

**CONTRIBUTIONS TO THE STUDY OF CHALCEDONY AND OPAL  
QUARTERED IN THE ANDESITES FROM BUCURESCI-CRISCIOR  
PERIMETER (BRAD, HUNEDOARA COUNTY) – PART 1**

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**Abstract**

The opal and chalcedony described in the Bucuresci - Criscior perimeter present a series of particularities that differentiate them from the characteristics of other areas of Romania and even from the neighbour areas. The present study offered a series of new data regarding the geochemistry, the genesis and the coloration of the “solidified silica gels” quartered in the andesites from the Bucuresci - Criscior perimeter. The following aspects were particularly approached: 1) the content and the manner of distribution of some minor elements (Na, K, Ca, Mg, Fe, Cr, Ni, Co, Zn, Cu) according to the relation between the opal and chalcedony contents, the distribution rate of the “solidified silica gels”; 2) establishing some minor correlations between the minor elements content (especially those with chromophore role) and the relation between the opal and chalcedony contents; and 3) some aspects referring to the mechanisms of genesis and coloration of the “solidified silica gels” from the perimeter mentioned. The interpretations and conclusions formulated were based on the results of the chemical and instrumental analyses completed on 16 samples selected from those assayed from Bucuresci-Criscior perimeter.

KEY WORDS: chalcedony, opal, agates

**Introduction**

Numerous studies regarding the geology, the petrography and the mineralogy of Brad area (Hunedoara county) mention the presence of the quartered opal and the chalcedony, both in the quartz andesites with hornblende and biotite, and also in the andesites with hornblende and quartz (Rădulescu & Dimitrescu (1966), Ghițulescu & Borcoș (1966), Mutihac & Ionesi (1974), Ianovici et al. (1976), Berbeleac et al. (1979),

Mutihac (1982, 1990), Rădulescu & Dimitrescu (1982), Borcoş et al. (1986), Mârza (1999)). These studies discuss in detail the mineralogy and geochemistry of the opal and chalcedony from the area mentioned and the fundamental aspects referring to the genesis of these minerals, respectively.

The opal and chalcedony described in the Bucuresti-Criscior perimeter present a series of particularities that differentiate them from the occurrences from other areas of Romania (Ghiorghiu & Mareş (1966), Moţiu & Ghiurcă (1979), Ilinca (1989), Iancu & Mihăşan (1991), Iancu et al. (1999), Iancu & Bulgariu (2003)) and even from the neighbour areas. Although according to some people, the opals and chalcedonies from the Bucuresti - Criscior perimeter belong to the category of agates, our studies showed that they present a series of structural, mineralogical and chemical atypical characteristics, according to which the placement in the category of agates is questionable.

The present study brings a series of new data referring to the geochemistry, genesis and coloration of the “solidified silica gels” quartered in the andesites from the Bucuresti-Criscior perimeter. The following aspects were particularly studied: (1) the content and the manner of distribution of some minor elements (Na, K, CA, Mg, Al, Fe, Cr, Ni, Zn, Cu, Co, V) according to the relation between the opal and chalcedony contents, the rate of “solidified silica gels” distribution, respectively; (2) establishing some minor correlations between the minor elements content (especially those with chromophore role) and the relation between the opal and chalcedony contents; (3) some aspects referring to the mechanisms of genesis and coloration of the “solidified silica gels” from the perimeter mentioned. The interpretations and conclusions formulated were based on the results of the chemical and instrumental analyses designed on 16 samples selected from the samples assayed from Bucuresti-Criscior perimeter.

### Experimental

**1. The samples of work.** For designing the study, several rock samples from the Bucuresti-Criscior perimeter were assayed, of which, a number of 16 samples were selected afterwards for carrying out the studies (figure 1). The rock samples were processed in the following manner:

a) *The creation of lapidary sections* – for the microscopic studies at the binocular eyeglass.

b) *The preparation of average samples for the chemical and instrumental analyses.* For this purpose, the rock was sectioned in three successive stages: crushing, grinding operation in a ball mill (Fritsch model) - 30 minutes at 600 rotative speeds / minute; grinding in agate mortar under acetone. From the milled material (with the granulation < 2 µ) the average samples were obtained (through the method of quarters) used at the chemical analysis, through diffraction with X-rays and absorption spectrometry in IR (Demetrescu et al. (1966), Bulgariu & Rusu (2005)).

