

# X-ray diffraction study and luminescence of agates of Southern Siberia

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**Abstract.** Central part of Kuznetsk Basin is known in the narrow circle of researchers as one of the regions of Siberia where agate mineralization is widespread. In spite of rather wide distribution of these quartz-chalcedony aggregates, still there are some unresolved issues about their origin. In this context it may be informative to use such methods as luminescence analysis and estimation of crystallinity indexes of minerals which constitute agates. Layer-by-layer X-ray diffraction study of minerals which make up distinct layers of agates and onyxes allowed identifying three minerals alternating: chalcedony, quartz and (less frequently) cristobalite. Calculation of crystallinity indexes of all of the layers with use of X-ray diffraction analysis helped to find changes of proportion between two states of silica – high-molecular (polymerized) and monomeric. X-ray luminescence analysis results confirmed this finding. Authors suppose that monomeric state is particularly related to high value of crystallinity index and presence of defects which are responsible for short-wavelength luminescence (280 nm).

## 1. Introduction

Agates are rhythmically zonal (concentrically zonal and parallel-layered) aggregates of different silica minerals, among which quartz and chalcedony prevail. Sometimes there are also zones and inclusions of other minerals: (carbonates, goethite, zeolites, celadonite and so on). Textural and morphological features of agates may be conditioned by cavities morphology, silica minerals structural features and pigments composition and concentration [1]. Despite these quartz-chalcedony formations wide distribution their origin issues are unresolved still. X-ray luminescence study and crystallinity index calculation may be helpful in finding the answer. Nowadays most of researchers accept secretion way of agates formation: sequential deposition of chalcedony, quartz and other minerals layers due to solutions circulating throughout previously formed cavities and canals [2, 3]. The purpose of this work is to ascertain textural and morphological features of South Kuzbass magmatic area (Southern Siberia) agates and layer-by-layer study of their composition with use of X-ray luminescence and X-ray diffraction analyses.

## 2. Methods

X-ray diffraction and X-ray luminescence analyses were carried out. X-ray diffraction analysis results were obtained with use of X\*Pert PRO, PANalytical diffractometer. Analysis was carried out in normal conditions by Bragg-Brentano geometry with use of  $\text{CuK}\alpha$ -radiation. Tube voltage is 40 kV, amperage is 30 mA. Crystallinity index ( $K_{ci}$ ) values were calculated in accordance with multiplet reflection position in  $67^\circ \dots 69^\circ$  range on powder X-ray diffractogram of quartz-chalcedony phase



with use of  $K_{ci}=10 F a/b$  formula, which was suggested by Murata & Norman and is successfully used by other researchers [4-7]. X-ray luminescence (XRL) spectra were recorded with use of device made on the base of MDR 12 monochromator with computer control according to previously outlined method [8, 9]. XRL spectra were obtained in optical wave-length range from 200 to 800 nm. Mo-anticathode X-ray tube BSV-2 of URS-55 apparatus was an excitation source. All the work was carried out with use of equipment of “Analytical center of geochemistry of natural systems” of Tomsk State University.

### 3. Objects of the study

Kuzbass agate-bearing volcanites (Kuznetsk zone) are included in Altai-Sayan gems and ornamental stones bearing region, which is the part of South Siberian province. Agates formation is associated with amygdaloidal early Mesozoic basalts of so called «melaphyric horseshoe», which is located within Bungarap syncline among lower Triassic terrigenous sedimentary rocks [10, 11]. Amygdaloidal kinds of basalts formed close to the roofs and to the floors of bed-like bodies. In terms of orography this «melaphyric horseshoe» consists of Saltymakovsky, Agendarovsky, Karakansky, Taradanovsky ridges, Kaylot mountains, Ostashkinsky stone and belongs to South Kuzbass magmatic area. Basalts and dolerites of the area belong to Kuzbass trap formation, which includes saltymakovsky and syrkashevsky complexes. Besides Permian and Triassic basalts there are also Devonian ones, which also contain veins of quartz and chalcedony. At the present moment a number of spots of quartz and chalcedony appearing within South Kuzbass magmatic area boundaries are known. Let's take a look at some of them.

