PERSPECTIVES FOR THE PRODUCTION OF INDUSTRIAL MINERALS FROM THE EXPLOITATION OF THE WASTE STEMMING DURING THE EXTRACTION OF GREEK WHITE CALCITIC MARBLES (EASTERN MACEDONIA)

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ABSTRACT

Considerable amounts of white marble waste with a high calcite content ($CaCO_3$>98%) exhibiting high reflectance values (Y>94%) and low Einlehner abrasiveness (<40mg) are found in the area of Eastern Macedonia, the major marble production center of Greece. IGME is currently investigating the perspectives for feasible co-management of the waste produced by 126 calcitic marble quarries permitted in the regions of the Falakro and Lekani's mountains located in Eastern Macedonia. These marbles are white – semi-white calcitic rocks (calcite content ~95-98%) that belong in the carbonate formation of the Rodopian zone, with a maximum thickness of 1.500m of equigranular structure and massive texture. According to estimations performed by the authors, ~6.000.000m^3 of rocks have been extracted so far in the area under study, but only ~450.000m^3 have been exploited for decorative purposes. The remaining amounts equal to 5.550.000m^3 or ~15.000.000 tons have been stockpiled as rejects. The low recovery percentage (<10%) is due mainly to the strong deformation that the carbonate rock has undergone by the faults and joints. Currently, approximately ~300.000m^3 of rocks are being extracted annually, coming from 11 quarries which are operating today. Thus, an amount of more than ~270.000m^3 or ~700.000 tons of materials are added annually in the waste stockpiles of the region. Aiming at the investigation of the commercial exploitation of the above rejects, in the framework of the National Strategic Reference Framework (NSRF) IGME has focused on the specific region. Based on the research conducted so far, these rejects are appropriate for the production of added-value materials, namely fillers for the chemical industry, while their application as aggregates is questionable since preliminary examination of the materials mechanical features concluded in negative results.

Key words: mining waste, marble, fillers, Greece

1. INTRODUCTION

Mining waste has become a major concern for Europe, not only because of the considerable volumes produced (30% of the whole wastes stream) but also due to steadily growing needs for their sustainable management, including their exploitation as secondary resources. Vigorous action has been taken by the new EU member States (e.g. SEE countries) in order to transpose the EU relevant legislation into their national legislation, to conduct special plans for the management of mining waste and compile cadastres. Although the focus is on the waste stemming from the exploitation of metallic minerals due to increased environmental impacts and the potential to produce Critical Raw Materials (CRM), the non-metallic quarrying activity is also of interest.

Regarding Greece increased emphasis is put on the production of marbles, an activity which results in large amounts of waste rocks equal to 95% of the extracted rock. Many Greek

marble types are characterised as having high whiteness values (>90%) and high calcite content ($CaCO_3$>98%). Those intrinsic characteristics of the Greek marbles, especially in Northern Greece, make them ideal candidates as raw materials for the production of added-value products in the market of industrial minerals. Considering the above, IGME is currently investigating the possibility for feasible co-management of the waste produced by the marble quarries of the Eastern Macedonia Region. This paper presents the main findings concerning the utilisation of the specific waste as raw material for the production of fillers.

2. MATERIAL AND METHODS

Following up previous research, IGME is currently involved in the preparation of a feasibility study specifically for the Eastern Macedonia marble rejects which have been produced form the past and current activity of 126 marble quarries located in the area (Falakro and Lekani Mountains), based on sustainable management principles. According to estimations performed by the authors, a volume of 6.000.000m^3 of rocks has already been extracted so far here, but only 450.000m^3 were exploited for decorative purposes. The rest equal to 5.550.000m^3 or 15.000.000 tons have been stockpiled. An average quantity of 300.000m^3 (700.000 tons) rejects is currently being stockpiled annually, coming from only 11 quarries which are still operating today.

The aforementioned study constitutes part of a project which is implemented in the framework of the National Strategic Reference Framework (NSRF) 2007-2013 and focus on the management and commercial exploitation of the mining waste, mainly as fillers for the chemical industry addressing international markets, and in the field of construction, addressing mainly local markets.

To this end, hand samples as well as bulk samples of marble rejects were taken from six (6) sub areas of the study area: (1. Disvato, 2. Stenopos, 3. Komnina, 4. Limnia, 5. Falakro Mt, 6. Kechrokampos).

