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## ARCHAEOMETRIC INVESTIGATIONS ON CINNABAR PROVENANCE AND ORIGIN BY X-RAY POWDER DIFFRACTION: PRELIMINARY DATA

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### *Abstract*

*This study aims to focus on cinnabar extraction and trade routes in the Roman Age, when the pigment had its maximum spread, also to clarify if the practice of mixing sources from different quarries is reliable. X-ray powder diffraction (XRPD) has been used as a preliminary test to underline structural variation connected to cinnabar provenance: data from 14 mineralogical samples, coming from 11 different localities, were compared showing that detectable differences exist in terms of unit cell parameters and volume. The results highlight the potentiality of X-ray diffraction for provenance analysis.*

**Keywords:** *Cinnabar; Red pigment; X-ray powder diffraction; Deterioration; Provenance*

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### **Introduction**

The use of cinnabar, *i.e.* vermilion, as a pigment is first historically documented in Theophrastus (315 A.C.). It is thanks to its work that the term “cenobrium” starts spreading in the occidental culture.

Aside from the written records, several artefacts give evidence of an earlier use of cinnabar as a brilliant and vivid red pigment, although it reached its peak in the Roman culture. In his masterpiece “De Architectura” (about 15 A.C.), Vitruvius suggests the presence of many workshops in Rome for the pigment production, probably mixing together cinnabar coming from different quarries to obtain the best dyes. Reported localities are the Roman province “Hispania Baetica” (almost surely corresponding to Almadén, Spain), Ephesus and Colchid regions. No references exist for closer quarries, such as Monte Amiata (Italy) or Idrija (Slovenia). Therefore, the problem of provenance of vermilion on Roman paintings is still an open question. Trace element analysis has been applied in recent years [1, 2], the best results being obtained with instruments not easily available, especially for their high price, and with low reliability. Therefore, it can be claimed that at present there is no reliable way to determine the provenance of vermilion samples. Thus, the aim of this work is to test the potentiality of a more common technique, X-ray powder diffraction (XRPD) coupled with Rietveld refinement, to provide valuable information to help answering this question through the analysis of small amounts of mineral samples from different known localities.

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## Materials and Methods

Fourteen cinnabar mineralogical samples (Table 1) have been selected from the collection of the Mineralogical Museum of the University of Rome (MMUR), in order to analyse at least one sample from eleven different mining localities (Almadén, Spain; Lucca, Grosseto and Monte Amiata, Italy; Idrija, Slovenia; Carnia, Austria; Moschellandsberg, Germany; Avala, Serbia; Nikitowska, Russia; Honan, China). These mines have been chosen for their high probability of being used as a primary source in the production of vermilion, based on their distance from Rome and from historical references. The only exception is represented by the sample from Tsar Lien Mine, Honan, China, specifically added to obtain a feedback from a non-European mine.

Three samples come from the largest district, Almadén (Spain), which is known for its complexity, showing the coexistence of 11 deposits in a restricted area [3]. The purpose is to test our experimental procedure efficiency not only for different quarries but also for samples from the same mining district. This is also valid for sample GR from Grosseto, added at a later stage of the research as a donation from a private collector.

**Table 1.** List of the analyzed cinnabar samples

Sample	Provenance	Museum Inventory	Description
AS54	Almadén, Spain	1182/54	In big crystals with quartz on the pyritiferous rock. Small amounts of native mercury. Big sample.
AS60	Almadén, Spain	1188/60	Crystals and leaves, with crystallized quartz, in a pyritiferous rock.
AS76	Almadén, Spain	1204/76	In leaves with massive quartz in a pyritiferous rock.
C34	Carnia, Austria	1162/34	Lamellar, massive; with white spathic calcite in a grey blackish calcareous.
CH124	Tsar Lien Mine, Honan, China	22367/124	Twinned crystals diving on crystallized quartz; partially covered by a limonite patina. Big sample, 1910
GE46	Moschellandsberg, Germany	1174/46	Massive on a red or brown kaolinitic rock.
GR141	Cerretto Piano, Grosseto, Italy	24048/141	Ing. Testa's donation, 1945.
GR	Cerretto Piano, Grosseto, Italy	Private Collection	Pedone Collection, Casteldelpiano (GR), Italy.
I24	Idrija, Slovenia	1152/24	Granular in a bituminous pyritiferous schist (deteriorated).
LU10	Val di Castello, Lucca, Italy	1138/10	Lamellar within the quartz forming nuclei in a white micaschist (partially yellow for the presence of limonite).
MA2G	Sele Mine, Castell' Azzara, Monte Amiata, Italy	Not catalogued	Microcrystals, Galvani Collection.
R110	Nikitowska, Charkov railway station, Russia	18878/110	Crystallized with yellow limonite. Acquired from Th. Schuchardt, 1889.
S113	Avala, Serbia	19289/113	In crystals {111} on crystallized quartz forming veins in the matrix. Big sample acquired from L. Eger, Vienna, 1889.
U37	Rosenau, Romania	1165/37	Lamellar and massive with calcite, (110) (211) dolomite (100), massive quartz and pyrite, both in crystals (210) (111) (100) and massive.

