

ON THE DISTRIBUTION OF IRON IN MINERALS FROM JASPERS FROM THE EASTERN RHODOPES ACCORDING TO SPECTROSCOPIC DATA

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ABSTRACT. The Eastern Rhodopes are the main area of distribution of various in color and genesis jaspers in Bulgaria. With the help of Mössbauer spectroscopy and Electron Paramagnetic Resonance (EPR) spectroscopy, the iron status and distribution of different valence states of iron were studied in the three most important impurity phases of jasper – hematite, goethite and celadonite, which are associated with red, yellow to yellowish-brown and green coloration, respectively. In the Mössbauer spectrum of red jasper, Fe³⁺ sextets characteristic of hematite and goethite are detected, in the spectrum of yellow jasper – Fe³⁺ sextets characteristic only of goethite, and in the green jasper spectrum – dominant Fe³⁺ and Fe²⁺ doublets associated with celadonite. The EPR spectra of jasper samples reveal information about the concentration of iron-bearing phases and iron ions in tetrahedral coordination.

Key words: jasper, hematite, goethite, celadonite, Eastern Rhodopes

ВЪРХУ РАЗПРЕДЕЛЕНИЕТО НА ЖЕЛЯЗОТО В МИНЕРАЛИ ОТ ЯСПИСИ ОТ ИЗТОЧНИТЕ РОДОПИ ПО СПЕКТРОСКОПСКИ ДАННИ

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РЕЗЮМЕ. Източните Родопи са главния район на разпространение на разнообразни по цвят и генезис ясписи в България. Чрез помощта на Мьосбауерова спектроскопия и чрез Електронен парамагнитен резонанс (ЕПР) са изследвани статута и разпределението на разновалентни желязни йони в трите най-важни примесни фази на ясписите – хематит, гьотит и селадонит, които са свързани съответно с червено, жълто до жълтокафяво и зелено оцветяване. В Мьосбауеровия спектър на червен яспис се отбелязват Fe³⁺ секстети, характерни за хематит и гьотит, в този на жълт яспис – Fe³⁺ секстети, характерни само за гьотит, а в този на зелен яспис – доминиращи дублети от Fe³⁺ и Fe²⁺, свързани със селадонит. ЕПР спектрите на пробите от ясписи разкриват информация за концентрацията на желязо-съдържащи фази и тетраедрично координирани желязни йони.

Ключови думи: яспис, хематит, гьотит, селадонит, Източни Родопи

Introduction

The Eastern Rhodopes are the main region of localization of various in color and genesis jaspers in Bulgaria (Atanasov and Yordanov, 1986). In recent years their widespread distribution has been established both in the host rocks and in deluvial and alluvial manifestations along the main river valleys of the Eastern Rhodopes (Kostov et al., 2016a). At the same time, differently colored jaspers in the form of artifacts are found both in random finds and as a result of detailed archaeological studies of prehistoric settlements in the region (Kostov et al., 2016b). The mineralogy of jasper is poorly studied on an international scale and the existing systems are based on mineralogical or genetic traits without being universally accepted (Kostov, 2006; 2010). To clarify the role and distribution of iron in the composition of the most common and frequently occurring iron-containing phases in jasper, spectroscopic studies were performed using Mössbauer spectroscopy and Electronic Paramagnetic Resonance (EPR) spectroscopy. Both methods are complementary to the possibility of interpretations of valence, position and type of iron in the respective mineral phases or in the SiO₂ matrix

itself, represented most commonly by fine grained quartz, chalcedony and various opals.