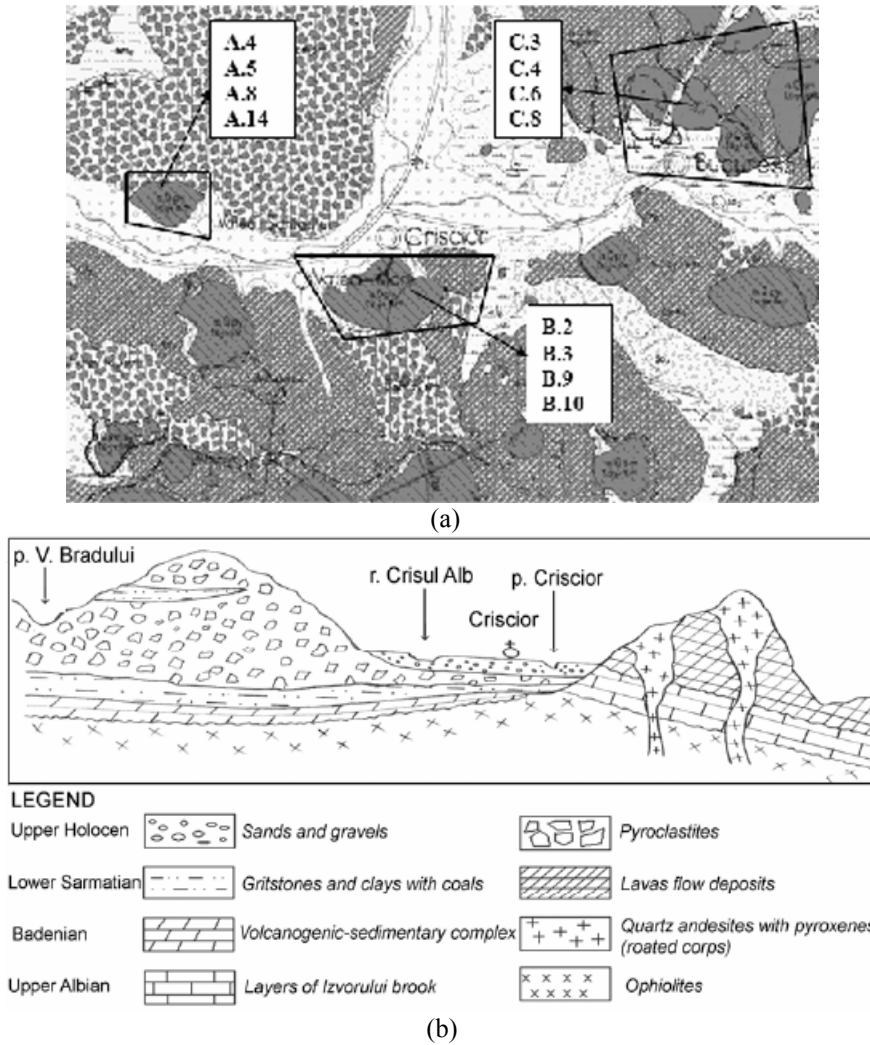


Fig. 1. (a) The relative localization of areas of assay from the studied perimeter (Geological map of Romania, scale 1:200,000). On the map, the selected samples for carrying out the laboratory samples are specified. (b) Geological profile between Bradului Valley – Criscior – Bucuresci. The samples were drawing from routed corps of volcanic apparatus from each sector (Criscior, Bucuresci, Scheaului Valley).

Table 1. The attribution of absorption bands in infrared according to the vibration and the analytical information they provide

Vibration types	Observations
<b>Si – O – Si (Al; Fe) bonds vibrations</b>	
Valence vibrations 700 ÷ 1200 cm <sup>-1</sup> v <sub>asym</sub> = 970 ÷ 1100 cm <sup>-1</sup> v <sub>sym</sub> = 600 ÷ 800 cm <sup>-1</sup>	Weak coupling with: the vibrations of HO <sup>-</sup> and H <sub>2</sub> O bonded by easy exchangeable cations; network vibrations. In 500 ÷ 540 cm <sup>-1</sup> domain: the mixt absorption bands (the Si – O bond deformation vibrations; the cations in octahedral coordination stretching, network vibrations etc.). [SiO <sub>4</sub> ] <sub>isolate</sub> : v <sub>asym</sub> = 800 ÷ 1000 cm <sup>-1</sup> ; [SiO <sub>4</sub> ] <sub>condensate</sub> : v <sub>asym</sub> = 200 ÷ 900 cm <sup>-1</sup> ; [SiO <sub>6</sub> ] <sub>condensate</sub> : v <sub>asym</sub> = 600 ÷ 950 cm <sup>-1</sup> ; [AlO <sub>4</sub> ] <sub>isolate</sub> : v <sub>asym</sub> = 650 ÷ 800 cm <sup>-1</sup> ; [AlO <sub>4</sub> ] <sub>condensate</sub> : v <sub>asym</sub> = 700 ÷ 900 cm <sup>-1</sup> ; [AlO <sub>6</sub> ] <sub>isolate</sub> : v <sub>asym</sub> = 400 ÷ 450 cm <sup>-1</sup> ; [AlO <sub>6</sub> ] <sub>condensate</sub> : v <sub>asym</sub> = 500 ÷ 650 cm <sup>-1</sup> .
Deformation vibrations δ = 150 ÷ 600 cm <sup>-1</sup>	Strong coupling with: vibrations of cations in octahedral coordination; apparent translation vibrations of HO <sup>-</sup> .
<b>Water vibrations</b>	
Valence vibrations (H–O) 3400 ÷ 3750 cm <sup>-1</sup>	Vibrations of H–O groups: free (3700 cm <sup>-1</sup> , 3540 ÷ 3675 cm <sup>-1</sup> ) and bonded (2500 ÷ 3400 cm <sup>-1</sup> ). Si–OH: ν = 3700 ÷ 3750 cm <sup>-1</sup> ; Al–OH: ν = 3680 ÷ 3710 cm <sup>-1</sup> ; (Cation)–OH: ν = 3540 ÷ 3650 cm <sup>-1</sup> .
Deformation vibrations (free) 600 ÷ 950 cm <sup>-1</sup>	Vibrations of H–O groups: free (3700 cm <sup>-1</sup> , 1610 ÷ 1700 cm <sup>-1</sup> ) and in octahedral positions (800 ÷ 950 cm <sup>-1</sup> ). (Fe <sup>2+</sup> Fe <sup>3+</sup> )–OH: ≈ 800 cm <sup>-1</sup> ; (MgFe <sup>3+</sup> )–OH: ≈ 815 cm <sup>-1</sup> ; (MgAl)–OH: ≈ 840 cm <sup>-1</sup> ; (Fe <sup>3+</sup> Al)–OH: ≈ 890 cm <sup>-1</sup> ; (Al <sup>IV</sup> Al <sup>VI</sup> )–OH: 910 ÷ 950 cm <sup>-1</sup> .
<b>Network vibrations</b>	
300 ÷ 420; 500 ÷ 650 cm <sup>-1</sup>	Deformation vibrations. Mixt absorption bands.
<b>Diagnosis bands</b>	
Quartz	(405; 470; 515; 590; 615; 650; 700); (790; 810); (1100; 1180); 1630
Chalcedony	(415; 470; 525; 585; 610; 640; 650; 690); (790; 810); (1100; 1180; 1450; 1530); 1650
Opal	(405; 470; 525; 600; 700); (720; 790; 810); (1110; 1180; 1450); 1630

*Reference:* Hunt & Salisbury (1970), Wilkins et al. (1974), Farmer (1974), Gadsden (1975), Hlavay & Inczdey (1979), Matei et al. (1986), Calas & Howthorne (1988), Mozgawa et al. (1999), Bulgariu (2005).

