8th Global Stone Congress
Drama, Greece | 16th – 20th June 20

Stone composites made with waste from the carbonate ornamental stone extraction and processing industry

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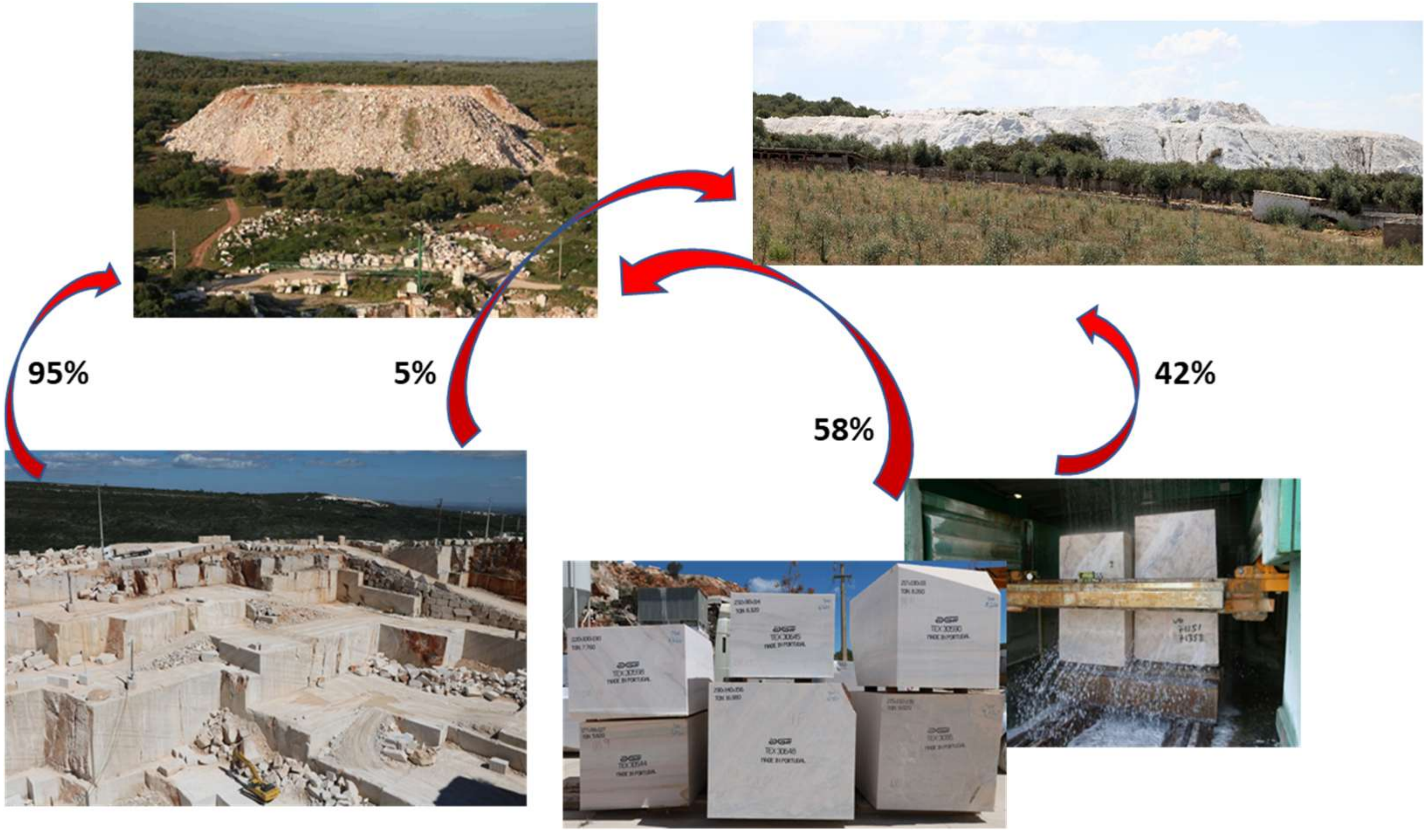
1. Introduction

The carbonate dimension stone extractive and processing industry produces large amounts of wastes later deposited in heaps and deposits of carbonate sludge.

