

Geochemistry and material science for cultural heritage preservation: a case study of sulfur isotopes tracing the source of tuffeau limestone weathering

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Safeguarding historical stone buildings requires collaboration of conservators, architects, stone restorers, with a multitude of scientific disciplines, including geology, geomechanics, mineralogy, and geochemistry to obtain a detailed, multi-method diagnosis of stone weathering. Isotope geochemistry can provide answers on the reasons of stone degradation, notably on salt crystallisation, one of the most disastrous deterioration mechanisms [1]. Soluble salts can stem from air, water and soil pollution, but also a large diversity of intrinsic sources from materials like plaster and other mortars.

Many landmark structures in France, including the famous Loire castles, are built from tuffeau, a fine-grained Turonian limestone native to the Loire Valley. Characterized by its high porosity (approximately 45%) and relatively low durability, tuffeau is composed primarily of calcite, along with quartz, opal, micas, and clay minerals [2]. This inherent porosity makes it particularly susceptible to capillary rise and various weathering phenomena, such as granular disintegration, flaking, black crust formation, scaling, and, most notably, spalling [3].

During restoration work, samples were collected from a medieval building in Orléans and the Castles of Chambord and Chaumont-sur-Loire (France) to determine the sources and mechanisms of weathering. These samples were analyzed using energy-dispersive X-ray spectrometry (EDS), backscattered electrons imaging (BSE), and micro-XRF mapping. Sulfur and oxygen isotope analyses were conducted to trace the origin of gypsum formation. At a depth of 1.5 cm from the surface, the stone becomes more porous, with calcite dissolution and re-crystallization driven by capillary water. Near the surface, fine gypsum grains accumulate, forming sometimes a black crust. Sulfur and oxygen isotopes indicate several sulfate sources, including atmospheric pollution and plaster dissolution.

The (re)crystallization processes of calcite and gypsum might constitute an initial trigger of spalling, the main degradation pattern of tuffeau. Its precise mechanisms still need to be elucidated, which is the aim of the ongoing DETRESSE project funded by the French Centre-Val de Loire region.