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## Mansfieldite ( $\text{AlAsO}_4 \cdot 2\text{H}_2\text{O}$ ): a new white pigment in Himalayan artwork

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### ABSTRACT

An unusual arsenate mineral, mansfieldite ( $\text{AlAsO}_4 \cdot 2\text{H}_2\text{O}$ ), was identified as a pigment for the first time as the principal white colorant on two Himalayan thangka paintings at the Indianapolis Museum of Art at Newfields. The co-occurrence of this unusual mineral pigment provides support for the belief that the two artworks are members of a cycle of paintings originating from the same workshop, perhaps from Chamdo, Tibet. The complete palettes of both artworks are identical, including the use of mansfieldite, brochantite, malachite, azurite, vermilion, gold, orpiment, and a carbon-based black in a glue binder on a gypsum-primed cotton fabric.

### INTRODUCTION

The Indianapolis Museum of Art at Newfields (IMA) accessioned two Himalayan thangkas into its collection in 2016, Figure 1. As part of a conservation assessment of the pieces, routine scientific analysis detected the anomalous presence of arsenic in white areas of both paintings. The subsequent investigation detailed in this report ultimately identified the material as mansfieldite, ( $\text{AlAsO}_4 \cdot 2\text{H}_2\text{O}$ ), a mineral which has never before been identified as an artist's pigment.

Thangkas are religious paintings associated with Vajrayana, the style of Buddhism prevalent in Himalayan cultures.<sup>1</sup> They are displayed as wall hangings, sewn within a frame-like mount of fabrics incorporating a hanging bar at the top and a heavier dowel, or roller, at the bottom. Contemplation of the paintings is central to the meditative practices and rituals of Buddhist practitioners. Thangkas in active religious use are consecrated by a qualified Lama and an 'awakening' mantra is brushed onto the back of the painting to give it power.

The imagery of the thangkas purportedly stems from the visions of fully realized tantric masters. The two IMA paintings are mandalas, which are symbolic diagrams that reveal an alternative universe powered by the enlightened mind of the central deity depicted. Understanding Buddhist teaching and gaining sufficient proficiency in meditation practices makes it possible to enter the energetic space that the mandala represents. The imagery often portrays a stylized celestial palace, rendered in bird's eye view (Figure 1b), with four gates and multiple rings of protection.



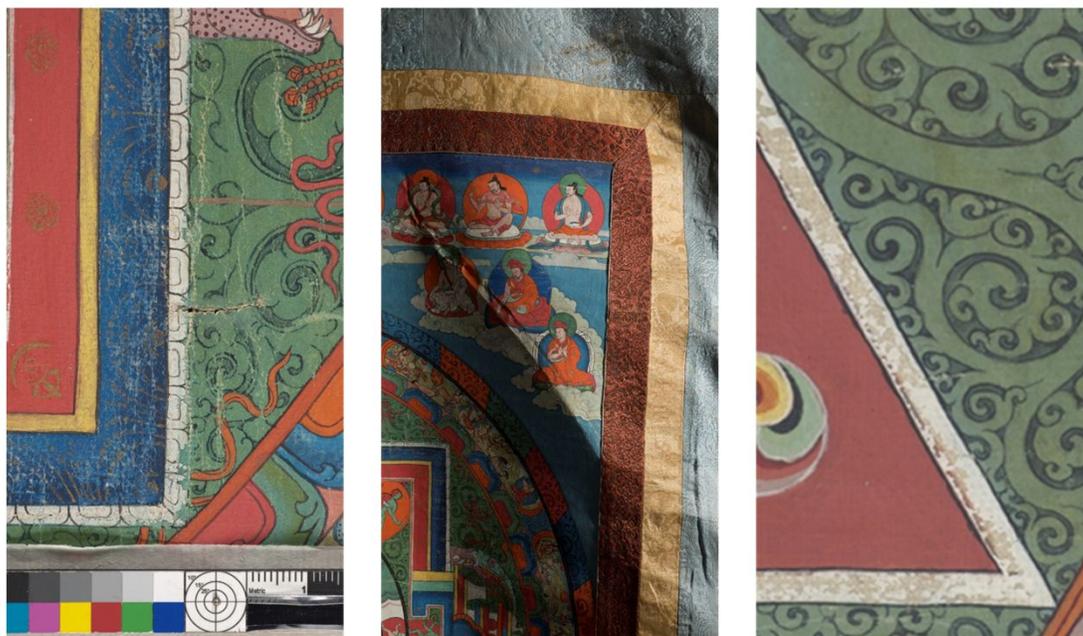
**Figure 1.** Two thangkas accessioned by the IMA: (a) 2016.71, Vajravarahi mandala, and (b) 2016.72, Chakrasamvara mandala.

The works in question did not have a known provenance, or history of ownership, other than they had been at the institution for many decades, perhaps since the 1970s, as part of the “study collection,” a grouping of artworks and fragments used in the museum for didactic purposes. There was no record of how they came to be at the museum, or who previously owned the thangkas. Works classified as study pieces do not benefit from the same level of stewardship as artworks fully accessioned into the collection because of their intended use as didactic and test specimens. The decision to elevate these two items was prompted by a casual review of the museum’s Himalayan artworks by a visiting Himalayan art expert, Dr. Katherine Anne Paul, during a speaking engagement. The specialist curator was surprised the pieces were not already part of the permanent collection since they seemed to be museum quality, worthy of exhibition, and appeared to be made for actual religious practice rather than having been produced for the tourist trade. The two items were described as part of a larger cycle of paintings hung during special occasions, probably from the same workshop. Three consecration syllables are inscribed on the verso of each painting in an identical script. Although Dr. Paul could not be certain of their origin, she suggested the pieces could be Qing Dynasty (1800-1899) from Tibet or Bhutan based on imagery and style. Objective dating through radiocarbon analysis, however, has not been done to confirm this assignment.

