REVIEW ARTICLE

DOI: https://doi.org/10.18599/grs.2024.2.1 Russian Original 2024. Vol. 26. Is. 2. Pp. 135–154

Opoka: Polymorphic Composition, Genesis, Problems of Study

P.V. Smirnov[1,2]
Tyumen Scientific Center of the Siberian Branch of the Russian Academy of Sciences, Tyumen, Russian Federation
Kazan Federal University, Kazan, Russiam Federation
e-mail: geolog.08@mail.ru

Abstract. This paper is a comprehensive review devoted to topical issues in the study of opoka – marine sedimentary siliceous rocks of the Cretaceous-Paleogene age. For almost two hundred years of studying these sedimentary formations, the term “opoka” itself has not received proper recognition globally due to the lack of a detailed mineralogical definition and the general imperfection of the systematics of siliceous rocks. A distinctive feature of the opoka is the presence of opal-CT lepispheres, which form a recognizable framework of siliceous rock or form an obscure lepispheric/cryptocrystalline mass. The article discusses various aspects of opoka – history of study, nomenclature, mineralogical composition, microtexture, the distribution of Cretaceous-Paleogene opoka, etc. The etymology of the genesis of the opoka and models of its origin at the early and late stages of diagenesis are critically discussed. In this review, attention is focused on recent studies, that provide detailed information about silica polymorphic forms distributed in the opoka, as well as its typical microtexture types. A model of the genesis of opoka and the relationship with global biogeochemical cycle of silica is presented. Differences recorded in opoka of different ages, geological and tectonic positions, indicate both the predetermination of many parameters of the mineral composition from the very genesis, and the disproportionate contribution of individual factors to the evolution of opoka rocks, namely the source of silicic acid, the role of siliceous bios in the mobilization of dissolved silica, the nature and volume of terrigenous influx from the adjacent landmass, secondary changes and mineral formation, etc.

Keywords: opoka, silicites, opal-CT, opal, cristobalite, silicic rocks, silica cycle, Trans-Urals

Recommended citation: Smirnov P.V. (2024). Opoka: Polymorphic Composition, Genesis, Problems of Study. *Georesursy = Georesources*, 26(2), pp. 135–154. https://doi.org/10.18599/grs.2024.2.1

Introduction

A distinctive feature of the Upper Cretaceous and Paleogene marine deposits in Northern Eurasia is the widespread occurrence of carbonate-siliceous and siliceous sediments. These siliceous deposits are primarily composed of biogenic and chemogenic silica, encompassing a range of sedimentary rocks from diatomites and diatomaceous shale to tripoli and opoka. Among the diverse group of siliceous rock, opoka hold a unique position. These rocks are distinguished by their opal-cristobalite-tridymite phase composition. Despite two centuries of research on these sedimentary formations, many aspects of their nature – including their genesis, structural properties, and physicochemical parameters – remain topics of intense scientific debate. The term “opoka” itself presents a challenge in the global scientific community. Due to imperfections in the international nomenclature of siliceous rocks, “opoka” is not universally accepted and is interpreted in various ways. As a result, this sedimentary formation type is often associated with rocks that differ significantly in appearance, physicochemical parameters, and mineral composition (Peryt, 2000; Machalski, 2012; Jurkowska, 2016; Malchyk et al., 2017).

Opoka have achieved widespread geographical and stratigraphic distribution, forming substantial Cretaceous and Paleogene layers up to 700 meters thick. These formations have been documented and studied across modern-day France, Poland, Germany, Belarus, Ukraine, Russia, and Central Asian countries, corresponding to the regions of ancient epicontinental basins (Figure 1). These rock formations serve as unique archives of the oceanographic conditions that prevailed in epicontinental marine basins during specific periods of geological time. These periods were characterized by significant changes in the scale of sedimentary silica accumulation and the global silicon cycle. Despite the seemingly extensive body of factual material, many properties, parameters, and formation mechanisms of opoka remain insufficiently understood. All aspects of this issue are closely interrelated, making it challenging to achieve significant progress by studying these aspects

---

in isolation. For decades, the debate over the genesis of various types of opoka rocks has remained a contentious issue. Earlier, it was commonly accepted that opoka is the product of diagenetic "maturation" of diatomites, a view that has since been questioned and criticized by certain experts.

This paper provides a comprehensive review that consolidates information on the history of opoka research, their mineral composition, structural and textural parameters, and formation mechanisms. To better understand the current state of knowledge on this subject, we propose the following structure for our discussion: (1) the history of opoka research; (2) silica polymorphs in opoka; (3) terminology, nomenclature, and synonymy; (4) sources of silica in opoka formation; (5) mechanisms of crystallization of silica polymorphs in opoka; (6) structural and textural parameters of opoka and their relationship to genesis; and (7) genetic models of opoka.

History of Opoka Research

The term "opoka" has Polish origins and likely began to be used as early as the 13th century to describe hard rocks that could be used as building materials (Jurkowska, Świerczewska-Gładysz, 2022). The term was introduced into scientific literature by geologist and paleontologist Georg Gottlieb Pusch, who borrowed it from Polish miners. These miners commonly used the term to describe chalky carbonate marls found within the Małopolska Upland (Pusch, 1833, 1836). Pusch used the term "opok" to refer to "*Grube und Chloritishe Kreide*", which he called "*Polnische Opoka*" (Polish Opoka), covering most of the Małopolska and Lublin Uplands in northeastern Poland (Jurkowska, Świerczewska-Gładysz, 2022).

Based on the similar facies observed in England and France, Georg Gottlieb Pusch pointed out that chalk and opoka represent laterally successive facies. Despite the lack of detailed mineralogical and petrographic descriptions, the term "opoka" received widespread acceptance in the literature and was widely used to describe various carbonate-siliceous rocks not only in Poland but also in the Russian Empire and later in the Soviet Union (e.g., Zejszner, 1847; Siemiradzki, 1905; Smoleński, 1906; Arkhangelsky, 1912; Samoylov, Rozhkova, 1925). In 1931, Sujkowski (Sujkowski, 1931) presented an extensive study of Upper Cretaceous opoka within the Małopolska Upland, including the results of macroscopic and microscopic observations. The compilation of these data allowed for the identification of typical features of these sedimentary formations, particularly the presence of "dispersed biogenic silica" (derived from sponge spicules), which prevents the rock from disintegrating after treatment with hydrochloric acid. In subsequent years, many researchers attempted to identify the type and origin of the polymorphic modifications of silica, as well as the mineralogical composition of opoka (e.g., Poaryski, 1948; Poaryska, 1952). However, an exact petrographic definition was never established. Overall, the term "opoka" was used in Northeastern Europe to refer to all types of hard Upper Cretaceous rocks that are not chalk, as well as to rocks

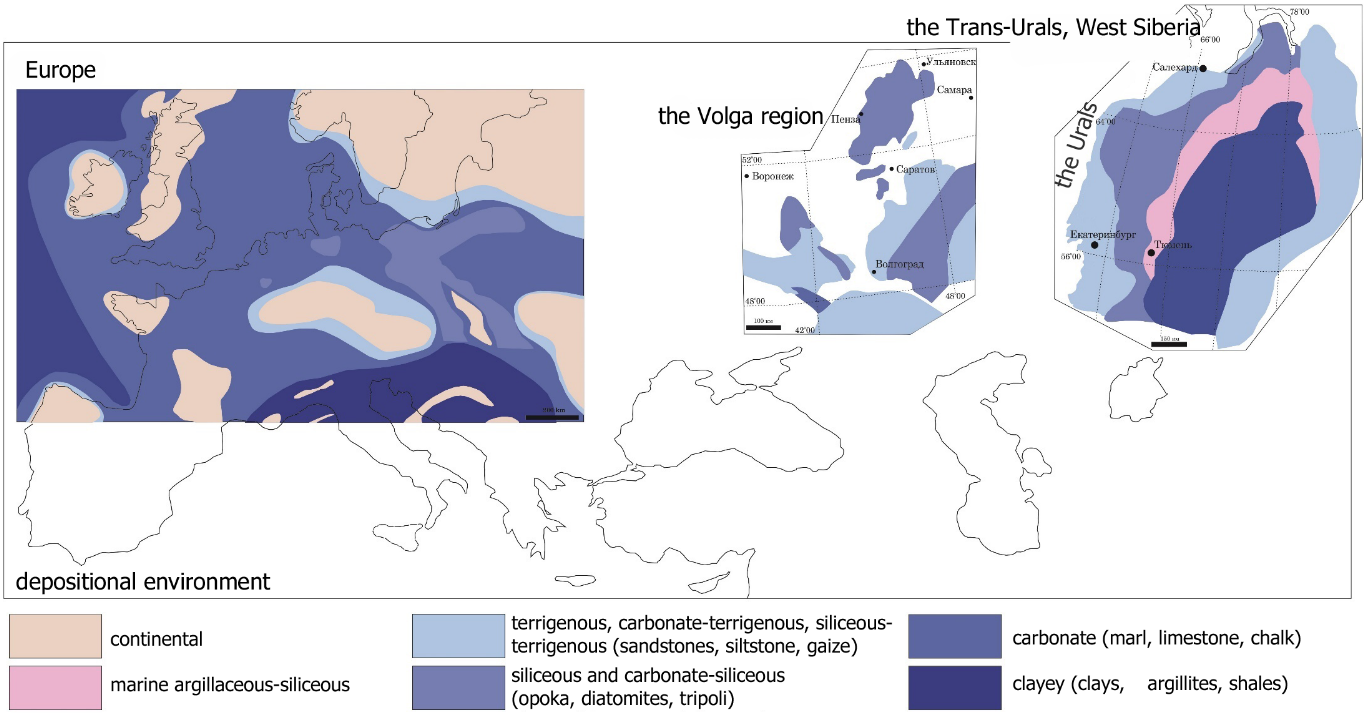

Fig. 1. A schematic representation of the distribution of sedimentary formations in the Cretaceous-Paleogene sediments of Europe, the Volga region, the Trans-Urals, and West Siberia

enriched with biogenic silica (opal) that contain less calcium carbonate and are less porous than typical chalk.

In subsequent years, many researchers attempted to identify the type and origin of the polymorphic modifications of silica, as well as the mineralogical composition of opoka (e.g., Poaryski, 1948; Poaryska, 1952). However, an exact petrographic definition was never established. Overall, the term "opoka" was used in Northeastern Europe to refer to all types of hard Upper Cretaceous rocks that are not chalk, as well as to rocks enriched with biogenic silica (opal) that contain less calcium carbonate and are less porous than typical chalk.

Silica Polymorphs in Opoka

A detailed study of opoka cannot overlook their polymorphic composition – neglecting the distribution of polymorphic modifications within the rock has contributed to the incorrect application of the term "opoka" to a wide range of other siliceous or carbonate-siliceous rocks.

It is well known that silica precipitates in crystalline, non-crystalline, and paracrystalline phases. The most common polymorphs in the crystalline group include quartz, moganite, cristobalite, and tridymite. Among the paracrystalline forms, opal-CT (opal-cristobalite-tridymite, opal-cristobalite-tridymite phase, syn. OCT-phase) and opal-C are predominant, while the non-crystalline forms are represented by opal-A (Jones, Segnit, 1971; Williams, Crerar, 1985; Flörke et al., 1991; Jones, 2021).

In geyserites (siliceous hot sinters), and during sediment burial, opal-A transforms into more ordered forms such as opal-CT and opal-C, and eventually into quartz due to progressively increasing temperature (Lynne, Campbell, 2004; Lynne et al., 2007; Rodgers et al., 2004). These mineralogical transformations can be traced using X-ray diffraction studies (Jones, Segnit, 1971; Flörke et al., 1991; Smith, 1998; Rodgers et al., 2004). The increasing crystalline lattice order during the transformational transitions from opal-A to opal-CT and quartz is recorded in X-ray diffractograms as an increase in sharpness and narrowing of peaks (Jones, Segnit, 1971; Williams, Crerar, 1985; Flörke et al., 1991). To identify different types of opals, FWHM (Full Width at Half Maximum) analysis of the 4 Å diffraction band has been performed, with narrower FWHM values indicating a greater degree of order and more mature phases (Graetsch et al., 1994; Elzea, Rice, 1996).

The X-ray diffraction profile of the OCT phase is characterized by the superimposition of SiO_2 polymorph reflections – opal (a broad, diffuse halo of low intensity peaking around 4,10 Å), cristobalite (a well-defined peak with an interplanar spacing of approximately $d \sim 4{,}05$ Å), and tridymite (a triplet of reflections with values of approximately $d \sim 4{,}31$; 4,07; 3,81 Å). Various types of opaline and crystalline silica can precipitate directly from solution, depending on the concentration of DSi. Quartz precipitates at low DSi concentrations (< 20 ppm), whereas opal-CT requires higher concentrations (20–60 ppm), and opal-A necessitates the highest concentrations (> 60 ppm) (Morey et al., 1962; Mackenzie, Gees, 1971; Williams & Crerar, 1985). Other crystalline silica polymorphs – tridymite and cristobalite – are associated with silica-rich volcanic rocks and form at elevated temperatures (~ 1470 °C) (Smith, 1998). Although several studies have convincingly demonstrated that cristobalite can be genetically linked to low-temperature conditions in soils and marine deposits (zeolites and clays) (Flörke, 1955; Jones, Segnit, 1971; Brindley, 1980), it is often the result of its mixing with opal-C, with which it has been identified for many years (Frondel, 1962; Flörke et al., 1991; Smith, 1998).

It's worth noting that recently, the informativeness of X-ray diffraction methods for short-range silica network polymerization continues to be critically discussed. Alternative techniques being considered include: infrared spectroscopy, Raman spectroscopy, nuclear magnetic resonance spectroscopy. These methods are being applied to analyze the structural environment of silicon, bond characteristics, and unit cell parameters of opaline silica (Curtis et al., 2019, 2021; Liesegang & Tomaschek, 2020).

