New occurrence of gypsum in Belgrade city (Serbia)

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Introduction

During geological prospecting of the Belgrade city center in 2006 a new occurrence of gypsum was found in one borehole. Gypsum is rarely occurred mineral in Serbia, therefore every new occurrence of this mineral is of special interest. The last find of gypsum in Belgrade city, however, is not so surprising, because quite recently the mineral was found in the close proximity to Belgrade city — in Jajinci village (Tancic and Ilic, 2003). Gypsum occurrences are important because they can help in better understanding the geology of the studied areas, in reconstructing the climate and other circumstances related to the origin of gypsum.

For precise determining the mineral and chemical composition of the sampled borehole, X-ray powder diffraction, DTA, TGA, and chemical methods were employed.

Material preparation and applied investigation methods

X-ray powder diffraction patterns were recorded on Philips PW 1009 and PW 1051 X-ray diffractometers using Fe β-filtered CoKα irradiation (l = 1.79026 E) at U = 35 kV and I = 8 mA, 2θ range from 4 to 80°, goniometer speed V_g = 1/8° 2θ/min, and running paper speed 400 mm/h. It was used GM counter with mean plateau at 1550 V, sensitivity 320 imp/s for full scales, and RC constant of 4s. The sample was powdered and incorporated into standard aluminum holder with dimensions (in mm) 20x10x1.5. Metallic Si was used as standard to control the diffractometer precision before and after the experiments. The recorded patterns were further processed using a conventional procedure including measurement of the peak positions (2θ), calculation of the corresponding interplanar d-spacings, and identification of the present mineral phases comparing the experimental d-spacings and relative intensities (I) with those in the ICDD PDF database.

Differential thermal analysis (DTA) was performed using an ADAMEL LHOMARGY ATD 67 apparatus with sensitivity of 0.1 mV. Temperature was measured with a Pt-PtRh thermocouple.

Thermogravimetrical analysis (TGA) was carried out on a STANTON apparatus with 10°C/min heating speed and for temperature range from 20 to 1000°C.

Chemical methods were used for quantitative determination of SiO_2, SO_3, H_2O^-, and ignition losses (I.L.) — by gravimetrical method, and Al_2O_3, Fe_2O_3, CaO, MgO, K_2O, and Na_2O, and soluble Fe_2O_3, CaO, and MgO (after dissolving the sample in 2N HCl) — by atomic absorption spectrometric (AAS) method.

Results and discussion

The performed X-ray diffraction analysis of the sample (the corresponding pattern with measured d_{obs} is shown in fig. 1) allowed one to identify the following minerals ordered according to their quantity: calcite (peaks and their d-spacings are marked by letter C in fig. 1), gypsum (G), quartz (Q), clays/micas (CM), zeolites (Z), goethite (GE), lepidocrocite (L), and feldspars (F). Calcite, gypsum and quartz were found to be dominating minerals.

The results of the DTA and TGA investigations are represented at figure 2 and table 1.

In figure 2a it can be seen one essentially large endothermic peak at around 100-200°C and two smaller endothermic peaks in the temperature interval of 800-900°C (marked with arrows). According to the literature data (Mackenzie, 1957), the DTA curve of gypsum contains a double endothermic peak in the range of 100-200°C corresponding to loss of water in two stages: loss of 1 1/2 molecule transforming gypsum into bassanite and then total dehydration of the latter to anhydrite. At the same time, according to Janjic and Ristic (1989) gypsum transforms into bassanite at about 70°C. Taking into account this fact, we heated the original sample at 80°C and then performed the DTA (figure 2b) and TGA (table 1, columns b) investigations once again. The obtained results allowed us to suppose that the first large endothermic peak in the temperature range 100-200°C corresponds to the formation of bassan-

