Angewandte Chemie International Edition

DOI: 10.1002/anie.201205461

Art Conservation

A Chemist Remains a Chemist[**]

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1991

Raman spectroscopy · art conservation

My life, so far, was full of chemical excitements, and I can confirm: A chemist remains a chemist!

I have told my life story hundreds of times already, but the accidental beginning of my scientific career still fascinates me:[1a] A curious, 12 year old boy discovering, in 1945, in the attic of his house in Winterthur, Switzerland, chemicals collected by an uncle, Karl Ernst, who died in 1923, and whom he obviously never met. The chemicals were originally used for developing photo plates. In the hands of an adventurous boy, their mixing often led to unexpected reactions and explosions that stimulated his desire to lift all chemical mysteries.

Our house, built 1898 by my grandfather, Walter Ernst, was originally enlightened by city-gas illumination. The original tubing still existed in my time, 1945. So it was easy to attach a Bunsen burner for converting a storage room in the basement into a veritable chemistry lab. Running water was a bit more difficult to come by. But the abandoned tiny photographic darkroom, used by my deceased uncle, still survived after more than twenty years, and served as my source for tap water. Our house was, from the basement to its attic, an inexhaustible treasury, an environment in which one would wish all young people to grow up. How in such a paradise could they miss the chance of becoming explorers or, in the best case, experimental chemists? And it worked, unintentionally, in my case, to all extents and I became a passionate spare-time chemist, of course without anticipating ever receiving great science prizes for my curiosity.

Later, while working at the ETH Zürich, I had no longer a need for a "hobby-chemistry lab". Not much remained of it, except for some pre-1923 bottles that moved in 1977 with us to our newly built home, again in Winterthur. At that time, I did not plan for another hobby-chemistry lab. Chemistry had long before turned into my "earnest" profession. My other passions, emerging besides chemistry, playing the cello, and much later collecting Tibetan painting art did not require chemical facilities. The passions were rather complementary to my "professional" activities, each with its own personal relevance and fascination, as I will explain briefly in the following.

Playing music already fascinated me very early in my youth, much before my interest for chemistry emerged from the mentioned discovery in the attic. I was born as an introverted person with difficulties to establish verbal human contacts. Music became a way to live out my inhibited emotions. Fortunately, I grew up in the midst of a spectacular musical atmosphere; our old house stood just 100 meters from the home of the legendary music patron of Winterthur, Werner Reinhart.[2] Many world-famous musicians were guests in his hospitable house just across the street from ours, and some of them were composing immortal music for him and for the Winterthur symphony orchestra in which he occasionally played the basset horn and the bass clarinet. Among them were Igor Stravinsky, Anton Webern, Paul Hindemith, Arthur Honegger, Frank Martin, Adolf Busch, and Othmar Schoeck.[2] Inspired by these musical heroes, whom I often met at the frequently closed railroad gate when going to school, I started to play the cello and to compose music myself. Most of it has never been performed nor deserves a performance. But looking back, the creativity of composing music was for me similarly satisfactory as writing a scientific manuscript in my later years.

Music developed for me into a most relevant societal link, also towards my wife Magdalena as her love for music exceeds the one for chemistry. Actually, we met for the very first time at a private musical party; she played the violin and I the cello, and it seemed to harmonize. My attraction to music also possesses historical aspects. The Musikkollegium Winterthur[3] is an ancient institution, dating back to 1629. From its beginning, gifted members of the family Ernst were actively taking part in musical performances. My musical interests developed, so to say, by default and were relevant for my participation in local social activities. They also allowed me to interact with my "non-chemical" fellow-citizens. I still remember how some passengers in the commuter train wrinkled their noses and even opened the windows near to me, during my returning in the evening to Winterthur after having spent 8–10 h in a smelly chemistry lab at ETH Zürich! This revealed to me how much chemistry was disliked by my philistine compatriots!

A scientific link between music and chemistry can easily be found. It is provided by spectroscopy: spectroscopy serves as an analytical tool in chemistry for elucidating molecular structures, and serves as a physical basis for comprehending music, written for one or for several voices. In a remote sense, music is indeed even anticipating multi-dimensional nuclear magnetic resonance (NMR) spectroscopy. For a long time I have been intrigued by the correspondences between music and physical chemistry.

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[**] The author acknowledges numerous enlightening discussions with Dr. Amy Heller (Nyon, CH) on Tibetan art and culture.

