Tracing Alabaster (Gypsum or Anhydrite) Artwork Using Trace Element Analysis and a Multi-Isotope Approach (Sr, S, O)

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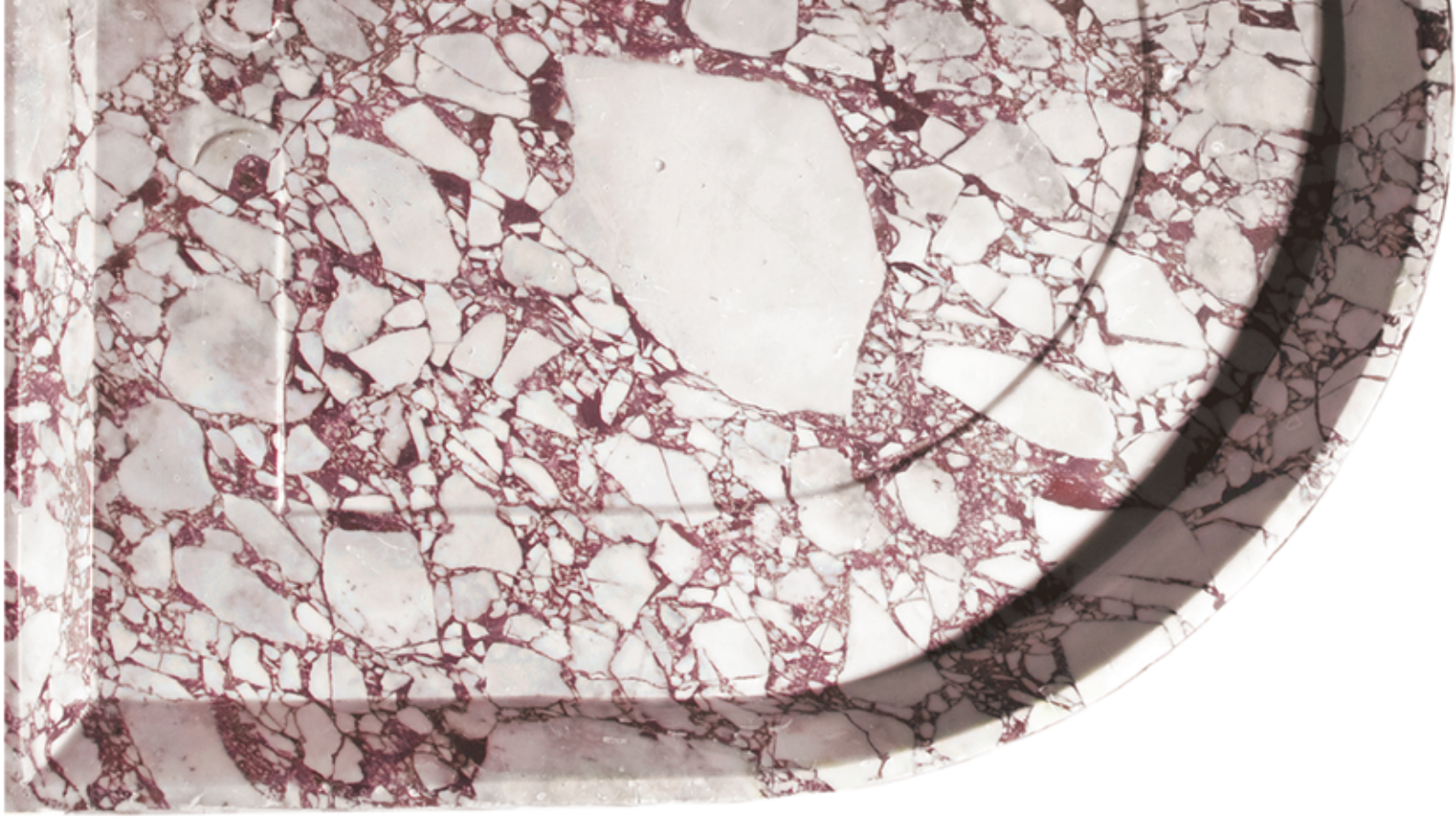

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CONTENT

3. PROVENANCE IDENTIFICATION II: (OTHER STONES)

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TRACING ALABASTER (GYPSUM OR ANHYDRITE) ARTWORK USING TRACE ELEMENT ANALYSIS AND A MULTI-ISOTOPE APPROACH (SR, S, O)

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Abstract

Since Antiquity, gypsum and anhydrite alabaster have been carved, as an alternative to white marble. Before 2010, the few mineralogical and chemical provenance studies produced unconvincing results. A large study has been undertaken, concerning several European quarries and involving about 30 samples of both quarries and artworks. These were analysed using mineralogical (XRD), chemical (ICP-AES) and isotopic (CF-IRMS and TIMS) methods. Multi-isotope fingerprinting (S, O and Sr) proved to be the most suitable methodology. The results have established highly specific isotope signatures for English, French and Spanish alabaster especially for Sr and S, with strong intra-group homogeneity and inter-group contrasts. A further investigation of 12th to 16th century sculptures from several French museums and monuments validates this methodology for identifying the provenance of the raw material. It is planned to enlarge the database with isotope analyses from historical alabaster quarries across Western Europe.

