

Article

Silification of the Mesozoic Rocks Accompanying the Bełchatów Lignite Deposit, Central Poland

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Abstract: Fieldwork and exploratory study of Poland's Bełchatów lignite deposit reveals that the Jurassic and Cretaceous sediments with overlying Neogene clays include rocks of greater hardness than the primary composition would indicate. Mineralogical and petrographic tests show the impact of secondary mineralization involving silification in particular. Transitional and carbonate rocks observed microscopically and subjected to X-ray examination show numerous polymorphic forms of silica replacing carbonate minerals. Opal types A and CT, chalcedony, quartz and microcrystalline quartz are all present. The process of silification observed is a selective and multistage one, with selective activity entailing the displacement and replacement of carbonates from older rocks, mainly Cretaceous opoka-rocks and marls, and Jurassic limestones. The opal fills tectonic fractures and has cemented cracked grains. Cathodoluminescence analysis identifies several generations of silica. The rocks have undergone advanced diagenesis as is evidenced by the recorded metasomatic reactions between minerals. They can further be assumed to be in the locomorphic stage. Such observations are relevant to efforts to reconstruct the origin of the rock matrix, and to the study of its textural features. In addition, the tests run on rocks of the lignite series would seem to be of significant value in identifying and developing associated rocks.

Keywords: cristobalite; opal; raw materials; diagenesis; Neogene–Mesozoic contact zone

1. Introduction

Silification is an allochemical diagenetic process in which solutions enriched with Si ions, usually in the form of silicic acid (H_4SiO_4), suppress calcite, aragonite and dolomite in carbonate rocks with opal, chalcedony or low-temperature quartz and dissolved carbonate species (e.g., Ca-hydrogen carbonate) [1]. Factors controlling silification are those that influence the dissolution/precipitation process, i.e., shell mineralogy and ultrastructure (and therefore surface area), the amount and location of organic matter, and the nature of the enclosing matrix. Silification, like all types of fossilization, can produce taphonomic biases; it is far more common in Paleozoic than younger deposits, and is more likely to occur where organisms had low-magnesium calcite shells, in carbonate sediments, and in environments with elevated dissolved silica [2]. SiO_2 (solid) actually represents a complex of crystallochemical compounds whose composition depends on the environmental conditions under which crystallization takes place. Different mineral phases in rocks can be formed. During diagenesis, silica minerals follow an opal-A, opal-CT/C microcrystalline quartz transformation [3]. The process of silification of rocks, silica stabilization in the context of the transition of opal into quartz, and the metasomatic silification of different rocks have all been discussed in the literature [4–6], while latest studies relate mainly to fossilized trees [7–10].

In Poland, lignite is mined in the Bełchatów, Konin, Turek, Turów and Sieniawa regions (Figure 1) [11–13]. The deposits there display diversity in terms of their geological forms of

occurrence [14–16], while differences also relate to age and the types of rock building the substrate, and thus the diversity of weathered deposits lying in the contact zone between the Neogene and substrate rocks. Previous studies have focused more on the geology of the lignite-mining area [17–19] than on issues viewed as marginal, since they relate to rock not mined directly. Thus, while the value of the latter aspects of geological study was never really in doubt, little actual development of research could be noted, hence an ongoing aim that more attention should finally be given to these rocks.