From the rock average samples, through magnetic separation (Franz isodynamic separator, model L.1), after Bulgariu's method (2002, 2005), we obtained mineral fractions with a content of > 98.75 % from the solidified silica gels, used for carrying out the chemical and instrumental analyses (the analyses on average samples).

c) *The separation of solidified silica gels.* The differential samples for analysing the solidified silica gels were collected through hewing and polishing. Afterwards, the collected material was chipped until granulation  $< 2 \mu$  according to the method described previously. According to the studies carried out at the binocular eyeglass on each sample the areas in which the opal predominates quantitatively and the areas where the chalcedony predominates were delimited. Differential samples were collected from these areas and they were used for carrying out the analyses.

Table 2. The water, silica, and specific weight content of the solidified silica gels from the Bucuresti-Criscior perimeter

Sample		H <sub>2</sub> O				Silica				G.s; g/cm <sup>3</sup>
		Total	H <sub>2</sub> O	(HO) <sup>(1)</sup>	(HO) <sup>(2)</sup>	Total	Q	Op	Cal.	
<b>A.4</b>	A S	6.58	5.15	0.94	14.25	99.57	1.14	62.37	35.40	2.21
<b>A.5</b>	A S	4.15	3.20	0.45	10.75	99.26	0.80	58.91	38.75	2.36
<b>A.8</b>	A S	5.93	4.91	0.78	15.00	97.85	2.08	61.70	33.39	2.19
<b>A.1 4</b>	A S	6.37	5.05	1.10	17.00	98.62	0.75	63.15	34.05	2.27
<b>B.2</b>	A S	3.95	3.64	0.51	15.60	98.70	1.48	38.95	57.73	2.38
	I	5.22	4.17	0.65	12.55	98.21	0.55	70.25	26.14	2.17
	II	3.25	2.10	0.71	21.00	99.68	3.18	25.94	68.56	2.57
<b>B.3</b>	A S	3.75	3.75	0.55	16.85	99.12	2.41	31.26	64.05	3.41
	I	4.75	3.90	0.60	13.10	97.89	0.67	65.00	31.47	2.20
	II	2.70	1.95	0.58	18.55	99.75	4.00	18.12	76.55	2.61
<b>C.3</b>	A S	2.81	2.63	0.28	11.35	99.56	5.88	25.74	69.19	2.56
	I	4.58	4.25	0.40	8.50	99.35	2.90	54.79	40.80	2.21
	II	2.10	1.55	0.35	17.90	99.80	6.15	12.36	79.75	2.59
<b>C.4</b>	A S	1.96	1.83	0.26	9.88	99.63	8.21	18.00	72.87	2.58
	I	4.85	3.95	0.52	10.15	98.45	3.75	56.35	37.65	2.23
	II	1.60	1.10	0.37	13.75	99.59	9.40	7.73	82.10	2.65

H<sub>2</sub>O-total: evaluated from the thermal analysis data; H<sub>2</sub>O - water present in non-dissociated form; estimation from the chemical analysis data (at 105<sup>0</sup> C) and the absorption spectres in infrared; (HO): dissociated water (quantified as HO groups);

estimation from the absorption spectres in IR (see table 1); (1) related to the total quantity of analysed sample; (2) related to the total quantity of water contained in the sample; Q-quartz; Op-opal; Cal-chalcedony; AS-average sample; I-opal area; II-chalcedony area.

**2. The chemical analyses** – were carried out, both on average samples, and also on differential samples obtained from each rock sample. The samples were decomposed by treating them with a mixture of HCl (conc.), HNO<sub>3</sub> (conc.) and H<sub>2</sub>SO<sub>4</sub> (conc.). The silica (the total content) was determined by the other elements (tables 2; 3). In order to establish the provenience of silica from the residues obtained, we recurred to an ulterior decomposed with NaOH 20 % (3 hours at 100°C). The work method used is well described in the specialty literature (Demetrescu et al. (1966), Jones & Dreher (1996), Sparks (1997), Bulgariu & Rusu (2005)). The minor elements were determined after a previous concentration from the work solutions through extraction in the system with two polyethylene glycol water phases 1550 (20 %) – Na<sub>2</sub>SO<sub>4</sub> 20 % (Bulgariu (2006)).

Table 3. The chemical composition of the studied silica gels samples  
(average samples analyses)

	A.4	A.5	A.8	A.14	B2	B3	C3	C4
SiO <sub>2</sub>	99.57	99.26	97.85	98.62	98.70	99.12	99.56	99.63
Al <sub>2</sub> O <sub>3</sub>	0.11	0.14	0.05	0.17	0.69	0.54	0.09	0.06
Fe <sub>2</sub> O <sub>3</sub>	0.02	0.02	0.01	0.05	0.12	0.27	0.07	0.10
Na*	335	274	219	305	754	681	206	188
K*	41	68	55	37	110	117	46	52
Ca*	152	135	178	160	397	443	202	194
Mg*	35	27	31	33	101	109	38	32
Cr*	6	8	11	6	n.d.	n.d.	22	27
Co*	5	5	3	4	n.d.	n.d.	9	11
V*	22	29	14	17	n.d.	n.d.	15	12
Ni*	9	13	8	9	2	n.d.	2	4
Zn*	6	6	3	8	19	24	11	15

\*in ppm. I–opal area; II–chalcedony area. *Analysis methods*: SiO<sub>2</sub> – microgravimetric; Al; Fe - spectrophotometrical; Na, K - flamphotometrical; Ca, Mg - potentiometric titration; Cr, Co, V, Ni, Zn - atomic absorption (after pre-concentration); n.d.-not detected through the utilized analysis methods.

