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The carbonate rocks of Kozani area (NW Greece) in regard to certain industrial applications

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Abstract. The suitability of Kozani's broader area carbonate rocks for use in industrial applications is examined on the basis of their mineralogical, chemical and technical features. The studied carbonate rocks belong to the Pelagonian zone and are represented mainly by pure limestones with minor dolomites and dolomitic limestones. Examination concerning their insoluble residue, organic matter and whiteness together with their mineralogical and chemical composition satisfy specific requirements for use in certain industrial applications. As it was resulted, nearly all carbonate formations, except some of the Siatista formations and the dolomitic or dolomite containing formations of Vermion, satisfy the requirements for paint industry. Three formations (one from Vermion, one from Kozani and one from Vourinos) are suitable for paper industry. Only the Siatista carbonate rocks can be used in rubber industry. The most suitable rocks for flue gas desulfurisation are one formation from Siatista and one from Vermion. Finally, all the dolomitic formations of the area meet the requirements for fertiliser industry.

Key words: *Northwestern Greece, carbonate rocks, dolomite, industrial applications.*

Introduction

General

Naturally occurring carbonate rocks, which include limestones, marbles and dolomites, are extremely important natural resources finding widespread applications and thus being placed among the most important raw materials. This is due to their application in many uses usually after mechanical and/or chemical treatment. The main use of limestone as crushed stone is in constructions, mainly as an aggregate and filler, providing strength and hardness, ideal particle shape and resistance to weathering. Limestones along with marbles are used as decorative stones because they show ideal colors and mechanical strength. In addition, significant amounts of limestone are used in the metal refining, in the flue gas desulfurisation and as inert fillers extending further in numerous industrial products (i. e. paper, paint, glass, plastic, etc), (Boynton, 1980, Pentarakis, 1981, Laskaridis, 1994, Oates, 1998, Tsirambides, 2001). Dolomite is the raw material for the production of MgO and it is necessary to alloys, paints and developed products. It is used in desulfurisation of iron and steel, in the manufacture of special cements, refractories, pharmaceuticals, glass industry, fertilizers, etc. Carbonate rocks are finally used in chemical industry for the production of $Mg(OH)_2$ and chemical $MgCO_3$ (Anani, 1984, Tsirambides, 1996). The carbonate rocks often contain impurities which depending on the frequency of their appearance and contribution into the rock, can affect their exploitation (Katerinopoulos & Stamatakis, 1995).

Greece is a country with many carbonate formations. Having marble production equal to 2,05 million tones possess the third place in the European Union and the eighth in the world. It is estimated that the deposits of dolomites in Greece are about 10 million tones while the deposits of limestones and marbles are virtually unlimited (Laskaridis, 1994, Tsirambides, 1996).

In this paper some of the most significant carbonate rock formations of Kozani area (NW Greece) are mineralogically, chemically and technologically studied in order to determine their suitability for several industrial applications, as in paper, paint and rubber industry, as well as in flue gas desulfurisation and in fertilizers industry. It must be mentioned that the carbonate rocks of Kozani broaded area have stimulated recently the strong interest of several researchers concerning their potential use in industry (Laskaridis, 1989, Laskaridis, 1994, Laskaridis, 1996, Laskaridis, 2000, Dagounaki, 2001).

Geological Setting

Geotectonically, the broader area belongs to the Pelagonian zone. The crystalline unit of the Pelagonian pre-Upper Carboniferous basement includes a series of metamorphic rocks intruded in several places by large masses of Upper Carboniferous granites. Two separate carbonate covers were deposited on the margins east and west of the Pelagonian zone during the Triassic-Jurassic. The cover of the eastern margin is a neritic carbonate sequence which thrusted westward onto the Pelagonian crystalline basement in the Late Jurassic-Early Cretaceous. The autochthonous neritic carbonate cover of the western Pe-