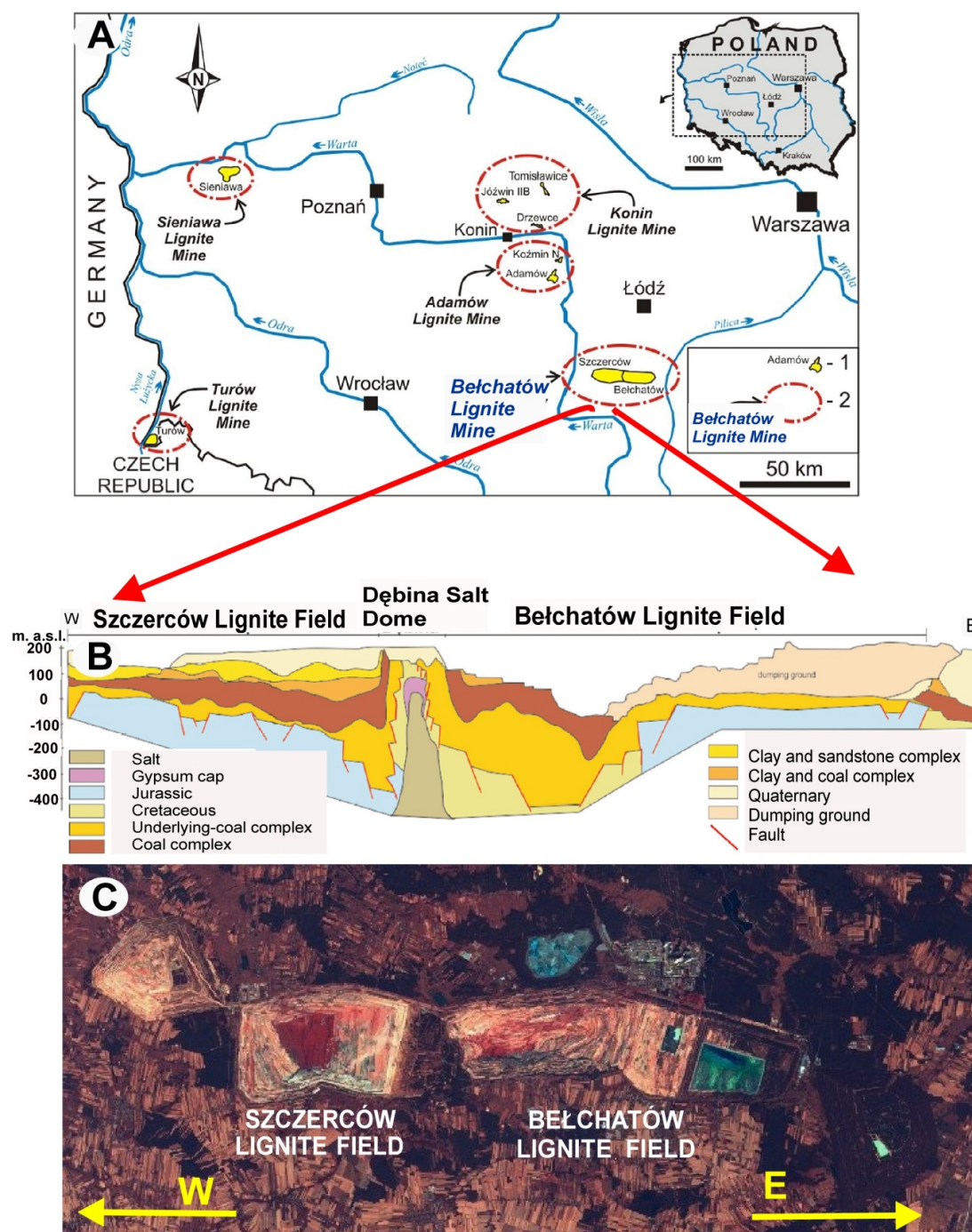


Figure 1. The Bełchatów and Szczerców deposits: (A) Map of Poland showing locations of some mined deposits [13]; (B) Cross-section through the Bełchatów lignite deposit [18]; (C) Location of the study area depicted on the color composition of a Sentinel satellite image.

Ultimately, the long-term nature of open-cast mining operations involving the Bełchatów lignite do necessitate basic, raw-material-related research on the accompanying deposits, hence this paper's presentation of the current state of knowledge of rocks in the Neogene–Mesozoic zone of contact, as well as provisioning of new information. Thus, the geological and geochemical background is first presented here, followed by the results of our own mineralogical and petrographic studies.

Presented here are indications of silification in rocks of Mesozoic substrate in which the process seemed most noticeable and significant. The sediments in question include Jurassic limestones, as well as Cretaceous marls and opoka-rocks.

2. Geological Setting

The deposits studied in the present work are located in the main fault zone bounding the deposit from the south. At the sampling site, contact between the Neogene and Mesozoic sediments is disturbed, and tectonic in nature, running along a NE–SW fault. The Mesozoic relief of the Bełchatów region, formed as a result of Laramide-age movements, underwent very strong peneplenization in the Paleogene [20]. As a result, the Cretaceous deposits in the west and southwest of the region under study were destroyed completely. The period of peneplenization probably lasted throughout the Paleogene, as no sediments of this age are found in the Bełchatów region. Only the more erosion-resistant silicified sponge and reef limestones of the Upper Jurassic were preserved from the destruction [17].

Silification is characteristic of deposits from the Neogene–Mesozoic contact zone in the area of the Bełchatów lignite deposit. The lithology and petrography of these rocks, and the nature of the genetic and diagenetic processes affecting them, have been the subject of research for years. The first examples of the presence of this type of silicified rock were identified around the town of Bełchatów at a depth of 14 meters, the geological description being as light opoka-rocks [21]. The Bełchatów lignite opencast and drilling profiles from the Szczerców field pointed to the occurrence of sediments difficult to diagnose unequivocally in a lithological, and especially a petrographic, sense. The initial reference was to “weathered rocks,” which were thought to represent a decalcified opoka enriched in Ca-beidellite [22,23]. Testing allowed for the identification of these rocks as opoka-rocks, light opoka-rocks, gaizes and marls [24].

