Characterization of Pararealgar and Other Light-Induced Transformation Products from Realgar by Raman Microspectroscopy

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Characterization of Pararealgar and Other Light-Induced Transformation Products from Realgar by Raman Microspectroscopy

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Naturally occurring arsenic sulfide minerals are brightly colored and consequently have been used as artists' pigments since ancient times. Orpiment, As_2S_3, is yellow and is often found associated with realgar, As_4S_4, which is red to red-orange. When exposed to sunlight, unprotected realgar develops a surface coating of friable yellow material that, until recently, had generally been assumed to be orpiment. However, it has been determined that this material is pararealgar, a light-induced polymorph of realgar. We have identified pararealgar in a major work by the Renaissance master, Tintoretto. The accurate identification of pigments in artistic and historic works is of great importance for determining the construction, history, and future preservation of these works. We report here the characterization by Raman microspectroscopy of pararealgar and the various intermediate species involved in the light-induced transformation of realgar to pararealgar. The relative merits of Raman microspectroscopy and X-ray diffraction for the accurate and efficient characterization of these arsenic sulfide compounds are discussed.

The identification and characterization of pigments found in artistic and historic works is an important aspect of the care and preservation of museum collections, yielding information on the artists' materials and techniques, authenticity, previous restoration history, and present condition of works of art. *The Dreams of Men*[1] (ca. 1547), a painting by the Venetian artist Jacopo Robusti (1518−1594), known as Tintoretto, recently underwent extensive study and conservation[2] in the Conservation Services Laboratory at the Detroit Institute of Arts. The large ceiling painting, which is over 12 ft long and 7 ft wide, depicts the interaction of human dreams, fortune, and the cycles governing heaven and earth through complicated mythological and astrological symbols. Extremely small paint samples, with surface areas of 0.5 mm[2] or less, were removed from a few carefully selected sites on the painting. Upon sectioning, between 5 and 15 discernable layers of varnish, glaze, paint, and glue were exposed in the resulting cross section. Analysis of the materials in each layer revealed the sequence in which paint layers of different colors and opacity were applied to create the desired overall tonal effect.

During our study of one small fragment removed from *The Dreams of Men*, elemental analysis[3] showed the presence of arsenic and sulfur in the top yellow paint layer. We initially interpreted this information as indicating that the artist had used orpiment, As_2S_3, a yellow pigment known to have been used by Venetian painters during the Renaissance. The few yellow pigment particles in the layer were carefully isolated and subjected to X-ray powder diffraction analysis, which revealed that the material was not orpiment but rather was pararealgar, a naturally occurring yellow mineral characterized only recently. Pararealgar is a light-induced polymorph of the red mineral realgar, As_4S_4, that readily forms on surfaces of realgar exposed to light. The discovery of an alteration product of a well-known pigment in this painting by Tintoretto raises an interesting question: When did the alteration occur? Specifically, did the artist initially use pararealgar as a yellow pigment (possibly mistaken for orpiment), or was the area originally painted red with realgar that subsequently transformed to yellow pararealgar? Unfortunately, no studies have been published to date on the light-induced transformation of realgar contained in oil or any other paint medium.

Whereas only a few particles of pararealgar were removed from *The Dreams of Men*, large amounts of relatively pure pararealgar were easily obtained from mineralogical specimens of realgar that had been exposed to light. We describe here the results of our study using the technique of Raman microspectroscopy to characterize pararealgar and the intermediate species involved in its formation from realgar. Raman microspectroscopy is ideally suited for the identification and study of many artists' pigments in that it can probe microscopic quantities of material, or even single crystals of individual components within a mixture, thereby reducing the size of samples that must be removed from a valuable work of art.

BACKGROUND

Raman Microspectroscopy. Raman spectroscopy has long been used for the identification of minerals.[4] However, because of the low sensitivity and relatively large amount of sample

(1) Jacopo Tintoretto, *The Dreams of Men*, ca. 1547; oil on canvas. The Detroit Institute of Arts, Detroit, MI; City of Detroit Purchase (23.11).

(2) Moreno, J. *AIC Paintings Specialty Group Postprints*; Papers Presented at the 23rd Annual Meeting of the American Institute for Conservation, St. Paul, MN, June 10, 1995; American Institute for Conservation of Historic and Artistic Works: Washington, DC (in press).

(3) Elemental analysis of paint cross section performed on an Amray 1830I scanning electron microscope equipped with an EDAX PV9800 energy-dispersive X-ray analyzer.

