

UDC 55

CODEN – GEOME 2

ISSN 0352 – 1206

# GEOLOGICA MACEDONICA



Geologica Macedonica	Год.	20	стр.	1–53	Штип	2006
Geologica Macedonica	Vol.		pp.		Štip	

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		pp.	Štip

## GEOLOGICA MACEDONICA

Издава: Published by:  
Рударско-геолошки факултет – Штип Faculty of Mining and Geology – Štip

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РЕДАКЦИЈА  
Рударско-геолошки факултет  
пошт. фах. 96  
МК-2000 Штип, Република Македонија  
Тел. 032 391 379  
E-mail: seraft@rgf.ukim.edu.mk

Address  
GEOLOGICA MACEDONICA  
EDITORIAL BOARD  
Faculty of Mining and Geology  
P. O. Box 96  
MK-2000 Štip, Republic of Macedonia  
Tel. ++ 389 32 391 379

Тираж: 400

Излегува еднаш годишно

Печати:

2<sup>ри</sup> Август „С“ – Штип

400 copies

Published yearly

Printed by:

2<sup>nd</sup> August "S" – Štip

Цена: 500 ден.

Бројот е отпечатен во декември 2006

Price: 500 den.

The edition was published in December 2006

На корицата:

Панорамска снимка на вулканската калдера Плавица

Photo on the cover:

Panoramic view of Plavica volcanic caldera



## MINERALOGICAL-CHEMICAL CHARACTERISTICS OF CALCITE FROM ZLETOVO, SASA AND BUČIM DEPOSITS

Tena Šijakova-Ivanova<sup>1</sup>, Vesna Zajkova-Paneva<sup>1</sup>, Ilinka Donova<sup>2</sup>

<sup>1</sup>*Faculty of Mining and Geology, "Sts. Cyril and Methodius" University,  
Goce Delčev 89, MK–2000 Štip, Republic of Macedonia*

<sup>2</sup>*Institute of Chemistry, Faculty of Natural Sciences and Mathematics, "Sts. Cyril and Methodius" University,  
P.O. Box 162, MK–1001, Skopje, Republic of Macedonia  
tena@rgf.ukim.edu.mk*

**Abstract:** The paper presents mineralogical-chemical characteristics, dependence between some elements and concentration of some calcite elements of Zletovo, Sasa and Bučim deposits. Calcite from Sasa, Zletovo and Bučim occurs in rhombohedral crystals of different size. The colour is white, but in Bučim it is white, pink, and yellow. Their twinning is very common. Chemical composition of calcite was determined by AES–ICP. Results show that in calcite from Bučim the concentration of Ba is much higher in pink calcite from than in white or yellow. The concentration of Zn and Pb is the lowest in white calcite. The calcite from Zletovo contains much higher concentrations of Pb, Zn, Sr, but calcite of Bučim which is pink contains higher amounts of Ba and Co. The concentrations of CaO, MgO, and MnO in all calcite samples are approximately equal. Concentration of all other elements in calcite of Sasa, Zletovo and Bučim is approximately equal. TG and DTA curves out on all samples were recorded. The decompositions of the samples of calcite starts at different temperature and it is not finish until 1000 °C.

**Key words:** calcite; crystal; colour; cleavage; thermal analysis

### INTRODUCTION

The present of calcite in the Zletovo and Sasa lead zinc deposits as well as in the Bučim copper deposit is mentioned in several papers such as [1], [2], [3], [5], [6], [7].

The mineralogical-chemical characteristics of the calcite from these deposits have not been determined so far. In the papers mentioned above, only ore minerals have been analyzed.

In the Sasa ore field, especially in the Svinja River, calcite is the most important of all non-ore minerals. It occurs together with dolomite, rhodochrosite, siderite, barite, quartz, calciton, opal and so on.

Calcite in Zletovo formed in the final phases of the hydrothermal stage.

Hydrothermal mineralization stage commenced with a manifestation of high temperature pre-ore alterations of surrounding volcanic rocks present as chloritizations, epidotizations, pyritizations, in part calcitization, silifications and terminates with separation of low temperature oxide carbonate paragenesis present as calcite, siderite, rhodochrosite, quartz, chalcedon and opal.

In the Bučim ore field calcite formed in hydrothermal stage. It occurs together with feldspar, biotite, chlorite, muscovite, sericite, epidot, quartz. Very often is found as smaller and larger net-like concentrations.