Further research into the rocks exposed on the sub-Neogene surface of the zone of contact within the Bełchatów lignite deposit allowed a lithologically much broader group of rocks to be distinguished within the Mesozoic substrate [25]. In addition to the opoka-rocks, gaizes and marls recognized originally; limestones, diatomites, flints and sandstones were also found. In turn, sediments identified as formed through weathering included decalcified opoka-rocks, sedimentary breccias and kaolinite clays [26].

The limestones referred to (inter alia in the context of their possible use as sorbents) were classified as biomicrites and biointramicrites, with amounts of allochemical components in the 10–40 vol.% range. These are mainly represented by calcite-type bioclasts, and only less often by silica or phosphate, as well as ooids and intraclasts. The mineral composition of the limestone so characterized proves to be diverse. Besides calcite as the main phase, SiO₂ group minerals are also present, i.e., opal, chalcedony and quartz. Also identifiable are clay minerals represented mainly by kaolinite, as well as pyrite, siderite, hematite, barite, celestine, gypsum, feldspar and apatite.

The CaCO₃ content varies across a wide range, from 48.67 to 98.61 wt.% (mean 70.90 wt.%). Among other chemical components, silica reaches almost 30 wt.%, while iron and aluminum are also found [27]. Such rocks could be used to reduce SO₂ emissions in fluidized furnaces. Values noted for the reactivity index (RI)—which describes the ratio of calcium in a sample to sulfur following the sorption process (mol Ca/mol S)—are 4.47–1.55. In turn, values for the absolute sorption coefficient (CI)—which determines the amount of sulfur absorbed (in g S/1000 g sorbent)—are in the range 62–150. Such values for coefficients correspond to “excellent” to “sufficient” qualitative assessments of sorption capacity in these limestones [28].

Accompanying rocks were characterized mineralogically and geochemically [29,30], it being shown that the group of transitional rocks (opoka, gaizes and marls) have SiO_2 and CaO as their main components. Silica is present in transitional formations as opal-A, opal-CT, chalcedony, quartz and microcrystalline quartz. The calcium carbonate present also displays genetic diversity. Calcite of red and yellow luminescence has formed via secondary mineralization processes, the former being affected by diagenetic solutions rich in Fe^{2+} , the latter seen to have crystallized in conditions of Fe^{2+} deficiency—such that the share of Mn^{2+} is considerable. Research has further shown marls, gaizes, limestones and above all opoka-rocks subject to silification.

Mean cadmium concentrations are 0.55 ppm in the marls, 0.4 ppm in the opoka-rocks and 0.05 ppm in the gaizes. This relationship may reflect the status of Cd as an element highly dispersed in the rocks and mobilized readily by weathering. It goes on to bind to clay minerals, iron hydroxides and organic matter.

A matter of economic importance currently concerns the way in which the aforementioned rocks exposed during lignite mining may be utilized. Natural resources are protected where the area mined is kept in check, and economic significance arises should demand for minerals or materials made from them increase. Environmental goals can therefore be achieved, in part at least, if certain exploited rocks can be transformed into environment-friendly materials [31,32].

In general, observations of rock formations from the Mesozoic to Cenozoic transition are crucial for paleogeographic and paleoecological interpretations and correlations on a global scale. Furthermore, relevant research offers important insights into the impact of silification on primary structural and textural features, allowing for a determination of the influence of sedimentology and diagenesis on properties of the rocks studied. The recognition of changes in the primary sediment matrix is significant as the history of diagenesis is studied [33–36].

3. Materials and Methods

Samples for testing came from both the excavation of the Bełchatów lignite field and drilling cores obtained from the operational front of the Szczerców lignite field. Macroscopic study offered the basis for selecting research material. Rock hardness was most often found to be greater in the upper parts of the Jurassic and Cretaceous deposits with the overlying Neogene clays. From among the 60 samples analyzed, selection for detailed testing involved 4 samples of decalcified opoka-rock, 8 of opoka-rock samples, 6 of marl and 15 of limestone.

Mineralogical and petrographic analysis needed to be wide-ranging in terms of its methodology. An FEI Quanta 200FEG scanning electron microscope (SEM) equipped with an X-ray spectrometer (EDX Genesis) and a backscattered electron detector (BSE) were used. Observations were carried out on fresh fractures of carbon-coated samples (done with a JEE – SS Vacuum Jeol).

Microscopic observations in reflected and transmitted light accompanied by quantitative analysis were carried out using a Nikon Optiphot 2 polarizing microscope. Thin sections were used in the tests.

Mineral phases were identified using a PHILIPS X'PERT PW 3020 X-ray diffractometer using Ni-filtered $\text{Cu K}\alpha$ radiation. Diffraction images were recorded across a 30° – 70° range of angles (Θ).