(4) Carmichael, R. S., Ed. *Handbook of Physical Properties of Rocks*; CRC Press Inc.: Boca Raton, FL, 1982; Vol. 1, pp 355−359.

required for analysis, it has generally not been of much utility for studying the thin layers of pigments present in art objects. These problems have, for the most part, been overcome by the development of Raman microspectroscopy,[5] in which a microscope coupled to a Raman spectrometer is used to probe the sample. Raman microspectroscopy is capable of nondestructive in situ analysis with a high degree of specificity, excellent spatial resolution (on the order of 1 μm or less), and relatively high sensitivity (samples on the order of picograms can be successfully analyzed).[5,6]

In the materials analysis of works of art, the removal of samples of any size is generally undesirable. Raman microspectroscopy has been used to analyze pigments in situ in illuminated manuscripts, where the paint layer is so thin that it would be impossible to remove a sample without causing considerable damage to the object.[7,8] However, most objects cannot be placed safely under a microscope for in situ analysis. Painted surfaces often are built up by the successive application of layers of paint, each layer ranging from 2 to 50 μm in thickness and possibly containing a mixture of several different pigments. Therefore, if a sample can be removed from the object, a detailed analysis of the layer structure can be performed by using the high spatial resolution of the Raman microscope to study individual pigment particles isolated from each layer. Raman microspectroscopy has been shown to be especially effective in the identification of pigments derived from natural mineral sources, such as lapis lazuli (ultramarine), azurite, malachite, and cinnabar (vermillion).[6]

Light-Induced Transformation of Realgar to Pararealgar. Realgar (As_4S_4) is a red, naturally occurring arsenic(II) sulfide mineral, often found with the yellow arsenic(III) sulfide mineral, orpiment (As_2S_3). On surfaces exposed to light, realgar is known to develop a coating of a friable bright yellow material.[9] To explain this phenomenon, it has been stated that realgar undergoes a light-induced decomposition to yellow orpiment with subsequent oxidation to colorless arsenic oxide, arsenolite (As_4O_6).[9-12] However, this statement appears to be based on visual examination alone, for while the light-induced formation of arsenolite from realgar has been confirmed,[13] no spectroscopic evidence of the formation of orpiment could be found in the literature. X-ray diffraction (XRD) studies have shown that the yellow material is, in fact, pararealgar, a polymorph of realgar.[14]

Pararealgar was first identified as a distinct mineralogical species by Roberts et al. in 1980,[14] and the crystal structure was published by Bonazzi et al.[15] in 1995. It is not surprising to find earlier reports in the literature indicating that pararealgar had been observed but not identified as such. For example, Cahoon[16] and Keneman et al.,[17] in separate studies on the effect of light exposure on arsenic sulfides, each reported an XRD powder pattern of a transformation product they could not identify: the patterns clearly match that of pararealgar. Interestingly, following intense light exposure of a realgar sample, Keneman et al. also noted the appearance of lines corresponding to arsenolite in addition to the transformation product. In a study by Stodulski et al.[18] of a realgar sample removed from the ancient Persian city of Persepolis, the XRD powder pattern of a light-irradiated sample could, at that time, be identified only as an unknown photochemical product. As a final example, in their paper characterizing and naming pararealgar, Roberts et al. state: "Owing to the similar physical appearance and mode of occurrence of the two minerals, pararealgar has been misidentified as orpiment on several geological specimens at the Geological Survey of Canada."[14] Clearly, the misidentification of pararealgar as orpiment, or its identification simply as an "unknown photochemical product", has occurred repeatedly over the past several decades.

The misidentification of pararealgar as orpiment certainly has not been limited to mineralogical specimens. In the study of artists' materials and their methods, it has generally been assumed that yellow arsenic-containing pigments are orpiment and that red or orange arsenic-containing pigments are realgar. However, as demonstrated by our findings in *The Dreams of Men*, pararealgar has begun to be recognized in artistic works.[19]

As_4S_4 Polymorphs. There are several known As_4S_4 polymorphs. Natural realgar is a low-temperature phase termed α-As_4S_4. A metastable high-temperature phase, termed β-As_4S_4,[20] can be synthetically produced by heating stoichiometric amounts of As and S above the transition temperature, 252 °C. The β phase can also be produced by heating natural low-temperature phase realgar above the transition temperature (but below the melting point, 306 °C) for ~40 days.[21] Pararealgar is a light-induced polymorph of both the high- and low-temperature phases of realgar. A second light-induced phase, termed χ, a precursor to pararealgar, has recently been identified.[22] The literature also contains reports of two synthetically produced phases, named $As_4S_4(II)$[23] and γ-As_4S_4,[24] which have been shown to be the same as pararealgar.[15,22]

All three phases, α-As_4S_4, β-As_4S_4, and pararealgar, are made up of discrete, covalently bonded As_4S_4 molecules held in a lattice by van der Waals forces.[15,25-27] The high- and low-temperature phases have the same molecular structure, illustrated in Figure

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(16) Cahoon, B. G. In *Research of Chemistry and Physics of Inorganic Systems under Extreme High Pressure and Temperature;* Hurlburt, C. S., Ed.; Final Report, Contract AF 19 (604)-7319, prepared for Office of Aerospace Research; Air Force Cambridge Research Laboratories, USAF: Bedford, MA, 1965; pp 42−52.

