

Sulfur isotope analysis of cinnabar from Roman wall paintings by elemental analysis/isotope ratio mass spectrometry – tracking the origin of archaeological red pigments and their authenticity

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The most valuable pigment of the Roman wall paintings was the red color obtained from powdered cinnabar (*Minium Cinnabaris* pigment), the red mercury sulfide (HgS), which was brought from mercury (Hg) deposits in the Roman Empire. To address the question of whether sulfur isotope signatures can serve as a rapid method to establish the provenance of the red pigment in Roman frescoes, we have measured the sulfur isotope composition ($\delta^{34}\text{S}$ value in ‰ VCDT) in samples of wall painting from the Roman city Aventicum (Avenches, Vaud, Switzerland) and compared them with values from cinnabar from European mercury deposits (Almadén in Spain, Idria in Slovenia, Monte Amiata in Italy, Moschellandsberg in Germany, and Genepy in France). Our study shows that the $\delta^{34}\text{S}$ values of cinnabar from the studied Roman wall paintings fall within or near to the composition of Almadén cinnabar; thus, the provenance of the raw material may be deduced. This approach may provide information on provenance and authenticity in archaeological, restoration and forensic studies of Roman and Greek frescoes.

The finest Greek and Roman houses were frequently decorated with mosaic floors and wall paintings (frescoes). Studies of archaeological wall paintings often aim to determinate the origin of the pigments and the techniques used to apply the different colors. This is of major relevance in cultural heritage studies because it (a) provides historical information on early technologies (i.e., raw material processing, painting techniques) and ancient trading patterns (i.e., origin of raw materials, trade and commercial routes), (b) helps detect past restoration of frescoes and authenticity of works, and (c) gives an approximate maximal age for the painting through the determination of the cinnabar origin. Such studies applying different techniques – including optical microscopy (OM), scanning-electron microscopy (SEM), X-ray diffraction (XRD), electron microprobe analysis (EMA), diffuse reflectance infrared Fourier transform spectroscopy and gas chromatography/mass spectrometry (GC/MS) – were performed on Roman wall paintings recovered from archaeological sites in France,¹⁻⁴ Switzerland,⁵ Spain,⁶⁻¹⁰ Italy¹¹⁻¹⁷ and Croatia.¹⁸ The mineralogical and physicochemical analyses of ancient paintings

are often difficult to interpret as they reveal only the average composition of a mixture of materials and pigments.

The most valuable pigment used in Roman wall paintings was the red pigment *Minium Cinnabaris* (called also *Vermilion*), containing principally cinnabar, the red mercury sulfide (HgS).¹³⁻¹⁶ Cinnabar was used pure for a light red pigment or mixed with *Rubrica* (also called *Red Ochre*), composed mainly of hematite (Fe₂O₃), to obtain a darker red. Cinnabar, used all over the Roman world in small quantities for high-quality paintings, was an expensive raw material, since this mercury ore was not abundant inside the borders of the Roman Empire.³ The largest known cinnabar deposits in the Mediterranean region are Almadén in the province of Castilla la Nueva, Spain (300 000 metric tons of Hg),^{19,20} Idria in Slovenia (145 000 t Hg),^{21,22} and Monte Amiata in Grosseto, Italy (117 707 t Hg).^{23,24} Epigraphic, literary and archaeological evidence corroborates ore extraction in Almadén since at least 500 BC. The other two deposits are thought to have been mined by the Romans, but the archaeological studies are scarce, and the earliest records are from Christopher Columbus' notes in 1492 and 1499. Almadén cinnabar exploitation through the ages was two and a half times greater than at Idria and nearly four times greater than at Monte Amiata. Other smaller cinnabar mines that were in operation during the Roman period include Karaburun, İzmir, and Sızma (Konya province) in Turkey,²⁵ Medjerda in Tunisia, Moschellandsberg in Germany,²⁶ and Genepy (La Mure

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region) in France.²⁷ The exploitation history of these deposits is poorly known. The cinnabar ore was brought to Rome for processing; therefore, the cinnabar used in the wall painting of the Roman Empires may be of different origins.