Samples and methods

Five samples of single coloured jasper of three different colours (two with red, one with yellow to yellowish-brown and two with green colour) were studied from artefacts from regions of their maximum concentration around the town of Momchilgrad (Chukovo – aCh, Varhari – aVu) and the village of Nanovitsa in the Krumovgrad region. Similar in colour jaspers found in the host rocks (Piyavets, Neophyt Bozvelievo and Pazartsi, marked correspondently Pi, Ne and Pa) were used for comparison. On the geological map of Bulgaria at a scale of 1:50000, in the region are revealed predominantly materials from the Lower and Upper Tuff epiclastic batch, as well as basic to medium-acid volcanic rocks of the upper effusion, all of them with an Oligocene age (Yordanov et al., 2008). The samples were analyzed by X-ray in order to determine the mineral phases contained in them and the distribution of dominant microcrystalline quartz or chalcedony (Kostov et al., 2017b). The data from the X-ray diffraction

analyses show a similar and relatively homogeneous phase composition: in the green varieties – quartz (\pm chalcedony, opal) with celadonite $K(\text{MgFe}^{3+})[\text{Si}_4\text{O}_{10}](\text{OH})_2$, in the yellow ones – quartz (\pm chalcedony) with goethite $\alpha\text{-FeOOH}$, and in red ones – quartz (\pm chalcedony, opal) with hematite $\alpha\text{-Fe}_2\text{O}_3$.

The Mössbauer spectra were measured on an electromechanical spectrometer (Wissenschaftliche Elektronik GMBN, Germany), operating in steady-state mode at room temperature. The source is $^{57}\text{Co}/\text{Rh}$ (activity $\cong 25$ mCi) and an $\alpha\text{-Fe}$ standard has been used (Institute of Catalysis of the Bulgarian Academy of Sciences). Experimentally obtained spectra were processed with the program CONFIT2000 (Žák and Jirásková, 2006). The parameters of the hyperfine interactions – isomer shift (δ), quadrupole splitting (Δ), effective internal magnetic field (B) as well as line width (Γ_{exp}) and relative influence of the partial components (G) are determined.

The samples, that were pre-ground (60 mg) in an agate mortar, were examined for impurity and electrone-hole defects, mostly at room temperature (294 K) on a Bruker EMXplus-10/12/P/L Spectrometer System in different mode (modulation amplitude of 2 G; microwave power 2 mW and 0.6 mW) (IGIC BAS) and on a JEOL JES-FA100 spectrometer both operating in the X-band (IC BAS). Electron Paramagnetic Resonance (EPR) spectra were recorded at a magnetic field width of 4000 G (in the range $\sim 4100\text{-}8000$ G for the diagnosis of broad lines associated with iron ions and iron impurities; 150 s) and at 200 G (in the range $\sim 3200\text{-}3400$ G for diagnostics of electrone-hole centers in the range of $g\text{-}2$; 60 s).

Results and Discussion

The experimental Mössbauer spectrum of a red jasper specimen (hematite-containing; sample aCh2) is a combination of a sextet and a doublet (Figure 1). Mathematical processing was performed using a model of two sextets and one doublet. As a result of the treatment, parameters of the sextet components corresponding to hematite $\alpha\text{-Fe}_2\text{O}_3$ and goethite $\alpha\text{-FeOH}$ were obtained (Table 1). The doublet component has Fe^{3+} ions parameters in a compound with paramagnetic or superparamagnetic behavior. A distinction between the two alternatives (paramagnetic phase/superparamagnetic particles) can be made after measuring spectra at a liquid nitrogen temperature.

The experimental Mössbauer spectrum of a yellow jasper (goethite-bearing; sample aYu3) is composed of broad sextet lines with distribution of the magnetic field (Figure 2). The spectrum processing uses a combination of two sextets, one of which has a magnetic field distribution ($Sx2$). The sextet parameters are typical for the mineral goethite (Fe^{3+} ions in octahedral environment), and the decreasing internal magnetic field ($Sx2$) is probably due to an isomorphic substitution of iron with an element, for example Al. The lower internal magnetic field value is indicative of a reduction in the magnitude of magnetic interactions due to the magnetic discharging of the chemical system with diamagnetic Al^{3+} ions. With such a substitution in the structure of goethite, there is a presence of

iron ions with different number of iron and aluminum closest neighbours, whose iron nuclei are located in a different internal magnetic field, respectively. The function of the internal magnetic field distribution for $Sx2$ is presented (Figure 3). Similar spectra have been reported for solid solutions in the system of compositions $\alpha\text{-FeOH}$ - $\alpha\text{-AlOH}$ (Fysh and Clark, 1982).

