

3rd INTERNATIONAL CONFERENCE on Sustainable Solid Waste Management

Production of high value added carbonate fillers from the treatment of white calcitic marble waste: the case of Eastern Macedonia and Thrace of Greece

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Objective

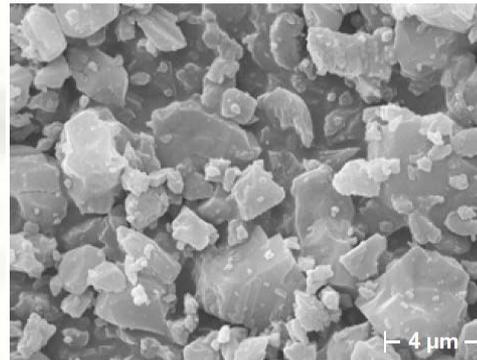
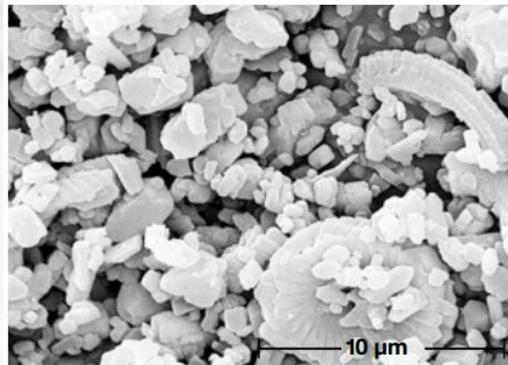


.....to investigate the potential of using **marble rejects** from the past and current activities **from Eastern Macedonia** as **fillers** based on laboratory analysis and also on market research mainly of the current domestic market of fillers...

Fillers - 1

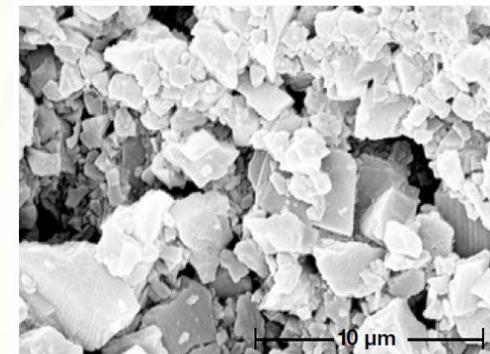
- A **filler** is a substance consisting of particles which is virtually insoluble in the application medium and which is used to enlarge the volume, to achieve or improve technical properties and/or to influence optical characteristics (DIN 55943)
- **Raw Materials:** globally, the most commonly used fillers:
Ground Calcium Carbonate (GCC) > Precipitated Calcium Carbonate (PCC) > carbon black > kaolin > talcum