(17) Keneman, S. A.; Bordogna, J.; Zemel, J. N. *J. Appl. Phys.* **1978**, *49*, 4663−4673.

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(19) Corbeil, M.-C.; Helwig, K. *Stud. Conserv.* **1995**, *40*, 133−138.

(20) Earlier papers generally refer to the low-temperature phase of realgar as β-As_4S_4 and the high-temperature phase as α-As_4S_4, while more recently the opposite notation is generally used. We will adopt the more recent convention for our discussions here; that is, that the low-temperature phase is designated as α-As_4S_4 and the high-temperature phase as β-As_4S_4.

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(22) Douglass, D. L.; Shing, C.; Wang, G. *Am. Mineral.* **1992**, *77*, 1266−1274.

(23) Kotoglu, A. *Z. Anorg. Allg. Chem.* **1976**, *419*, 176−184.

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(26) Mullen, D. J. E.; Nowacki, W. *Z. Kristallogr.* **1972**, *136*, 48−65.

(27) Porter, E. J.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1972**, 1347.
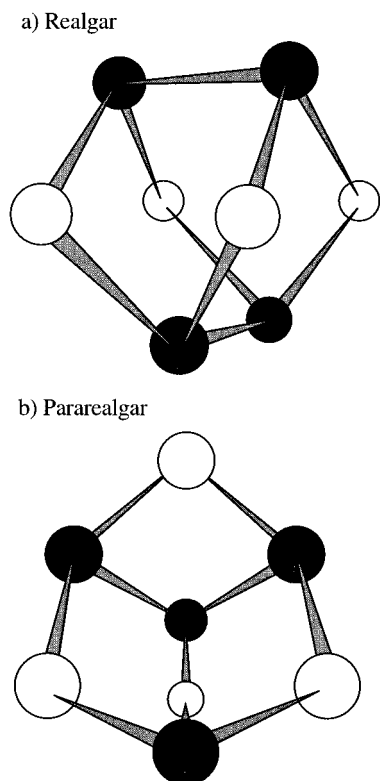
a) Realgar

b) Pararealgar

Figure 1. (a) Structure of As_4S_4 molecules in both the α and β phases of realgar. The low-temperature α phase is monoclinic, with unit cell parameters $a = 9.325$ Å, $b = 13.571$ Å, $c = 6.587$ Å, and $\beta = 106.38°$.[26] The high-temperature β phase is also monoclinic, with $a = 9.957$ Å, $b = 9.335$ Å, $c = 8.889$ Å, and $\beta = 102.48°$.[27] (b) Structure of As_4S_4 molecules in pararealgar. Pararealgar is also monoclinic, with $a = 9.909$ Å, $b = 9.655$ Å, $c = 8.502$ Å, and $\beta = 97.29°$.[15] ●, Arsenic; ○, sulfur.

1a. In these phases, the arsenic atoms are arranged in a tetrahedron and the sulfur atoms in a square bisecting one of the C_2 axes of the arsenic tetrahedron.[26,27] All four As atoms are in equivalent environments, and the molecule exhibits overall D_{2d} symmetry. The main structural difference between the α and β phases is the way they are packed in the lattice, evidenced by their different unit cell parameters (listed in the caption to Figure 1). The transition between α and β, therefore, involves only the breaking of van der Waals bonds and rearrangement of the As_4S_4 molecules.

While the cell parameters of pararealgar are similar to those of the high-temperature β phase, the structures are clearly quite different. The structure of pararealgar, illustrated in Figure 1b, does not exhibit a high degree of molecular symmetry: there are three different As atom environments, and the only symmetry element present is a pseudo-mirror plane.[15] The conversion of realgar to pararealgar clearly must involve the breaking and reforming of As−As and As−S bonds.

There is some contradictory evidence in the literature regarding the light-induced transformation of realgar. In particular, samples of realgar from Mina Alacrán, Pampa Larga, Chile, containing the high-temperature phase did not transform when exposed to light.[28] Notably, this appears to be the first and only mention in the literature of naturally occurring high-temperature phase realgar, reflecting its rarity. It has been postulated that the presence of the high-temperature phase, having lattice

parameters similar to those of pararealgar, might have precluded the formation of pararealgar.[22] However, subsequent studies have shown that the molecular structure of pararealgar is actually quite different from that of the high-temperature phase (see Figure 1). Furthermore, it has been shown[22,27] that both the high- and low-temperature phases undergo transformation to pararealgar. The question as to why no transformation was observed in the Mina Alacrán samples remains unanswered.