Regarding the siliceous rocks of the Trans-Urals region, including opoka, it has been established that the following features indicate the predominant silica modification in opal-cristobalite rocks is opal with initial signs of cristobalite lattice formation: A broad X-ray diffraction scattering reflex in the 2Θ range from 20° to 26° on X-ray diffractograms (known as the "amorphous halo"), Bands at 525, 800, and 1630 cm^{-1} on infrared spectra, Chemical composition analysis. (Ushatinsky, 1987; Smirnov, 2017; Smirnov et al., 2017)

Opal-CT in the form of lepispheres is often referred to as opal-CT$_{M}$ (massive or lepidospheric) (Flörke et al., 1991; Smith, 1998). The size of opal-CT/C lepispheres varies from 2 to 30 micrometers in different types of opoka. V.I. Muraviev (1983) interpreted the texture of the primary component of opoka and tripoli as spherical grains with a ribbed cristobalite shell surrounding an opal core. Crystallographic studies have identified a distinct symmetrical ultrastructure in the lepispheres, characterized by consistent angles between the interpenetrating plate-like crystals (Il'icheva, 2013). The lepispheres are composed of plates that have coalesced according to the tridymite twinning laws (3034) and (1016) (Il'icheva, 2013). The size of opal-CT lepispheres typically ranges from 0.05 to 0.5 micrometers (Wise, Kelts, 1972; Jurkowska, Świerczewska-Gładysz, 2020a). Opal-CT$_{M}$ differs significantly from opal-CT$_{LF}$ (lengthslow fibers) (Flörke et al., 1991; Smith, 1998), which consists of fibrous and parallel plates, also known as lussatine (Flörke et al., 1991).

The lepispheric structure of opal-CT$_M$, composed of lepispheres, has been observed in Cretaceous and Paleogene opoka across various regions, including Poland, the Volga region, Western Siberia, and the Trans-Urals. A similar microtexture has also been identified in the Miocene Monterey Formation in California, USA (Bramlette, 1946; Oehler, 1975). Depending on the degree of maturity (increasing order), opal-CT$_M$ forms barely distinguishable macrostructures of lepispheres (Williams, Crerar, 1985; Lynne et al., 2007; Jones, 2021). In samples from Trans-Ural opoka, poorly developed lepispheres of opal-CT and magnesium-rich clay minerals have been observed. Similar poorly developed lepispheres have also been noted in Cretaceous marl complexes in Poland (Jurkowska, Świerczewska-Gładysz, 2020b), likely representing a primary or early diagenetic form of opal-CT$_M$ (Kastner et al., 1977; Kastner, Clark, 1982; Minde et al., 2018). Additionally, Polish opoka have revealed lepispheres with distinctive cross-hatched structures, indicating mature phases (Jurkowska, Świerczewska-Gładysz, 2020a), which indicate mature phases of opal-CT/C (Lynne et al., 2007). In the Trans-Ural opoka, instead of a lepispheric framework, one may also observe homogeneous, vaguely lepispheric, cryptocrystalline silica masses, where the evolution of silica phases has led to the merging of lepispheres into a continuous surface, making the boundaries between particles indistinguishable. In such samples, opal-CT$_M$ lepispheres are identifiable only within the cavities of bioclasts (e.g., in the relics or replicas of diatom frustules) (Nesterov et al., 2021).

Terminology, Nomenclature, and Synonymy

In scientific practice, numerous examples of terminological and conceptual discrepancies exist between different scientific schools in the identification of opoka. The reasons for such discrepancies, as noted earlier, are closely linked to the history of studying these rocks and the inherent geological and tectonic differences in the positioning of opoka formations across various regions of the world. However, the presence of a siliceous lepispheric framework, where the opal-CT/C lepispheres are tightly packed, should likely be considered the primary distinguishing feature of opoka (Wise, Kelts, 1972; Jurkowska et al., 2019a; Jurkowska, Świerczewska-Gładysz, 2020a,b; Nesterov et al., 2021).

From the perspective of Polish researchers, opoka should be defined as a rock composed of calcite (38–90%) and an insoluble residue, the main component of which is authigenic opal-CT (40–46%), forming the siliceous matrix of the rocks made up of adjoining lepispheres (definition by A. Jurkowska). The presence of a characteristic framework of opal-CT and a minimal amount of terrigenous components distinguish this rock from others (for example, from chalk or siliceous marl) (Jurkowska et al., 2019a; Jurkowska, 2022). In a series of works led by A. Jurkowska, which included analysis of data from opoka samples collected in Europe, it is asserted that opoka was a widespread facies in the European basin during the Late Cretaceous. The studies suggest the appropriateness of using the term for all carbonate rocks from this time interval that contain opal-CT as a major component (Jurkowska et al., 2019a). In Russian scientific literature, the term opoka refers to lightweight, finely porous (3–5 nm) siliceous rocks composed predominantly of opal-CT (up to 98%) with admixtures of clays, detrital, or authigenic minerals (quartz, feldspars, clay minerals) (Distanov et al., 1976; Senkovsky, 1977; Nesterov et al., 2021). In the Russian literature, color-based classification has been used to distinguish subtypes of opoka. For instance, a classification system identifies three color types: white, cream-white, gray-white, and yellow-gray ("light opoka"); gray and dark gray ("gray opoka"); and black-gray ("dark opoka") (Distanov et al., 1976) (Figure 2). It should be noticed that opoka with different color characteristics and structural-textural parameters are often found at the same depth levels and frequently form cohesive aggregates (Figures 2e–f). Additionally, in Russian scientific practice, dark gray and black opoka are generally considered to be of the same type.

In Central European scientific literature, some of the most commonly used synonyms for Upper Cretaceous opoka are "siliceous chalk" (Machalski, Malchyk, 2016) and "siliceous limestone" (Jurkowska, 2016; Remin, 2018). From a mineralogical perspective, siliceous chalk is defined as a type of chalk (i.e., a carbonate rock containing more than 95% calcium carbonate in the form of coccoliths) (Fabricius, 2007) with aggregates of chalcedony (Faÿ-Gomord et al., 2016) and authigenic nano-α-quartz (Jakobsen et al., 2000). This definition clearly indicates that opoka and siliceous chalk are entirely different rocks, as reflected in the mineralogical composition of their polymorphic modifications.

Unlike chalk, opoka has a different microstructure that includes a framework of opal-CT lepispheres, which provides the rock with a high degree of cohesion. This cohesion prevents opoka from disintegrating after treatment with HCl, as its framework is siliceous, formed by opal-CT particles (Jurkowska, Świerczewska-Gładysz, 2020a, b). The second term, "siliceous limestone," implies that the rock is a siliceous-carbonate formation primarily composed of crystalline aggregates of calcite/aragonite and silica minerals. In this sense, according to Jurkowska and colleagues (2019b, 2021, 2022), both chalk and opoka represent a distinct type of limestone, in which calcite is mainly derived from

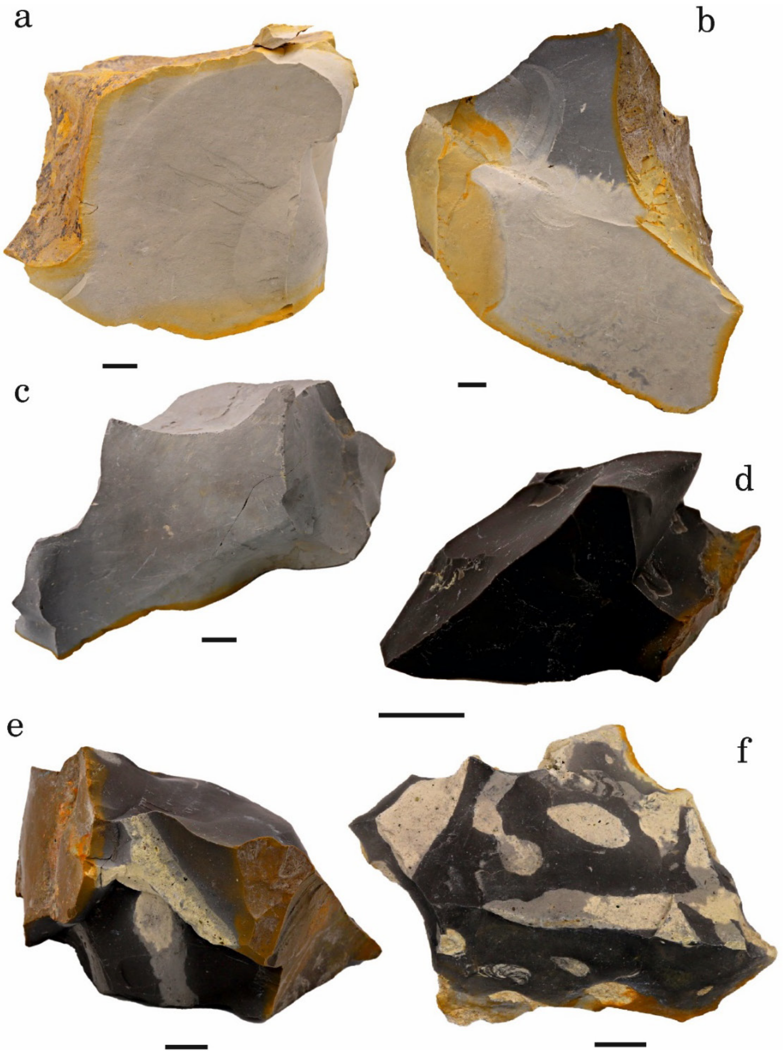

Fig. 2. The external appearance of opoka from the Reutinskoye site exhibits notable variation. Section 3. The locality is situated in the Kamyshlov District of the Sverdlovsk Region, which is located in the Trans-Urals. The line length is 1 cm. The transition from light-colored opoka to gray and black is clearly evident in e and f

coccolith skeletons.

However, the term "siliceous limestone" does not reflect the significant features of "Polish" opoka – namely, the microstructure of polymorphic silica forms. It is generally acceptable only if the carbonate component in the rock retains an organogenic texture. Clearly, in Russian terminology practice, opoka is not associated with siliceous limestones. Such naming or comparative practices have not been used in Russia, even in cases where carbonate minerals are present in significant quantities (e.g., in sections of European Russia, Belarus, and Ukraine).

The French term "gaize", often used in the context of studying opoka, typically denotes carbonate-siliceous rocks with a significant amount (up to a quarter of the total composition) of fragmental quartz (Cayeux, 1929; Jurkowska, Świerczewska-Gładysz, 2022). As evident from the mentioned mineralogical characteristics, the presence of detrital quartz allows for easy distinction between gaizes and opoka. The use of this term in relation to opoka by some authors is only associated with previous incorrect practices of applying the term. Summary information on the group of siliceous rocks is presented in Table 1.

Another term from the nomenclature of siliceous rocks that has been used as a synonym for opoka is "porcellanite". In European geological practice, porcellanites often refer to siliceous concretions that consist of more than 50% opal-CT and can be considered analogous to opoka (known as "kremni" in Russian literature) (Bramlette, 1946; Calvert, 1975, 1977; Jeans, 1978; Riech, von Rad, 1979; Clayton, 1984; Hesse, Schacht, 2011; Maliva, Siever, 1989; Behl, 2011; Jurkowska, Świerczewska-Gładysz, 2020b). Moreover, scanning electron microscopy data of deep-water porcellanites has revealed the development of these textures from individual plates to large coagulated aggregates (Muraviev, 1983), which differ from those observed in the lepispheric (formed by lepispheres) texture of opoka.

	Gaize	Chert	Flint	Opoka	Porcellanite
General characterization	Carbonate-siliceous rocks with significant amounts of clastic quartz	Carbonate-free siliceous rock with prevalence of opal-CT	Carbonate-free siliceous rock with quartz\ chalcedony predominance	Siliceous rocks with opal-CT$_M$ frame	Siliceous rock
Microtexture	Clastic, granular	Granular	Granular	Lepispheric, cryptocristalline	lamellar, coagulative
Mineral composition, %	Quartz (18–20), opal-CT (14–26), clays (1–18), zeolites (0–4)	Opal-CT (> 50)	Quartz, chalcedony (up to 90–100%)	Opal-CT (> 20)* Opal-CT (> 50)**	Opal-CT (> 50)
SiO$_2$ content, %	30–45	65–99	87–99	up to 50* up to 90–95**	50–90

*Table 1. Comparison of the main parameters of the siliceous rocks. * – according to Jurkowska et al., 2019a,b; ** – according to Russian practice*

In studies of the Miocene Monterey Formation in California, high-resolution electron microscopy revealed differences between opoka (> 90 wt. % SiO$_2$) and porcellanites (50–90 wt. % SiO$_2$) in terms of the degree of structural disorder and the coherence of lamellar intergrowths of microcrystalline opal (Cady et al., 1996; Il'icheva, 2013).

Let's consider another example of terminological confusion, which is perhaps the most problematic in the context of studying opoka: the identification of rocks as *chert* and *flint*. Some authors equate chert (often referred to as "кремень" in Russian) with flint, since the latter was originally understood merely as a local Danish term for chert. It was believed that mineralogically, flint is essentially the same type of rock as chert, predominantly composed of quartz. However, other researchers view *chert* and *flint* as mineralogically distinct sedimentary formations: chert being formed from opal-CT and flint from quartz (see, for example, Jeans, 1978; Clayton, 1984; Maliva, Siever, 1987; Behl, 2011; Jurkowska, Świerczewska-Gładysz, 2020b). In this nomenclature system, chert, according to Behl (2011), becomes synonymous with a rock that would predominantly be diagnosed as opoka in the Paleogene sedimentary sections of the Trans-Urals region (with a similar dominance of opal-CT in its mineral composition) and, from a mineralogical perspective, though without considering microstructure, could even be classified as porcellanite. This discrepancy arises from the fact that "Polish" opoka is a two-component system in which the carbonate component quantitatively exceeds or is comparable to the siliceous opal-CT (Jurkowska, Świerczewska-Gładysz, 2022). In contrast, in the Trans-Ural sections, opoka refers to rocks where silica in the form of opal-CT overwhelmingly dominates over all other components, such as clay minerals, zeolites, carbonates, and others. The distribution of the main phases in the mineral composition of opoka, compared to other siliceous and carbonate-siliceous opoka, is presented in the diagrams shown in Figures 3 and 4. For constructing the diagrams, our unpublished data were used, as well as the results of determining the mineral composition of opoka and the corresponding systematics of Polish geologists (Jurkowska et al., 2019a; Jurkowska, Świerczewska-Gładysz, 2020a; Jurkowska, Świerczewska-Gładysz, 2020b; Jurkowska, 2022).