Chalk



Limestone

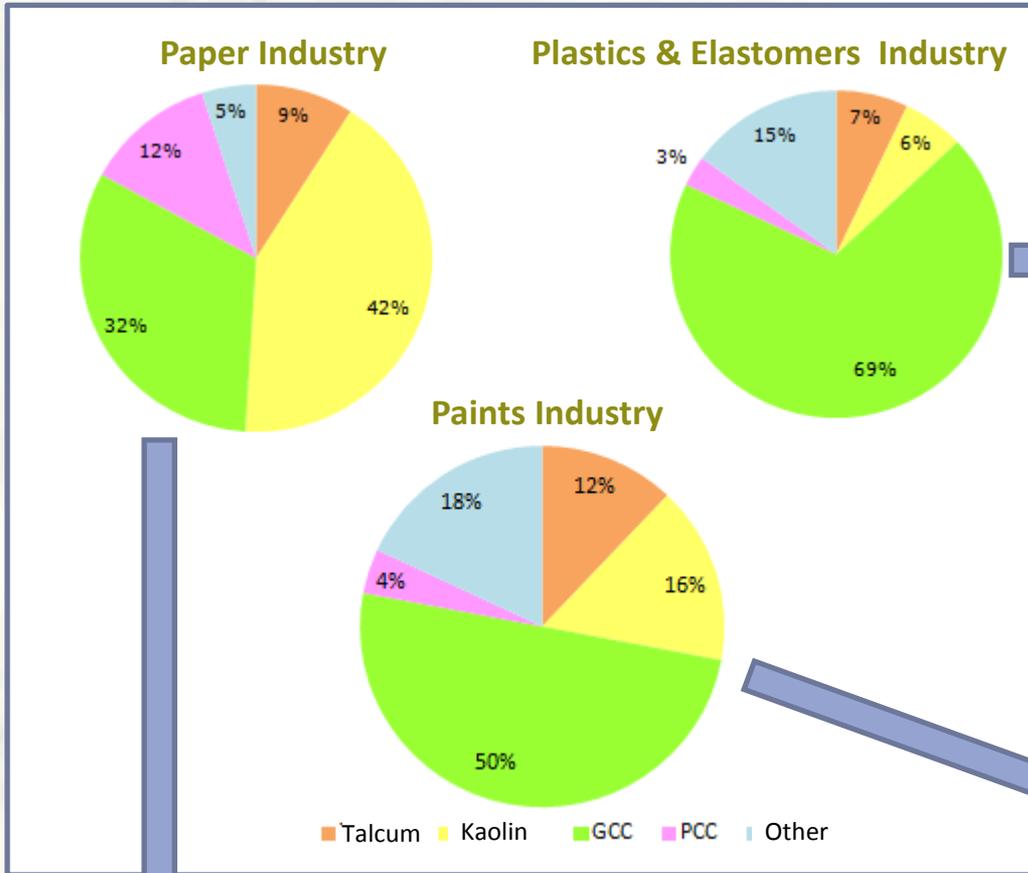
Marble



Fillers - 2



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- ✓ 50-60% tyres production
- ✓ 40 – 60% floor covering
- ✓ 35 – 55% roofing sheets
- ✓ 5 – 15% shoe soles
- ✓ 60 – 80% arpets
- ✓ 20-40% PP garden furniture
- ✓ 3 – 30% PVC pipe production
- ✓ 2-30% PE film



- ✓ 50-70% emulsion paints
- ✓ 70-80% plasters and stoppers
- ✓ 30 – 40% road-marking paints
- ✓ 10 – 20% powder coatings



- ✓ 12% for newsprint
- ✓ 35% for Supercalendered papers

Marble waste rock, Greece



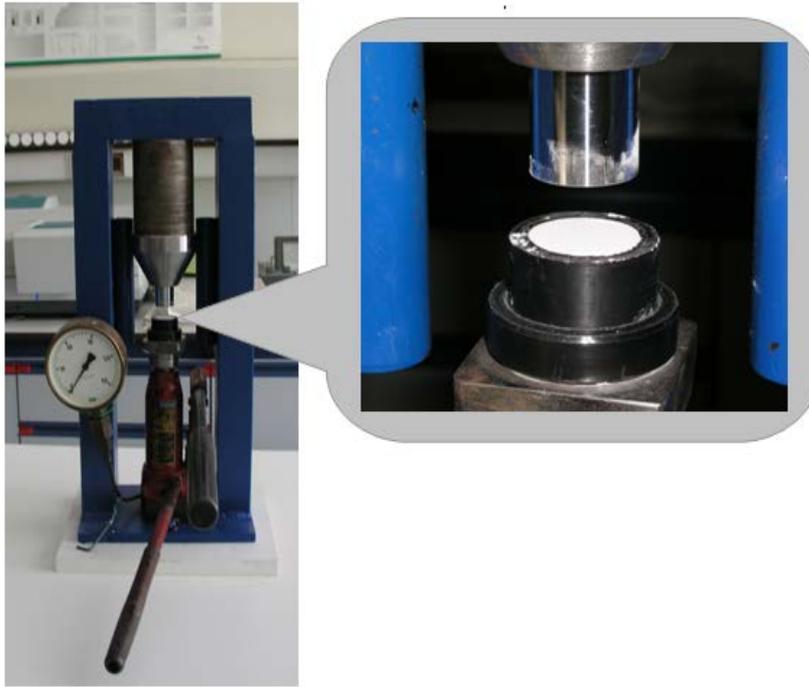
- Mining waste has become a major concern for EU since it accounts for 30% of the total waste
- Production of marbles → Waste rocks equal to 95% of extracted rock.
- The region of Eastern Macedonia (constitutes the most important quarry center of the country where the problem of rejection of marble waste rock is particularly acute.
- IGME investigating the possibility for feasible co-management of the wastes.
- Ideal candidates as raw materials for the production of added-value products (for the production of fillers) in the market of industrial minerals.