Keywords
alabaster, provenance, isotopic analysis

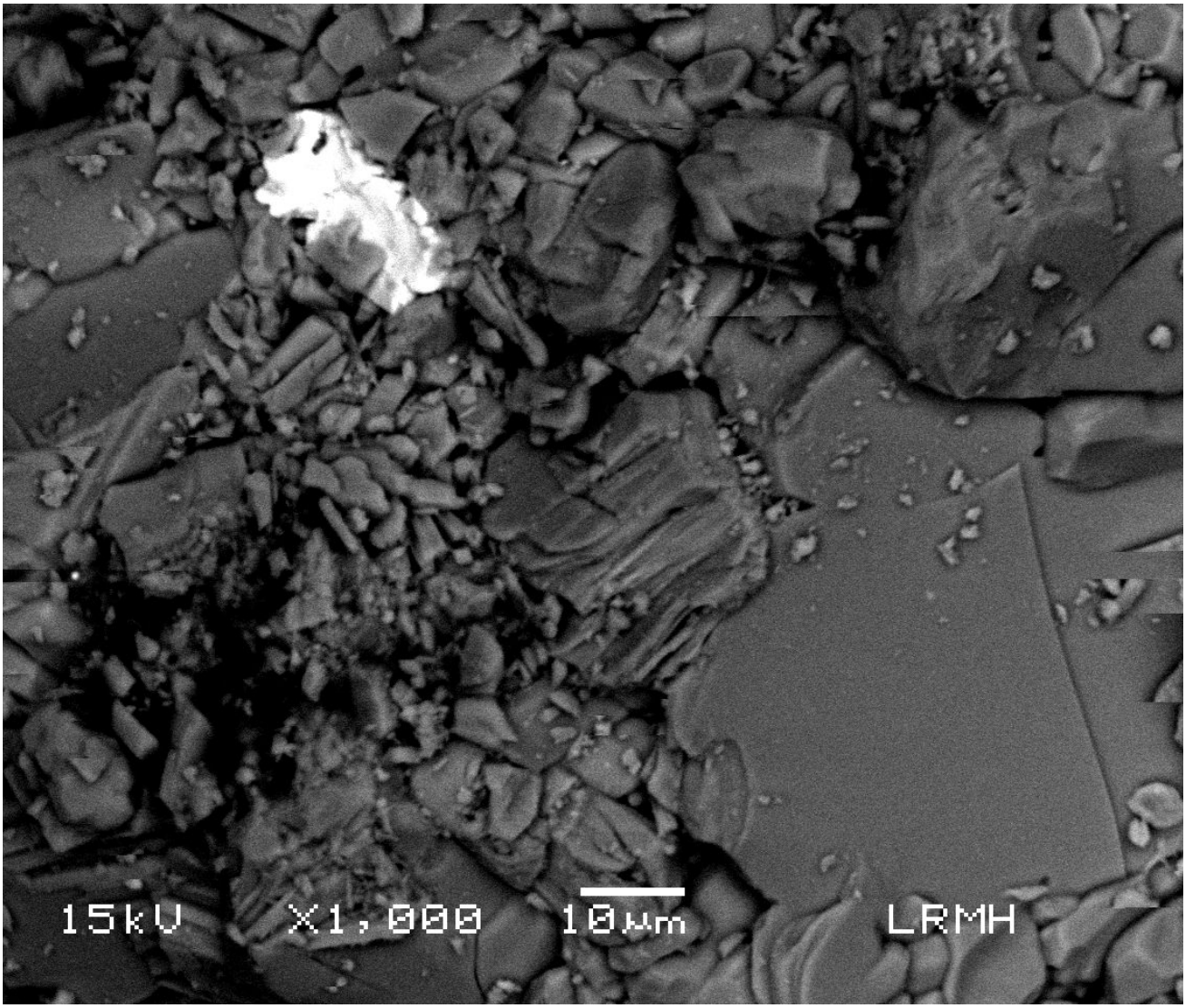
Introduction

Due to their fine-grained texture and white colour, gypsum ($CaSO_4,2H_2O$) and anhydrite ($CaSO_4$) alabasters have been used throughout history for sculptures and ornamental stone. Alabaster is similar in appearance to marble, but its softness makes it easier to work. There is no reliable petrographical indicator of geographic provenance for these relatively homogeneous rocks. It is critical for archaeologists and art historians to be able correctly to assign the provenance of the raw materials. In the absence of textual evidence, hypotheses of provenance are therefore often based on stylistic indications, or inferred by the geographical proximity of quarries.

In contrast to white marble artworks, only a few studies have addressed the mineralogical, geochemical and isotopic fingerprints of the raw alabaster sources compared to those of alabaster sculptures (COSTAGLIOLA *et al.* 2001, 421–428; LIGEZA *et al.* 2001, 71-74; PLAYA *et al.* 2012, 50–51).

Systematic shifts of $\delta^{34}S$ and $\delta^{18}O$ of SO_4 in seawater over the geological timescale (CLAYPOOL *et al.* 1980, 199-260; UTRILLA *et al.* 1992, 229-44) characterize marine gypsum deposits of different ages. Local variations in S and O isotopes also occur, caused by non-marine sulphur, from continental inputs, oxidation of sulphides and the presence of isotopically light biogenic organic sulphur; typically these are depleted in ^{34}S with respect to marine sulphate. Recycling of older sulphate deposits causes further variations (TAYLOR 1983, 11-31).

Sr commonly substitutes for Ca in the gypsum crystal lattice, and is commonly found as celestine ($SrSO_4$) (Fig.1). Isotopes of Sr reflect the age of gypsum and anhydrite deposits, varying just as the $^{87}Sr/^{86}Sr$ ratios of seawater have varied through geological time (DENISON, KIRKLAND, EVANS 1998, 1-17; MCARTHUR, HOWARTH, SHIELDS 2012, 127-144). Sr also originates from the weathering of continental rocks becoming mixed with marine Sr in coastal evaporite basins. Sr derived from Rb-containing silicate weathering tends to have higher $^{87}Sr/^{86}Sr$ ratios, as ^{87}Rb decay produces radiogenic ^{87}Sr.



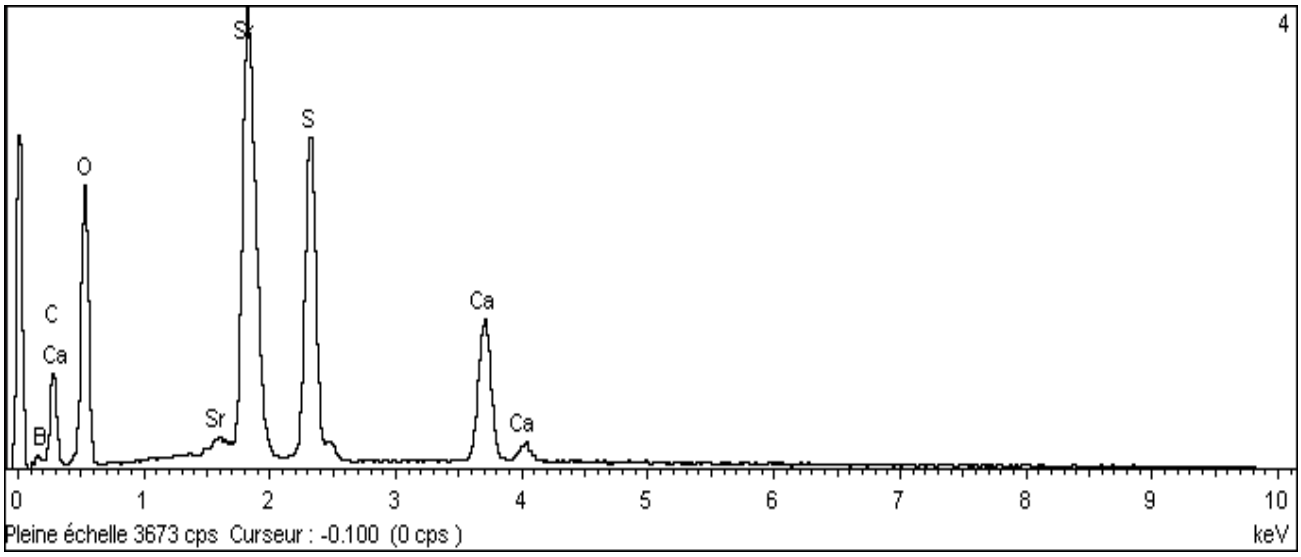


Fig. 1. Celestine (SrSO4) is highlighted by MEB (a; bright mineral among gypsum crystals) and EDS (b) analysis of an alabaster sample from the statue St Antoine, from the rood screen of the Royal Monastery of Brou (Bourg-en-Bresse, France)