Small fragments of crystals, carefully picked-up from each sample, were crushed with an agate mortar and pestle in deionized water. Each resultant powder was deposited onto a flat sample holder, after admixture with silicon NBS640c as internal standard, for X-ray powder diffraction analysis.

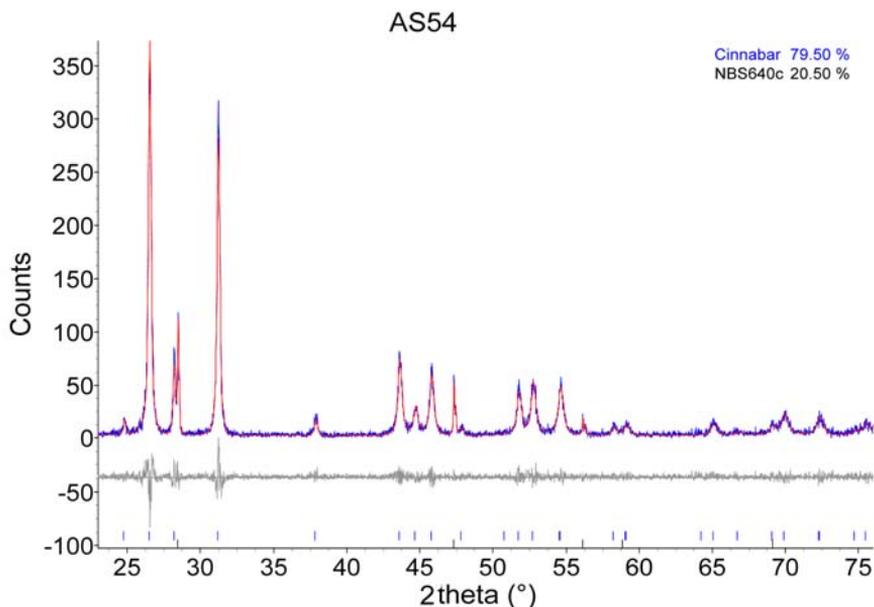
XRPD data were collected at the Department of Earth Sciences of Sapienza University of Rome, using a  $\theta/2\theta$  Bragg-Brentano Seifert MZ IV diffractometer. The operating conditions were 40 kV and 30 mA. Samples were analysed in the  $23\text{-}76^\circ$   $2\theta$  range, with a step scan of  $0.02^\circ$   $2\theta$  and a counting time of 3s. A preliminary careful scrutiny of the various diffraction patterns was performed, using DIFFRAC<sup>PLUS</sup> 10.0 [4] software and the Powder Diffraction File (PDF) database, in order to identify the possible occurrence of impurities.

Finally, the sample from Idrija, I24, was analysed with two Bruker AXS D8 instruments (Focus and Advance), to assess the possibilities of high-quality refinements in this archaeometric topic. Both diffractometers operate in transmission mode on capillaries, with an overall counting time of 2 days per pattern.

