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CHARACTERISTICS OF A CALCITE "LIMESTONE"-MARBLE FROM MACEDONIA, USED AS FLUX MATERIAL

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Abstract

The phase characteristics of calcite "limestone"-marble from Banjany area village (near Skopje, Macedonia) were examined by means of XRD, SEM, microscope in polarizing and reflected lights, chemical, DT/TG-analyses. It was concluded as follows:

- *calcite ($CaCO_3$) is a major mineral component (cca 80-90 %) prevailing in the marble over the other minerals*
- *dolomite is generally of minor importance (cca 10-20 %) in the rock*
- *quartz, micas, graphite, pyrite represent typical accessories.*

As result of the mentioned phase characteristics, this raw materials was for a long time (more than 30 years) used as flux in the iron and steel metallurgy in Macedonia.

Keywords: "limestone‰marble, calcite, dolomite, quartz, micas, graphite, flux, Macedonia

1. Introduction

In the metallurgical smelting process usually are included special raw

materials as fluxes, the purpose of which is slag formation. The selection of the material as flux, depends of the gangue mineral composition. So, the basic fluxes (limenstones) are usually used in the smelting process for metals obtaining.

The preliminary geological investigations (M.Stojanovic, 1967) reveal that the limenstones-marbles deposits at the vicinity of Banjany village, Skopje contain a lot of reserves and quality characteristics as follows:

- CaO (52-54 %) and MgO (0.37-2.89 %) contents are uniformly distributed and ranged inside mentioned limits.
- SiO_2 (1-2.5 %) and R_2O_3 (0.33-0.63 %) are of minor importance and also uniformly distributed.

Since 1965, as flux materials have been used the limenstones near Banjany village, in the working process of the „Mining and iron works · Skopje‰ Skopje, although the phase characteristics of these raw materials were not determined in details.

2. Experimental

The determination of the phase characteristics of the mentioned „limestone‰from Banjany village were determined by means of complex analytical procedures using XRD, SEM, microscopic, DT/TG, as well as chemical analyses.

3. Results and discussion

3.1. Macroscopic description

Brownish-white and grayish-white „limestone‰samples are two distinct types treated in this work, although the first mentioned species is predominant in the mine.

The brownish-white and white samples show a finegrained structure and homogenous massive texture with grains ranged between 0.5-1.0 mm., because this rock is treated as marble. Here and there these rock samples are

cutted with brown-yellowish veinlets of limonite (to 1 mm. in thickness).

The grayish-white samples have also finegrained structure and slightly schistose texture.

Both rock samples show very intensive reaction with 10 % cold HCl due to the calcite predomination over dolomite.

3.2. Microscopic examinations

By means of a LEITZ SM-POL equipment, in transmitted and reflected lights were performed microscopic examinations on the treated marble samples.

In the both rock samples (brownish-white and grayish-white marble) calcite is a major mineral component against dolomite, which contents are of minor importance.

Calcite is presented by xenomorphic grains of cca 0.03 to cca 1.0 mm filled with submicroscopic inclusions of graphite substance. The graphitic substance is more encountered component in the grayish-white marble samples. (Fig. 1 and Fig. 2)

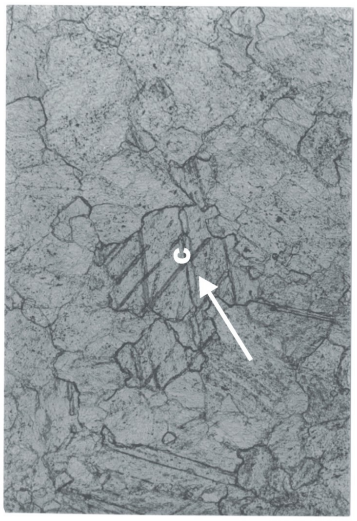

Figure 1. White "limestone" – xenomorphic calcite grains (c) with rombohedral sections filled with superfine grained graphitic materials (black spots)