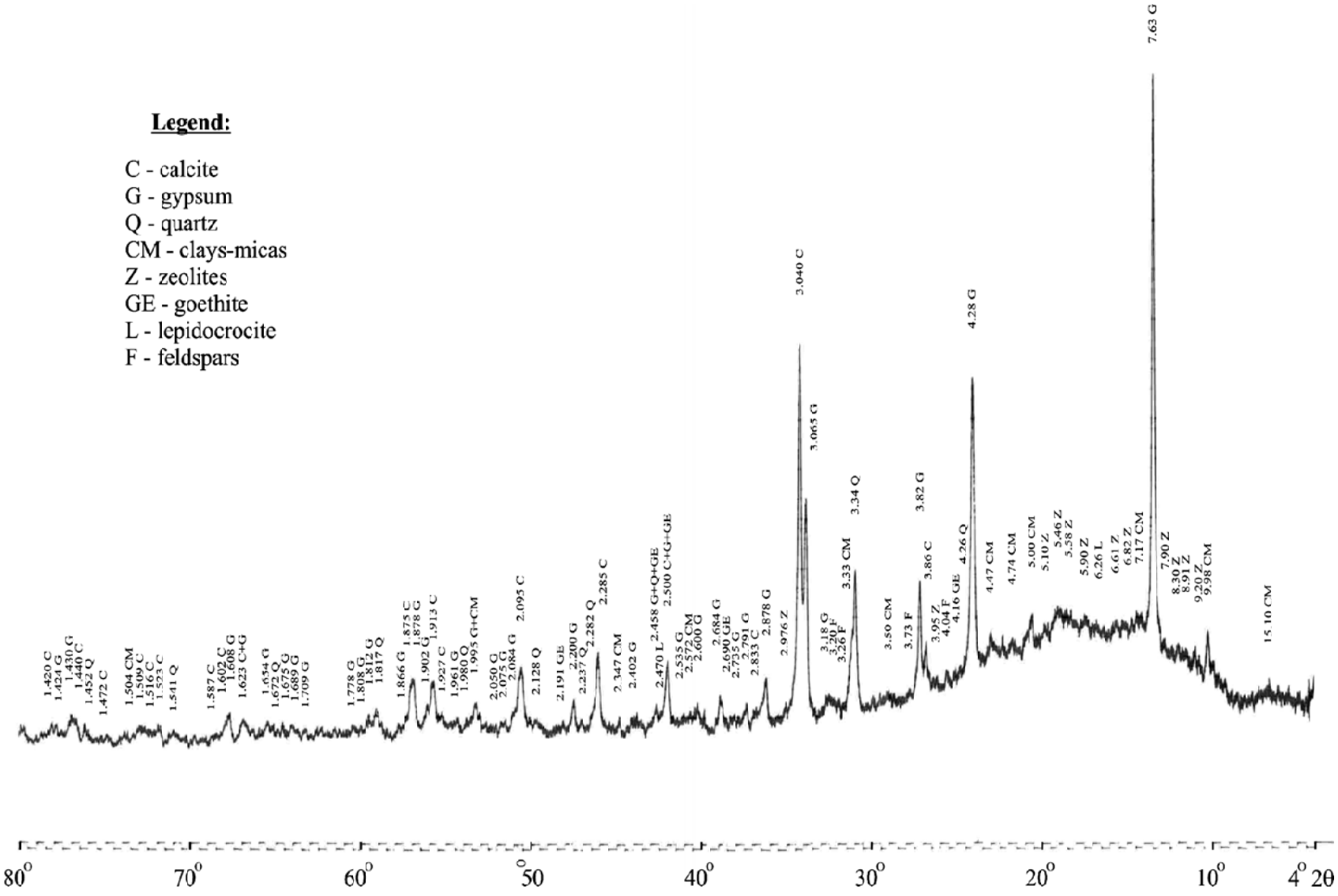

Fig. 1. X-ray powder diffraction pattern of the studied sample

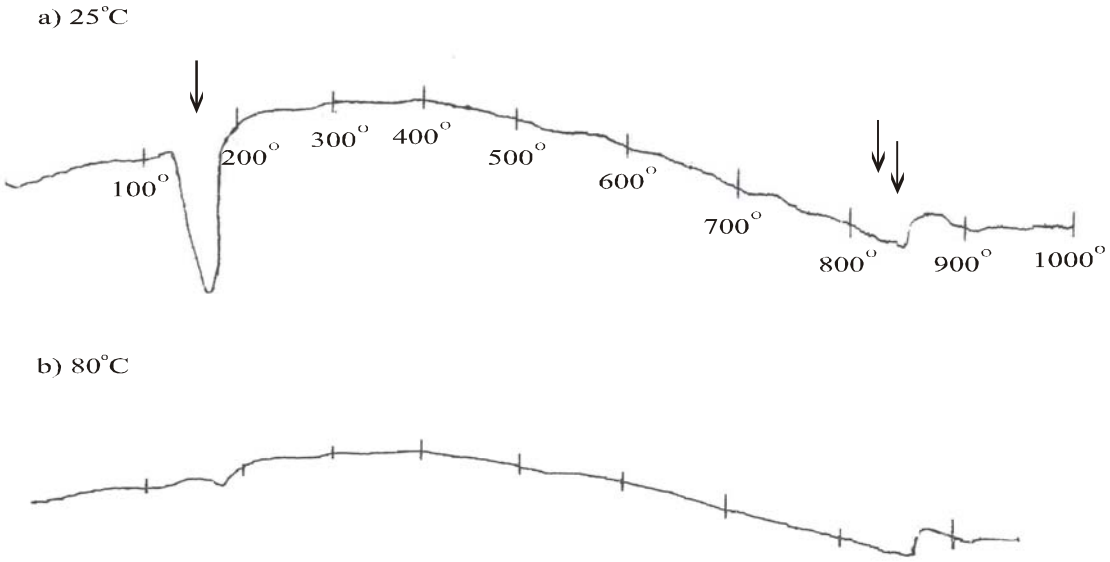

Fig. 2. DTA curves of the original sample (a) and that after treating at 80°C (b)

Table 1. TG analysis of the original sample (a) and that preliminary treated at 80°C (b)

Temperature (°C)	Loss (a)	Σ loss(a)	Loss (b)	Σ loss(b)
100	4.48	**4.48**	2.07	**2.07**
150	6.03	**3.10**	3.11	**2.77**
200	7.58		4.84	
250	11.20		4.84	
300	11.55		4.84	
350	11.55		4.84	
400	11.72	**6.04**	5.19	**1.73**
450	12.24		5.19	
500	13.10		5.88	
550	13.62		6.57	
600	14.48		6.92	
650	15.86		8.30	
700	18.44	**19.82**	9.86	**14.88**
750	22.06		13.14	
800	30.68		17.64	
850	33.44		21.45	
900	33.79		21.45	
950	33.79	**0.35**	21.45	**0.00**
1000	33.79		21.45	

ite after gypsum (at temperature 80°C), while the other two smaller endothermic peaks are related to calcite.

The observed differences between the weight losses (a) and (b) in table 1 seem to be due to complicated mineral composition of the studied sample including a lot of minerals, every one being with individual and not similar contribution to the total thermochemical characteristics of the sample. We suppose that the main difference in the obtained weight losses originates from the water of zeolites known as minerals easily losing and accepting the water molecules.

The weight loss difference of 14.88 wt.% for the temperature range 600-1000°C (table 1, columns b) can be related to CO_2 of calcite. Recalculation of