## Results and Discussion

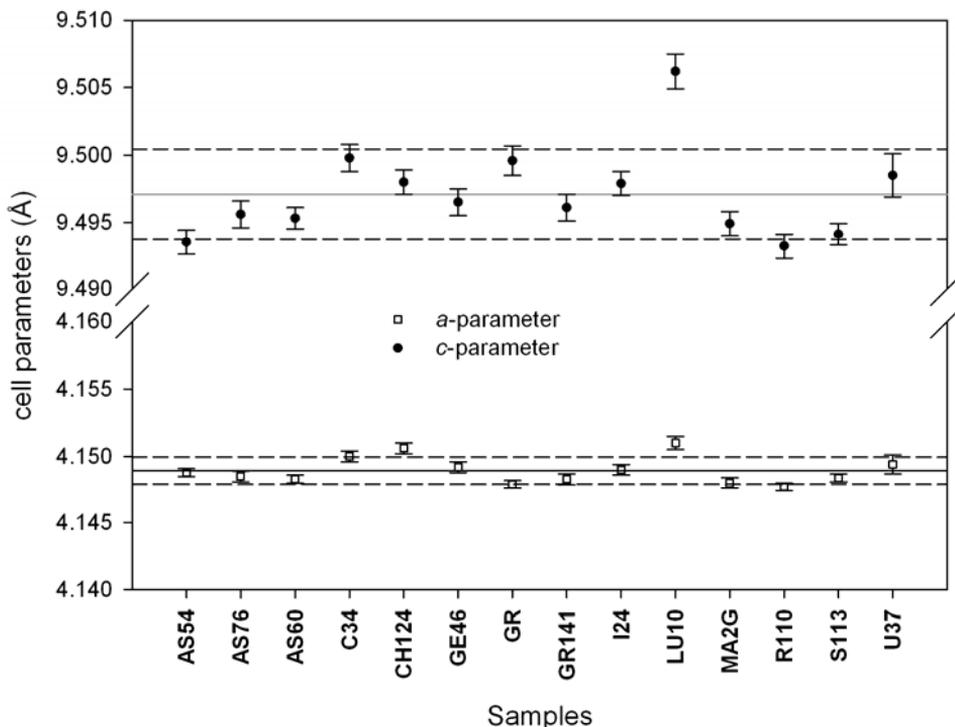
XRPD shows that almost all powdered cinnabar samples are pure, the only exceptions being represented by samples C34 from Carnia, GR from Grosseto, Italy, containing traces of quartz, albite, and muscovite, and sample MA2G from Monte Amiata, Italy, in which minor amounts of both dolomite and calcite have been identified.

Diffraction data were evaluated, by the Rietveld method, using Topas V.4.2 [5] for cell parameters and volume extraction. No structure refinements were performed due to the limited angular range explored. Structural data were taken from [6]. An example of the conventional Rietveld plots is reported in Fig. 1.



**Fig. 1.** Conventional Rietveld plots (blue line: experimental; red line: calculated; grey line: difference) of the refinement of the diffraction pattern collected for sample A54. The vertical bars represent the position of calculated Bragg reflections (blue: cinnabar; black: silicon).