My relation to Tibetan and Central Asian painting art has a more direct chemical relevance. The fascination for Asian art developed accidentally during a tourist journey through Asia, and particularly Nepal, in 1968, while returning to Switzerland after having spent four and a half professional years at Varian Associates in Palo Alto, California. At Varian, I was successful by introducing the Fourier transform concept that increased the sensitivity by several orders of magnitude.[4] It gave NMR a major push and finally led to my "little Prize" received in Stockholm in December 1991.[1b,c] In order to keep this short Essay in bounds, I refrain from a discussion of my research work in NMR spectroscopy.

My unexpected encounter with Tibetan Buddhist art[5–7] in Nepal was indeed "love on the first sight". I was immediately fascinated by the bold colorfulness of the paintings and the skillful drawing of great details. This art has at the same time the qualities of naive children's art, and of most sophisticated and expressive mediaeval European art. It is art conceived and executed by "unspoiled" pure minds that have not yet learned to depicture pseudo-feelings of a decadent and money-minded Western "high" society. Although Tibetan art from beyond the Himalayas is reflecting a culture shockingly alien to ours, the colorful paintings allow for a direct non-verbal access, revealing an enormously rich world. It was for me a true discovery opening the door to a marvelous spiritual and artistic domain. I felt like a "profane chemist" having gotten access to a spiritual paradise, to the "Pure Land" or Sukhavati, to use a Sanskrit Buddhist term.[8]

No, I did not convert into a Buddhist, nor am I particularly religiously inclined, but this experience widened my perception for spiritual concepts and for non-verbal expressions of eternal truths. While we chemists are using chemical formulas for representing structures and chemical reaction pathways, in the spiritual context, metaphors, symbols, and rituals have equal importance to express abstract philosophical concepts independently of a particular language, and become universally understandable. I was struck by a wealth of similarities and correspondences between Eastern and Western philosophies and religions. Having once become acquainted with one particular language or philosophy, one may comprehend others without much difficulty; they all emerge from similar human minds and use related symbols or metaphors.

Since 1968, Magdalena and I have established in our home a sizeable collection of ancient Tibetan and Central Asian, mostly Buddhist, paintings from the 12th to the 19th century. Today, they decorate virtually all the available walls. My curiosity was stimulated as much as by my first encounter with chemistry in the attic of our old house in 1945. I was inspired to acquaint myself with the complexity of Central Asian history that evolved during the past 1000 years; I had to learn about the depth of Buddhist philosophy[9] and symbolism in order to comprehend the secret messages of the beautiful paintings; and I gained insight into the Tibetan life style that is depicted in all its details within the religious and historical pictures. All aspects of the Tibetan daily life are intimately related to the Buddhist view of life and tradition. This makes these paintings invaluable sources on Tibetan culture and philosophy in the past and present.

Technically speaking, the paintings[10] are skillful products of "applied chemistry", or to use the German term "Angewandte Chemie". In this case, the relation between chemistry and painting art is becoming obvious and highly relevant for art conservation. In the course of maintaining our precious collection of Central Asian paintings I started to realize that art conservation is one of the most demanding scientific occupations conceivable. The range of relevant scientific aspects is breathtaking, from knowledge of the painting materials: support, grounding of the support (the so-called gesso), to the traditional binders and to a wide variety of natural and synthetic pigments. The application of quite delicate natural pigments requires a lot of skill and experience, and chemical knowledge is indeed indispensable.

After my compulsory professional retirement in 1998, I set out to properly equip a small "art-conservation laboratory" within our private home, converting a hobby crafting room into a tiny specialized analytical spectroscopy and restoration lab. I needed to add facilities for the chemical, microscopic, and spectroscopic analysis of the paintings, for cleaning the painting's surface from centuries of surface soiling, for retouching minor damage of the pigment layer, and for repairs of the Chinese silk framing of the paintings. Each step comprises highly delicate and demanding aspects that can be handled only by experienced experts, who themselves are often coming to their own limits of skill and expertise.

Before attempting to consolidate or restore damaged details within a precious ancient painting, it is necessary to learn as much as possible on the chemical aspects of the painting materials that have been applied by the ancient artists. Obviously, of primary interest are the painting pigments.[11] My first acquired optical tool was a Stereomicroscope Zeiss Stemi SV11 with objectives, polarizer and photographic equipment. The microscope was mounted on a sufficiently large and stable mobile gantry to cover paintings up to 2 m^2. A stereo microscope is indispensable for the study of pigment layers and for the restoration of minor damages by a very fine brush and a tungsten needle.