Methodology - 1

- Conduction of domestic market research.
- Hand samples' collection of 3-5 kg weight each, correspondent to the materials rejected in the different quarrying sites of six major sub-areas in Eastern Macedonia Thrace: 1. Disvato, 2. Stenopos, 3. Komnina, 4. Limnia, 5. E. Falakro, 6. Kechrokambos.
- Targeted bulk sampling by collecting samples of 500kg each, representing the six sub-areas



Methodology - 2

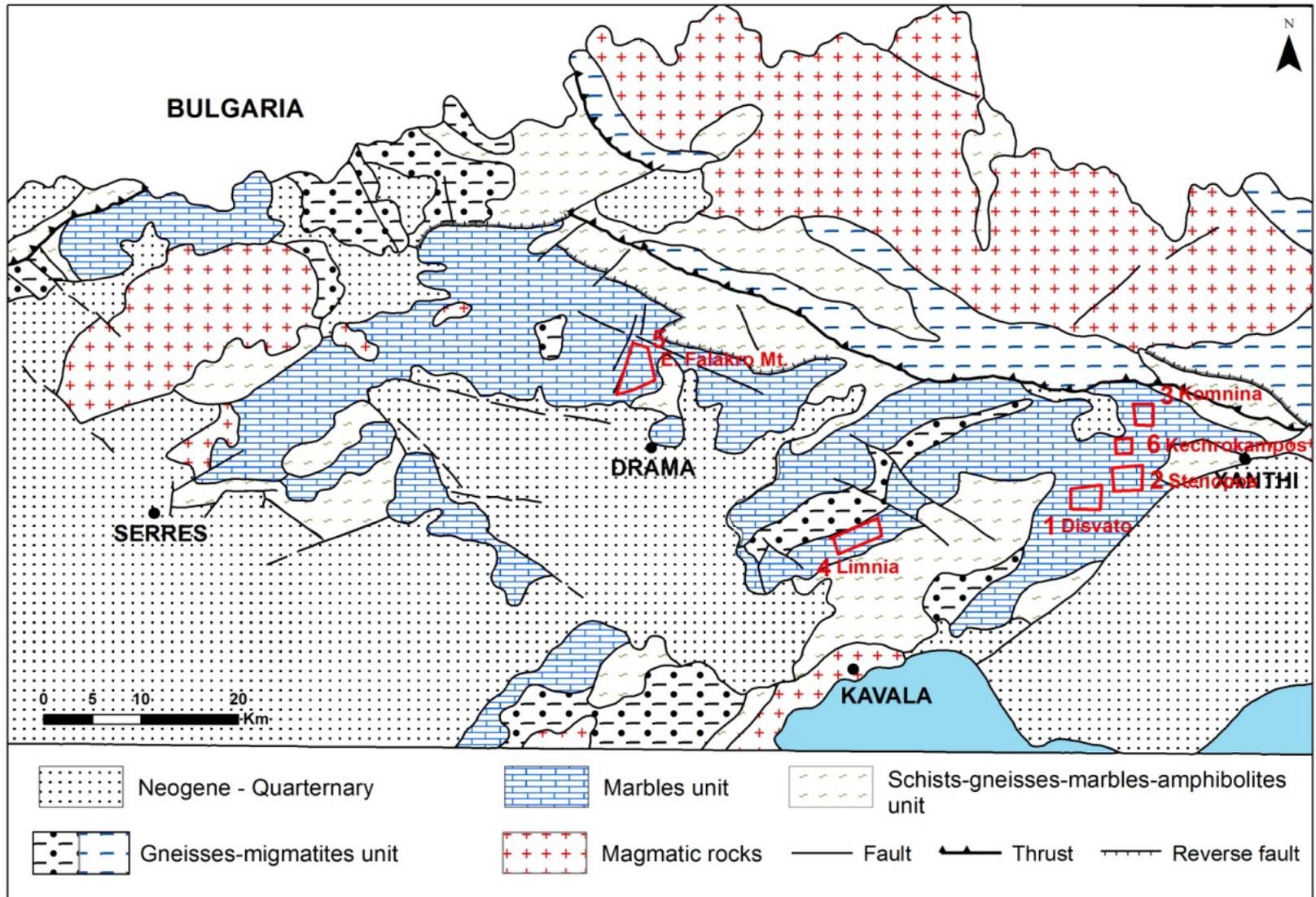


- CaCO_3 content based on XRF measurements, mineralogical examinations and chemical analysis
- Abrasion behaviour with an Einlehner Abrasion Tester and
- Whiteness by measuring the reflectance factor $R, \%$ with a spectrophotometer.