In order to assess the suitability of rejects as fillers (Ground Calcium Carbonate, GCC) determination of the calcium carbonate content and the purity in general was conducted by synthesis of the assay results and mineralogical analysis (XRD). It should be noted here that the geological study of the area under investigation is of extreme importance for the following reasons:

(1) Access to stockpiles of marble waste is often difficult and collection of representative samples is not possible;
(2) Study of the qualitative characteristics of the marble waste material is based on hand samples typical of the rock formations that occur in the area;
(3) Exploitation of rejects for specific applications depends on: a) the availability of materials that own the necessary specifications, and b) the possibility to select and remove the desirable qualities;
(4) Correlation between qualities and quantities must be accomplished with the help of an expert geologist in co-operation of course with a mineralogist;
(5) Further proposals for management and exploitation of the marble waste should be based on the results of such investigation.

Moreover, whiteness in terms of CIEL*a*b* measurements of the powdered material was also performed with a spectrophotometer CARY 100. Specific tests were also implemented in order to investigate the adequacy of those materials as aggregates to be used in the local market for constructive purposes. To this end, bulk samples representing the six (6) sub-areas were submitted in mechanical / physical, as well as thermal / weathering tests in accordance with: a) EN 1097.02:2011 (Methods for the determination of resistance to

fragmentation - Los Angeles test); b) EN 1097.06:2000 (Determination of particle density and water absorption); c) EN 1367.02:1999 (Magnesium sulfate test).

Further to the technical investigation mentioned above, a market research is envisaged for the accomplishment of the feasibility study, as well as the development of the potential flow diagram, for the treatment of the rejects, including the necessary equipment specifications.

3. THE AREA OF INTEREST

Following a long period of research within the framework of many national co-funded projects, IGME decided to mark out an area of increased interest in order to develop strategies for management and exploitation of marble waste. Specifically, this area is part of the Eastern Macedonia Region, where the marble extraction activity constitutes 70% of the overall annual marble production in Greece. Moreover it is often the case that these marbles are white with high calcium carbonate content.

3.1. Geological information

The metamorphic rocks of the Western Rhodope Zone consist of two tectonic units, on the basis of geological, structural and petrographic data (Papanikolaou & Panagopoulos, 1981, Papanikolaou et al, 1982, Chatzipanagis et al, 1983), Zachos & Dimadis, 1983, Liati and Mposkos, 1989):

a) The lower unit (Pangaeon Unit) of low grade metamorphic rocks (greenschist facies).
b) The upper unit (Sidironero Unit) of higher grade metamorphic rocks, compared to the previous ones (intermediate-higher amphibolite facies).

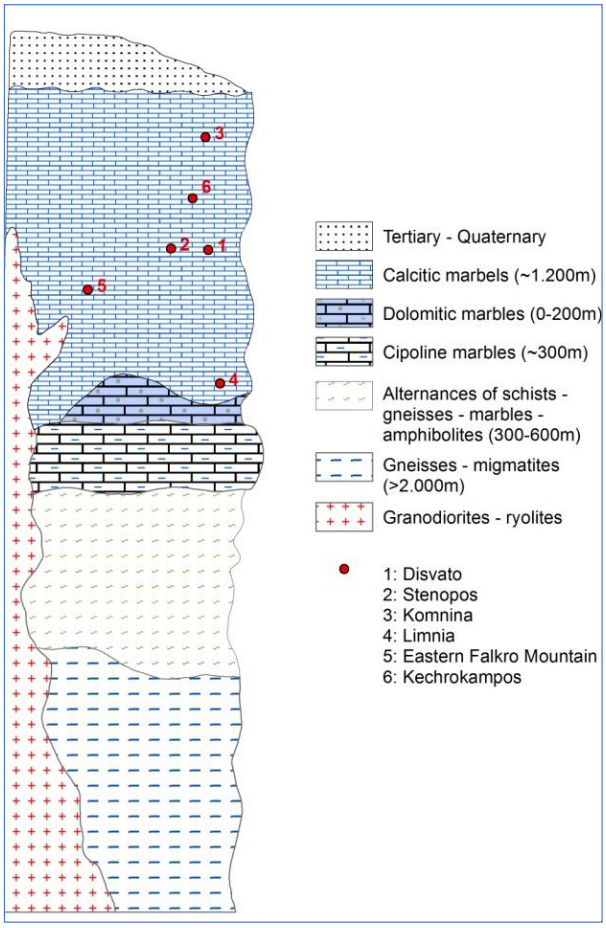

Fig. 1: Lithostratigraphic Column of Western Rodope showing the stratigraphic position of the exploitation areas

The tectonic position of the two units seems to be defined by an overthrust structure with a NNW-SSE direction and a SW incline which follows the extension of the imaginary line of K. Nevrokopi - Livadero - Paranesti (Mposkos et al, 1998) (Fig.1). The ductile as well as the brittle deformations have same style in both units, with four systems of faults and fractures, having NW-SE, NE-SW, N-S and E-W directions (Chatzipanagis, 1991).