It is also common to distinguish various types of opoka based on macroscopic field observations: "pure" (high-silica, also known as "resonant") opoka, as well as marl, clayey opoka, and others (Walaszczyk, 2004; Leszczyński, 2010; Jurkowska et al., 2019a; Nesterov et al., 2021, etc.). While this "color-based" classification is certainly not without merit and can be quite useful in the initial study of rocks, it cannot be considered reliable, as it does not reflect the typical mineralogical characteristics of opoka. The parameters used for description are "non-petrographic", as they do not account for microtexture and mineral composition. Therefore, such a classification at a minimum requires substantial support from chemical and mineralogical data.

It is important to note that in contemporary Russian scientific practice, the term "opoka" has been unjustifiably and repeatedly used in the diagnosis of rocks forming the Cretaceous horizons productive for hydrocarbon resources in Western Siberia (Karymova, 2020). In the Cretaceous rocks she studied, silica is mainly (up to 70%) represented not by opal-CT, but by quartz (authigenic and detrital), which makes the initial application of the term "opoka" to such sedimentary formations incorrect.

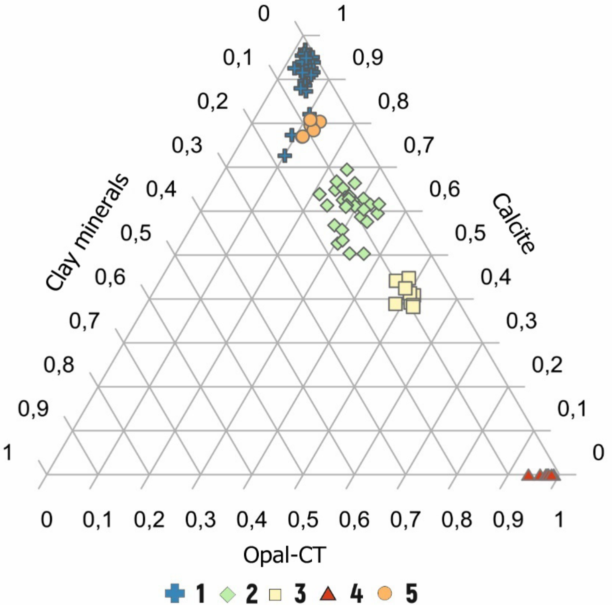

Fig. 3. Simplified diagram of the mineral composition of opoka is based on our unpublished data and the published findings of (Jurkowska, 2016; Jurkowska, Świerczewska-Gładysz, 2022). 1. Highly carbonate opoka, comprising up to 90% calcite and up to 10% opal-CT. 2. Opoka with opal-CT content of 20–35%. 3. Opoka with opal-CT content of 43–48%. In these samples, opal-CT quantitatively dominates over calcite. 4. Carbonate-free opoka, in which opal-CT is the dominant component, are referred to as "Trans-Ural opoka." 5. Opoka that exhibit a dominance of carbonate minerals (73–78%) and a content of clay minerals (up to 10–12%) are also observed

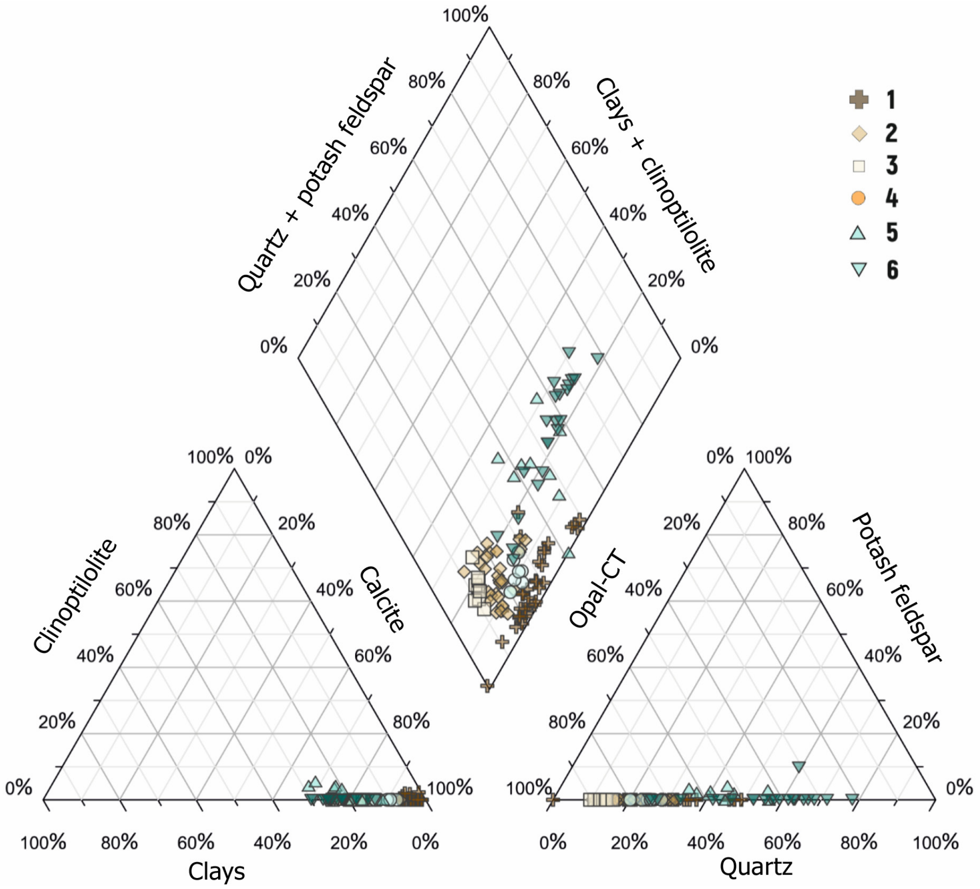

Fig. 4. Mineral composition of the opoka and adjacent carbonate-siliceous rocks. The data presented here are based on our own unpublished findings and those of Jurkowska et al. (2019a) and Świerczewska-Gładysz (2022). In particular, the diagrams take into account the content of zeolites, quartz, and feldspars. 1. High carbonate rock (up to 90% $CaCO_3$, opal-CT content up to 10%); 2. Rock with opal-CT content of 20–35%; 3. Rock with opal-CT content of 43–48%; opal-CT quantitatively dominates over carbonate minerals; 4. Rock dominated by carbonate minerals (73–78%) and containing clay minerals (up to 10–12%); 5. Gaize; 6. Marls

Sources of Silica in the Formation of Opoka rocks

Let's examine the sources of silica involved in the formation of opoka rocks, as this is directly connected to the role of opoka in the global silicon cycle. Three well-known sources of silica in the marine environment are: (1) the skeletons of siliceous organisms, such as diatoms, siliceous sponges, and radiolarians (Yool, Tyrrell, 2003); (2) extensive weathering crusts on adjacent landmasses; and (3) volcanogenic-hydrothermal processes driven by global tectonic shifts (Racki, Cordey, 2000; Penman, 2016; Jurkowska, Świerczewska-Gładysz, 2020a; Tréguer et al., 2021). In the context of the global silica cycle, the significance of each source has varied throughout Earth's history, influenced by both the biological evolution of silicification and major paleogeographic transformations. These factors have impacted the scale and intensity of terrestrial weathering and submarine volcanogenic-hydrothermal activity (Kitchell, Clark, 1982; Siever, 1991; Racki, Cordey, 2000; Conley et al., 2017; Gao et al., 2020).

The presence of numerous remains of siliceous sponges (Hurcewicz, 1968; Świerczewska-Gładysz, 2006; 2012) and voids formed by the dissolution of spicules in Cretaceous opoka (Sujkowski, 1926; 1931; Pożaryska, 1952; Pożaryski, 1960; Jurkowska et al., 2019a), as well as the stratigraphic distribution of these rocks during periods of significant siliceous sponge development (Jurkowska, Świerczewska-Gładysz, 2020a), provide compelling evidence for the biogenic origin of silica (Sujkowski, 1931; Pożaryska, 1952; Rutkowski, 1965; Maliva, Sievier, 1989). Similarly, for Paleogene opoka in the Trans-Urals sections, the combined presence of diatom frustules with numerous spicules of siliceous sponges (Distanov et al., 1976; Aleksandrova et al., 2012) has been interpreted as an indication of a biogenic source of silica. A key concept in these studies is that after the decomposition of organic opal-A membranes, the silica from the siliceous biota dissolved and, in the form of DSi saturated the pore waters to levels sufficient for the early precipitation of opal-CT during diagenesis (Jurkowska, Świerczewska-Gładysz, 2020a).

In the proposed concept, there must be a biogenic source of silica supplying significant amounts of DSi to the pore water. Microstructural studies of Cretaceous opoka have shown that the varying microstructure of opal-CT lepispheres observed in opoka deposits and silica-rich horizons (opoka) is likely related to different mechanisms of Si condensation and diffusion in pore waters of sedimentary layers (Jurkowska, Świerczewska-Gładysz, 2020b). The presence of densely packed large (up to 300 μm) opal-CT lepispheres found in Cretaceous chert nodules indicates rapid opal-CT precipitation, which is characteristic of high DSi concentrations over a short period (Kastner et al., 1977). The presence of elevated Si can be caused by temporal events (e.g., oceanic influxes of DSi of volcanogenic-hydrothermal origin). In this concept, the biogenic source of silica plays a subordinate role in the formation of chert horizons (Jurkowska, Świerczewska-Gładysz, 2020b).

According to laboratory experiments (Kastner et al., 1977), loosely packed small (1–10 μm) lepispheres found in Cretaceous opoka are characteristic of conditions where DSi is continuously present at levels sufficient to precipitate opal-CT. Such conditions could have been maintained by a constant influx of siliceous sponge spicules into the sediment, which would have occurred during the ongoing formation of opoka deposits. However, these hypotheses should be approached with caution, as other environmental factors (such as the presence of detrital clays or diagenetic processes) could also influence the microstructure of lepispheres (Kastner et al., 1977).

In the younger (Paleocene-Eocene) opoka deposits of the Russian Platform, biogenic sources of DSi, such as diatoms and siliceous sponges, have also been identified (Kidder, Erwin, 2001). N.M. Strakhov (1963, 1965) believed that the formation of siliceous rocks was driven biogenically through the dissolution of the shells of silicifying organisms. S.I. Shumenko (1978), who studied the composition, texture features of opoka using scanning electron microscopy, proved their planktonic nature. The hypothesis developed by Y.V. Samoylov and E.V. Rozhkova (1925) and N.M. Strakhov (1965) suggests secondary redistribution of biogenic silica during diagenesis. Relics of organic material within the cryptocrystalline siliceous mass were interpreted as evidence of opoka formation from diatomites (Strakhov, 1965). The co-occurrence of opoka and diatomite in a single stratigraphic section, noted by M. Bramlette (1946) in the Miocene Monterey Formation in California, V.P. Kazarinov et al. (Kazarinov, 1958; Kazarinov et al., 1969) in Paleogene sections of Western Siberia, N.G. Brodskaya (1966) in Miocene Sakhalin, V.I. Grechin (1971) in Miocene Western Kamchatka, and V.I. Muraviev (1983) in Paleogene sections of the Pre-Mugodzharskaya Uplift, further supports the presence of a genetic link between these rocks.

Another hypothesis attributed the primary role of DSi in the genesis of opoka to continental weathering. This idea was first presented by A.D. Arkhangelsky (1936) and later elaborated upon by Kazarinov et al. (1969). Arkhangelsky was among the first to notice the synchronicity between the accumulation of siliceous rocks in platform basins and periods of peneplane and the formation of weathering crusts on land. This observation led to the identification of two key factors that contributed to the accumulation of siliceous clays: (1) the scale of chemical weathering on the adjacent land, which supplied the necessary silicic acid through river waters, and (2) the minimal influx of detrital particles from the land, which prevented the “dilution” of sediments (Volokhin, 2013; Smirnov, Konstantinov, 2017; Amon, 2018). The authors of the study (Kazarinov et al., 1969) indicated that massive weathering within the Ural region, and to a lesser extent the Kazakhstan and Altai orogenic structures, served as a source of silica for the Trans-Ural Basin. According to this work, during periods of significant terrestrial input of DSi, marine silicifiers could not assimilate the entire amount. Consequently, biogenic silica deposition was quantitatively overshadowed by abiotic (chemical) processes on the seafloor, which is why Kazarinov interpreted opoka as a chemical rock. In the subsequent and final stages of such a transfer of silica from land, the development and abundance of siliceous organisms reached such a scale as to allow the deposition of excess silica mass by biogenic means, giving rise to diatomites.

V.P. Kazarinov (1969) specifically emphasized the stratigraphic asynchrony between diatomites and opoka – highlighting the association of diatomites and radiolarites with higher stratigraphic levels, while opoka were concentrated in the lower parts of the sequences. Currently, this theory is actively challenged by Agata Jurkowska’s body of work. According to her, a terrestrial source of DSi is unlikely for the Cretaceous opoka of Poland due to the rising sea levels and significant reduction in land area/islands during that time in Central Europe, which led to a considerable decrease in terrestrial weathering (Jurkowska et al., 2019b). However, this assertion requires further clarification, as increased sediment transfer could have occurred due to the erosional encroachment of marine waters onto the land during transgressions. Petrographic studies of Cretaceous opoka from coastal regions indicate that the skeletons of siliceous sponges, transported from pelagic zones, were a primary source of silica for areas adjacent to the land (Jurkowska et al., 2019b). When analysing the stratigraphic non-synchrony of diatomites and opoka, it is worth noting that in the Trans-Urals sections this regularity is also often violated and “atypical” sections are recorded, where opokas occur on diatomites or are interlayered with them (sections near the villages of Shipitsyna and Shilkina, Kamyshlovsky District, Sverdlovsk Region).