Initially, I applied my practical chemical knowledge in wet chemistry, remaining from my first semester chemistry lab course, to identify under a Zeiss Axiolab microscope some of the pigments.[12] In many cases, it was sufficient to identify a characteristic metal ion that, uniquely identified, together with its color, the inorganic natural or synthetic pigment.[12] In the case of blue pigments, for example, the presence of copper verified azurite, iron led to Prussian blue, and aluminum to ultramarine or natural lapis lazuli.[12] However the application of my first-semester chemistry was invasive and required appreciable amounts of sample to be taken crudely from the painting. Performing characteristic color reactions under a stereo microscope reduces the need for large samples; but in the case of the extremely fine Tibetan and Mongolian paintings, where a painted eye might consist just of a single grain of pigment, the limits of tolerable sampling are rapidly approached.

My respect for the integrity of ancient paintings forced me to switch as soon as possible to non-invasive modes of spectroscopy without any need of sample-taking.[13] Not all kinds of spectroscopy are applicable for non-invasively examining painting art. For example, my beloved NMR spectroscopy, is often unsuited because paintings are too bulky for fitting into a narrow-gap NMR spectrometer; and NMR techniques are frequently not sensitive enough for examining the thin layers of pigments applied by the artist.[14]

Infrared spectroscopy has much higher sensitivity and specificity for inorganic and organic pigments. But many of the standard IR measurements are to all extent destructive: Pigment samples are mixed with an optically inert matrix, such as KBr, into pellets and measured in transmission.[15] The most suitable IR technique is attenuated total reflection, ATR,[16,17] where the painting surface is pressed strongly against a diamond or zinc selenide crystal for achieving intimate contact. The light internally reflected in the crystal is penetrating only by a few wave lengths into the surface layer of the painting. ATR is nearly "non-destructive" but still leaves noticeable and irreversible pressure marks in the painting. In addition, only small paintings or regions near their edges are accessible with today's FTIR microscopes.

Few non-invasive techniques are left for serious consideration. For example, X-ray fluorescence can be used quite conveniently in situ on large paintings without causing noticeable damage of the paint layer. XRF has frequently been applied to art works by means of mobile X-ray fluorescence equipment.[18] But the information obtained is atomic rather than chemical and does not allow one to identify uniquely chemical compounds. For example the composition As_xS_y can represent either orpiment (As_4S_6), realgar (As_4S_4), or *para*-realgar (As_4S_4). Problematic is also the analysis of pigment mixtures, not knowing which of the elements found belong to the same compound. The high penetration depth of X-ray irradiation renders it difficult to distinguish the various pigment layers of the painting.

The most ideal known analytical technique for pigment studies is Raman spectroscopy.[19,20] Molecular vibrations are excited by a laser beam and the specific emission lines are observed. Raman is non-destructive, if used with some care not to burn holes into the canvas by excessive laser power, and it is truly a molecular analysis technique, measuring indirectly the vibration frequencies of molecules or crystalline material. Raman spectroscopy can also be implemented on relatively small space, becoming the method of choice for the narrow analytical laboratory in my private home.[21] It was not too difficult to adapt a commercial Raman microscope to the study of quite large scroll paintings. The Bruker-Optics Senterra Raman microscope was mounted on a sufficiently spacious gantry[21] to accommodate paintings up to one square meter or more. Any desired spot could then be reached by the microscope objective under computer control. Sometimes, it is not even necessary to unframe a painting as the Raman measurement is also possible through a painting's mineral cover glass, but not through Plexiglas.

The potential of combining analytical chemistry with art history is demonstrated in the following on a particularly informative and valuable 13th century painting from Central Tibet. In order to appreciate the scientific possibilities, it is necessary to provide some historical background information.[22] Buddhism reached Tibet in two phases. The first one took place around 650 during the reign of King Song-tsen Gam-po (617–650) and two of his followers. The political strength of Tibet during this early period was due to a unified Tibetan empire under an absolute ruler, extending over a huge area. The most influencial Indian teacher during this period was Padmasambhava and the teaching followed the lines of the traditional Buddhist Nyingmapa school. Two hundred years later, during the rein of Lang-dharma (838–841), the situation was radically different. Buddhism was persecuted and almost extinguished, the rescued holy books where hidden (as "terma"), and the former Bon religion took over again.