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3 After conducting the necessary legal steps to obtain clear title to the artworks,<sup>2</sup> the two paintings were  
4 assigned accession numbers (2016.71 & 2016.72), and images of the works were populated to the  
5 museum's website. This attracted the attention of Dr. John Henry Rice, Curator of South Asian and  
6 Islamic Art at the Virginia Museum of Fine Arts, who was able to shed light on the early history of these  
7 pieces. He had been studying a local collection of Buddhist artworks in Richmond, Virginia that were  
8 acquired by a local businessman, Mr. Harry O. Stone, around 1913 during a trip to China to represent US  
9 and British tobacco trading interests. According to a 1923 newspaper report,  
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12  
13 *"Mr. Stone's collection consists of sixteen wonderful paintings, which came originally*  
14 *from the great Lamasery of Chiamdo in Tibet. In 1913 they were stolen from the*  
15 *lamasery by Chinese officers of an invading army, at the same time the lamasery was*  
16 *plundered, and all the lamas were killed. At a later date they were sold to the American*  
17 *by some of these officers. Since that time the lamasery has never been restored, and so*  
18 *these glorious and proud paintings are still in the possession of Mr. Stone."*<sup>3</sup>  
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21  
22 Eight thangkas were pictured in the article, including the two accessioned by the IMA. A later article in  
23 the *Richmond Times-Dispatch* from 1953 mentions that two of the paintings had been subsequently sold  
24 by the owner prior to his death in 1947,<sup>4</sup> and it is thought that these two are the ones now in  
25 Indianapolis.  
26



48  
49 (a)

50 (b)

51 (c)

52 **Figure 2.** Photomicrographs of condition issues affecting the thangkas including (a) abrasion and tears,  
53 (b) distortions and creases, and (c) flaking paint, particularly in the white areas as seen in the triangular  
54 border.  
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3 IMA curators decided to exhibit the thangkas within the galleries devoted to Asian artworks, which  
4 necessitated a comprehensive conservation review prior to installation. During that examination,  
5 several condition issues were noted such as abraded paint layers, minor tears, creasing, and an overall  
6 lack of planarity to the picture surface, Figure 2a-b. Of immediate concern, however, was the presence  
7 of lifting and flaking paint, Figure 2c, that threatened further losses of the painted surface, particularly in  
8 the areas of the white pigment. Although a conservation treatment was devised to gently consolidate  
9 the loose paint fragments using a dilute solution of Methocel A4C carefully wicked under the lifting paint  
10 surface, a scientific analysis was requested of the white paint to see if the composition of the pigment,  
11 binder, or gesso surface could explain the particularly localized friability of the white passages in the  
12 artwork.  
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## 16 17 **EXPERIMENTAL**

### 18 19 *Samples*

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21 A sample of flaking white paint from 2016.71, less than 200  $\mu\text{m}$  across, was made available for invasive  
22 analyses. A hand specimen of mansfieldite with minor scorodite ( $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ) collected from Hobart  
23 Butte, Oregon was purchased from M & W Minerals for spectroscopic comparison.  
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### 26 27 *X-ray Fluorescence Spectroscopy (XRF)*

28 Three Bruker XRF instruments were used in the study. Initially, a survey of the elemental signatures of  
29 the various pigments was made in the paper conservation studios at the IMA using a Tracer III-V  
30 portable XRF (pXRF) unit with Si pin diode detector and Rh x-ray tube connected to a vacuum pump.  
31 The thangkas were analyzed in their hanging position with care taken not to touch the instrument to the  
32 artwork's surface. As a result, small air gaps limited the effectiveness of the vacuum pump in reducing  
33 atmospheric absorption of characteristic x-rays from light elements. Instrument parameters included 60  
34 sec acquisitions, 40 keV accelerating voltage, and 3.1  $\mu\text{A}$  current for the unfiltered x-ray beam. The  
35 analysis spot was roughly an 8 x 10 mm oval. Minor Cu and Ni peaks appear in the blank for this  
36 instrument.  
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39 An Artax microfocus instrument ( $\mu\text{XRF}$ ) with Rh x-ray tube, 10  $\text{mm}^2$  silicon-drift detector (SDD), and  
40 polycapillary focusing lens ( $\sim 70 \mu\text{m}$  spot) was used to refine the analysis on one thangka (2016.72) and  
41 to pinpoint smaller painted features that could not be cleanly analyzed using pXRF (gold, black, gesso).  
42 Experimental parameters included 50 keV tube voltage, 600  $\mu\text{A}$  current, and 60 sec live time  
43 acquisitions. A helium purge gas allowed for light element detection. Elemental survey spectra were  
44 collected in the region from 0 to 50 keV.  
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46

47 A macro-scanning M6 Jetstream XRF (MA-XRF) acquired after the study was initiated allowed the  
48 elemental composition of larger areas of one of the thangkas (2016.71) to be mapped. The instrument  
49 consists of a Rh x-ray tube with dual 60  $\text{mm}^2$  SDD detectors. The excitation beam was again 50 keV and  
50 600  $\mu\text{A}$ . A larger beam size (190  $\mu\text{m}$ ) was scanned continually over the sampled area at a rate of 45  
51 ms/pixel without a He purge. A beam limiting aperture of 1000  $\mu\text{m}$  was used to minimize changes in the  
52 spot size as the instrument scanned over the gently undulating surface of the painting. False color  
53 elemental maps were generated for each element from the characteristic x-ray peak with the least  
54 interferences following spectral deconvolution. Relative intensities of each map were manipulated to  
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3 enhance readability. The instrument operation and data manipulation were accomplished using Bruker  
4 M6 version 1.6.611.0 software.  
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#### 6 *Scanning Electron Microscopy – Energy Dispersive Spectrometry (SEM-EDS)*

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8 Electron micrographs of flaking paint were created using a Zeiss EVO MA15 scanning electron  
9 microscope operated in variable pressure mode at 50 Pa of room air. A Zeiss five segment  
10 backscattered electron detector (BSE) and a Bruker Quantax 200 EDS were used to acquire images.  
11 Electron accelerating voltage was set at 20 keV to ensure generation of x-rays for all elements in the  
12 sample while a beam current of 1 nA yielded ~ 6 kcps detector signal with a few percent dead time. A  
13 sample working distance of 8.5 mm optimized EDS detection. The SEM was controlled using Zeiss  
14 SmartSEM software while the EDS spectra were collected and analyzed using Bruker Esprit 1.9.4  
15 software. Semi-quantitation of selected elements was achieved using an automated PB-ZAF algorithm  
16 to yield mass percent composition of the sample.  
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#### 21 *Reflected infrared digital photography*

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23 Near-infrared reflectograms (IRR) were captured with a modified Nikon D610 camera equipped with a  
24 Coastal Optics UV-VIS-IR apochromatic 60mm macro lens at f-stop 8. The infrared images were acquired  
25 using an X-nite 830 cut-on filter (MaxMax) at 1/8 sec exposure. The longest wavelength sensitivity of  
26 the camera is approximately 1000nm.<sup>5</sup> The object was diffusely illuminated at 45 degrees from both  
27 sides with a pair of Lowel DP halogen lamps.  
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#### 30 *Fourier Transform Infrared Microspectroscopy (FTIR)*

