**Layered manganese oxides structures: Micro-Raman and selected mobile Raman spectroscopic studies**

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***Abstract***

The main structural building blocks that form manganese oxides are MnO6 octahedra, these share corners and edges to construct specific structures which can either be tunneled or layered. In the layered structures, i.e., phyllomanganates, the MnO6 octahedra form sheets which in turn alternate with sheets of metal oxides and H2O. These metal ions can vary (Zn, Co, Ni, Al, Li,…) and give rise to an entire range of different metal oxides. The characterization of these layered materials is important as they have various economical/industrial applications. Birnessite-type materials, a specific type of layered manganese oxides, are widely studied for their use as cathode materials in alkali-ion batteries. Phyllomanganates are also commonly found as constituents in sediments and soils or as coatings on rock surfaces. Their natural occurrence as black colored components have ensured that these minerals were also applied as pigments in archaeological and historical contexts. They are, for example, often found in rock art paintings and on pottery. As the oxides are used in unique archaeological objects, Raman spectroscopy is an evident choice for characterization due to its non-destructive nature of analysis. In the current study, five mineral samples of (layered) manganese oxides are analyzed with different Raman instrumentations, including mobile systems and a benchtop micro-Raman set-up. The characterization of each selected manganese oxide and their comparison with literature data is discussed for the micro-Raman instrumentation. In addition, the ability of identifying and characterizing layered manganese oxides and the possible challenges when using mobile instrumentation are discussed as well.

***Keywords:*** Phyllomanganates; manganese oxides; Archaeological heritage; mobile Raman equipment

***Introduction***

Manganese oxides and oxyhydroxides are abundant minerals that can be found in various geological settings, such as coatings on rock surfaces, nodules in lakes and oceans and fine-grained sediments in soils1,2­. These minerals are composed of main structural building blocks, i.e. MnO6 octahedra, that are arranged in a particular order. This structure can either be tunneled in which cations can be encapsulated (tectomanganates)3 or layered (phyllomanganates) in which sheets of MnO6 octahedra alternate with metal oxide layers and H2O2.

Both layered and tunneled Mn oxides became increasingly popular, owing to their widespread applications and specific properties. These applications range from the industrial to the archaeological field. In the context of industrial applications, layered metal manganese oxides of the birnessite-type (Na,Ca)(Mn4+,Mn3+)2O4$ ∙$ 3/2 H2O have attracted interest as cathode materials for Na and K batteries and pseudocapacitors4. The layered manganese oxides typically have favorable electrochemical properties, and have economic and environmental advantages over more toxic compounds such as cobalt or nickel5. Recently, these types of manganese oxides have been shown to be promising compounds for heterogeneous water-oxidation catalysis6. Moreover, manganese oxides can also play an important role in mitigating climate change in the perspective of mineral-carbon reactions as they have a high reactivity with organic carbon1. Besides this broad application range and the promising properties of manganese oxides, for many years, these minerals have also been observed in an archaeological context. For example, in research into Neanderthal communities and cultures, the use of black manganese oxide minerals as pigments has been linked to the direct application of the pigmented mineral onto the skin, in the form of a body drawing or painting. Manganese oxides have also been documented as a fire accelerator7-9. The latter authors have also highlighted the overall cultural significance and change of the use of the manganese oxide minerals in these Neanderthal communities9. As another example, the ancient Chinchorro people who inhabited the Atacama Desert in northern Chile and Southern Peru ornamented their dead by covering the body with various types of clays, minerals, sticks, and reeds. This tradition began in 6950 BP and the coloring of the body was exclusively done with black manganese oxides10,11. Further knowledge of the different manganese oxides used and found in soils can help unravel new insights into these traditions. In addition, throughout the archaeological record, manganese oxides have been implemented widely as dark pigments alongside others, such as carbon black and iron oxides12,13,14. The knowledge of combining the two main sources of black pigments, iron and manganese oxides, to form a mixed black Mn,Fe-oxide has been known since ancient times as well13. In various rock art paintings, the black drawings were obtained by applying some type of manganese oxides15-17. Also on decorated pottery, manganese oxides fulfill their role as the black chromophore18-20. However, manganese oxides can also involuntary be the colorant. It is known that manganese oxides precipitate on ancient artefacts over time, rendering the original artefact with a different hue. This is for example the case for Mesopotamian clay tablets. Portable X-Ray fluorescence (pXRF) revealed that indeed in the darkened surfaces, an elevated Mn amount was found21. It is evident that the characterization of different types of manganese oxides can be very useful for various branches in archaeometrical research.