Another possibility for explanation of the broad spectral lines is the manifestation of the dimensional effect of the goethite particles, i.e. presence of particle size distribution, in size from fine dispersed to ultra-dispersed, for example from ~ 70 nm to ~ 10 nm). This is the so-called collective magnetic excitation effect. Measuring spectra at low temperatures can confirm or reject its presence.

In the case of Mössbauer spectroscopy of goethite in the form of yellow ocher from the supergenic area of the Sakhalin nickel deposit, it is found that the spectrum (sextet, sextet with doublet or doublet) is not constant and changes in the samples from one point to another at the same horizon, as well as in the transition at different horizons (Bobkovskii and Yalovoi, 1987). It is noted that two factors can influence the goethite spectrum: the degree of substitution of iron by a non-magnetic element (in this case, aluminum up to 16%) and the degree of dispersion (crystallinity) of the goethite. To elucidate the two main factors, experimental studies were conducted simultaneously using Mössbauer spectroscopy and X-ray diffraction analysis, as there are a number of contradictory and ambiguous data regarding alumina-containing and fine disperse goethite and hematite (Tkacheva and Umnova, 1982). Upon increase in the aluminum content at 8 mol%, a B parameter narrowing from 37.5 T to 24.2 T is noted and a change in the geometry of the peaks of the sextet in the spectrum is observed (the second and fifth lines have a higher intensity compared to the first and sixth lines), and at >18 mol% of aluminum appears a doublet. The X-ray diffraction analysis of the specimens showed that with the Fe-Al increased isomorphic substitution, a reducing of the parameters of the elementary cell is observed, associated with the interplanar distances of the reflections 110 and 111 (they decreased and widened, the substitution was also influenced by the higher dispersion of the sample). The doublet in the goethite spectra with a high degree of isomorphic impurity is explained by the disruption of the spines of antiferromagnetic subcells. It should be noted that the Mössbauer spectra of goethite $\alpha\text{-FeOOH}$ and lepidocrocite $\gamma\text{-FeOOH}$ differ significantly – for the first mineral is typical a sextet, and for the second one – a quadruple doublet. More recent studies on both hematite and goethite indicate that the parameters of the Mössbauer spectra depend to a higher degree on structural factors than on the aluminum content and the degree of crystallinity (Vandenberghe et al., 2000).

The experimental Mössbauer spectrum of green jasper (celadonite-bearing; sample aNa8) is a combination of sextets and doublets (Figure 4). Mathematical processing was performed using a model with two sextets and two doublets. As a result of the processing, parameters of sextet components corresponding to $\alpha\text{-Fe}_2\text{O}_3$ (hematite) and $\alpha\text{-FeOOH}$ (goethite) were obtained. The parameters of the two doublets correspond to Fe^{3+} and Fe^{2+} ions in octahedral coordination, probably

introduced into the structure of celadonite. The ratio of the relative values of the two-component components is $Fe^{3+}/Fe^{2+}=2.35$. The low iron content of the specimen, as well as the presence of other iron-containing phases (hematite and goethite) in the sample, impedes the correct use of more sophisticated processing patterns (such as those in Daynyak and Drits, 1987). The possible positions of Fe^{3+} in the structure of the celadonite are described in detail (Drits et al., 1997).

Earlier published Mössbauer spectra of jasper samples from the Eastern Rhodopes show some close-up data but are with no relevant parameters, and were used mainly for diagnosis of the admixed mineral phase in the quartz matrix (Atanasov and Yordanov, 1986).