31  
32 FTIR microspectroscopy was performed on a Nicolet Continuum microscope with a liquid nitrogen  
33 cooled MCT-A detector coupled to a Nicolet 6700 spectrometer purged with dry, CO<sub>2</sub>-free air. The  
34 spectra are the sum of 32 coadditions at 4 cm<sup>-1</sup> spectral resolution. Microsamples were crushed on a  
35 diamond compression cell and held on a single diamond window during the analysis. Unknown spectra  
36 were compared to in-house as well as the Infrared and Raman Users Group (IRUG) spectral libraries. To  
37 remove interfering mid-IR bands from inorganic compounds (carbonates, clays, silicates), microsamples  
38 of paint were treated with 10% HF in the vapor phase according to the procedure by Smith et al. prior to  
39 FTIR analysis.<sup>6</sup>  
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#### 43 *Raman microspectroscopy*

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45 Raman spectra were acquired using a Bruker Senterra microspectrometer on a Z-axis gantry. The  
46 spectrometer utilizes 3 selectable excitation lasers (532, 633, and 785 nm), an Andor Peltier-cooled CCD  
47 detector, and a 50 μm confocal pinhole. A 50X ultra-long working distance objective was used to focus  
48 on in situ pigment particles with the artwork laying partially rolled from both ends on the sample  
49 platform. Small weights were placed on glassine papers on the surface of the painting to keep it flat  
50 during the analysis. Laser power at the sample was below 1 mW. The spectra are the result of 2 to 5 sec  
51 integrations with 25-50 coadditions. The analysis spot size was on the order of 1 μm, and the spectral  
52 resolution was in the range of 9-18 cm<sup>-1</sup>. OPUS v8 software allowed for automated cosmic spike  
53 removal, peak shape correction, and spectral calibration.  
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### *Powder X-ray Diffraction (XRD)*

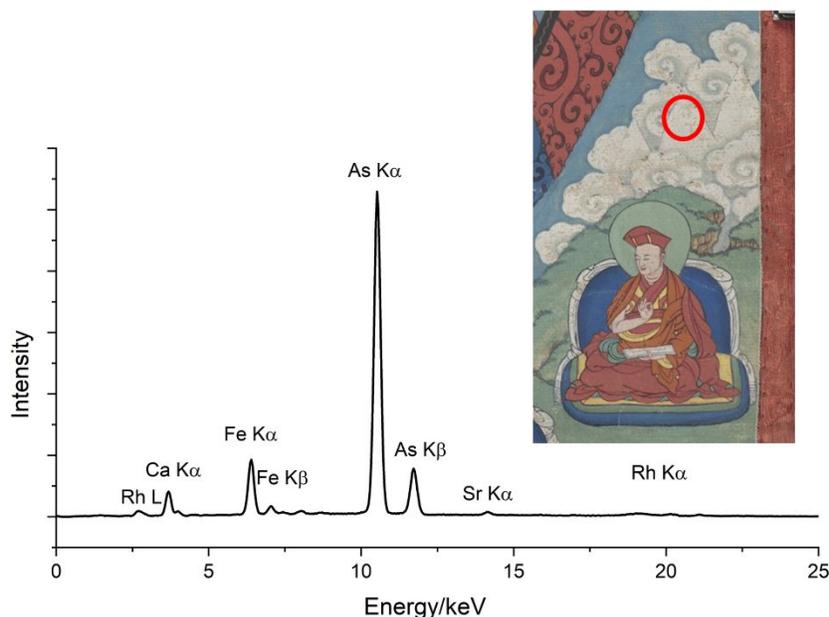
Minor crumbles of white flaking paint collected from thangka 2016.71 were placed onto a quartz zero diffraction plate (30mm x 30mm x 2.5mm) and wetted with a drop of methanol to adhere them. The sample was mounted in the Eulerian cradle of a Bruker D8 Discover XRD, an  $\mu$ S X-ray source with a 2mm beam was aligned to the sample and the sample rotated ( $360^\circ$  at  $1200^\circ/\text{minute}$ ) with  $\phi$  varying from 0 to 60 degrees for a gimbling action to further randomize particulate orientation relative to the X-Ray source. The data was captured on a Vantec 500 2D detector; X-ray diffraction cones displayed good continuity across detector space, and a standard diffraction pattern was generated using Bruker Eva software v4.0. The diffraction pattern from the sample was matched to reference patterns in the Crystallography Open Database (COD) both by a standard search/match routine that identified mansfieldite and by comparison to other possible arsenic phases in the database including scorodite, arsenolite (hexoctahedral  $\text{As}_2\text{O}_3$ ), or claudetite (monoclinic  $\text{As}_2\text{O}_3$ ). The diffractogram was plotted using CrystalDiffract v6.9.3.

## **RESULTS & DISCUSSION**

### *Discrete in situ analysis by XRF*

The white pigment was initially investigated by pXRF within the conservation studios. Analysis of larger white patches matching the size of the sampling window of the handheld pXRF unit generated intense signals for As with minor Ca, Fe, and Sr, Figure 3. The air gap between instrument and the hanging thangka prevented the efficient detection of light elements like Al, Si, and S. The dominant As signal did not agree with any of the anticipated white colorants for thangka paintings: Jackson and Jackson list the common whites as kaolin (aluminosilicate), chalk (trigonal  $\text{CaCO}_3$ ), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), bone ash ( $\text{Ca}_3(\text{PO}_4)_2$ ), and later lead white ( $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ ),<sup>1</sup> while aragonite (orthorhombic  $\text{CaCO}_3$  from mollusk shells) has been previously identified on one example,<sup>7</sup> and barytes ( $\text{BaSO}_4$ ) and titanium dioxide ( $\text{TiO}_2$ ) has been documented in modern examples.<sup>8</sup> Arsenic is, however, commonly found in brightly colored artists' pigments including natural yellow orpiment ( $\text{As}_2\text{S}_3$ ) and red realgar ( $\alpha\text{-As}_4\text{S}_4$ ),<sup>9</sup> as well as synthetic pigments like cobalt violet ( $\text{Co}_3(\text{AsO}_4)_2$ ) and emerald green ( $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 3\text{Cu}(\text{AsO}_2)_2$ ),<sup>10</sup> but not generally in white artists' pigments.