### EXPERIMENTAL PART

Concentration of elements determined were made using Liberty 220 ICP–AES (Varian, Australia) at optimized conditions. Lost of ignition were made using thermal furnace Nabertherm in the temperature 1100 °C.

TG and DTA curves were obtained by using a Netzsch thermoanalyser in dry air in the temperature range 20–1000 °C, at a heating rate of 10 ° min<sup>-1</sup>. All solutes used for preparing the calibration curve for the elements determined, were made with diluting

of multielement standard solution (CertiPUR, ICP–multi–element standard solution IV, Merck, Germany), which contains 23 elements in dissolved nitric acid the concentration being 1000 mg/l. For preparing the calibration curve of As, solutes were used obtained by dilution of the basic standard solute (Titrisol, As<sub>2</sub>O<sub>3</sub> in H<sub>2</sub>O, 1000 mg/l, Merck, Germany).

All standard solutes and those of sample studied are acidified with 5% nitric acid.

0.5 of the sample studied is weighted in volumetric flask and 20 ml HNO<sub>3</sub> (1 : 1) is added. The mixture is left overnight. The following day it is warmed on electric heater at 1500 °C to wet salts. 5 ml concentrated nitric acid is added to the volumetric flask and filled with 100 mg/l redistill water.

## RESULTS AND DISCUSSION

Calcite from Sasa ore field occurs in good rhombohedral crystals of different sizes. The colour is white. Cleavage is perfect on (1011). Interference colours are white and of higher order.  $Nm = 1.658$ ,  $Np = 1.486$ ,  $Nm - Np = 0.172$ . [4]. Optically is negative.

Calcite from Zletovo occurs in good rhombohedral translucent crystals. The colour is white. Cleavage is perfect on (1011), hardness 3, density 2.71 g/cm<sup>3</sup>.

Calcite from Bučim occurs in rhombohedral crystals. The colour is white, but in Čukar II part 555/579 it is white, yellow and pink. Size of crystals is small. Their twinning is very common.

Proportional depends between some elements are shown on Figs. 1–6.

Table 1

### Chemistry of calcite from Sasa and Zletovo

	Sasa – Svinja River hor. XII k. 1318	Sasa – Svinja River hor. XV k. 1190 900–900'	Sasa – Svinja River hor. XIII k. 1254 p. 1000–1000'	Zletovo vein 1B, hor. pot. 2 etage II 2–460'
CaO	54.67	53.68	53.02	53.47
MgO	0.03	0.086	0.11	0.22
MnO	1.13	2.77	2.87	1.35
FeO	0.05	0.10	0.16	1.39
Lost of ignition CaO	42.89	42.11	41.60	41.95
Lost of ignition MgO	0.03	0.09	0.12	0.24
Lost of ignition MnO	0.70	1.72	1.78	0.84
Lost of ignition FeO	0.03	0.06	0.10	0.85
<b>Total</b>	<b>99.54</b>	<b>100.62</b>	<b>99.73</b>	<b>100.30</b>
Sr	49.84	78.55	110.76	537.86
Ba	10.67	27.37	10.59	15.23
Zn	<1.66	2.33	1.44	139.98
Pb	2.189	6.09	12.85	1030.73
Ag	1.84	4.05	4.33	3.23
Au	0.92	1.86	6.76	1.53
Na	57.38	55.40	36.22	30.90
K	100.01	98.44	90.60	97.32
Al	65.42	65.43	67.79	61.47
P	5.91	0.55	4.06	3.42
Cd	0.09	<0.07	<0.07	3.41
Cu	0.25	<0.2	0.47	0.27
Ni	<0.49	<0.49	<0.49	<0.49
Cr	<0.13	0.88	<0.13	<0.13
Co	<0.27	<0.27	<0.27	<0.26
Li	1.15	0.76	0.56	1.16
V	3.00	7.88	8.30	5.38
Mo	<6.00	<6.004	<6.004	<6.00
W	<0.23	<0.23	<0.23	<0.23
Ti	<0.043	<0.04	<0.04	<0.043
Se	<7.43	7.58	9.12	<7.43
As	<1.85	<1.85	8.69	11.92