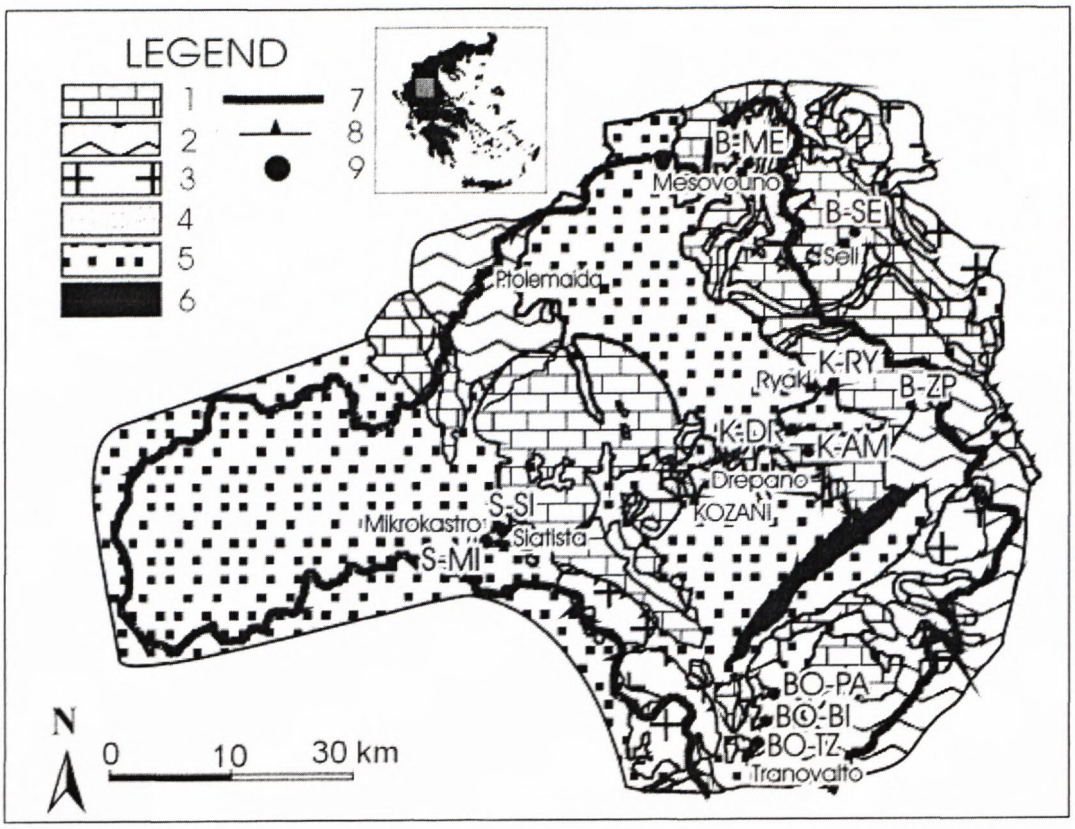

Figure 1. Geological sketch map of the Kozani broader area and sample locations.
1 = Limestones-marbles, 2 = Metamorphic rocks, 3 = Igneous rocks, 4 = Flysch, 5 = Alluvial deposits, 6 = Polyfytos lake, 7 = Kozani prefecture borders, 8 = Obduction, 9 = Sample locations.

lagonian margin was deposited on the Upper Paleozoic metaclastics (Mountrakis, 1984, Mountrakis, 1986). Big ophiolitic complexes were obducted on the Triassic-Jurassic carbonate formations of the Pelagonian zone. Ophiolites are overlained by Middle-Upper Cretaceous sediments and Early Paleocene flysch deposits (Mountrakis, 1985).

Two metamorphic events are inferred, a pre-Upper Carboniferous metamorphism of mainly upper greenschist facies which affected the crystalline basement and a post-Jurassic which resulted in a weak, low-grade greenschist fabric in the Upper Paleozoic and Mesozoic rocks (Mountrakis, 1984, Mountrakis, 1986, Nance, 1981).

Materials and methods

Representative carbonate samples were collected from the whole area of Kozani prefecture (Fig. 1). Samples S-MI and S-SI were collected from the formations near the town of Siatista. Samples B-SE, B-ME and B-ZP derive from carbonate formations of the Vermion mountain. Samples K-RY, K-DR and K-AM were collected from carbonate formations near the town of Kozani. Samples BO-BI, BO-TZ, BO-PA1 and BO-PA2 belong to the quarried limestone formations of Vourinos.

Thin sections were prepared for microscope examination in order to examine their texture and mineralogical composition. Part of each carbonate sample was ground in an agate mortar for X-Ray Diffraction (XRD) analysis, as well as for chemical and whiteness determinations. XRD analyses were performed using a Phillips type diffractometer with Ni-filtered $CuK_{\acute{a}}$ radiation. Randomly oriented samples were scanned over the interval 3-63° of 2č at a scanning speed of 1.2°/min. Semi-quantitative estimation of the abundances of the minerals was made from the XRD data.