**3. Instrumental analyses** - were carried out in order to: (a) establish the chemical-mineralogical composition; (b) estimate the opal, chalcedony, and quartz composition; (c) determine the total content of water and its intra crystalline speciation forms (Bulgariu (2005)); (d) study the structure and mechanisms of colouring the solidified silica gels.

The analyses through X rays diffraction were carried out through the powder method (Straumanis method) under the following conditions: FeK $\alpha$  radiation (Mn filter), 35 kV, 20 mA, 4 hours time of exposure, camera diameter  $\Phi_2 = 114.60$  mm, apparatus: DRON 2.0 (Jones & Dreher (1996), Sparks (1997), Bulgariu (2005)). The differentiation of silica polymorphs through diffraction with X rays was achieved based on the process described by Iakovleeva et al. (1976). Basically, the method consists of differentiating the spectres of X rays diffraction of diffraction lines intensities (110), (102) and (111) for the silica polymorphs. The method allows determining the quartz and the chalcedony with an acceptable precision. In the case of the opal it is less precise (Pelto (1954), Iakovleeva (1976), Bobyshev & Radzig (1988)).

The spectral analyses in the infrared field were carried out through the process of tablet forming in KBr (relation sample KBr = 1:100), the method of adding a blank matrix, apparatus: spectrometer of absorption in IR, model Bio-Rad (Bulgariu (2005)). The method of interpreting the absorption spectres in infrared and the absorption bands used for determinations are indicated in table 1. The spectral analyses in the UV-VIS field were carried out through a similar process in this case the tablet forming process of the samples being made in the polyethylene glycol (relation sample/matrix= 1:10); UV-VIS spectrophotometer apparatus, model UNICAM SP.800). The spectres obtained both the ones in IR and those in UV-VIS, were used for determining the transition energies corresponding to the absorption bands from the respective fields and to the relative estimation in the width of bands prohibited for the studied solidified silica gels (Farmer (1974), Willkin et al. (1974), Garofalini (1982, 1983), Griffen (1992)).

The differential thermal analyses were carried out for determining the total content of water from the samples (Todor (1972)) and for differentiating the intra - crystalline speciation forms of the water molecules (Bulgariu (2005)). The determinations were carried out with a Derivatograph MOM Budapest Paulik-Paulik – Erdey.2, under the following circumstances: normal atmosphere, platinum caster, reference  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, warming speed 2.5÷5°C / min., DTG: 1 / 2; TG: 100÷150 mg.

## Results and discussions

1. *The quartz andesite with hornblende and biotite* is a rock of grey or grey-whitish colour, with a porphyric structure and massive texture. The microscopic analyses, through X rays diffraction and absorption spectrometry in infrared have indicated the presence of the following minerals: plagioclase feldspars 23.50÷27 %; quartz: 10÷18.75 %; biotite: 9.5÷14 %; green hornblende: 2.65÷4.25 % (partially substituted by chlorite or carbonates). These values represent the limits of variation of the contents for 6 samples of analysed rock (2 samples of each work area delimited by us in the studied perimeter – figure 1). The fundamental mass of the rock presents the holocrystalline-micro granular structure, being composed of quartz microlites, feldspar, hornblende and magnetite. In some cases, clay and carbonations were also noticed.

The solidified silica gels, frequently associated with calcite, iron oxyhydroxides and other neoformation minerals, appear as deposits in the gaps and cracks from the rock mass. Although there are occurrences of zeolites associated to the deposits from the gaps and cracks in this area, in the andesite samples from the Bucuresti-Criscior perimeter (Bedelean & Nedopaca (1975), Berbeleac et al. (1979), Bedelean (1982), Bulgariu (2005)), the studies carried out by us did not discover the presence of these minerals. According to the manner of distribution in the rock mass and the physical-chemical characteristics, the solidified silica gels were divided into 3 classes corresponding to the three areas delimited by us in the Bucuresti-Criscior perimeter.

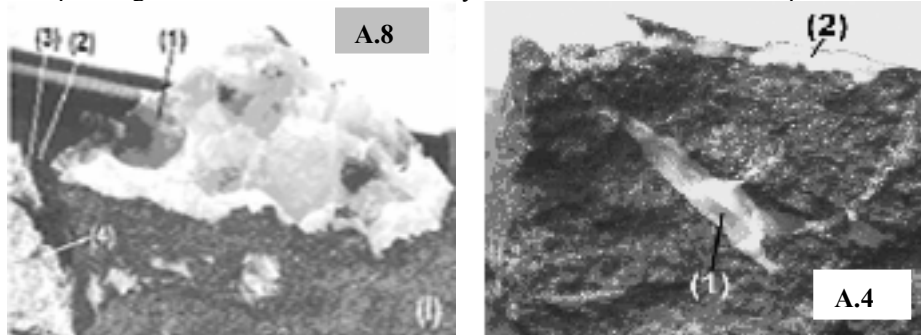


Fig. 2. Samples with solidified silica gels from the A area (Scheaului Valley). *Sample A.8*: (1) and (2) solidified silica gels (the two areas have different physical-chemical characteristics – see tables 2 and 3); (3) carbonates (predominantly calcite); (4) iron oxyhydroxides; (1) - the host rock. *Sample A.4*: (1) and (2) solidified silica gels (they have similar physical-chemical properties); (3) calcite and clay mineral deposits.

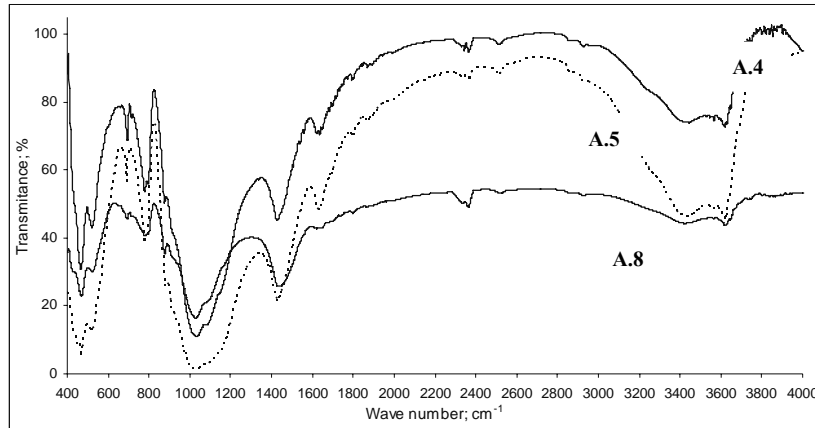


Fig. 3. The absorption spectra in infrared for the silica gels samples from the Bucuresti-Criscior perimeter (A area).



