Soluble salt sources in medieval porous limestone sculptures: A multi-isotope (N, O, S) approach

Wolfram Kloppmann, Olivier Rolland, Anne-Thérèse Montech, Eric Proust

Soluble salt sources in medieval porous limestone sculptures: A multi-isotope (N, O, S) approach.

W. Kloppmann[a]*, *O. Rolland*[b], *E. Proust*[a], *A.T. Montech*[a]

[a] BRGM, Direction des Laboratoires, Unité Isotopes, BP 6009, F-45060 Orléans cedex 2, France, [b] Specialist in stone restoration, Montlouis-sur-Loire, France, olivierrolland@wanadoo.fr

* Corresponding author; e-mail: w.kloppmann@brgm.fr BRGM

Abstract

The sources and mechanisms of soluble salt uptake by porous limestone and the associated degradation patterns were investigated for the life-sized 15th century "entombment of Christ" sculpture group located in Pont-à-Mousson, France, using a multi-isotope approach on sulfates ($\delta^{34}S$ and $\delta^{18}O$) and nitrates ($\delta^{15}N$ and $\delta^{18}O$). The sculpture group, near the border of the Moselle River, is within the potential reach of capillary rise from the alluvial aquifer. Chemical analyses show a vertical zonation of soluble salts with a predominance of sulphates in the lower parts of the statues where crumbling and blistering prevail, and higher concentrations of nitrates and chloride in the high parts affected by powdering and efflorescence. Isotope fingerprints of sulphates suggest a triple origin: (1) the lower parts are dominated by capillary rise of dissolved sulphate from the Moselle water with characteristic

Keuper evaporite signatures that progressively decreases with height; (2) in the higher parts affected by powdering the impact of atmospheric sulphur becomes detectable; and (3) locally, plaster reparations impact the neighbouring limestone through dissolution and re-precipitation of gypsum. Nitrogen and oxygen isotopes ~~of nitrates~~ suggest an organic origin of nitrates ~~of~~ in all samples. N isotope signatures are compatible with those measured in the alluvial aquifer of the Moselle River further downstream. This indicates contamination by sewage or organic fertilizers. Significant isotopic contrasts are observed between the different degradation features depending on the height and suggest historical changes of nitrate sources.

Keywords: stone degradation, sulphate, nitrate, capillary rise, cultural heritage, isotope fingerprinting, sulphur, oxygen, nitrogen.

1. Historical and environmental context

The "Entombment of the Christ" is a recurrent motive of French statuary of the 15th and 16th century (Forsyth, 1970). The studied group in St. Martin's Church in Pont-à-Mousson, North-eastern France (Figure 1, Figure 1S, Supplementary Information) is supposed to have been ordered for the funerary monument of Baldemar-Johannis of Biebelnheim and executed between 1425 and 1430 (Karsallah, 2009, Fréchet, 1991) supposedly by an east-European artist. The group of sculptures comprises 13 standing or lying life-size statues and 8 smaller statues of angles suspended at the vault. It is likely that the present day emplacement is the historical one even if important modifications in the 19th century are reported (partial replacement of the soldier group, De Sansonetti 1844). The last restoration campaign took place in 1973. This campaign was limited to replacing lost parts and ignored soluble salts as the principal cause of those losses. The gradual evolution of salt degradation can be followed from the very first photographs around 1900. As early in 1844, the text by de Sansonetti (1844) stated that "the group is more damaged by frost than by man" which has to be

interpreted in the light of the fact that before the last quarter of the twentieth century damages due to salts were often attributed to frost or to wind erosion.

The original material of the sculptures is a fine-grained limestone; some recent replacements are made of oolithic limestone (summit of the cross, elbow of the second female saint). Several reparations and replacements made use of gypsum plaster. The monument has alterations of different types (ICOMOS, 2008): disintegration and superficial cracks, powdering in the higher parts, efflorescences (chemical precipitates), and fragmentation (Figure 1).

The church is situated in the direct vicinity (50 m) of the Moselle River around 3 m above mean base level. The statues are in contact, directly or indirectly via a mortar layer, with a soil made of calcareous dressed stone or, in some places, made of a compacted mix of earth and calcareous stone fragments. This soil is visibly porous and hydrophilic but its basic properties are unknown. Spots of humidity on the soil elsewhere in the church indicate capillary rise.

Alluvial aquifers are generally hydraulically connected to the river; it is therefore likely that accompanying groundwater has similar contents of major ions especially during high-flow conditions where river water inflow predominates compared to local recharge. Supplementary input of nitrates is possible via the sewer network and diffuse agricultural pollution but the decomposition of human corpses in tombs can also play a role as nitrogen source (WHO, 1998). Dissolved ions may contribute to the degradation of the “Entombment of the Christ” through capillary rise of groundwater. Air pollution is another source of soluble salts and has been strong in the past as witnessed by thick black crusts on the Southern facade of the church. Air pollution is mainly a source of sulphates, to a much lesser extent of nitrates and chlorides. Air pollution mainly affects the exterior of buildings but also, to a minor but still measurable extent, their interior (e.g. Kramar *et al.*, 2011). Indeed, Pont à Mousson became, from 1856 onward, the most important centre of cast iron tube production in France with up

to five blast furnaces in activity, reduced to two in 2009 and one in 2011. Other factors of local air pollution are heavy car traffic and a nearby thermal power plant (DRIRE, 2004). Gypsum plaster reparations which have been identified in several places (Rolland, 2012) represent a supplementary risk of sulphate contamination (Kloppmann *et al.*, 2011, Vallet *et al.*, 2006), in particular in the context of capillary rise which may lead to dissolution, mobilisation and recrystallization of the calcium sulphates which constitute gypsum plaster.

The present multi-isotope study is part of the pre-restoration assessment currently conducted by O. Rolland on account of the DRAC (Regional Division of Cultural Affairs) Lorraine. The choice of the isotope tracers, employed in the aim of elucidating sources and mechanisms of weathering, was guided by the nature of the observed soluble salts. Preliminary investigations found mainly sulphates and nitrates with some chlorides, so we combined $\delta^{34}S$ and $\delta^{18}O_{(SO4)}$ with $\delta^{15}N$ and $\delta^{18}O_{(NO3)}$ with the aim of constraining the sources of soluble salts inducing different types of alteration. Curiously enough, given the widespread occurrence of both Na- and K-nitrate salts (nitre, nitratine), alums and Ca-, Mg-, Na-sulphates in building stones (mainly gypsum, thenardite, mirabilite, hexahydrite and epsomite, Flatt, 2002), this combination of tools has, to our knowledge, never been applied before. There is a long record of isotope studies using $\delta^{34}S$ signatures of black crusts and other alteration features of building stones and sculptures since the early works in Salt Lake City (Dequasie and Grey, 1970), Venice (Longinelli and Bartelloni, 1978), and Prague (Šrámek, 1980; Buzek and Šrámek, 1985; Buzek et al., 1991; for a more complete bibliography refer to Kloppmann *et al.*, 2011, and Sanjurjo-Sanchez & Alves, 2012). The ambiguity of mono-isotope studies (overlap of signatures of a large diversity of sources) can be overcome by combining several tracers. After rare precursor studies in Venice (Longinelli and Bartelloni, 1978), and Antwerp (Torfs et al., 1997), recent works on stone decay combine oxygen and sulphur isotopes in sulphate to discriminate pollution sources in urban environment (Vallet et al., 2006,

Schweigstillova *et al.*, 2009, Schleicher and Hernandez, 2010, Kloppmann *et al.*, 2011). Less "traditional" isotopes have been recently combined with sulphur and oxygen, like boron (Kloppmann *et al.*, 2011) giving hints to the relative role of air pollution (coal combustion), and sea-salts on monument in a coastal setting. Strontium and sulphur isotopes were analysed together in salt efflorescences degrading the Angkor monuments and indicated bat guano as main source of salts (sulphates, phosphates, carbonates, Hosono et al., 2006). Lead and strontium isotopes were combined (Åberg et al., 1999) to investigate the role of traffic in the degradation of Norwegian rock carvings. Steelman *et al.*, (2002) is a rare example for the use of nitrogen isotopes in stone degradation studies. Using nitrogen combined with carbon isotopes they revealed animal origin of black crusts on cave paintings in Idaho.