However, the use of sodium arsenide ( $\text{Na}_3\text{As}$ ) has been recommended as a biocide in starch pastes used to reline thangkas onto new cotton supports,<sup>11</sup> and several arsenic salts have been liberally applied to organic artworks as pesticides historically.<sup>12</sup> To rule out contamination of the thangkas by these sources, analyses were also conducted on other colored areas of the paintings as well as the wood hanging bar and the fabric mounts. However, no strong As signal was detected in any of these areas with the exception of the pink paint, surmised to be a mixture of the main white colorant with a red pigment, and the yellow paint, anticipated to be the traditional mineral yellow colorant, orpiment.<sup>1,9</sup> Based on this elemental survey, the white pigment in both thangkas appeared to be a purposefully applied arsenic-based white colorant.



**Figure 3.** Handheld XRF spectrum of white clouds in 2016.71, Vajravahri mandala, showing strong As signal. The red circle shows the approximate analysis location.

The other paint colors for the two objects were also analyzed at the same time using pXRF to provide a general palette survey, and then later using a higher spatial resolution Artax instrument ( $\sim 70 \mu\text{m}$ ). The pigments seemed to be identical between the two artworks, and the inorganic colorants, inferred from their elemental signatures as determined by XRF spectroscopy, appeared to be those commonly encountered in thangka artworks.<sup>1</sup> A strong Pb signal from the orange areas suggested minium ( $\text{Pb}_3\text{O}_4$ ), whereas the dominant Hg in the red passages indicated vermilion ( $\text{HgS}$ ). Both blue and green paints presented spectra containing characteristic x-rays from Cu, likely azurite ( $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ) and malachite ( $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ), respectively. In addition, gold highlights yielded strong Cu, Zn, and Au fluorescence indicating a debased gold. Finally, the spectra from black outlines and passages gave strong signals for Ca alongside those elements from the colors used underneath or in the vicinity, suggesting the application of a carbon-based black pigment overtop of other passages of paint. The gesso, where it could be analyzed from areas of loss, contained equally strong signals for Ca and As, as well as S and Fe, indicating the likely use of calcite or gypsum perhaps mixed with the arsenic white pigment to make the ground used to prepare the canvas. Table 1 lists the elements identified using pXRF in the initial survey.

**Table 1.** Analytical results for each color. Analyses were similar for each artwork studied. Notations for XRF indicate signal strength as **major**, minor, and (trace).

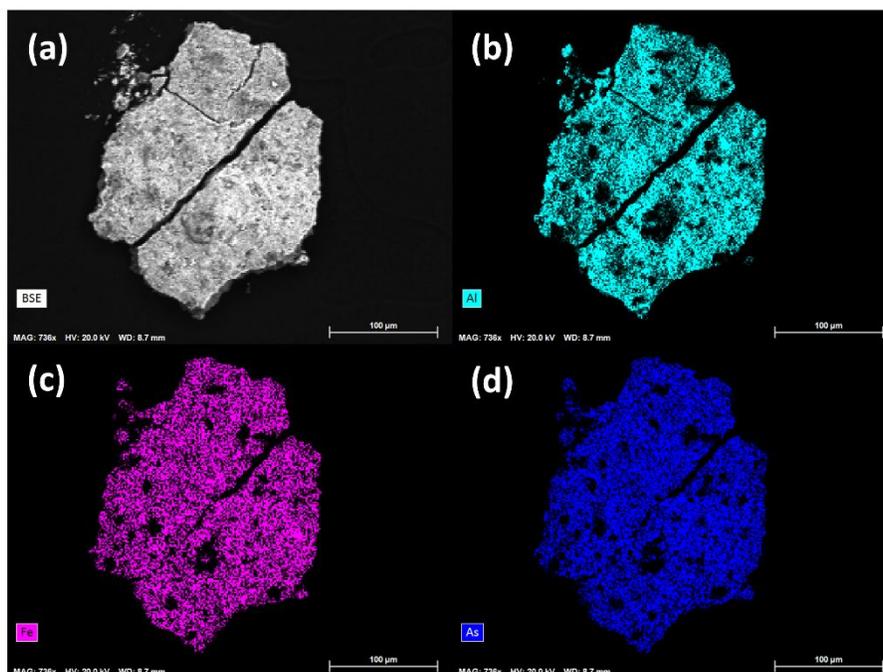
Color	Instrumental Results	
	pXRF	Raman
white	As, Ca, Fe (Al*, Cu, Sr)	mansfieldite
red	Hg, S, Ca, Sr (Ti, Fe, Ni, Cu)	vermilion
orange	Pb, Ca (Fe, Ni, Cu, Sr)	minium

yellow	<b>As, S, Ca</b> (Ti, Fe, Sr)	orpiment
blue	<b>Cu, Ca, Fe</b> (S, Ni, Sr)	azurite
green	<b>Cu, Ca, Fe</b> (As, Sr)	malachite
dk. blue-green	<b>Cu, Ca, Fe</b> (Ti, Ni, Sr)	brochantite
black* (used over other colors)	<b>Ca, Cu, Fe, Pb</b> (K, As, Sr)	soot black
gold* (used over other colors)	<b>Cu, Au, Zn</b> (Ca, Fe, As, Sr)	no signal
gesso* (near loss in white)	<b>Ca, As, S, Fe</b> (Cu, Sr)	calcite + some gypsum

\*Identified using the Artax  $\mu$ XRF with He purge on 2016.72 only.

### Elemental microanalysis by SEM-EDS

To better characterize the unusual white pigment, a microsample of paint, approximately 200  $\mu\text{m}$  in diameter, was made available for laboratory analysis from the Vajravarahi mandala (2016.71). This sample was found detached from the artwork and could not be relocated and adhered during the consolidation treatment. The sample was mounted on a graphite stub and analyzed by SEM-EDS mapping as shown in Figure 4. The strongest signals (mass %) arose from O (39.1), C (33.7), As (16.7), Al (5.6), Si (2.2) and Fe (2.1), although Ca (0.2), S (0.2), and K (0.1) were also observed. The maps of the major elements Al, As, and Fe, Fig4b-d), show a consistent composition across the majority of the white paint flake and highlight the prevalence of Al in the sample, which was otherwise difficult to detect in air by pXRF. This analysis also ruled out minor arsenic contamination of an otherwise typical white Himalayan pigment like clay, gypsum, or chalk.