Unfortunately, identification of these minerals is quite tedious and using X-ray diffraction (XRD) for example can be difficult22-25 as phyllomanganates often have highly disordered crystalline structures, resulting in ambiguous XRD spectra with broad and/or overlapping peaks1,2,26. Other techniques have therefore often been applied, such as X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS) and electron microprobe analysis (EMPA)1,24,25. These techniques have proven to be very useful, however, advanced sample preparation, large sample sizes or the use of synchrotron X-ray sources can complicate the analysis2,27 and for some samples, especially unique archaeological ones, these prove to be too much of a limitation. Raman spectroscopy can be a technique that can circumvent some of these limitations with respect to sample consumption and large sample sizes.

The characterization of manganese oxides with Raman spectroscopy has a proven track record2,3,5,26-28 and the technique can be used to analyze both tunnel3,27 and layered structures2 in natural samples2,3,26,27 and synthetic manganese oxides4,29,30. From an archaeological point of view, the non-destructive nature and *in situ* measurement capability of Raman spectroscopy adds an extra advantage17.

However, the characterization of manganese oxides with Raman spectroscopy, especially when using portable Raman equipment can be quite difficult due to multiple factors. Many different phases of manganese oxides exist, and various cations can be encapsulated into the framework. This often results in Raman spectra with minimal differences between the various manganese oxides. In mobile instrumentation, these minor variations can even be invisible due to the lower spectral resolution. Secondly, manganese oxides are known to be weak Raman scatterers3. An increase in measuring time and/or power is then often imposed. Mobile instrumentation is, however, typically used for its relatively quick analysis17. Long measuring times are thus not preferred. In addition, manganese oxides are quite susceptible to the laser light and power that can inflict a transformation and/or degradation of the original component, and can thus lead to mischaracterization. Mobile instrumentation typically uses a higher laser power and is hence disadvantageous31.

In the current study, micro-Raman spectroscopy was used to characterize five mineral samples of layered manganese oxide. These mineral samples were selected based on their common occurrence as weathering products in many Mn-bearing base metal deposits2,32. As these minerals are commonly found in soil and sediments, it is logical to hypothesize that these components were used when dark pigmented minerals were required. Many of the tunneled structures (i.e. pyrolusite, hausmannite, manganite) have already been extensively studied and characterized3,26,27,29,33. Due to its industrial applications, birnessite is one of the most widely studied layered manganese oxide. However, ambiguous Raman data for this mineral have been reported4,26,28.It is thus interesting to characterize these layered structures with Raman spectroscopy in more detail. In addition, this study also tests the ability of mobile Raman instrumentation to differentiate and characterize layered manganese oxides that are often found in the archaeological context11,16,20,34-36. The manganese oxides were first identified with micro-Raman spectroscopy paying special attention not to degrade or alter the samples in the process. The experimental conditions (e.g., power and measuring time) were carefully selected. The obtained results are compared with existing data from literature. The mineral samples were subsequently tested with three different mobile Raman set-ups.

***Experimental***

*Samples*

A total of five natural Mn oxide minerals were analyzed in this study. One sample comes from the collection of the Geology department at Ghent University and was labelled as chalcophanite (sample 13487). Two samples were obtained from the Mineralogical museum of the Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University (Prague), i.e., an asbolane specimen and vernadite (Fig. 1a). The remaining two samples, birnessite and ranciéite, were obtained as weathering products from manganese-rich veins in Kutná Hora, Czech Republic.