We hypothesized use of the constituent isotopes of the observed nitrate and sulphate salts would provide better constraints for disentangling the potential pollution sources impacting the sculpture group. Our sampling strategy focused on the different degradation features, including disintegration, powdering and efflorescences, and on the supposed contamination end members: (1) Black crusts which can be considered as representative of air pollution and integrating the pollution signal over long periods (Camuffo *et al.,* 1983; Ausset *et al.,* 1998, Kloppmann *et al.*, 2011), (2) Moselle water potentially contributing salts from its dissolved load through capillary rises, and (3) gypsum plaster used abundantly for reparations as potential sulphate source.

2. Materials and Methods

2.1. Sampling

Sampling was limited to the surface of the degraded parts of the limestone, by superficial scraping of the disintegrated parts and brushing of the disintegrated powdering parts and of efflorescences (Figure 1). A grab sample of River water was taken on June 17, 2011 on the

right bank of the Moselle 20 cm below the surface close to the bridge in the vicinity of St. Martin's Church. .

2.2. Analytical methods

After crushing of the solid samples, nitrates and sulphates were solubilised by lixiviation with 250 ml of Millipore® highly distilled water over 72 h on an agitation table. Lixiviates are then filtered at 0.45 µm. Chemical composition was then determined by Inductively coupled plasma atomic emission spectroscopy (ICP-AES, Horiba Ultima 2) for major cations and ion chromatography (Cl^-, NO_3^-, SO_4^{2-}, limits of quantification: 0.5 mg/L) or titration (HCO_3^-, limits of quantification limit 5 mg/L) for major anions. All chemical analyses follow international standard procedures (NF EN ISO/CEI 17025 : 2005).

The isotopic compositions are expressed in the usual delta notation as a per mil (‰) deviation of the heavy-to-light isotope abundance ratio ($^{34}S/^{32}S$, $^{18}O/^{16}O$, and $^{15}N/^{14}N$) in the sample from an international standard, sulphur isotopes as $\delta^{34}S$ with respect to the CDT standard, oxygen isotopes as $\delta^{18}O$ with respect to the SMOW, nitrogen isotopes with respect to the AIR standard.

Sulphur and oxygen isotopes of sulphates; For sulphur and oxygen isotope ratio determination lixiviate was filtered at 0.22 µm and acidified before adding $BaCl_2$. The precipitate of $BaSO_4$ is then recovered on a 0.45 µm filter, dried at 60°C for at least one night.

Sulphur: 300 µg of $BaSO_4$ is mixed with V_2O_5 in a tin capsule. The capsule is then introduced in the elemental analyser (Flash EA) and the $BaSO_4$ reduced to SO_2 at 900°C. The SO_2 gas, purified by gas chromatography is then analysed on a Thermo Scientific DELTAplus XP continuous flow mass spectrometer (CF-IRMS).

Oxygen: A 200 µg aliquot of the previously obtained $BaSO_4$ in a silver capsule are injected into a graphite pyrolysis oven at 1450°C. The oxygen reacts with the graphite and forms CO

gas which is, after purification by gas chromatography, analysed by CF-IRMS (DELTAplus XP).

The standard analytical error between duplicate analyses is lower than ±0.3 ‰ for both sulphur and oxygen.

Nitrogen and oxygen isotopes of nitrates:. The lixiviate was purified by several subsequent steps of ion exchange and precipitation of chlorides, carbonates, sulphates and phosphates by adding AgCl and $BaCl_2$ (modified after Chang *et al.*, 1999, Silva *et al.*, 2000). Solid nitrates are then obtained as $AgNO_3$ by lyophilisation.

The solid $AgNO_3$ in a silver capsule is then injected in a graphite pyrolysis oven at 1450°C. The gases obtained (CO and N_2) are separated by gas chromatography and analysed successively by CF-IRMS (Thermo Scientific DELTA V).

All samples were measured as duplicates with a standard analytical error of lower than 0.5 ‰.

3. Results and Discussion

3.1. Chemistry of soluble salts

Major ions (Table 2, providing solid/solid concentrations of the leachable fraction of the total rock), with exception of bivalent cations (Ca, Mg) and bicarbonates, which are related to the mineralogical nature of the limestone used for the group of sculptures, discriminate several types of alteration. Disintegrated stones without powdering (PA1, 3, 5) from the base of the statues are rich in sulphates (concentrations higher than 40 mg/g) but poor in Na, K, NO_3, and Cl. Powdering stones from the upper parts of the statues are rather low in sulphates, with exception of sample PA7, but contain significant amounts of K, Na, NO_3^-, and Cl which are more or less correlated (Figure 2). Efflorescences are mainly KNO_3 with negligible concentrations of other elements so that they plot outside the tendencies observed for the altered stone samples. Sample EF1 is somewhat richer compared to sample EF2 in sulphates

and chlorides (25 mg/g and 4 mg/g respectively, Figure 2). Both the black crust CN1 and the plaster of Paris PL1 contained more than 50% calcium sulphate;

The water sample from the Moselle river, taken in November 2010 (Table 2) is quite rich in chloride (400 mg/L) and sulphates (113 mg/L) compared to the typical calcium-bicarbonate waters from catchments mainly built of carbonate rocks (median values for sulphate concentrations on French carbonate rock catchments range from 10 to 48 mg/L, whereas Cl concentrations corrected for precipitations are nil (cf. Meybeck, 1986). This is due to the presence of Triassic evaporites upstream of Pont-à-Mousson containing gypsum and halite (Brenot *et al.*, 2010). Nitrate and potassium contents were, on the contrary, quite low at the moment of sampling (3.4 and 1 mg/L respectively). The river water could therefore represent an important source of sulphates and chlorides, via groundwater and capillary rise. It has to be stated that nitrate concentrations in the river, mainly related to agricultural activities, are bound to vary strongly over the year (a range of 0.7 to 15 mg/L has been measured at Pont St. Vincent from March 2002 to September 2003, Brenot *et al.*, 2007). Supplementary input is possible directly into the alluvial aquifer (sewage, agricultural pollution) leading to higher concentrations. Up to 104 mg/L of nitrate were measured in the alluvial groundwater body accompanying the Moselle at Yutz (Widory and Nguyen-Thé, 2006). Thus, the measured Moselle water is very rich in sulphate and chloride, less in nitrates but the concentrations could be highly variable over the year.

Spatial patterns of soluble salt concentrations as well as the identified alteration types vary in function of height (Figure 1). Close to the base of the statues, stones are disintegrated but not powdering; they are rich in sulphates and calcium, pointing to gypsum as main mineral, but low in nitrates and chlorides. In the higher parts, the sculptures are disintegrated and powdering, rich in chlorides, nitrates, sodium, and potassium. Chlorides represent a good

tracer of Moselle water and of the accompanying alluvial groundwater as it can be expected that atmospheric inputs are not a significant source of chloride in a continental context. Regional rainwater has in fact chloride concentrations < 3 mg/L in the studied zone (Blum *et al.*, 2002). The influence of river water/groundwater is perceptible for all sampling points but concentrations of chlorides and nitrates are higher in the upper parts of the statues. Less soluble salts (calcium sulphates) precipitate first during capillary rise whereas more soluble salts (nitrates and chlorides) stay mobile and crystallise later, leading to the formation of efflorescence and powdering. Such a zonation has been reported for stone monuments concerned by capillary rise (Arnold, 2004)

3.2. Sulphur and oxygen isotopes of sulphates

Potential sources of sulphates including air pollution, Moselle water, and groundwater, as well as gypsum plasters used for reparations may be distinguished isotopically (Table 2). As the origin and geological age of the limestone material used for the sculptures is not known, it is difficult to estimate *a priori* the potential isotopic signatures of carbonate associated sulfates (CAS) and sulphides that may give rise to sulphate formation. Measurements were impossible as this would have implied drilling into non-altered material. However, no macroscopic observation of sulphide oxidation was made (e.g. FeIII-hydroxides) and CAS concentrations in chemically precipitated micritic limestones, as probably used for the sculptures, are generally low (few tens of ppm, Kampschulte & Strauss, 2004 and references therein) so that their impact can be considered as minor.