The waste and residues are basically divided into two types:

1 – In quarries:
i) Rock fragments that contribute with around 95%;
ii) Carbonated sludge with 5% contribution.

2 – In processing units:
i) Rock fragments - 58%;
ii) Carbonated sludge - 42%.



Environmental impacts are inevitable, the main ones being:

- reduction of vegetation cover;
- decrease in agricultural activity;
- soil sealing;
- alteration of water lines with a significant reduction in its quality;
- alteration of ecosystems;
- decrease in air quality;
- reduction in the photosynthetic process of plants;
- visual impact.

Carbonate sludge is considered waste because it has not yet been used industrially to give it an economic value. However, they have high degrees of purity and relevant physical and chemical characteristics that make them materials with high potential for use in various industries, especially those that include calcium carbonate ($CaCO_3$) in their production processes.

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2. Objectives

The Geosciences Department at the University of Évora, has a line of research that studies the potential of these wastes as raw materials in other industrial applications.

Calcinata research project proposed to study the application of carbonated sludge from the processing of marble and limestone, as an integral part of resinous binders with polyester resin, later incorporated into stone composites with agregates.

Polyester Resin

+

Dry, Disintegrated Carbonate Sludge

=

Binder

+

Marble Agregates

Gravel 0,5 (2/6,3)

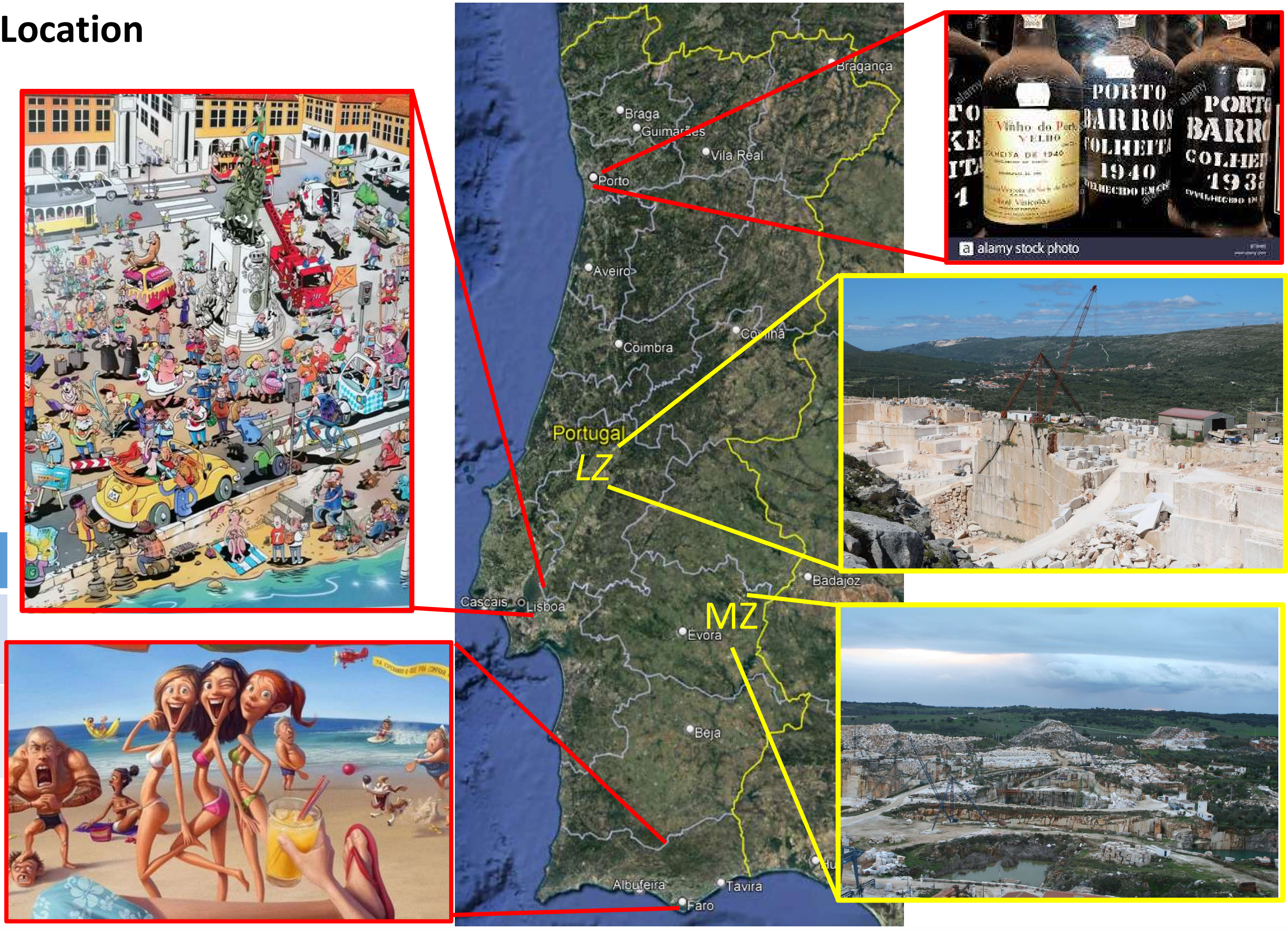
Gravel 1 (6,3/12,5)