*X-Ray powder diffraction*

X-ray diffraction was performed as a supporting method of analysis to confirm the mineral composition of the samples. The samples were crushed in an agate mortar and analyses were carried out using a PANalytical X’Pert Pro diffractometer, equipped with a diffracted-beam monochromator and X’Celerator multichannel detector (CuKα radiation, 40 kV, 30 mA, 3–80° 2θ, step scanning at 0.02°/200 s). The obtained diffractograms were analyzed using X'Pert HighScore Plus software version 1.0d equipped with a PDF-2 database.

*Raman spectroscopy*

*Bruker Senterra*

The Raman spectra obtained with a benchtop instrument were acquired with a confocal Bruker Senterra R200-L spectrometer. The system is equipped with two laser excitation wavelengths, i.e. 532 nm (frequency doubled Nd:YAG) and a 785 nm diode laser. A thermoelectrically cooled (-65°C) charge-coupled-device (CCD) detector was used. The micro-Raman spectrometer is coupled with an Olympus microscope equipped with an XYZ motorized stage. The microscope turret contains the following objectives 5x, 20x, 50x and 100x, with respectively numerical apertures (NA): 0.1; 0.4; 0.75; 0.9. Spot sizes were estimated to be 50 µm, 10 µm, 4 µm and 2 µm, respectively. Neutral density filters are used to control the laser output. A spectral resolution of 3-5 cm1 can be achieved. The system is controlled by OPUS software (Bruker).

Samples were obtained as fragments. Small grains were measured as such, after positioning them on a glass slide, requiring no further sample preparation for further Raman analysis. A magnification of 50x was used to focus the laser on the minerals. Both lasers were used for characterization and identification of the mineral manganese oxide samples. The laser power was kept at the lowest (1%), in order not to hinder correct identification due to degradation bands and patterns. The laser output on the manganese oxide samples was, 0.12 mW (50x) and 0.73 mW (50x) for the 532 and 785 nm laser, respectively. Other experimental parameters included: spectral resolution of 3-5 cm-1, spectral range: 40-1540 cm-1 and 80-1530 cm-1 for the 532 and 785 nm laser respectively, while the confocal pinhole was kept at 50 µm. The obtained spectra were post-processed using the Thermo Grams/AI 8.0® suite software (Thermo Fischer Scientific).

*Bravo*

The handheld Bravo (Bruker Optik GmbH, Ettlingen, Germany) Raman spectrometer weighs ca. 1.5 kg and has a fixed optical head. The instrument is equipped with two lasers in order to suppress fluorescence by using a sequentially shifted excitation mode (SSE). Both laser wavelengths operate in the near infrared region, i.e. 785 and 853 nm. A CCD detector, cooled to 15°C, is used for collecting the signal. The spectral range is 170–3200 cm−1, with a resolution of 10–12 cm−1. The instrument automatically chooses the laser power with a maximum capacity of 100 mW, the user cannot adjust the power. The spectra were recorded using the automated settings. The spectra can be exported by OPUSTM software for further data processing with the Thermo Grams/AI 8.0® suite software (Thermo Fischer Scientific). The wavenumber positions were checked with a calcite standard provided by Bruker.

*i-RAMAN EX*

The i-Raman® EX portable system (BWTek, Newark, USA) is a dispersive fibre optics spectrometer, which works on net power. The spectrometer has a 1064 nm excitation laser, with a spectral range from 100 to 2500 cm−1 and a spectral resolution of less than 10 cm-1. A high-sensitivity TE-cooled InGaAs detector is used for collecting the Raman scattering. The laser power has a maximum output of 330 mW at the exiting probe. The experimental conditions (such as accumulation times and power) can be chosen by the operator with the software BWSpec (v.4.10\_4). The laser power was kept at a minimum to not induce any degradation and/or alteration to the susceptible manganese oxide minerals. No external calibration is required but the wavenumber calibration was checked with cyclohexane (Kaiser). Posttreatment of the acquired spectra was performed by using Thermo Grams/AI 8.0® suite software (Thermo Fischer Scientific).