In fact, the two-part model of “bio-chemical + biogenic silicite” (Kazarinov et al., 1969) has proven valid in explaining mechanisms of alternative abiogenic hypotheses, where the primary role in the transfer of silica to marine basins was attributed not to weathering crusts but to various volcanic ash and pyroclastic materials and hydrothermal processes. Volcanogenic-hydrothermal processes indeed represent an alternative abiotic source of silica in marine environments. These processes include the transfer of DSi, the dissolution of silica-rich volcanic pyroclastic material, and underwater weathering of volcanic rocks (Maliva, Siever, 1989; Siever, 1992; Racki, Cordey, 2000). Such processes supply sufficient amounts of DSi to seawater to initiate the spontaneous precipitation of silica (Akhlestina, Ivanov, 2002; Tsekhovsky, 2015a,b, 2017a,b), and pyroclastic material, capable of being dispersed over long distances, served as an additional source of silica (Krasny et al., 1962). The hypothesis regarding the key role of volcanic origins of silica was actively supported by V.I. Muraviev (1983), based on his research of siliceous Paleogene rocks in the European part of Russia. He argued that, in addition to the relatively close proximity of volcanic centers, the scale and intensity of volcanic activity were also significant factors in the formation of opoka over the vast territories of the Siberian and Russian platforms. This idea was further supported by the analysis of “masked” pyroclastic material in Cretaceous-Palaeogenic rocks of the Volga region (Zorina et al., 2012; Zorina, Afanas’eva, 2015). According to these studies, during diagenesis, pyroclastic material transformed into more stable minerals, including associations of opal-CT with zeolites and clays. This transformation is widely regarded as a reliable proxy indicator of volcanic processes (Strelichik, 2004; Tsekhovsky, 2017a, 2017b; Zorina et al., 2012; Akhlestina, Ivanov, 2000; Akhlestina, Ivanov, 2002; Berger, von Rad, 1972; Pomerol, Aubry, 1977; Kastner et al., 1977).

This view is opposed by Jurkowska et al. (2019b), who note that in coastal environments, the association of biogenic silica (spicules of siliceous sponges) with terrigenous aluminum input can initiate diagenetic formation of zeolites and opal-CT without any connection to volcanic processes. However, this does not exclude that such a mineral association is indeed quite typical of volcanic deposits.

Examining genetic types of siliceous rocks (tuffaceous siliceous rocks, phthanites, and biogenic siliceous rocks) and their localization, N.G. Brodskaya (1966) used biostratigraphic data from complexes in Kamchatka and Georgia to establish that volcanic rocks are typically overlain by opoka and diatomites. She found that periods of intense volcanic activity correlate with the presence of siliceous rocks. A similar observation was made for late Cretaceous horizons of siliceous concretions containing quartz and opal-CT. The characteristic microtexture of authigenic quartz and opal-CT lepispheres is associated with the presence of silica (in quartz and opal-CT sediments, respectively) over short time intervals and likely reflects a significant oceanic influx of volcanic-hydrothermal silica (Jurkowska, Świerczewska-Gładysz, 2020b).

Mechanisms of Silica Polymorph Crystallization in Opoka

To date, two main theories have gained significant support in explaining the mechanisms of diagenetic silica precipitation. These theories have been developed through the study of the origins of siliceous concretions and sediments from the Cretaceous and Paleogene periods (Bromley, 1975; Calvert, 1975, 1977; Riech, von Rad, 1979; Clayton, 1984, 1986; Maliva, Siever, 1989; Wise, Weaver, 1974; Kastner et al., 1977; Madsen, Stemmerik, 2010; Hesse, Schacht, 2011; Lindgreen, Jakobsen, 2012). The first theory is the maturation theory of silica polymorphs (Barton, 1918; Bramlette, 1946), and the second is the direct precipitation theory (Lancelot, 1973). Key differences between these theories lie in their explanations of the physical and chemical mechanisms and the rates of precipitation. The maturation theory suggests that opoka forms through multiple phase transformations during late diagenetic processes. In contrast, the direct precipitation theory argues for the early diagenetic origin of opoka.

The previously predominant maturation theory (Barton, 1918; Bramlette, 1946) is based on observations of the diagenetic transformation of silica. According to this theory, silica undergoes a series of transformations from opal-A to opal-CT and eventually to quartz through processes of dissolution and re-precipitation (Wise, Weaver, 1974; Williams et al., 1985; Maliva, Siever, 1989). In the classic interpretation of the Monterey Formation (Bramlette, 1946), factors controlling the maturation sequence of silica include temperature, which increases with depth, and time (Keller, Isaacs, 1985; Wise, Weaver, 1974; Williams et al., 1985; Maliva, Siever, 1989). The maturation theory was developed based on observations that quartz-bearing siliceous concretions are typically found in older Upper Cretaceous deposits subjected to higher burial temperatures, whereas opal-CT concretions are more commonly found in younger Eocene to Pliocene layers (Bramlette, 1946). Temperature estimates for the transformation of opal-CT to quartz in the Monterey Formation vary widely. Studies have reported a range from 55–110 °C (Murata, Larson, 1975; Murata et al., 1977) to 35–61 °C (Pisciotto, 1981). Some studies have also postulated lower transformation temperatures of opal-CT to quartz (17–48 °C) (e.g. Behl, 1992; Madsen, Stemmerik, 2010).

The diagenetic polymerization of silica and its phase transitions are interpreted as being governed by the Ostwald process. Ostwald ripening, or recondensation, occurs when larger particles grow at the expense of smaller ones. This process drives the growth of silica polymers from solution and the increase in size of newly precipitated forms (Williams, Crerar, 1985). The phase transitions of silica – from the amorphous opal-A (an unstable phase) through the intermediate opal-CT to quartz (a crystalline and stable phase) – are seen as examples of the Ostwald's step rule (Williams, Crerar, 1985; Hesse, Schacht, 2011). According to the maturation theory, after the dissolution of opal-A, opal-CT begins to precipitate as the concentration of DSi in the pore water drops to a level that inhibits the precipitation of opal-A. Once all the opal-A has dissolved, opal-CT reprecipitates in more ordered forms, either as opal-CT or quartz. Finally, when all the opal-CT has dissolved, the DSi concentration drops to a level where only quartz can precipitate (Williams et al., 1985; Williams, Crerar, 1985; Madsen, Stemmerik, 2010). Studies of the Monterey Formation in California, Cretaceous horizons in Europe, and deep-sea cores consistently show that at shallow burial depths, opal-A is found together with opal-CT. In the underlying horizons, opal-CT is found alongside quartz, while at even greater depths, opal-CT is entirely absent due to its phase transition into quartz. The theory of diagenetic maturation of silica polymorphs has been employed to explain the coexistence of opoka and diatomite, including in Paleogene sedimentary sequences of the Volga region and Trans-Urals, where opoka is considered a diagenetic product of diatomite (Ushatinsky, Gavrilova, 1985; Zorina et al., 2012; Nesterov et al., 2021). According to Jurkowska and Świerczewska-Gładysz (2020b), the maturation theory contradicts observations of sedimentary sections where opoka coexists with Late Cretaceous siliceous concretions. Under ideal conditions, these studied deposits should contain only authigenic quartz, not the metastable opal-CT.

Additionally, petrographic analysis of Late Cretaceous siliceous concretions and opoka revealed the lack of microtextural evidence for the transformation of silica polymorph (such as co-occurrence of remnants of primary textures, intermediate phases, weakly developed phases and outgrowths), which should be established during phase transitions the phase transitions from opal-A to opal-CT to quartz (Lynne et al., 2007; Jurkowska, Świerczewska-Gładysz, 2020b). In the Trans-Urals region, this pattern is sometimes disrupted, with "atypical" sequences observed where opoka are found on diatomites or interlayered with them. Moreover, different color variations of opoka are found within the same aggregate (Fig. 2e–f). The observation that opoka of varying colors exhibit different distributions of silica polymorphs suggests that other factors might be influencing the processes governing the genesis of these opoka, necessitating further investigation.

Another concept is the quartz precipitation theory (Tarr, 1917; Lancelot, 1973) (see also the discussion in (Jurkowska, Świerczewska-Gładysz, 2020a)). This hypothesis suggests that both silica polymorphs, opal-CT and quartz, can precipitate during early diagenesis, depending on the geochemical conditions of sedimentation, such as the concentration of DSi in pore water (Kastner et al., 1977). Unlike the maturation theory, Lancelot's research (1973) questioned the dominant role of temperature and time during deep diagenesis, thereby rejecting the maturation pathway of silica controlled by dissolution and reprecipitation processes. In the classical interpretation of Lancelot's quartz precipitation theory (1973), the lithology of the inclosing deposits was the key factor determining the precipitation of silica polymorphs. This assumption was based on the observation that horizons containing siliceous (opal-CT) concretions are exclusively found in layers of zeolitic clays and marly tuffaceous limestones, while quartz-bearing siliceous concretions occur in chalks and limestones.

The process of direct precipitation of opal-CT from a DSi-saturated solution at room temperature was experimentally confirmed by Kastner et al. (1977), while the direct crystallization of quartz from seawater at room temperature was demonstrated by Mackenzie and Gees (1971). Moreover, the direct precipitation of quartz without an intermediate opal-CT stage is also indicated by Meister et al. (2014) in Miocene deposits. The occurrence of direct precipitation of opal-CT and quartz during early diagenesis, without the involvement of dissolution-recrystallization processes, has also been observed in the sedimentary sections of siliceous concretions and opoka within Late Cretaceous strata (Lindgreen, Jakobsen, 2012; Jurkowska, Świerczewska-Gładysz, 2020b).

In the maturation theory, Ostwald's step rule was employed to explain the phase transformation of silica, where the sequence of maturation involves the precipitation of less stable polymorphs (opal-CT) and their subsequent transformation into stable quartz (Wise, Weaver, 1974; Clayton, 1984; Williams et al., 1985; Maliva, Siever, 1989). In the quartz precipitation theory, Ostwald's step rule can also be applied to explain the crystallization mechanisms of silica polymorphs, with the caveat that supersaturation with a metastable phase may inhibit the formation of a stable phase (Meister et al., 2014). In other words, opal-CT will precipitate directly from pore water saturated with opal-CT.

The precipitation mechanism of early diagenetic silica polymorphs requires clarification of the mobilization and migration dynamics of DSi in aqueous solutions. The chemical mechanism that facilitates the mobility and condensation of DSi – resulting in the formation of concretions and silica-rich layers – is described by Landmesser's diffusion process (Landmesser, 1995). This process occurs between two objects connected by a water film and possessing different chemical potentials (e.g., silica phases with varying solubility or degrees of crystalline imperfection). One object acts as the source of DSi (such as siliceous skeletal remains containing opal-A), while the other serves as a sink area where a silica "nucleus" of opal-CT forms. Unlike Ostwald's maturation process, Landmesser diffusion can operate over greater distances between different silica polymorph phases without limiting the size of the final product (Rodgers et al., 2004).

The quartz precipitation hypothesis (Lancelot, 1973) provides an explanation for the occurrence of different silica polymorphs within the same stratigraphic intervals. This theory suggests that the variation is due to differences in the geochemistry of pore waters rather than the transformation of one silica polymorph into another.

Recent studies of the microtexture and mineralogical parameters of Late Cretaceous opoka and siliceous concretions indicate that the direct precipitation of silica from pore waters occurred during the early diagenesis of these rocks (Jurkowska, Świerczewska-Gładysz, 2020b). Furthermore, this direct silica precipitation did not follow the Ostwald's step rule, as previously suggested in many studies (Clayton, 1984, 1986; Maliva, Siever, 1989; Madsen, Stemmerik, 2010), but occurred through the Landmesser diffusion process (1995).

Structural and textural parameters of opoka and their relation to genesis

The structural parameters of opoka have been described at different times by scientific groups, which have produced very substantial reports for specific regions of the world: for Western and Central Europe, these are (Jurkowska et al., 2019a, Jurkowska, Świerczewska-Gładysz, 2022); for the Volga region – (Akhlestina, Ivanov, 2002; Zorina et al., 2012; Zorina, Afanas'eva, 2015); for the Trans-Urals and Western Siberia – (Generalov, Drozhashchikh, 1987; Sidorenkov et al., 1989; Smirnov, 2017; Nesterov et al., 2021), etc.

The light-colored Paleogene opoka of the Trans-Urals region exhibit various cryptocrystalline textures, where lepispheric silica is the primary structural component (Figure 5). The most common structural patterns include:

1) lepispheric;
2) clastic-lepispheric;
3) organogenic(biomorphic)-lepispheric;
4) biomorphic-lepispheric;
5) flake-lepispheric;
6) clastic-flake-biomorphic-lepispheric;
7) clastic-(clastogenic)-lepispheric and other combinations of these microtextures.