Sulfur has four stable isotopes, ³²S, ³³S, ³⁴S, and ³⁵S, with naturally occurring abundances on earth of 95.02, 0.75, 4.21, and 0.02%, respectively. The stable isotope composition of sulfur is reported in the delta (δ) notation as the per mil (‰) deviation of the isotope ratio relative to known standards: $\delta = [(R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}}] \times 1000$, where R is the ratio of the heavy to light most abundant isotopes (³⁴S/³²S). The sulfur standard is the Vienna Cañón Diablo Troilite (VCDT).

Sulfur isotope compositions have many different applications in Earth Sciences with particular attention given to the isotopic variations among the different sulfur phases (sulfides and sulfates). The stable sulfur isotope ratio can be used to identify sources, mixing processes, and the fate of sulfur species in the environment, and particularly in deposits of metallic sulfides.²⁸ Knowledge of the sulfur isotope composition of the potential sources allows their relative contribution to the sulfur at the final site to be assessed. The sulfur isotope composition of cinnabar in the pigments of the Roman frescoes discovered at the House of Diana (Crosseto, Italy) were measured and used in combination with OM, SEM and EMA data to obtain insight into the origin of the red pigment.¹³ Mazzochin *et al.*²⁹ compared the isotopic composition of lead present in cinnabar of Roman wall paintings from the Xth Regio of the Roman Italy with that of samples from the mercury deposits at Almadén, Monte Amiata, and Idria. In this study, we explore the discriminating potential of the sulfur isotope composition for tracking the provenance of cinnabar present in Roman wall paintings from Avenicum (Avenches, Vaud, Switzerland), the most important city of central Switzerland during the Early Roman Empire (1st and 2nd centuries AD). The sulfur isotope composition of the red pigments was compared with that of cinnabar samples from major European mercury deposits.

EXPERIMENTAL

Eight fragments of painting from the collection of the Roman Museum of Avenches were selected for sulfur isotope study. The surface of the fragments was cleaned of visible foreign material with organic solvents-washed stainless steel tweezers. Red painting samples were collected using a micro drill to avoid contamination with material not containing cinnabar.

The cinnabar samples from the mercury deposits were obtained from collections of the Department of Geology and the Museum of Geology of the University of Lausanne. There were 13 mercury ore samples from Almadén (Spain), 24 from Idria (Slovenia), 9 from Monte Amiata (Italy), 2 from Moschellandsberg (Germany), and 2 from Genepy (France). The cinnabar samples were checked for impurities under a binocular microscope, and manually homogenized using an agate mortar and pestle.

All archaeological pigment samples were analyzed by powder X-ray diffraction (XRD) using a Philips[®] PW 1830 diffractometer (PANalytical, Almelo, The Netherlands) equipped with monochromated CuKα ($\lambda = 1.54056 \text{ \AA}$) X-radiation to determine the presence of different sulfur phases. The scan settings were 5–65° 2θ, 0.5° step size, 1.5-s count time per step.

Sulfur isotope analyses were performed using a Carlo Erba 1108 elemental analyzer (EA, Fisons Instruments, Milan, Italy) connected to a Thermo Fisher (formerly ThermoQuest/Finnigan, Bremen, Germany) Delta S isotope ratio mass spectrometer that was operated in the continuous helium flow mode via a Thermo Fisher Conflo III split interface³⁰. Aliquots of the sample and of the calibration standards (200 to 600 μg) were weighed in tin cups (Säntis Analytical AG, Teufen, Switzerland). Vanadium pentoxide was added as an oxidation catalyst in an amount approximately twice the weight of the sample. The tin cups of the samples and the calibration standards were closed, crushed to a small size and loaded into an AS 200 autosampler (Fisons Instruments). They were flash-combusted sequentially under a stream of helium and oxygen at 1030°C in a single oxidation-reduction quartz tube filled with high purity oxidizing (tungsten trioxide, WO₃) and reducing (elemental Cu) agents, both from Säntis Analytical AG. Combustion-derived gases (SO₂, H₂O, CO₂, N₂) were first dried by passing them through a 10 cm long column filled with anhydrous Mg(ClO₄)₂, and then directed through a 0.8 m PTFE chromatographic column packed with Porapak 50–80 mesh (Fisons Instruments) at 70°C for the separation of SO₂ which was isotopically analyzed by isotope ratio mass spectrometry (IRMS). Pure SO₂ gas was inserted into the He carrier flow as pulses of reference gas. The reference SO₂ gas was calibrated against the IAEA-S-1 sulfur isotope reference standard (Ag₂S) with δ³⁴S value of −0.3‰.³¹ The overall analytical reproducibility of the EA-IRMS analyses, assessed by replicate analyses of three laboratory standards (synthetic cinnabar, with δ³⁴S value of +15.5‰; barium sulfate, +12.5‰; pyrite Ch, +6.1‰; pyrite E, −7.0‰) and the Avenicum cinnabar samples, is better