Methodology - 3



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Results – PART A - Market Study

Domestic Fillers Producers



- ❖ DIONYSSOMARBLE
- ❖ IONIAN KALK SA
- ❖ MICROFILL SA
- ❖ KARBOKAL SA
- ❖ OMYA HELLAS SA.
- ❖ WHITE MINERALS SA
- ❖ INDUSTRIAL MINERALS SA

DIONYSSOMARBLE

Marble waste rock and microcrystalline limestone

Trade name: NOVOCARB	Fineness			γ^*	Applications
	$d_{0,97}$ μm	$d_{0,50}$ μm	$\%<2$		
<i>Uncoated</i>					
No 10	8 - 12	3 - 5	25 - 35	98.0	Paints, Plastics and Adhesives
No 20	16 - 20	4 - 6	14 - 26	97.5	Paints, PVC, Adhesives, Stucco with polyester base
No 25	23 - 27	5 - 8	12 - 18	97.0	Paints, PVC, Adhesives, Stucco with polyester base
No 40	38 - 42	11 - 14	7 - 10	97.0	Paints, Plastics, Carpets, Tyres, Insecticides, Pesticides
No 60	58 - 62	12 - 18	5 - 8	96.5	Acrylic stucco, Carpets, Detergents, Insecticides, Pesticides, Tyres
No 80	78 - 82	21 - 24	5 - 7	96.0	Acrylic stucco, Carpets, Detergents, Insecticides, Pesticides, Fertilisers, Feeds
No 120	115 - 125	30 - 35	4 - 6	96.0	Carpets, Detergents, Insecticides, Pesticides, Fertilizers, Feeds, Tyres
SoftGrade no 100	58 - 62	12 - 18	5 - 8	96.0	Putties, Roofs covering, Films for greenhouse covers
<i>Coated</i>					
No 10c	8 - 12	3 - 5	25 - 35	98.0	Cable, PVC tube, Paints
No 20c	16 - 20	4 - 6	14 - 26	97.5	Cable, PVC tube, Paints
No 25c	23 - 27	5 - 8	12 - 18	97.0	Cable, PVC tube, Paints

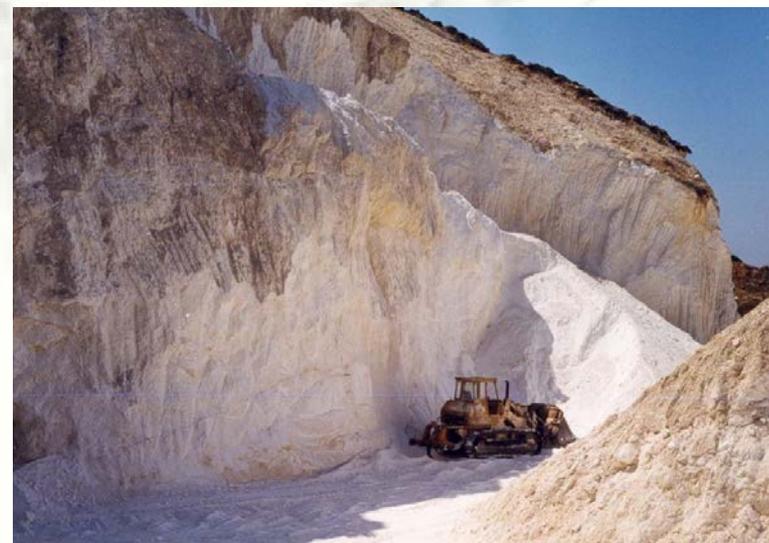
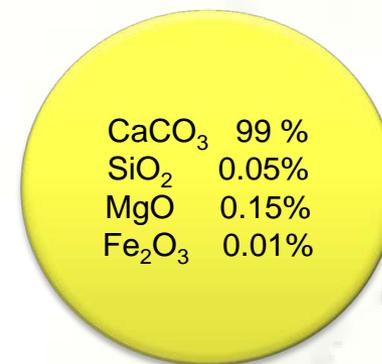


