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Tracing internal sulphate sources (plasters mortars) involved in stone degradation: Environmental isotopes (S. O) applied to French monuments

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Objectives:

Gypsum is one of the most common soluble minerals involved in the decay of stone monuments. Gypsum is particularly concentrated in the black crusts on the stone surface and in an epigenic layer just beneath, which are typical of urban or industrial environments. It is also located in fissures inside the damaged stones. Previous studies using sulphur isotopes demonstrated the important role of atmospheric sulphur in black crust formation (Longinelli & Barteloni 1978, Šrámek 1980, Buzek & Šrámek 1985, Nord 1985, Šrámek 1988, Pye & Schiavon 1989, Rösch & Schwarz 1993, Torfs & Van Grieken 1997, Siedel 2000). An alternative hypothesis concerning the gypsum crystallisations responsible for the degradation of stones (scaling and spalling) consists in assuming an internal source of sulphates: Plasters and mortars containing gypsum and other sulphate species have been frequently used during restorations and stone degradation seems often spatially linked to these materials. In the aim to better constrain the sources of newly formed gypsum on the western facade of the gothic cathedral of Bourges, a stable isotope study has been undertaken. Studies of other French monuments (marble statues of Versailles, Chartres Cathedral, Chenonceau castle, Marseilles Cathedral) using oxygen, sulphur and boron isotopes are underway.

Methods and results:

Black crusts, plasters, mortars and decayed stone samples were analysed for both sulphur and oxygen isotopes. The different types of sulphate containing materials have very clearly defined isotopic signatures. As can be expected for atmospheric sulphates, the black crusts show δ^{34}S values close to 0 $\%_0$ *vs.* CDT and δ^{18}O ranges from 10.7 to 12.4 per mille *vs.* VSMOW. Mortars are strongly depleted in ^{34}S with δ^{34}S values around -20 per mille and enriched in ^{18}O (17.7 to 19 per mille. The isotopic depletion of sulphur can be explained by admixture of crushed brick to these mortars, containing clay minerals and isotopically light sulphur of sedimentray origin. Plasters are strongly enriched in heavy sulphur with δ^{34}S ranging from 15.8 to 20.8 per mille and δ^{18}O values in the same range as the mortars (15.8 to 21.5 per mille. Their isotopic composition is identical to that of Eocene gypsum in the central Paris Basin (Fontes & Thoulemont, 1987). At least since the 19th century, these marine evaporites were used as base for the so called "Paris plaster" frequently employed in restoration. Sulphates from decayed parts of the building stone, a Jurassic limestone, are well constrained by the three potential pollution endmembers: Their isotopic signatures can be explained by a ternary mixing with variable contributions of the atmospheric sulphates, mortars and plasters.

Conclusions: The results suggest that a part of the gypsum involved in the stone degradation process could be provided by gypsum based plasters and mortars. The findings of the isotope study have implications for the restoration and conservation strategy: Whereas external, atmospheric sources cannot be controlled, internal sources of sulphur can be eliminated during restoration or its use for stone restoration works be avoided.

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