remained after siliceous sponge spicule dissolution occurred, which indicates that they dissolved after burial and were the primary source of DSI in porewater within Late Cretaceous seabed mud (Clayton, 1986; Jeans, 1978; Maliva et al., 1989; Sujkowski, 1931; Zijlstra, 1994). Similar mechanisms have been observed in modern deep-sea areas with abundant siliceous sponges (Maldonado et al., 2005, 2019). Unfortunately, the mechanisms of DSI utilization by sponges followed by BSi sinks (in the form of sponge skeletons) in sediments do not explain why abiotic DSI precipitation did not occur in Late Cretaceous seabed mud. Moreover, if diffusion between DSI-enriched seawater and porewater existed, the additional DSI derived from the dissolution of sponge skeletons composed of BSi would have significantly elevated the DSI concentration to a level at whichopal-A would have been precipitated instead of opal-CT (>60 ppm; Calvert, 1974; Kastner et al., 1977; Mackenzie & Gees, 1971; Williams & Crerar, 1985). This was not confirmed by the mineralogical studies, according to which opal-CT was the only phase of silica that precipitated straight from the porewater in the Late Cretaceous seabed mud of the European Basin (Jurkowska & Świerczewska-Gładysz, 2020a). These features indicate that DSI diffusion between seawater and porewater was strongly limited by existing physical (e.g., impermeable sediment layer) or chemical barriers (low DSI concentration of seawater). Generally, sediment within Late Cretaceous seaboards was not impermeable because it was composed of calcareous mud, which would have been very porous and permeable (Hjuler & Fabricius, 2009). In fact, a physical barrier that would have limited seawater/porewater exchange naturally existed within the sediment because the geochemical zone in which the DSI concentration was elevated due to sponge spicule dissolution was 10–15 cm below the seabed surface (Figure 5). This indicates that in a seabed sediment column, the zone in which the sponge spicules were preserved as BSI (opal-A) had existed, and in that zone, abiotic silica precipitation did not occur, although DSI diffusion from seawater to porewater was possible. The limited diffusion between seawater and porewater could be explained by the existence of a zone of depleted DSI concentration in a belt laying slightly above the seabed surface. This decrease in DSI concentration could have been caused by massive DSI consumption by siliceous sponges, which acted as a barrier and significantly limited the diffusion between seawater and porewater. The mechanism that could also have prevented seawater-porewater diffusion was silica polymorph precipitation. The rapid rate of opal-CT precipitation, which exceeded the rate of
BSi dissolution, could have favored the downward migration of DSi from the source (spicules in the Fe-Mn reduction zone) to the sulphate reduction zone with silica crystallization. This would have been in agreement with the Landmesser (1995) diffusion process, which is a mechanism of DSi migration between sites with different chemical potentials. The downward DSi migration to the zone of silica precipitation could have strongly limited seawater-porewater diffusion but does not explain why abiotic DSI crystallization in the uppermost geochemical zones did not occur unless the zone of depleted DSI concentration existed slightly above and below the seabed mud.

The mechanisms of decreasing DSI concentration by siliceous sponges in a zone close to the seabed surface contradict the processes noted in modern deep sea environments with siliceous sponge aggregations. Modern sponge aggregations enrich local DSI concentrations through a feedback mechanism from porewater (Maldonado et al., 2021). The DSI derived from dissolution of siliceous sponge skeletons is recycled to seawater before its complete burial via crystallization. This mechanism could not have occurred in Late Cretaceous sponge aggregations due to elevated overall seawater DSI concentrations, which could have caused sluggishness of the DSI diffusion and distinctive mineralogical composition of the seabed, enabling opal-CT crystallization under geochemical conditions mediated by bacterial decomposition of organic matter.