At the beginning of the new millennium, a second wave of Indian teachers reached Tibet, partially due to the Muslim pressure onto India from the West. Tibet became a refuge for Buddhists that still persists today, although for different reasons. One of the great Indian teachers of that time was Atisha (982–1054). He became highly influential for establishing the Kadampa and the emerging Kagyupa schools in Tibet.

The painting to be discussed stems from the Kagyu school and has been painted around 1200 during the early period of an emerging new tradition in Central Tibet. Beginning with the 11th century, a number of important monasteries of the Kadampa and Kagyu schools have been founded in Central Tibet. Among them were the monasteries of Nyethang Dolma Lhakhang (founded 1045 by Atisha himself), Reting and Radreng (founded 1056–57 by Atisha's student, Drom-tönpa, 1004–1064), Daglha Gampo (founded 1121 by Gampopa, 1079–1153), Densa Thil (founded 1158 by Phagmodrupa, 1110–1170), Drigung (founded 1179 by Jigten Gonpo, 1143–1217), Taglung (founded 1180 by Taglung Thangpa Chenpo, 1142–1210), and Ralung (founded 1180 by Lingrepa Padma Dorje, 1128–1188). Many of them established painting schools for documenting their history and illustrating their dogma. The historical paintings consist often of a lineage tree putting into evidence the descent of the particular teaching tradition from Buddha. Such paintings are historically highly revealing and show the development through many generations.

The painting of Figure 1 (see also Refs. [5] p. 83, [6] p. 196–197, [23], and [24] p. 146–148) shows four major teachers of the Kagyu tradition, pair wise in discussion, together with six smaller figures. Buddha is represented here by Vajrasattva/Vajradhara in the center of the top row. He is flanked by the two Indian Mahasiddhas: Tilopa on the left and Naropa on the right side who formulated in North India the Buddhist creed in the form it reached Tibet. The second row of small figures in the middle of the painting shows in the center the great Indian teacher Atisha. He could be convinced, after several unsuccessful attempts, to come to Tibet and to bring the current Buddhist creed. On the left side is Marpa (1012–1097), a renouned translator who was essential for rendering the teaching understood by the Tibetans; and on the right side is his student, Milarepa, the great and famous Tibetan poet (1052–1123). He has written immortal poems; and he is always clad in white. So far, the identification of the personalities is relatively easy, even without any inscriptions at hand.

The identification of the four major hierarchs on this painting, continuing the lineage tree, can be based on

Figure 1. Four Kagyupa Lamas, Thangka, Central Tibet around 1229 (by ^{14}C dating). Collection R.R.E., ET69. The pigments found by Raman spectroscopy, are indicated in the text. The thangka displays the lineage leading from Vajrasattva-Vadjradhara (1) via Tilopa (2), Naropa (3), Atisha (4), Marpa (5), Milarepa (6), Gampopa (7), Phagmo Drupa (8a), Dusum Khyenpa (8b) to the youthful founder of the Drigung monastery (1179), Jigten Gonpo (9). For the identification of the ten personalities, a scheme, chronologically numbered from 1–9, is given in the text.

numerous contemporary portraits[24] and on traditional knowledge. The gray-haired teacher on the upper left must be the important spiritual leader Gampopa (1079–1153). He was the most famous student of Milarepa. Gampopa himself had many students, and he is the origin of four major Kagyu schools: the Karmapas, the Phagmodrupas, the Tsalpas, and the Bahrampas.[25] His gray hair and his characteristic physiognomy allow his convincing identification.[26]

His discussion partner on the right side must be the head of one of the four great Kagyu schools. According to his physiognomy and his characteristic headdress, he likely represents Gampopa's foremost student Phagmo Drupa (1110–1170).[24] The latter had a large number of highly gifted students, eight of whom became the founders of eight influential Kagyu schools, among them Taglung Thangpa Chenpo and Jigten Gonpo, mentioned above.

The second gray-haired hierarch on the lower left seems to be, on the first sight, a teacher of Gampopa's generation. However, there is none who would match Gampopa in importance. It is more likely that he is another disciple of Gampopa. In fact, Dusum Khyenpa (1110–1193), the founder of the highly influencial Karmapa school, is known to have been gray haired already as a young monk and was often called Khampa Özer, the "gray-haired Khampa".[27] There is little doubt that he is shown on this thangka. Dusum Khyenpa had an influence reaching far beyond his own school.