Tersyuk district is located in Novokuznetsk rayon of Kemerovo region. It adjoins to the west flank of Kuznetsk Alatau and locates within Kuznetsk sink. Exposure is located at the right bank of Tersyuk river, which flows in Middle and Lower Tersey rivers lower courses interfluve. Triassic, Jurassic and Quaternary sediments take part in geological composition of the district. Triassic system is presented by its lower series, sosnovskaya and jaminskaya suites in particular. Sosnovskaya suite (T1ss) doesn't contain any basalts. Jaminskaya suite (T1jam) contains amygdaloidal basalts with color from dirty-green to black, massive texture, aphanitic and brecciform structure. Tersyuk occurrence is known as most promising agates bearing one in Kemerovo region.

Triassic trap formation rocks are present at Saltymakovsky ridge territory (Tom River right bank). Most of cross section rocks are vitroclastic aleurolitic tuffs. Basalts are almost untouched by metamorphic processes so they have fresh cenotypal outlook. Oftentimes there is intensively developed zeolitization in upper parts of the bodies and also in fracturing zones in middle and lower parts of the bodies. These occurrences agates mostly are onyxes and have bluish grey color. Oftentimes there is white and blue or grey and white layers alternation. Also there is quartz in central parts of some amygdules.

The occurrence near Zelenogorsky settlement is included to structure of so called Krapivinsky dome, which is made up of Devonian rocks. Silica minerals veins are found within greenish black basalts. Filled with variously coloured (reddish, blueish, grey of green) chalcedony veins are occurring. Again there are central parts made up of quartz in some of samples. Calcite crystals appear sometimes. Oftentimes there are basalt xenoliths inside the chalcedony veins. Most of samples have onyx pattern, but some of them have distinct agate one.

### 4. Results and discussion

There are three patterns types of studied agates: first type – concentrically zonal amygdule one, second type – combined type (onyx pattern and within the same amygdule), third type – onyx pattern. Most of Tersyuk agates have concentrically zonal pattern, less often there is combined type appearance. Low onyxes (parallel-layered agates) content may evidence rather low silica concentrations in hydrothermal solutions, which hinder colloidal component gravitational deposition [12, 13]. And on the contrary, onyxes prevalence among Saltymakovsky ridge chalcedonies and at Zelenogorsky settlement occurrence indicates that there was high silica concentration in solution. Moreover there was high-

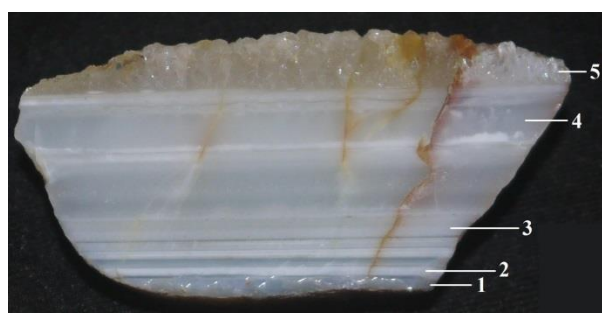
molecular (polymerized) state of silica that contributed to gravitational deposition of colloidal component of solutions. Chalcedony fibres growth proceeded by means of polymeric component (by way of whole polymeric chains connection). In turn polymerization was supported by high silica concentration [14]. High silica concentrations finding for this region corresponds to other researchers findings on petrological and mineralogical features of Kuzbass central part volcanites [10]. Onyxes share decrease among quartz-chalcedony rocks at Tersyuk occurrences may be caused by silica concentration decrease in the latest amounts of hydrothermal solutions.

Layer-by-layer X-ray diffraction study of minerals which make up separate layers in agates and onyxes allowed proving three minerals presence: chalcedony, quartz and (less often) cristobalite. The latter was found in Tersyuk agates (figure 1).



**Figure 1.** Concentrically zonal agate of Tersyuk district: 1 – cristobalite and quartz ( $K_{ci} = 1,8$ ), 2 – chalcedony ( $K_{ci} = 1,2$ ), 3 – chalcedony ( $K_{ci} = 1,5$ ), 4 – chalcedony ( $K_{ci} = 2,9$ )