Gravel 2 (10/20)

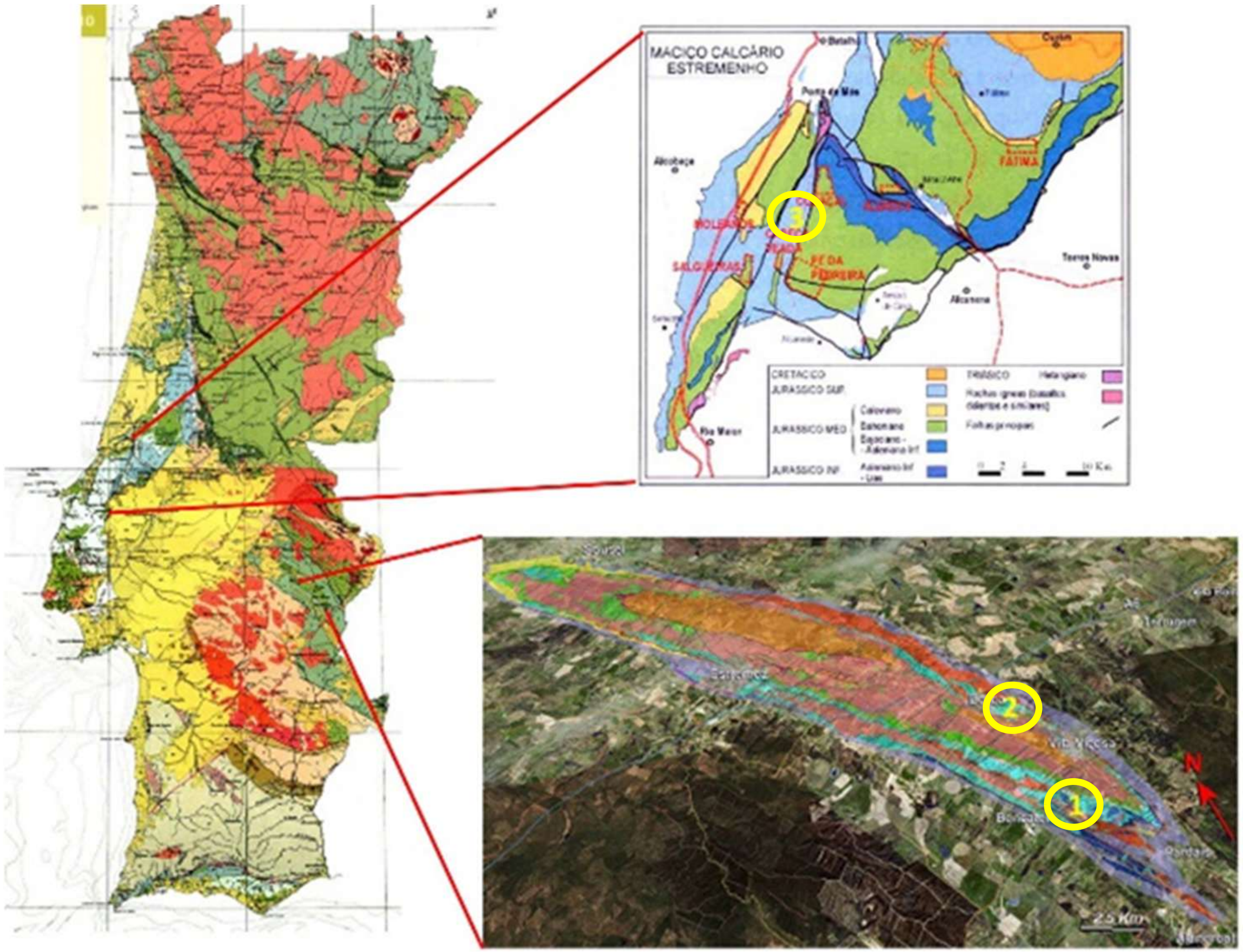
3. Geographic Location

A sampling campaign was carried out in the Marble Zone (MZ), between the municipalities of Estremoz, Borba and Vila Viçosa, and in the Limestone Zone (LZ) including the municipalities of Rio Maior, Porto de Mós, Batalha and Leiria.

	Lisbon	Porto	Algarve
Marbles Zone (MZ)	150 km	270 km	190 km
Limestone Zone (LZ)	130 km	190 km	340 km



4. The Geological Framework of the Sampling



- Estremoz Anticline; is an elliptical-shaped geological structure, about 42 km long and 8 km wide, NW-SE orientation. / Estremoz Carbonated Sedimentary Volcanic Complex; Paleozoic calcitic marbles:

Carbonate sludge from:

