

## Stone decay in two-mica granite buildings of Northern Portugal

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The application of the natural stone as a building material catalyzes the deterioration process due to the reactivity between the rock minerals and industrial mortars and to the exposure to particular environmental conditions. Among the main factors in the origin of stone decay, the intrinsic characteristics of the rock are determinant in the behaviour of its constituents. Three historical granite monuments from the Oporto region, largely affected by a diversity of stone deterioration types, have been selected in order to illustrate the combination of the intrinsic factors with weathering and environmental agents, responsible for the susceptibility of granite stones to deterioration: a millenarian Xth century Romanic church, a XVIIIth century Baroque church and a XIXth century neoclassical building. The granite the selected monuments are built with is classified as a medium- to coarse-grained leucogranite, syn-tectonic in relation with the third Hercynian deformation phase. This granite exhibits a non-porphyrific hypidiomorphic granular texture and a mineral association of quartz, orthoclase, perthitic microcline, albite, muscovite and biotite. Apatite, zircon, monazite, ilmenite, and scarce tourmaline and garnet are accessory minerals. The granite is affected by late-to post-magmatic alteration as well as by weathering processes to various extents. In some outcrops the potassic feldspar is intensely kaolinized. The A/KCN molar ratio between 1.3 and 1.5 is an evidence of a strong peraluminous character due to the presence of primary muscovite. A U-Pb geochronological study on zircon and monazite indicates a minimum emplacement age of  $318 \pm 2$  Ma (Almeida, 2001). The granite stones applied in the selected monuments display different weathering degrees, as a consequence of different susceptibility to deterioration. Granular disintegration, plates, flakes, black crusts, thin black layers, efflorescences and biological colonization are the main deterioration types. Gypsum, halite, niter, glauberite, singenite, calcite, aptitalite, thenardite, arcanite and mirabilite have been detected by X-ray diffraction and SEM analyses and play an important role in the stone decay (Silva, 2005). The main source of salts is rainwater, affected by the proximity with the Atlantic Ocean. Carbon and sulphur rich porous fly ashes and silicon and aluminium rich smooth fly ashes are also present, in the thin black films, produced by air pollution agents.

### References

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## The CaCO<sub>3</sub> saturation state of Phanerozoic oceans

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Geochemical models suggest that perturbations of the global carbonate cycle in the geologic past resulted in large variations in the CaCO<sub>3</sub> saturation state ( $\Omega_c$ ) of the ocean (Zeebe and Westbroek, 2003; Ridgwell, 2005). These variations may have influenced the evolution of biocalcifying organisms and global sedimentation patterns. To independently test these ideas, I deduce information on past oceanic  $\Omega_c$  from the geological record of calcified cyanobacteria and a numerical model of cyanobacterial mat calcification. A curve of threshold oceanic  $\Omega_c$  needed for cyanobacterial calcification is derived and compared to the Phanerozoic distribution of calcified cyanobacteria, providing some constraint on past oceanic  $\Omega_c$  levels. To this curve correspond threshold curves of pH and total alkalinity (TA). The emerging picture of considerable oceanic  $\Omega_c$  variation through time matches the long-term tectonic, geochemical and biological evolution of the Earth System:  $\Omega_c$  maxima at the base of the Cambrian (545 Ma;  $\Omega_c > 12$ ), most of the Carboniferous (330-300 Ma;  $\Omega_c > 7$ ), the mid Permian (280-260 Ma;  $\Omega_c > 9$ ) and the late Triassic (210-200 Ma;  $\Omega_c > 7$ ) correspond to periods of increased continental weathering or decreased neritic depositional space. A prominent drop in oceanic  $\Omega_c$  starting from an early Jurassic high ( $\Omega_c > 7$ ) to a mid-Cretaceous low ( $\Omega_c < 3$ ) records the advent of planktic calcifiers during the "mid-Mesozoic revolution". Low and relatively stable oceanic  $\Omega_c$  after this event confirms the efficiency of the carbonate compensation mechanism in stabilising the global carbonate cycle. Both the "Cambrian Explosion" and key moments of the "mid-Mesozoic revolution" took place in highly supersaturated oceans, suggesting a link between these major evolutionary events and changes in ocean chemistry. Global biocalcification crises associated with Mesozoic oceanic anoxic events took place in poorly supersaturated oceans, when short-lived (< 1 Ma) perturbations of the global carbon cycle would have been most effective in inhibiting biocalcification.

### References

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