The fourth hierarch on the lower right, undoubtedly, is a disciple of one of the two shown masters Phagmo Drupa and Dusum Khyenpa. Because of the less direct succession and student-master relationship within the Karmapa school, he is more likely one of the many disciples of Phagmo Drupa.[25] We may consider identifying him with Taglung Thangpa Chenpo, with Jigten Gonpo, or possibly with Lingrepa Padma Dorje. We can exclude the founder of the Drukpa school in Bhutan, Lingrepa Padma Dorje, as he is mostly clad in white, like Milarepa. Based on his physiognomy,[24] one is tempted to identify the fourth hierarch with Jigten Gonpo (or Jigten Sumgon) (1143–1217), the founder of Drigung (bri gung) monastery in 1179, 150 km east of Lhasa, rather than with Taglung Thangpa Chenpo (1142–1210), the famous founder of Taglung monastery 120 km north of Lhasa in 1180. The round and smooth face of hierarch four fits the known portrait of Jigten Gonpo well.[24]

In addition, it is known that towards the end of his long life, Dusum Khyenpa (1110–1193, later recognized as the first Karmapa) visited Drigung monastery, and he was deeply impressed by the radiance of Jigten Gonpo, recognizing in him (on two occasions) an incarnation of Buddha himself.[28] Dusum Khyenpa became, so to say, a second spiritual Guru of Jigten Gonpo. This would well justify to show Dusum Khyenpa on this thangka together with Phagmo Drupa as the co-teachers of Jigten Gonpo. This completes satisfactorily the assignment of all ten figures, however without conclusively proving their identities.

This thangka has been published already four times, with some differences in the given assignments: Amy Heller[5] was cautious enough to restrain from a full assignment in 1999. She identified only Tilopa, Naropa, and Atisha, and left the four dominant hierarchs unassigned. Pratapaditya Pal,[6] supported by other experts, risked a complete assignment, and proposed no. 8b to be Jigten Gonpo, while no. 9 he assigned to Taglung Thangpa Chenpo. Richard R. Ernst[23] misinterpreted 2001 a left/right ambiguity in literature[29] and correspondingly identified no. 7 with Phagmo Drupa and no. 8a with Taglung Thangpa Chenpo. In addition, no. 4 was identified, lacking an alternative, with Gampopa. Finally, David Jackson[24] saw in no. 8b a yet unidentified disciple of Phagmo Drupa and left the identification of no. 9 open. There are good reasons to doubt these previous attempts of identification and to accept for the moment the new assignment proposed in this paper as the most consistent interpretation of today's knowledge, summarized by the following scheme with a chronological numbering:

2 Tilopa (928–1009) 1 Vajrasattva-Vajradhara 3 Naropa (956–1040)
7 **Gampopa** (1079–1153) 8a **Phagmo Drupa** (1110–1170)
5 Marpa (1012–1097) 4 Atisha (980–1054) 6 Milarepa (1052–1123)
8b **Dusum Khyenpa** (1110–1193) 9 **Jigten Gonpo** (1143–1217)

It is likely that the thangka has been painted after the death of Jigten Gonpo, 1217, around the year 1220. This can be verified by a ^{14}C age determination of the canvas of the painting by accelerator mass spectroscopy: For harvesting the cotton of this painting, a time span of 1229 ± 61 years has been determined by Dr. Georges Bonani, Institut für Teilchenphysik, ETH Zürich. The identification of the figures and their life data are at least not in apparent contradiction with this ^{14}C dating.

The determination of the main pigments in this painting based on Raman spectroscopy leads to a rather restrictive palette of colors: a) The dominant dark red of the monk's undergarment and of the back seats in the form of shields relies on cinnabar (HgS), as so often in thangkas. b) The orange of the outer clothes is implemented by mixing yellow orpiment (As_4S_6) and red cinnabar. In later paintings usually red lead (Pb_3O_4) is the common orange pigment that is however not used here. c) Pure orpiment is found in the yellow borders of the pedestals. d) The damped green of the seats and of the aura of Hierarchs (7) and (8b) consists of a mixture of yellow orpiment and of blue Indigo ($C_{16}H_{10}O_2N_2$). No pure green pigment, such as malachite ($CuCO_3{\cdot}Cu(OH)_2$), which has been mined since centuries in the copper mines of Nyemo County in Tibet, or Brochantite ($Cu_4(OH)_6SO_4$), or Botallackite ($Cu_2(OH)_3Cl$) can not be found in this thangka. e) Pure Indigo has been applied to the blue Vajrasattva/Vajradhara, for the blue lion heads in the aprons and for the stylistic blue mountains in the aprons. f) In addition, there is an intense blue being used for the background sky. It consists of high quality azurite ($2\,CuCO_3{\cdot}Cu(OH)_2$) that was mined also in Nyemo County. g) The white areas of the Aura of Hierarchs (8a) and (8b), the seat of Marpa (4), and the dress of Milarepa (5) are colored with calcium carbonate ($CaCO_3$).