Country	Sample	Provenance	Geological age	Legend
France	39-02 white	Salins-les-Bains, Jura	Trias, Middle Keuper	F-Jura1
	39-02 veined		Trias, Middle Keuper	F-Jura2
	39-14a		Trias, Middle Keuper	F-Jura3
	73-06a	Saint-Jean-de-Maurienne, Savoie	Trias	F-Maur1
	73-06c	Saint-Jean-de-Maurienne, Savoie	Trias	F-Maur2
	Mâlain	Mâlain, Côte d'Or	Trias, Keuper	F-Mala1
	84-70a	Beaumes-de-Venise, Vaucluse	Trias	F-Beau1
	84-70b	Beaumes-de-Venise, Vaucluse	Trias	F-Beau2
	38-32	Notre-Dame-de-Mésage, Isère	Trias, Keuper	F-Mésa1
	57-17	Klang, Moselle	Trias, Upper Keuper	F-Mose1
Spain	Quinto de Ebro	Quinto de Ebro, Aragon	Miocene	E-QEbr1
	Fuentes de Ebro	Fuentes de Ebro, Aragon	Miocene	E-FEbr1
	Sarral	Sarral, Catalogne	Eocene	E-Sarra1
	Beuda 1	Beuda, Catalogne	Eocene	E-Beud1
	Beuda 2	Beuda, Catalogne	Eocene	E-Beud2
	Beuda 3	Beuda, Catalogne	Eocene	E-Beud3
England	Nottingham	Outcrop near a medieval quarry	Trias, Keuper	GB-Nott1
	Triassic 3	Newark, Nottinghamshire	Trias, Keuper	GB-Nott2
	Tutbury 6, white part	Fauld Mine, Tutbury, Burton-up-on-Trent, Staffordshire	Trias, Keuper	GB-Nott3a
	Tutbury6, brown veins		Trias, Keuper	GB-Nott3b
	Tutbury 7		Trias, Keuper	GB-Nott4

Table 1. List of the 21 samples from gypsum and anhydrite quarries

Country	Sample	Provenance	Legend
France	TOB Lion 4	Tomb of Oudart de Bournonville, Museum of Fine Arts, Arras	TOB-4
	TOB Fragment C	First location = Church St-Martin, Hénin-Beaumont	TOB-C
	71-09	Jacques d'Amboise palace, Cluny	PJA
	Inv. 61-9-13	Déploration altarpiece, Musée Lorrain, Nancy First location unknown	RDD
	Bg. B Jub. Ant.	Statue of St Antoine, Jube of Royal Monastery of Brou, Bourg-en-Bresse	STA
	11-49a	Statue of ND of Bethlehem, Cathedral of Narbonne	NDB
	PER-1	Main altar, Cathedral of Perpignan	PER-1
	PER-B		PER-B
Sweden	UPPS1	Gustav Vasa monument,Uppsala Cathedral	UPPS

Table 2. List of the 9 samples from artworks

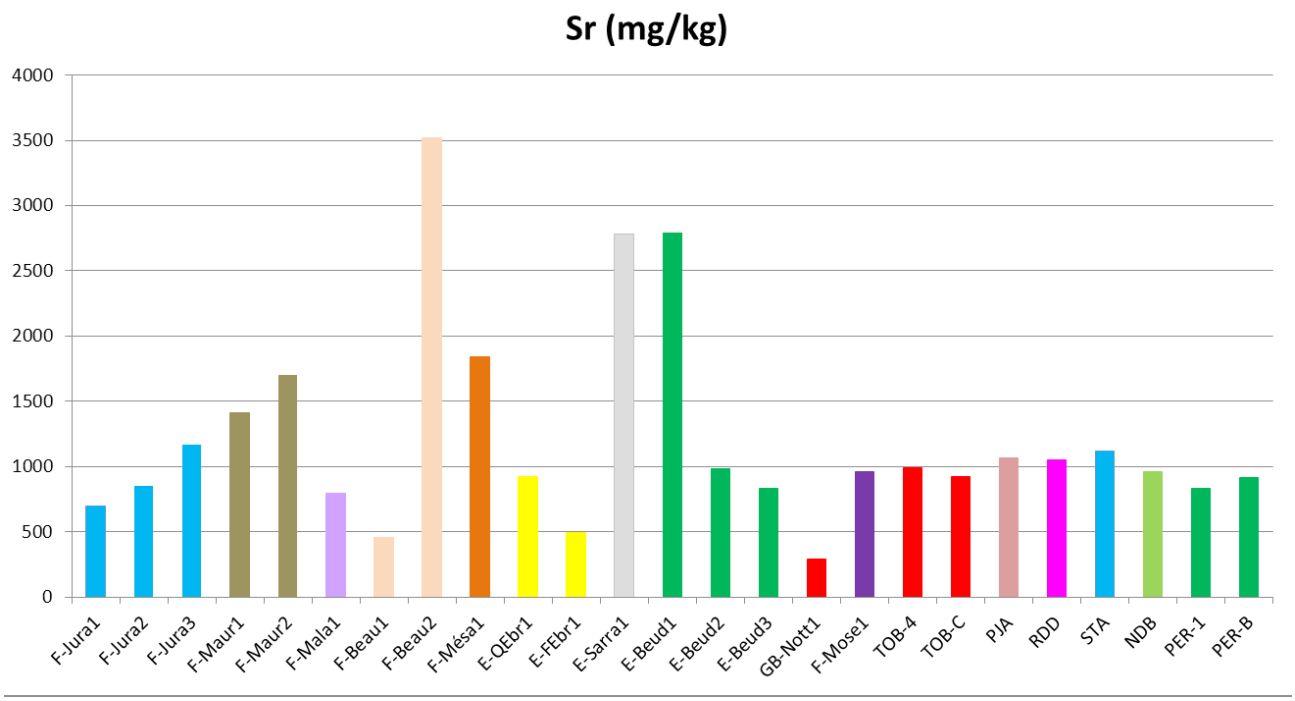


Fig. 2. Strontium contents (mg/kg) of alabaster from quarries and artworks (ICP-AES)

GALE *et al.* (1988, 57-72) pioneered the combination of Sr isotopes with S isotopes to assess the provenance of Minoan alabaster artefacts. The isotopic contrasts of marine Mio-Pliocene gypsum with Triassic or Permo-Triassic evaporites confirms a Cretan provenance both for the Cretan and some Mycenaean works of art.

The isotopic signature variations of S, O and Sr are highly specific and enable the geographical differentiation of gypsum and anhydrite deposits. However, as distinct from the case of white marbles, no geochemical and isotopic signature database existed for known quarries of these minerals.

This study defines a methodology for tracing alabaster artworks using mineralogy, trace elements and a multi-isotope approach. It is the start of a reference database for the main source quarries and a case study test of the methodology.

Material and methods

A pilot study (KLOPPMANN *et al.* 2014, 203-219) analysed 21 samples taken from gypsum and anhydrite quarries in France, Spain and England, plus 9 samples from sculpture in France and Sweden, including some of known supply provenance (Tables 1 and 2).