The separation into three discrete lithological units of metamorphic rocks was performed with geological mapping (Chatzipanagis, 1991 (Fig. 2), as follows: a) Marbles unit (Upper unit); b) Alternances unit (Middle unit), and c) Gneisses unit (Lower unit).

3.2 The marbles' unit in the area of Eastern Macedonia

The highest stratigraphic unit or the Marbles unit, which is of interest for the present, comprises the series of: 1) The Falakro massif calcitic marbles with a

thickness of about 1.000m; 2) Dolomitic marbles with a thickness from 0 to 200m, and 3) Banded cipoline marbles with a thickness of about 300m.

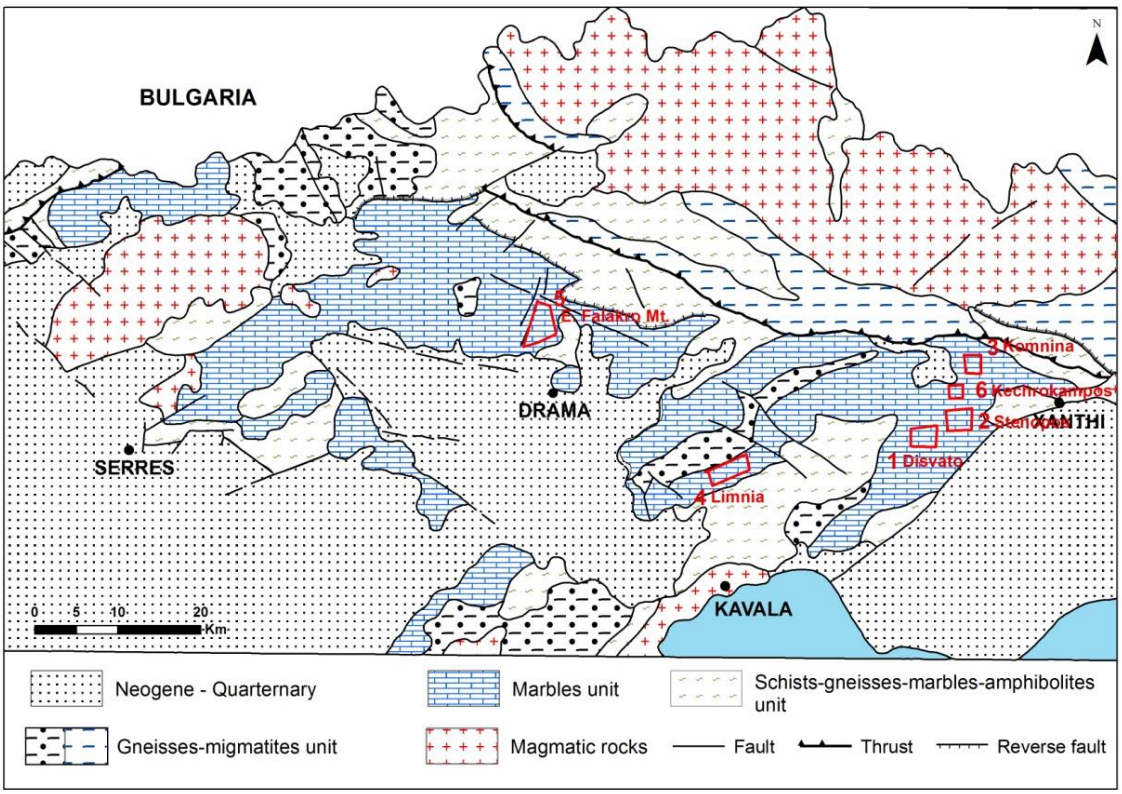

Fig. 2: Location of major white calcitic marble producing sites in Northern Greece – Main geological formations (I. Chatzipanagis, C. Christidis, 2015)

The Falakro massif calcitic marbles are holocrystalline and are almost entirely consistent of pure calcite. They are strongly deformed with intense brittle and ductile tectonic phenomena. The color of the marbles varies by location from grey to white, with banded and speckled texture depending on the concentration of bituminous materials, micro-crystallic graphite or flake graphite.

Besides the calcitic marbles, crystalline dolomites occur in the western section of the wider area mainly as lenses and forming a stratigraphic horizon between the Falakro and the banded cipoline marbles. The last are dark colored rocks with grey bands comprising fine-grained quartz and graphite, have a thickness of 300m and constitute a geologic 'marker', since they appear in the whole area, maintaining their stratigraphic position.