In fact, this variability reflects the distribution of specific mineral components with distinct morphologies: lepispheres of opal-CT form lepispheric textures; biomorphic textures indicate the presence of numerous opal-CT replicas of siliceous biota fragments (sponge spicules are easily identified by narrow, elongated voids on the rock surface, while replicas of diatom algae

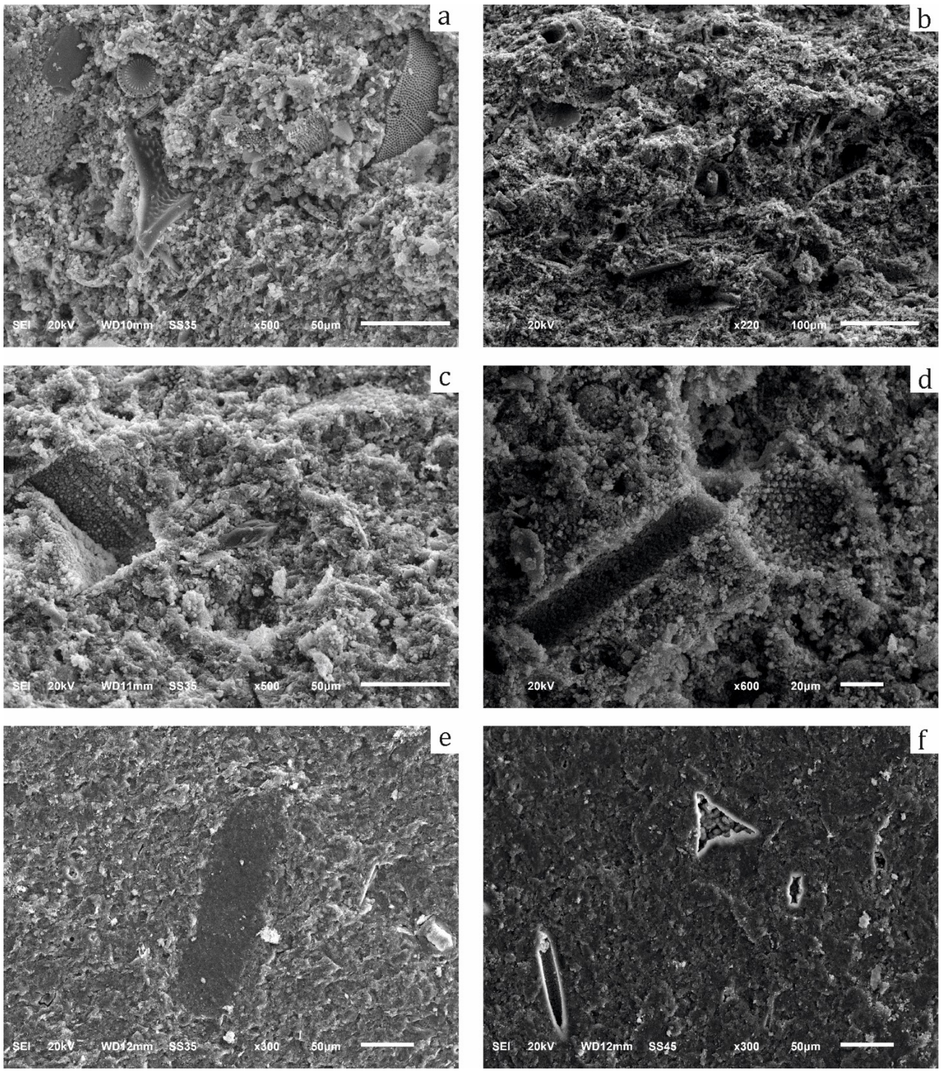

Fig. 5. Typical microtextures of opoka in the Trans-Urals from different sites. a – organogenic-lepispheric (Ozhgikha); b – biomorphic-lepispheric (Ipatova 5,6); c – clastic-biomorphic-lepispheric (Ipatova 5,6); d – biomorphic-lepispheric (in the center of the mass of lepispheric silica, replicas of spiculae from sponges and diatoms can be easily distinguished (Ipatova 2.3-2.4); e – cryptocrystalline (Reutinskoye 3-2,8); f – biomorphic- cryptocrystalline (Reutinskoye 3-2,8)

correspond to the morphology of diatoms and exhibit rounded, triangular, barrel-shaped, and other forms); clay minerals predominantly form flake-like, leafy, or platy aggregates; quartz fragments, and less frequently feldspar, create clastic textures, and so on. Despite this diversity, the textures observed in the studied Paleogene opoka can be categorized into three main types: biomorphic-lepispheric, (clastic)-organogenic-lepispheric, and indistinct lepispheric/cryptocrystalline.

The "organogenic-lepispheric" texture of opoka is relatively rare. It is characterized by lepispheric textures containing well-preserved large siliceous microfossils (Fig. 4a), notably diatom valves that show no signs of degradation or loss of their original biogenic texture. Lepispheric textures with clearly discernible replicas of siliceous skeletal fossils are typical of light-colored opoka (Fig. 4b–d) and are interpreted as biomorphic-lepispheric. This means they replicate the morphology of bioclasts and create "replicas" of bioclasts even in their actual absence.

In the opoka of the Trans-Urals region, instead of a lepispheric framework, one can observe homogeneous, cryptocrystalline, glassy silica masses, where the poorly defined lepispheric/cryptocrystalline opal-CT is prevalent, and the boundaries between particles are indistinguishable within the overall homogeneous matrix. In such samples, opal-CT lepispheres are only identifiable within the cavities of bioclasts (e.g., in replicas of diatom frustules). Macroscopically, these opoka are almost always dark-colored; however, according to foreign rock classifications, they might be described differently from opoka, often classified as porcelanites (see above).

Recent studies of Cretaceous opoka from European areas have revealed that the distinctive microtexture, composed of opal-CT_M lepispheres, is characteristic of early diagenetic silica precipitation, which occurred directly from silica-saturated pore waters (Lancelot, 1973). There is no microstructural evidence to suggest that opal-CT lepispheres form as a result of maturation and serve as a precursor to quartz-rich opoka (Jurkowska, Świerczewska-Gładysz, 2020b). A similar conclusion was reached in the work of Oehler (1975) based on studies of opal-CT lepispheres in the Monterey Formation. Moreover, Kastner et al. (1977) demonstrated in laboratory experiments that opal-CT lepispheres could precipitate directly from carbonate ooze containing diatoms under marine conditions. he second microstructure of opal-CT_M, consisting of a homogeneous silica matrix and cavities filled with opal-CT lepispheres, may have formed as a result of prolonged early diagenetic silica crystallization. This process causes the opal-CT lepispheres to accumulate on top of one another, leading to the formation of a uniform mass. In close microenvironments, such as within the shells of diatoms, opal-CT lepispheres precipitate more slowly, thereby preserving their original texture. A similar pattern is observed in Cretaceous opoka, where opal-CT lepispheres that precipitate in close proximity to the chambers of foraminifera are significantly larger (200–300 µm) and more developed compared to the surrounding opal-CT matrix (Jurkowska, Świerczewska-Gładysz, 2020a). Another interpretation of the genesis of this homogeneous opal-CT_M microstructure is that it forms as a result of secondary lepisphere precipitation following the dissolution of the initial homogeneous silica matrix at a later stage of diagenesis (Oehler, 1975).

Genetic Models of Opoka

The collective data we have gathered suggests that the rocks in question are predominantly formed through early diagenetic processes with limited post-diagenetic alterations.

For the crystallization of polymorphic modifications of silica, three factors are important (Williams et al., 1985; Kastner et al., 1977):

1) concentration of soluble silica;
2) high alkalinity and pH;
3) Mg^{2+} ions.

The concentration of DSi determines which type of silica polymorphs will precipitate: quartz predominantly crystallizes at low DSi concentrations (below 20 ppm) (Mackenzie, Gees, 1971; Lindgreen, Jakobsen, 2012; Meister et al., 2014), while opal-CT tends to precipitate at higher DSi concentrations (20–60 ppm) (Mackenzie, Gees, 1971).

For the polymerization of silica, a high level of alkalinity is required (here alkalinity refers to the capacity of water to buffer changes in acidity, essentially its ability to neutralize acids. This is distinct from pH, which measures the acidity or basicity of a solution based on the concentration of H+ and OH– ions formed during water dissociation). Additionally, Mg^{2+} ions are essential for the crystallization of silica polymorphs in the form of lepispheres (Iler, 1979; William, Crerar, 1985; Kastner et al., 1977).

The model of opoka formation through early diagenetic silica precipitation, reconstructed from the study of Cretaceous formations in Poland, suggests that the source of silica in pore waters is the dissolution of biogenic silica (in the form of opal-A) from the skeletons of siliceous sponges. A critical aspect of this process is that during diagenesis, the concentrations of dissolved silica (DSi) in the pore water reach levels sufficient to enable the crystallization of opal-CT/C. The geochemical conditions necessary for this precipitation are achieved in the sulfate-reducing zone of the sediment (Clayton, 1984, 1986; Zijlstra, 1987, 1994; Jurkowska et al., 2019b; Jurkowska, Świerczewska-Gładysz, 2020a). Reconstructed from studies of Cretaceous formations in Poland, the model for opoka formation through early diagenetic silica precipitation suggests that the dissolution of biogenic silica (in the form of opal-A) from the skeletons of siliceous sponges is the source of silica in pore waters. A critical factor is that during diagenesis, the concentration of DSi in the pore water reaches levels sufficient for the crystallization of opal-CT/C. The geochemical conditions necessary for this precipitation are achieved within the sulfate-reducing sediment zone (Clayton, 1984, 1986; Zijlstra, 1987, 1994; Jurkowska et al., 2019b; Jurkowska, Świerczewska-Gładysz, 2020a). Geochemical zonation is established in the uppermost layer near the seafloor, where oxygen is consumed during the aerobic degradation of organic matter. In deeper, suboxic zones, Mn and Fe take over as electron acceptors in place of oxygen. Further down, in the sulfate-reduction zone, similar processes occur through the anaerobic decomposition of organic matter. Beyond the sulfate reduction zone, the remaining organic matter may be converted into CO_2 and methane. The sequence of geochemical zones in sediments is well-documented based on the composition of pore water in modern deposits (Curtis et al., 1986; Balzer et al., 1987; Middleton, Nelson, 1996) and is primarily controlled by bacterial decomposition of organic material.

The process of the oxidation–reduction cascades alters the pH and Eh of pore water, which triggers the authigenic precipitation of minerals. In this early diagenetic model for opok formation, geochemical changes occurring within the first few centimeters below the seafloor surface lead to the dissolution of calcite, precipitation of polymorphic forms of silica, and further recrystallization of calcite into micrite grains (Clayton, 1984; Zijlstra, 1987; 1994; Jurkowska et al., 2019a,b; Jurkowska, Świerczewska-Gladysz, 2020a). Due to bacterial decomposition of organic matter in the uppermost geochemical zone, hydrogen sulfide (H_2S) formed in the underlying sulfate-reducing zone diffuses upward and oxidizes to sulfuric acid, which acidifies the pore water and affects the pH. As a result, more soluble aragonite and high-magnesium calcite skeletons initially dissolve, releasing Mg^{2+} into the solution (Jurkowska et al., 2019a).

In the upper zone, the decomposition of the organic sheath covering spicules, the complete dissolution of metastable biogenic opal (opal-A), and the saturation of pore waters with DSi occur. Within the upper oxygenated zone, two crucial factors contribute to silica crystallization: DSi concentration and Mg^{2+} ions. The final necessary factor, alkalinity, is observed in the sulfate-reducing zone, located approximately 25 cm below the seafloor surface. Alkalinity in this zone is due to sulfate reduction and anaerobic oxidation of methane (which diffused from the underlying methanogenic zone) (Wetzel, Allia, 2000). The precipitation of polymorphic forms of silica began in the upper part of the sulfate-reducing zone.

Considering that only authigenic polymorphous modifications of silica – opal-CT/C – are observed in the opoka, the DSi concentration in pore waters must reach values of 20–40 ppm, which is the level required for opal-CT/C crystallization (Mackenzie, Gees, 1971; Kastner et al., 1977). As the DSi concentration in pore waters decreases due to the precipitation of authigenic silica polymorphs and the subsequent reduction in alkalinity, calcite recrystallizes into micrite (Bojanowski et al., 2016; Jurkowska et al., 2019a). A reduction in DSi concentration below the level required for opal-CT precipitation (<40 ppm – 8 ppm) (Mackenzie, Gees, 1971) could potentially trigger quartz deposition; however, this was not observed in the opoka of Europe and Russia. This absence might be due to a lack of iron, which is necessary to catalyze quartz crystallization (Williams, Crerar, 1985; Meister et al., 2014). A conceptual model of opoka genesis considering the silica cycle is presented in Fig. 6.

The formation mechanisms of Paleogene non-carbonate opoka likely differed somewhat from those proposed by Polish geologists for Cretaceous opoka (Jurkowska et al., 2019a; Jurkowska, Świerczewska-Gładysz, 2022). The actual absence of a carbonate biota in sedimentary processes in the early Paleogene epicontinental basin of the Transural region should

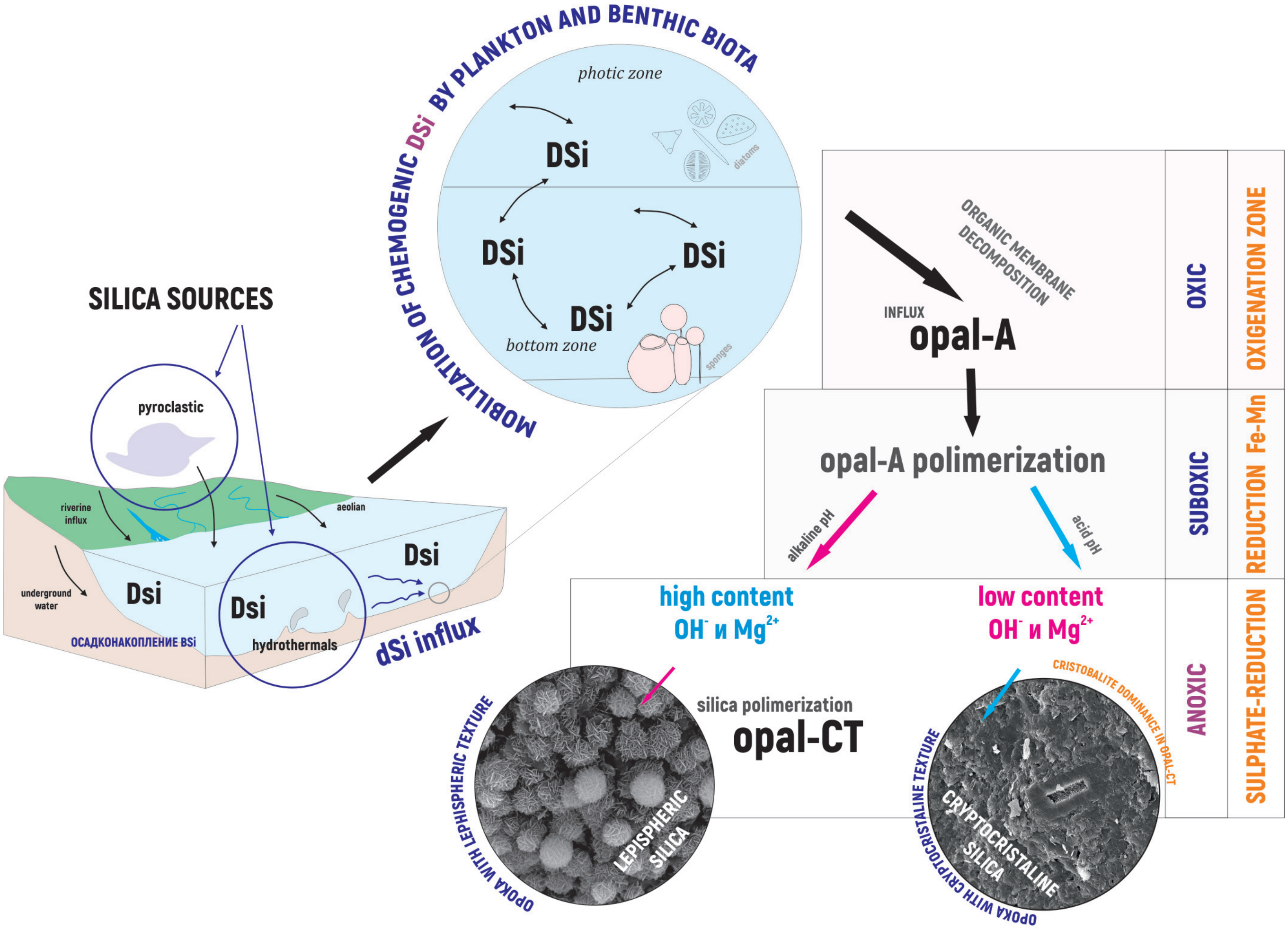

Fig. 6. General conceptual scheme of the opoka genesis with of different microtextures. The following section presents an overview of the elements of the silica cycle, as outlined by Frings et al. (2016)