EXPERIMENTAL SECTION

A large specimen of natural realgar from Manhattan, NV, on display near a window since 1967 in the Karl E. Limper Geology Museum, Department of Geology, Miami University, Oxford, OH, exhibited a spectacular coating of bright yellow material. The yellow material had been periodically removed, but it always quickly reformed.[29] Samples from this specimen were collected simply by lightly brushing the surface. Underlying the yellow material was a dark red crystalline material, some crystals of which were also collected during the sampling and subsequently separated and isolated. Upon microscopic examination, it was apparent that the yellow material formed as flakes and consisted of more than one component. On many of the yellow flakes, spots of an orange material were observed to be attached to one side, and a thin layer of a colorless or white material was attached to the other. The significance of this "layered" structure will be discussed in the next section. Mineral specimens containing untransformed natural realgar (stored in darkness) and orpiment were also obtained. Small single crystals of realgar and orpiment were removed from the specimens, placed on glass microscope slides, and analyzed without further preparation.

X-ray diffraction analysis was performed using a Philips PN 3550 vertical goniometer equipped with a Cu Kα radiation source operated at 40 kV, 20 mA. The powder samples were mounted in collodion on an ordinary glass microscope slide. Diffraction patterns were recorded on a strip chart recorder, and the peak heights were used to determine the relative line intensities.

Raman spectra were obtained with a Renishaw Ramascope System 2000, equipped with a helium−neon (632.8 nm) laser excitation source, an Olympus BH2 microscope, a single spectrometer (250 mm focal length, 20 μm slit width), and a Peltier-cooled CCD detector. A more detailed description of the spectrometer and its operation can be found elsewhere.[30] The laser power at the sample for all spectra presented here was 0.6 mW, focussed using a 20× objective to a spot size ~4.5 μm in diameter. Exposure times for all spectra were on the order of 1.5−2.5 s. The same samples that had been analyzed by XRD were subsequently analyzed by Raman microspectroscopy, and, to serve as a control, Raman spectra of portions of the original sample not subjected to X-ray analysis were also obtained. All samples were placed on glass microscope slides and studied without further preparation.

RESULTS AND DISCUSSION

XRD and Raman Analysis of Red Crystals. The dark red crystals underlying the yellow flakes on the light-irradiated realgar sample were identified, on the basis of their XRD pattern, as the

(28) Clark, A. H. *Am. Mineral.* **1970**, *55*, 1338−1344.

(29) Mr. Joe Marak, curator, Karl E. Limper Geology Museum, Department of Geology, Miami University, Oxford, OH, personal communication, June 1995.

(30) For a full discussion of the capabilities of the spectrometer, see: Williams, K. P. J.; Pitt, G. D.; Smith, B. J. E.; Whitley, A.; Batchelder, D. N.; Hayward, I. P. *J. Raman Spectrosc.* **1994**, *25*, 131−138.
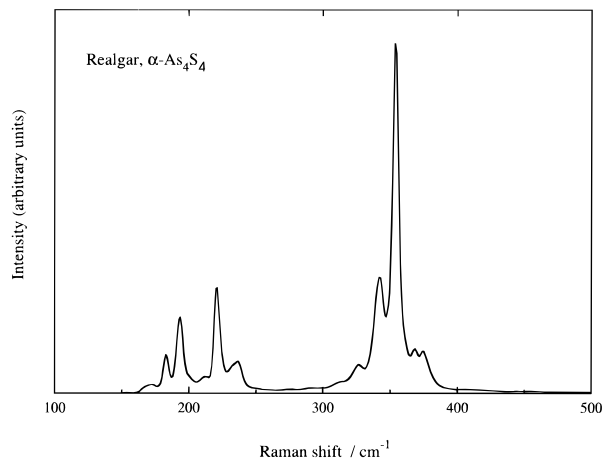
Figure 2. Raman spectrum of red crystals from realgar sample. This spectrum is identified as that of the low-temperature phase of realgar, α-As$_4$S$_4$.

Figure 3. Raman spectrum of yellow material removed from surface of light-irradiated realgar sample. The material is identified as pararealgar.

Figure 4. Raman spectrum of orpiment.

low-temperature phase of realgar, α-As$_4$S$_4$.[31] The Raman spectrum obtained from these crystals is presented in Figure 2, and the peak positions and relative intensities are listed in Table 1. This Raman spectrum agrees very well with previously published spectra of realgar[27,32] and also with the Raman spectrum we obtained from the sample of untransformed natural realgar, confirming the assignment made on the basis of the XRD data. Raman spectra obtained from samples that had previously been subjected to XRD analysis were identical to those of samples that had not, demonstrating that the realgar was not altered by exposure to X-radiation during the XRD analysis.