Cathodoluminescence analyses (CL) were performed using a Cambridge Image Technology Ltd. Model CCL 8200 mk3. This was coupled with an Optiphot 2 microscope equipped with a Canon EOS 600D digital camera. Tests were carried out on exposed hard plates with a polished surface. Heat-resistant resin was used to make these.

4. Results

4.1. Diffraction

The enrichment of rocks with silica is seen to have taken place through the filling of pores and karst voids, fractures and compacting gaps (Figure 2A,B). In limestones and marls, silica mineralization occurred in the form of concretions, with flints of an early diagenetic and less often an epigenetic

character taking shape. Silica in opoka-rocks and limestones has in turn replaced carbonate minerals in organic debris. Rocks in which silica originally disrupted the carbonate rock matrix were also encountered, with the original structural and textural nature of the rock blurred in this way.

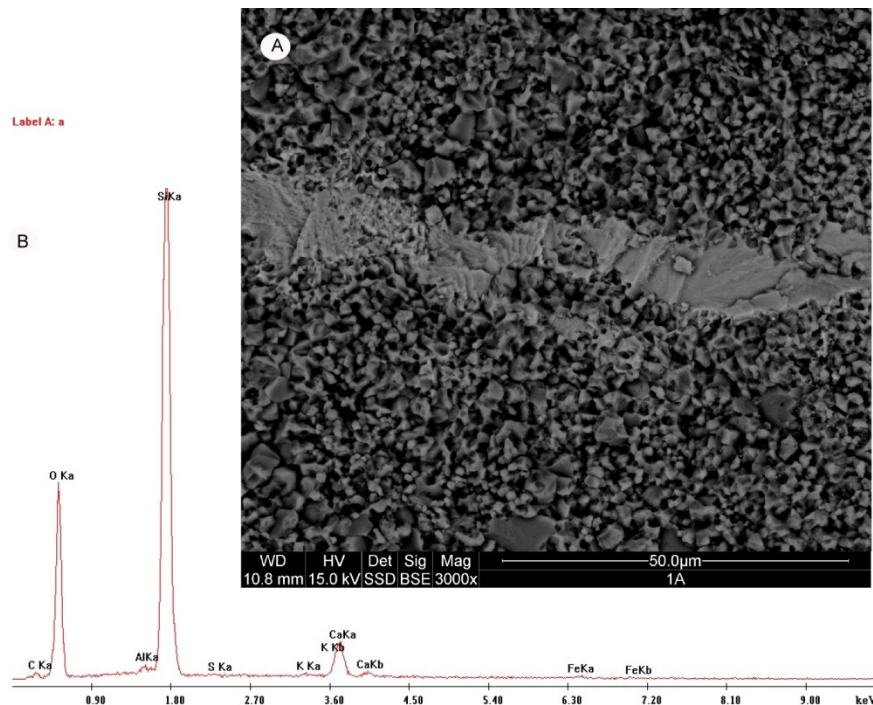


Figure 2. Tectonic fractures filled with an opal-like phase: (A) Image SEM, (B) Spectrum EDX.

X-ray examination identifies the opal-filling tectonic fractures as an intermediate phase between opal-CT (cristobalite–tridymite) and opal-C (cristobalite) (Figure 3). In scanning images, it is noted in massive crystalline aggregates, with traces of dissolution visible in many places.

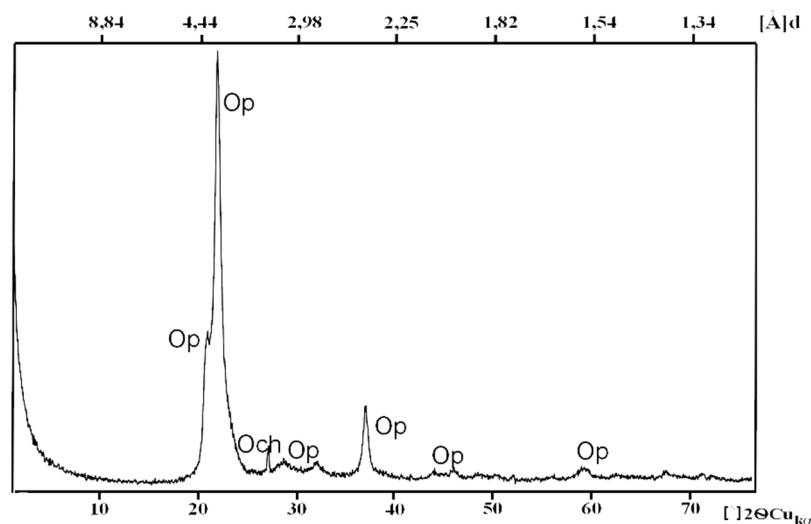


Figure 3. Diffraction pattern of the separated mineral phases. Explanations: Op–opal, Och–chalcedony.