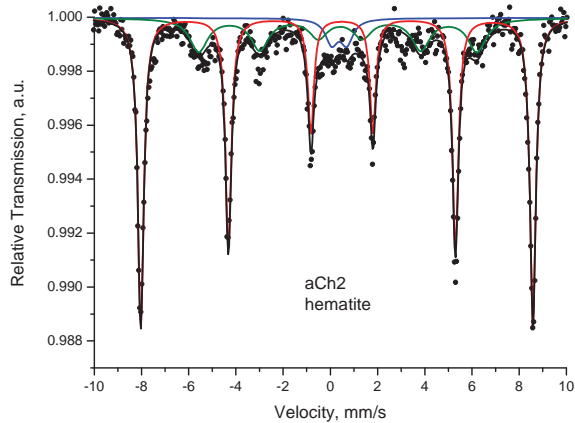


Fig. 1. Mössbauer spectrum of sample aCh2 (red jasper; hematite-bearing)

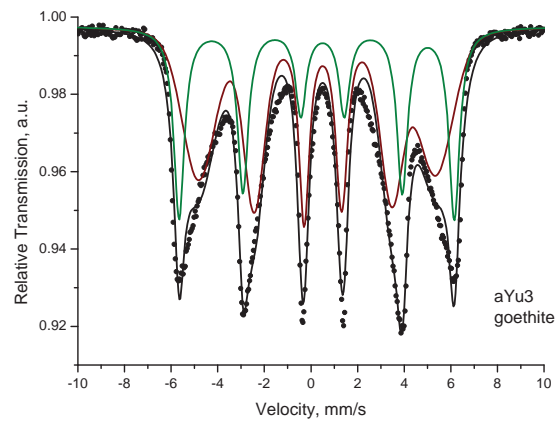


Fig. 2. Mössbauer spectrum of sample aYu3 (yellow jasper; goethite-bearing)

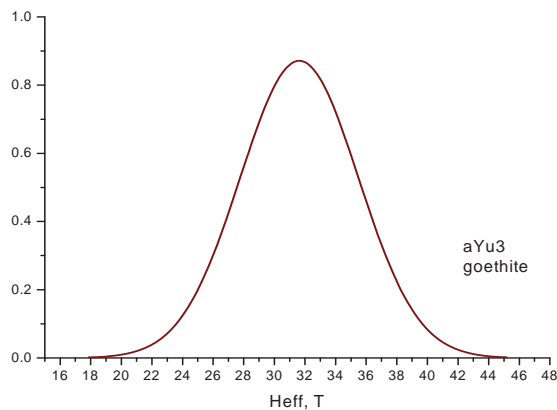


Fig. 3. Function of internal magnetic field distribution of Sx2 in the sample aYu3 spectrum (yellow jasper, goethite-bearing)

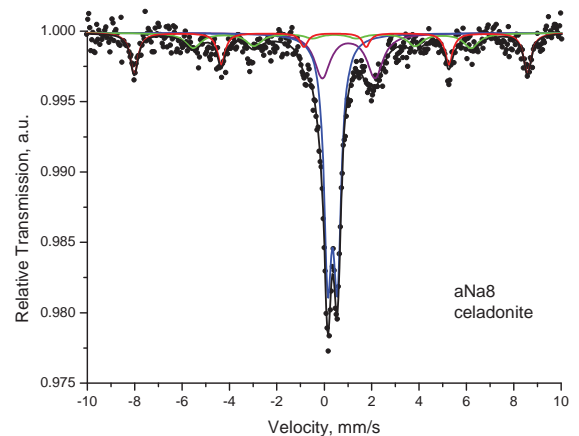


Fig. 4. Mössbauer spectrum of sample aNa8 (green jasper, celadonite-bearing)