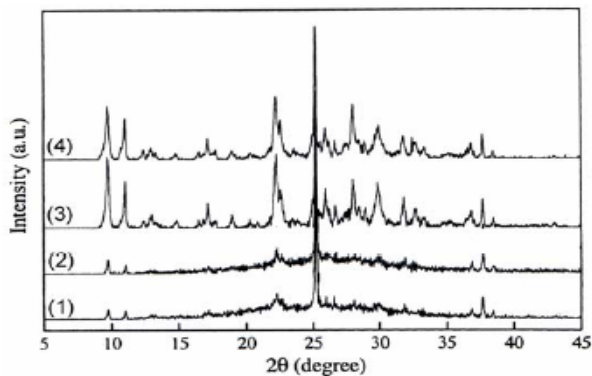


Fig. 4. The diffraction spectra with X rays of the solidified silica gels from the A area – the samples: A.4 (1), A.5 (2), A.8 (3) and A.14 (4).

2. The solidified silica gels in the A area have the colour of light blue to mat white (figure 2), the colour being inequable in the gel mass, does not present petrographic fibrousnesses or zonations (typical to the agates described in this Brad by several authors). In these samples, the opal is dominating in quantity (58.91÷63.15 %) compared to the chalcedony (33.39÷38.75 %), the quartz being present in insignificant quantities (0.75÷2.08 %). The opal identified in the A area samples appears in a shapeless form and not under microcrystalline form (as it usually appears in the agates). Compared to the solidified silica gels from the B and C areas, those from the A areas have a more reduced distribution rate, and the percentage of neoformation minerals they are associated with is very small. Both in the mass of these silica gels and in their contact with the guest rock, deposits of iron or calcite ox hydroxides were not observed.

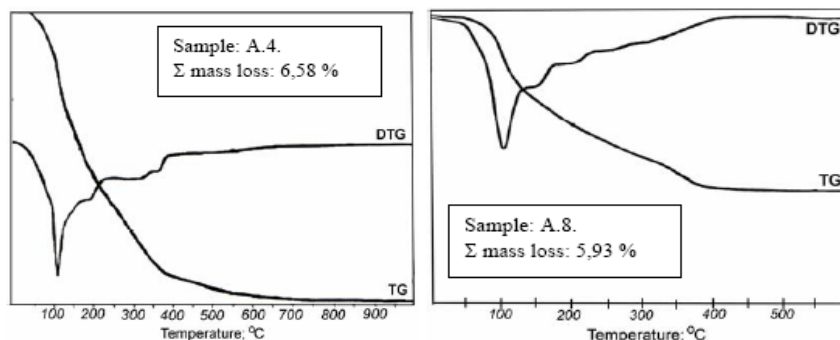


Fig. 5. The derivatograms for the solidified silica gels A4 and A8 (A area). Experimental conditions: the warming speed  $5^{\circ}\text{C}/\text{min.}$ ; caster: Pt; reference  $\alpha\text{-Al}_2\text{O}_3$ .

The specific weight of the silica gels from the A area varies between  $19\div 2.36\text{ g.cm}^{-3}$ , generally in accordance with the chalcedony and opal contents. According to the

differential thermal analyses and to the spectral analyses in infrared, corroborated with the chemical analyses, the total content of water varies between  $4.15 \div 6.58$  %, of which the water present under dissociated form (determined under grouping form HO) represents  $10.75 \div 17.00$  %. These results are confirmed by the existence of two-dehydration stages on the thermal curves (figure 5), respectively on the souses from the water absorption bands (figure 3), corresponding to the dissociated water vibrations.

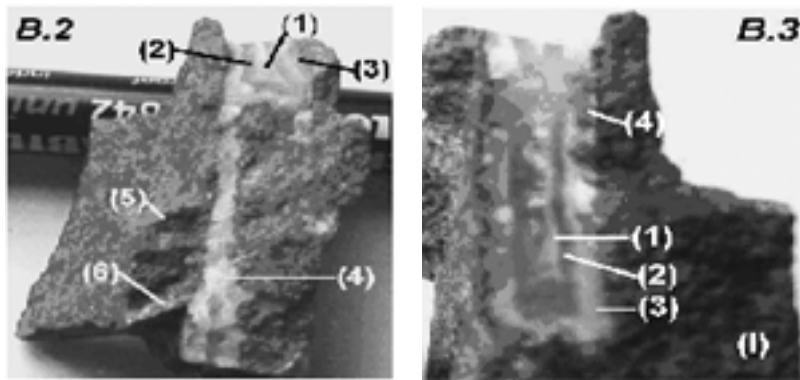


Fig. 6. Samples with solidified silica gels from the B area (Scheaului Valley). *Sample B.2*: (1); (3) - areas with chalcedony; (2); (4) - areas with opal; (5) - iron oxyhydroxides; (6) - calcite and clay mineral deposits. *Sample B.3*: (1), (3) - areas with opal; (2) - areas with chalcedony; (4) - iron oxyhydroxides; (I) - the host rock.