XRD Analysis of Yellow Flakes. The X-ray powder diffraction pattern of the yellow flakes (and inseparable orange and colorless/white material) is presented in Table 2. Since this sample contains a mixture of materials, the XRD pattern must be deconvoluted into its individual components. The diffraction pattern of pararealgar is clearly evident within our pattern. The lines not attributable to the yellow pararealgar are assumed to be due to the orange and colorless/white material.

The high-temperature β phase is described as being more yellow than the red low-temperature phase,[28] and although the color of the χ phase was not noted,[22] since it is an intermediate between red realgar and yellow pararealgar it is reasonable to assume that it is intermediate in color as well. Therefore, we must initially consider both the χ and β phases as possible identities for the orange material. The reported XRD patterns of these two phases are quite similar, each accounting reasonably well for most of the lines in our pattern not attributable to pararealgar (see Table 2). The XRD pattern alone, therefore, is not sufficient to definitively distinguish between these two species.

Arsenolite is colorless or white, and its presence in our sample is suggested by the XRD line at 6.36 Å and the anomalously high intensity of the line at 3.19 Å. Arsenolite was conclusively identified by Keneman et al. on films of polycrystalline As$_x$S$_x$ subjected to intense light exposure.[17] They determined that the As$_4$O$_6$ crystals were preferentially oriented in the (111) direction, giving rise to the strongest reflections along the (111) and (222) directions, corresponding to lattice spacings of 6.394 and 3.195
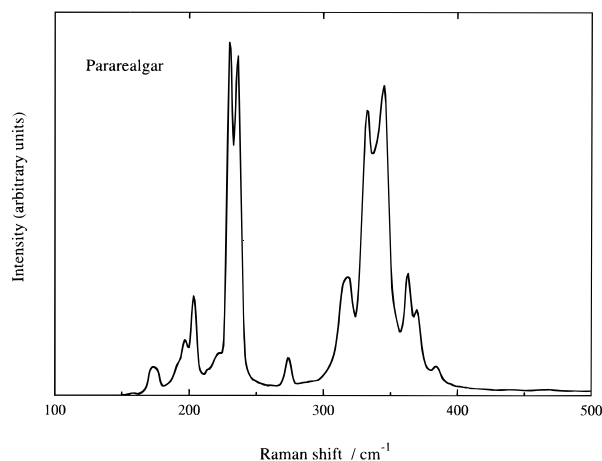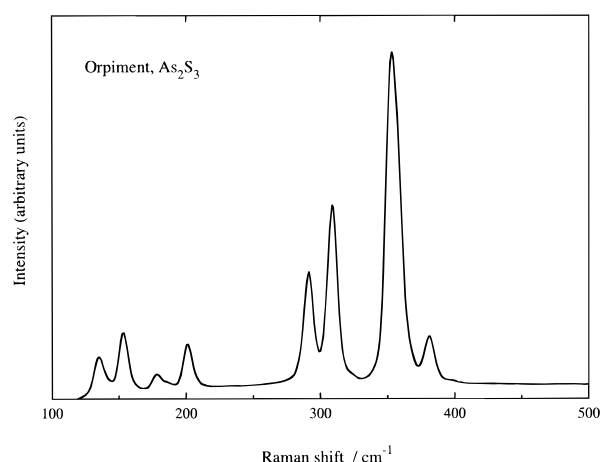
Å, respectively. This is in complete agreement with our XRD results, further indicating that arsenolite is present in our sample.

Raman Microspectroscopic Analysis of Yellow Material. Although the yellow, orange, and colorless/white materials could not be physically separated for XRD analysis, we were able to optically isolate them with the Raman microscope for spectroscopic analysis. The Raman spectrum of the yellow pararealgar is presented in Figure 3; the peak positions and relative intensities are listed in Table 1. This spectrum represents the first reported Raman spectrum of pararealgar. The Raman spectrum of pararealgar is easily distinguishable from that of untransformed realgar (Figure 2), and also from that of orpiment (Figure 4), for which it has often been mistaken. The Raman spectrum we obtained from the yellow material removed from *The Dreams of Men* was identical to the spectrum shown in Figure 3, confirming that the material was pararealgar.

The Raman spectrum of pararealgar is characterized by a pair of strong peaks near 230 cm^{-1} and a grouping of four distinguishable peaks centered at about 330 cm^{-1}. In comparison to the Raman spectrum of realgar, the pararealgar spectrum has a greater number of bands of strong or medium intensity, reflecting the reduced molecular symmetry of pararealgar with respect to realgar.