Table 1.
Values of the specified Mössbauer parameters

Sample, colour	Components	δ , mm/s	Δ , mm/s	B, T	Γ , mm/s	Γ_{exp} , mm/s	G, %
aCh2 red	Sx1 – Fe^{3+} , hematite	0.38	-0.22	51.6	-	0.31	69
	Sx2 – Fe^{3+} , goethite	0.37	-0.11	36.6	-	0.92	26
	Db1 – Fe^{3+}	0.38	0.65	-	-	0.64	5
aVu3 yellow	Sx1 – Fe^{3+} , goethite	0.37	-0.25	36.7	-	0.55	36
	Sx2 – Fe^{3+} , goethite	0.39	-0.25	31.6	1.1	0.47	64
aNa8 green	Sx1 – Fe^{3+} , hematite	0.37	-0.18	51.6	-	0.40	19
	Sx2 – Fe^{3+} , goethite	0.39	-0.10	36.5	-	0.80	14
	Db1 – Fe^{3+} , celadonite	0.35	0.40	-	-	0.39	47
	Db2 – Fe^{2+} , celadonite	1.03	2.22	-	-	0.82	20

In the Mössbauer spectrum of the red jasper sample dominates the presence of hematite, in the yellow jasper sample – of goethite, and in the green jasper sample – of celadonite with doublets of iron of varying valency, predominantly Fe³⁺ and subordinate Fe²⁺ in structural position. Apparently, in the so-called brocade jaspers with yellowish and reddish spots, the ratio of hematite to goethite can be different. The presence in the Mössbauer spectra of green jasper of Fe³⁺ sextets associated with hematite and goethite indicates the presence of these minerals in the SiO₂ matrix, even when they are not visually (initiation of heliotrope) observed. Increasing their content leads to the formation of a visually distinct heliotrope.

In the EPR spectra of the jaspers (Figs. 5-9), the following main types of signals are distinguished: N1 – signal, sometimes with large width and intensity at g~10; N2 – signal at g=4.3 attributed to structural Fe³⁺; N3 – a wide signal ~1000 G at g ~2.3-2.1 attributed to Fe impurity; N4 – signal at g~2.1-2.0; N5 – signal at g=2 attributed to the presence of hole centers in the SiO₂ matrix (in each figure is given at a smaller scale a detailed spectrum within this range, with the corresponding electron-hole centers, characteristic of SiO₂ and not being discussed here).

The results are reported in Table 2, with data from earlier EPR studies of chalcedony (Plyusnina and Kostov, 1988) and jasper (Hemantha Kumar et al., 2010). The interpretation of the

EPR spectra is made according to the existing system and methodology of description of electron-hole centers in polycrystalline quartz samples (Kostov and Bershov, 1987; Lyutov, 2004). The obtained ESR spectra of jasper can be compared with other ones – for example, of jaspers with the same three colours from occurrences in the same region in Momchilgrad in the Eastern Rhodopes (Kostov and Pazderov, 2016).

The wide signal N1 is recorded in samples of any colour and therefore can not be used as a typomorphic spectroscopic sign. The signal N2 at g=4.3 is associated with structural iron in tetrahedral coordination in the quartz matrix and apparently is not associated with any of the admixing mineral phases. The wide signal N3 in the range of g~2.3-2.1 is not noted in red hematite-bearing jaspers, but it may be associated with a goethite impurity. The signal N4 at g~2.1-2.0 is present in all jasper samples (with maximum intensity in red hematite-bearing samples) and its intensity may possibly correlate with the N5 signal intensity, which is interpreted as a total amount of defect hole centers in SiO₂ matrix. According to EPR data for synthetic hematite and goethite specimens, both minerals have only one signal of varying width, centered at g~2, while magnetite gives broad lines in different magnetic field ranges (Guskos et al., 2002). The latter phase may be the cause of EPR signals N1 and/or N3. Visually magnetite is found in samples of red jasper from the area of Zvezdel.