*EnSpectr RaPort*

EnSpectr RaPort (Enhanced Spectrometry, Inc., San Jose, CA, USA) is designed as a field-portable lightweight (2 kg) instrument of pistol-like design, which is equipped with an Nd:YAG 532 nm wavelength laser and an output of up to 120 mW. Spectra were recorded in the range of 150 – 1800 cm-1 with an operational resolution in the range of 6 – 9 cm-1 and an attenuation factor of 30, which roughly translates into the 15 mW output (checked with the LaserCheck power meter, Coherent, Santa Clara, CA, USA). The laser spot size is less than 0.1 mm. The system is controlled through a USB 2.0 port connection to a laptop that runs the control software. The measurement setup was 30 accumulations of 3 seconds each. This spectrometer does not require a wavenumber calibration procedure; however, a polystyrene standard was used to check the correct wavenumber positions of the Raman bands.

***Results and discussion***

 The current research is focused on the accurate characterization of layered manganese oxides using Raman spectroscopy (benchtop equipment and mobile systems), the characterization of these layered structures is of relevance for both industrial as well as archaeological applications5,6,10,14,21. To confirm the composition of the five mineral samples, the manganese oxides were additionally analyzed with powder X-ray diffraction (pXRD). However, natural manganese oxides are often difficult to identify and distinguish using X-ray diffraction because of issues of crystal size and disordered and similar structures, which may result in diffraction patterns exhibiting broad peaks2. In our samples, chalcophanite is easily distinguished by the strong diffraction peaks at 6.925 Å, 4.067 Å, 3.511 Å, 3.469 Å, and 2.767Å (JCPDS 01-084-1692 reference) (Figure S1a). Magnetite was identified as the admixture in the sample. Both phases have high crystallinity considering the sharp peaks. Ranciéite was also detected along with other Mn-oxide, todorokite, and haematite. Each of these phases exhibits broad peaks, suggesting some level of disordered structures. Ranciéite is identified by the peaks at 7.473Å and 3.732Å (JCPDS 00-022-0718 reference) (Figure S1b). Other layered Mn oxides were more difficult to recognize. The detection of birnessite in the sample used was problematic because the main phase of the sample is muscovite, along with ramsdellite and fluorapatite. A broad peak at 7.214Å could be attributed to a disordered birnessite phase (JCPDS 00-043-1456 reference) (Figure S1c). The sample labelled as 'vernadite' showed a complex composition. Romanéchite is likely to be one of the Mn phases in the sample (Figure S1d) with peaks at 6.984Å, 3.493Å, 2,396Å, 2.245Å, and 2.160Å (JCPDS 00-014-0627 reference). Coronadite and/or hollandite could also be present. The small peaks of 7.612Å, 2.823Å, and 1.960Å can correspond to the vernadite signal37. The result for the asbolane sample is inconclusive. The only main phases detected are magnetite and enstatite. The presence of asbolane cannot be completely ruled out, but it remains unconfirmed (Figure S1e).

In the following paragraphs, the characterization of the manganese oxides with micro-Raman spectroscopy and their comparison to literature data will be discussed first. For each manganese oxide phase, a table with the corresponding Raman wavenumbers is given together with a figure of the corresponding spectra recorded with the two different lasers (785 and 532 nm, Senterra). Lastly, the characterization with mobile Raman equipment is discussed for the five mineral samples.

Chalcophanite Zn2+Mn3O7 · 3H2O

 Chalcophanite, Zn2+Mn3O7 · 3H2O is a hydrated phyllomanganate that is constructed out of sheets of edge-sharing Mn4+O6 octahedra alternating with ZnO6 octahedra and H2O2,22,26. In this framework, one out of seven octahedra of the manganese oxide layer is left vacant. The Zn2+ cations are found above and below these vacancies in an ordered pattern. These ions in turn form an octahedron by binding with 3 oxygen atoms from the manganese octahedra and 3 oxygen atoms originating from water molecules. The stacking sequence is of the order $∙∙∙$Mn-O-Zn-H2O-Zn-O-Mn$∙∙∙$. In comparison to other layered manganese oxide structures, chalcophanite is characterized by a well-defined crystallinity and forms euhedral platy crystals due to its highly ordered structure. The XRD pattern of this mineral is therefore defined by strong and narrow diffraction peaks22, as was confirmed by the pXRD obtained from our mineral sample.