The X-ray diffraction patterns of the substance separated from places covered in the process of silification (Figure 4) attested to an increase of background in the $2\theta_{CuK\alpha}$ 18° – 24° angular range, suggesting the presence of opal-A [37]. However, more attention should be paid to clear peaks at $2\theta_{CuK\alpha}$ 22.5° and $2\theta_{CuK\alpha}$ 36° , as associated with partially ordered varieties of minerals from the SiO_2

group, i.e., opal-CT (cristobalite–tridymite) and opal-C (cristobalite). The opal-CT mineral phases in the graphs analyzed often show an affinity for minerals of the smectite group (Figure 5). As in the case of the smectite–tridymite/cristobalite association [38], a structural relationship between these minerals and smectite cannot be precluded. Weak and blurry peaks, appearing on the X-ray diffraction patterns at a maximum of about 10.5 Å, point to the presence of a mixed packet of illite/smectite minerals.



Figure 4. Precipitation of opal on the slope of the opencast mine in the Bełchatów lignite deposit. Explanation of symbols: Op–opal, Cl–claystone.

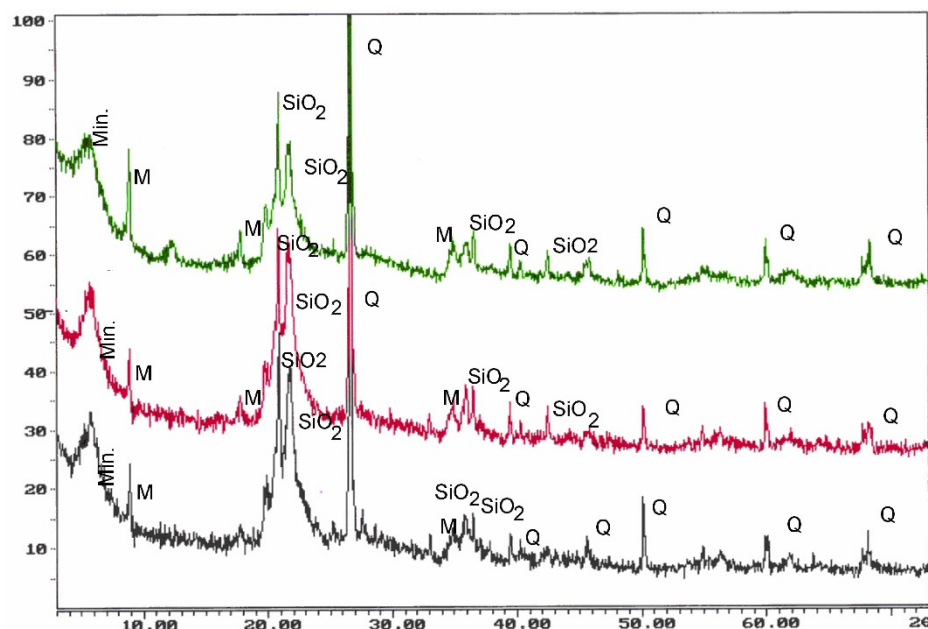


Figure 5. Example diffractometric curves. Explanation of symbols: SiO₂—silica phases in the form of opal (CT varieties relative to C), Q—quartz, M—mica, Min.—clayey minerals.

4.2. Microscopy

In limestones, opal of both types A and CT filled bioclast primary pores, such as intercellular spaces in sponge skeletons or the insides of mussel shells. In the opoka-rocks, it replaced carbonate organic debris and also formed the rock matrix. In addition, low-crystalline silica-filled rock pores

arising through karst phenomena, as well as the stylolites, crevices and fractures generated by tectonic stress (Figure 6A–E).

