Guessing stone behaviour before extraction

L. Dias[1*], R. Silva[1], L. Lopes[2,3], A. Candeias[1,4], J. Mirão[1,3]

[1] HERCULES Laboratory, University of Évora, Portugal

[2] Institute of Earth Sciences, University of Évora, Portugal

[3] Geosciences Department, Sciences and Technology School, University of Évora, Portugal

[4] Chemistry Department, Sciences and Technology School, University of Évora, Portugal

* e-mail address: luisdias@uevora.pt

* CienciaVitae ID: 3B14-2FD7-627F

Introduction

In the ornamental stone industry, Portuguese companies have a great exporting capability, which recently reached 400 million EUR in 2019 [1]. In fact, the Portuguese industry of ornamental stones is traditionally an exporting sector, with manufactured products appreciated internationally. It is extremely important that the stone purchased by the consumers meets the expectations for which it was chosen, being colour one of the main aspects. Currently, there are Portuguese companies with very high costs in the replacement of altered stone.

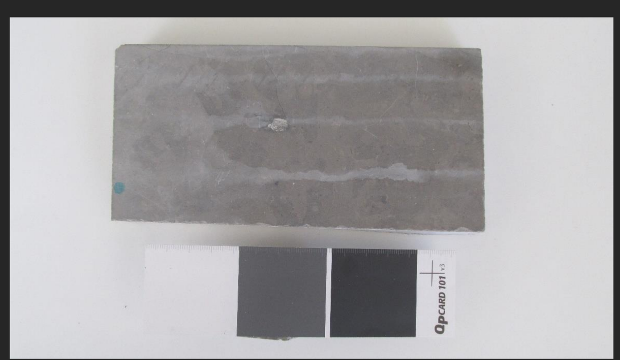
The recent emergence of new players in the ornamental stone industry, namely China, Brazil and Turkey, characterised by distinctly lower labour costs, has been reshaping the role of Europe in this industry [2]. The unpredictability, inherent to the use of a natural stone material is, thus, being considered a penalising factor by the construction industry. This unpredictability can, however, be reduced and controlled through the knowledge of the stone's weatherability, mineralogy and chemical composition, factors that lead the material's certification and are essential in defining its exploitation plan.

This work arises from the companies' need to seek the extraction of stone blocks that ensure a lower susceptibility to colour change after application.

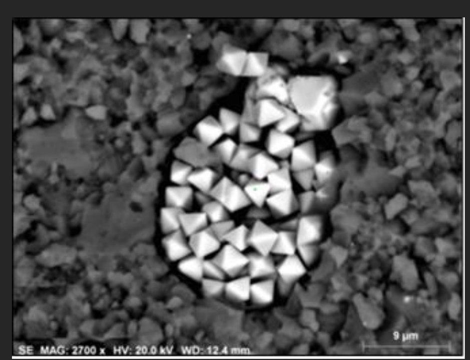
Material and Methods

A geochemical/mineralogical study was applied in a quarry located in the "Maciço Calcário Estremenho" (MCE, northern region of Lisbon), where one of the most important Portuguese lithotypes is currently explored. Featured by its excellent physico-chemical characteristics, this lithotype is further characterised by the coexistence of a blue and cream colour [3]. The work aimed to study the chemical composition of each exploitation level blocks, emphasizing the mineral, pyrite, responsible for the natural discolouration of this construction resource.

Quarry in study, located at the MCE, Portugal



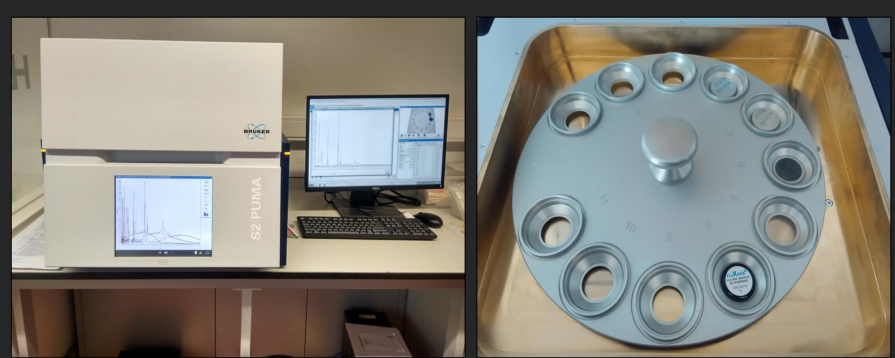
Colour alteration occurred, after application on site



Pyrite, present in stone in large amounts

The sampling was done across all the exploration levels of the quarry, which 5 samples were tooked by each exploration level. The samples were powdered to make glass beads that allowed the geochemical/mineralogical analyses by X-ray Fluorescence S2-PUMA and X-ray diffraction. The level "0" corresponds to the surface of the quarry.