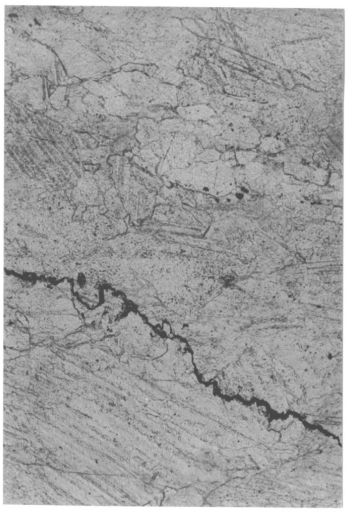

Figure 2. Thin veinlets of limonite enclosed in calcite "limestone" associated with disperged graphitic material as well as pyrite in form of coarse-grained black spots

Here and there in rock samples can be encountered accessories of pyrite · isometric forms of cca 0.005 · 0.02 mm (Fig.3). Accessories of micas (to 0.1 mm) can be seen also in the grayish-white marble samples.

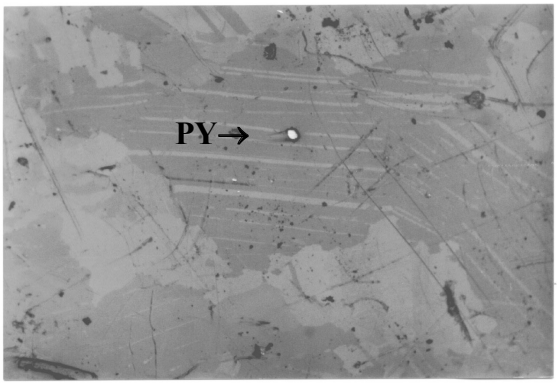

Figure 3. Pyrite (py) – inclusion enclosed in the polysynthetic calcite (c) twins in the grayish- calcite limestone (N – reflected lights).

Granulometric examinations of examined marble samples were preformed by means of direct optical measurements using an object-micrometer scale. The obtained results (Fig.4) show that both marble samples are characterized with an average grain size ranged between 0.1-0.25 mm.

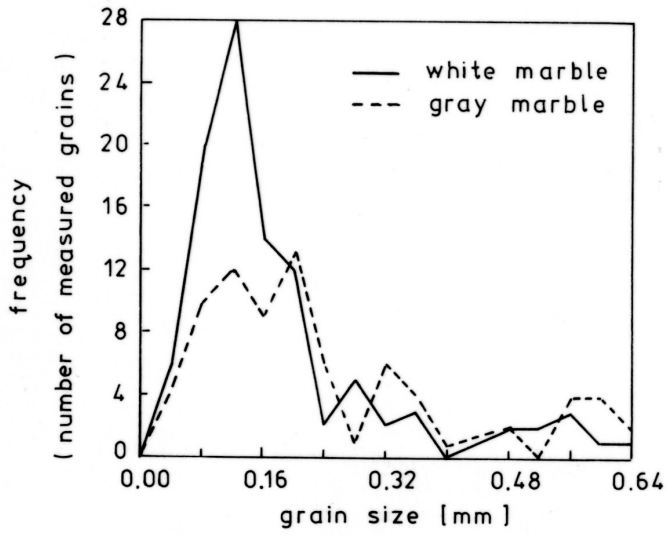

Figure 4. Granulometric curve for white and gray marble

3.3. Chemical examinations

The chemical examinations were performed by complete chemical analyses of 12 randomly selected marble samples.