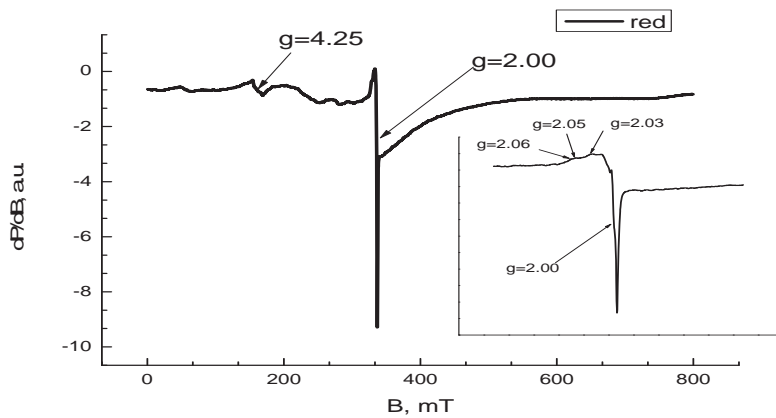


Fig. 5. EPR spectrum of green jasper (aVu1); second smaller spectrum – detail in the g=2 range

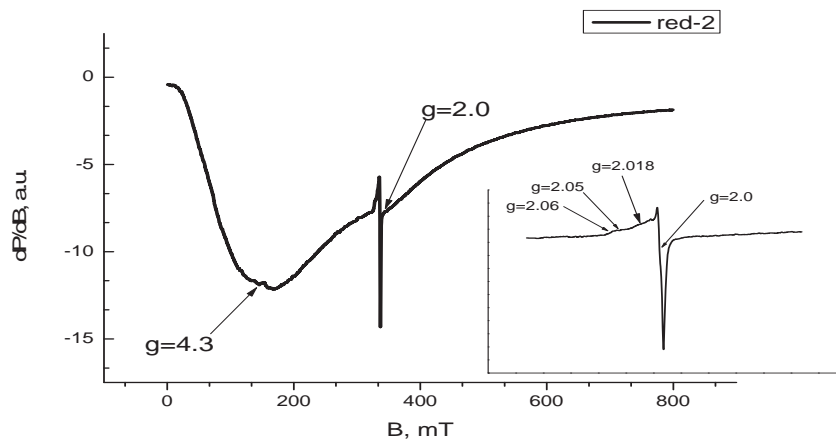


Fig. 6. EPR spectrum of red jasper (aCh2); second smaller spectrum – detail in the g=2 range

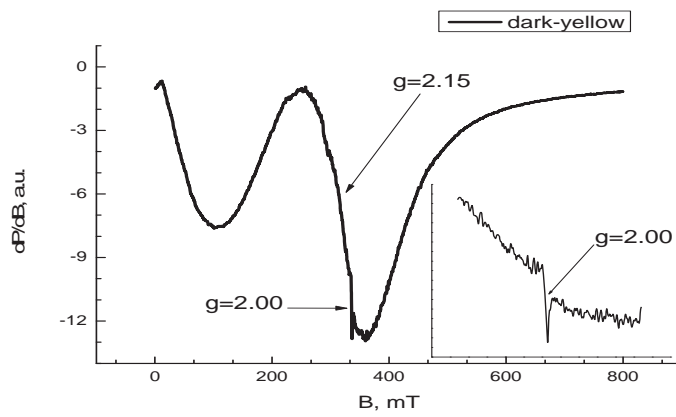


Fig. 7. EPR spectrum of yellow jasper (aVu3); second smaller spectrum – detail in the g=2 range