1 - *Texugo* quarry (*António Galego & Filhos S.A.);*
2 - JPL quarry (*Marmetal S.A.);*
2 - *Factory (A.L.A. Almeida Lda.)*.

- Estremenho Limestone Massif; Area with 800 km^2 consisting of Jurassic limestones with about 160 million years:

Carbonate sludge from:

3 - Cabeça Veada quarry
(*Solancis* S.A.);
(MVC Lda).

5. Sampling and Sample Preparation

Solancis - Sociedade Exploradora de Pedreiras SA, referenced as **C(S)**.

António Galego & Filhos – Mármores SA, referred to as **M(AGF).**

Manual disaggregation and drying at room temperature

MVC - Mármores de Alcobaça Lda., referenced as **C(MVC).**

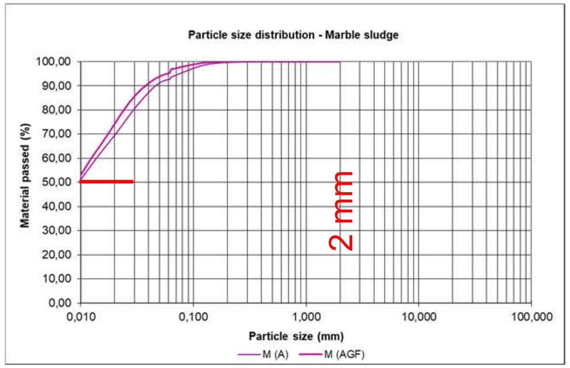
A.L.A. de Almeida SA., referred to as **M(A).**