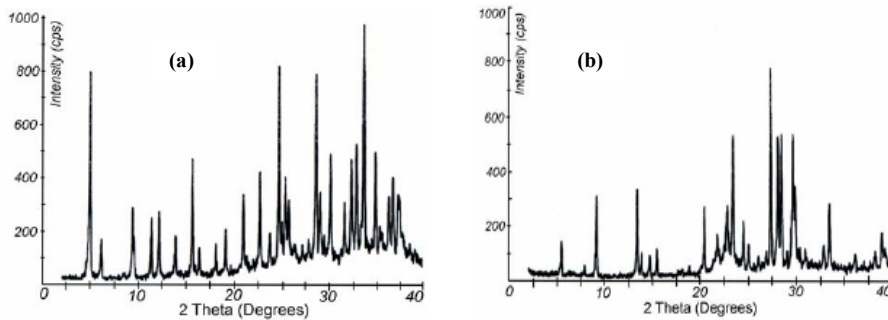


Fig. 7. The X rays diffraction spectres of the solidified silica gels from the B area - B.3 sample: (a) chalcedony portion; (b) opal portion.

**3.** *The solidified silica gels from the B area have a white colour with an obvious zonality given by the alternation of some transparent bands and opaque bands.*

The limit between these two bands is generally clearly marked (figure 6). The percentage with neoformation minerals that the silica gels from the B area are associated with is greater than in the case of silica gels from A area, these being represented by the iron oxyhydroxides, calcite; clay minerals and chlorites also appear, but more seldom (predominantly magnesium varieties) and sericite. The neoformation minerals are concentrated especially at the limit of separation between the silica gels and the host rock and with a more reduced percentage in the gels mass (on the cracks). The distribution rate is higher in the case of transparent bands, in which the chalcedony is predominant quantitatively (68.56÷76.55 %) compared to the opal (18.12÷25.94 %), and the quartz is encountered in larger quantities (2.61÷3.88 %) than in the A area samples, respectively the opaque portions. In the case of opaque portions the variation of opaque contents, chalcedony and quartz is contrary to the transparent portions.

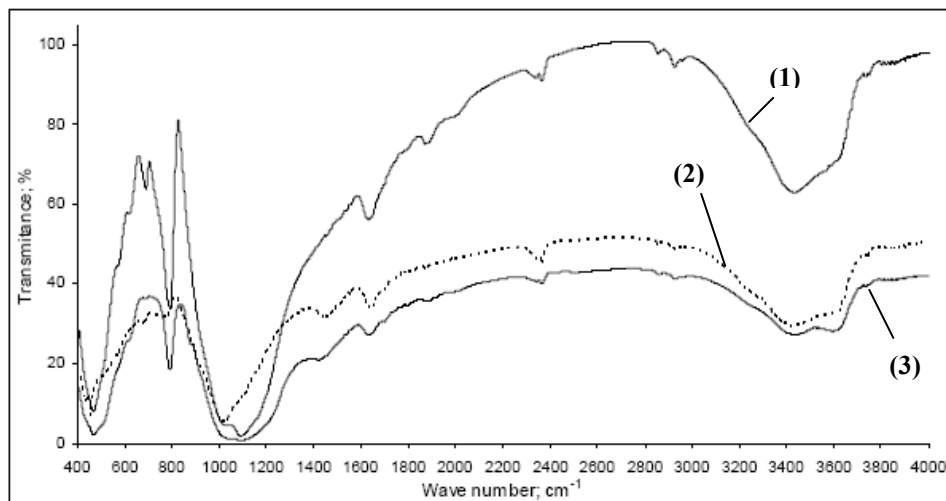


Fig. 8. Samples with solidified silica gels from the B area (Scheaului Valley) - The B.2 sample: (1) area with chalcedony; (2) and (3) area with opal areas.

The specific weight determined on average samples varies between  $2.38 \div 2.61 \text{ g.cm}^{-3}$ , in accordance with the opal, the chalcedony and quartz contents of the samples. The total content of water determined on average samples varies very little ( $3.75 \div 3.95 \%$ ), being slightly smaller than in the case of samples from the A area. The dissociated water represents  $15.60 \div 16.85 \%$  from the total content of water, higher values compared to the A area samples. We also noticed the fact that, in the portions where the opal predominates from the quantity point of view, the total content of water is a little higher,

and the water content under dissociate form and the specific weight are slightly smaller, compared to the portions where the chalcedony is predominant quantitatively.

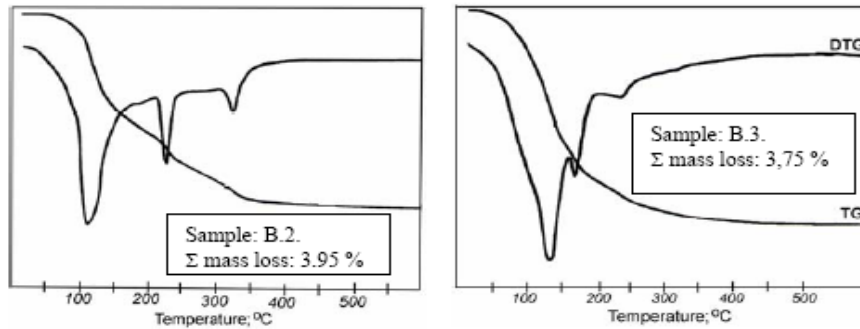


Fig. 9. The derivatograms for the solidified silica gels B.2 and B.3 (B area).  
Experimental conditions: the warming speed  $5^{\circ}\text{C}/\text{min.}$ ; caster: Pt; reference  $\alpha\text{-Al}_2\text{O}_3$ .

4. *The solidified silica gels from C area* – present a larger variety of colours, from white-mat, brown (with different shades), grey-grizzle that alternates in clearly delimited bands (figure 11). The zoning observed in these samples is different from the one observed in the B area samples.