It is speculated that this thangka was painted by a Nepalese painter, working, like many skilled Nepalese painters at that time, for a Tibetan sponsor in a Tibetan monastery or workshop. Such foreign labor was common at that time when the Nepalese painters were better skilled in comparison with the less developed Tibetan artists. This seems to explain the abundant usage of the typical Nepalese pigment indigo and the absence of malachite.

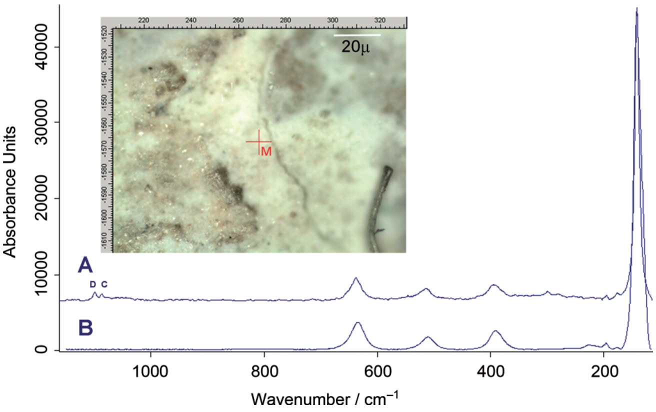

Figure 2. Pigment used (by an unknown 20th century restorer) for minor repairs of some eye whites. A) Raman spectrum of a repair of the eye white of Marpa (5), recorded with 785 nm laser and ×50 objective on a Senterra Raman Microscope, measurement time: 10 × 1 s. Laser power: 10 mW. The small peak C stems from $CaCO_3$, the original white pigment, while the small peak D corresponds to Dolomit ($CaMg(CO_3)_2$) which seems to have been mixed into the correcting paint. B) Reference spectrum, RRUFF Project R070582, Raman spectrum of Anatase, TiO_2, unoriented (780 nm laser).[31]

Already several years ago, the author has noticed that the eyes of the monks have been painted with a special pigment that could be identified only very recently by Raman spectroscopy. The usage of an unusual pigment for the eyes was not unexpected as the eyes are regularly inserted by the master painter as a last step in the painting process. So it was not surprising that he might have used his own proprietary pigments. However, to the author's great surprise, the Raman spectrum of Figure 2 A identifies this pigment without doubt as anatase by comparing with the reference spectrum in Figur 2 B and its four characteristic peaks at 148, 390, 511, and 634 cm^{-1}. Anatase is one of the three modifications of titanium dioxide (TiO_2) that was commercially available only since 1916, and that was replaced already 1938 by the modification rutile which possesses more favorable pigment properties. Although anatase is known to occur as a natural mineral, it has, without doubt, to be concluded that the eyes have been restored in the 20th century. Fortunately, no traces of further restorations have been found in this thangka. And the restoration of the eyes has been done rather skillfully, although using a modern foreign pigment. The tiny peak at 1084 cm^{-1} in Figure 2 A stems from the original white paint layer that consists of chalk, $CaCO_3$. More enigmatic is the second small peak at 1089 cm^{-1}. It occurs exclusively in the repainted areas and appears to be a component of the restorer's paint. It seems to match the spectrum of dolomite ($CaMg(CO_3)_2$). In Tibetan art, this white pigment is rarely used. One may ask whether the restorer purposely applied pigments that can not be mistaken as parts of the original painting. More likely, it is just what he had available at that moment.