Table 2

## Chemistry of calcite from Bučim

	Central body 540/333 c-71 white	Čukar II west part 555/579 pink	Čukar II west part 555/579 yellow
CaO	55.35	46.27	50.27
MgO	0.03	4.22	2.85
MnO	0.27	1.09	0.38
FeO	0.21	5.41	3.62
Lost of ignition. CaO	43.43	36.30	39.44
Lost of ignition MgO	0.03	4.60	3.11
Lost of ignition MnO	0.17	0.67	0.23
Lost of ignition FeO	0.13	3.31	2.22
Total	99.62	101.88	102.13
Sr	94.03	105.22	109.32
Ba	13.54	568.55	0.10
Zn	2.28	45.08	28.41
Pb	2.83	26.97	24.06
Ag	0.62	0.54	<0.60
Au	6.88	3.96	<0.320
Na	<1.68	31.33	45.00
K	95.54	113.39	38.40
Al	70.34	1.57	26.90
P	16.26	14.32	21.88
Cd	0.37	2.34	3.42
Cu	7.99	1.44	1.33
Ni	0.84	<0.49	<0.49
Cr	0.52	<0.13	<0.13
Co	<0.27	0.70	<0.27
Li	0.63	1.15	1.48
V	<0.45	21.49	6.14
Mo	<6.00	<6.00	<6.00
W	<0.23	<0.23	<0.23
Ti	<0.04	0.09	<0.04
Se	<7.43	<7.43	<7.43
As	<1.85	<1.85	<1.85

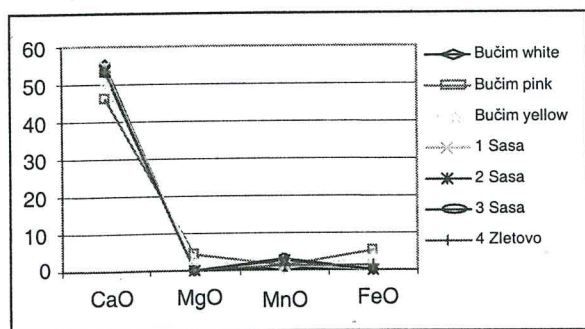


Fig. 1. Proportional depends between CaO, MgO, MnO, FeO

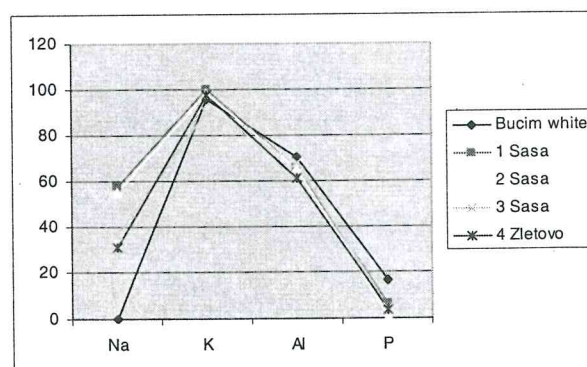


Fig. 2. Proportional depends between Na, K, Al, P

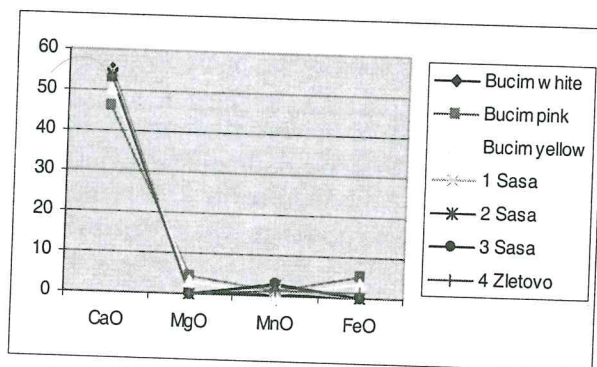


Fig. 3. Proportional depend between lost of ignition CaO, MgO, MnO, FeO

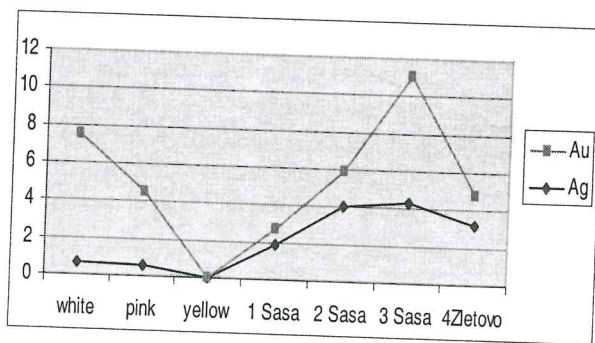


Fig. 4. Proportional depends between Au and Ag

#### Thermal decomposition of the calcites

DTA, TGA curves show the decompositions of the all samples of calcite starts at different temperature and it is not finish until 1000 °C.