The geologic sampling included notable and/or historic quarry areas in the East Midlands in England (Fauld Mine, Chellaston, Kilvington), north-east Spain (Beuda, Sarral, Quinto de Ebro, Fuentes de Ebro), and France (Notre-Dame-de-Mésage, Saint-Jean-de-Maurienne, Salins-les-Bains). In addition the samples included some French gypsum quarries not historically recorded as having been used for sculpting (Malain, Klang, Beaumes-de-Venise). The geological ages cover the Triassic to Miocene periods. The French Triassic outcrops are geographically dispersed, probably inducing variations due to extra-seawater inputs.

Historic quarries in the East Midlands (UK) and Catalonia and Aragon (Spain) have been studied by geologists and historians (TAYLOR 1982; 11-31; FIRMAN 1984, 161–178; UTRILLA *et al.* 1992, 229–244; EDWARDS 1966, 231–5 and 241; ESPAÑOL 2003; ORTI IGLESIAS 2005, 45–61; LAPUENTE *et al.* 2009; WOODS 2010, 86–93; PLAYA *et al.* 2012, 50–51). The Notre-Dame-de-Mésage quarries, near Vizille (French Alps), were worked mainly during the 19th century (DEBELMAS 1990), but earlier 14thcentury uses are also suspected (POIRET 2003, 85-103). Quarries in the Maurienne valley (French Alps) are currently worked for gypsum plaster manufacture. These Triassic deposits have most likely supplied gypsum or anhydrite alabaster used in local architecture, and for sculptural use since the 10th century, notably in Saint-Jean-de-Maurienne Cathedral. The Middle Keuper gypsum and anhydrite at Salins-les-Bains (French Jura), was exploited until the mid 20th century, both for gypsum plaster and sculpture. The art of works were chosen for the following reasons:

Sample	Provenance / Quarry	Art of work / location	Gypsum	Anhydrite	Others
39-02 white	Salins-les-Bains, Jura, France		+++		
39-13a			+++		
39-14a			+++	+	
73-06a	Saint-Jean-de-Maurienne, Savoie, France		+++	+	
73-06b			+	+++	
38-32	Notre-Dame-de-Mésage, Isère, France		+	+++	
Saint-Firmin white			+++		
84-70b	Beaumes-de-Venise, Vaucluse, France		+++	+	quartz
57-17	Klang, Moselle, France		+++		
71-09	Supposed quarry = Berzé-la-Ville, Saône-et-Loire, France	Jacques d'Amboise palace, Cluny	+++	+	quartz, dolomite, illite
Quinto de Ebro	Quinto de Ebro, Aragon, France		+++		
Fuentes de Ebro	Fuentes de Ebro, Aragon, Spain		+++	+	
Sarral	Sarral, Catalonia, Spain		+++		quartz
Beuda 1	Beuda, Catalonia, Spain		+++	+	
Beuda 2			+++		
Beuda 3			+++	+	
11-49a	Supposed supply = Catalonia, Spain	Statue of ND of Bethleem, Cathedral of Narbonne	+++	+	

Table 3. Mineralogical data: XRD analysis of alabaster from quarries and artworks

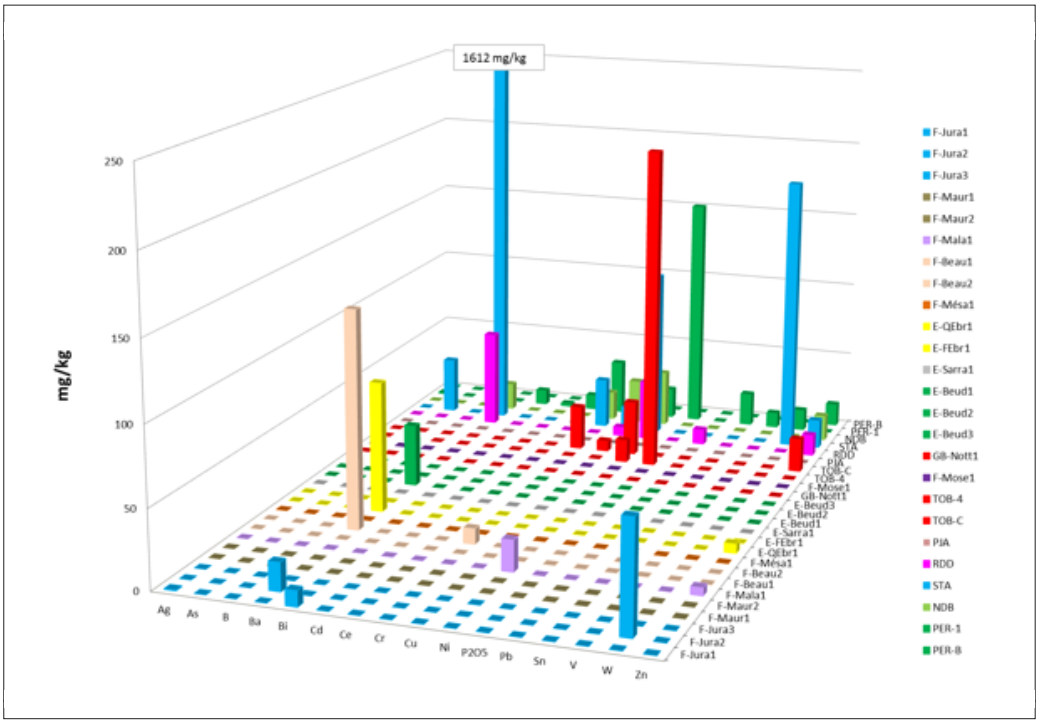


Fig. 3.
Contents of trace elements (mg/kg) of alabaster from quarries and artworks (ICP-AES) are shown only the elements detected in at least once among the 25 samples. Sr is presented apart, in fig. 2

Fig. 4.
Palais Jacques d'Amboise (Cluny, France), facade ornamented with alabaster sculptures dating from the early 16th century, and restored in 1938 (photos: W. Kloppmann)

The statue of St Antoine, from the rood screen of the Royal Monastery of Brou (Bourg-en-Bresse, France), belongs to a 16th century architectural ensemble, made from alabaster extracted from the Saint-Lothain quarries (POIRET 2003, 85-103). The ancient quarries are now inaccessible, but were about 30 km from the sampled quarries in Salins-les-Bains, and in the same Triassic gypsum sequence.

The façades of the Palais Jacques d'Amboise (Cluny, France) (15th to 16th century) are ornamented with alabaster sculptures. The raw material is likely to have come from the nearby Berzé-la-Ville quarries, located on the Abbey territory in Keuper gypsum, exploited in the 16th century (POIRET 2003, 85-103).

The high altar of Perpignan Cathedral (France) was carved over a long period (1573-1631), using a white alabaster from Beuda (Catalonia, Spain) (HERNANDEZ 2002, 109-138).

The statue of Notre Dame of Bethlehem was sculpted for Narbonne Cathedral (France) during the 14th century (PRADALIER-SCHLUMBERGER 1998, 360), when Narbonne was still culturally close to Catalonia.