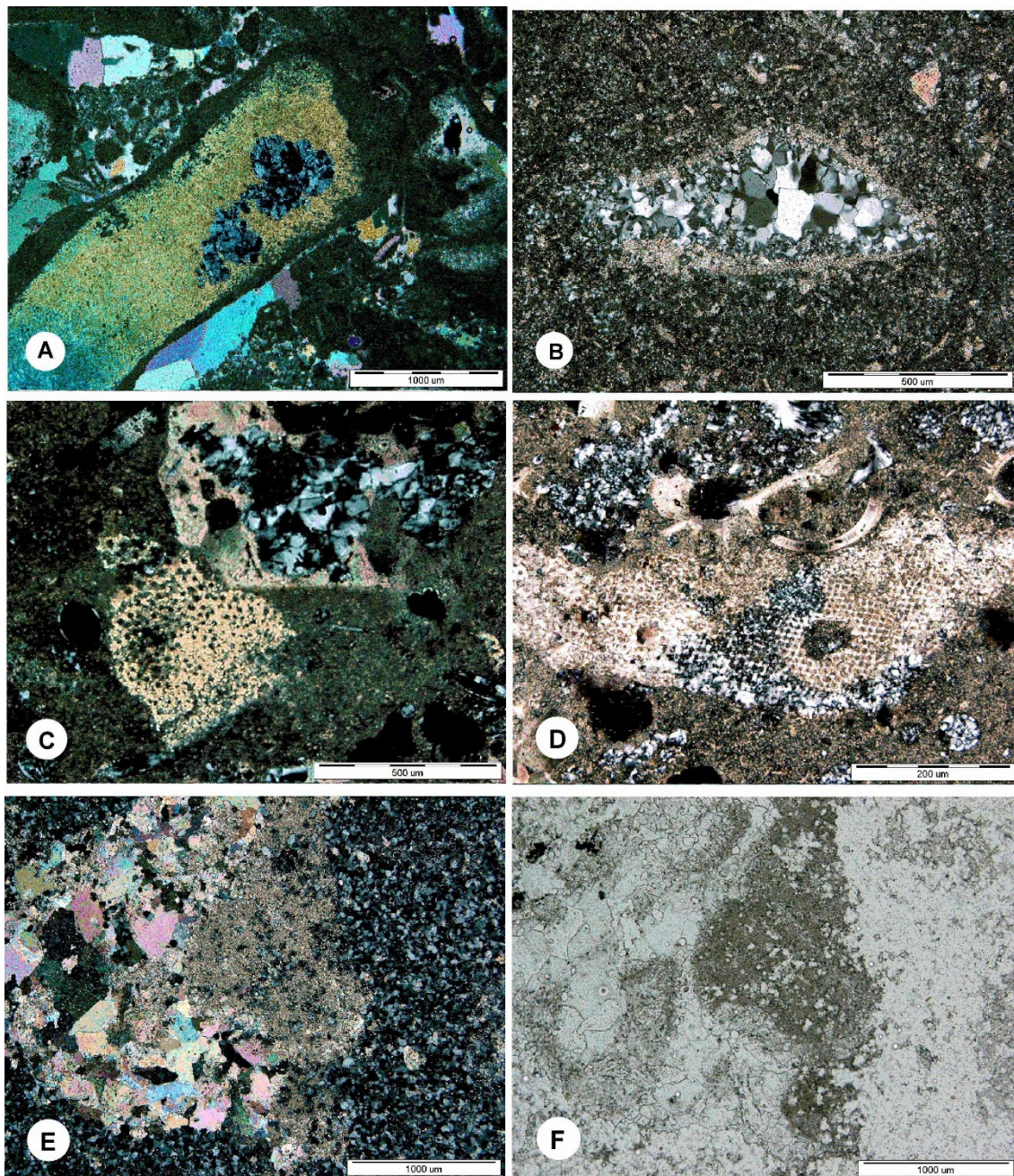


Figure 6. Examples of silification. Polarizing microscope: (A) A carbonate bioclast with traces of silification in organogenic limestone, 2P; (B) Relics of carbonate minerals in limestone encompassed by the silification process, 2P; (C) Replacing carbonates with microcrystalline chalcedony; (D) Silica filling of the intercellular space of the sponge skeleton; (E) Calcite relics, 2P; (F) Calcite relics, 1P.

Minerals of the SiO_2 group are also shown to take the form of chalcedony, quartz or microquartz in the Mesozoic bedrocks. Chalcedony crystallized in the form of spherulitic clusters, displacing micrites from bioclasts in limestones (Figure 6A,C,D). It also built silica sponge needles. The microstructural forms of quartz found are of an impregnating nature, being accumulations of the grain-mosaic quartz or pseudodruding quartz types (Figure 6B). These filled the voids left by granular components, bioclasts or fractures in the rock. The second form is quartz, occurring as a crypto- and microcrystalline “salt

and pepper” mass (Figure 6B). Quartz grains also form skeletons of decalcified opoka-rocks, and are present in limestones.

Cathodoluminescent analyses confirm the presence of different generations of silica. The oldest take the form of brown-luminescence quartz. The CL image mainly shows chalcedony-building nonluminescent sponge needles. Blue-luminescence opal-CT is observed in bioclasts. Silica of pink-blue luminescence constituting the rock matrix suggests its opaline nature. It is the youngest generation of silica most likely associated with the action of hydrothermal solutions (Figure 7B). Penetrating primary calcite cement of red luminescence is visible in the observed rock matrix.