have influenced the crystallization of polymorphous forms of silica due to a reduction in the availability of Mg^{2+} and possibly OH^{-} ions. Typically, these factors, combined with high DSi concentrations, would initiate the polymerization of silica and the crystallization of opal-CT in a form different from lepispheres. Under this genetic scenario, the basin would simultaneously exhibit high silica content and a deficiency of elements (such as Mg^{2+}) that promote lepisphere formation. In the absence of carbonate accumulation in this sector of the marine basin, other elements ensuring silica polymerization and the formation of lepisphere-like structures must be present. Potential sources for these elements include sulfate reduction and anaerobic methane oxidation, which diffuses from the underlying methanogenic zone.

The presence of lepisphere and bioclastic silica in opoka with an organogenic-lepisphere texture is feasible under conditions where the primary mass of silica was introduced into the sedimentary basin in a swell-like manner. This process did not involve the transfer of the necessary nutrients that would allow silicifying organisms (such as diatoms and sponges) to utilize the excess silica for active proliferation in the basin. Other mechanisms explaining the lack of diatom destruction in such opoka, given the overall OCT-lepisphere framework, are not evident. Geological settings are more likely associated with the swell-like transfer of silica into the sedimentary basin during volcanic activity.

When studying opoka that form a single depth profile, a general decrease in quartz content is observed, rather than in opal-CT, which typically increases. Such a distribution of mineral components is possible under two conditions: an initial predetermination of this polymorphic composition distribution in the rocks and throughout the stratigraphic section, or in conditions of extremely intensive hydrothermal alteration of such rocks, which should be accompanied by corresponding mineralogical or geochemical signals.

Our unpublished data on the mineral composition of opoka from the Trans-Urals region (Sverdlovsk and Chelyabinsk Regions) indicate that an increase in the overall silica content in opoka with cryptocrystalline textures is not accompanied by a rise in the amount of crystalline silica phases such as quartz. The quartz observed in Trans-Ural opoka primarily originates from terrigenous sources (data are from well 15 of the Artemovsky profile, drilled by the Ural Comprehensive Geological Survey Expedition, Yekaterinburg). Depth profiles show changes in the distribution of mineral components within the opal-CT phase. For light-colored opoka with lepispheric textures, the ratio of opal to cristobalite to tridymite (O:C:T) varies between (36–10) : (46–60) : (18–30). In underlying opoka with cryptocrystalline textures, the composition ranges from (11–14) : (83–87) : (1–2). However, in all types of opoka, the OCT phase remains the predominant component.

For opoka with an organogenic-lepispheric texture, which as previously noted, are a specific case characterized by a significant presence of bioclasts, the ratio of opal to cristobalite to tridymite (O:C:T) falls within the range of 58:30:12.

Below, we present a generalized schematic for the step formation of opoka deposits, based not only on our own data but also on materials from Russian and international colleagues. The proposed model views the formation of opoka as early-diagenetic processes within the context of the recirculation of chemogenic silica from biosilica (partially or nearly completely) followed by the deposition of lepispheric silica in the bottom zone, resulting in the formation of geochemical stratification within this layer. This model also accommodates progressive phase transitions of silica within substantial thicknesses, as observed in the reduction of metastable silica phases with depth, while being consistent with the overall increase in opal-CT with depth.

To develop a conceptual genetic model for opoka formation, key factors influencing the process have been identified, including the source of dissolved silica, depth, the role of the biosphere in mobilizing dissolved silica dSi, the availability of nutrients for biosphere development, and the transfer of sedimentary material from adjacent land areas. In addition to the existing and presented genetic models (from researchers such as A. Jurkowska, E. Świerczewska-Gładysz, N.I. Afanas’eva, S.O. Zorina et al.), attention should also be given to the following aspects.

1. In the Paleogene opoka of the Trans-Urals and Western Siberia regions, diatoms have traditionally been considered the primary biotic agents responsible for mobilizing chemogenic silica. It is well-known that diatoms attained a dominant position in these epicontinental marine basins. However, the uptake of silicic acid and the production of biogenic silica by diatoms are confined to the photic layer of the sea, and the mobilization of silica by both phototrophic and non-phototrophic organisms in deeper water conditions occurred differently, depending on the availability of other components necessary for this process. Sponges, as benthic organisms, naturally remobilize chemogenic silica in areas where it is eventually buried. In contrast, diatoms, being planktonic organisms, participate in the silica cycle within a different bionomic zone. Despite the recognized role of diatoms in siliciclastic sedimentation in the Trans-Urals and Western Siberia regions during the early Paleogene, their contribution to opoka formation was likely secondary and far from leading.

2. The occurrence of different types of opoka within a single sample is often underrepresented in genetic models of opoka formation. Notably, this phenomenon was observed during the study of opoka from the Serov

Formation, collected by our team in 2019 near the city of Kamyshlov, in the outcrops along the Reutinka River (Sverdlovsk Region). These samples later became the subject of biosedimentological research (Trubin, Yan, 2020). Within the dark-gray opoka matrix, channel-like inclusions of light-gray and cream-colored opoka are distinctly visible (see photographs from Trubin, Yan, 2020, and Figure 2). The light-colored opoka inclusions within the darker host opoka matrix were interpreted as burrow systems of *Thalassinoides* (Ehrenberg, 1944), most closely resembling the ichnogenus *Thalassinoides suevicus*. These burrows are filled with light opoka exhibiting a lepispheric texture, within which relics of diatom valves, as well as plate-like and flaky aggregates of clay minerals, are observed.

The enclosing rock surrounding the burrows is a "typical" dark opoka composed of a structureless silica mass. Evidence presented in Clayton (1984) supports the connection between the formation of siliceous deposits and animal burrows, as these burrows facilitate silica precipitation and contribute to elevated concentrations of dissolved silica DSi within the channels, creating conditions favorable for the formation of opal-CT in lepispheric textures. However, this phenomenon has only recently been discussed in greater detail. Meysman and Montserrat (2017) described it as a "benthic weathering engine," suggesting that organisms can accelerate mineral dissolution and act as catalysts for alkalinization. According to this approach, the contrasting lithologies and colors observed in the opoka layers we studied are formed under variable conditions and are also the result of intense bioturbation.

Conclusion

This study has thoroughly examined the key challenges encountered in the investigation of opoka. Addressing the issues raised in this work lies in the unification and agreement of methodological approaches with international practices, particularly for those rock formations for which detailed genetic models already exist. The integration of these models with the extensive factual data on the mineralogy and structural-textural characteristics of opoka, gathered by domestic researchers, will bring us closer to understanding of their genesis and evolution. The validation of existing genetic models is particularly recommended for the Cretaceous deposits of Western Siberia, such as the Lower Berezovskaya Formation, where the section is composed of siliceous rocks. Continued research into the relationships, genesis, and other parameters of these sedimentary rocks from various interpretative perspectives will further enhance our understanding.

The available data indicate both the initial determination of many mineral composition parameters and the disproportionate contribution of individual factors to the evolution of opoka formations. These factors include:

1) the source of silica;

2) the role of siliceous biota in mobilizing silica for further rock formation;

3) the nature and volume of terrigenous input from adjacent landmasses;

4) the extent of secondary alterations, among others.

Determining the nomenclature of rocks remains critical due to uncertainties related to the diverse and highly debated synonyms for sedimentary rocks, particularly those with negligible carbonate content and primarily composed of silica minerals (such as chert, flint, and opoka). In the classification system proposed by Polish scientists, rocks are still referred to as "opoka" if they are predominantly composed of calcite with a strongly dominated OCT-phase content.

In general, addressing the question of the immediate source of DSi for the formation of opoka requires consideration of the fact that silicifiers absorb DSi from seawater enriched with silica of volcanic, hydrothermal, and oceanic (upwelling) origins. Existing analytical methods for diagnosing biogenic, volcanic, or hydrothermal sources of silica are primarily based on the analysis of stable oxygen and silicon isotopes, as well as the elemental composition of silica. These methods are applicable to primary silica polymorphs (such as opal-A) but are less effective for opal-CT, which undergoes transformation during diagenesis. Phase transitions in silica can alter the original isotopic composition and the elemental composition of newly formed silica polymorphs. Exploring these mechanisms to determine the primary nature of silica sources appears to be a promising approach.

Acknowledgements

The study was supported by the grant from the Russian Science Foundation 22-77-00056.

The author expresses his sincere gratitude to A.O. Konstantinov for help with illustrations.

The author expresses his deep gratitude for professional advice and assistance in the selection of literature to my colleague, Agata Jurkowska from Stanisław Staszic Academy of Mining and Metallurgy in Krakow (Poland), cooperation with whom in terms of studying opoka rocks was extremely fruitful and without whose professional advice this work would not take place.

References

Akhlestina E.F., Ivanov, A.V. (2000). Atlas of Cretaceous and Paleogene siliceous rocks of the Volga region. Saratov, 166 p. (In Russ.)

Akhlestina E.F., Ivanov, A.V. (2002). Silica accumulation models in the sea basins of the Lower Volga region. *Izvestiya of Saratov University*, 2(2), pp. 91–95. (In Russ.)

Aleksandrova G.N., Oreshkina T.V., Iakovleva A.I., Radionova, E.P. (2012). Late Paleocene-Early Eocene diatoms and dinocysts from biosiliceous facies of the middle Trans-Urals region. *Stratigraphy and Geological Correlation*, 20(4), pp. 380–404. https://doi.org/10.1134/S0869593812030021

Amon E.O. (2018). Factors and conditions for the accumulation of biogenic silicites in the Paleogene basin of Western Siberia. *Byulleten' Moskovskogo obshchestva ispytatelei prirody = Bulletin of the Moscow Society of Natural Scientists*, 93(4), pp. 51–67. (In Russ.)

Arkhangelsky A.D. (1912). Upper Cretaceous deposits of Eastern European Russia. St.Petersburg, 631 p. (In Russ.)

Balzer W., Erlenkeuser H., Hartmann M., Müller P.J., Pollehne, F. (1987). Diagenesis and exchange processes at the benthic boundary layer. Rumohr J., Walger E., Zeitschel B. (Eds.). *Seawater-Sediment Interactions in Coastal Waters*. Berlin, Springer, pp. 111–161. https://doi.org/10.1029/LN013p0111

Barton D.C. (1918). Notes on the Mississippian chert of St. Louis area. *The Journal of Geology*, 26(4), pp. 361–374.

Berger W.H., von Rad U. (1972). Cretaceous and Cenozoic sediments from the Atlantic Ocean. *Initial Reports of the Deep Sea Drilling Project*, 14, pp. 787–954.

Bojanowski M.J., Dubicka Z., Minoletti F., Olszewska-Nejbert D., Surowski M. (2016). Stable C and O isotopic study of the Campanian chalk from the Mielnik section (Eastern Poland): signals from bulk rock, belemnite. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 465, pp. 193–211. https://doi.org/10.1016/j.palaeo.2016.10.032

Bramlette M.N. (1946). The Monterey Formation of California and the origin of its siliceous rocks: Professional Paper 212. Washington, DC: USGS, 57 p. https://doi.org/10.3133/pp212

Brindley G.W. (1980). Quantitative X-ray analysis of Clays. Brindley G.W., Brown G. (Eds.). *Crystal Structures of Clay Minerals and Their X-ray Identification*. London: Mineralogical Society, pp. 411–438.

Brodskaya N.G. (1966). About three genetic types of siliceous rocks in geosynclinal formations in book: Geochemistry of silicon. Moscow: Nauka, pp. 394–401. (In Russ.)

Bromley R.G. (1975). Trace fossils at omission surfaces. Frey R.W. (Ed.). *The Study of Trace Fossils*. Berlin, Heidelberg: Springer, pp. 399–428. https://doi.org/10.1007/978-3-642-65923-2_18

Cady S.L., Wenk H.R., Downing K.H. (1996). HRTEM of microcrystalline opal in chert and porcelanite from the Monterey Formation California. *American Mineralogist*, 81(11–12), pp. 1380–1395. https://doi.org/10.2138/am-1996-11-1211

Calvert S.E. (1975). Deposition and diagenesis of silica in marine sediments. Hsü K.J., Jenkyns H.C. (Eds.). *Pelagic Sediments: On Land and under the Sea*, pp. 273–299. https://doi.org/10.1002/9781444304855.ch12

Calvert S.E. (1977). Mineralogy of silica phases in deep-sea cherts and porcelanites. *Philosophical Transactions for the Royal Society of London. Series A, Mathematical and Physical Sciences*, 286, pp. 239–252.

Clayton C.J. (1984). The Geochemistry of Chert Formation in Upper Cretaceous Chalk: PhD Thesis. London: King's College London, 394 p.