The Oudart de Bournonville tomb (Museum of Fine Arts, Arras, France) and the Gustav Vasa monument (Uppsala Cathedral, Sweden) are supposed to have been carved in the 16th century from alabaster shipped from the East Midlands (UK). The first one shows polychromatic traces typical of the "Nottingham style", suggesting reuse of an English artwork (SAUTEREAU 2008). The second one was carved by the Flemish sculptor Willem Boy from Mechelen, and it is stated that he went to England to obtain the alabaster (BURKE 1998, 300; BENGTSSON 2010, 541). Mechelen was a hub for the re-export of English alabaster during the 16th century (WUSTRACK 1982, 422).

The Déploration altarpiece, conserved in the Musée Lorrain in Nancy (France), was sculpted in the 16th century. The sculptural origin of this piece is unknown, but it is stylistically attributed to a south Netherlands workshop, which

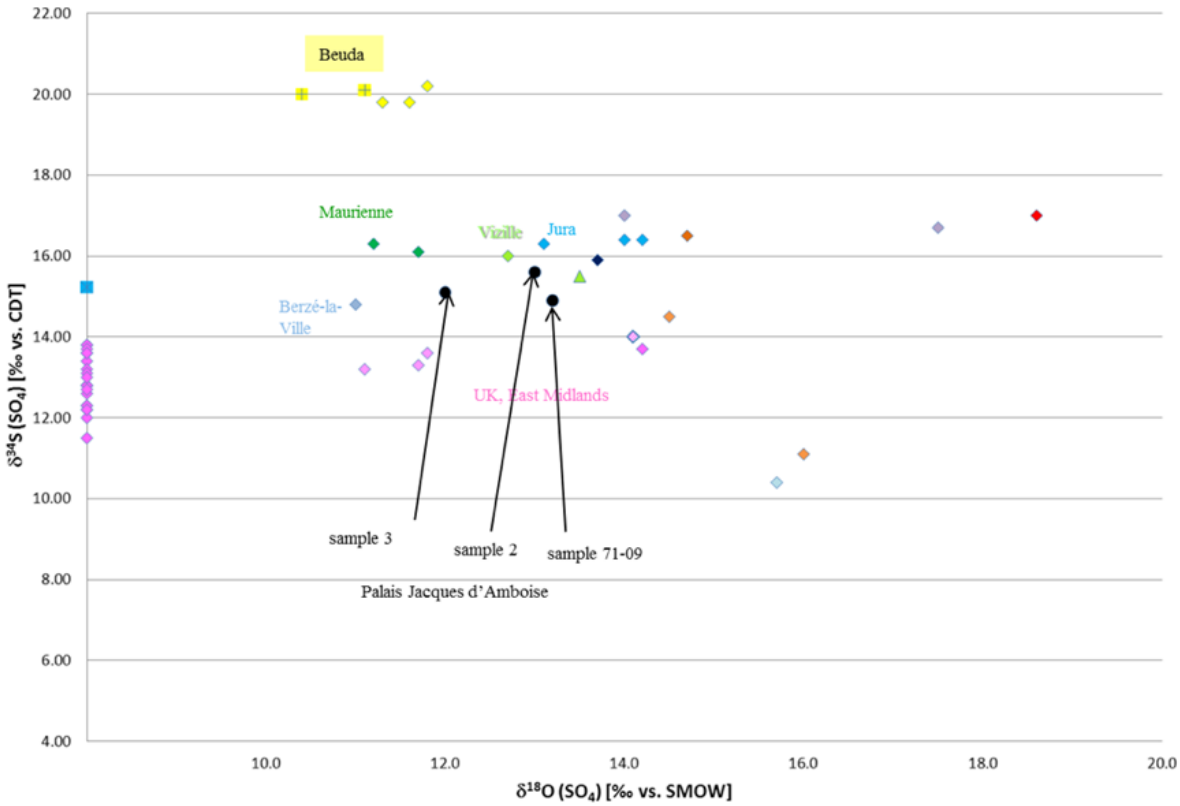


Fig. 5. Sulphur and oxygen isotope ratios of alabaster from Palais Jacques d'Amboise and from quarries published by KLOPPMANN *et al.* (2014, 203-219). Sulphur bibliographic data from Tutbury gypsum (TAYLOR 1982, 1983) are artificially represented on the ordinate axis, as well as those of the statue of St Antoine from Bourg-en-Bresse (STA) assumed to be a Jura gypsum

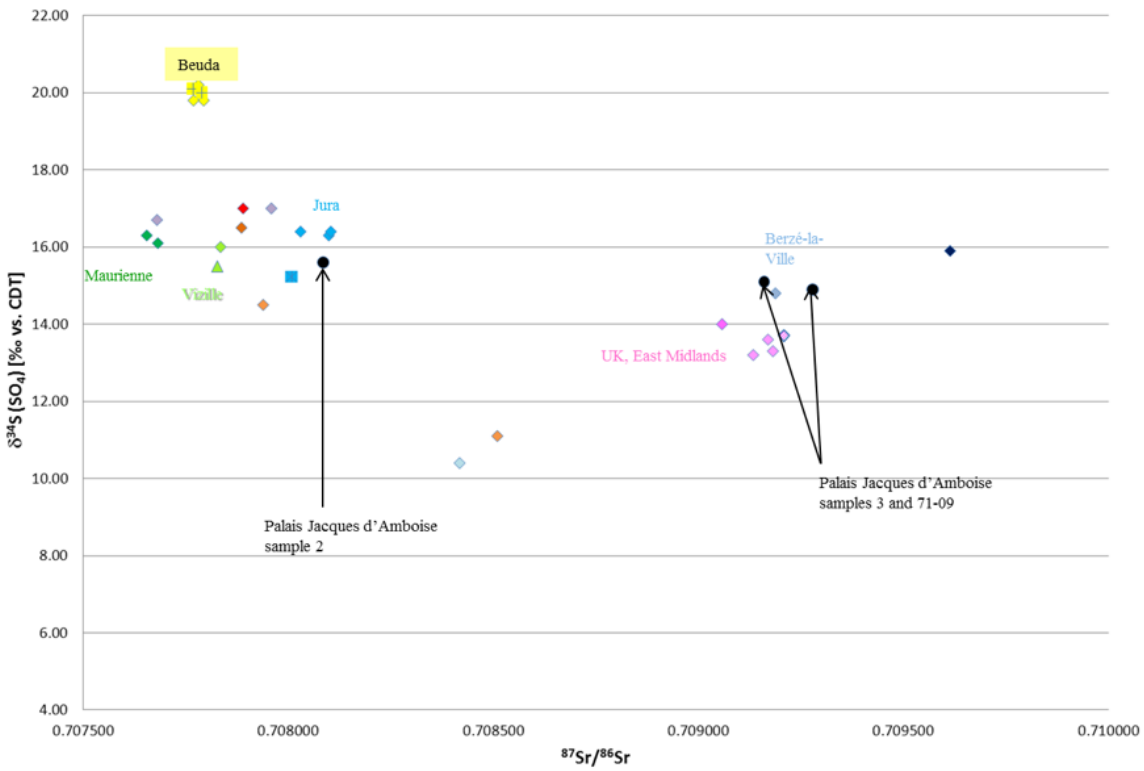


Fig. 6. Sulphur and strontium isotope ratios of alabaster from Palais Jacques d'Amboise and from quarries published by KLOPPMANN *et al.* (2014, 203-219)

is why an East Midlands supply is suggested.