Chemical analyses of the rock samples were performed by Atomic Absorption Spectrophotometry (AAS) using a PERKIN-ELMER 5000 apparatus. Ground samples were heated at 450° C for two hours in order to remove the organic matter and were treated by 1N HCl solution for the determination of the insoluble residue and its mineral content. Finally, pellets of 5 cm diameter and 0.5 cm thickness were prepared from the ground samples and their whiteness were measured using a DIFFUSION SYSTEMS, Model 99 spectrometer.

Results and discussion

Macroscopically, the studied carbonate samples display a distinctive variation in color and appearance. Samples S-MI, S-SI, B-SE, B-ME and K-DR are dark gray with white veinlets, samples K-RY and BO-PA2 are light gray and samples B-ZP, K-AM, BO-BI, BO-TZ and BO-PA1 are white in color. Microscopic examination of thin sections revealed a coarse-grained holocrystalline texture-

for B-ZP, K-AM, BO-BI, BO-TZ, BO-PA1 and BO-PA2 and a micritic texture for S-MI, B-ME, K-RY. Finally, the S-SI, B-SE, K-DR are consisted of medium and coarse grains, often tectonized.

The mineralogical composition (semi-quantitative determination by XRD) of the samples is shown in Table 1. The majority of the samples (S-MI, S-SI, B-SE, B-ZP, K-DR, BO-BI, BO-TZ, BO-PA1) are limestones with calcite content between 93-99% and only the B-ME, K-RY and K-AM are dolomitic rocks with dolomite content ranging between 92-96%. The sample BO-PA2 is characterized as dolomitic limestone with calcite content 83% and dolomite 17% (Harben 1992). The maximum percentage of impurities (minerals except of calcite and dolomite) was observed in sample B-ME (3%).

Table 1. Mineralogical composition (wt.%) of the Kozani carbonate rocks.

	Calcite	Dolomite	Quartz	Chlorite	Muscovite
S-MI	99		1		
S-SI	99		1		
B-SE	93	6	1		
B-ME	5	92		3	
B-ZP	99		1		
K-RY	4	96			
K-DR	99		1		
K-AM	5	95			
BO-BI	99		1		
BO-TZ	97	3			
BO-PA1	97		1		2
BO-PA2	83	17			

S-MI and S-SI=Siatista (Upper Jurassic-Lower Cretaceous and Middle Triassic-Lower Liassium limestones, respectively)
B-SE, B-ME and B-ZP=Vermion (limestone from Axios zone, Upper Cretaceous dolomite and quarried limestone, respectively)
K-RY, K-AM and K-DR =Kozani (Triassic-Lower Jurassic dolomites and Middle-Upper Cretaceous limestone, respectively)
BO-BI, BO-TZ, BO-PA1 and BO-PA2=Vourinos (Middle Triassic-Jurassic quarried limestones)

The results of chemical analyses are consistent with the mineralogical composition (Table 2). The amount of impurities (oxides except of CaO and MgO) ranges between 1.14% and 3.22%, which is explained by the low grade of metamorphism (greenschist face) of the rocks. Chemical analyses for the amount of trace elements show that only two samples (B-SE and B-ME) present higher concentrations of Cr and all the samples except S-SI, B-ME, K-RY and K-AM present higher concentrations of Ni compared to average composition given for commercial limestones. K-DR presents higher concentration of Co compared to the other samples. These relatively higher concentrations of the above trace elements are attributed to the direct contact of the limestone formations with the ophiolitic complexes.

Table 3 shows the insoluble residue with the corresponding mineralogical composition for each sample, as well as the organic matter content and the values of whiteness determined. The insoluble residue presents low values ranging between 0.09% wt. and 1.73% wt. and contains mainly quartz, chlorite and muscovite and less albite. The paragenesis quartz+chlorite+muscovite+albite confirms the greenschist metamorphic phase of the carbonate formations. The organic matter ranges between 0 and 1.07%, remaining thus within the limits given for carbonate rocks (Boynton, 1980).