Table 1. Sulfur isotope composition of the cinnabar from Roman wall paintings in Avenicum

Sample	Provenance	δ ³⁴ S (‰, VCDT)	
		Average ^a	σ
K4605	Avenicum 1	+10.5 (2)	0.15
K4665-1	Avenicum 2	+10.4(2)	0.13
K4665-2	Avenicum 2	+10.2(3)	0.26
K4665-3	Avenicum 2	+9.7 (2)	0.10
K9510/46-1	Avenicum 3	+9.6 (3)	0.18
K9510/46-2	Avenicum 3	+10.9 (2)	0.27
KA4117-1	Avenicum 4	+9.6 (2)	0.21
KA4117-2	Avenicum 4	+8.9 (2)	0.16
K4687	Avenicum 5	+10.7 (3)	0.25
K4686	Avenicum 6	+10.6 (2)	0.17
K9915-1	Avenicum 7	+9.2 (3)	0.28
K9915-2	Avenicum 7	+8.7 (3)	0.31
		+9.9 ± 0.7 (12) ^b	

^a Number in parentheses stands for number of replicate analyses.

^b Number of samples.

Table 2. Sulfur isotope data ($\delta^{34}\text{S}$ in ‰ VCDT) of cinnabar from mercury deposits obtained in this study

Almadén (Spain)		Idria (Slovenia)		Monte Amiata (Italy)	
Sample	$\delta^{34}\text{S}$	Sample	$\delta^{34}\text{S}$	Sample	$\delta^{34}\text{S}$
MGL25234	+6.6	MGL51355	+8.2	MGL-Bickel	-1.6
MGL40128-1	+6.2	MGL51357	+5.9	MGL-Bickel	-1.7
MGL40128-2	+5.4	MGL51357	+5.1	MGL-SGAM1	+2.3
MGL25229	+6.3	MGL51361	+8.5	MGL-SGAM2	+2.4
MGL14308-1	+8.8	MGL51361	+9.1	MGL-NM-1	-5.0
MGL14308-2	+8.0	MGL51366	+3.1	MGL-ICMA	-0.8
MGL51356	+0.6	MGL30392	+6.0	MGL-IMP	+0.1
MGL51349	+4.6	MGL30392	+7.7	MGL-NM-2	-7.6
MGL34986-1	+4.4	MGL51478	+1.2	MGL-SGAM3	+0.9
MGL34986-2	+5.1	MGL51478	+1.5		-1.0 ± 3.2
MGL34986-3	+4.6	MGL51478	+6.1		
MGL34986-4	+5.4	MGL51478	+7.0		
MGL34986-5	+7.0	MGL51639	+0.0	Moschellandsberg (Germany)	
+5.6 ± 2.0		MGL51639	-0.9	MGL3499-1	-19.6
		MGL52647	+8.9	MGL3499-2	-15.6
		MGL34995	+1.3		-17.6 ± 2.8
		MGL34995	+0.5		
		MGL34995	+4.1		
		MGL34989	+0.0	Genepy (France)	
		MGL34989	-0.5	MGL58789	-2.2
		MGL34976	+7.1	1 Aupt	-3.5
		MGL34996	+7.6		-2.9 ± 0.9
		MGL34981	+1.0		
		JSID26	+3.8		
			+4.3 ± 3.5		

than $\pm 0.3\text{‰}$ (1 SD). The accuracy of the $\delta^{34}\text{S}$ analyses was checked periodically by analyses of the international reference materials IAEA-S-1 and IAEA-S-2 silver sulfides (-0.3‰ and $+22.7 \pm 0.2\text{‰}$, respectively, values from IAEA-Catalogue and Documents) and NBS-123 sphalerite ($+17.09 \pm 0.31\text{‰}$, value from NIST-Catalogue and Documents).