The sulphates which constituted the major part of the black crust CN1 (37% of sulphate or 67% of gypsum), sampled on the external wall of the southern facade are considered as representative of local air pollution as the sampling location was potentially out of reach of capillary rise and no gypsum plaster was used in the surroundings. Their isotopic composition with a $\delta^{34}S$ of 0.8 ‰ *vs.* CDT and a $\delta^{18}O$ of 8.5 ‰ *vs.* SMOW ~~falling~~ falls indeed in the

relatively narrow range typical for air pollution-derived black crusts measured on other French monuments out of the coastal zone potentially influenced by sea salts (Bourges and Chartres cathedrals, Chenonceau and Versailles castles, Kloppmann *et al.*, 2011) (Figure 3).

Moselle water (E1) falls, with a $\delta^{34}S$ of 13.6 ‰ and a $\delta^{18}O$ of 12.3 ‰, in the field of Upper Triassic evaporites (Pearson *et al.*, 1991). This composition is similar to the range of values measured for Moselle water 45 to 50 km upstream from Pont-à-Mousson (Pont St. Vincent, Messein, Brenot *et al.*, 2007). Moselle water contains significant sulphate concentrations (113 mg/L for our sample) due to the fact that Upper Triassic (Keuper) evaporites outcrop in some upstream parts of the Moselle catchment. They are dissolved by runoff and within the groundwater bodies which in turn feed tributaries and the Moselle River.

The gypsum plaster sample (PL1) is the sample which is most enriched in ^{34}S and ^{18}O with a $\delta^{34}S$ of 17.2 ‰ and a $\delta^{18}O$ of 22.6 ‰. It falls in the range of $\delta^{34}S$ values measured for the Tertiary (Lutetian and Ludian) gypsum of the Paris basin (Fontes and Letolle, 1976, Fontes and Nielsen, 1966; Fontes and Thoulemont, 1987) but shows a slightly higher $\delta^{18}O$. Most gypsum plasters, commonly referred to as "Paris plaster" show in fact the isotope signature of Tertiary gypsum from the town of Paris (Kloppmann *et al.*, 2011). For CAS of Jurassic age, $\delta^{34}S$ values of 14.2 to 18 ‰ could be expected (Kampschulte & Strauss, 2004) in the same range as observed for the plaster endmember.

All stone samples fall clearly off a mixing line for $\delta^{18}O$ and $\delta^{34}S$ of the atmospheric and the plaster endmember. We observe two mixing trends requiring a third endmember which is compatible with mean Moselle water at Messein and Pont-St-Vincent ($\delta^{34}S$ = 11.1 ‰ and $\delta^{18}O$ =13 ‰). Nevertheless, the approximate co-linearity of the three end members makes it difficult to quantify their respective contributions (Figure 3).The disintegrated stone samples close to the base of the statues (PA1, 3, 5) fall in the field of Keuper gypsum, confirming the influence of groundwater through capillary rise (Figure 3). Samples of powdering stone taken

on the upper parts of the statues (PA2, 4, 6, 8) show a good correlation (r^2=0.93, n=4, p-value=0.036 , statistics performed with XLSTAT software package) in the $\delta^{34}S$ *vs.* $\delta^{18}O$ diagram (Figure 3) suggesting mixing between two end members, "Moselle water" and "air pollution" represented respectively by samples E1 and CN1. Sulphates in sample PA4 appear to be nearly exclusively dominated by air pollution. Indoor sulfation of carbonates can be favoured by particulate matter (Grau-Bové and Strlic, 2013), itself containing oxidised sulphur compounds (e.g. for diesel particulate matter) or acting as catalyser of SO_2 fixation, and gypsum formation (Rogriguez-Navarro and Sebastian, 1996, Cultrone et al., 2008). It needs to be stated, though, that this group of powdering stone samples is rather poor in sulphates (0.4 to 16 mg/g). The powdering sample PA7 presents a singularity as it is shifted towards the signature of the plaster sample PL1 and is rich in sulphates (>45 mg/L). It was taken from the back of John (Mary and John are carved in a single bloc; Figure 1 and Supplemental Information Photograph) in the vicinity of the plaster reparation which provided PL1 and may contain plaster-derived sulphates, dissolved by capillary rising groundwater, and then transported by diffusion in the interstitial porosity of the fine-grained limestone.

Sample PA9 taken from the external wall of the St. Martin church at the base of the northern facade of the north tower is, isotopically speaking, very close to the black crust of the southern facade and shows a predominance of atmospheric sulphates, in spite of its proximity to the soil and the obvious signs of capillary rise at the sampling spot (Figure 3). It seems that the strong environmental pressure from local air pollution (smelters) dominates sulphate formation at the exterior of the building.

Salt efflorescences at the internal wall of the chapel hosting the sculpture group (sample EF1) contained enough sulphates (26 mg/g) to allow for isotope analysis of sulphates. Their signature is very close to the black crust, suggesting atmospheric origin for the sulphate

contents of the efflorescences which are weak (5 to 26 mg/g) compared to nitrate (472 to 482 mg/g).

It is likely that isotope signatures of neoformed sulphates in the stone samples reflect closely those of dissolved sulphate in the pore water as isotope fractionation accompanying precipitation of solid sulphates is low (< +2 ‰ enrichment in ^{34}S of the solid phase in most studies, Raab & Spiro, 1999 and references therein, around +3.5 ‰ enrichment in ^{18}O, Claypool *et al*., 1980), lower than the potential variability of the end members (e.g. Moselle water: range of 4.2 ‰ for $\delta^{18}O$ and of 3.3 ‰ for $\delta^{34}S$, Brenot *et al.* 2006). Oxygen isotope composition of sulphate can be expected to be stable over time as water-sulphate equilibrium exchange at ambient temperatures will take $>10^7$ years (Chiba and Sakai, 1985).

Judging from the isotopic composition of sulphates of the "Entombment of the Christ" we can derive the following conclusions on their origin: Sulphates contained in the altered parts at the base of the statues show the influence of Moselle water or of river-derived groundwater in the alluvial aquifer, dominated by the dissolution of Keuper gypsum in the upstream parts of the catchment. The influence of river water can be explained by capillary rise of groundwater, in particular during high-water conditions that lead to rising groundwater levels. During the winter months the total sulphate concentrations will be lowered by dilution and the relative contribution of agricultural input increased (Brenot *et al.,* 2007). The powdering alteration in the higher parts of the statues falls between Moselle water and the "air pollution" endmember represented by the black crust CN1. The highest sample (PA4, female saint above the right breast) reveals to be closest to the atmospheric endmember. The influence of capillary rise is visible, for sulphate salts, up to the mid-height of the statues due to preferential precipitation of gypsum in the lower parts and overrides to varying extents the atmospheric signatures. Air pollution seems to have impacted the statues in spite of their sheltered situation in the interior of the church which can be explained by the strong local

environmental pressure of metal industry and car exhausts. Indeed, the outdoor samples fall in the range of $\delta^{34}S$ values reported for "pure" car traffic sulphur by Torfs *et al.*, (1997) between -2.1 ‰ and +2.8 ‰. Gypsum plaster reparations constitute a significant source of calcium sulphate with a relatively limited spatial range of influence via dissolution, transport by diffusion or capillarity and reprecipitation at the stone surface.