Concerning the whiteness of the studied samples, it was found that the color of B-ZP, K-RY, K-AM, BO-TZ and BO-PA1 is approaching the 'pure white color', the color of S-SI, K-DR, BO-BI and BO-PA2 is in the wavelength of yellow, the color of B-ME and B-SE is in the wavelength of blue-green and the color of S-MI is in the wavelength of orange.

The main quality requirements for use of carbonate rocks on the basis of their chemical composition (wt.%) and values of their whiteness are (Boynton, 1980, Power, 1985, Harben, 1992, Oates, 1998):

- Paper industry:

for limestones:>96% $CaCO_3$, for dolomites:>53% $CaCO_3$, >44.5% $MgCO_3$.

- Paint industry:

($CaCO_3$ + $MgCO_3$)>95%, $MgCO_3$>3%, brightness 80% (putty) to 96% (paper coating).

- Rubber industry:

Cu < 40 ppm, MnO < 0.02%, ($CaCO_3$ + $MgCO_3$) > 98%.

- Flue gas desulfurisation:

CaO>53.2%, MgO>0.5%, SiO_2>0.65%, CO_2>41.8% whiteness > 80%, insoluble residue < 1%.

- Fertilisers: Coarsely pulverised dolomitic limestone and dolomite are frequently added to fertilisers. High-calcium limestone is rarely used in fertiliser formulations, because it can release ammonia from nitrogenous compounds.

According to the experimental results and the established standards the studied carbonate rocks can be used for the following industrial applications:

- The samples K-RY, B-ZP and BO-TZ are suitable for the paper industry. Comparing the chemical composition of these samples to the requirements, it is shown that they are very close to the necessary standards. The sample K-RY contains up to 96.9% ($CaCO_3$ + $MgCO_3$) and this is above the established limit of 53% $CaCO_3$ and 44.5% $MgCO_3$. The sample B-ZP is a pure limestone containing more than 96% $CaCO_3$, therefore, it is suitable for the manufacture of paper. The sample BO-TZ has a content of $CaCO_3$ almost 96%, a fact which is not forbidding for its use to the paper industry.
- Furthermore, the samples S-SI, B-ZP, K-RY, K-DR, K-AM, BO-BI, BO-PA1 and BO-PA2 can be used in the paint industry, since they fulfil the chemical specifications and the whiteness limits. The content of ($CaCO_3$ + $MgCO_3$) of these samples exceeds the limit of 95%, the lowest value is observed in BO-PA1 (96.76%) and the highest one in S-SI (98.71%). Their whiteness values are also within the limits, as the lowest one is 82.2% (K-DR) and the highest one is 95.1% (B-ZP).

Table 2. Chemical composition of the Kozani carbonate rocks.

(wt. %)	*S-MI*	*S-SI*	*B-SE*	*B-ME*	*B-ZP*	*K-RY*	*K-DR*	*K-AM*	*BO-BI*	*BO-TZ*	*BO-PA1*	*BO-PA2*	*(Mason & Moore 1982)**
SiO_2	0.54	0.70	2.41	2.14	2.14	2.41	1.88	2.41	2.94	2.67	2.67	2.14	5.19
Al_2O_3	0.10	0.00	0.12	0.15	0.00	0.00	0.00	0.00	0.00	0.00	0.17	0.00	0.81
TiO_2	0.016	0.290	0.016	0.000	0.000	0.000	0.016	0.100	0.000	0.000	0.000	0.000	0.060
MnO	0.010	0.002	0.010	0.004	0.005	0.002	0.007	0.002	0.007	0.002	0.002	0.004	
Fe_2O_3t	0.15	0.07	0.13	0.07	0.00	0.00	0.06	0.00	0.04	0.00	0.07	0.00	0.54
CaO	54.30	55.20	51.25	31.15	54.60	31.85	53.03	30.45	52.58	53.90	52.80	49.80	42.57
MgO	0.56	0.29	2.08	21.33	0.40	20.00	0.62	21.75	1.38	0.92	0.82	4.62	7.89
K_2O	0.03	0.03	0.19	0.06	0.14	0.10	0.11	0.09	0.05	0.09	0.11	0.05	0.33
Na_2O	0.16	0.22	0.30	0.09	0.23	0.21	0.26	0.19	0.10	0.07	0.08	0.12	0.05
P_2O_5	0.14	0.19	0.04	0.03	0.045	0.02	0.03	0.03	0.03	0.02	0.02	0.025	0.04
CO_2	43.52	43.22	43.36	44.88	42.34	45.06	43.60	44.86	42.81	42.14	43.14	42.85	
(ppm)													*(Oates 1998)***
Co	28	22	16	b.d.l.	b.d.l.	16	46	b.d.l.	b.d.l.	b.d.l.	19	b.d.l.	
Cr	11	12	23	27	15	13	17	15	15	15	15	12	3-15
Ni	21	b.d.l.	28	b.d.l.	17	b.d.l.	21	b.d.l.	21	21	21	17	0.5-15
Rb	58	60	84	28	64	54	36	24	29	38	38	26	
Sr	213	185	358	168	228	153	518	102	440	210	213	250	
Zn	17	6	7	13	14	16	5	8	7	6	7	7	3-500