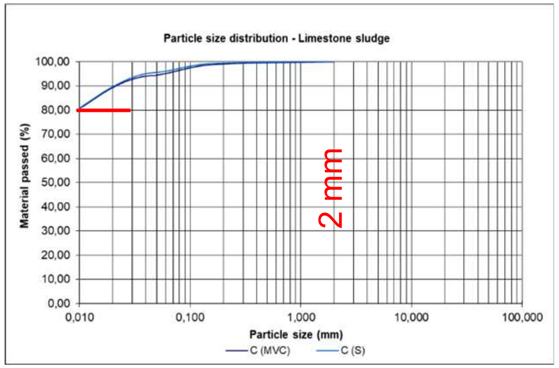
Mechanical disaggregation in jaw mill

Bagging in 5 kg bags

6. Some Characterisation

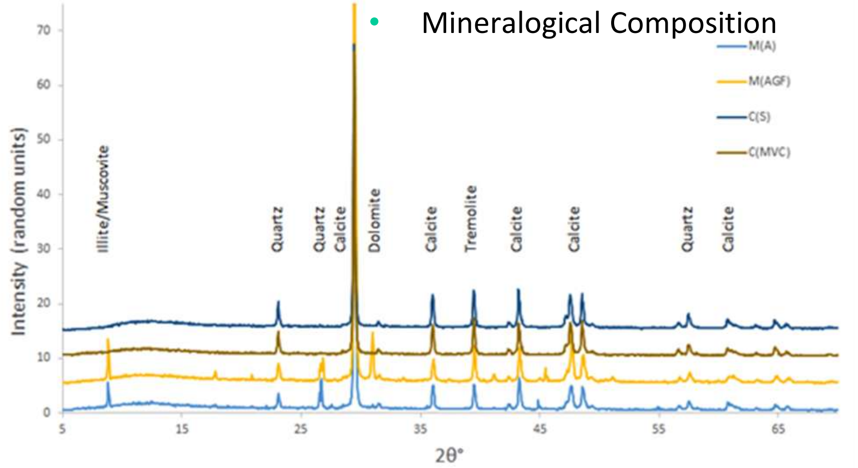
- The particle size distribution





Similar granulometric curves between the two limestone samples and the two marble samples. Limestone muds are slightly finer than marble muds.

- Mineralogical Composition



M(A), M(AGF), C(S) and C(MVC) markedly carbonated muds, with well-defined x-ray diffraction peaks in Calcite.

- Chemical Characterization

Samples	Al_2O_3	SiO_2	CaO	MgO	Fe_2O_3	K_2O	Na_2O	MnO	TiO_2	Loss on Ignition (%)
M(AGF)	0.545	2.549	45.504	3.156	0.228	0.253	0.564	0.030	0.017	42,97
C(MVC)	0.278	0.357	52.580	0.337	0.089	0.092	0.583	0.004	0.006	43,50
C(S)	0.276	0.297	54.189	0.301	0.089	0.143	0.620	0.004	0.011	43,30
M(A)	0.716	3.537	51.555	0.829	0.274	0.362	0.670	0.008	0.026	42,15

All carbonated sludges have significant percentages of **CaO** and in the **loss of ignition test**. M(AGF) and M(A) expressed in SiO_2 and M(AGF) something magnesium (**MgO**).

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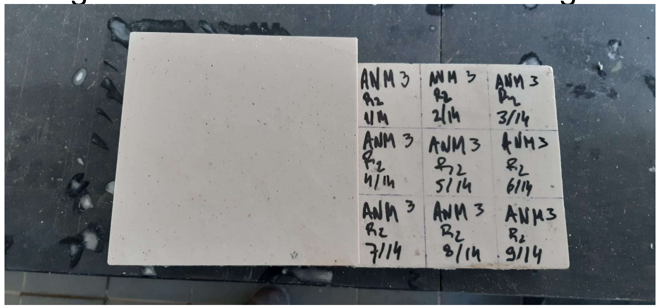
7. Binder Formulations

Constitution of formulations with different percentage contributions of carbonate sludge and polyester resin, branded Recapoli 2196.



Mortar Formulations	NM (Marble Sludge)	NC (Limstone Sludge)	Resine (Polyester)	R (MPa)
ANM3	54,43%		45,57%	102.73
ANM4	50%		50%	98.35
ANM5	47%		53%	96.23
ANM6	**52%**		**48€**	106.37
ANC3		**52%**	**48%**	103.20
ANC4		50%	50%	102.12
ANC5		47%	53%	96.04

Mechanical Characterization of Binders

After demolding, the specimens kept for curing in air and were evaluated at 7, 14 and 28 days, with increasing uniaxial compressive strength over this period, reaching higher uniaxial compression values at 28 days.