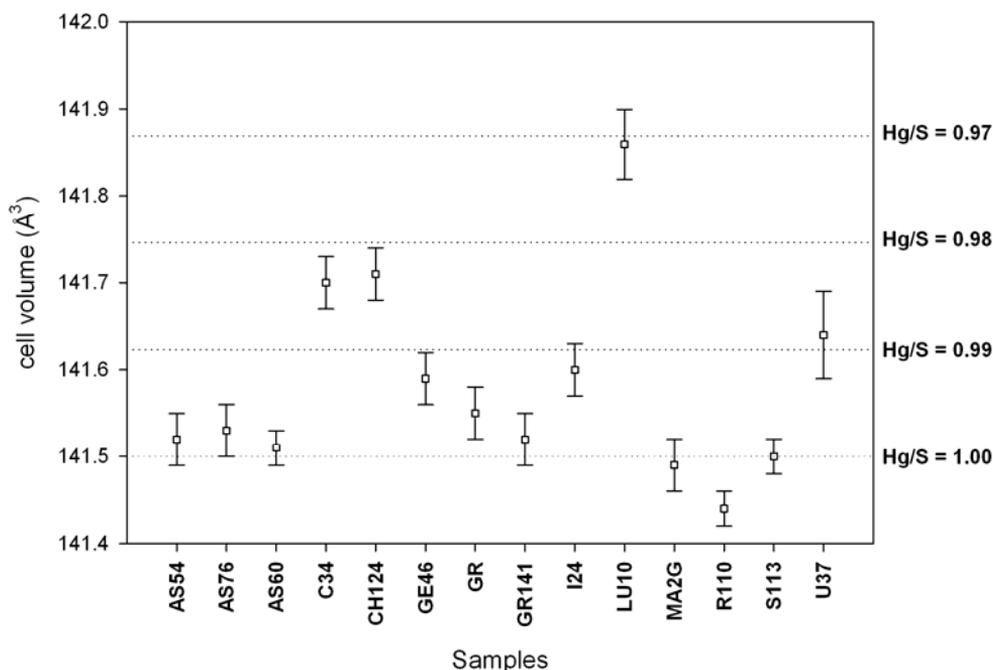
The calculated cell parameters of the various samples have been compared to detect differences to be possibly related to provenance. Indeed, unit cell parameters variation can be substantially attributed to two factors: compositional variability or different thermobaric conditions occurring during crystallization. The first factor refers to cation/anion substitution processes or/and defectivity occurring within the cinnabar structure. In fact, it has been shown that a deviation of the Hg/S ratio from the ideal value of 1.00 is responsible for detectable variation of cell parameters [7, 8]. The second factor includes the thermodynamic parameters, *i.e.* temperature, pressure, influencing crystallization, and affecting microstructural parameters as micro-strain [9] as well. In particular, micro-strain can be extracted from profile fitting of diffraction patterns collected up to a high  $\sin\theta/\lambda$  value and, therefore cannot be reliably obtained from our present preliminary data set. In the case of the sample from Almadén, AS60, a room temperature XRPD pattern was collected, in the 20-140° 2 $\theta$  angular range, on the same parallel-beam diffractometer used to undertake the high temperature experiment. From the Rietveld refinement the cell parameters  $a = 4.1483(1)$  Å,  $c = 9.4953(4)$  Å, volume = 141.51(1) Å<sup>3</sup> were obtained [6] almost coincident with those from the data collected on the conventional diffractometer. According to Potter and Barnes [7], those cell parameters are consistent with an Hg/S ratio very close to 1.00. Such values were used to normalize the cell parameters of all samples in order, to compensate for small systematic errors possibly occurring because of the limited 2 $\theta$  angular range investigated. Finally, the normalized data have been plotted for comparison purposes (Figs. 2-3).



**Fig. 2.** Cell parameters of all investigated samples. Horizontal lines represent respectively: a) solid line: mean value of the data set; short-dashed lines: confidence interval (95% level).

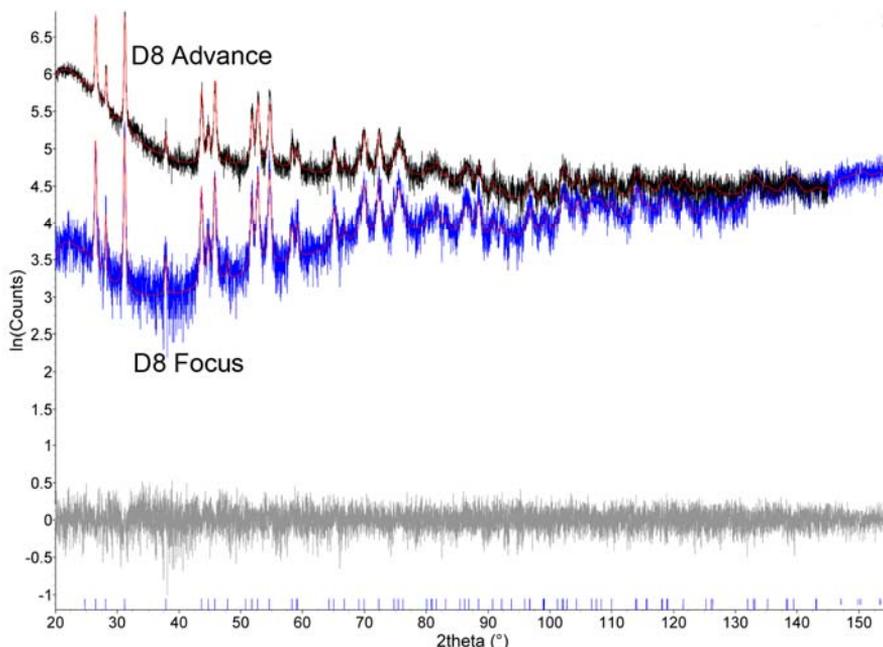
The graphs show that cell parameters and volume of the various samples are characterized by a moderate variability. However, samples from the same localities *i.e.* Almadén and Grosseto, show very small differences, both in terms of unit cell parameters and volume. Besides, sample LU10 from Lucca, Italy, is characterized by an expanded unit cell as compared to that of the remaining samples. By evaluation of reference data [7], the regression equation, relating Hg/S ratio and unit cell volume,  $V (\text{Å}^3) = 153.8(5) - 12.3(5) x [\text{Hg/S ratio}]$ , has been devised and graphically superimposed to figure 3.