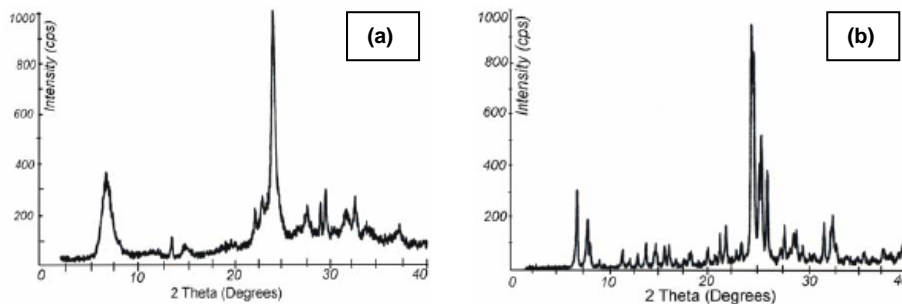


Fig. 10. The X rays diffraction spectres of the solidified silica gels from the C area - B.3 sample: (a) chalcedony portion; (b) opal portion.

For the majority of samples from the C area, we noticed the existence of a “nucleus” constituted predominantly from chalcedony (transparent or semi-transparent, slightly coloured). Then, a narrow area follows, where the opal is predominant (with turbid aspect, grey-grizzle) and a relatively extended area where the chalcedony (semitransparent, specifically coloured predominates) is predominant. At the contact between the silica gels from the C area and the host rock (which is mostly achieved through an area with chalcedony) we can notice deposits of iron oxyhydroxides,

carbonates and clay minerals. Generally, the percentage of neoformation minerals that the silica gels from the C area are associated with, is higher than in the case of silica gels from the A and B areas, these being represented by iron oxyhydroxides, calcite, clay minerals and chlorites subordinately (predominantly magnesium varieties) and sericite. The neoformation minerals are concentrated especially at the separation limit between the silica gels and the host rock and on the cracks from the gel mass.

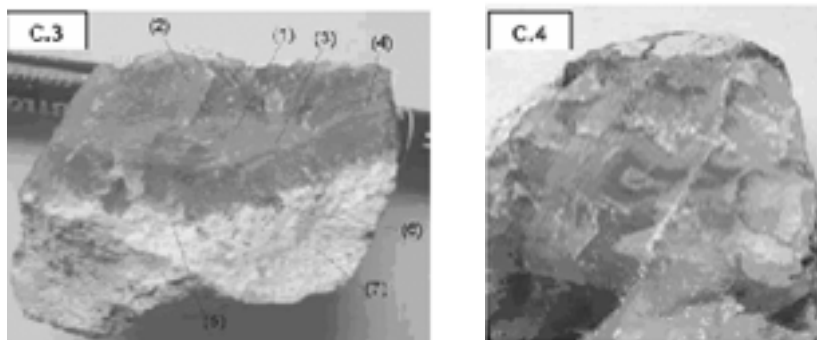


Fig. 11. Samples with solidified silica gels from the C area. *Sample C.3*: (1), (2) - areas with chalcedony (the two areas have different physical-chemical characteristics – see tables 2; 3); (3), (4) - areas with opal; (5), (6) - iron oxyhydroxides; (7) - the host rock.

The distribution rate is higher in the case of transparent bands, where the chalcedony is predominant quantitatively (79.75÷82.10 %) compared to the opal (7.73÷12.36 %), and the quartz is present in higher quantities (6.15÷9.40 %) than in the opaque portions. In the case of opaque portions, the variation of opal, chalcedony and quartz contents is the opposite for the transparent portions. Generally, the chalcedony and quartz contents are higher than in the A and B areas samples, and the total content of water is smaller.

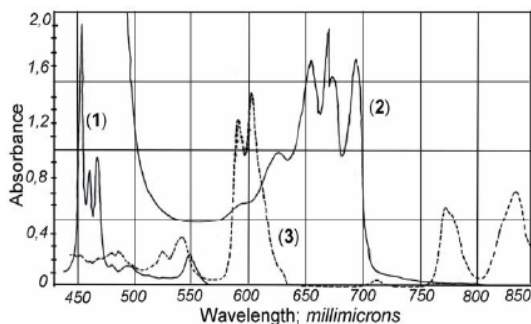


Fig. 12. The absorption spectres in UV-VIS for the silica gels samples from the A area (Bucuresci-Criscior perimeter): (1) sample C.3; (2) sample C.4; (3) sample C.6.

The specific weight, determined on average samples, varies between  $2.56 \div 2.58 \text{ g.cm}^{-3}$ , in accordance with the opal, chalcedony and opal contents of the samples. The total content of water on average samples varies between  $1.96 \div 2.81 \%$ , being slightly smaller than in the case of samples from A and B areas; the dissociated water represents  $11.35 \div 13.75 \%$  from the total content of water, smaller values compared to the A and B samples. Similar to the B area samples, we notice significant variations of the water content (total and dissociated) and specific weights from one portion to another of the same sample according to the opal and chalcedony content.

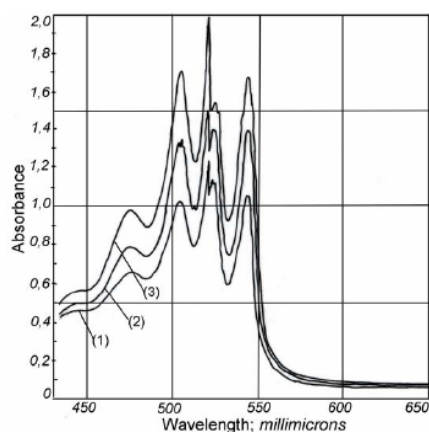


Fig. 13. The absorption spectres in UV-VIS for the silica gels samples from the A area (Bucuresci - Criscior perimeter): (1) sample A.4; (2) sample A.5; (3) sample A.8.

5. The minor elements and traces content do not indicate the existence of some specific correlations according to the opal / chalcedony relationship. In addition, the correlations between the elements presented in table 3 are insignificant and do not seem to have clear geochemical implications. We notice higher values of the Al, Fe, Na, K, Ca and Mg contents in the B area samples, and in the case of samples from the A and C areas we notice higher values of the Cr, Co, Cu, V contents (elements that are not present in the B area samples).