3.3. Nitrogen and oxygen isotopes in nitrates

As Moselle water (E1) could not be analysed for nitrogen and oxygen isotopes in nitrates due to the very low concentrations (2.8 mg/L), values for Moselle catchment are provided by the report of Widory and Nguyen-Thé (2006) who determined $\delta^{15}N$ of the alluvial groundwater of the Moselle at Yutz, situated around 60 km further downstream. The reported values are highly variable, between 4.3 ‰ and 22 ‰ (n=4), samples with high NO_3^- showing $\delta^{15}N$ in the lower range (4.3 to 6.7 ‰). The variability of signatures is explained by the variability of nitrate sources, mainly mineral fertilisers and animal or human faeces (via sewage and organic fertilisers).

The analysed black crust CN1 was too low in nitrate to be analysed isotopically so that we lack the pure "air pollution" endmember for nitrate. In fact, "air pollution nitrate", if present in the chapel, would not be expected to be concentrated in black crusts. In fact, black crust formation is strongly linked to sulphur oxides and distribution of airborne nitrogen deposits would be probably very different from those of sulphates. $\delta^{15}N$ values of NOx compounds, derived from coal combustion show isotope rations similar to modern urban atmospheric particles, ranging from 5 to 13 ‰ (Heaton, 1987, Kiga *et al.*, 2000, Widory, 2007). References on $\delta^{18}O$ of particle-bound nitrates are rather rare (Elliot *et al.*, 2009) and much higher than those encountered in our study. Gaseous $\delta^{18}O_{HNO3}$ and particle-bound $\delta^{18}O_{NO3}$ fall between 45 and 94 ‰ due to the role of ozone, strongly enriched in ^{18}O, in the oxidation of nitrogen (Elliot *et al.*, 2009). To our knowledge, no reference exists on nitrogen and oxygen

isotopes in altered calcareous building stones and the mechanisms of NO_x oxidation, and interactions with ozone, SO_x, and limestone are complex (Massey, 1999).

The isotope signatures of nitrates (Table 2) differentiate two groups of disintegrated stone samples at the base of the statues (PA1, 3, 5) fall in a restricted range of $\delta^{15}N$ values from 5.7 to 6.3 ‰. The signatures of the most nitrate-rich alluvial groundwaters at Yutz (Widory and Nguyen-Thé, 2006) are compatible with those measured at the lower part of the statues. The efflorescences EF1 and EF2 as well as sample PA9, sampled at the external wall of the church within the potential zone of capillary rise, show a $\delta^{15}N$ somewhat enriched in ^{15}N ranging from 7.3 to 9.5 ‰ (Figure 4).The disintegrated powdering stone samples from the upper part of the statues (PA2, 4, 8) form a well-defined group with a $\delta^{15}N$ between 11.6 and 12.3 ‰ and $\delta^{18}O$ between 5.4 and 8.9 ‰. Since measured $\delta^{18}O_{(NO3)}$ values are incompatible with an atmospheric origin of nitrates as they are much to low compared with the range of air pollution derived NO_3 (Elliot *et al.*, 2009) this indicates that the predominant agents of air pollution in the sector were SO_x which is compatible with contamination from smelters.

Nitrates from all altered stone samples as well as the K-nitrate efflorescences fall in the field of animal waste (Figure 4, Kendall *et al.*, 2007) and are comparable to the signatures measured in the alluvial aquifer of the Moselle river further downstream. The nitrate contents of the altered stones seems therefore to stem from human faeces or animal waste, either via local sewage input or diffuse agricultural pollution of the riverine water by manure spreading in the upstream parts of the catchment. The fact that the measured Moselle water is richer in Na than in K is not incompatible with the preferential formation of nitre (KNO_3) in the efflorescences as solubility of nitre is by a factor of 2 (at 20°C) to 4 (at 0°C) lower than that of nitratine ($NaNO_3$) so that nitre will form first (Laue, 2005).

We were not able to analyse the gypsum plaster sample given the low nitrate contents. Gypsum plaster could be *a priori* an important source of sulphates due to its chemical

composition ($CaSO_4 \cdot 2H_2O$) but is unlikely to deliver much nitrate given the low measured concentrations (6.2 mg/g in PL1). Even though, as nitrates are easily leachable and very mobile, the initial nitrate contents of PL1 could have been diminished by dissolution and diffusion. Point PA9 (altered stone at the exterior wall of the North tower) shows capillary rise as main source of nitrates whereas its sulphate signatures indicate the impact of air pollution.

On the whole, it is therefore likely that all nitrates are derived from capillary rise contrarily to sulphates where three sources have been identified (capillary rise, air pollution and gypsum plaster leaching).

The observed range in isotopic values of nitrates in the alluvial aquifer are too low to associate a distinct origin of nitrate salts with the different types of degradation (efflorescences, powdering, disintegration) or to the location of the samples (upper and lower parts of the statues). The reasons for the clumping of data for specific materials in Figure 4 is not totally clear. One hypothesis might be a succession of contamination with slightly different sources (eg. contribution of mineral fertilisers in the alluvial aquifer).

4. Conclusions and recommendations

Chemical major ion analyses (Cl, NO_3, SO_4, Na, K, Mg) of the soluble fraction in the decayed parts of limestone sculptures highlight a clear differentiation between the disintegrated but not powdering stone at the base of the statues and the upper parts where stones show powdering. Lower parts, mainly impacted by disintegration, are rich in gypsum but contain low nitrates and chlorides. Powdering stones are rich in chlorides, nitrates, sodium and potassium. Since Moselle water has high sulphate and chloride, and variable nitrate concentrations this trend in major ion concentrations indicates that capillary rise via the alluvial aquifer can contribute to the salt contents even in the higher parts of the statues. Sulphates precipitate in the lower parts whereas more soluble salts rise higher and contribute to the powdering alteration.

Neoformation of sulphates in the "Entombment of the Christ" group has a triple origin: (1) Moselle water contained in the alluvial aquifer in the disintegrated and powdering stones due to capillary rise, (2) air pollution which is superposed on the other sources and becomes progressively predominant in the higher parts less rich in sulphate, (3) dissolution of gypsum plaster used for restorations.

Nitrates are likely to be brought into the system by groundwater contaminated by sewage or diffuse agricultural pollution (isotope signature of "organic waste" type). Sepulchres with decomposed human material might also explain part of the observed saltpetre. The origin of the slight but significant differences between the isotope signatures of the different types of alteration is not fully elucidated. They could be historical resulting from successive pollution phases. Atmospheric input is not significant for the nitrate balance in the decayed parts of the sculptures. Isotope signatures of nitrates are less conclusive than S and O isotopes in our study as there is one predominating (organic) nitrate source. In another, multi-source context they may be more discriminating.

From a practical point of view, the restoration strategy has to include hydraulic isolation of the statues from the soil. Plaster reparations should be eliminated as they contribute locally to the neoformation of sulphates. The impact of air pollution is detectable but appears less important than the other soluble salt sources. As the industrial activity in the area has significantly decreased, this contamination pathway may be considered as historical.

Acknowledgements

This study was supported by the DRAC Lorraine and co-financed by the Research Division of BRGM. We wish to warmly thank Veronique Verges-Belmin and Lise Leroux from LRMH (Laboratoire de Recherche des Monuments Historiques, Champs sur Marne, France) for fruitful discussions on the manuscript.

5. Bibliography

Åberg G, Stray H, Dahlin E. Impact of Pollution at a Stone Age Rock Art Site in Oslo, Norway, Studied using Lead and Strontium Isotopes. Journal of Archaeological Science 1999; 26: 1483-1488.

Arnold A. Evolution des sels solubles dans l'altération et la conservation des monuments. Enduits dégradés par les sels : pathologies et traitements. ICOMOS-France, report Dossier Technique n°6-2004, 2004.

Ausset P, Bannery F, Del Monte M, Lefevre RA. Recording of pre-industrial atmospheric environment by ancient crusts on stone monuments. Atmospheric Environment 1998; 32: 2859-2863.