In areas where the white calcitic marble variety dominates, such as Stenopos, Disvato, Kechrokampos, Komnina, Limnia and Eastern Falakro Mountain, the marbles are exploited as ornamental stones (Fig. 1, 2). However, the low rate of exploitation for ornamental purposes (6-7%), due to the existence of intense faulting, deformation and other weathering factors such as erosion and karstification, result in rejection of significant quantities of white to semi-white marble fragments as unusable materials.

3.3 Key features of the white calcitic marble residues in Eastern Macedonia

The photos that follow (Figures 3-6) were taken during the field work accomplished by the scientific personnel of the research project mentioned above and they illustrate the waste management issues arising in the area due to marble exploitation.

Fig.3 (on the left): Stockpiled marble waste (E. Falakro – Vathilakkos / Monastiraki)

Fig.4 (on the right): Stenopos – general view and detail from stockpiled marble waste

Fig.5 (on the left): Working in the field (Limnia)

Fig.6 (on the right): Stockpiled marble waste (Disvato)

Key properties of marble rejects from the area under study, regarding their application in the calcium carbonate fillers industry are summarised in Tables 1 and 2 below. The results are based on examinations performed at IGME's laboratories on hand samples and bulk samples collected during the years 2013 and 2014. It is obvious that these materials are of great interest to the fillers industry, since they are pure calcitic, having $CaCO_3$>98%, with high reflectance values (Y =90-96%) for the powdered material.

Table 1: Optical properties and $CaCO_3$ content of the materials in the area under study

Sub- area of interest	**Abrasiveness** [(a)]		**Optical Properties** [(b)]				**Purity**
	Einlehner, mg	VWB_{120}	L* (%)	a*	b*	Tristimulus value Y (%)	$CaCO_3$, %
1. Disvato	n/a	n/a	96,9-97,8	-0,092 to -0,046	0,042 to 0,114	92,2-94,5	99
2. Stenopos (white)	n/a	n/a	97,6-98,2	0,001 to 0,052	-0,027 to 0,592	93,9 – 95,6	98-99
3. Komnina (white)	n/a	n/a	98,3-98,4	0,020	0,564 to 0,695	95,7-95,9	99
4. Limnia (white and semi-white varieties)	21,6	70,8	96,8-98,1	-0,098 to 0,088	-0,229 to 0,632	90,0-95,2	99-100
5. E. Falakro (white and semi-white varieties)	19,0	62,3	96,5-98,5	-0,077 to 0,075	-0,019 to 0,0556	91,2-95,8	98-99
6. Kechrokambos (white)	n/a	n/a	98,3	0,020	0,499	95,7	98

(a)	*Grain size d_{90}=30μm*
(b)	*Grain size d_{90}=30μm, 8° Diffuse Reflectance Spectrophotometry CIE 10° Observer, Illuminant D65, Standard: $BaSO_4$ powdered*

Table 2: Mineralogical composition of the materials in the area under study

Sub- area of interest	Mineralogical composition		
	Calcite, %	Dolomite, %	Others (mainly quartz), %
2. Disvato	96,9-97,3	2,4-2,6	0,3-0,8
2. Stenopos	96,3-96,9	2,7-3	0-0,7
3. Komnina	97-97,3	1,7-2,3	0,6-1
4. Limnia	97-98%	1,5-2,5	0-1
5. E. Falakro	95-97,5	1,3-3,1	1-1,3
6. Kechrokambos	96,5	1,5	0,7-1,8

3.4. Current evolutions in the calcium carbonate fillers' market

As mentioned above (paragraph 2), a market research was conducted very recently (2015) focusing on the potential of producing Ground Calcium Carbonate Fillers (GCC) by using white calcitic marble. The scope of this work was to update the findings of a report entitled "*The White Carbonate Fillers' Production in Greece"* issued by IGME in 2008. Based on the conclusions of this report, the Greek Calcium Carbonate Industry was expected to develop further with increase of the marble waste share in the feed of the Industry's mills (Fig. 7) (Chalkiopoulou, F., 2008, Chalkiopoulou, F. et al, 2009,).