 In Figure 2, both spectra are depicted, as obtained with the 785 nm and 532 nm laser from the Senterra Bruker benchtop system. Both spectra display well pronounced bands with a good signal-to-noise ratio. These well-defined bands reflect a highly crystalline order, and show that manganese is only present in the +IV oxidation state2,22. Post et al. (2021) have shown that the band around 670 cm‑1 highly depends on the polarization of the laser. In a crossed polarized beam, the band almost completely disappears2. It is evident that the mineral sample can easily be identified by its high intensity bands at 670 and 570 cm‑1. However, some minor differences are noticeable in the spectra acquired with the two lasers of the system. Depending on the laser wavelength, some relative band intensities change. This is particularly noticeable for the bands in the region 400-280 cm-1. In this region, the bending vibrations of the Mn-O and Zn-O octahedra are found2. In the spectrum acquired with the 785 nm laser, two bands are visible in this region, one at 379 cm-1 and one at 298 cm-1. Whereas for the 532 nm laser, only the 392 cm-1 band is found. This effect was noticed in multiple spectra obtained with the 532 nm laser.

In Table 1, the identified Raman band positions for chalcophanite are compared to published data and a good agreement with the results is shown.

Asbolane (Ni, Co)xMn4+(O,OH)4·nH2O

Asbolane is a lithiophorite-like phase. In lithiophorite, alternating layers of MnO6 octahedra and (Al,Li)(OH)6 octahedra sheets are present. In the case of asbolane, some of the Al and Mn ions are replaced with cations of transition-metals such as Co, Cu and Ni2,38. The structure of asbolane has not yet been determined, but it has been proposed that the sheets of (Al,Li)(OH)6, characteristic for lithiophorite, are replaced by poorly structured islands of (Co,Ni,Cu)O6 octahedra2. Hence, the Raman spectra of asbolane species typically have very broad bands. As asbolane is a lithiophorite phase in which sorption of other metal cations has taken place, mixed intermediate phases of these two manganese oxides are also quite common38. This results in various Raman band patterns depending on the substitution ratio of the heavier transition metals38.

 In Figure 3, Raman spectra acquired with the 785 and 532 nm lasers of the benchtop instrument Senterra are shown. Broad bands are clearly visible and the lack of bands below 400 cm‑1 is obvious. A band around 498 cm-1 is observed for both lasers (785 and 532 nm, Senterra). Different band intensities can be noticed for both lasers in the range of 800-500 cm-1. In the spectrum obtained with the 785 nm laser, a band around 590 cm-1 is the most pronounced, whereas for the 532 nm laser this band is found at 620 cm-1.

The Raman band positions for our sample, as well as literature data are given in Table 2. Not all the data is comparable. Possible explanations are that the mineral exists in various mixed states between lithiophorite and asbolane, and the substitution with the heavy transition metals most likely also plays a role2,38,39.

Ranciéite (Ca,Mn2+,K,Ba)(Mn4+, Mn3+)4°9 · n H2O

Ranciéite is a calcium-rich layered manganese oxide. Although calcium is the predominant interlayer cation, sometimes magnesium, barium and/or potassium are also found inside the lattice2. The mineral has a similar structure as chalcophanite but has only 1 out of 10 or 11 vacant positions in the MnO6 octahedra sheet. Due to the lesser number of vacant positions, the framework is not as ordered as in the case of chalcophanite and the mineral is characterized by a lower crystallinity2,26.

In Figure 4, spectra obtained with both lasers (Senterra, benchtop) are shown. A slight similarity between the spectra obtained for chalcophanite and ranciéite can be observed. For example, both minerals show the main Raman band around 670 cm-1. This is a consequence of the similarity in their framework, however due to the lesser degree of ordering in ranciéite the bands of the latter are broader2. Another observation is that by increasing the acquisition time with the 785 nm laser, the intensity of the band around 580 cm-1 dropped in comparison to the band at *circa* 670 cm-1. Moreover, in both spectra the noise, linked to the low crystallinity, was unavoidable.