The methods of sample preparation for isotope analyses are described by KLOPPMANN *et al.* (2014, 203-219). TIMS (Finnigan MAT262) is used to measure $^{87}Sr/^{86}Sr$ and CF-IRMS (Thermo Delta Plus XP) to dose S and O isotopes. The isotopic composition of S and O are expressed in the usual delta notation, as a per mil (‰) deviation of isotope abundance ratio ($^{34}S/^{32}S$, $^{18}O/^{16}O$) in the sample: $\delta^{34}S$ with respect to the CDT standard, $\delta^{18}O$ with respect to the SMOW standard.

Twenty-five alabaster samples were analysed by ICP-AES in order to determine the contents of trace elements.

Seventeen samples were analysed by XRD in order to identify the mineralogy, using Bruker D8 Advance (Co tube), and Brucker D2 Phaser (Cu tube), both with Lynx Eye detector.

Results of the pilot study

The isotopic results were published by KLOPPMANN *et al.* (2014, 203-219).

The $\delta^{34}S$ vs. CDT values of the French samples from the Alps, Provence and Jura are in a narrow range (+15.9‰ to +17.0‰), whereas the $\delta^{18}O$ vs. SMOW values are much more variable for this group (+11.2‰ to +17.5‰), falling in the typical range for Keuper evaporites. Samples from Burgundy (France) plot in the same characteristic range as other samples of Upper Triassic age (PEARSON *et al.* 1991). Catalan samples from Beuda are significantly enriched in ^{34}S ($\delta^{34}S$ around +20‰), with $\delta^{18}O$ values among the lowest of the data set (+11.3‰ to +11.8‰), similar to values reported in the bibliography for this quarry (UTRILLA *et al.* 1992, 229-244; INGLÈS *et al.* 2009). The English samples of Triassic Chellaston and Tutbury gypsum fall within the previously published $\delta^{34}S$ range of +12‰ to +14‰ (TAYLOR 1983).

$^{87}Sr/^{86}Sr$ ratios for raw alabaster vary significantly, from 0.707655 to 0.709614, and allow the discrimination of French Alps alabaster from the Upper Triassic East Midlands alabaster, which has a well defined radiogenic signature (mean value = 0.709151). This is again very similar to the previous work on the Tutbury and Fauld gypsum deposits (TAYLOR 1982), which had a mean value of 0.709156. The East Midlands samples and the Burgundy samples contain much more radiogenic ^{87}Sr. Continental influence is suspected, with significant input from silicate weathering. The Spanish Catalan marine Eocene alabaster from Beuda has a mean value of 0.707781 and falls in the range of Triassic gypsum from the French Alps and foreland, but can be discriminated by its higher $\delta^{34}S$ values. The Ebro basin Miocene gypsum shows a relatively wide range for both $\delta^{34}S$ and $^{87}Sr/^{86}Sr$. The depletion in ^{34}S of the continental Miocene gypsum of the central Ebro basin is interpreted as being caused by S reduction in organic-rich lake sediments and subsequent oxidation (UTRILLA *et al.* 1992, 229-244).

Combining $\delta^{34}S$ and $^{87}Sr/^{86}Sr$ leads to a strong discrimination, with well-defined and clearly distinguished fields, partly due to the temporal variations of seawater signals, and also the influence of non-marine sources, especially for strontium. Sr concentrations (Fig. 2) however are much less discriminating, as local variations can be quite significant (e.g. by a factor of 3 for the Beuda quarry). Generally the $^{87}Sr/^{86}Sr$ ratios are very homogeneous for each site.

The studied sculptures from Narbonne (NDB) and Perpignan (PER-1 and PER-B) show a clear Beuda signature for all three isotope systems, as was expected on the basis of stylistic and historical studies. An English origin is confirmed for the tombstone sculpture of Oudart de Bournonville (TOB) and for the monument of Gustav Vasa of Uppsala (UPPS). A local origin is possible for the analysed works of art from Burgundy and Jura: as expected, the statue of St Antoine from Bourg-en-Bresse (STA) shows isotopic similarities to the Jura gypsum; the alabaster from the Palais Jacques d'Amboise (PJA) at Cluny is quite enriched in ^{87}Sr, a feature that characterizes the quarry sample from Burgundy. The alabaster used for the Deploration altarpiece (RDD) is probably Triassic gypsum, but the provenance could not be identified in the current study.

The XRD analysis of these alabasters (Table 3) provided few discriminating features concerning the geologic and geographical origin of the samples. It is suggested that this reflects the high mineralogical purity and homogeneity of the materials selected for sculpture, where whiteness and the absence of inclusions may have been the criteria of choice. The alpine alabasters may have an anhydritic composition.

The trace element contents (Fig. 3) show a great variability, and are not discriminating, mainly due to the low concentrations, in most cases below the quantification limit (QL) of the ICP-AES method employed. For the samples and parameters above QL, there is no reproducibility among samples from the same quarry area. Only the bivalent cations barium and strontium are frequently (Ba) or systematically (Sr) above the QL of respectively 10 and 5 mg/kg. Strontium contents showed little consistency (Fig. 2) where several samples were collected from the same quarry, for example the three samples from Salins-les-Bains area (F-Jura1 and F-Jura2 taken from white and veined parts from the same alabaster block, and F-Jura3 from a nearby quarry) or the data from the Beuda group (E-Beud1, E-Beud2 and E-Beud3 from the quarry; PER-1 and PER-B, from the Perpignan Cathedral).

In conclusion, this first pilot study, comprising mineralogical determinations, analysis of trace elements and isotopes, shows the benefit of using the isotopic analysis of sulphur ($\delta^{34}S$), oxygen ($\delta^{18}O$) and strontium

Fig. 7. Recumbent effigy of cardinal Jean de Lagrange (inv. N52), Musée du Petit Palais, (Avignon, France) (photo: O. Guillon)

($^{87}Sr/^{86}Sr$). The results from trace element analysis by ICP-AES and mineralogical composition by XRD are not sufficiently sensitive or discriminatory for our purpose. However a systematic screening of trace elements by ICP-MS on quarry material, and application of statistical analysis, might allow the identification of deposit-specific parameters.

Case studies

The multi-isotopic method proved by the pilot study has been tested and applied for restoration projects and in response to art history issues.