Fig.7: Marble waste prepared to feed a fillers producing mill (Stenopos)

The abovementioned recent market study on fillers, which was accomplished within the framework of a National Strategic Reference Frame-work (NSRF) project for Non-Energy Mineral Raw Materials (MEOPY) which is run by IGME, confirmed these predictions. In particular, based on the conclusions of the study, the following can be underlined as major outcomes (Valta, K. 2015):

1) Apart from limestone used for the production of carbonate fillers, the utilization of marble waste has become a common practice for the production of Ground Calcium Carbonate in Greece (Fig. 7);
2) The total annual capacity (2015) of the Greek companies producing fillers is almost the same with the annual capacity of 2008 and equal to 0,8 Mt;
3) Despite the economic crisis, the domestic fillers' production has shown slightly upward trends for applications in Chemical Industry (paints, plastics, e.t.c.). The sector is highly depending on exports (80%) all over the world.
4) The global market of Ground Calcium Carbonate (GCC) is driven mainly by the paper and plastic industries. Moreover the global use of Ground Calcium Carbonate (GCC) was 74 Mt in 2011, while the global use of calcium carbonate fillers is expected to reach 98,7 Mt until 2020, including also Precipitated Calcium Carbonate (PCC) (Roskil, 2012).

5. DISCUSSION

The sustainable management of mining waste has become a major goal in Europe with a priority to prevent their production and if produced to pursue their exploitation as secondary resources. Regarding Greece, extraction of marbles is an activity which results in large amounts of waste rocks equal to 95% of the extracted rock. Eastern Macedonia especially, among the various exploitation areas of the country, is of great interest due to the occurrence of abundant waste materials coming from the extraction of white calcitic marbles. Extensive long-time investigation which has been accomplished by IGME, within numerous projects, shows that it is feasible to use this material in order to feed Ground Calcium Carbonate Fillers Mills. The industry has made use of the research findings and invested in the field. Currently, the Greek Ground Calcium Carbonate Fillers' sector is healthy and growing steadily. Incorporation of best practices in the management of marble waste by marble quarry operators, taking into account their potential future utilization, needs further promotion.

5. REFERENCES

CHALKIOPOULOU, F. (2008): "The White Carbonate Fillers' Production in Greece", IGME, Internal Market Research Report, CSF III, Subproject: "Greek Ornamental Stones' By-products and Wastes Management and Utilization Study – Contribution in the Sector's Viable Growth"

CHALKIOPOULOU, F., KARADASSI, S., VOUJOUKAS, D., LASKARIDIS, C., AGGELOPOULOS, C., (2009): "Potential of the Greek White and Semi-White Marble Residues Under the Prism of Updated Information", 3rd AMIREG International Conference (2009), 'Resource Utilization and Hazardous Waste Management', Athens, Greece

CHALKIOPOULOU, F., LASKARIDIS, C., HATZILAZARIDOU, K., (2008): "Status and trends of white carbonate fillers' supply and demand in Greece - focus on GCC", 19th INDUSTRIAL MINERALS CONGRESS, ATHENS 2008

CHATZIPANAGIS I., COMPAGNONI R., SANDRONE R. (1983): "Studio geologic – petrografico del Bos-Dag settentrionale (Macedonia greca)", Bollet. Dell' Assoc. Miner. Subaplina

CHATZIPANAGIS I. (1991): "Geotectonic evolution of Falakro Mountain area (W. Rhodope)", Ph.D Thessis, Technical University of Athens, 171

LIATI, A., MPOSKOS, E. (1989): "Preliminary results on The Petrology and Geochemistry of amphibolitic rocks in W. Rhodope, Drama area" IGME - EEC. Regional Geology Subgroup, Athens, p 27.

MPOSKOS E., CHATZIPANAGIS I., PAPADOPOULOS P. (1998): "New data on the boundaring of the Pangaeon and Sidironero tectonic Units in Western Rhodope", 8th Inter. Cong. of the Geol. Soc. of Greece, 32/1, 13-22.

PAPANIKOLAOU, D., PANAGOPOULOS, A., (1981): "The structural style of Southern Rhodope, Greece", Geologica Balcanica, 11: 3, 13-22.

PAPANIKOLAOU, D., SASSI, F. P., SCARPELIS N. (1982): "Outlines of The pre-Alpine metamorphisms in Greece", in SASSI and VARGA, IGCP No 5, 56-62.

VALTA, K. (2015): "Study on the Greek and the Global Fillers Market" in the framework of the project entitled: "Research and evaluation of selected non-energy mineral raw materials of Greece for the sustainable operation of the extractive industries"

ROSKIL (2012): "Industrial Minerals / Ground & Precipitated Calcium Carbonate: Global Industry Markets & Outlook", 1st edition 2012. http://www.roskill.com/reports/industrial-minerals/ground-and-precipitated-calcium-carbonate-1.

ZACHOS, S., DIMADIS E. (1983): "The geotectonic position of the Skaloti-Echinos granite and its relations to the metamorphic formations of Greek Western and Central Rhodope", Geologica Balcanica, 13:5, 17-24.