Chemical mobility of major elements during lixiviation experiments, in magmatic ornamental stones from Portugal
Joaquim Simão, Nuno Leal, Carlos Galhano

Synopsis
Six Portuguese magmatic ornamental stones were submitted to Soxhlet experiments during 10000 hours (approximately 416 days) in order to evaluate how the rain water affects the rock behavior as a dimension stone. Macroscopic alterations were observed in the rock fragments and chemical analysis of leaching water solutions revealed how major elements were mobilized from rock-forming minerals allowing to compare weathering susceptibilities between different natural stones.

Keywords
Soxhlet experiment, granite, leaching, natural stone, dimension stone.

Introduction
Water is the main solvent present at Earth surface, thus playing a determinant role in the alteration of rocks. Rain is a major agent for such changes, and their intensity strongly depends upon the available quantity of water that drains through rocks. During the last decades, due to their granted durability and inalterability, silicate ornamental stones, often referred as “granites”, have been more exploited than ever. However, when used as exterior claddings, they are subject to the action of weathering agents. In order to simulate the effect of atmospheric water action on rocks, a Soxhlet extractor has been used, during a total time of 10000 hours. Experiments of the same kind have been performed by Simão (2003), Simão (2003a), Simão & Silva (2003), Galembeck et al. (2009), Costa et al. (2010) and Oliveira (2017), to evaluate the alterability of silicate ornamental stones, trying to find relationships between similar stones with different origins, and to help in the correct choose of applications for such materials. They also allow the identification of the way factors like mineralogy, texture, original state of degradation, climate condition and atmospheric pollutants contribute to mineral instability, and thus may change the physical characteristics and mechanical properties of rocks. When such features are known and considered by producers, architects, civil engineers and constructors, a correct choice for application can be achieved, with a good performance, both in terms of durability and safety. So, it is most useful that ornamental stone transformation industry gets information on the limitations that some kinds of exploited stone materials may exhibit as a result of the presence of minerals that will become unstable on specific environmental conditions.

Petrography
Six “granites” have been selected for the present study, named after their origin location regions: the Monção (MnGr), the Vila Real (VRGr), the Castelo de Vide (CVGr) and the Monforte (MfGr) granites, the Odivelas gabbro (OdGb) and the Monchique Nepheline Syenite (MoNS).
MnGr is a porphyritic, medium- to coarse-grain, leucocratic, biotitic, pinkish (due to microperthitic microcline phenocrysts) calco-alcaline granite. VRGr is a two micas (mainly muscovite), sometimes porphyritic, medium- to coarse-grain, leucocratic, yellowish (due to strong alteration) granite. CVGr is a two micas (mainly biotite), porphyritic (microcline phenocrysts), medium- to coarse-grain, white granite. MfGr is an homogeneous medium-grain, leucocratic, reddish pink coloured (abundant pinkish feldspar) granite, with biotite and hornblende. OdGb is an homogeneous medium-grain, melanocratic, olivine gabbro, with greyish plagioclase and black pyroxene crystals. MoSN is a greyish, medium- to coarse-grain, leucocratic nepheline syenite, with prominent elongated tabular K-feldspar crystals and (sometimes well-developed) reddish brown nepheline crystals.

Methodology

The Soxhlet extractor is used to simulate the action of atmospheric precipitation, in order to promote rocks and/or minerals leaching during a certain period of time. Water is initially distilled, and then evaporated and condensed, and finally it will circulate through the sample. This experiment will accelerate the natural alteration process and has been used in several types of rocks. The methodology is described by Aires-Barros (1991) & Simão (2003), according to these authors, the experiment simulates higher-temperature (60°) and more acidic rain than natural ones, humid atmosphere, hydrostatic level fluctuation, percolation through the porous rock-system and leaching and reprecipitation of materials. The studied rocks have been subjected to the action of a Soxhlet extractor, in which previously fragmented samples (about 25g each) suffer draining processes during 10 successive cycles, 1000 hours each. At the end of each cycle, percolation water has been analysed, so Si, Al, Fe, Mg, Ca, Na and K chemical mobility can be evaluated. Then, new, fresh, distilled water was added to the rock-system.

Results

Major changes were found for OdGb and MoSN. At the end of the experiment, homogeneous, black, gabbro fragments exhibited reddish-brown patches, mainly composed by residual Fe-oxides, as a result of olivine and pyroxene alteration. By its turn, MoNS nepheline crystals turned from reddish-brown to light-yellow colour, with intense alveolization and disaggregation; pyroxene crystals got reddish-brown colouration and K-feldspar became lighter relative to the original colour. In granites, changes were less marked, mainly consisting in the alteration of feldspar and biotite on CVGr and VRGr. Here (VRGr), the enhancement of the original colour is the result of continuous degradation of biotite, with the resulting dissolution and leaching of Fe-oxides, and their precipitation on feldspar, which became altered. MnGr and MfGr were less altered, reflecting stronger resistance to the experiment conditions.

At the end of each cycle, water coming from the leaching of each rock-type was analysed by Atomic Absorption Spectrophotometry, and the results can be shown as charts (Fig. 1), in which Si, Al, Fe, Mg, Ca, Na, and K (recalculated as oxides), accumulated and absolute variations are expressed as ratios between each end-of-cycle and original values. These values reflect the ease of dissolution of each analysed element. Due to dissolution of
nepheline and feldspar, Na and K that more change show in MoNS, and Al values are due to nepheline dissolution. In OdGb, K, Na and Si are the most prominent elements in terms of change; although Si leaching tends to be slow, destruction of olivine and pyroxene crystals, as well as plagioclase leaching lead to significant values for the element. These effects in olivine grains were recorded in a more intense way by Simão (1996), Simão & Silva (1999) and Silva & Simão (1995). In granites, Na was the more mobilized element, due to feldspar leaching, followed by Si, and then by K, Mg and Ca. In all samples, Fe exists in very low amounts in solution, staying as residual deposit in the rocks, after oxidation and precipitation.

Fig. 1 Accumulated variation for Si, Al, Fe, Mg, Ca, Na and K (major elements oxides) in the cycles of the Soxhlet experiment waters.

Conclusions
Alteration and alterability studies evaluated and compared the different rock-types behaviour when exposed to the action of conditions similar to atmospheric precipitation, and allowed the prediction of their behaviour in real natural conditions. Among the studied rocks, MoNS and OdGb include minerals with a high susceptibility to alteration, respectively nepheline and olivine, thus suffering more damages than granites, which gave a better response. In granites, it is possible to distinguish two main different behaviours: MnGr and MfGr are highly-resistant rocks, while CVGr and VRGr are less resistant. Apparently CVGr seems like a solid rock, but when exposed to disequilibrium conditions shows changes that decline its behaviour as an ornamental stone. VRGr is a rock that suffered significant meteoric alteration that diminished its response capacity and prejudiced its behaviour when exposed to new aggressive environments. This kind of alteration studies show that even apparently solid rocks may develop fast degradation patterns, when submitted to environments with specific characteristics. These changes are reflected in loose of quality,
both in aesthetic terms and physical-chemical behaviour, and thus this kind of studies must act as an indicator of the rock quality, being critical its inclusion in the characterization and recommendation (or not) of each ornamental stone, for a determined application.

Acknowledgements


References


About the author(s)

Joaquim Simão, Professor; Nuno Leal, Professor; Carlos Galhano, Professor.

University Nova de Lisboa, Department of Earth Sciences and GeoBioTec, Campus de Caparica, Almada 2829-516, Portugal. jars@fct.unl.pt; n.leal@fct.unl.pt; acag@fct.unl.pt.