Table 2. Chemical composition of the studied sample (in wt.%)

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	I.L.$^{(500)}$	I.L.$^{(1000)}$	H_2O^-	Σ
%	24.22	8.81	4.21	25.73	1.14	2.30	0.29	10.44	4.24	15.90	3.46	100.74

this value gives content of calcite in the sample 33.84 wt.%, which corresponds to 18.96 wt.% of CaO (+ MgO).

The results of chemical investigations performed for the sample preliminary heated at 80°C are presented in table 2.

The SO_3 content of 10.44 wt% could be entirely recalculated into the gypsum content giving 22.45 wt.%, which is adequate to 7.31 wt.% of CaO and 4.69 wt.% of H_2O (1.17 wt.% of H_2O^- and 3.52% of I.L.^{500}). The rest quantities of CaO and MgO (0.54 wt. %), I.L.^{500} (0.72 wt.%), I.L.^{1000} (1.02 wt.%) and H_2O^- (2.29 wt.%), as well as the contents of all other oxides (SiO_2, Al_2O_3, Fe_2O_3, K_2O and Na_2O) can be related to the other minerals, i.e. quartz, clays/micas, zeolites, goethite, lepidocrocite and feldspars.

Conclusion

During geological prospecting of the Belgrade city center a new occurrence of gypsum was found in one borehole. The sample investigated with the X-ray powder diffraction, DTA, TGA and chemical methods contains mainly calcite (about 34%), gypsum (about 22.5%), quartz (15-20%) as well as, in smaller quantities, other minerals as clays/micas, zeolites, limonite (goethite and lepidocrocite) and feldspars.

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