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Moganite in selected Polish chert samples: The evidence from MIR, Raman and X-ray studies

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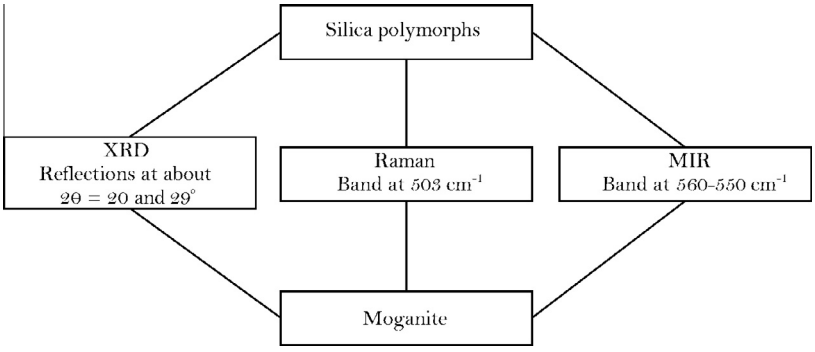
HIGHLIGHTS

- The X-ray powder diffraction measurements have shown that moganite most probably exists in the selected Polish cherts.
- The MIR spectra have revealed the presence of an analytical band (characteristic of moganite).
- Raman spectroscopic studies confirmed the presence of moganite in tested cherts.

GRAPHICAL ABSTRACT



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ABSTRACT

The authors discuss the results of structural investigations (XRD, MIR, Raman) of Polish cherts from different geological formations. The X-ray diffraction analyses explicitly confirmed the presence of moganite, which was identified on the basis of satellite XRD peaks positioned/occurring close to the quartz reflections and the additional reflections with the d_{hkl} values 4.456 and 3.101 Å, and established its amounts as varying between about 1 and above 17 wt%. The mid-infrared and Raman spectroscopy also proved the presence of moganite, indicated by the 695 and 560–555 cm^{-1} bands, respectively. These analytical finds allow to identify moganite in samples containing various SiO_2 polymorphs.

Introduction

The term *chert* refers to siliceous concretions and other siliceous bodies of minor sizes occurring within sedimentary rocks, most often in carbonate ones, marls and opokas. The chert bodies markedly differ from their host rocks, mainly due to colour differences of the two. Microquartz and chalcedony, accompanied by opal-A or opal-CT, are principal mineral components of cherts, and the list of admixtures usually includes iron oxides and oxide–hydroxides (hematite, goethite), bituminous or carbonaceous matter, pyrite and carbonate minerals. The colour of cherts is diversified: black, brownish, grey, bluish, green, yellow, white, being often variable: spotty or concentric. The latter is characteristic of the variety called striped cherts.

A new siliceous phase – moganite – was identified relatively not so long ago (in 1976) by Flörke et al. [1] in ignimbrites from the Mogan Formation, Gran Canaria. This mineral, only occasionally occurring on its own, usually forms intergrowths with other minerals of the SiO_2 group, as it has been found, among others, in agates [2–4]. The investigations carried out by Flörke et al. [5] revealed in the X-ray patterns of moganite few characteristic reflections not existing in other low-temperature minerals of the SiO_2 group. Other moganite diffraction lines overlap the reflections

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of these minerals, particularly those of chalcedony LF, chalcedony LS and β-quartz. Therefore, the identification of moganite, if this phase occurs in trace or minor amounts, is difficult. The same applies to the cherts from Poland, which for many years – and also recently – have been described by various authors [6–8]. As moganite has not been identified so far in the siliceous rocks of this type, the present authors carried out investigations of cherts from various regions of Poland using chemical methods and the selected methods of phase analysis: X-ray diffraction (XRD), mid-infrared spectroscopy (MIR) and Raman spectroscopy.

The main objective of the study was to demonstrate the existence of moganite in Polish cherts, especially using MIR spectroscopy.

Experimental

The cherts to be studied were selected from the geological formations of Poland of various age (Fig. 1): Jurassic (samples 1, 2, 3), Neogene (sample 4) and Quaternary (sample 5). One of them (sample 3 from Śródborze) represents the striped cherts occurring within Upper Jurassic limestones from the NE margin of the Holy Cross Mts. These cherts, by far most often described in the Polish mineralogical and geochemical papers, are characterized by the presence of usually light grey, grey and dark grey, irregular and alternating, onion-resembling bands (*onion-skin* [9]). According to Migaszewski et al. [7], such a chert structure results from a different degree of impregnating rock pores with secondary silica, because of which the light reflection also differs. The bands containing few micropores are dark grey of brownish, whereas those rich in micropores are light grey or white. These authors do not found any dependence between the colour of the cherts and the contents of organic matter, clay minerals or iron oxide–hydroxides. Lately Graetsch and Grünberg [10] stated on the basis of XRD studies that the content of moganite in a striped chert sample from the NE margin of Holy Cross Mts is diversified. The grey bands contain rather low (1.1%), whereas the white ones distinctly higher (11.1%) amounts of this mineral.