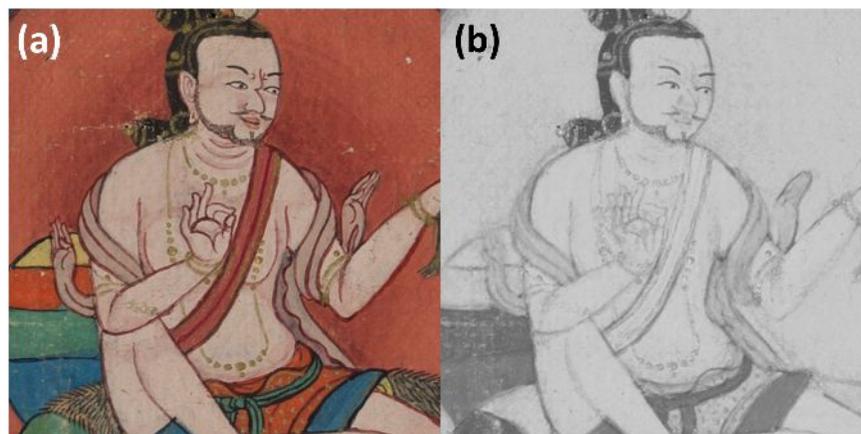


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3 **Figure 4.** SEM-EDS chemical maps of a white paint chip from 2016.71  
4 Vajravarahi mandala including (a) backscattered electrons, (b) Al, (c) Fe,  
5 and (d) As. Scale bar is 100  $\mu\text{m}$ .  
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8 *Underdrawing imaging by near infrared reflectography*  
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10 Technical analysis of thangkas by infrared reflectography has on occasion identified color notations  
11 related to pigment usage hidden under the opaque paints.<sup>13-16</sup> For instance, Duffy and Elgar examined a  
12 large corpus of thangkas with IRR and discovered pigment names written on compositional elements of  
13 the artwork during the underdrawing stage presumably to inform apprentices as to the color scheme of  
14 the painting. Interestingly, in one colorless (white?) sample, the authors observed the notation “se” for  
15 yellow orpiment, although XRD identified only arsenolite ( $\text{As}_2\text{O}_3$ ) as present.<sup>13</sup> The explanation was  
16 made that the orpiment must have thoroughly degraded to white arsenolite.  
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20 The IMA thangkas were examined using IRR to see if any descriptive notations might suggest an identity  
21 for the white pigment. No such annotations were observed; however, evidence of artist’s changes could  
22 be seen in the underdrawing, presumably executed in an inorganic carbon-based pigment because of  
23 the drawing’s strong NIR absorption. Figure 5 shows (a) a detail photograph of 2016.71 of a seated male  
24 compared to (b) the IRR of the same area. The sitter’s proper right hand and facial features were  
25 repositioned during the compositional planning stage.  
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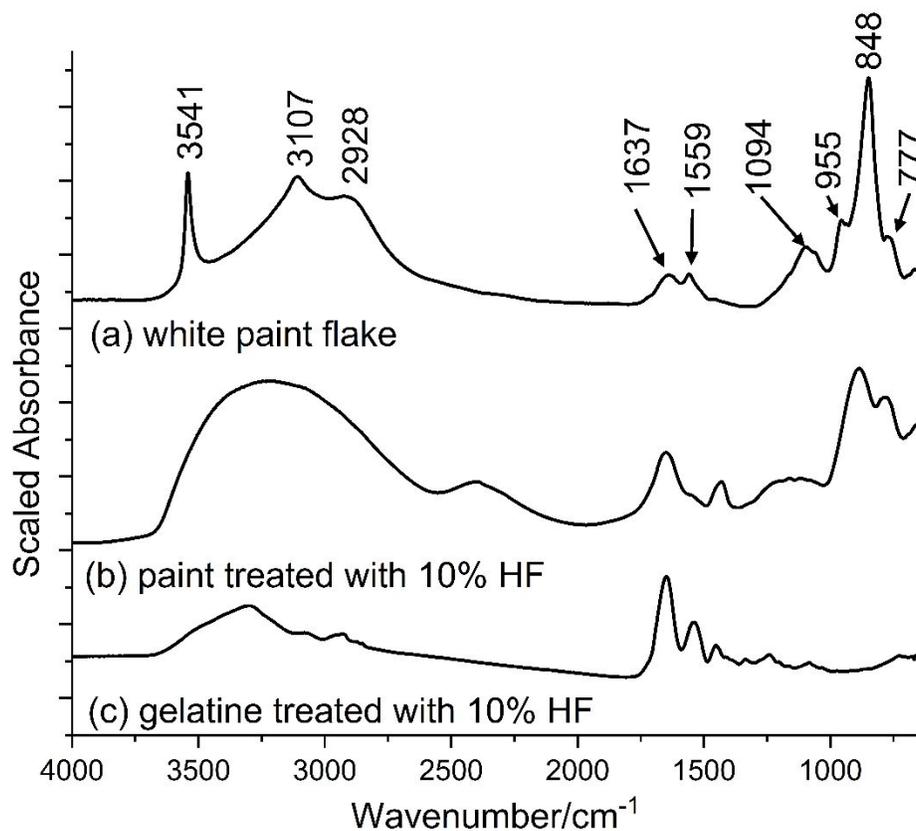


43 **Figure 5.** (a) Visible detail image and (b) infrared reflectogram in the 830  
44 to  $\sim 1000$  nm region.  
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46 *Molecular analysis by FTIR and Raman spectroscopies*  
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48 A minor fragment of the same microsample was analyzed by FTIR and Raman microspectroscopies. The  
49 FTIR spectrum shown in Figure 6a reveals a strong stretching mode quartet centered at  $848\text{ cm}^{-1}$ ,  
50 attributable to inorganic arsenates, although no exact match could be identified in the Infrared and  
51 Raman Users Group (IRUG) spectral library or any of the commercial spectral libraries available in-house.  
52 The intense, sharp feature at  $3541\text{ cm}^{-1}$  and the two weaker bands at  $3107$  and  $2928\text{ cm}^{-1}$  are indicative  
53 of a mineral hydrate. The feature at  $1637\text{ cm}^{-1}$  could correlate to the strongest absorption of a  
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3 proteinaceous binding medium, the amide I band. Traditionally, a distemper-based glue made from  
4 boiled yak skins was used as the binder in thangka paints,<sup>1</sup> however a proteomics analysis of a glue  
5 sample would be required to confirm that here. The visibility of these protein modes was somewhat  
6 improved by allowing the vapor from a drop of dilute HF (10% v/v) to react with the inorganic  
7 components of the sample and shift their infrared frequencies, Figure 6b.<sup>6</sup> This compares favorably in  
8 the amide stretching region with a similarly treated mockup sample of gelatin, Figure 6c.  
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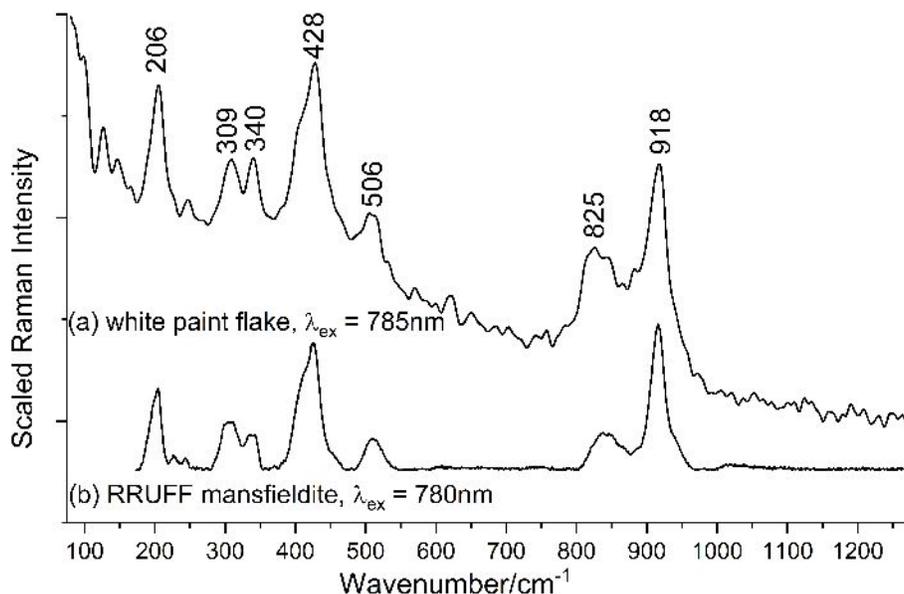