Glass beads preparation, using 12g flux + 1,2g sample



Glass beads analyses, using a X-ray Fluorescence S2-PUMA

Preliminary findings

✓ The stone blocks extracted from the deepest exploration levels of the quarry seem to have more content of pyrite and aluminum and silicate oxides, specially in the darker fractions of the stone;

✓ A higher content of pyrite in the stone will trigger its weathering more quickly;

✓ The information obtained is extremely important, since these findings will influence the exploitation plan of the quarry in the future.

References

[1] Website assimagra.pt, accessed at December 2019;

[2] Montani C. (2014) XXV Report Marble and Stones in the World 2014, Aldus Casa di Edizioni in Carrara, Italy;

[3] Dias L, Rosado T, Coelho A et al. (2018). Natural limestone discolouration triggered by microbial activity—a contribution. AIMS Microbiology 4 (4): 594-607;

Acknowledgments

The authors gratefully acknowledge the following funding sources: ColourStone—Colour of commercial marbles and limestone: causes and changings (ALT20-03-0145-FEDER-000017) and INOVSTONE4.0 (POCI-01-0247-FEDER-024535) co-financed by the European Union through the European Regional Development Fund ALENTEJO 2020 and Fundação para a Ciência e Tecnologia (FCT). The authors acknowledge to the National Museum of Ancient Art in Lisbon for allowing this study. Luís Dias acknowledges FCT for the grant SFRH/BD/111498/2015 co-funded by the European Social Fund (ESF) and MEC national funds.

Chemical characterisation

The quarry under study has currently 13 exploration levels, with the level designated B13 the deepest exploration level in the quarry stratigraphy. In this way it is possible to state that:

- Through the results obtained by the X-ray fluorescence S2-PUMA it seems that the Fe_2O_3 and SO_3 levels tend to increase with the exploration level increasing (Figure 1). The same phenomenon seems to occur with the aluminum and silicon oxides (Figure 2)