Facades of Palais Jacques d'Amboise in Cluny (Burgundy, France)

The 15th to 16th century facades of Palais Jacques d'Amboise (Cluny, France) are ornamented with alabaster sculptures (Fig. 4). The quarry in Lower Keuper gypsum located at Berzé-la-Ville, less than 10 km distant, is suspected to be the alabaster source. The facade was restored at the beginning of the 20th century, and some ornamentation was replaced with alabaster of unknown provenance. Prior to further restoration, a review of sculpture authenticity was required, and isotopic analyses were performed on two alabasters sampled on the facade and one in the Berzé-la-Ville quarry: "sample 2", probably introduced in 1938; "sample 3", brought before 1938; Berzé-la-Ville", gypsum from the quarry. Previously, "sample 71-09", removed from the facade during a previous restoration (1938?), conserved in the LRMH collection of stones, was analysed in the pilot study.

The results are reported in Figs. 5 and 6. The $\delta^{34}S$ vs. CDT and $\delta^{18}O$ vs. SMOW values of the samples from the Palais Jacques d'Amboise and the Berzé-la-Ville quarry ($\delta^{34}S$ = +14.8‰ to +15.6‰; $\delta^{18}O$ = +11.0‰ to +13.2‰) plot in the typical range for Keuper evaporites. The Sr isotopy provides a diagnosis, because the $^{87}Sr/^{86}Sr$ ratio is higher in the Berzé-la-Ville gypsum (0.709188± 0.000007), confirming that the Burgundy samples contain much more radiogenic ^{87}Sr. Samples 3 (0.709161± 0.000007) and 71-09 (0.709279 ± 0.000008) could be associated with this original quarry, and probably came from blocks carved in the 16th century. Sample 2 ($^{87}Sr/^{86}Sr$ = 0.708085 ± 0.000009), supposed to be a substituted alabaster, could be related to a Jura deposit, where quarries were being exploited at the beginning of the 20th century.

Tomb of Cardinal Jean de Lagrange, recumbent effigy (inv. N52), Musée du Petit Palais, (Avignon, France)

This recumbent effigy (Fig. 7) is a sculpture that was part of the monumental tomb (reaching a height of 15 meters) that Cardinal Jean de Lagrange erected around 1388-1389 at Saint Martial Church in Avignon (France). This funerary monument, carved in alabaster, reflects the wealth of Avignon buildings during the Papal era. It was destroyed during the Revolution, and fragments are preserved at the Musée du Petit Palais, as are many sculptures from other Avignon tombs of the 14th century. The alabaster provenance has never been determined before.

A small flake (±100 mg) was sampled from a broken surface of the statue, and analysed to obtain $\delta^{34}S$ vs. CDT and $\delta^{18}O$ vs. SMOW values and $^{87}Sr/^{86}Sr$ ratio. These were compared with an enlarged database of isotope analyses of samples from known or suspected historical alabaster workings in France (KLOPPMANN *et al.* 2015)

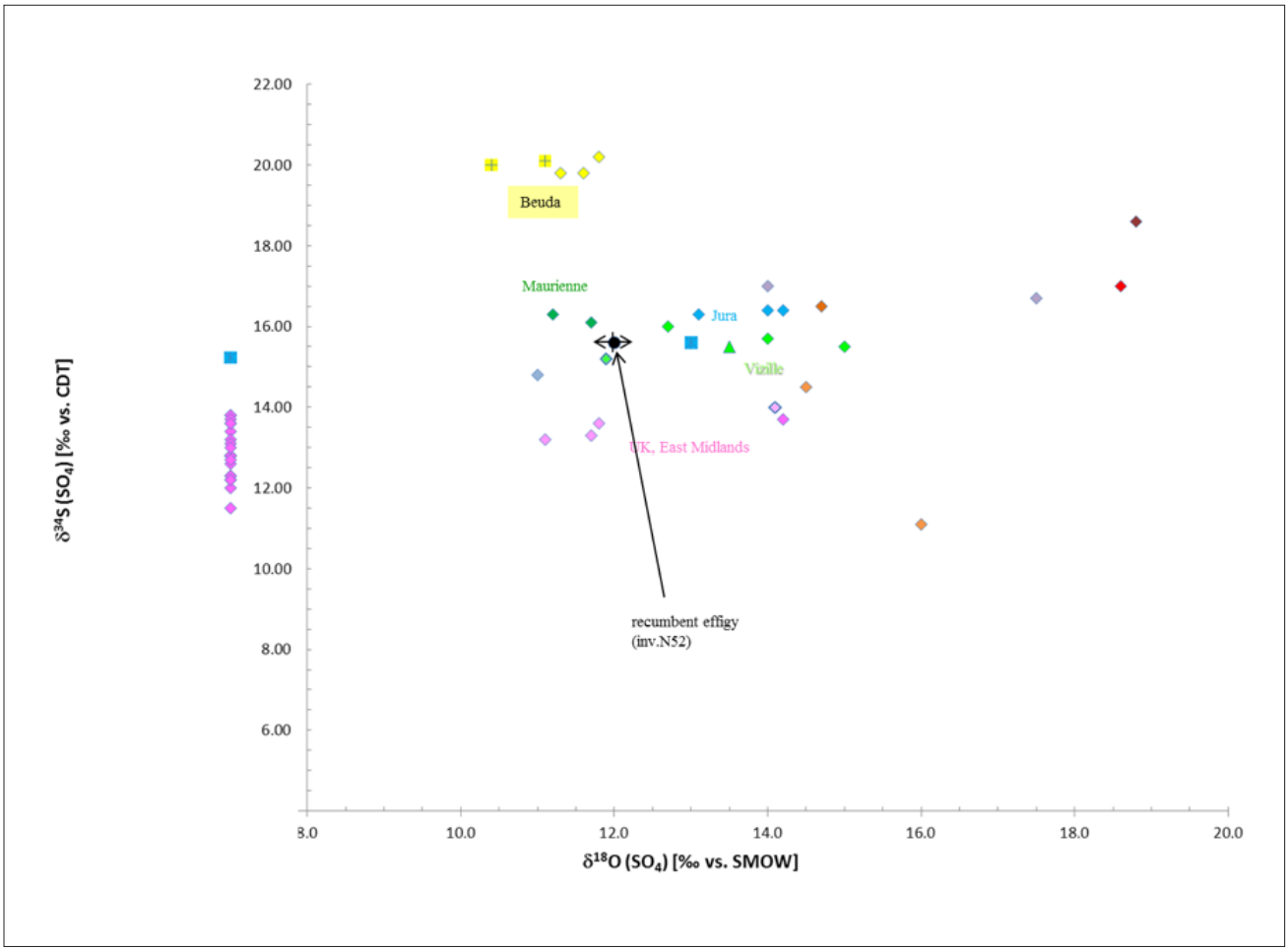


Fig. 8. Sulphur and oxygen isotope ratios of alabaster from recumbent effigy of cardinal Jean de Lagrange (inv. N52) (Musée du Petit Palais, Avignon, France) (• ; arrows represent analytical error) and from quarries (KLOPPMANN *et al.* 2014, 203-219; 2015).Sulfur bibliographic data of Tutbury gypsum (TAYLOR 1982, 1983) are artificially represented on the left of the ordinate axis, as well as those of the statue of St Antoine from Bourg-en-Bresse (STA) assumed to be a Jura gypsum

(Figs. 8 and 9). Sulphur and oxygen isotopy results ($\delta^{34}S$ = +15.6‰; $\delta^{18}O$ = +12.0‰) reveal that the raw material used for the effigy is in the range for Keuper evaporites, therefore excluding Tertiary alabasters from Spain. Strontium isotopy ($^{87}Sr/^{86}Sr$ = 0.707793 ± 0.000008) combined to $\delta^{34}S$ correlates the effigy closely with samples coming from the quarries of the Vizille area.