The assignment of Raman bands in molecular solids is complicated by the breakdown of selection rules: at best, only general assignments of groups of bands can be made. Forneris,[32]

(31) The X-ray powder diffraction pattern for natural, low-temperature realgar, α-As$_4$S$_4$, is listed under JCPDS 24-77.

(32) Forneris, R. *Am. Mineral.* **1969**, *54*, 1062−1074.

Table 1. Peak Positions and Relative Intensities[a] of Raman Spectra

red (α-As$_4$S$_4$) (Figure 2)		yellow (pararealgar) (Figure 3)		orpiment (As$_2$S$_3$) (Figure 4)		orange (χ phase) (Figure 5a)		orange (χ phase + pararealgar) (Figure 5b)	
cm^{-1}	I_{rel}	cm^{-1}	I_{rel}	cm^{-1}	I_{rel}	cm^{-1}	I_{rel}	cm^{-1}	I_{rel}
				135	m				
				154	m				
						166	w		
172	vw	173	w						
				179	w			177	w
183	m								
						186	m		
194	m	197	m			193	m (sh)	190	m
		203	m	202	m	202	vw	203	m
212	vw								
221	m	222	w (sh)			218	ms	220	ms
		230	vs					231	s
235	w	236	vs			234	m	235	s
		274	w					274	w
				292	ms				
				309	s				
		318	m			314	w (sh)	319	m (sh)
327	w	332	vs			331	m (sh)	331	s (sh)
342	m	345	vs			343	s	344	vs
354	vs			353	vs	352	s		
		363	m			361	vs	360	vs
369	w	369	m						
375	w					377	m (sh)	375	m (sh)
		384	w	381	m				

[a] I_{rel}: w, weak; m, medium; s, strong; v, very; sh, shoulder.

in his study of the Raman spectrum of realgar, noted a grouping of peaks similar to that which we observe in pararealgar. Forneris assigned the higher frequency bands as As−S stretching modes and the lower frequency bands as S−As−S bending modes. However, based on extended X-ray absorption fine structure (EXAFS) data,[33] the lower frequency group has been assigned as As−As stretching modes and the strongest band, at 354 cm^{-1}, as the totally symmetric vibration of the covalently bonded S−As−S−As chain.

Porter and Sheldrick[27] measured the Raman spectra of both the low- and high-temperature phases of realgar and also noticed the formation of a transformation product after prolonged irradiation with the helium−neon laser excitation source of their Raman spectrometer. Although they incorrectly identified the transformation product as a polymer, their lower resolution spectra are similar in appearance to our spectrum of pararealgar. They reported similar Raman spectra for the transformation product from both the α and β phases, indicating that both phases transformed to the same product. This observation was also made in the later studies by Douglass et al.,[22] who used XRD to characterize the products.

Raman Microspectroscopic Analysis of Orange Material. The orange material yielded two apparently different Raman spectra, representative examples of which are presented in Figure 5. The spectrum in Figure 5a exhibits well-resolved peaks. The features in this spectrum that clearly distinguish it from pararealgar (as well as the α phase and orpiment) are a strong peak at 361 cm^{-1} and a weaker peak at 186 cm^{-1}. The spectrum presented in Figure 5b exhibits similar features but contains additional peaks.

As discussed above, the orange material is most likely either the high-temperature β phase or the χ phase, the immediate

precursor to pararealgar. The position and orientation of the orange material within the sample may contain important information as to its identity. The orange material was found only in intimate contact with flakes of pararealgar and only on one side of each flake. This proximity to pararealgar suggests that the orange material is actively undergoing transformation. Although the β phase has been shown to transform to pararealgar, Raman spectra and XRD analysis of the untransformed red crystals from our sample indicated the presence of only the low-temperature α phase. Our samples were never subjected to the conditions necessary to induce the transition from α to β.[21] Furthermore, Raman spectra exhibiting the characteristic features of the orange material were obtained both from samples that had undergone previous X-ray analysis and from those that had never been exposed to X-rays, thus eliminating the unlikely possibility of an X-ray-induced transition from α to β. Since the β phase was not initially present in our sample, nor was it produced during subsequent handling or analysis, we conclude that the orange material must, therefore, be the χ phase.

While the spectrum in Figure 5a appears to be of "pure" χ, several of our spectra also exhibited features attributable to the underlying pararealgar, as demonstrated by the spectrum presented in Figure 5b. Indeed, the spectrum in Figure 5b can be accurately modeled by a weighted average of the spectrum of χ, shown in Figure 5a, and that of pararealgar. The fit is shown as a dotted line in Figure 5b. Even in these "mixed" spectra, the strong peak near 360 cm^{-1} is quite distinct, allowing the presence of χ to be easily identified.