The average sulfur isotope values for cinnabar in the Roman wall paintings and the mercury deposits were compared by means of *t*-tests using the SAS software (version 9.1, SAS Institute Inc., Cary, NC, USA) and MatLab[®] software package (version 7.2, MathWorks Inc., Natick, MA, USA).

RESULTS AND DISCUSSION

The results of the XRD analyses have shown that the only sulfur-containing phase in the red painting samples from Aventicum was cinnabar. The sulfur isotope ratios and the standard deviation (SD) of the replicate measurements of the 12 cinnabar samples from the wall paintings recovered in Aventicum, Switzerland, are presented in Table 1. The $\delta^{34}\text{S}$ values range between $+8.7$ and $+10.9\text{‰}$ (average ± 1 SD, $+9.9 \pm 0.7\text{‰}$). Table 2 contains the $\delta^{34}\text{S}$ values of cinnabar ore from the Mediterranean region mercury deposits obtained in this study. A set of 47 sulfur isotope ratios for Almadén cinnabar was compiled from published data^{32–35} and the data obtained in this study. The unimodally distributed $\delta^{34}\text{S}$ values range from -1.6 to $+13.0\text{‰}$ ($+6.6 \pm 3.7\text{‰}$, $n = 47$) (Fig. 1). The mode peaks at about $+7\text{‰}$ (median = $+7.0\text{‰}$) and two smaller maxima appears near 0 and $+12\text{‰}$. For the Idria deposit, a set of

187 $\delta^{34}\text{S}$ values was compiled from published data^{36–39} and data from this study. The distribution of these $\delta^{34}\text{S}$ values is summarized as histogram in Fig. 2. The $\delta^{34}\text{S}$ values for cinnabar samples range from -19.1 to $+22.8\text{‰}$ ($+2.2 \pm 6.0\text{‰}$), with an unimodal distribution peaking at about $+3\text{‰}$ (median = $+2.4\text{‰}$). The data sets from Almadén and Idria (Figs. 1 and 2) represent the entire spectrum of syngenetic (e.g., formed contemporaneously with the sedimentary host rock) and epigenetic (e.g., formed by post-depositional processes) cinnabar-containing rock bodies. The important

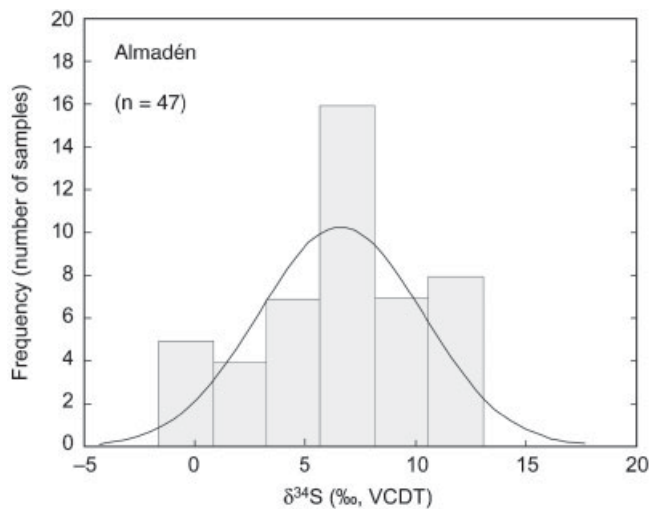


Figure 1. Frequency distribution of $\delta^{34}\text{S}$ values for cinnabar from Almadén deposit, Spain. Data from Rytuba *et al.*,³² Saupé and Arnold,³³ Higuera *et al.*,³⁴ Jébrak *et al.*,³⁵ and this study.