Blum A, Chery L, Babrier J, Baudry D, Petelet-Giraud E, Ruppert N, et al. Contribution à la caractérisation des états de référence géochimique des eaux souterraines. Outils et méthodologie. Rapport final, report BRGM/RP-51549-FR, 2002.

Brenot A, Carignan J, France-Lanord C, Benoit M. Geological and land use control on delta S-34 and delta O-18 of river dissolved sulfate: The Moselle river basin, France. Chemical Geology 2007; 244: 25-41.

Buzek F, Cerny J, Sramek J. Sulphur isotope studies of atmospheric S and the corrosion of monuments in Prague, Czechoslovakia. In: Krouse HR, Grinenko VA, editors. Stable isotopes, natural and anthropogenic sulphur in the environment. Wiley and Sons, Chichester, 1991, pp. 399-405.

Buzek F, Šrámek J. Sulphur isotopes in the study of stone monument conservation. Studies in Conservation. Studies in Conservation 1985; 30: 171-176.

Camuffo D, Delmonte M, Sabbioni C. Origin and growth mechanisms of the sulfated crusts on urban limestone. Water Air and Soil Pollution 1983; 19: 351-359.

Chang CCY, Langston J, Riggs M, Campbell DH, Silva SR, Kendall C. A method for nitrate collection for δ15N and δ18O analysis for water with low nitrate concentrations. Canadian Journal of Fisheries and Aquatic Sciences 1999; 56: 1856-1864.

Chiba H, Sakai H. Oxygen isotope exchange-rate between dissolved sulfate and water at hydrothermal temperatures. Geochimica Et Cosmochimica Acta 1985; 49: 993-1000.

Cultrone G, Arizzi A, Sebastian E, Rodriguez-Navarro C. Sulfation of calcitic and dolomitic lime mortars in the presence of diesel particulate matter. Environmental Geology 2008; 56: 741-752

de Sansonetti V. Description de l'ancienne église des Antonistes maintenant paroisse Saint-Martin de Pont-à-Mousson. Nancy: Grimblot, Raybois et Cie, Imprimeurs-Libraires, 1844.

Dequasie HL, Grey DC. Stable isotopes applied to pollution studies. American Laboratory 1970; 2: 19–27.

DRIRE. Environnement Industriel en Lorraine - Bilan 2004 - Perspectives 2005. La pollution de l'air. DRIRE, report, 2004.

Elliott EM, Kendall C, Boyer EW, Burns DA, Lear GG, Golden HE, et al. Dual nitrate isotopes in dry deposition: Utility for partitioning NOx source contributions to landscape nitrogen deposition. Journal of Geophysical Research-Biogeosciences 2009; 114.

Flatt RJ. Salt damage in porous materials: how high supersaturations are generated. Journal of Crystal Growth 2002; 242: 435-454.

Fontes JC, Letolle R. O-18 and S-34 in Upper Bartonian gypsum deposits of Paris basin. Chemical Geology 1976; 18: 285-295

Fontes JC, Nielsen H. Isotopes de l'oxygène et du soufre dans le gypse parisien. C.R. Acad. Sc. Paris Serie D 1966; 262: 2685-2687.

Fontes J-C, Toulemont M. Facies, pétrologie et teneurs en isotopes lourds 18O, 13C, 34S des niveaux évaporitiques lutétiens supérieurs du bassin de Paris : Interprétation paléohydrologique. Bull. Centres Rech. Explor.-Prod. Elf-Aquitaine 1987; 11: 39-64.

Forsyth WJ. The entombment of Christ. French sculptures of the fifteenth and sixteenth centuries. Cambridge (Massachussetts): Harvard University Press, 1970.

Fréchet G. La Mise au tombeau de l'église Saint-Martin de Pont-à-Mousson (ancienne commanderie des Antonins). Bulletin de la Société de l'Histoire de l'Art français 1991; 1991: 9-20.

Grau-Bove J, Strlic M. Fine particulate matter in indoor cultural heritage: a literature review. Heritage Science 2013; 1: 8.

Heaton THE. 15N/14N ratios of NOx from vehicle engines andcoal-fired power stations. Tellus Series B-Chemical and Physical Meteorology 1990; 42: 304- 307.

Holser WT, Kaplan IR, Sakai H, Zak I. Isotope geochemistry of oxygen in the sedimentary sulfate cycle. Chemical Geology 1979; 25: 1-17.

Hosono T, Uchida E, Suda C, Ueno A, Nakagawa T. Salt weathering of sandstone at the Angkor monuments, Cambodia: identification of the origins of salts using sulfur and strontium isotopes. Journal of Archaeological Science 2006; 33: 1541-1551.

ICOMOS-ISCS Illustrated glossary on stone deterioration patterns = Glossaire illustré sur les formes d'altération de la pierre. English-French version - Version Anglais-Français. Verges-Belmin V. ed. Paris: ICOMOS-ISCS, 2008. 78 p. (Monuments and Sites; XV). ISBN: 978-2-918086-00-0.

Kampschulte A, Strauss H. The sulfur isotopic evolution of Phanerozoic seawater based on the analysis of structurally substituted sulfate in carbonates. Chemical Geology 2004; 204: 255-286.

Karsallah E. Les Mises au tombeau monumentales du Christ en France (XVe-XVIe siècles): enjeux iconographique, funéraire et dévotionnel. Thèse de doctorat. Université de Paris IV, 2009, pp. 362.

Kendall C, Elliott EM, Wankel SD. Tracing Anthropogenic Inputs of Nitrogen to Ecosystems. In: Lajtha K, Michener RH, editors. Stable Isotopes in Ecology and Environmental Science 2nd ed. Blackwell Scientific Publications, 2007.

Kloppmann W, Bromblet P, Vallet JM, Verges-Belmin V, Rolland O, Guerrot C, et al. Building materials as intrinsic sources of sulphate: A hidden face of salt weathering of historical monuments investigated through multi-isotope tracing (B, O, S). Science of the Total Environment 2011; 409: 1658-1669.

Kramar S, Mirtic B, Knoeller K, Rogan-Smuc N. Weathering of the black limestone of historical monuments (Ljubljana, Slovenia): Oxygen and sulfur isotope composition of sulfate salts. Applied Geochemistry 2011; 26: 1632-1638.

Laue S. Salt Weathering of Porous Structures Related to Climate Changes. Restoration of Buildings and Monuments/Bauinstandsetzen und Baudenkmalpflege 2005; 11: 381-390.

Longinelli A, Bartelloni M. Atmospheric pollution in Venice, Italy, as indicated by isotope analyses. Water Air and Soil Pollution 1978; 10: 335-341.

Massey SW. The effects of ozone and NOx on the deterioration of calcareous stone. Science of the Total Environment 1999; 227: 109-121.

Meybeck M. (1986) Composition chimique des ruisseaux non pollués de France. Sci. Geol. Bull. 39, 3-77.

Nguyen-Thé D, Widory D. Etude isotopique de l'origine des nitrates dans l'aquifère calcaire situé entre l'Aire et la Cousances (Meuse). BRGM, report BRGM/RP-54410-FR, 2006, pp. 38.

Pearson FJ, Balderer J, W., Loosli HH, Lehmann BE, Matter A, Peters T, et al. Applied isotope hydrology - A case study in Northern Switzerland edited by. Studies in Environmental Sciences. Vol. 43. Elsevier Science Publishers B.V., Amsterdam-London-New York-Tokyo, 1991, pp. 460.

Raab M, Spiro B. Sulfur isotopic variations during seawater evaporation with fractional crystallization. Chemical Geology 1991; 86: 323-333.

RodriguezNavarro C, Sebastian E. Role of particulate matter from vehicle exhaust on porous building stones (limestone) sulfation. Science of the Total Environment 1996; 187: 79-91.

Sanjurjo-Sanchez J, Alves C. Decay effects of pollutants on stony materials in the built environment. Environmental Chemistry Letters 2012; 10: 131-143.