Raman Microspectroscopic Analysis of Colorless/White Material. The colorless/white material was observed to be present only as an extremely thin layer on one side of a given flake of pararealgar, and in many cases spots of the orange

(33) Yang, C. Y.; Paesler, M. A.; Sayers, D. E. *Phys. Rev. B* **1987**, *36*, 980−988.

Table 2. X-ray Powder Diffraction Data for Yellow Flakes (with Inseparable Orange and White/Colorless Material) Taken from Light-Irradiated Realgar Sample[a]

yellow powder, inseparable orange and white material[b]		pararealgar JCPDS 33-127		χ phase (Douglass et al.[22])		β-As$_4$S$_4$ JCPDS 25−57		arsenolite, As$_4$O$_6$ JCPDS 36-1490	
d (Å)	I_{rel}	d (Å)	I_{rel}	d (Å)	I_{rel}	d (Å)	I_{rel}	d (Å)	I_{rel}
6.70	10					6.76	10		
6.36	20								
								6.399	44
5.73	15			5.81	100	5.75	80		
				5.74	60				
5.56	30	5.56	91						
5.09	45	5.14	100						
5.03	25			5.05	45	5.01	40		
4.90	10	4.90	29			4.85	20		
4.79	20			4.77	15				
4.69	10					4.69	20		
4.52	10								
4.13	10 (b)					4.15	20		
3.95	20			3.96	25	3.93	70		
3.92	30								
3.73	50	3.75	78						
3.44	10	3.44	27			3.44	10		
						3.39	5		
3.29	60	3.299	50	3.30	10	3.33	10		
3.22	25			3.24	25				
3.19	85	3.184	3	3.19	10	3.20	80	3.199	100
3.10	25	3.105	33			3.08	70		
3.02	100	3.025	51	3.01	60	3.01	100		
2.91	40	2.905	30			2.95	30		
2.87	50			2.87	55	2.89	100		
2.79	70	2.795	71			2.82	60	2.770	26
						2.76	10		
						2.74	10		
2.66	10								
2.53	35	2.525	18			2.53	30	2.542	34
						2.50	20		
						2.47	5		
2.41	15 (b)	2.445	28			2.44	10		
		2.377	11			2.39	30		
2.31	10								
2.26	10 (b)	2.278	30			2.25	20	2.262	6
						2.21	20		
2.18	10	2.208	11			2.17	20		
						2.15	20		
2.12	15	2.106	2			2.11	1	2.1328	12
2.06	15	2.069	6						
2.02	20 (b)	2.030	22			2.01	5		
1.97	15	1.976	16						
1.96	30							1.9588	22
1.92	15								
1.86	15 (b)	1.862	11					1.8728	4
								1.8466	4
1.74	20 (b)	1.744	6						
1.71	25 (b)	1.710	10						
1.67	35 (b)	1.682	11					1.6702	14
1.59	15 (b)							1.5991	5
1.55	20							1.5515	14
1.44	10							1.4422	7

[a] The published XRD patterns for pararealgar, the χ and β phases of realgar, and arsenolite are listed for comparison. [b] The resolution of our diffraction pattern is estimated to be $\pm 0.1°$ 2θ. (b) indicates a broad line.

material could be seen attached to the opposite side of the same flake. If, as hypothesized above, the orange material is the χ phase, the immediate precursor to pararealgar, it would naturally occur only on the side of a pararealgar flake nearest the untransformed realgar. The thin colorless/white layer, on the opposite side of the pararealgar flake from the orange material, would, therefore, necessarily be on the surface exposed to light and air. The thickness, color, and orientation of this material with respect to the pararealgar flakes are consistent with those of an oxide layer, most likely arsenolite, As$_4$O$_6$, as suggested by the XRD data discussed in the previous section.