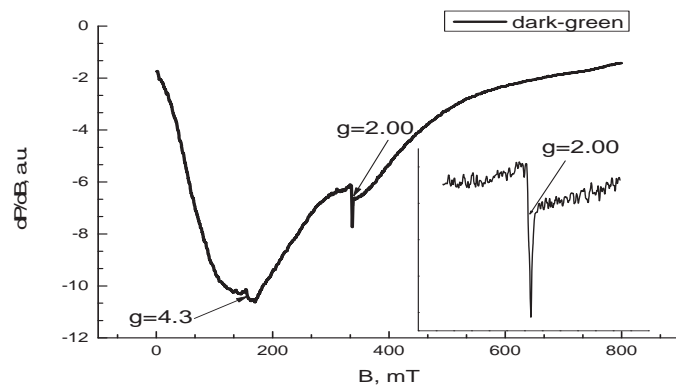


Fig. 8. EPR spectrum of dark green jasper (aNa8); second smaller spectrum – detail in the g=2 range

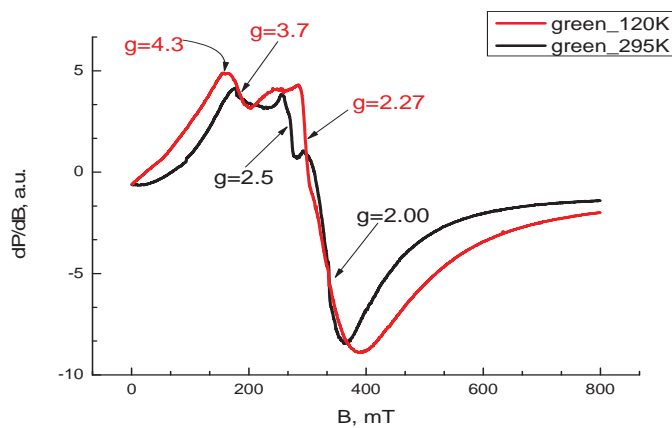


Fig. 9. EPR spectrum of green jasper (aVu4); upper line – at temperature 120 K

Table 2.

EPR data (g factor) and intensity (in arbitrary units) of signals in the EPR spectra ($g_q - g=2$ of importance for the silica phase)

Sample, colour	$g \sim 10$	$g=4.3$	$g \sim 2.3-2.1$	$g \sim 2.1-2.0$	$g_q=2$
aVu1 red	-	0.6	-	9.4	2.7
aCh2 red	+	0.3	-	8.5	1.1
aVu3 yellow	+	-	+	3.0	0.8
aNa8 dark green	+	0.5	-	1.6	0.4
aVu4 green	-	+	+	0.8	+
Pi1 red	+	++	-	+	+
Ne1 green	-	+	-	+	+
Ne2 yellow	-	+	+	+	+
Ne3 red	-	+	-	++	++
Pa1 green	-	-	-	+	-
X* colourless	n.a.	n.a.	+	-	+
XX** red	+	+	-	+	+

*Colourless chalcedony from the Momchilgrad area (Plyusnina and Kostov, 1988; n.a. – not analyzed); **Red jasper from Taiwan (Hemantha Kumar et al., 2010).

Conclusion

Through Mössbauer spectroscopy and through Electronic Paramagnetic Resonance (EPR), the iron status and distribution of different in valence iron ions in the three most important impurity phases of jasper from the Eastern Rhodopes – hematite, goethite and celadonite are studied, which are related to red, yellow to yellowishbrown and green colouration, respectively. In the Mössbauer spectrum of red jasper, Fe³⁺ sextets characteristic of hematite and goethite are detected, in the spectrum of yellow jasper – Fe³⁺ sextets characteristic only of goethite, and in the green jasper spectrum – Fe³⁺ and Fe²⁺ doublets associated with celadonite, as well as at a lower degree Fe³⁺ sextets characteristic of hematite and goethite.

The EPR spectra data helps to establish the role of iron in the SiO₂ matrix or in the impurity mineral phases responsible for one or another coloration of the jasper. The distribution and intensity of the EPR signals in the respective spectra can be used in the correlation of geological and archaeological samples, as well as a guide in the search for the source of raw material or local geochemical anomalies.

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