Table1. Chemical analyses of marble samples from "Banjany" area, Skopje (%)

Samples	SiO_2	CaO	MgO	loss.ign.	Total	Calcite	Dolomite
1	1.24	40.51	11.16	45.5	98.41	49	51
2	0.60	39.69	12.58	45.77	98.64	42.5	57.5
3	0.71	44.94	9.65	44.10	99.40	56	44
4	0.77	44.01	9.06	44.66	98.50	58.5	47.5
5	1.08	49.61	4.36	44.00	99.05	80	20
6	0.27	50.78	3.77	44.10	98.92	83	17
7	0.41	52.53	2.10	43.97	99.01	90.5	9.5
8	0.42	52.50	2.85	43.30	99.07	87	13
9	0.28	52.55	2.10	44.34	99.27	90.5	9.5
10	0.47	51.96	1.67	43.53	97.63	92.5	7.5
11	0.30	48.10	3.02	46.98	98.40	86	14
12	0.34	50.20	3.75	44.38	98.67	83	17
Avarage	0.60	48.10	5.50	44.55	98.75	75	25

According to Table1, could be concluded as follows:

- Calcite component in examined marble samples is predominant mineral phase (more than 80%) in respect of cca 70% of the total number. Average calcite content amounts 75%.
- Dolomite mineral component is of minor importance, although this mineral phase represents a major mineral component only in four examined samples (1; 2; 3; 4).
- The other components (SiO_2 ; Al_2O_3 ; Fe_2O_3 ; K_2O ; Na_2O) are ranged below 1%, representing typical contents of minor importance (Table 2)

Table 2. Complete chemical analyses of a marble sample from Banjany area, Skopje (%)

SiO_2	CaO	MgO	Al_2O_3	Fe_2O_3	K_2O	Na_2O	loss.ign.
0.60	51.90	2.30	1.20	0.36	0.081	0.1	43.20

3.4. Quantitative SEM – Analyses

Fine-grained (cca 0.005 · 0.02 mm) pyrite inclusions in calcite grains of examined marbles were preliminary indicated by the methods of ore microscopy and more exactly determined by means of SEM-analyses.

Table 3 Representative SEM-analyses of pyrite (%)

Elements	1	2	3
S	53.72	54.40	54.35
Fe	45.52	45.08	45.00
Cu	0.36	0.37	0.36
Ni	0.18	0.18	0.19
Total	99.78	100.03	99.90

According to aforementioned data pyrite formula was calculated:

$$(Fe_{0.95}Cu_{0.006}Ni_{0.003})_{0.96}S_2$$

3.5. X-ray powder diffraction phase analyses

The X-ray powder diffraction analyses of the examined rock samples were performed by the difractometer method, according to the working conditions as follows:

- Philips X-ray difractometer equipment
- Cu/Kα/Ni monochromatic X-rays obtained at 40 kV and 20 mA
- working area 12-45^o 2θ.

On the basis of obtained X-ray powder diagram (fig.5) in the examined rock samples, these mineral phases were determined:

Calcite (c) , dolomite (d) , quartz (q)

Starting of the contributed X-ray diagram, could be concluded that calcite represents a major mineral phase, while dolomite and quartz are of minor importance what is compatible with chemical data.