The dotted lines represent compositional variations, at the 0.01 level, of the Hg/S ratio. According to the above-cited relationship, 11 of the 14 samples should approximately lie in the 0.99-1.00 Hg/S ratio compositional field. Differently, the volume of sample LU10 is consistent with an Hg/S ratio of ca. 0.97. Besides, samples C34 from Carnia, Austria, and CH124, from China should be characterized by an intermediate Hg/S ratio. Analogous compositions have been calculated using the regression equations  $a (\text{Å}) = 4.264(5) - 0.116(5) x [\text{Hg/S ratio}]$  and  $c (\text{Å}) = 9.787(12) - 0.292(13) x [\text{Hg/S ratio}]$  similarly devised from reference data [7]. Encouraged by those promising preliminary results, we are currently recollecting the XRPD data, using the same experimental set up previously used to obtain data of very high quality of other pigments [10, 11]. The instrument, a parallel-beam Bruker AXS D8 Focus, operates in transmission mode on capillary sample in Debye-Scherrer geometry, using  $\text{CuK}\alpha$  radiation.



**Fig. 3.** Calculated unit cell volumes of all investigated samples. Dotted lines represent compositional variations, at the 0.01 level, of the Hg/S ratio calculated from the regression equation  $V (\text{Å}^3) = 153.8(5) - 12.3(5) x [\text{Hg/S ratio}]$ .

It is fitted with a solid-state detector and it is especially suitable for the extraction of more accurate cell parameters and microstructural parameters by significantly extending the accessible  $\sin\theta/\lambda$  range to ca.  $0.6 \text{ \AA}^{-1}$ . In principle, microstructural parameters could be able to provide further evaluable variables for provenance identification. The almost complete removal of the parasitic effects of preferred orientation renders those data perfectly suited for full structural refinements of high quality [12] possibly directly proving deviation of the Hg/S ratios from unity. An example of a combined Rietveld refinement of two data sets for sample I24 is reported in Fig. 4.



**Fig. 4.** Conventional Rietveld plots (blue and black lines: experimental; red lines: calculated; grey line: difference) of the refinement of the diffraction patterns collected for sample I24 with two instruments (Bruker AXS D8, Focus and Advance) both operating in transmission mode on capillaries (overall counting time of 2 days/pattern).

## Conclusions

Present preliminary data have demonstrated that conventional XRPD coupled to Rietveld refinements is capable to individuate differences in unit cell parameters and volume among cinnabar samples of different provenance. Those differences have been possibly attributed to variations of the Hg/S ratio that have been shown to produce significant modifications of the unit cell parameters.

Three of the fourteen analysed samples of cinnabar show fairly large differences of the cell parameters that could be used as an identification tool. Thus, it is desirable to plan further XRPD experiments aimed at increasing the quality of the diffraction patterns for extraction of microstructural parameters as well that, in principle, could be able to provide valuable extra

information. However, a severe drawback is represented by the relevant increase of the collection time for a single pattern (> 2 days), due to the very large linear absorption coefficient of cinnabar that forces the preparation of the samples in capillaries as thin as 0.3 mm of diameter. Moreover, XRPD data should be collected from a statistically significant sampling, increasing the number of samples from the same locality, and complemented by chemical analyses at the trace level. Only in this case we expect to be able to obtain a combined set of parameters suggesting a univocal identification of the provenance.

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