In the context of studies of other Tibetan paintings,[30] a remarkable glittering effect has occasionally been found in areas painted with orpiment. It could be shown that it is due to a natural, but very slow, conversion process of orpiment (As_4S_6) into crystalline sulfur (S) and into crystalline arsenolite (As_2O_3),[30] possibly by the two chemical processes $As_4S_6 \rightarrow As_4S_4 + 2\,S$, and $As_4S_6 + 9\,O_2 \rightarrow 2\,As_2O_3 + 6\,SO_2$. Sulfur and arsenolite crystals could be found and identified by Raman spectroscopy in the present thangka as well, as shown in Figure 3, with the three characteristic sulfur peaks at 157, 224, and 476 cm^{-1}, and in Figure 4, with the six typical arsenolite lines at 183, 268, 369, 470, 560, and 780 cm^{-1}. (The byproduct As_4S_4 is expected to occur as realgar or pararealgar. However, Raman signals of these two compounds could not be detected, possibly because they are spatially very thinly dispersed.) The sulfur crystals are quite abundant in the orpiment regions and can easily be found, while the Arsenolite crystals are rarer. The latter exhibit invariably relatively strong signals of remaining orpiment (*) and of the simultaneously present cinnabar component (C).

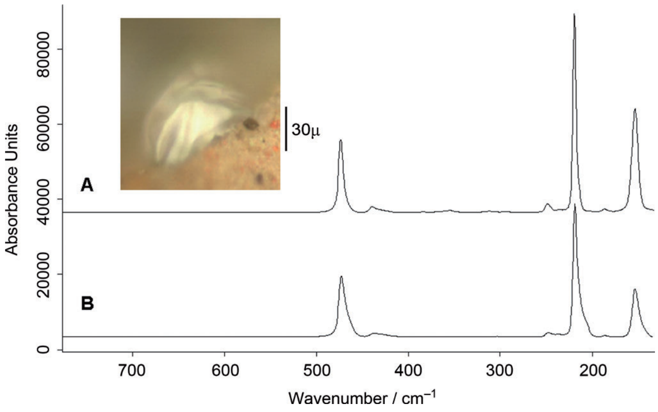

Figure 3. Identification of glitter within the orpiment areas in the thangka of Figure 1. A) Sulfur crystal and its Raman spectrum with the same parameters as used for Figure 2. B) Reference spectrum, RRUFF Project R040135 Raman spectrum of sulfur unoriented (780 nm laser).[31]

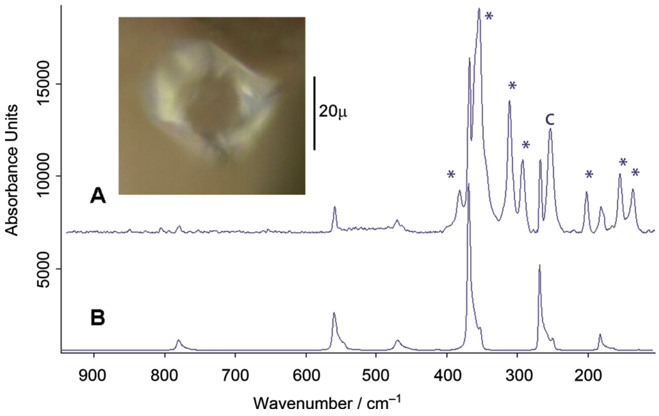

Figure 4. Arsenolite (As_2O_3) glitter within orpiment areas. A) Raman spectrum of the arsenolite crystal shown in an orpiment + cinnabar area recorded under the conditions of Figure 2. In the spectrum, the remaining orpiment peaks are marked with a star (*) and the cinnabar peak with a letter C. B) Reference spectrum, RRUFF Project R050383 Raman spectrum of arsenolite unoriented (780 nm).[31]

Indeed, Raman spectroscopy and analytical chemistry are highly informative in art conservation. For a researcher, it is rewarding to bring his scientific and artistic inclinations on a single denominator, rendering it feasible to develop a more coherent view of our wide-spread human endeavors.

Who would expect a retired professor of chemistry being able of handling professionally all the demanding skills and knowledge in history, arts, spectroscopy, and chemistry, needed for success in art conservation? So I am back where I started from: a passionate amateur of chemistry and humanities with rather high ambitions, but with limited skills, limited time, limited finances, and limited laboratory space. The circle is closing: I am living today within one kilometer from where I was born. However, my ambitions extend far beyond the "frontiers" of traditional chemistry. It is true, chemistry itself does not know any "limits"; and I still consider myself a curious chemist in agreement with the title of this Essay: "*A chemist remains a chemist*".

Received: July 11, 2012
Revised: September 11, 2012

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