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**Figure 6.** FTIR spectrum of (a) a white paint flake, (b) the same sample treated with dilute HF, and (c) a hide glue sample treated with dilute HF.

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Using Raman microspectroscopy, a fresh microsample of the white pigment from thangka 2016.71 gave a reasonably strong Raman spectrum with 785nm excitation, Figure 7a, although it could not be matched to any artists' pigment in the in-house spectral library or the IRUG online library. After the analysis of the same sample by XRD (*vide infra*), which identified the pigment as the aluminum arsenate dihydrate mineral mansfieldite, a matching Raman spectrum was obtained from the online RRUFF database at the University of Arizona, Figure 7b, for a mansfieldite sample collected at Djebel Debagh, Constantine, Algeria (R060409).<sup>17</sup> A similar spectrum with 785 nm excitation was also obtained in-house from a hand specimen of mansfieldite purchased online. The vibrational spectra of mansfieldite and its iron analog scorodite were reported by Kloprogge and Wood in 2017 after the initial discovery of the pigment in these thangkass.<sup>18</sup> Based on those published spectra, scorodite can be ruled out.

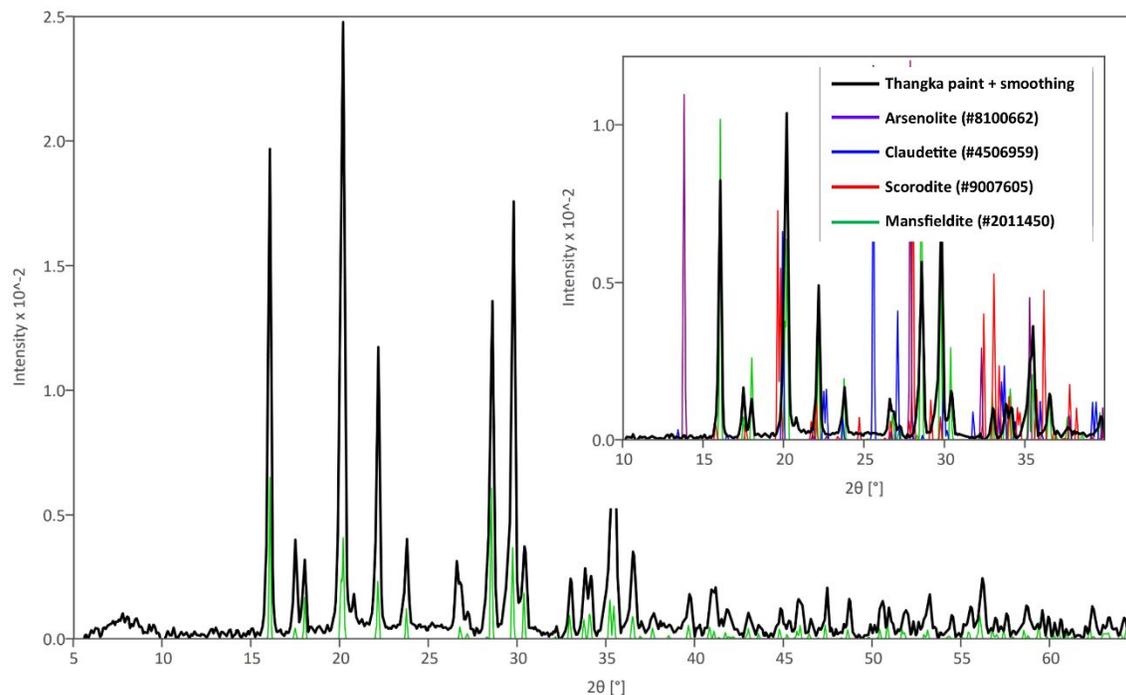


**Figure 7.** Raman spectrum of (a) the unknown white pigment using 785 nm excitation and (b) a RRUFF reference spectrum for mansfieldite ( $\text{AlAsO}_4 \cdot 2\text{H}_2\text{O}$ ) collected using 780 nm excitation.<sup>17</sup>

In situ analysis of all colors on both paintings was also undertaken using Raman spectroscopy. Table 1 summarizes the pigments identified for the major colors used on the two thangkas. The pigments and their manner of application were identical in both works and largely confirmed the earlier presumptions based on the discrete analyses using XRF. One exception was the identification of brochantite ( $\text{Cu}_4(\text{SO}_4)(\text{OH})_6$ ) in the darker blue-green color on the thangkas. Although more rarely identified than malachite for green in these historic works, brochantite has been previously found on thangkas.<sup>8,13,19</sup> Importantly, the co-occurrence of the previously unknown pigment mansfieldite as the principle white pigment in both paintings, as well as the similar palettes overall, supports the original curatorial inclination that the two paintings originated from the same workshop.