Thermal decomposition of the calcite from Bučim (pink) becomes at about 510 °C followed by two endothermic peaks, the first once at 770 °C, and the second at about 930 °C. The thermal de-

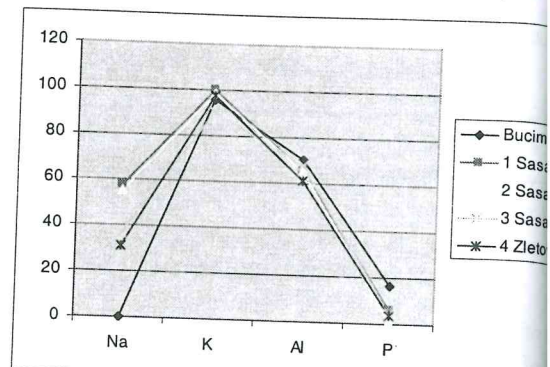


Fig. 5. Proportional depend between K, Na, Al and P

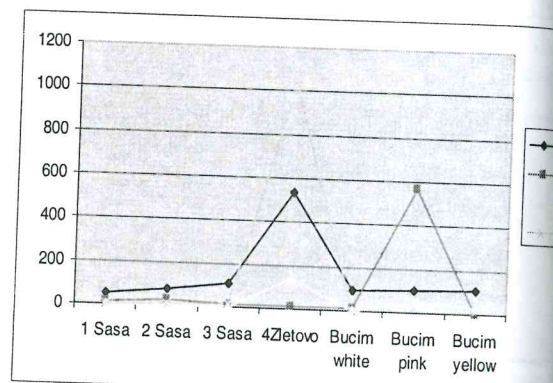


Fig. 6. Proportional depend between Sr, Ba, Pb, Zn

composition of calcite from Bučim (yellow) becomes at 670 °C and takes place also in two steps. One endothermic peak appears at 750 °C, and the other at about 958 °C.

The thermal decomposition of calcite from Sasa is at 720 °C. The sample decompose in the two steps to 1000 °C, followed with endothermic peak at about 1000 °C, and at 975 °C appropriately.

#### CONCLUSION

Our investigation shows proportional dependence between:

- CaO, MgO, MnO, and FeO,
- Na, K, Al, and P except in yellow and pink calcite from Bučim,
- Au and Ag in all samples,
- Sr, Ba, Pb and Zn in all samples.

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## Резиме

## МИНЕРАЛОШКО-ХЕМИСКИ КАРАКТЕРИСТИКИ НА КАЛЦИТОТ ОД НАОЃАЛИШТАТА ЗЛЕТОВО, САСА И БУЧИМ

Тена Шијакова-Иванова<sup>1</sup>, Весна Зајкова-Панева<sup>1</sup>, Илинка Донова<sup>2</sup><sup>1</sup>Рударско-геолошки факултет, Универзитет "Св. Кирил и Методиј", Гоце Делчев 89, МК-2000 Штип, Република Македонија,<sup>2</sup>Институт за хемија, Природно-математички факултет, Универзитет "Св. Кирил и Методиј", б. фах 162, МК-1001, Скопје, Република Македонија  
tena@rgf.ukim.edu.mk**Клучни зборови:** калцит; кристал; цеplивост; боја; термална анализа

Во овој труд се презентирани минералогско-хемиските карактеристики на калцитот од Злетово, Саса и Бучим како и, зависноста меѓу одделните елементи и нивната концентрација.

Калцитот од Злетово, Саса и Бучим се јавува во ромбодарски кристали со различна големина. По боја е бел, но во Бучим се јавува и како розов и жолт. Испитувањата покажаа дека кај калцитот од Бучим концентрацијата на Ва е многу повисока во розовиот отколку во белиот и жолтиот. Концентрацијата на Zn и Pb е повисока во белиот калцит.

Најголема концентрација на Sr, Pb и Zn има во калцитот од Злетово, додека кај розовиот калцит од Бучим најголема е концентрацијата на Ва и Со. Концентрацијата на СаО, MgO и MnO, како и загубите при жарење во сите примероци се речиси идентични.

Пропорционална зависност е констатирана меѓу:

– СаО, MgO, MnO, и FeO,

– Na, K, Al и P, освен во жолтиот и розовиот калцит од Бучим,

– Au и Ag,

– Sr, Ba, Pb и Zn.