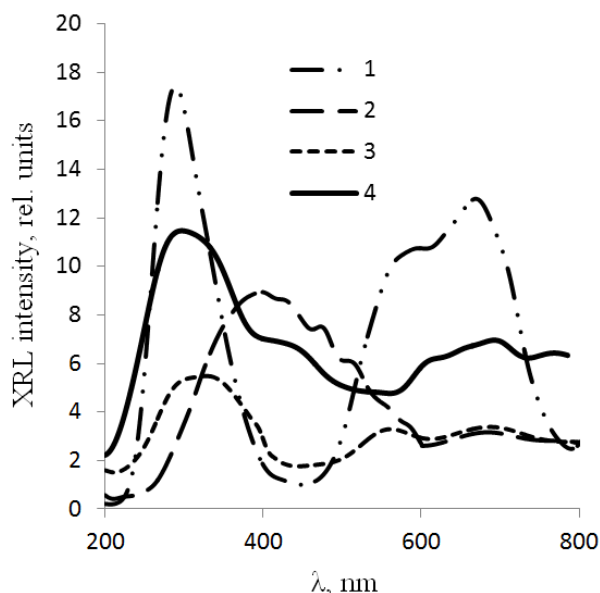
Besides that crystallinity index ( $K_{ci}$ ) was calculated for quartz and chalcedony parts of every sample with use of powder X-ray diffraction analysis. This analysis results show that quartz-chalcedony samples differ from each other by crystallinity indexes. Quartz from amygdules inner parts have high crystallinity index values (from 11,0 to 12,6).  $K_{ci}$  of chalcedony is always significantly lower than that of quartz, but none the less its values vary noticeably. Saltymakovsky ridge onyxes have the highest  $K_{ci}$ . Samples with high  $K_{ci}$  values both of quartz component and chalcedony component are distinguished with their vivid blue, bluish grey, bluish white colour. It's noteworthy that Saltymakovsky ridge onyxes usually consist of quartz mostly (figure 2). Their  $K_{ci}$  vary from 6 to 12.



**Figure 2.** Tersyuk district onyx: 1 – quartz ( $K_{ci} = 5,61$ ), 2 – quartz ( $K_{ci} = 6,86$ ), 3 – quartz ( $K_{ci} = 6,53$ ), 4 – quartz ( $K_{ci} = 6,87$ ), 5 – quartz ( $K_{ci} = 8,7$ )

In the authors' opinion crystallinity index may reflect change of proportion between high-molecular (polymerized) and monomeric states of silica. Probably it's monomeric state that is responsible for high crystallinity index values.

X-ray luminescence spectra were recorded for all of the samples within optical wave-lengths range from 200 to 800 nm. XRL spectra of agates are rather complicated and include emission bands with their maxima at following bands (nm): 180-190, 280-300, 320-350, 390-400, 420-450, 540-590, 640 (figure 3).



**Figure 3.** XRL spectra of quartz-chalcedony formations of South Kuzbass magmatic area: 1 – quartz of Tersyuk agates (amygdule upper part), 2 – cristobalite and quartz of Tersyuk concentrically zonal agate, 3 – chalcedony of Tersyuk concentrically zonal agate, 4 – quartz and chalcedony of Saltymakovsky ridge onyx.

All the luminescence centers, which are responsible for XRL bands mentioned above appearing, are intrinsic defects mostly [15]. Emission band at 280-300 nm is related to oxygen deficiency state (oxygen vacancy). 540-700 nm band may appear due to non-bridging OH centers or non-bridging oxygen centers presence. A number of bands in 300-450 nm range may be related to not only intrinsic defects, but also to presence of such admixtures as Al and Na, which take part in formation of traps for electrons and holes [9, 15, 16]. Differences between luminescence spectral composition and intensity of different layers of agates and onyxes may be caused by acidity and alkalinity changes, oxidation potential change, silica concentration and may reflect changes of proportion between high-molecular (polymerized) and monomeric states of silica.

## 5. Conclusion

According to the purpose of the present work textural and morphological features of South Kuzbass magmatic area agates and their composition were studied with use of X-ray luminescence and X-ray diffraction analyses. Agates formation is associated with amygdaloidal early Mesozoic basalts of so called «melaphyric horseshoe». There are three patterns types of studied agates: first type – concentrically zonal amygdule one, second type – combined type (onyx pattern and within the same amygdule), third type – onyx (parallel-layered) pattern. Low onyxes content may evidence rather low silica concentrations in hydrothermal solutions, while high onyxes content indicates that there was high silica concentration. X-ray diffraction study allowed proving three minerals presence: chalcedony, quartz and (less often) cristobalite. Quartz-chalcedony samples differ from each other by crystallinity indexes. Quartz from amygdules inner parts has high crystallinity index.  $K_{ci}$  of chalcedony is always significantly lower than that of quartz, but it varies noticeably. X-ray luminescence study allowed recording a number of luminescence bands that may be related to not only intrinsic defects, but also to presence of admixtures, which take part in formation of traps for electrons

and holes. Differences between luminescence spectral composition of different layers may be caused by formation conditions change and may reflect changes of proportion between high-molecular (polymerized) and monomeric states of silica.

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