Schleicher N, Hernandez CR. Source identification of sulphate forming salts on sandstones from monuments in Salamanca, Spain-a stable isotope approach. Environmental Science and Pollution Research 2010; 17: 770-778.

Schweigstillova J, Prikryl R, Novotna M. Isotopic composition of salt efflorescence from the sandstone castellated rocks of the Bohemian Cretaceous Basin (Czech Republic). Environmental Geology 2009; 58: 217-225.

Silva SR, Kendall C, Wilkinson DH, Ziegler AC, Chang CCY, Avanzino RJ. A new method for collection of nitrate from fresh water and the analysis of nitrogen and oxygen isotope ratios. Journal of Hydrology 2000; 228: 22-36.

Šrámek J. Determination of the source of surface deterioration of surface deterioration of tombstones at the old Jewish cemetery in Prague. Studies in Conservation 1980; 25: 47-52.

Steelman K, Rowe MW, Boutton TW, Southon JR, Merrel CL, Hill RD. Stable Isotope and Radiocarbon Analyses of a Black Deposit associated with Pictographs at Little Lost River Cave, Idaho. J. Archaeological Sci. 2002; 19: 1189-1198.

Torfs KM, Van Grieken RE, Buzek F. Use of Stable Isotope Measurements To Evaluate the Origin of Sulfur in Gypsum Layers on Limestone Buildings. Environmental Science & Technology 1997; 31: 2650-2655.

Vallet JM, Gosselin C, Bromblet P, Rolland O, Verges-Belmin V, Kloppmann W. Origin of salts in stone monument degradation using sulphur and oxygen isotopes: First results of the Bourges cathedral (France). Journal of Geochemical Exploration 2006; 88: 358-362.

Verges-Belmin V. Deterioration of Stone in Monuments. In: Schrefler B, Delage P, editors. Environmental Geomechanics. John Wiley & Sons, 2010, pp. 201-245.

WHO. The impact of cemeteries on the environment and public health. WHO report EUR/ICP/EHNA 01 04 01(A), 1998.

Widory D. Nitrogen isotopes: Tracers of origin and processes affecting PM10 in the atmosphere of Paris. Atmospheric Environment 2007; 41: 2382-2390.

Widory D, Nguyen-Thé D. Etude isotopique de l'origine des nitrates dans la nappe alluviale de la Moselle dans le secteur de Yutz (Moselle). BRGM, report BRGM/RP-54409-FR, 2006, pp. 34.

Figure captions

Figure 1: Mapping of alteration types and superficial deposits (modified after Rolland, 2012). The brown patches are places where the surface of the sculpture is covered with a brownish natural patina. Examples of the two main degradation features are provided with powdering (above) and disintegration (below). Arrows indicate sampling points for isotope analyses (rear= rear surface of the statue)

Figure 2: Chemical contents of solid samples (altered stones, efflorescences and plaster) in the Saint Martin church of Pont-à-Mousson.

Figure 3: Isotopes signatures ($\delta^{34}S$ vs. $\delta^{18}O$) of black crusts, altered stones, efflorescences and plaster in the Saint Martin church of Pont-à-Mousson. For comparison: gypsum crusts in Antwerpen (Torfs et al., 1997), Venice (Longinelli et Bartelloni, 1978) and different French inland monuments (Kloppmann et al., 2011), Keuper aquifer groundwaters (Pearson et al., 1991), Mosel river water at Pont St. Vincent and Messein 45-50 km upstream of Pont-à-Mousson (Brenot et al., 2007) and atmospheric oxygen.

Figure 4: Isotopes signatures ($\delta^{15}N$ vs. $\delta^{18}O$) of black crusts, altered stones, efflorescences and plaster in the Saint Martin church of Pont-à-Mousson. Fields of $\delta^{18}O$ and $\delta^{15}N$ of nitrates originating form atmospheric sources, soils, mineral and organic fertilisers and sewage (after Kendall et al., 2007)

Supplementary Information Figure 1S: General view of the « Entobment of the Christ » group in the Saint Martin church of Pont-à-Mousson (photo : O. Rolland); inserted map of France with situation of Pont-à-Mousson

Table captions

Table 1: Samples of pollution sources and altered stones

Table 2: Major ion and isotopic analyses on stone and river samples with standard analytical errors

Tables

Click here to download Table: Kloppmannet_al_STOTEN-D-12-03739R2_tables.doc

Table 1: Samples of pollution sources and altered stones

Sample	Description	Emplacement
CN1	Black crust	Exterior of the chapel, southern facade, eastern pilaster, base of the solid arched bay
E1	Moselle water	Moselle river, right shore near the bridge, 20 cm below surface
EF1	Efflorescence	Eastern wall behind the purse of Joseph of Arimathea
EF2	Efflorescence	Interior of the right sleeve of Joseph of Arimathea
PA1	Disintegrated stone without powdering	Below the folds between the feet of Joseph of Arimathea
PA2	Powdering disintegrated stone	Below the right breast of the holy woman rising her right hand
PA3	Disintegrated stone without powdering	Under the base of the tombstone, southern surface, eastern edge
PA4	Powdering disintegrated stone	Below the right breast of the holy woman rising her right hand
PA5	Disintegrated stone without powdering	Under the lower edge of the gown of Nicodemus, fold nearest to the eastern leg of the funerary table
PA6	Powdering disintegrated stone	Right lower part of the back of Mary
PA7	Powdering disintegrated stone	Back of Saint John
PA8	Powdering disintegrated stone	Veil of Mary below the right breast
PA9	Disintegrated stone without powdering	North tower, northern facade, near the basis.
PL1	Gypsum Plaster	Back of Saint John

Table 2 : Major ion and isotopic analyses on stone and river samples with standard analytical errors

Sample	Ca	Mg	Na	K	HCO_3	Cl	SO_4	NO_3	$\delta^{34}S$	$\delta^{18}O$ (SO_4)	$\delta^{15}N$	$\delta^{18}O$ (NO_3)
	mg/g total	mg/g total	mg/g total	mg/g total	mg/g total	mg/g total	mg/g total	mg/g total	‰ vs. CDT	‰ vs. SMOW	‰ vs. AIR	‰ vs. SMOW
	± 5%	± 5%	± 5%	± 5%	± 5%	± 5%	± 5%	± 5%	± 0.3 ‰	± 0.3 ‰	± 0.5 ‰	± 0.5 ‰
CN1	156,5	0,2	0,6	0,5	3,8	0,8	371,1	1,6	0,8	8,5	nd	nd
EF1	15,4	0,2	0,8	263,5	3,7	4,1	25,6	472,5	0,4	8,9	7,3	8,7
EF2	6,9	0,6	0,6	273,6	18,1	1,3	5,0	482,1	nd	nd	9,5	3,8
PA1	16,5	0,2	0,1	0,5	0,6	0,3	> 39*	3,5	11,2	14,8	5,7	9,9
PA2	5,8	0,1	3,2	2,2	1,1	2,9	11,5	10,4	7,8	11,4	12,3	8,9
PA3	28,5	0,5	0,2	0,3	1,7	0,2	>70*	2,7	12,8	13,9	5,9	11,3
PA4	4,2	0,1	3,8	2,4	2,6	3,0	6,6	12,2	4,1	8,4	11,8	8,2
PA5	20,3	0,3	0,4	0,6	0,6	0,2	> 50*	5,1	13,7	16,7	6,3	12,8
PA6	1,1	0,1	2,5	1,4	1,2	2,1	0,4	8,2	6,6	10,6	nd	nd
PA7	18,5	0,0	2,9	3,1	0,4	2,4	> 45*	11,8	16,2	19,1	8,4	5,0
PA8	7,2	0,1	3,7	6,6	1,3	2,9	16,4	19,2	10,7	12,3	11,6	5,4
PA9	3,6	0,1	0,5	0,5	0,9	0,8	6,7	3,9	2,6	9,2	9,1	3,7
PL1	187,1	0,2	1,6	1,2	2,7	1,7	469,4	6,2	17,2	22,6	nd	nd
E1	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L				
	152	14,4	131	5,9	133	400	113	2,8	13,6	12,3	nd	nd

