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Micro-porosity and minero-petrographic features influences on decay: Experimental data from four dimension stones

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HIGHLIGHTS

- Associated MIP and hygroscopic sorption are effective in the characterisation of micro-porosity.
- Joint MIP and hygroscopic sorption allowed detecting the presence of hygroscopic clay minerals.
- Mineralogical and petrographic features allowed interpreting the results of the two techniques, when contrasting.
- On the whole the suggested methodology allowed deciphering the simulated weathering processes.

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ABSTRACT

Sedimentary stones have been used since long as dimension stones, constituting the primary building material of several monumental structures all over the world. The understanding of their behaviour when exposed to weathering factors is crucial for preservation, replacement and restoration intervention. Although not directly involved with decay mechanisms, micro-pores (*i.e.* open pores with radius <0.1 μm) and their interconnection to the wider ones are important for air and water flow inside rocks. In fact, micro-pores are not directly the site of ice or salt crystallization, nor of oil and gas entrapment, but are the main pathway for fluids during both adsorption and evaporation processes. The study of narrow pores is therefore crucial to predict *e.g.* stone durability and physical properties. This study presents the study on four different sedimentary lithotypes vastly employed as dimension or ornamental stones in Italy, both sound and artificially weathered. In particular, coupled MIP and hygroscopic sorption based micro-porosimetry were used to uncover liability to relative humidity variation, in association with a thorough mineralogical characterization. The MIP intrusion pattern attained pore shapes and typology description for the different rock types; but only the hygroscopic sorption helped deciphering the on-going processes. Moreover, the coupling of petrography and petro-physical analyses (*i.e.* MIP and hygroscopic sorption based micro-porosimetry) pointed out that phyllosilicates have a role in decay processes of rocks due to swelling and/or suturing of the adjacent voids.

1. Introduction

Availability, workability, mechanical performances and appearance are some of the factors that, for centuries, induced selection and usage of natural lithic materials to build or ornate structures [1,2]. Even if, generally, sedimentary stones present lower durability and mechanical performances if compared to volcanic or metamorphic lithotypes their availability as raw materials, aptitude for workability, and visual appearance allowed sedimentary stones wide employment throughout men's history as dimension and ornamental stones. In order to be able to perform adequate replacement and restoration intervention, or to plan preventive care and monitoring it is necessary to characterize the main internal factors leading to decay when exposed to weathering factors [3]. The mineralogy of the diverse rock typology comprised under this genetic category has high variability as well as diverse textures and structures. One of the most variable factor is porosity, ranging from low values in compact sandstones and limestones to high values in less compacted sediments (*e.g.* biocalcarenites, bioclastic limestones) [4]. The bearing of pore size distribution to different kind of weathering has been since long addressed [5–9]. Several analytical techniques providing a precise evaluation of the pore space and other related values as tortuosity, formation factor, etc.

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were implemented for their high-resolution performances in describing pore networks (in particular: X-ray Computed Tomography, NMR, ultrasounds, and resistivity) [10,11].

Several authors recognize the importance of predicting rock durability when dealing with Cultural Heritage, stating that the analysis of porosity is crucial to foresee rock performances [8,12]. In particular micro-pores (*i.e.* open pores with radius < 0.1 μm) even if not connected with the main fluid flow processes, as capillary rise, are the main pathway for air, water and their solutes (*i.e.* water vapour, pollutants etc.). Accordingly micro-pores are the site of the processes related to fluid-rock interaction (*i.e.* evaporation, hydration, deposition, etc.), having a major role in weathering mechanisms [13,14]. Micro-pores, being the site of condensation, are also important to describe the thermo-hygrometric properties of buildings [15,16]. Several techniques are currently applied to get information about micro-pores (*e.g.* size, shape, distribution). Between 0.001 and 0.1 μm the relative pore volume and the opening size distribution can be determined by means of Mercury Intrusion Porosimetry (MIP), Brunauer-Emmet Teller (BET), small-angle neutron scattering (SANS), image analysis and techniques based on the hygroscopic behaviour of micro-pores [11,17,18]. These techniques could also be efficiently combined between them [8] or with opportune image analysis [9] or physical techniques (*e.g.* ultrasounds [19,20], and permeametry [21]), in their resolution ranges, to define the micro-pore space. MIP is a popular technique to characterise porous materials, allowing the reconstruction of open pore radius distribution generally from c. 0.01 to c. 70 μm. It is to take into account that the required calculation introduces approximations by simplifying the real geometry of the pore network (*i.e.* the calculations are based on input parameters (γ, θ) with questionable values, refer to cylindrical voids and do not take into account the so-called ink-bottle effect). Moreover structural features of the samples are usually not considered (*e.g.* the risk of damaging the material by exerting high pressure) [22–24]. However, mathematical models are used to correct these approximations, and to recast several parameters, as pore typology and shape, tortuosity and grain-size [18]. A process similar to the BET technique of adsorption controls the hygroscopic behaviour of micro-porous materials (Fig. 1): the surfaces of the porous system accumulate water molecules until the equilibrium moisture content is reached. At increasing relative humidity (RH), the adsorption continues with the formation of subsequent molecular layers with lower binding forces, until equilibrium state is reached. Assuming isothermal conditions, the sorption isotherm describes the accumulated water volume vs. the relative humidity value. The Kelvin equation correlates RH and capillary radius allowing the construction of a micro-porosimetric curve reflecting the hygroscopic behaviour of the analysed material.