CaCO_3 98 %
 SiO_2 0.35%
 MgO 0.75%
 Fe_2O_3 0.07%
 Mn_2O_3 0.01%

IONIAN KALK SA

Microcrystalline limestone

Trade Name: IOKAL	Top cut $d_{97} \mu\text{m}$	Median size $d_{50} \mu\text{m}$	L*	Y (%)	Abrasion Einlehner mg
<i>Uncoated</i>					
ULTRA FINE	3.5 (d_{98})	0.75	98.5	≥ 96.0	2.3
SPECIAL CHALK	17.5	2.3	96.5	≥ 92.0	8.0
TYP 5C	7	1.9	98.5	≥ 95.5	4.2
TYP 10C	10.0	2.4	98.0	≥ 95.5	5.6
No 20	20.0	3.7	98.0	≥ 94.5	11.4
No 40	30.0	4.5	98.0	≥ 94.0	14.5
KALKOLIN	32.0	6.0	96.0	≥ 90.0	11.0
No 63	48.0	6.5	97.0	≥ 93.0	21.1
TYP RL	50.0	7.0	97.5	≥ 93.5	26.4
No100	63.0	-	96.5	≥ 93.0	19.0
<i>Coated</i>					
ULTRA FINE	3.5 (d_{98})	0.75	98.5	≥ 96.0	2.3
TYP 5C	7	1.9	98.5	≥ 95.5	4.2
TYP 10C	10.0	2.4	98.0	≥ 95.5	5.6
TYP 15C	13.5	2.9	98.0	≥ 95.0	8.3
IOKALITA	10.0	3.7	97.5	≥ 94.0	6.5
KALKOLIN	23	4.5	96.0	≥ 90.0	11



Other Greek filler companies



Raw Material	Trade Name	Median size $d_{50} \mu\text{m}$	Top cut $d_{97} \mu\text{m}$	Whitiness L*	Main Applications
<i>Uncoated CaCO₃ grades – MICROBLANC</i>					
Very white Calcite of highest purity	X-treme	1.0	5	98.0	Paints as TiO ₂ extender, jnpaper
	1	1.6	7.5	97.5	Paints, PO/PE masterbatch
	2	2.0	10	97.0	Paints, Paper, Food
	3	3.5	15	96.5	Paints, Sealants
	5	4.5	22	96.5	Paints, Sealants, Adhesives, Food
	130	85	300	93.0	Paints, Adhesives, Putties
	20	11	85	93.0	Adhesives, Putties, Glass, Rubber
	Matting	24	55	95.5	Emulsion paints as matting agent
<i>Double Coated CaCO₃ grades – ZETAFIL</i>					
Very white Calcite coated by Stearic acid	cst 1	1.1	3.5	98.0	PVC window profiles
	cst CA	1.7	6.5	97.5	PVC profiles, pipes, cables, PO MB
	cst 2	3.0	10	97.0	Masterbatch, PVC pipes, cables
	cst 3	3.5	14	97.0	Masterbatch, PVC pipes, cables
	MST	5.5	22	96.5	PVC pipes, Solvent based paints
<i>Talcum grades – ZETATALC</i>					
Extremely white macrocrystalline Talcum	EW 10	4.0	13	97.0	Paints, PO/PE masterbatch
	EW 20	6.0	22	96.5	Paints, PO/PE masterbatch
	EW 40	16	60	95.0	Paints, Cables

MICROFILL SA

Limestone and Talcum

CaCO_3 99.5 %
 SiO_2 0.04%
 MgO 0.32%
 Fe_2O_3 0.01%
 Fe_2O_3 0.003%

OMYA SA and **KARBOKAL SA** use marble waste rocks as raw material for fillers production



Domestic Filler Market Trends

- Today (2015) the total annual capacity of Greek enterprises producing fillers estimated to have remained at the same level as that of 2008, i.e. about 0,8Mt.
- The utilization of marble waste has become a common practice for the production of Ground Calcium Carbonate in Greece.
- Despite the fact that the economic crisis negatively affected the Greek industry, domestic production of fillers showed a slightly upward trend in prices before the crisis (2008), ranging from 35 to 320 €/ t.
- It is estimated that over 80% of the production volume is exported.
- As for the domestic use, it is mainly consumed by the paints and plastics industry, since the domestic paper industry uses little mineral fillers.