The southern part of the Częstochowa–Cracow Upland and adjacent regions are the second area rich in Jurassic cherts. The most widespread cherts are brownish and occur in Upper Jurassic (Oxfordian) rocky limestones and in secondary deposits, represented by alluvial loams, conglomerates and gravels [11]. A sample typical of the first of these types was taken in the Będkowska Valley (sample 1), the sample of the other type comes from Dąbrowa Szlachecka near Skawina (sample 2).

Cherts also occur in the overburden of the lignite deposit in Bełchatów, where they form a characteristic layer of rock fragments called the *chert pavement*. They represent an Upper Miocene, coarse-grain sediment in the bottom part of the clay–sandy complex of the deposit [12]. The sample numbered 4 comes just from this part of the Bełchatów open pit.

The list of the material studied is completed by cherts (sample 5) collected from the Quaternary overburden of the deposit of Triassic red clays in Woźniki (Silesian–Cracow Monocline).

Chemical analyses were made using Fusion ICP–OES (Inductively Coupled Plasma–Optical Emission Spectrometry). Samples were prepared and analyzed in a batch system. Each batch contained a method reagent blank, certified reference material and 17% replicates. Samples were mixed with a flux of lithium metaborate and lithium tetraborate and fused in an induction furnace. The melt was immediately poured into a solution of 5% nitric acid containing an internal standard and mixed continuously until completely dissolved (~30 min). The samples were then analyzed for major oxides and selected trace elements with a combination simultaneous/sequential Thermo Jarrell-Ash ENVIRO II ICP spectrometer. Reagent blanks with and without the lithium borate flux as well as the method reagent blanks were also analyzed. Interference correction verification standards were analyzed, too. Calibration was performed using the multiple USGS- and Canmet-certified reference materials.

The X-ray powder diffraction measurements were performed using a Philips X'Pert Pro MD diffractometer. The Cu $K\alpha_1$ radiation obtained with a Ge(111) monochromator was used. Standard Bragg–Brentano geometry with a θ–2θ setup was applied (0.008° step and 10–90°2θ range).

The IR spectroscopic measurements (MIR – Mid-infrared) were made with a Bio-Rad FTS 60 V spectrometer using the transmission technique. Samples were prepared as the standard KBr pellets. Spectra were collected after 128 scans at a 4 cm^{-1} resolution.

The Raman spectra were obtained using a Bio-Rad FTS 6000 spectrometer with the Nd–YAG laser system ($\lambda = 1064$ nm). The laser power was 200 MW. The spectra were collected at a 4 cm^{-1} resolution.

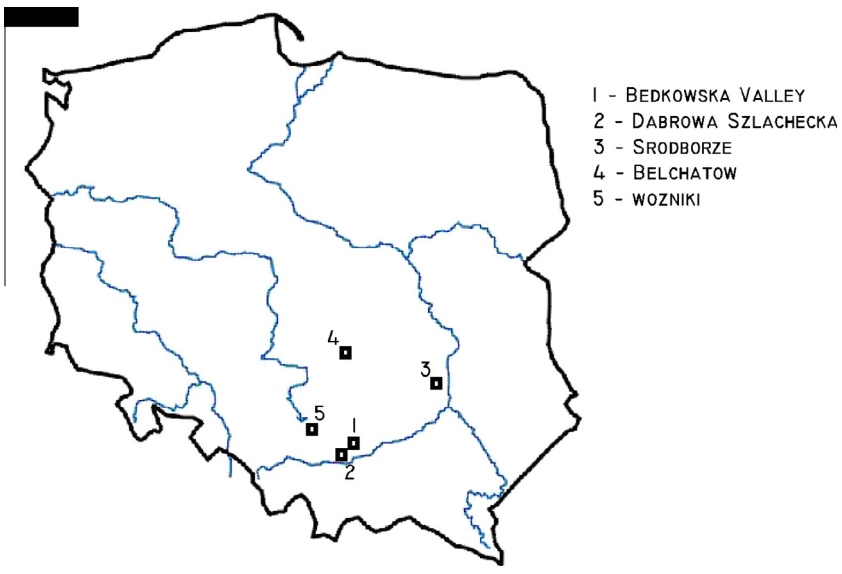

Fig. 1. Map with samples locations.