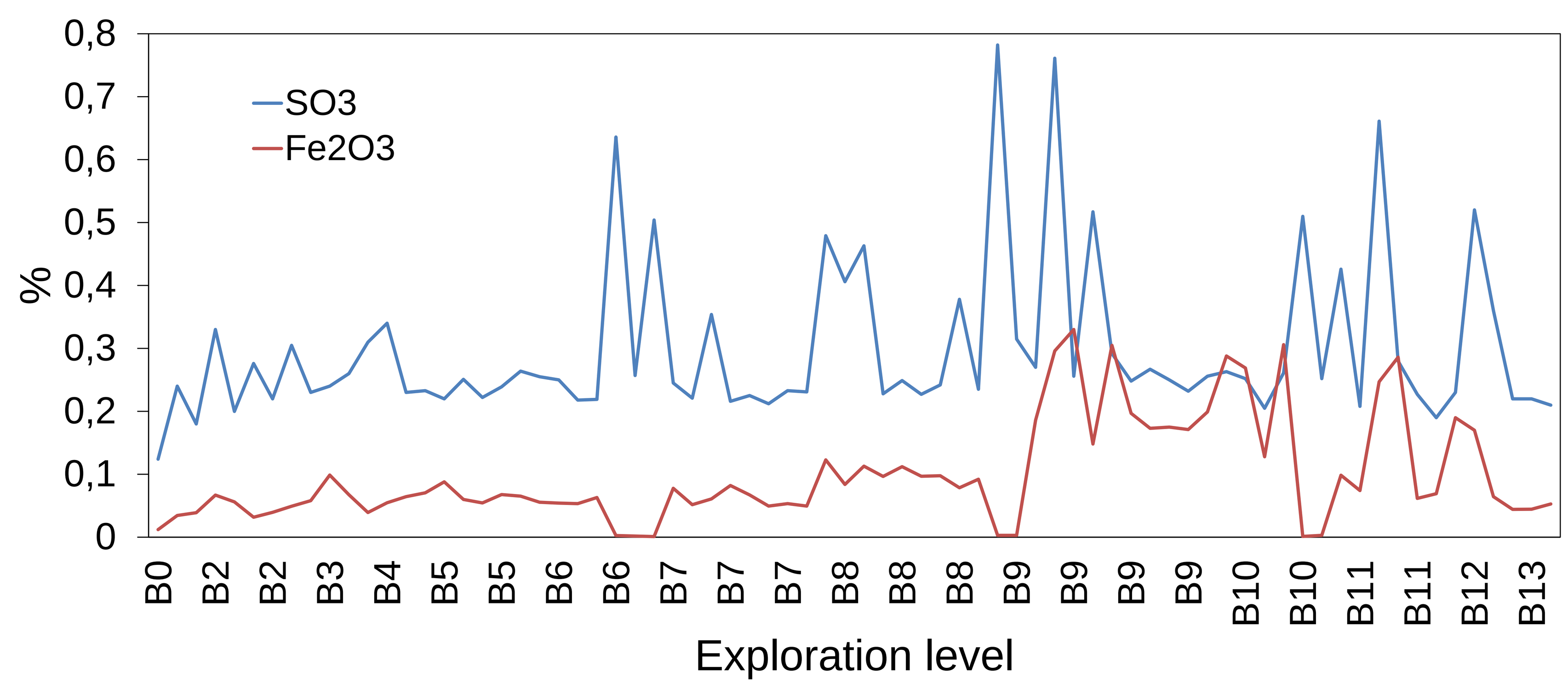


Figure 1: Variation of SO_3 and Fe_2O_3 content in the exploration levels of the quarry in study.