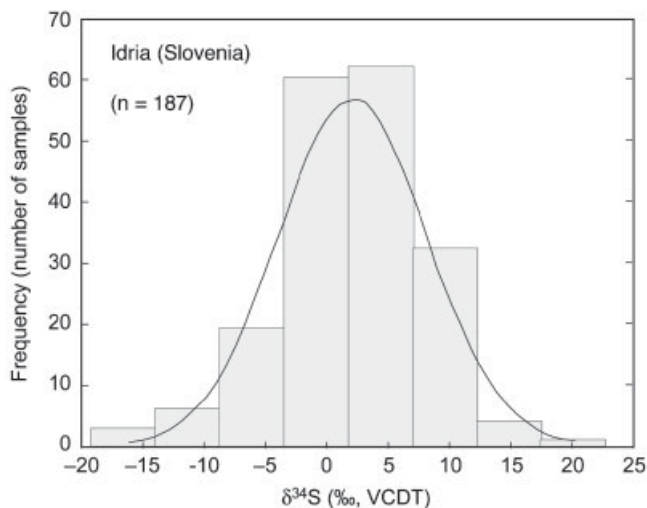


Figure 2. Frequency distribution of $\delta^{34}\text{S}$ values for cinnabar from Idria deposit, Slovenia. Data from Drovenik *et al.*,³⁶ Drovenik *et al.*,³⁷ Lavrič and Spangenberg,³⁸ Palinkaš *et al.*,³⁹ and this study.

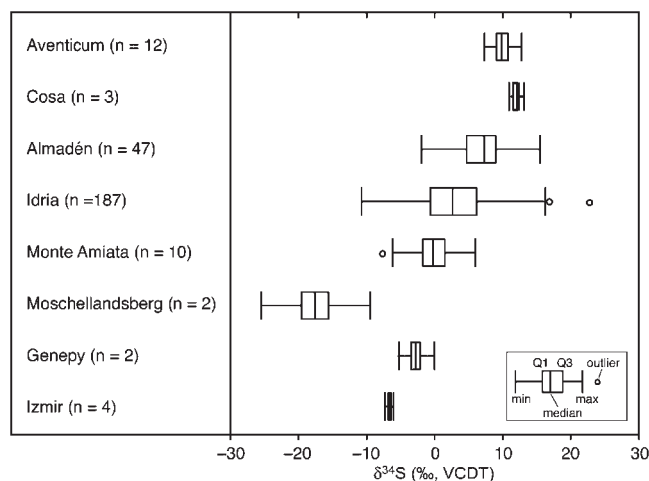


Figure 3. Box plot of $\delta^{34}\text{S}$ values for the cinnabar from the Roman paintings at Aventicum (Switzerland) and Cosa (Italy)¹³ and European Hg deposits, displaying the ranges, 25th (1st quartile, Q1) and 75th (3rd quartile, Q3) percentiles, median, and outliers.

amount of new published sulfur isotope data for cinnabar from Almadén and Idria motivated a reevaluation of the $\delta^{34}\text{S}$ values of cinnabar from frescoes in the House of Diana in Cosa, presented by Damiani *et al.*¹³

We used box plot charts, displaying the ranges, 25th and 75th percentiles (lower and upper quartiles; Q1, Q3), outliers, and median (50th percentile, Q2) to show the spread of $\delta^{34}\text{S}$ values between the cinnabar of Roman wall paintings from Aventicum (Switzerland) and Cosa (Italy) and the Hg ore deposits (Fig. 3). The statistical significance of the difference between the groups of $\delta^{34}\text{S}$ values was determined using a two-tailed Student's *t*-test adjusted after checking by Fisher test whether two samples have equal or different variances (homo- or heteroscedasticity, Table 3). The spread of the cinnabar $\delta^{34}\text{S}$ values of the Roman wall paintings from Aventicum are similar to those from