This study has provided fresh information concerning historical trade routes for building materials used in the papal city during the 14th century, via the Rhone navigation from the Alps. It also indicates the potential of the Vizille quarry area as a source of supply in this period.

Conclusions

Detecting the origin of raw materials used for sculpture is crucial for art historians and museums aiming to identify artists, rarely named and documented before the 16th century, the locations of workshops and historic trade routes. Before the 2010 pilot study started (KLOPPMANN *et al.* 2014, 203-219), the origin of the raw material for gypsum alabaster artworks was under-investigated. The trace element analyses by ICP-AES and mineralogical determinations have not yielded convincing results, due to low concentrations for most elements and the rather homogeneous mineralogical composition, especially within pure white alabaster varieties. However, trace element analysis could be refined, e.g. through the use of ICP-MS, and particularly the extension to REEs, as it is known that cathodoluminescence in sulphates is related to REE contents (BAUMER *et al.* 1997, 73-80).

The benefit of multi-isotope fingerprinting of alabaster provenance, using a combination of sulphur, oxygen and strontium isotopes, has been clearly demonstrated, yielding the first database of quarry samples, with validation by case studies. West European alabaster samples show age-specific differentiation. Additionally, non-marine sources such as sulphides, organic sulphur

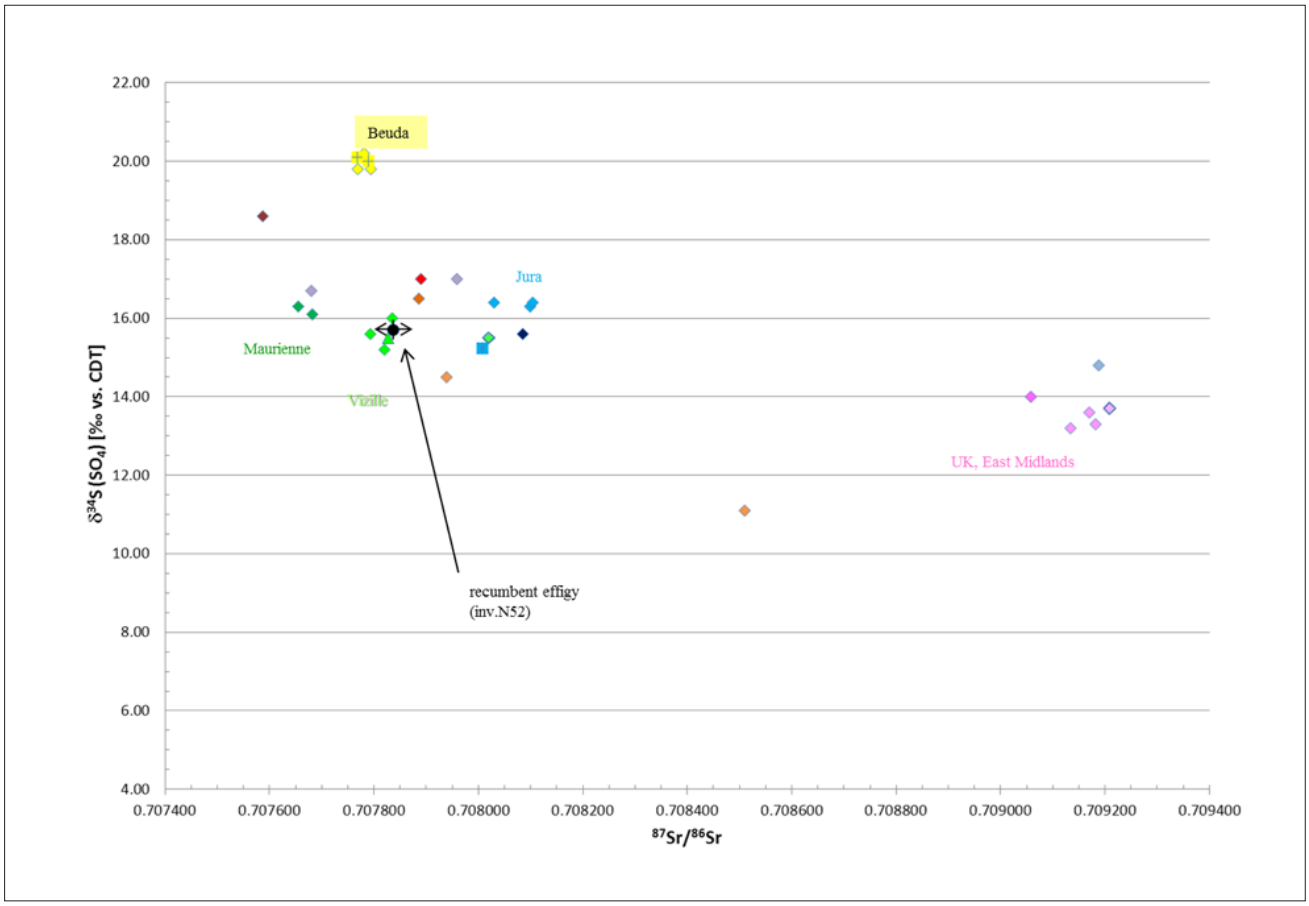


Fig. 9. Sulphur and strontium isotope ratios of alabaster from recumbent effigy of cardinal Jean de Lagrange (inv. N52) (Musée du Petit Palais, Avignon, France) (• ; arrows represent analytical error) and from quarries (KLOPPMANN *et al.* 2014, 203-219; 2015)

and strontium derived from mineral weathering, provide basin- or sub-basin-specific signatures, and can further refine discrimination of alabaster provenances. Oxygen isotopes provide supplementary evidence even if there is an overlap of signatures. The basic operational tool to distinguish the main alabaster sources for historical workshops (Middle Ages and Renaissance) in Western Europe has been established for the first time, but needs to be enhanced with more quarry samples to make it more statistically robust. The method would be applicable to Mesopotamian deposits and the Assyrian works of art for which the supply source and trade routes have yet to be determined.

The analytical method only requires the collection of micro-samples, which considerably limits the impact on the works of art. As sulphur and oxygen are major components in calcium sulphates and the content of Sr is rather important, a theoretical minimum of 5 mg of gypsum is required. In practice, in order to have unpolluted material, the sample flakes should weigh at least 50 mg.

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