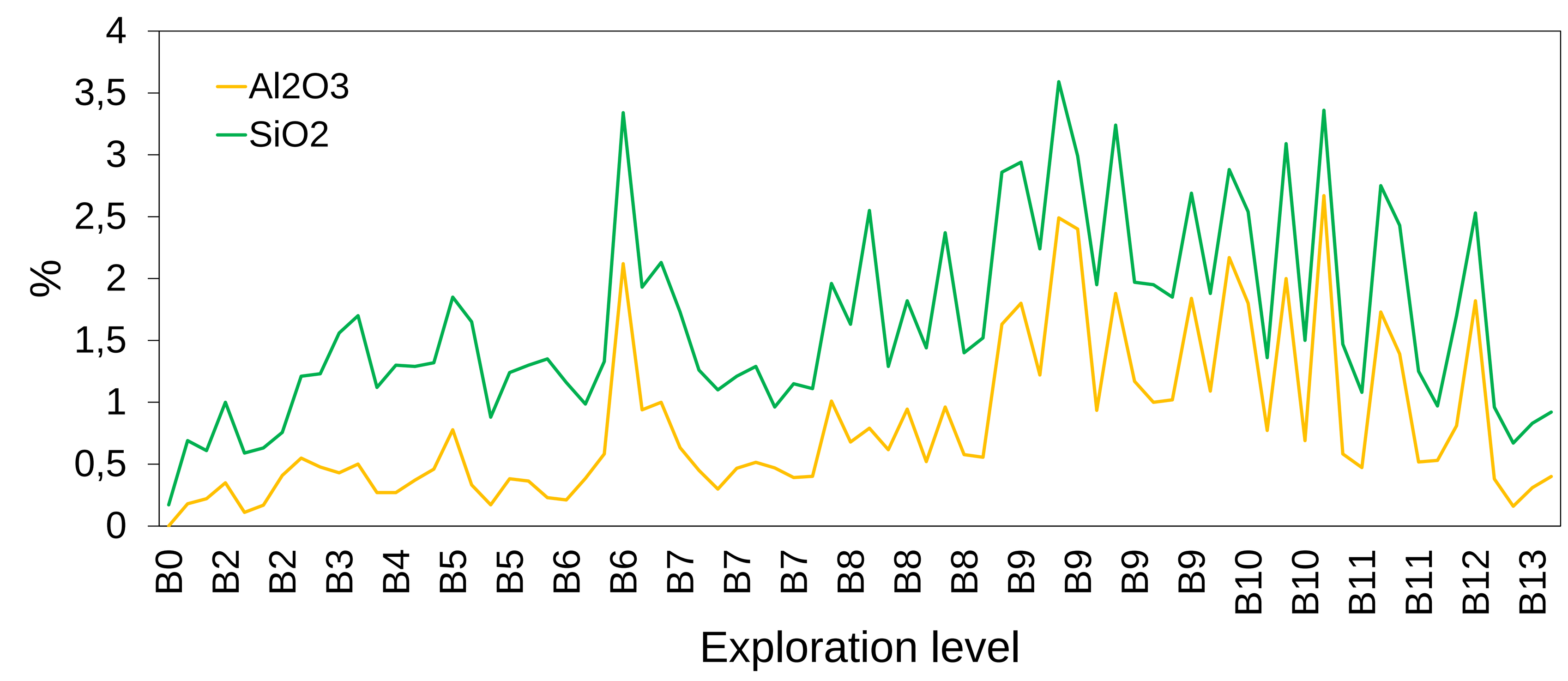


Figure 2: Variation of Al_2O_3 and SiO_2 content in the exploration levels of the quarry in study.

- Predominance of higher levels of pyrite in the darker fractions of the stone, represented in the cluster signalized at red in the figure 3, indicated by the enrichment in iron and sulfur. Another point is the predominance of hematite in the lightest fractions of the rock, represented in the cluster signalized at green, indicated by the iron enrichment.

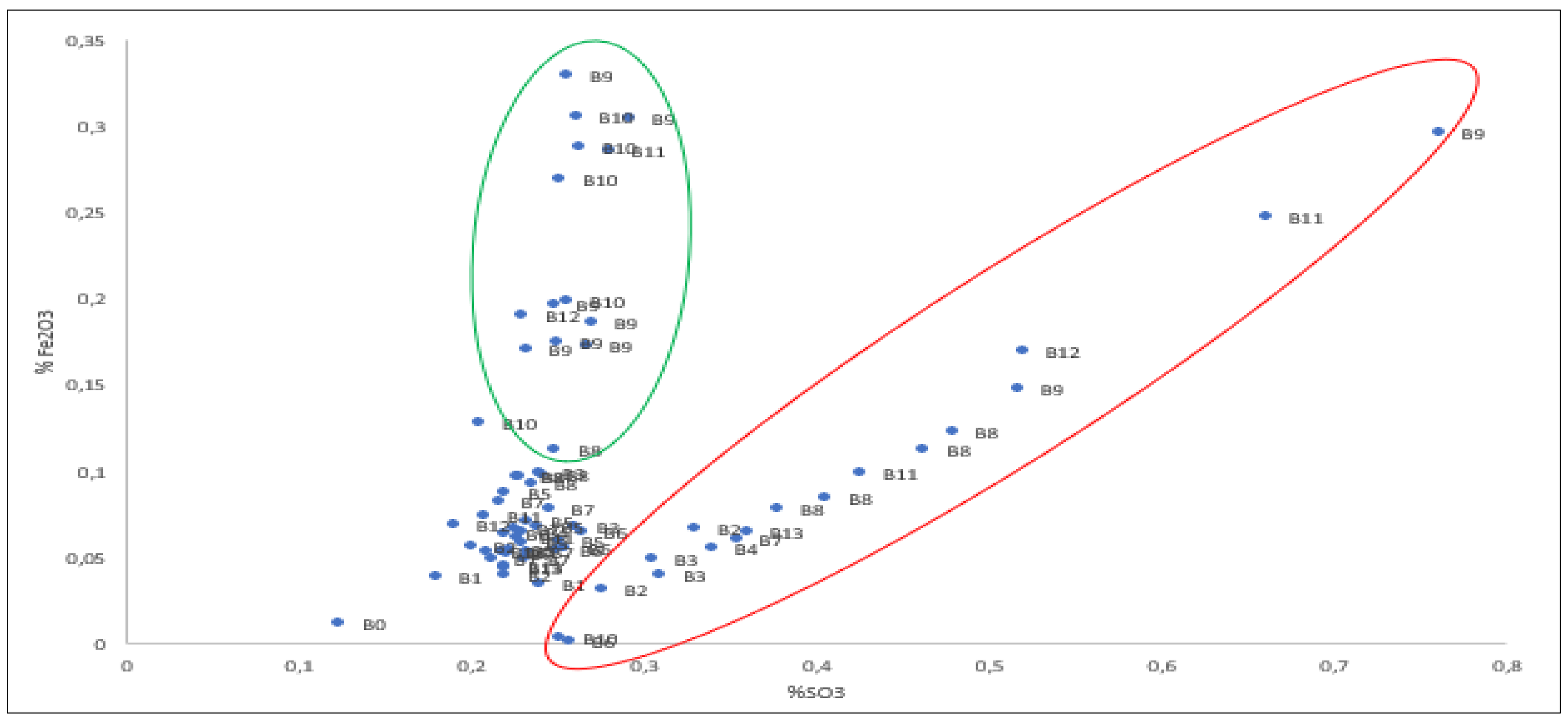


Figure 3: Fe_2O_3 vs SO_3 contents, originating clusters accordingly with the colour of the stone fraction. Lighter fraction – green cluster; Darker fraction – red cluster.