Cosa, and statistically different from the $\delta^{34}\text{S}$ values of cinnabar from the Hg deposits (Fig. 3, Table 3). The average $\delta^{34}\text{S}$ values for Aventicum ($+9.9 \pm 0.7\text{‰}$) and Cosa ($+11.8 \pm 0.3\text{‰}$) are close to those of Almadén ($+6.6 \pm 3.7\text{‰}$) and Idria ($+2.2 \pm 6.0\text{‰}$), and statistically different ($p < 0.05$) to the other Hg deposits (Monte Amiata, Moschellandsberg, Genepy, Izmir) (Table 3). The beginning of underground mining only in 1490 and the absence of superficial cinnabar exposures in Idria indicate Almadén as the source of cinnabar used for the Aventicum wall paintings. For any signature to be meaningful, its value must be uniform over the dimensions of the studied artifacts and, ideally, show only small variations on orebody and mining district scale. Detailed studies carried out in the Almadén district by Saupé and Arnold³³ showed the variations in $\delta^{34}\text{S}$ within mercury ore blocks to be less than 0.5‰ and less than 2‰

Table 3. Statistical *t*-test comparing the mean of the $\delta^{34}\text{S}$ values of the cinnabar from Roman wall paintings and cinnabar from mercury ore deposits

	α^a	ν^b	F-test ^c	P-value ^d	Accepted H ^e
Aventicum/Cosa (House of Diana)	0.05; 0.001	13	0.2131	0.000014 (0.00086)	HI; HI (HI; HI)
Aventicum/Almadén	0.05; 0.001	57	7.32E-08	0.0033	HI; HO
Aventicum/Idria	0.05	197	5.18E-08	3.64E-31	HI
Aventicum/Monte Amiata	0.05	20	4.00E-05	1.21E-06	HI
Aventicum/Moschellandsberg	0.05; 0.01	12	0.0057	0.0441(3.62E-13)	HI; HO (HI; HI)
Aventicum/Genepy	0.05; 0.01	12	0.5406	0.0168 (4.43E-11)	HI; HO (HI; HI)
Aventicum/Izmir	0.05	23	0.0142	4.36E-18 (2.65E-16)	HI (HI)
Cosa (House of Diana)/Almadén	0.05; 0.01	48	0.0092	2.49E-12 (0.0192)	HI; HI (HI; HO)
Cosa (House of Diana)/Idria	0.05; 0.001	188	0.0035	7.59E-40 (0.0062)	HI; HI (HI; HO)
Cosa (House of Diana)/Monte Amiata	0.05; 0.001	11	0.0122	3.86E-07 (0.000034)	HI; HI (HI; HI)
Cosa (House of Diana)/Moschellandsberg	0.05; 0.01	3	0.0155	0.0424 (0.000294)	HI; HO (HI; HI)
Cosa (House of Diana)/Genepy	0.05; 0.01	3	0.1448	0.0202 (0.000088)	HI; HO (HI; HI)
Cosa (House of Diana)/Izmir	0.05; 0.001	5	0.3011	3.10E-06(5.36E-10)	HI; HI (HI; HI)

^a α = significance level.

^b ν = degree of freedom.

^c Comparison of variance by Fisher test; $F > 1$: equal variance (homoscedasticity); $F < 1$: unequal variance (heteroscedasticity).

^d Probability; for F values relatively close to 1 a second *t* test was performed assuming $F > 1$ (homoscedasticity) and the P-values given in parentheses.

^e Hypothesis: HO = equal mean, HI = different mean; For $P > \alpha$ HO is accepted.

within an outcrop of most orebodies. However, the $\delta^{34}\text{S}$ average values between cinnabar orebodies in Almadén district vary between +0.2 and +13.6‰. Thus, the slight difference between the $\delta^{34}\text{S}$ average values from Aventicum and from Cosa could be explained by cinnabar coming from different Hg-mineralized bodies in the Almadén mine. An additional possible source of heterogeneity is the fact that the cinnabar ore was brought to Rome for processing. The average sulfur isotope composition of the two groups of cinnabar from Roman wall paintings (Aventicum in Switzerland, Cosa in Italy) cannot be statistically differentiated. The identification of not local (exotic) sources for cinnabar found at Aventicum adds substantially to our understanding of regional interaction and trade during the Roman period.

The results presented in this study indicate that the sulfur isotope composition provides further insights on the origin and authenticity of the red pigment produced from cinnabar in archaeological paintings. This approach may have important implications for archaeological, restoration and forensic studies. Very small amounts of sulfide are needed (down to 100 μg , 1 μmol) for sulfur isotope analysis by EA/IRMS, which is relatively fast and inexpensive, and permits a high throughput of samples.

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