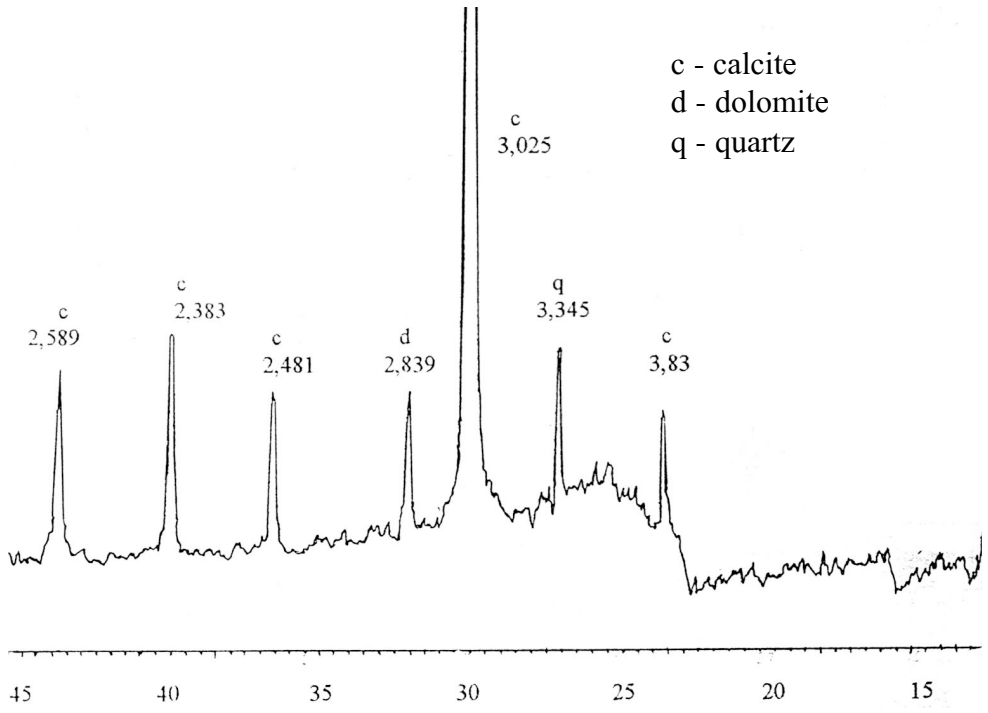

Figure 5. X-ray powder diagram of calcite-marble, near Banjany village, Skopje

3.6. DT/TG – examinations

Thermal examinations were performed by means of DT/TG · analyses at conditions of 0.5 g weight sample, Vt · 10°/min.

According to obtained DT/TG · diagram (Fig.6) can be seen that endotermal effects at 760 °C and 880 °C correspond to dolomite and calcite respectively. The most intensive endo-effect at 880 °C represents another proof, that calcite mineral component is quantitatively predominant over dolomite whatÎs compatible with X-ray, chemical etc. data. TG-data of 44.5 % loss of ign. also show that calcite is major mineral component in the examined marbles.

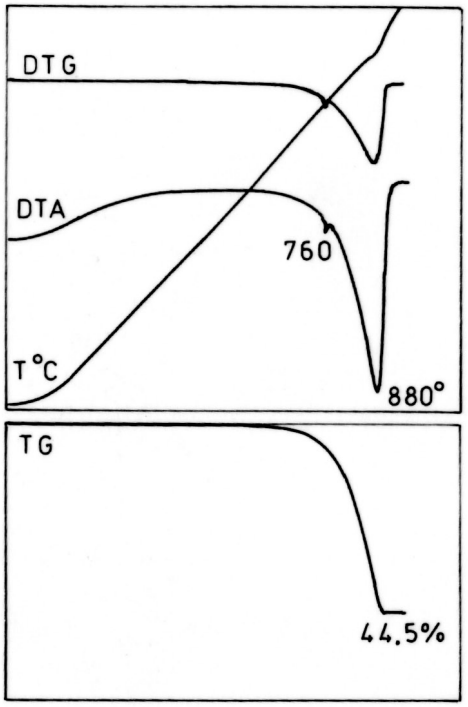

Figure 6. DT/TG – curve of calcite (c), dolomite (d), from a calcite marble from Banjany village near Skopje, Macedonia

4. Conclusion

The calcitic marbles from Banjany village region near Skopje, were for a long time period used as flux material in the iron and steel metallurgy in Macedonia, although the phase characteristics of these row materials were not examined in details.

According to XRD, SEM, Microscope, DT/TG, chemical examinations in the aforementioned marbles were determined:

- calcite as major mineral component (cca 80 · 90%)
- dolomite is generally of minor importance (cca 10 · 20%)
- quartz, micas, graphite, pyrite represent typical accessories

So, according to these phase characteristics, examined marbles represent an excellent raw material, as flux in the mentioned industry in Republic of Macedonia.

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