The results from both lasers largely corroborate the reported literature data2 (Table 3), but there are some discrepancies to be observed. The Raman wavenumbers of our sample do not match the band positions reported by Bernardini *et al*.26 and Fan *et al*.40. A possible explanation might be that the reported band positions in aforementioned studies originate from a degraded ranciéite as a consequence of the experimental conditions used. In the current study, when the power was increased to 10% (1.53 mW for the 532 nm laser), a spectrum was obtained with a broad band around 632 cm-1 (Figure S2), resembling other research26,40. In Bernardini et al. the laser (632.8 nm) power output was reduced to 1 mW, whereas in Fan et al. no laser (633 nm) power is mentioned.

Birnessite (Na,Ca)(Mn4+,Mn3+)2O4 ·3/2 H2O

Birnessite minerals are relatively common and can be found in various soils and surficial sediments6. They are often poorly crystalline and fine-grained and possess promising industrial qualities due to their high absorption properties and their easy participation in redox and cation-exchange reactions6, making them interesting compounds for batteries5,28. As such, many researchers have synthesized birnessite-like materials with a variety of transition metals and alkali and earth-alkali cations2.

Birnessite materials are composed of negatively charged stacked sheets of MnO6 octahedra. The resulting negative charge is counteracted by the inclusion of mono- or divalent cations (such as Na+, Ba2+, K+, Ca2+) or water molecules in the interlayer, and/or the partial substitution of Mn(+III) in the Mn(+IV)O6 octahedra2,41,42. Two different birnessite crystal structures (triclinic and hexagonal) exist and the differentiation between them is based on the origin of their negative charge, which is reflected in the nature of the interlayer cation and the oxidation state of the manganese ions42. In the triclinic structure, the negative charge originates from the substitution of Mn(+III) into the framework, which in this case is composed of two layers of Mn(+IV)O6 octahedra that alternate with one layer of Mn(+III)O6 octahedra. To compensate for the induced negative charge, hydrated cations such as Na+, Ba2+ are found in the interlayer42. Important to note is that the higher degree of Mn3+ substitution (triclinic structure) will result in a lower symmetry due to Jahn-Teller distortions caused by the manganese cation2. In the hexagonal structure, Mn(+IV)O6 octahedra are the main constituents. The negative charge is in this case induced by vacancies in the layered framework. Above and below these vacancies, Mn(+III) as well as some H+ ions, are found to compensate the charge41,42.

In this study, as evident from the XRD data, the sample material was found to contain birnessite. An additional manganese oxide was identified in this particular sample as well, and was identified as ramsdellite $γ$-MnO227. This is a polymorph of the most common manganese oxide, pyrolusite $β$-MnO23. The obtained Raman spectra, acquired with both the 785 nm and 532 nm lasers (Senterra, benchtop), can be found in the supplementary Figure S3.

Unfortunately, the Raman scattering properties of birnessite-type structures are rather low5, resulting in broad bands and quite some noise. In Figure 5, the spectra resulting from the two laser wavelengths are depicted. These exhibit an obvious variation in band patterns. In the spectrum acquired with the 785 nm laser, a pronounced band at circa 650 cm-1 is present, with a low intensity band around 580 cm-1. Whereas with the 532 nm laser, this band (577 cm-1) has an intensity which is relatively comparable to the band at circa 650 cm-1. The latter band might be resonance enhanced by the 532 nm laser but can also be a consequence of orientation as a result of shear motions of oxygen atoms parallel to the MnO6-octahedra layer2. Another difference between both spectra is the lack of a band at 499 cm-1 with the 785 nm laser. This might as well be a resonance effect caused by the 532 nm laser or an orientation-dependent band. This particular band has previously been attributed to be characteristic of a hexagonal structure28.