b.d.l.=below detection limit, *Average limestone composition (Mason & Moore, 1982), **Typical ranges of trace elements in commercial limestones (Oates, 1998)

Table 3. Insoluble residue (wt.%), mineralogical composition of insoluble residue (wt.%), organic matter (wt.%) and hiteness values (%) of the Kozani carbonate rocks.

		Mineralogical composition of the insoluble residue					
	Insoluble residue	Quartz	Chlorite	Muscovite	Albite	Organic matter	Whiteness*
S-MI	0.52	100				0.29	75.3
S-SI	0.16	100				0.20	84.5
B-SE	0.96	61	9	8	22	0.28	58.0
B-ME	1.22		100			0.61	67.2
B-ZP	0.20	1		99		0.19	95.1
K-RY	1.73	11	37	52		1.07	90.0
K-DR	0.09	100				0.20	82.2
K-AM	0.76		52	48		1.00	93.0
BO-BI	1.23	36		64		0.20	82.4
BO-TZ	0.26			97	3	0.00	90.0
BO-PA1	0.94	18	16	66		0.15	93.0
BO-PA2	1.03			100		0.19	85.3

*percentage reflectance value of sample

- The samples S-SI and S-MI are suitable for the rubber industry, as their content in CaO, MnO and Cu fulfil the requirements. The values are 54.3-55.2% for the CaO, 0.002-0.01% for the MnO and their concentration in Cu is below the detection limit (9 ppm) of the spectrophotometer for Cu. Their content in ($CaCO_3$ + $MgCO_3$) is ranging between 93.38% and 98.71%, values that are higher than the established ones.
- The samples S-SI and B-ZP can be used in the flue gas desulfurisation as their content in CaO is 55.2% and 54.6%, respectively, quantities much higher than the lowest limits. Their whiteness values (84.5% for S-SI and 95.1% for B-ZP) are above the limit of 80%. Their content in MgO is for S-SI 0.29% and for B-ZP 0.40%. They contain more SiO_2 than the established value and their content in CO_2 is above 41.8% (43.22% for S-SI and 42.34% for B-ZP). Finally, their insoluble residue is below 1%, (0.2% for S-SI and 0.19% for B-ZP).
- Finally, the samples B-ME, K-RY, K-AM and BO-PA2 are suitable as raw materials in fertilisers. The first three samples are dolomitic rocks with MgO content ranging between 20% and 21.75%, while the sample BO-PA2 is a dolomitic limestone containing 4.62% of MgO.

Conclusions

The carbonate rocks at the Kozani broader area represent a variety of carbonate formations ranging from pure limestones (which is the majority of the rock formations)

to dolomitic limestones and dolomites. Mineral impurities, such as quartz and other silicates, participate in minor or trace amounts, remaining in the majority of the samples below 0.5%.

Measurements concerning their insoluble residue, organic matter and whiteness together with their mineralogical and chemical composition satisfy special requirements for use in certain industrial applications. Thus, nearly all carbonate formations, except some of the Siatista formations and the dolomitic or dolomite containing formations of Vermion, are suitable for paint industry. On the contrary, only three formations (one from Vermion, one from Kozani and one from Vourinos) can be used in paper industry. Furthermore, only the Siatista carbonate rocks can be used in rubber industry while for flue gas desulfurisation the most proper rocks are one formation from Siatista and one from Vermion. Finally, all the dolomitic formations of the area are suitable for the fertiliser industry.

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