Clayton C.J. (1986). The chemical environment of flint formation in Upper Cretaceous Chalks. *The Scientific Study of Flint and Chert: Proc. of the Fourth Int. Flint Symposium Held at Brighton Polytechnic*. Cambridge: Cambridge Univ. Press, pp. 43–54.

Conley D.J., Frings P.J., Fontorbe G., Clymans W., Stadmark J., Hendry K.R., Marron A.O., De La Rocha, C.L. (2017). Biosilicification drives a decline of dissolved Si in the oceans through geologic time. *Frontiers in Marine Science*, 4, 397. https://doi.org/10.3389/fmars.2017.00397

Curtis C.D., Coleman M.L., Love L.G. (1986). Pore water evolution during sediment burial from isotopic and mineral chemistry of calcite, dolomite and siderite concretions. *Geochimica et Cosmochimica Acta*, 50(10), pp. 2321–2334. https://doi.org/10.1016/0016-7037(86)90085-2

Curtis N.J., Gascooke J.R., Johnson M.R., Pring A. (2019). A review of the classification of opal with reference to recent new localities. *Minerals*, 9(5), 299. https://doi.org/10.3390/min9050299

Curtis, N.J., Gascooke, J.R., Pring, A. (2021). Silicon-Oxygen Region Infrared and Raman Analysis of Opals: The Effect of Sample Preparation and Measurement Type. *Minerals*, 11, p. 173. https://doi.org/10.3390/min11020173

Distanov U.G. (1976). Siliceous rocks of USSR. Kazan, 411 p. (In Russ.)

Elzea J.M., Rice S.B. (1996). Tem and X-ray diffraction evidence for christobalite and tridymite stacking sequences in opal. *Clays and Clay Minerals*, 44, pp. 492–500. https://doi.org/10.1346/CCMN.1996.0440407

Fabricius I.L. (2007). Chalk: composition, diagenesis and physical properties. *Bulletin of the Geological Society of Denmark*, 55, pp. 97–128.

Faÿ-Gomord O., Descamps F., Tshibangu J.-P., Vandycke S., Swennen R. (2016). Unraveling chalk microtextural properties from indentation tests. *Engineering Geology*, 209, pp. 30–43. https://doi.org/10.1016/j.enggeo.2016.05.005

Flörke O.W. (1955). Zur frage des "Hoch-Cristobalit" in Opalen, Bentoniten and Glasern. *Neues Jahbruch für Mineralogie (Abhandlungen)*, 149, pp. 523–336.

Flörke O.W., Graetsch H., Martin B., Röller K., Wirth R. (1991). Nomenclature of micro- and non-crystalline silica minerals, based on structure and microstructre. *Neues Jahrbuch für Mineralogie (Abhandlungen)*, 163, pp. 19–42.

Frings P.J., Clyman W., Fontorbe G., De La Rocha Ch.L., Conley D.J. (2016). The continental Si cycle and its impact on the ocean Si isotope budget. *Chemical Geology*, 425, 12–36. https://doi.org/10.1016/j.chemgeo.2016.01.020

Frondel C. (1962). The system of mineralogy of James Dwight Dana and Edward Salisbury Dana, Yale University, 1837–1892, Vol. Ill: The Silica Minerals. N. Y., London: Wiley, 346 pp.

Gao P., S Lib S., Lashc G.G., Hed Z., Xiao X., Zhang D., Hao Y. (2020). Silicification and Si cycling in a silica-rich ocean during the Ediacaran-Cambrian transition. *Chemical Geology*, 552, 119787. https://doi.org/10.1016/j.chemgeo.2020.119787

Generalov P.P., Drozhashchikh N.B. (1987). Eocene opalites of Western Siberia. In: Opalite of Western Siberia. Tyumen, pp. 3–10. (In Russ.)

Graetsch H., Gies H., Topalović I. (1994). NMR, XRD, and IR study on microcrystalline opals. *Physics and Chemistry of Minerals*, 21, pp. 166–175. https://doi.org/10.1007/BF00203147

Grechin V.I. (1971). Miocene siliceous rocks of Western Kamchatka. *Litologiya i poleznye iskopaemye = Lithology and minerals*, (4), pp. 117–123. (In Russ.)

Hesse R., Schacht U. (2011). Chapter 9 – Early diagenesis of deep-sea sediments. In: Deep-Sea Sediments. HüNeke H., Mudler T. (Eds.). *Developments in Sedimentology.* V. 63. Amsterdam: Elsevier, pp. 557–713. https://doi.org/10.1016/B978-0-444-53000-4.00009-3

Hesse R., Schacht U. (2011). Early diagenesis of deep-sea sediments. In: Deep-Sea Sediments. *Developments in Sedimentology* (Eds. Hüneke, H., Mudler, T.), 63. Elsevier, Amsterdam, pp. 557–713.

Hurcewicz H. (1968). Siliceous sponges from the Upper Cretaceous of Poland; Part II, Monaxonia and Triaxonia. *Acta Palaeonologica Polonica*, 13, pp. 3–9.

Il'icheva O.M. (2013). Structural state and transformation of silica forms in siliceous and zeolite-containing carbonate-siliceous rocks. Cand. Geol. and Mineral. Sci. Diss. Kazan, 155 p. (In Russ.)

Jones B. (2021). Siliceous sinters in thermal spring systems: review of their mineralogy, diagenesis, and fabrics. *Sedimentary Geology*, 413, 105820. https://doi.org/10.1016/j.sedgeo.2020.105820

Jones J.B., Segnit, E.R. (1971). The nature of opal. I. Nomenclature and constituent phases. I. Nomenclature and constituent phases. *Journal of the Geological Society of Australia*, 18(1), pp. 57–68. https://doi.org/10.1080/00167617108728743

Jurkowska A. (2016). Inoceramid stratigraphy and depositional architecture of the Miechów Synclinorium (Southern Poland). *Acta geologica Polonica*, 66(1), pp. 59–84. https://doi.org/10.1515/agp-2015-0025

Jurkowska A. (2022). The biotic-abiotic control of Si burial in marine carbonate systems of the pre-Eocene Si cycle. *Global Biogeochemical Cycles*, 36, e2021GB007079. https://doi.org/10.1029/2021GB007079

Jurkowska A., Barski M., Worobiec E. (2019b). The relation of the coastal environment to early diagenetic clinoptilolite (zeolite) formation – New data from the Late Cretaceous European Basin. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 524, pp. 166–182. https://doi.org/10.1016/j.palaeo.2019.03.025

Jurkowska A., Świerczewska-Gładysz E. (2020a). New model of Si balance in the Late Cretaceous epiconinental European Basin. *Global and Planetary Change*, 186, 103108. https://doi.org/10.1016/j.gloplacha.2019.103108

Jurkowska A., Świerczewska-Gładysz E. (2020b). Evolution of Late Cretaceous Si cycling reflected in formation of siliceous nodules (flints and cherts). *Global and Planetary Change*, 195, 103334. https://doi.org/10.1016/j.gloplacha.2020.103334

Jurkowska A., Świerczewska-Gładysz E. (2022). Opoka – a mysterious carbonate-siliceous rock: an overview of general concepts. *Geology, Geophysics and Environment*, 48(3), pp. 257–278. https://doi.org/10.7494/geol.2022.48.3.257

Jurkowska A., Świerczewska-Gładysz E., Bąk M., Kowalik S. (2019a). The role of biogenic silica in formation of Upper Cretaceous pelagic carbonates and its paleoecological implications. *Cretaceous Research*, 93, pp. 170–187. https://doi.org/10.1016/j.cretres.2018.09.009

Kastner M., Keene J.B., Gieskes J.M. (1977). Diagenesis of siliceous oozes. – I. Chemical controls on the rate of opal-A to opal-CT transformation – an experimental study. *Geochimica et Cosmochimica. Acta*, 41(8), pp. 1041–1059. https://doi.org/10.1016/0016-7037(77)90099-0

Kazarinov V.P. (1958). Mesozoic and Cenozoic deposits of Western Siberia. Moscow, 322 p. (In Russ.)

Kazarinov V.P., Bgatov V.I., Gurova T.N. et al. (1969). Weathering and lithogenesis. Moscow: Nedra, 456 p. (In Russ.)

Keller M.A., Isaacs C.M. (1985). An evaluation of temperature scales for silica diagenesis in diatomaceous sequences including a new approach based on the Miocene Monterey Formation, California. *Geo-Marine Letters*, 5, pp. 31–35. https://doi.org/10.1007/BF02629794

Kidder D.L., Erwin D.H. (2001). Secular distribution of biogenic silica through the Phanerozoic: Comparison of silica-replaced fossils and bedded cherts at the series level. *The Journal of Geology*, 109(4), pp. 509–522.

Kitchell J.A., Clark D.L. (1982). Late Cretaceous–Paleogene paleogeography and paleocirculation: Evidence of north polar upwelling. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 40(1–3), pp. 135–65. https://doi.org/10.1016/0031-0182(82)90087-6

Krasny L.I., Zhamoyda A.I., Moiseeva A.I. (1962). On the relationship of the development of organisms with a silicon skeleton (radiolarians and diatoms) with tectonic and volcanic processes (on the example of the northwestern part of the Pacific belt). *Significance of the biosphere in geological processes: Questions of the relationship between paleontology and tectonics: Coll. papers*. Moscow, pp. 171–182. (In Russ.)

Lancelot Y. (1973). Chert and Silica Diagenesis in Sediments from the Central Pacific. *Deep Sea Drilling Project Reports and Publications*, Vol. 17, pp. 377–405.

Landmesser M. (1995). Mobilität durch Metastabilität: SiO_2 Transport und Akkumulation beiniedrigen Temperaturen. *Chemie der Erde*, 55(3), pp. 149–176.

Lindgreen H., Jakobsen F. (2012). Marine sedimentation of nano-quartz forming flint in North Sea Danian chalk. *Marine and Petroleum Geology*, 38(1), pp. 73–82. https://doi.org/10.1016/j.marpetgeo.2012.08.007

Lynne B.Y., Campbell K.A. (2004). Morphologic and mineralogic transitions from opal-A to opal-CT in low-temperature siliceous sinter diagenesis, Taupo Volcanic Zone, New Zealand. *Journal of Sedimentary Research*, 74, pp. 561-579. https://doi.org/10.1306/011704740561

Lynne B.Y., Campbell K.A., James B.J., Browne P.R.L., Moore J. (2007). Tracking crystallinity in siliceous hot-spring deposits. *American Journal of Science*, 307(3), pp. 612–641. https://doi.org/10.2475/03.2007.03

Machalski M., Malchyk O. (2016). Classic palaeontological sites in the Upper Cretaceous of western Ukraine: History of research and biostratigraphy. *Przeglad Geologiczny*, 64(8), pp. 570–576.

Mackenzie F.T., Gees R. (1971). Quartz: Synthesis at earth-surface conditions. *Science*, 173, pp. 533–535. https://doi.org/10.1126/science.173.3996.533

Madsen H.B., Stemmerik L. (2010). Diagenesis of flint and porcellanite in the Maastrichtian Chalk at Stevns Klint, Denmark. *Journal of Sedimentary Research*, 80(6), pp. 578–588. https://doi.org/10.2110/jsr.2010.052

Malchyk O., Machalski M., Waksmundzki B., Duda, M. (2017). Shell ornament, systematic position and hatching size of *Epicymatoceras vaelsense* (Nautilida): New insights based on specimens in mould preservation from the Upper Cretaceous of Poland. *Cretaceous Research*, 80, pp. 1–12. https://doi.org/10.1016/j.cretres.2017.08.006

Maliva R.G., Siever R. (1989). Nodular chert formation in carbonate rock. *The Journal of Geology*, 97(4), pp. 421–433.

Meister P., Chapligin B., Picard A., Meyer H., Fischer C., Rettenwander D., Amthauer G., Vogt Ch., Aiello I.W. (2014). Early diagenetic quartz formation at a deep iron oxidation front in the Eastern Equatorial Pacific – A modern analogue for banded iron/chert formations? *Geochemica et Cosmochimica Acta*, 137, pp. 188–207. https://doi.org/10.1016/j.gca.2014.03.035

Middleton H.A., Nelson C.S. (1996). Origin and timing of siderite and calcite concretions in late Palaeogene non- to marginal-marine facies of the Te Kuiti Group, New Zealand. *Sedimentary Geology*, 103(1–2), pp. 93–115. https://doi.org/10.1016/0037-0738(95)00092-5

Minde M.W., Wang W., Madland M.V., Zimmermann U., Korsnes R.I., Bertolino S.R.A., Andersen P.Ø. (2018). Temperature effects on rock engineering properties and rock-fluid chemistry in opal-CT-bearing chalk. *Journal of Petroleum Science and Engineering*, 169, pp. 454–470. https://doi.org/10.1016/j.petrol.2018.05.072

Morey G.W., Fournier R.O., Rowe J.J. (1962). The solubility of quartz in water in the temperature interval from 25° to 300° C. *Geochimica et Cosmochimca Acta*, 26(10), pp. 1029–1043. https://doi.org/10.1016/0016-7037(62)90027-3

Muraviev V.I. (1983). Mineral Parageneses of Glauconite-Siliceous Formations. Moscow, 218 p. (In Russ.)

Nesterov I.I., Smirnov P.V., Konstantinov A.O., Gursky H.-J. (2021). Types, features, and resource potential of Palaeocene–Eocene siliceous rock deposits of the West Siberian Province: A review. *International Geology Review*, 63(4), pp. 504–525, https://doi.org/10.1080/00206814.2020.1719370

Oehler J.H. (1975). Origin and distribution of silica lepispheres in porcelanite from the Monterey Formation of California. *Journal of Sedimentary Research*, 45(1), pp. 252–257. https://doi.org/10.1306/212F6D25-2B24-11D7-8648000102C1865D

Penman D.E. (2016). Silicate weathering and North Atlantic silica burial during the Paleocene–Eocene Thermal Maximum. *Geology*, 44(9), pp. 731–734. https://doi.org/10.1130/G37704.1

Peryt D. (2000). O wieku opok z Piotrawina nad Wisłą, Polska Środkowa. *Biuletyn Państwowego Instytutu Geologicznego*, 393, pp. 81–94.