8. Formulating Mixtures (Aggregate + Binder)

8 mixes were made with marble aggregate (Gravel 0,5, Gravel 1 and Gravel 2):
- 4 with limestone binder (limestone mud + polyester);
- 4 with marble binder (marble mud + polyester).

Preparing the Moulds
55 cm x 15 cm x 15 cm

Mixing

Filling the Mould

Vibration to Release Air Bubbles

NM – Formulation with Marble binder; **NC** – Formulation with Limestone binder.

Tests	Aggregate + Binder	
	NM	NC
Mechanical Resistance to Compression (MPa)	88.19	91.96
Mechanical Resistance to Bending (MPa)	15.49	13.49
Open Pore Volume (ml)	0.224	0.214
Apparent volume (ml)	117.01	104.59
Apparent density (g/m³)	2.279	2.263
Open porosity (%)	0.191	0.203
Water absorption at atmospheric pressure (%)	0.2	0.1
Absorption of water by capillarity (%)	0.088	0.062

Formulation Drying

9. Cutting and Polishing at the António Galego Factory

Received Blocks

Cutting the Blocks Into Slabs

Blocks With Cut Surfaces

Finished Slabs

Polishing

Finishing

From a chromatic point of view, there was a slight difference between the slabs with a binder incorporating marble mud and those with a binder incorporating limestone mud, the latter having a darker, beige-coloured matrix.

10. Conclusions

1 - It is possible to use carbonate sludge in composites, giving it economic value and making it possible to classify it as a by-product rather than waste.

2 - Comparing the mechanical resistance to compression with the values of some ornamental stones, it can be concluded that they are within the range of values for Natural Stone (Catalogue of Portuguese Ornamental Stones).

3 - Production in an industrial plant using a suitable mixer with a vacuum chamber will certainly ensure a more homogeneous product with a higher density and fewer structural defects, which will certainly lead to higher compressive and flexural strength values.

4 - The use in stone composites of aggregates from the fragmentation and rolling of blocks with no commercial value for ornamental purposes appears to be a possibility for this type of product.

5 - The use of polyester resin in stone composites has proved promising, with considerable economic advantages over epoxy resin.

6 - Reduction of environmental impacts caused by the open-air accumulation of tailings from the carbonate ornamental stone extraction and processing industry.

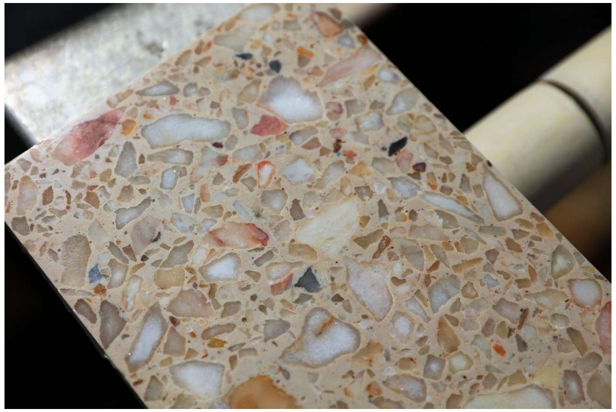
11. Acknowledgements

CALCINATA project (ALT20-03-0247-FEDER-072239) co-financed by the European Regional Development Fund (FEDER) under the ALENTEJO 2020 (Alentejo Regional Operational Programme).

To the Cluster Portugal Mineral Resources Association, co-manager of the project, and to the Project Support Office of the University of Évora.

Vera Pires would like to thank the Programme Contract between FCT and the University of Évora within the scope of the call for proposals to stimulate institutional scientific employment 2018, the Foundation for Science and Technology (FCT) within the scope of projects UIDB/04449/2020 and UIDP/04449/2020-through the HERCULES laboratory.

Special thanks to the companies: A.L.A. de Almeida SA, António Galego & Filhos - Mármores SA, Marvisa, Mármores Alentejanos Lda MVC - Mármores de Alcobaça Lda. Solancis - Sociedade Exploradora de Pedreiras SA,



Thank you for your attention