In the authors' opinion, both the variations of contents with minor elements and traces, and the correlations between them, cannot have certain geochemical significations for the moment. However, these aspects can be correlated with the structure and coloration of the studied silica gels. Thus, the appearance of the specific colorations and the zonation of silica gels can be attributed to the presence of metallic cationes with chromophore roles (ionic species with incomplete electronic structures present in the structure of silica gels in non-saturated states from the coordination point of view). This hypothesis is valid for the silica gels from the B area and partially for those in the C area. In the last case, the phenomena of emission/ absorption in VIS due

to the dispersion in the silica gels mass of some fine particles ( $\varnothing < 0.02 \mu\text{m}$ ), of some solid inclusions respectively, greatly contribute to the appearance of silica gels colorations. It is very difficult to differentiate the three mechanisms' contributions to colouring the silica gels.

Table 4. The transition energies and the width of prohibited bands for the studied silica gels.

Sample	$\Delta E$ ; eV	$\delta$ ; eV	Observations
A zone	2.55÷3.20	2.90	Strong absorptions in IR and UV-VIS (characteristics spectra). Chromophors: V (as $\text{VO}^+$ ion), $\text{Co}^{2+}$ , $\text{Cr}^{3+}$ (most probable in unsaturated coordination states).
B zone	0.39÷1.15	3.71	Don't take place absorptions in VIS (the silica gels don't have characteristic colours; they have a grey-troubled, in special in the zone with opal). Specific absorptions only in IR and partially in UV. The minor elements contents with chromophore role < the alkaline and earth-alkaline elements contents.
C Zone	1.43÷2.97	2.36	Strong absorptions in IR and UV-VIS (characteristics spectra). Chromophores: $\text{Cr}^{3+}$ , V (as $\text{VO}^{2+}$ ion), $\text{Co}^{2+}$ , $\text{Ni}^{2+}$ (probably in unsaturated coordination states). The complementary absorption mechanisms of electromagnetic radiation: the dispersion in silica gel mass of some powder particles ( $\varnothing < 0.02 \mu\text{m}$ ) and / or of some solid inclusions; the radiation absorption in VIS or elastic dispersion of photons on silica gel surface or on the microscopically fibres from structure.

$\Delta E$  (eV) – the transition energies;  $\delta$  (eV) – the prohibited bands width; eV – electron-volts. The calculus has been don eon the basis of obtained data from IR and UV-VIS spectra (figure 3; 8; 12; 13).

The calculations made through current mecano-quantic methods (the theory of the crystalline field; the theory of energy bands, the theory of frontier orbital) based on the spectres of absorption in infrared and UV-VIS, have indicated for the silica gels in the A and C areas values of the transition energies between 2.55÷3.20 eV, 1.43÷2.97 eV respectively, and values of the prohibited bands width between 2.36÷2.90 eV. These values largely explain the strong absorptions given by the silica gels in the A and C areas in the infrared field and UV-VIS, the appearance of specific colorations respectively.

In the case of silica gels from the B area, the transition energies have values between 0.39÷1.15 eV and values of the prohibited bands width of about 3.71 eV. These data largely explain the absence of specific colorations in the case of silica gels in the B area (there are no absorptions in VIS) and the existence of an absorption specific only to

IR (partially UV also). The aspects related to the genesis and mechanisms of colouring the silica gels from the Bucuresti-Criscior perimeter will be approached in more details in the second part of this study.

### Conclusions

1. The solidified silica gels from the Bucuresti-Criscior perimeter appear as deposits in the gaps and cracks of the rock mass (quartz andesite with hornblende and biotite), frequently associated with calcite, iron oxyhydroxides and other neoformation minerals.

2. According to the manner of distribution in the rock mass and the physical-chemical characteristics, the solidified silica gels from the Bucuresti-Criscior perimeter were divided in three classes, according to the three areas delimited by us in the studied perimeter):

(a) *The solidified silica gels from the A area* – have the colour of light blue to mat white, they do not present zonations or petrographic fibrousness (typical to the agates). The opal is dominant from the quantitative point of view compared to the chalcedony, the quartz being present in insignificant quantities. The identified opal is present under an amorphous form and not under microcrystalline form. The percentage of neoformation minerals they are associated with, is very small.

(b) *The solidified silica gels from the B area* – are uncoloured, with an obvious zonality given by the alternation of some transparent and opaque bands. The percentage of neoformation minerals they are associated with, is bigger, being represented by iron oxyhydroxides, calcite, clay minerals and chlorite subordinately (magnesium varieties) and sericite. The neoformation minerals are concentrated especially at the separation limit between the silica gels and the host rock and with a more reduced percentage in the mass of gels (on the cracks). In the case of transparent bands, the chalcedony predominates compared to the opal, and the quartz is present in larger quantities.

(c) *The solidified silica gels from the C area* – present a larger variety of colours, from white-mat, brown (with different shades), grey-grizzle, that alternates in clearly delimited bands. The zonation in these samples is different from the one observed in the B area sample: the chalcedony nucleus (transparent/semitransparent, slightly coloured)  $\Rightarrow$  narrow area with opal (cloudy aspect, grey-grizzle)  $\Rightarrow$  a large area with chalcedony (semitransparent, specifically coloured). At the contact between the silica gels and the host rock deposits of iron oxyhydroxides, carbonates and clay minerals appear.

3. The contents of minor elements and traces do not indicate the existence of a specific correlation according to the connection between opal/chalcedony. Also, the correlations between these elements are minor and do not seem to have clear geochemical significations.

4. The samples whose prohibited band width is about 3.5 eV, and whose transition energies are comprised between 0.5÷1 eV, do not absorb in VIS (they do not



present characteristic colorations; they have a grey-cloudy aspect, especially in the opal areas). They present specific absorptions only in IR and partially in UV. At these samples, the minor elements content with chromophore role > the content of alkaline elements and alkaline-earth content

5. The studied samples cannot be considered agates (in the strict sense) because they present a series of atypical chemical-mineralogical and structural characteristics.

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