Pomerol B., Aubry M.B. (1977). Relation between Western European chalks and opening of the North Atlantic. *Journal of Sedimentary Research*, 47(3), pp. 1027–1035. https://doi.org/10.1306/212F72CF-2B24-11D7-8648000102C1865D

Pożaryska K. (1952). The sedimentological problems of Upper Maastrichtian and Danian of the Pulawy Environment (Middle Vistula). *Biuletyn Panstwowego Instytutu Geologicznego*, 81, pp. 1–104.

Pożaryski W. (1960). An outline of stratigraphy and palaeogeography of the Cretaceous in the Polish Lowland. *Prace Instytutu Geologicznego*, 30, pp. 377–418.

Pusch G.G. (1833). Geognostische Beschreibung von Polen, so wie der übrigen Nordkarpathen–Länder. Stuttgart; Tübingen: J.G. Cotta'schen Buchhandlung, T. 1, 358 S.

Pusch G.G. (1836). Geognostische Beschreibung von Polen, so wie der übrigen Nordkarpathen–Länder. Stuttgart; Tübingen: J.G. CCotta'sche Buchhandlung, T. 2, 707 S.

Racki G., Cordey F. (2000). Radiolarian palaeoecology and radiolarites: is the present the key to the past? *Earth-Science Reviews*, 52(1–3), pp. 83–120. https://doi.org/10.1016/S0012-8252(00)00024-6

Remin Z. (2018). Understanding coleoid migration patterns between eastern and western Europe e belemnite faunas from the upper lower Maastrichtian of Hrebenne, Southeast Poland. *Cretaceous Research*, 87, pp. 368–384. https://doi.org/10.1016/j.cretres.2017.06.010

Riech V., von Rad U. (1979). Eocene porcellanites and Early Cretaceous cherts from the Western North Atlantic Basin. *Initial Report of Deep-Sea Drilling Project*, 43, pp. 437–455.

Rodgers K.A., Browne P.R.L., Buddle T.F., Cook K.L., Greatrex R.A., Hampton W.A., Herdianita, N.R., Holland G.R., Lynne B.Y., Martin R., Newton Z., Pastars, D., Sannazarro, K.L., Teece, C.I.A. (2004). Silica phases in sinters and residues from geothermal fields of New Zealand. *Earth Science Review*, 66(1–2), pp. 1–61. https://doi.org/10.1016/j.earscirev.2003.10.001

Rutkowski J. (1965). Senonian in the area of Miechów, southern Poland. *Rocznik Polskiego Towarzystwa Geologicznego*, 35, pp. 3–53.

Samoilov Ya.V., Rozhkova E.V. (1925). Deposits of silica of organogenic origin (siliceous bioliths – silicobiolites). Moscow, p. 71. (In Russ.)

Senkovsky Ju.N. (1977). Lithogenesis of the siliceous strata of the southwestern USSR. Kiev: Naukova dumka, 128 p. (In Russ.)

Shumenko S.I. (1978). Nanopetrography of tripolite and opoka in connection with the issue of their genesis. *Doklady Academy of Sciences*, 240(2), pp. 427–430. (In Russ.)

Sidorenkov, A.I., Zarubko N.S., Samoshkin A.A. (1985). Model of the mechanism of formation of tripolite and opoka. *Complex development of mineral resources of Western Siberia*. Tyumen: ZapSibNIGNI, pp. 46–63. (In Russ.)

Siemiradzki J. (1905). O utworach górnokredowych w Polsce. *Kosmos*, 30, pp. 471–492.

Siever R. (1991). Silica in the oceans: Biological-geochemical interplay. Schneider S.H., Boston P.J. (Eds.). *Scientists on Gaia*. Cambridge, MA: MIT Press, pp. 287–295.

Smirnov P.V., Konstantinov A.O. (2017). Biogenic siliceous accumulation in Early Paleogene marine basins of Western Siberia: Factors and stages. *Litosfera*, 17(4), pp. 26–47. (In Russ.)

Smirnov P.V., Konstantinov A.O., Gursky H.-J. (2017). Petrology and industrial application of main diatomite deposits in the Transuralian region (Russian Federation). *Environmental Earth Science*s, 76, 682.

Smirnov, P.V. (2017). Preliminary results of revision of mineral-raw material base of opal-cristobalite rocks in middle Trans-urals). *Bulletin of the Tomsk Polytechnic University: Geo Assets Engineering*, 328, pp. 28–37. (In Russ.)

Smith D.K. (1998). Opal, cristobalite and tridymite: Noncrystallinity versus crystallinity, nomenclature of the silica minerals and bibliography. *Powder Diffraction*, 13(1), pp. 2–19. https://doi.org/10.1017/S0885715600009696

Smoleński J. (1906). Dolny senon w Bonarce. 1. Głowonogi i inoceramy. *Rozprawy Wydziału Matematyczno-Przyrodniczego Akademii Umiejętności, Seryi B*, 46, 47 p.

Strakhov N.M. (1963). Types of lithogenesis and their evolution in the history of the Earth. Moscow, 536 p. (In Russ.)

Strakhov N.M. (1965). Problems of sedimentary rock formation in the coverage of V.P. Kazarinov. *Lithology and mineral resources*, 6, pp. 91–105. (In Russ.)

Strelchyk N.V. (2004). Peculiarities of composition and formation of upper cretaceous carbonate-siliceous rocks of the Stalnoye deposit in the east of Belarus. *Litasfera,* 1(20), pp. 69–76. (In Russ.)

Sujkowski Z. (1926). Sur le Jurassique, le Cretace' et le Quaternaire des environs de Wolbrom. *Sprawozdania Polskiego Instytutu Geologicznego*, 3, pp. 382–467.

Sujkowski Z. (1931). Petrografia kredy Polski. Kreda z głębokiego wiercenia w Lublinie w porównaniu z kredą niektórych innych obszarów Polski. *Sprawozdania Państwowego Instytutu Geologicznego*, 6, pp. 485–628.

Tarr W.A. (1917). Origin of chert in the Burlington Limestone. *American Journal of Sciences*, 44, pp. 409–452.

Tréguer P.J., Sutton J.N., Brzezinski M., Charette M.A., Devries T., Dutkiewicz S., Ehlert C., Hawkings J., Leynaert A., Liu S.M., Llopis Monferrer N., López-Acosta M., Maldonado M., Rahman S., Ran L., Rouxel O. (2021). Reviews and syntheses: The biogeochemical cycle of silicon in the modern ocean. *Biogeosciences*, 18, pp. 1269–1289. https://doi.org/10.5194/bg-18-1269-2021

Trubin Ya.S., Yan P.A. (2020). Fossil burrows of Thalassinoides in the opoks of the Serov Formation (Middle Trans-Urals, Upper Paleocene). *Bulletin of the Tomsk Polytechnic University: Geo Assets Engineering*, 331(6), pp. 32–40. (In Russ.) https://doi.org/10.18799/24131830/2020/6/2672

Tsekhovsky Y.G. (2015a). Sedimentogenesis and geodynamics in the Cretaceous-Paleogene boundary at the epoch of continental peneplanation. Article 1. Central and Eastern Eurasia. *Litosfera*, 1, pp. 5–23. (In Russ.)

Tsekhovsky Y.G. (2015b). Sedimentogenesis and geodynamics in the Cretaceous-Paleogene boundary at the epoch of continental peneplanation. Article 2. Platforms and mobile belts. *Litosfera*, 2, pp. 5–16. (In Russ.)

Tsekhovsky Y.G. (2017a). The participation of volcanism and hydrothermal in platform sedimentation of the boundary Cretaceous-Paleogene era of destructive tectogenesis in Central Eurasia. Article 1. Paleogeography, products of volcanism and hydrothermal activity. *Bulletin of Moscow Society of Naturalists. Geological series*, 92(4), pp. 34–48. (In Russ.)

Tsekhovsky Y.G. (2017b). The participation of volcanism and hydrothermal in platform sedimentation of the boundary Cretaceous-Paleogene era of destructive tectogenesis in Central Eurasia. Article 2. features of platform sedimentation. *Bulletin of Moscow Society of Naturalists. Geological series*, 92(6), pp. 3–13. (In Russ.)

Ushatinskii I.N. (1987). Composition and formation conditions of silica formations of West Siberia syneclise, in West Siberian opalites. Tyumen: ZapSibNIGNI, pp. 39–48. (In Russ.)

Ushatinskii I.N., Gavrilova L.M. (1985). Material composition and silica phases of siliceous rocks on Cenozoic and Mezozoic of Western Siberia. Complex development of mineral resources of Western Siberia. Tyumen: ZapSibNIGNI, 197, pp. 10–15. (In Russ.)

Volokhin Yu.G. (2013). Mesozoic and Cenozoic silica accumulation in the marginal basins of eastern Asia. Vladivostok: Dal'nauka, 434 p. (In Russ.)

Wetzel A., Allia V. (2000). The significance of hiatus beds in shallow-water mudstones: An example from the Middle Jurassic of Switzerland. *Journal of Sedimentary Research*, 70(1), pp. 170–180. https://doi.org/10.1306/2DC40908-0E47-11D7-8643000102C1865D

Williams L.A., Crerar D.A. (1985). Silica diagenesis; II. General mechanisms. *Journal of Sedimentary Research*, 55(3), pp. 312–321. https://doi.org/10.1306/212F86B1-2B24-11D7-8648000102C1865D

Williams L.A., Parks G.A., Crerar D.A. (1985). Silica diagenesis; I. Solubility controls. *Journal of Sedimentary Research*, 55(3), pp. 301–311. https://doi.org/10.1306/212F86AC-2B24-11D7-8648000102C1865D

Wise S.W. Jr., Kelts K.R. (1972). Inferred diagenetic history of a weakly silicified deep-sea chalk. *Gulf Coast Association of Geological Societies Transactions*, 22, pp. 177–203.

Wise S.W. Jr., Weaver F.M. (1974). Chertification of oceanic sediments. *Hsü, K.J., Jenkyns, H.C. (Eds.) Pelagic Sediments: On Land and under the Sea.* Int. Assoc. Sedimentolog., Spec. Publ., 1, pp. 301–326. https://doi.org/10.1002/9781444304855.ch13

Yool A., Tyrrell T. (2003). Role of diatoms in regulating the ocean's silicon cycle. *Global Biogeochemical Cycles*, 17(4), 1103. https://doi.org/10.1029/2002gb002018

Zejszner L. (1847). Ogniwa formacji kredy, czyli opoki Wyżyny Krakowskiej. *Przegląd Naukowy*, 1(7), s. 191–201; 1(8), pp. 223–234.

Zijlstra J.J.P. (1987). Early diagenetic silica precipitation, in relation to redox boundaries and bacterial metabolism in late Cretaceous chalk of the Maastrichtian type locality. *Geologie en Mijnbouw*, 66, pp. 343–355.

Zjilstra J.J.P. (1994). Sedimentology of the Late Cretaceous and Early Tertiary (Ttuffaceous) Chalk of Northwest Europe. *Geologica Ultraiect*, 119, pp. 1–192.

Zorina S.O., Afanas'eva, N.I. (2015). "Camouflaged" pyroclastic material in the Upper Cretaceous-Miocene deposits of the southeastern East European Craton. *Dokl. Earth Sc.,* 463, pp. 770–772. https://doi.org/10.1134/S1028334X15080085

Zorina S.O., Afanas'eva N.I., Zhabin A.V. (2012). Traces of pyroclastics in Santonian-Campanian deposits ("Vishnevoje" section, the Middle Volga). *Litosfera*, 3(3), pp. 3–13. (In Russ.)

About the Author

Pavel V. Smirnov – Cand. Sci. (Geology and Mineralogy), Leading Researcher, Tyumen Scientific Center of the Siberian Branch of the Russian Academy of Sciences

86, Malygina st., Tyumen, 625026, Russian Federation
e-mail: geolog.08@mail.ru

Manuscript received 14 June 2023;
Accepted 14 February 2024;
Published 30 June 2024

IN RUSSIAN

Опоки: полиморфный состав, генезис и проблемы их изучения

П.В. Смирнов[1,2]
[1]Тюменский научный центр СО РАН, Тюмень, Россия
[2]Казанский федеральный университет, Казань, Россия
e-mail: geolog.08@mail.ru

В работе дан комплексный обзор, посвященный актуальным вопросам изучения опок – морских осадочных кремневых пород мелового-палеогенового возраста. За почти двухсотлетнюю историю изучения этих осадочных образований сам термин «опока» не получил должного признания из-за отсутствия подробного минералогического определения и общего несовершенства систематики кремневых горных пород. Отличительной чертой опок является наличие леписфер опала-СТ, которые образуют узнаваемый каркас кремниевой породы или формируют неясно леписферную/скрытокристаллическую массу. Описана история изучения опок, перечислены номенклатуры, использующиеся для их классификации, охарактеризованы минералогический состав, микроструктура и микротекстура, распространение мел-палеогеновых опок и др. Критически рассмотрены этимология генезиса опоки и модели ее происхождения на ранней и поздней стадиях диагенеза. В обзоре особое внимание уделено недавним исследованиям, в результате которых установлены типы полиморфных форм кремнезема, встречающихся в опоке, а также его характерная микроструктура. Представлена модель генезиса опок с учетом взаимосвязи с глобальными процессами, включая биогеохимический круговорот кремния. Различия, фиксируемые в опоках разного возраста и геолого-тектонической позиции, указывают как на заданность многих параметров минерального состава изначально, так и на несоразмерность вклада отдельных факторов в эволюцию опоковых пород, а именно источника кремнекислоты, роли кремнистого биоса в мобилизации кремнекислоты для дальнейшего породообразования, характера и объема терригенного сноса с прилегающей суши, масштаба вторичных изменений и др.

Ключевые слова: опока, силициты, опал-СТ, опал, кристобалит, кремниевые породы, цикл кремнезема, Зауралье

Для цитирования: Смирнов П.В. (2024). Опоки: полиморфный состав, генезис и проблемы их изучения. *Георесурсы,* 26(2), с. 135–154. https://doi.org/10.18599/grs.2024.2.1