Mineralogical characterisation

- The behaviour of quartz content is random (figure 4) while pyrite is often below the detection limits of this technique, with exception in some darker fractions. This abundance of pyrite is more relevant in the deepest exploration levels of the quarry.

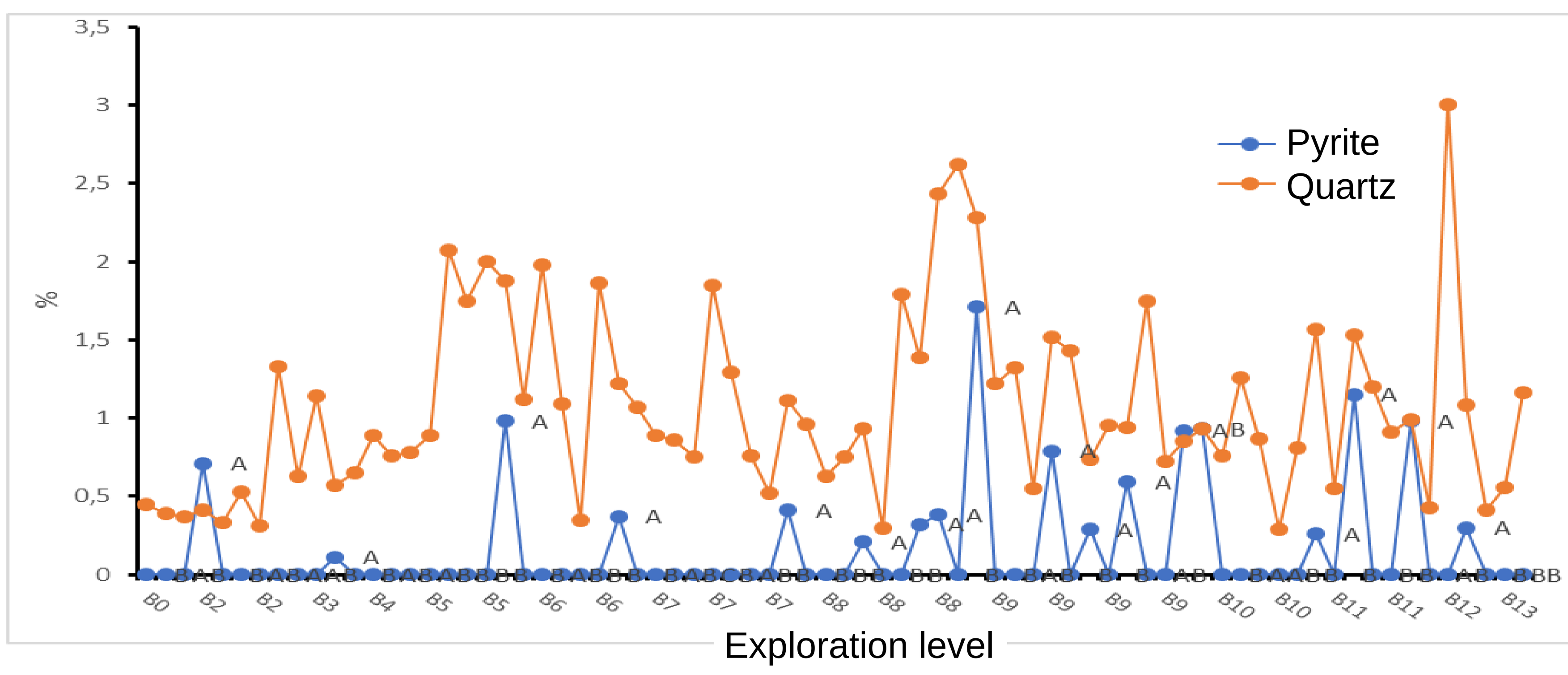


Figure 4: Pyrite and quartz abundance in function of the stratigraphy of the quarry, from B0 (more superficial) to B13 (deeper). A corresponds to darker fractions of the stone.