* lixiviate close to saturation with gypsum so that measured SO_4 contents are considered as minimum concentrations

Figure1

Click here to download high resolution image

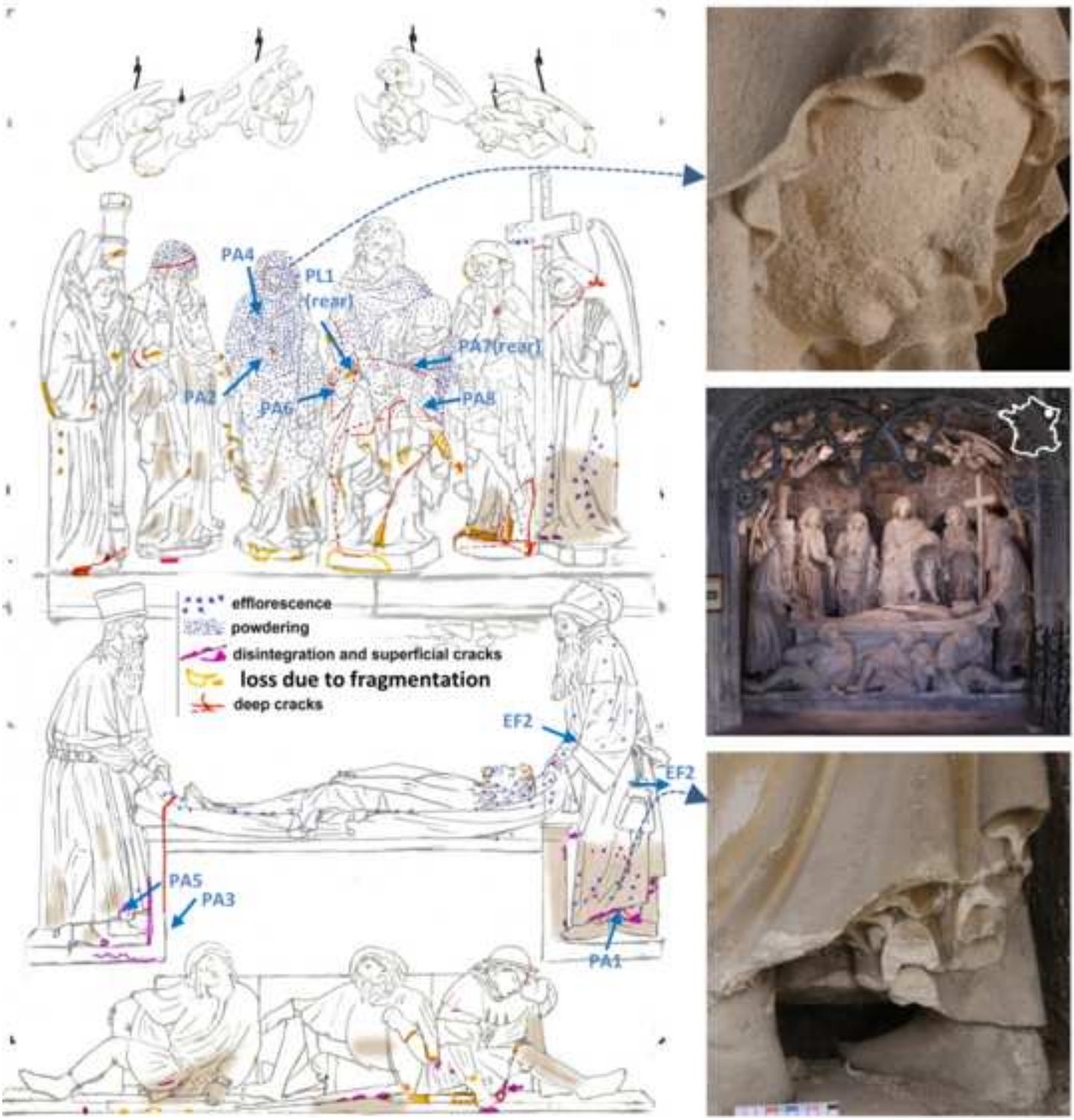


Figure2

Click here to download high resolution image

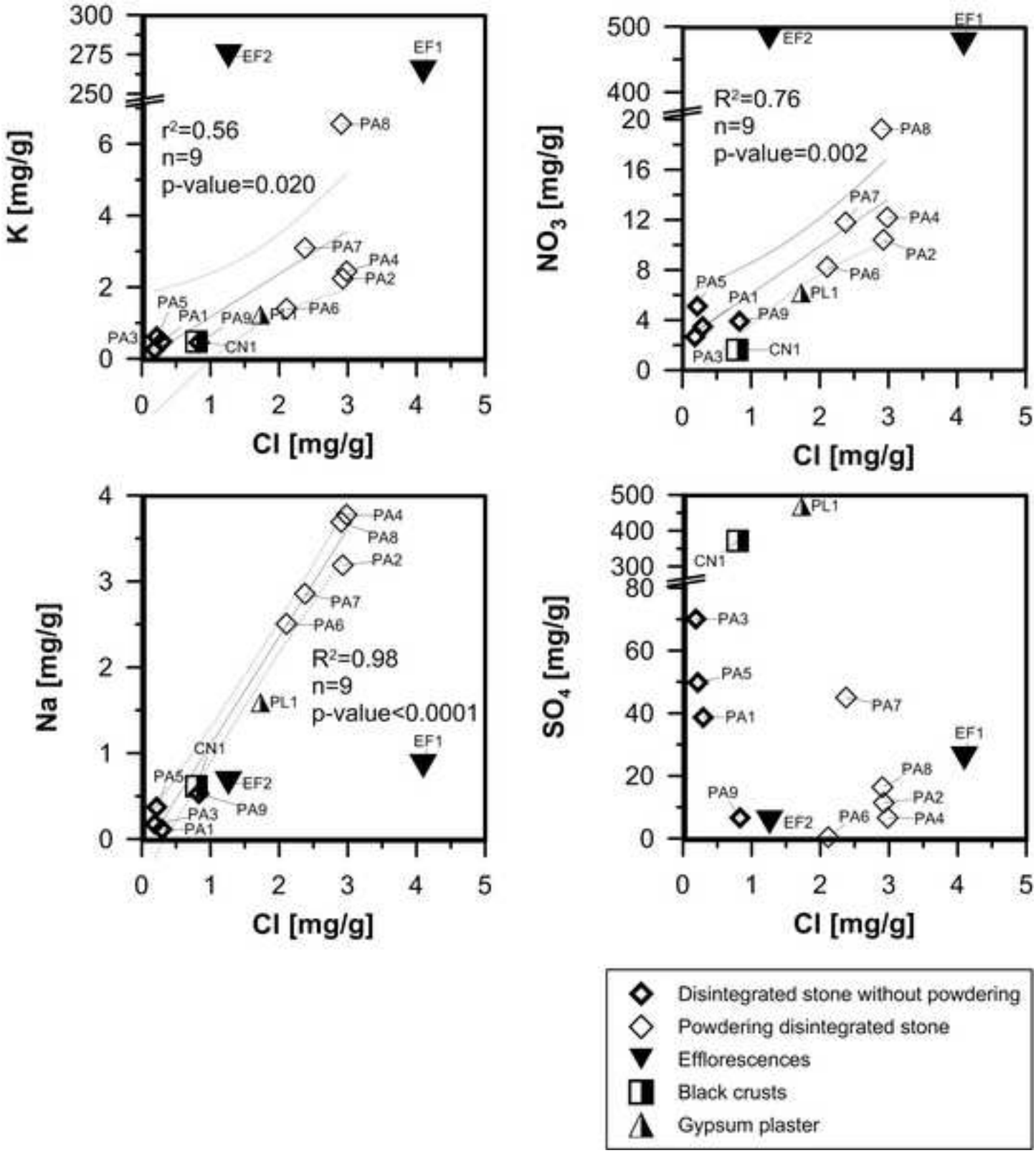


Figure3