#### *XRD analysis*

The microsample of white paint previously assessed by FTIR, Raman, and EDS spectroscopies was also analyzed by powder XRD. The sample diffractogram, Figure 8, provided an excellent match to mansfieldite in the Crystallography Open Database (#9011387), providing the first clear evidence of the identification of the mysterious white colorant during the project. Furthermore, scorodite, the iron analog of mansfieldite, could again be excluded, even though iron had been shown to overlap Al and As in the SEM-EDS map of the same paint flake, as could other arsenic species such as arsenolite and claudetite (Figure 8 inset).

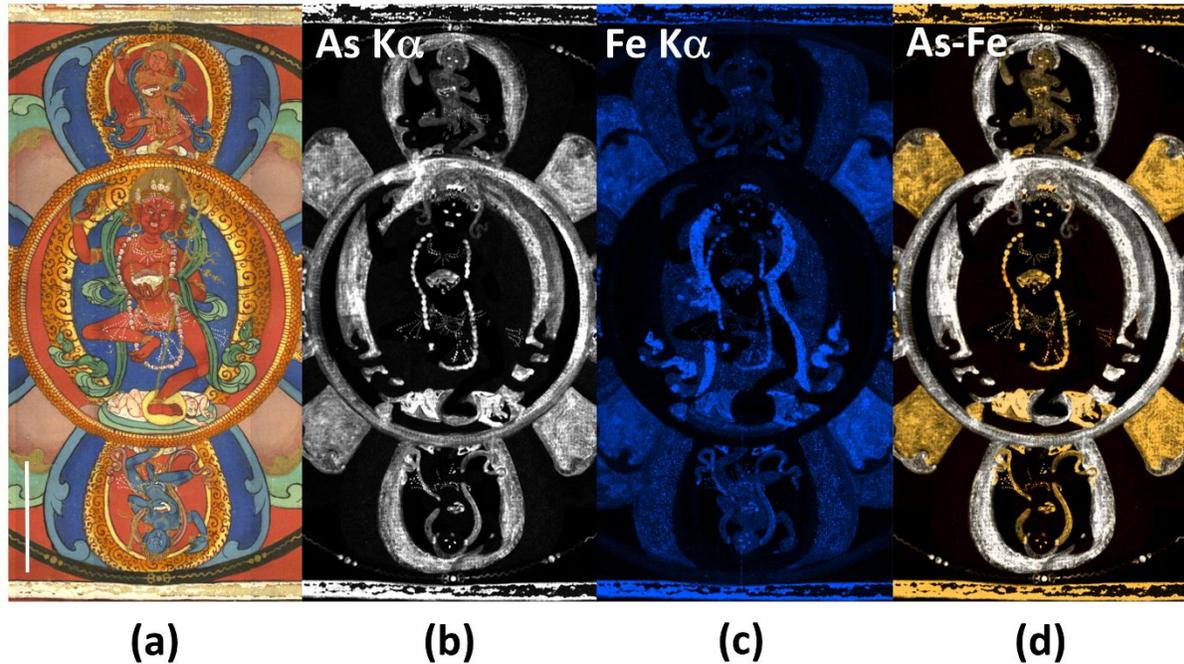


**Figure 8.** Powder diffractogram of the white paint chip compared to mansfieldite (green). Inset focused on major peaks between 10 and 40 degrees  $2\theta$  for mansfieldite, scorodite, arsenolite, and claudetite references with COD entry numbers.

#### MA-XRF mapping

After achieving the positive identification of the white pigment as mansfieldite, a new mapping XRF instrument became available in the laboratory. MA-XRF has previously been shown to reveal interesting spatial associations of pigment usages in thangkas.<sup>19</sup> The small central goddess medallion of the Vajravarahi mandala (2016.71) was scanned at a moderately high spatial resolution (190  $\mu\text{m}$ ) to detail the extent of application of the arsenic white pigment mansfieldite over this roughly 12 by 8 cm area, Figure 9a. Figure 9b, a false color map of the As  $K\alpha$  line intensity, reveals the presence of arsenic in the white areas of the painting, but also in the yellow-colored passages due to orpiment. The co-occurrence of iron in the white areas containing mansfieldite can be used to cleanly separate the two sources of arsenic. The false color map of the Fe  $K\alpha$  line, shown in Figure 9c, reveals an iron distribution overlapping the white areas of the painting as expected, for instance the bone necklace and trampled human figure under the goddess' feet, but also the blue and green painted areas, such as the floral backdrops and blue-skinned figure in the lower petal. Iron has been shown to be present in mineral azurite due to the natural inclusion of hematite ( $\text{Fe}_2\text{O}_3$ ) and goethite ( $\text{FeOOH}$ ),<sup>20</sup> and presumably this would be true for mineral malachite due to its natural association with azurite, although this has not yet been demonstrated. Subtracting the Fe false color map intensity from the As map separates the mansfieldite containing features, now shown in the complementary orange false-color in Figure 9d from

the orpiment containing features, which remain white in the subtraction map. This analysis combined with the discrete sampling mentioned earlier shows that the arsenic white pigment was used throughout the thangkas in white passages, highlights, lighter colors like pinks, and fine white details.



**Figure 9.** Visible mosaic image of (a) the area scanned by MA-XRF compared to false-color maps for (b) the As  $K\alpha$  line, (c) the Fe  $K\alpha$  line, and (d) the As map minus the Fe map intensity. The vertical white bar in (a) is 3 cm.

#### *Geology of mansfieldite*

Mansfieldite was discovered in 1942 and first recognized as a mineral in 1948 by Victor Allen and Joseph Fahey, who named it after one of their mentors Dr. George Rogers Mansfield.<sup>21</sup> The hydrated aluminum arsenate is part of the variscite mineral group, and one end of the solid solution series between mansfieldite and scorodite, the iron analog. That scorodite and mansfieldite are a solid solution series also means iron and aluminum (as  $Fe^{3+}$  and  $Al^{3+}$ ) more easily swap for each other in the mineral structure; in mineral systems this substitution often has a thermodynamic limit, as yet undefined here,<sup>22</sup> but significant Fe substitution is possible in a particular mansfieldite mineral grain. The iron detected alongside arsenic in the white pigment studied here as evidenced by SEM-EDS and MA-XRF mapping suggests that the pigment found in the thangkas is not high enough in iron to significantly alter the structure of the atoms from mansfieldite, as specific techniques like Raman spectroscopy and XRD are sensitive to these changes and the results here are consistent with the white material being primarily mansfieldite. Based on the semi-quantitation of the EDS spectrum converted to oxides and ignoring the