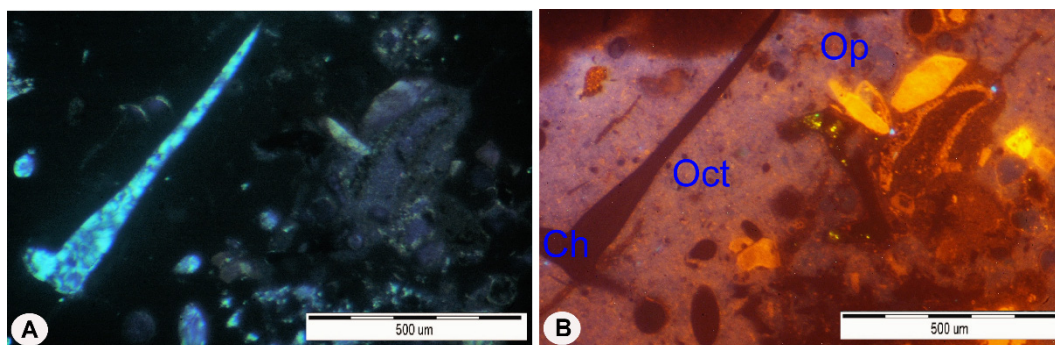


Figure 7. The silicified opoka-rock: (A) Polarizing microscope, 2P; (B) CL image revealing an opal rocky background–pink luminescence, and relics of feldspar and carbonate. Explanation of symbols: CL–cathodoluminescence, Ch–microcrystalline chalcedony, Oct–opal cristobalite–tridymite, Op–opal.

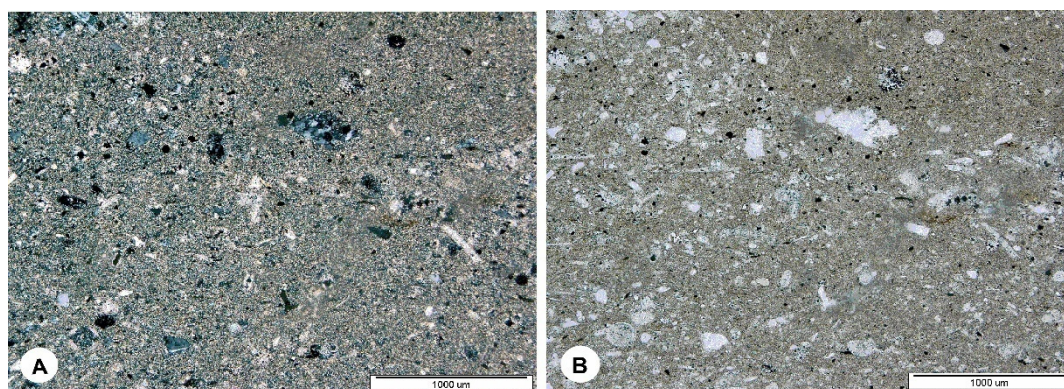
The generation of silica–carbonate binder, associated with the displacement of the latter by the former, indicates a syndeformation–early diagenetic stage. Observations in CL also disclose primary rocky components not visible previously in the microscopic image. These are mainly carbonate, recrystallized bioclasts and feldspars. Yellow-orange feldspar relics in CL have been completely replaced by silica (Figure 7A,B).

Previous studies have shown that the content of various silica polymorphs often determines geomechanical features of rocks. The possibility of the rocks studied having practical applications depends on the amount—and in particular on the phase nature—of the minerals from the SiO_2 group that are present. Transformation of silica mineral phases changes the rock’s physical and mechanical properties. Among other things, a higher value for the crystallinity coefficient (CI) is associated with higher values of parameters such as compressive strength in the air-dried state and apparent density, while porosity decreases (Table 1). The transition of opal-A into quartz results in reduced water content in rock, porosity and permeability. Such transformations are accelerated by higher temperature, pressure, alkalinity or the presence of different catalysts. Clay minerals in turn act to slow these processes down. The current study shows a fairly high degree of order for the silica phase in the gaizes, and a distinct difference in the silica formation that constitutes the transitional rocks examined. The rocks investigated are for the most part embraced by recrystallization processes, which have entailed the conversion of opal to chalcedony and microcrystalline quartz. This process is related to the gradual or total obliteration of original textures, and a transition from rock of amorphous to microcrystalline structure. Increased compaction and reduced porosity are consequences [39]. Thus, the silification process had a significant effect on the structural and textural features of the rock materials studied. Silica in the form of opal or chalcedony fills rock pores, tectonic fractures and stylolites (Figure 8A,B).

Table 1. Rocks accompanying the Bełchatów lignite deposit with dominant SiO₂-group mineral and designated parameters [39].

Parameters	Opoka-rocks (Opal Type A and CT)	Silicified Opoka-rocks (Opal Type CT Relative to Opal Type C)	Gaize (Chalcedony–Quartz)
Porosity (vol.%) DECREASE	44.5	24.3	10
Density (g/cm ³) INCREASE	1.32–1.41	1.9	n.d.
Compressive strength (MPa) INCREASE	31.9	52	55
Crystallinity index* INCREASE	1.8	2.17	7.8

* X-ray determined by Murat and Norman method [40] n.d.—not determined.