Click here to download high resolution image

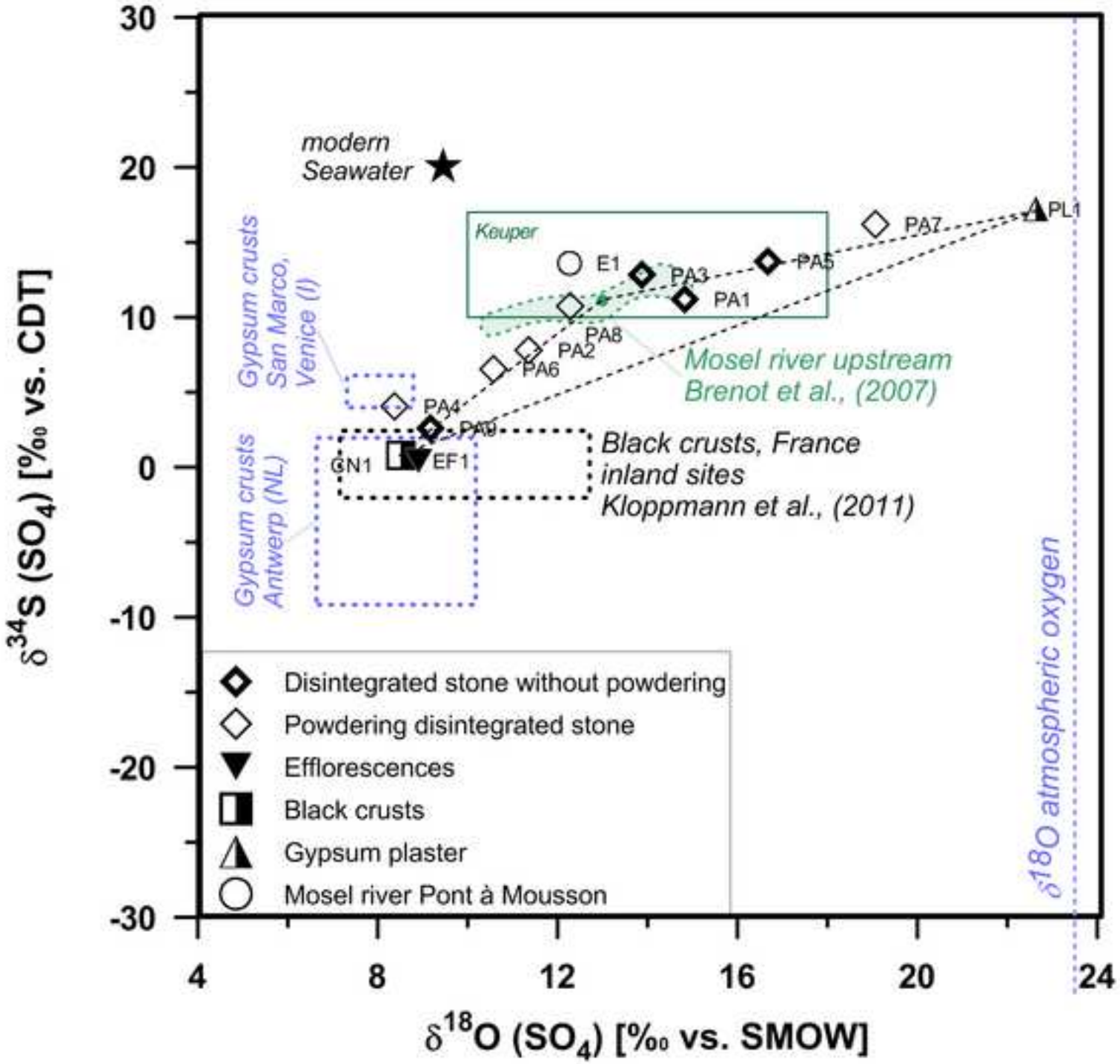
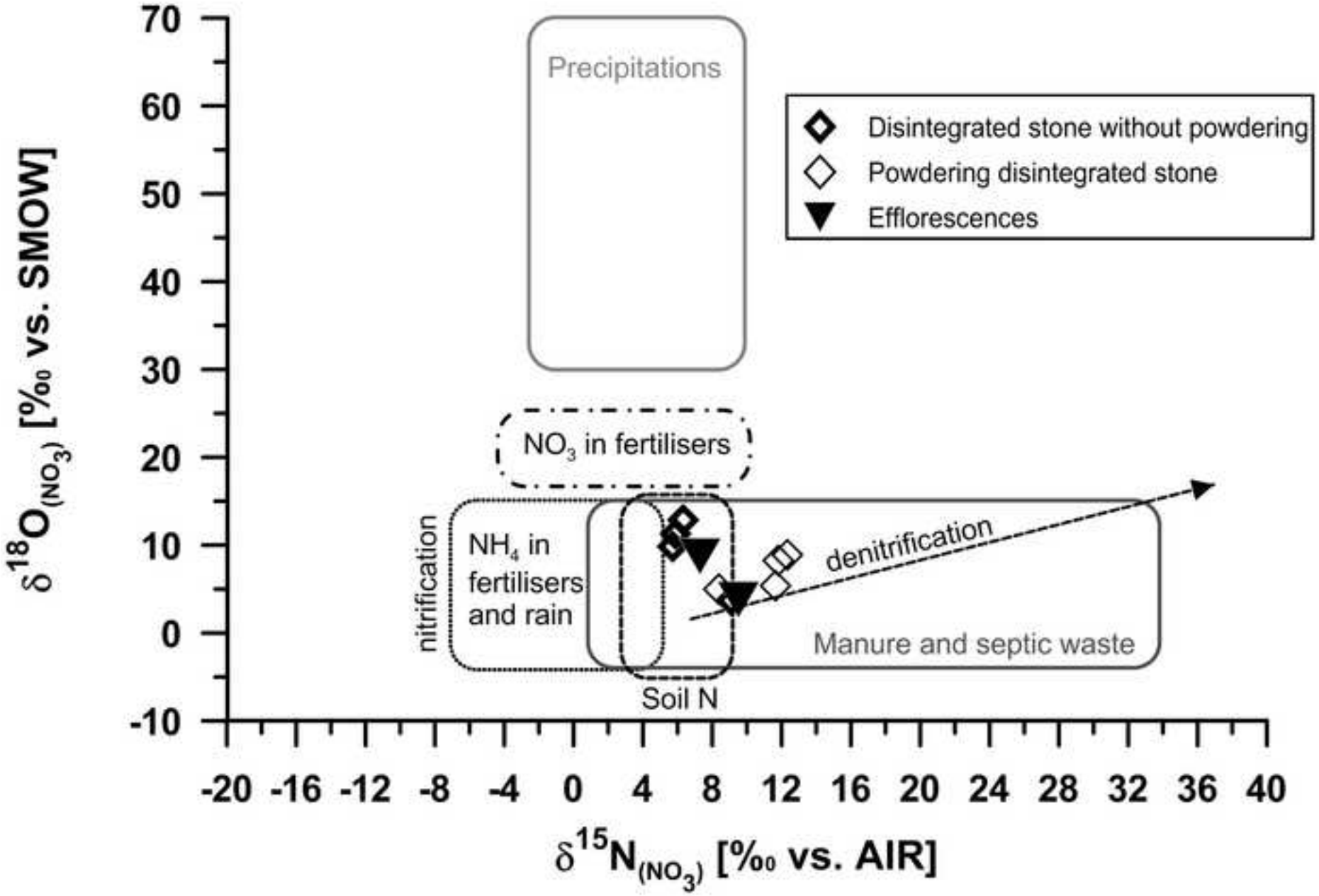


Figure4

Click here to download high resolution image



Supplementary Material

Click here to download Supplementary Material: Kloppmannet_al_STOTEN-D-12-03739R2-supplementary information.doc