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3 hydration water, the experimental composition of the sample here is calculated to be  $\text{Al}_{0.96}\text{Fe}_{0.16}\text{As}_{0.89}\text{O}_4$ ,  
4 close to the ideal composition of mansfieldite ( $\text{AlAsO}_4$ ).  
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7 Arsenate minerals often form at hydrothermal vents or from the weathering of the major arsenic sulfide  
8 minerals orpiment and realgar,<sup>10</sup> both minerals being common in Tibet's geology.<sup>1,9</sup> Claudetite and  
9 arsenolite are common weathering products of realgar and orpiment,<sup>23</sup> but mansfieldite as an aluminum  
10 arsenate mineral would form in a setting with more prevalent aluminum. The relative solubility of  
11 mansfieldite is decreased in a solution with even minor amounts of  $\text{Al}^{3+}$  based on calculations using  
12 available thermodynamic data.<sup>22</sup> Although sources of mansfieldite in Tibet have not to the authors'  
13 knowledge been specifically reported in the literature, it is conceivable that the mineral was procured  
14 locally from primary hydrothermal ore deposits or from the abundant deposits of weathered arsenic  
15 sulfides, likely associated with at least some aluminum-bearing minerals. According to the early 1900s  
16 Richmond, Virginia newspaper reports concerning the Stone collection of Himalayan paintings,<sup>3,4</sup> the  
17 artworks were procured in Chamdo in Tibet. Jackson and Jackson mention that the vicinity of Chamdo  
18 was noted as a historic source for orpiment:  
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24 *The chief yellow pigment of Tibetan painters was orpiment, a natural yellow trisulfide of*  
25 *arsenic,  $\text{As}_2\text{S}_3$ . Deposits of orpiment occur near the surface of the earth, especially near*  
26 *hot springs or in the vicinity of silver deposits. In Tibet the most famous deposits were*  
27 *found in East Tibet, near Chamdo.*<sup>1</sup> [pg. 82]  
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30 If the painting of the thangkas also occurred in Chamdo, then it is possible that this unusual white  
31 mineral was found locally in the orpiment mines that were already being used to supply thangka  
32 painters with their bright yellow pigment.  
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#### 35 *Other possible occurrences of mansfieldite in artworks*

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38 Careful technical analyses have been conducted on a large number of thangkas,<sup>7,8,13-16,19,24-26</sup> but  
39 mansfieldite has never before been identified in these works. However, in a few instances analysts have  
40 reported the uncharacteristic presence of arsenic in white pigments. Brochierri et al. describe an aged,  
41 darkened white pigment from an 18<sup>th</sup> century Vaisravana thangka as containing As, but they explain its  
42 presence as the white being contaminated with orpiment based on its off-white appearance and  
43 reflectance spectroscopy curves.<sup>19</sup> Colinart in her study of 10 thangkas from Paris' Musée National des  
44 Arts Asiatiques Guimet notes specifically the association of As and Al in the white face of a lama from  
45 the Taklung Monastery depicted in a thangka from around 1300 A.D. .<sup>14,24</sup> In this instance, the analyst  
46 hesitantly suggested the As could be present as a natural oxide, possibly arsenolite or claudetite,  
47 although she noted that neither has been identified as a purposeful pigment before. Finally, Tabasso et  
48 al. reported on the XRF analysis of several thangkas from the Giuseppe Tucci collection and noted the  
49 "not negligible quantities of arsenic" (translated) in pink areas of one thangka and also in the white  
50 grounds (Inv. 963, pg. 302), which they attributed to contamination with orpiment, but also high levels  
51 of arsenic in areas of another work where the color was not consistent with the use of orpiment (Inv.  
52 992, pg. 311).<sup>16</sup> It is possible that these previously puzzling results are other occurrences of mansfieldite  
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3 by Himalayan thangka painters that went unrecognized, although only a reanalysis of the paintings using  
4 molecular techniques can confirm this.  
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## 8 **CONCLUSION**

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10 Mansfieldite has been positively identified as a Himalayan artists' white pigment in two thangkas from  
11 the collection of the Indianapolis Museum of Art at Newfields probably dating to the 19<sup>th</sup> century. This  
12 is the first such identification of the mineral in any artwork from any time period or geographic region.  
13 The extent both geographically and temporally for the use of mansfieldite is unknown, but  
14 circumstantial evidence from the published analyses of a 13<sup>th</sup> and an 18<sup>th</sup> century thangka suggests that  
15 the identifications here are unlikely to be anomalous. The source of this white mineral has not been  
16 identified, although the geology of Tibet is right for its formation alongside deposits of other arsenic  
17 pigments utilized in traditional thangka painting. For the two artworks studied here, the presence of  
18 this seemingly rare white pigment, combined with stylistic similarities, adds credence to the theory that  
19 the two objects originated from the same artists' workshop, possibly in Chamdo, Tibet.  
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24 Importantly, this discovery adds yet another toxic pigment to the Himalayan palette alongside mercury  
25 rich vermilion red, lead containing minium orange, and arsenic-based orpiment yellow, requiring  
26 additional attention to health and safety when studying, storing, or conserving these paintings.  
27 Moreover, the comparatively poor condition of the flaking white passages of paint in the IMA thangkas  
28 may indicate an inherent vice to the use of mansfieldite in a distemper (glue-based) paint medium. The  
29 condition of other thangkas known to contain mansfieldite is required to clarify this potential  
30 conservation concern.  
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34 The results shown here indicate that XRF, preferably with a vacuum pump or He purge gas to facilitate  
35 the detection of aluminum, can be used noninvasively as a presumptive test for mansfieldite in passages  
36 of white paint on artworks, however Raman spectroscopy or XRD are required for confirmation. The use  
37 of portable XRF should allow quick and easy surveys of other Himalayan art collections to be conducted  
38 to better define the occurrences of this colorant and the condition of paints containing it. In fact, such a  
39 pXRF survey conducted at the IMA on the remaining three thangkas in our collection further identified  
40 an arsenic rich white pigment in a large 18<sup>th</sup> century Tibetan work, *Medicine Buddha (Bhaiṣajyaguru)*  
41 *and Buddhist Deities* (2016.384), and efforts are now underway to confirm the presence of mansfieldite  
42 by molecular techniques.  
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5

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7  
8 **G.D. Smith** Conceptualization; Formal analysis; Project administration; Original draft **C. Hoevel:**  
9 Conceptualization; Original draft; Review & editing **P. Cavanagh:** Formal analysis **G.K. Druschel:** Formal  
10 analysis; Original draft; Review & editing.  
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#### 13 **DECLARATION OF COMPETING INTEREST**

14  
15 The authors have no competing interests.  
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