**Figure 8.** (A) Rocky background of the opoka-rock, with visible filling of rocky pores by amorphous silica. Polarizing microscope, 2P; (B) Polarizing microscope, 1P.

5. Silification Pathway

Silification of rocks located at the point of contact between the Mesozoic and Cenozoic is associated with mobilization of silica from surrounding rocks, or with the interaction of SiO₂-rich solutions. The intensity of the silification process has undoubtedly been influenced by the overlying lignite series, whose presence has ensured the richness of solutions in CO₂, F, B, Li, Na and Ba migrating to the lower parts of the rock mass; with these therefore capable of generating multistage transformations in underlying rocks. When organic matter is oxidized, the carbon dioxide generated lowers pH, simultaneously dissolving calcium carbonate and precipitating silica. Bacterial degradation of organic matter in the course of this process cannot be precluded [41]. In the deposit reduction zone, anaerobic bacteria break down organic matter by consuming hydrogen to form hydrogen sulfide, ammonia and methane, which migrate up and are oxidized in the oxidative zone. In the reduction zone, alkaline conditions arise, silica polymerization ensues, and the polymers formed precipitate out at the border with the oxidation zone. At that time, silica diffuses to the precipitation site. Opal-A concretions grow until biogenic resources of silica in the sediment are exhausted, with these subsequently dissolving at the surface and precipitating out in the form of opal-CT. This then repeats in the context of the transition from opal-CT to quartz. Typical places in which such concretions form are:

- ichnofauna channels, as oxygen-rich water makes contact with the reducing sediment of the channel walls;
- the boundary of bioturbed, oxidized and nondisturbed sediment;
- the seabed, in places where erosion reaches the reduction zone;
- in the oxidative zone, where there are local concentrations of organic matter.

Silica may also be derived from the transformation and dissolution of terrigenous material, mainly feldspar grains and silica organic debris. Various studies confirm that amorphous silica (opal) is a common component of coal, including lignite, which was formed in the diagenetic stage of feldspar carbonation [42]. Meteoric waters may have been an additional source of silica. A sedimentation gap occurred in the Paleogene, when the Mesozoic rocks of the study area underwent intensive peneplenization. The intensity of silification processes then occurring in the zone studied can be attributed to opal clusters. There must have been direct precipitation from an aqueous solution in free spaces after recrystallization of previously formed amorphous opal-A. Precipitation of amorphous silica (opal) is promoted by a sharp drop in temperature and pressure near the surface. Silica and CaCO_3 are the subject of inverse trends, meaning that silica dissolves and CaCO_3 precipitates when pH increases [43,44].

The results of this research are also confirmed by modern studies on reactive silica transport. In line with that, conditions found to favor the replacement of carbonate by silica entail [45]:

- interaction of volcanic fluids and rocks producing silica-rich fluids;
- high CO_2 concentrations accelerating calcite dissolution;
- an increased geothermal gradient associated with fluid and heat transport;
- fast flow, for example, along faults or fault zones;
- cooling, for example, by infiltrating surface waters;
- the presence of silica in primary sediments.

6. Conclusions

In this study, the upper parts of the Jurassic and Cretaceous sediments with overlying Neogene clays were found to include rocks that were subject to silification. The main evidence for this process was noted in opoka-rocks, marls and limestones.

The enrichment of rocks in silica was followed by replacement of the carbonate organic debris filling voids and rocky pores. The silica replacing carbonates and forming a rock cement usually took the form of opal (of types A or CT) or chalcedony, and only sporadically microcrystalline quartz.

Areas encompassed by silification are associated with partially ordered varieties, that is, opal-CT (cristobalite–tridymite) relative to opal-C (cristobalite). This mineral phase has often been shown to have an affinity for minerals of the smectite group. Cristobalite and tridymite may have originally formed from opal-CT from the precipitation of excess silica that did not enter the structure of neogenic siliceous minerals. This occurred simultaneously with the crystallization of clay minerals. Crystallization of cristobalite and minor tridymite, as opposed to quartz, thus indicates the abundance of alkali solutions.

Cathodoluminescent analyses confirm the presence of silica of different generations. The youngest is opal-CT of pink-blue luminescence, which builds the rock matrix of the Cretaceous opoka-rocks, and most likely indicates interaction with hydrothermal solutions. The rock matrix in turn has a visible primary calcite cement of red luminescence. An opal-A bioclast builder luminesced blue in the CL image. The chalcedony present was nonluminescent.

CL observations revealed original rock clasts not previously visible in microscopic images. These were mainly carbonate bioclasts and feldspar completely replaced by silica. The processes inferred and revealed here may be combined with the locomorphic stage of diagenesis.

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