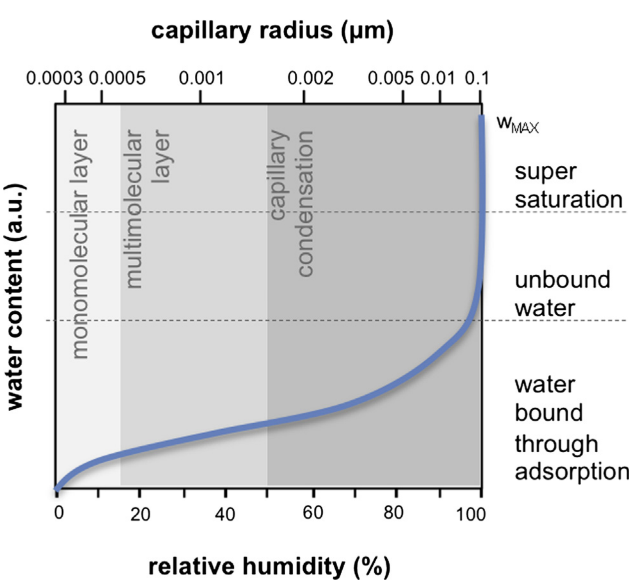

Fig. 1. Diagram showing the vapour/liquid equilibrium curve in confined spaces. The equivalence between humidity values and pore radius filled by liquid water is enlightened (after Kieβl, 1983).

The hygroscopic behaviour of materials as a key to interpret decay processes is critical for the following reasons: i) it is linked with the presence of micro-pores, and ii) it is connected with the presence of hygroscopic materials both as primary rock-forming minerals, or secondary minerals *e.g.* salts precipitated form circulating solutions. In fact the so-called hygroscopic minerals (*e.g.* phyllosilicates and salts) attract water into their structure, increasing their volume and causing a mechanical shock (*i.e.* micro-cracks) to the rock structure (*e.g.* turning from anhydrite to gypsum the crystal volume increases of about 60%) [25–27]. Usually, for a better understanding of the amount of stress induced by RH variation and the consequent moisture condensation or evaporation processes inside the rock core, swelling tests are performed, but this quantification is not the aim of this research.

This study addresses the micro-porous range by means of MIP and hygroscopic sorption based porosimetry in order to explore the advantages of coupling the techniques. Four different sedimentary lithotypes vastly used as dimension or ornamental stones, both sound and salt weathered, were analysed. The obtained porosimetric curves were associated with a detailed mineropetrographic analysis to investigate the micro-porosimetric characteristics of materials and their modification after salt crystallization. Following the preliminary characterization of the microporous network, the onset and development of a secondary porosity were detected, along with a revision of the application of MIP to investigate micro-porosity, and the disclosure of the potentiality of hygroscopic sorption in deciphering weathering mechanisms. Moreover, the coupling of petrography and petrophysical analysis (*i.e.* MIP and hygroscopic sorption based micro-porosimetry) allowed investigating the connection between phyllosilicate occurrence in the stone and decay processes.

2. Experimental

2.1. Materials

The addressed lithotypes, differing by relative abundance of components (*e.g.* minerals, fossils, oxides and hydroxides) or grain-size (Table 1), have widespread use as dimension and ornamental stones in the Italian Cultural Heritage. The selection criteria were i) difference in mineral-chemical composition, and ii) differentiation in the open porosity values, in order to establish correlations between these parameters and durability. Macigno Sandstone (MS), Breccia Aurora (BA), Rosso Verona (RV) and Vicenza Stone (VS) were the selected stones (Fig. 2).

MS is a turbiditic sandstone, with very fine to medium grained sandy clasts mainly of quartz (SiO_2) and feldspars (albite ($Na(AlSi_3O_8)$), orthoclase ($Al_2O_3|K_2O|6SiO_2$))), secondary calcite ($Ca(CO_3)$) and phyllosilicates of the montmorillonite-chlorite series (Na-Ca-Al-Si_4O_{10} - O) [28]. The lithotype presents bluish-grey fresh cut surfaces, and yellowish surfaces when weathered. The clayey cement is scarce and, with a few calcite, wraps the clasts. A net of narrow pores can be evidenced along grain boundaries and inside clay minerals, which wrap the main quartz grains. This rock, quarried in Tuscany, has been used since long time as dimension stone. It has been widely employed for architectural ornamental elements (*e.g.*, capitals, columns, corbels, etc.), and during the Florentine