

**Limestone weathering in the urban atmospheric
environment, a reactive transport model for unsaturated
porous medium**

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The preservation of the built heritage is a long term challenge with environmental, economic, and cultural issues at stake. Limestone is most widely used in historical buildings and its natural weathering causes a conservation problem. Moreover, the urban environment, where these buildings are (most often) located, is associated to anthropic pollutant emission (SO₂, CO₂, NO_x and particulate matter) that can enhance the initial weathering; by accelerating dissolution (acid deposits) and/or creating of a superficial crust and sub surface precipitates. Water, the main weathering agent, comes into contact with the limestone under the form of rain or gaseous condensation and can participate in the transport of the pollutants further into the porous network. The complex physical and hydrodynamic properties of its porous network play a key-role in the transfer of the dissolved species. In the context of an evolving environment (climate and pollution), the change of frequency (and duration) and/or intensity of rain events or the modification of local climatic conditions (RH or T°) have an impact on the deterioration of this heritage material over the course of centuries.

To assess the impact of atmospheric parameters (rain events frequency and relative humidity and pollution), a geochemical model of limestone alteration is required. The model is based on a description of the mechanisms and associated kinetics in relation to varying environmental parameters provided by atmospheric alteration chamber experiments. Preexisting models developed for a saturated aqueous medium (pure water, soil solution, seawater) cannot easily be adapted to the atmosphere due to unsaturated conditions and to the variability of relative humidity (RH) and of the rainfall patterns.

Our approach, using HYTEC reactive transport code, consists in two premises. The first one is based on the description of pore geometry and the chemical exchange at the pore interface, and concentrates on the full description the system, a macro-pore, in terms of hydrodynamic zones associated with global parameters (porosity, permeability, reactive surface, volume, grain effect...). The second is based on the description of imbibition and drying effects (flow, gas diffusion, advective transport) on the evolution of the solution chemistry as well as the phase transitions (evaporation, salt precipitation). The validation of model will be provided by comparison to thorough observations made on heritage samples altered for decades.