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Results – PART B – Laboratory Results

Area of Interest - 4 (E. Falakro)



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Stockpiled marble wastes

Area of Interest – 5 (Stenopos)



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Stockpiled marble wastes

Area of Interest – 6 (Limnia)



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Stockpiled marble wastes

Laboratory results -1



Optical properties and CaCO₃ content of the materials in the area under study, based on **hand** samples

Sub- area of interest	Abrasiveness ^(a)		Optical Properties ^(b)				Purity CaCO ₃ , %
	Einlehner mg	VWB ₁₂₀	L* (%)	a*	b*	Tristimulus value Y (%)	
1. Disvato	20.2-28.1 (24.6)	66.2-92.1 (80.7)	96.9-97.8	-0.092 to -0.046	0.042 to 0.114	92.2 - 94.5	99
2. Stenopos (white)	26.3-29.6 (27.9)	86.2-97.0 (91.5)	97.6-98.2	0.001 to 0.052	-0.027 to 0.592	93.9 - 95.6	98-99
3. Komnina (white)	24.6-28.2 (26.6)	80.7-92.5 (87,2)	98.3-98.4	0.020	0.564 to 0.695	95.7 - 95.9	99
4. Limnia (white and semi-white varieties)	23.5-29.0 (25,7)	77.0-95.1 (84.3)	96.8-98.1	-0.098 to 0.088	-0.229 to 0.632	90.0 - 95.2	99-100
5. E. Falakro (white & semi- white varieties)	25.3-28.0 (26.7)	83.0-91.8 (87.5)	96.5-98.5	-0.077 to 0.075	-0.019 to 0.0556	91.2 - 95.8	98-99
6. Kechrokambos (white)	24.7	81	98.3	0.020	0.499	95.7	98

Optical properties and CaCO₃ content of the materials in the area under study, based on **bulk** samples

Sub- area of interest	Abrasiveness ^(a)		Optical Properties ^(b)				Purity CaCO ₃ , %
	Einlehner mg	VWB ₁₂₀	L* (%)	a*	b*	Tristimulus value Y (%)	
1. Disvato	14.6	47.9	97.4	-0.0185	0.4757	93.6	99
2. Stenopos (white)	17.5	57.4	97.4	0.0376	0.8250	93.4	98
3. Komnina (white)	18.1	59.3	98.2	0.0714	0.8780	95.4	98
4. Limnia (white and semi-white varieties)	15.9	52.1	97.3	-0.0686	0.3419	93.2	99
5. E. Falakro (white & semi-white varieties)	17 (B) 19.3 (A)	55.7 (B) 63.3 (A)	96.2 (B) 95.9 (A)	-0.1334 (B) -0.1116 (A)	0.0610 (B) 0.0235 (A)	90.5 (B) 89.8 (A)	99 (B) 99 (A)
6. Kechrokambos (white)	19.0	62.3	97.9	0.0439	0.6930	94.8	99



Laboratory results - 2



Mineralogical composition of the materials in the area under study

Sub- area of interest	Mineralogical composition		
	Calcite, %	Dolomite, %	Others (mainly quartz), %
1. 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



Conclusions - 1

- The quarrying activity for marbles' production is still a significant industrial sector in Greece, however resulting in large amounts of waste rocks equal to 95% of the extracted rock.
- The GCC fillers sector has remained fundamentally sound with a total annual capacity (2015) equal to 0.8 Mt.
- The utilization of marble waste has become a common practice for the production of Ground Calcium Carbonate in Greece.
- Eastern Macedonia, is of great interest due to abundant waste materials coming from the extraction of white calcitic marbles.

Conclusions - 2



Taking into account the abundance of waste marble rocks of Eastern Macedonia and the laboratory results concerning the chemical and mineralogical composition of the materials under examination, showing a CaCO_3 content higher than 98%, as well as the reflectance factor measurements which have values greater than 90%, utilisation of these materials looks a promising and challenging opportunity in both financial and environmental terms.



Thank you for your attention



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