5.2. Si Burial in Late Cretaceous and Modern Marine Systems

Si cycling in the modern marine environment differs significantly from that in the Late Cretaceous, which represented pre-Eocene Si cycling and is mostly known from shielded epicontinental basins (Jurkowska & Świerczewska-Gładysz, 2020a). In modern seas and oceans, diatoms are the main biological controllers of DSI fluxes within the water column. These planktonic organisms, which are highly efficient in the molecular transport of DSI, fix the DSI circulation in the upper zone of the water column (Maldonado et al., 2020; Tréguer et al., 2021) and prevent DSI burial by reducing the amount of DSI delivered to the porewater (Tréguer et al., 2021). This mechanism of DSI transport to the seabed mud diminishes the possible DSI concentration able to be reached in porewaters within the seabed sediment, which strongly inhibits silica polymorph crystallization. In comparison to the Si cycling in the Late Cretaceous, the process of Si burial via early diagenetic crystallization is strongly limited in modern seas due to the recycling of DSI in the uppermost part of the water column and the feedback mechanism in deep sea areas with abundant siliceous sponges (Maldonado et al., 2021).

Although recent studies have revealed that siliceous sponges are highly inefficient both in the consumption of DSI from seawater and in the production of BSi in comparison to diatoms (Maldonado et al., 2020), when they live in extensive aggregations (mostly in restricted deep and shallow sea environments enriched with DSI), they transfer enormous amounts of Si to the sediments, and the effect can reach the regional scale (Maldonado et al., 2019, 2021). This last mechanism seems to be similar to the data from our studies, which indicate that in Late Cretaceous basins, the sponges were the main controllers of DSI porewater concentrations by removing DSI from the seawater and delivering it to the seabed mud via the dissolution of their skeletons. Considering the fact that DSI concentrations decreased during Earth history, it is highly probable that during the Late Cretaceous, siliceous sponges, due to the high concentration of DSI, had not developed more efficient mechanisms for the incorporation of DSI into their skeletons.

6. Conclusions

This study improves the understanding of both the mechanisms of Si burial within the marine environment and the influence of silica diagenesis on other authigenic minerals (calcite, clays) and rock fabrics. Increased knowledge of the mechanisms of DSI crystallization in carbonate seabed mud is essential for the recognition of biogeochemical Si cycling and reconstructing the diagenesis of carbonate-siliceous rocks. The collected data facilitate further discussion about the role of siliceous sponges in the pre-Eocene Si cycle, as well as a critical discussion concerning the fluctuations of DSI concentration in the water column in regard to the pre-Eocene Si cycle.

This study consisted of petrographic and mineralogical analyses of Upper Cretaceous carbonate-siliceous rocks that enabled the reconstruction of the biological and abiotic interplay that led to Si burial and that revealed the distinctive role of siliceous sponges in the pre-Eocene Si cycle in marine systems. It is highly probable that siliceous sponges, which had overgrown the seafloor surface in the part of the basin influenced by oceanic currents, diminished the DSI concentration by removing seawater DSI to build their skeletons in a zone close to the seabed.
surface, as well as a few centimeters below the surface, which prevented abiotic silica polymorph precipitation. These biological mechanisms not only caused vertical fluctuations in DSi concentrations within the water column but also controlled DSi concentrations in porewater trapped within the nonlithified carbonate mud. The DSi that saturated the porewater originated from the skeletons of siliceous sponges, which dissolved after the decomposition of the organic membrane. The new role regarding siliceous sponges and abiotic sources of DSi in Si burial presented here differs significantly from that presented in previous reconstructions of Si cycling. Previous authors presented the role of siliceous sponges only in a context of a biological source for DSi without the wider context of the global Si cycle comprising overall elevated DSi concentrations in Late Cretaceous marine systems. The model of Si burial reconstructed in these studies characterized the significance of interactions among the biological, biogenically mediated, and abiotic processes that enabled the complex mechanisms of DSi burial in sediments.

This study, which includes the largest petrographic data set of opoka samples, facilitates a formulation of the petrographic definition of this rock, therefore distinguishing it from other similar Upper Cretaceous chalks and gaizes. Opoka is a carbonate rock composed of calcite (38%–90%) and an insoluble residue (10%–62%) whose main component is authigenic opal-CT (4%–46%), forming rock networks consisting of adjoining lepispheres. The presence of the characteristic microtexture of the opal-CT rock framework and an insignificant amount of terrigenous components distinguish this rock from other carbonates (chalk and gaize).

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