Raman spectra of areas containing the colorless/white material showed only peaks attributable to the underlying pararealgar, indicating that the layer of white material is extremely thin. There are no available data on the relative Raman scattering cross sections of solid arsenic oxides versus sulfides. However, since the intensity of Raman scattering is dependent on polarizability, molecules containing the more polarizable S atoms might, in general, be expected to have a larger scattering cross section than similar molecules containing the less polarizable O atom. This trend has been documented for small gas phase molecules.[34] Additionally, Raman studies on the (100) crystal face of arsenolite[35]
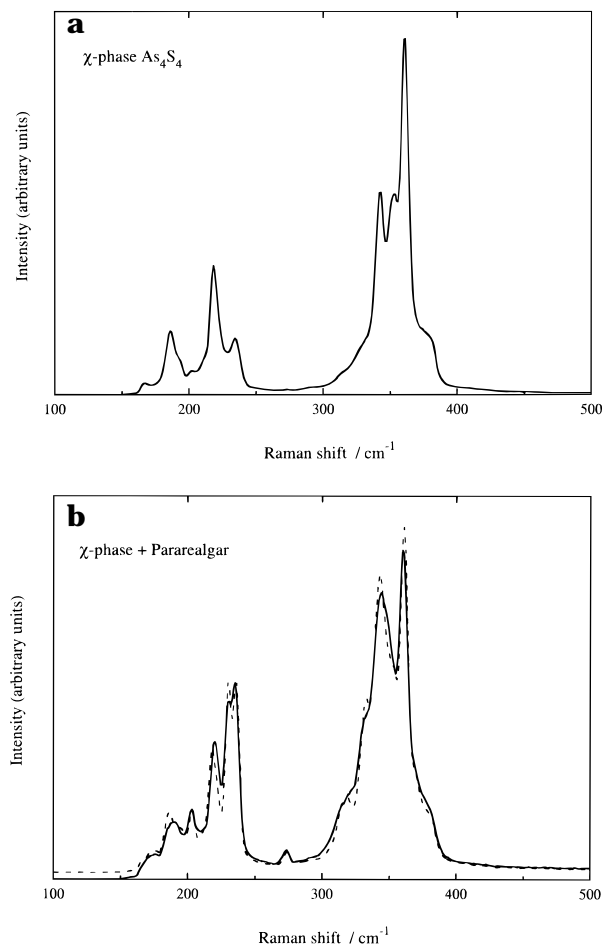
Figure 5. Raman spectra of orange material attached to yellow pararealgar flakes. (a) Well-defined spectrum, attributed to the χ phase. (b) Solid line: spectrum of orange material exhibiting additional peaks. Dotted line: fit to the data using a weighted average of the spectra in Figures 3 (pararealgar) and 5a (χ phase). Assuming that the Raman scattering cross sections of pararealgar and χ are approximately equal, this particular spectrum represents a mixture of approximately two-thirds χ and one-third pararealgar.

demonstrated that the scattering intensity can vary dramatically with the polarization of the excitation laser. Therefore, if the layer is arsenolite, the thinness of the layer combined with a greater scattering probability from the underlying pararealgar and possible preferred orientation effects may explain why we could not observe its Raman spectrum.

CONCLUSIONS

The Raman spectra of pararealgar and the intermediate χ phase, presented here for the first time, clearly provide a rapid, conclusive, and reliable means of identifying these species. X-ray diffraction, while undoubtedly suitable for the analysis of relatively pure samples, can yield confusing diffraction patterns if there are overlapping lines from multiple components that cannot be physically isolated. We have demonstrated that different components even in very small samples can be optically isolated by the Raman microscope and that the Raman spectra thus obtained

can be used to identify and characterize the species present. Of course, Raman microspectroscopy cannot completely replace X-ray diffraction for the identification of minerals and mineral-based pigments. Indeed, in the study presented here, Raman spectroscopy was unable to confirm the presence of arsenolite suggested by the X-ray diffraction data, whereas in the identification of pararealgar, Raman microspectroscopy was considerably more effective than XRD. Clearly, these techniques should be considered complementary.

In the materials analysis study of irreplaceable works of art, minimizing the invasiveness of the analytical technique is of primary importance. Therefore, techniques that can be performed in situ, or with the removal of a minimum amount of sample, are particularly desirable. Raman microspectroscopy has the potential to become an extremely valuable tool for the field of conservation science because it not only fulfills the sampling limitation requirements described above but also requires minimal sample preparation, is extremely quick and easy to perform, and provides a conclusive analysis with minimal data processing and interpretation. The advantages of Raman microspectroscopy were clearly demonstrated in our analysis of the sample of yellow material removed from Tintoretto's *The Dreams of Men*. Using a Gandolfi camera, the XRD powder pattern from the yellow pigment particles required a 6 h exposure, and its interpretation was complicated by lines from other crystalline components. By contrast, using the same sample, Raman spectra of a number of individual yellow particles within the sample were obtained in a matter of minutes, yielding sharp, well-defined spectra.

An understanding of the light-induced transformation of realgar is important for the study of artistic works and may influence steps taken toward their preservation. Realgar has not been frequently identified as a pigment,[12,36] whereas orpiment has been attributed as being widely used. Artists' manuals do not caution against the impermanence of realgar as a pigment, and therefore we suspect that the transformation is inhibited if the realgar is suspended in a binding medium for application as a paint, although this has yet to be rigorously investigated. Pararealgar itself may have been obtained by artists for use as a yellow pigment, in which case one must wonder, how much of what has been reputed to be orpiment in museum objects is, in fact, pararealgar?

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