The wavenumber values for our birnessite sample are compared to published data (Table 4) and seem to be inconsistent. However, as mentioned, depending on the degree of Mn3+ substitution, either a hexagonal (low ratio of Mn3+) or triclinic birnessite structure (high ratio of Mn3+) will be attained2, greatly affecting the Raman band positions42. As such, the data of our current study is in line with the reported wavenumbers from Post *et al.* in 2021, Scheitenberger *et al.* in 2021 for their hexagonal birnessite type mineral and Boumaiza *et al.* in 2019 for their synthetic hexagonal birnessite2,28,42. Thus, we conclude that the sample used in the current study is a hexagonal birnessite type. Julien *et al.* (2003) have shown that the counterion in the birnessite structure also has a large effect on the Raman spectrum: band position shifts as well as changing relative intensities were observed5.

Romanéchite (Ba,H2O)2(Mn4+,Mn3+)5°10

As previously mentioned, the sample labelled as vernadite was analyzed with pXRD to confirm the composition. However as layered structures are poorly crystalline, visual distinction in the field can be quite difficult and mischaracterization is possible2. Indeed, the pXRD analysis showed a complex composition. Romanéchite was likely to be the Mn phase, however coronadite and/or hollandite could also be present. Having mentioned that, XRD characterization can also be ambiguous, given the poor crystallinity of the material. Raman spectroscopy was subsequently performed and is in agreement with the result of the pXRD, confirming that the mineral contains romanéchite.

Romanéchite is a hydrated barium manganese oxide with a tunneled structure which consists of double and triple chains of MnO6 octahedra. The tunnels have dimensions of 2 x 3, reflecting the amount of MnO6 octahedra building blocks, and the Ba2+ cations and water molecules are arranged in a ratio of 1:22,26,27. Romanéchite has often been mischaracterized in the past and erroneously categorized as psilomelane, nowadays an obsolete and generic name referring to manganese oxides of the hollandite group $α$-MnO23,26,27.

The obtained Raman spectra for romanéchite are depicted in Figure 6. Both lasers provide a well resolved spectrum, with minor differences between the spectra regarding the relative intensities of the bands. In the spectrum obtained with the 532 nm laser, the band around 584 cm-1 is the most pronounced, whereas in the spectrum obtained with the 785 nm laser the bands (626 and 583 cm-1) have comparable intensities. This effect has been noticed in multiple spectra from the mineral sample, hence an orientation effect can be excluded. The 532 nm laser might thus enhance the band around 580 cm-1.

In Table 5, the Raman characterization of romanéchite is given in comparison with reported literature data and exhibit good agreement.

Mobile instrumentation

As manganese oxides are extensively present in many archaeological artefacts, such as rock art15,16,43-45, pottery18-20,46, glass ware47-50 and paintings51, it might be of interest to characterize them with mobile Raman instrumentation. Mobile equipment has the benefit that the investigated artefact does not need to be transported and *in situ* measurements implies that no sample needs to be taken from the precious artworks17. This approach has proven to be efficient in many cases and has been applied in various cultural heritage fields17. However, manganese oxides often prove difficult to characterize in detail with using mobile Raman instrumentation. In these cases, the characterization is based on broad and weak bands found in the region of 600‑700 cm‑1 16,48,50,51. This range is typical for the symmetric stretch vibration of the Mn-O bond5. Caggiani *et al.* have identified MnO2 in glass enamels based on two bands at a position of 475 and 685 cm-1 48. However, an exact determination of the manganese oxide phase could not be made based solely on these band positions as only minor differences exist for various manganese oxides2,3,20,27. Therefore, a more elaborated characterization of manganese oxides in artefacts has been performed with samples and micro-Raman systems15,20,43-46. The group of Pitarch performed an *in situ* measurement campaign in the Los Chaparros shelter (Spain) to characterize post-Paleolithic blackish pictograms using Raman spectroscopy and X-Ray fluorescence (XRF). The XRF results revealed that Mn was extensively present. This was confirmed with the mobile Raman equipment (785 nm, 10x objective probe head, <9.5 mW) as they were able to identify chalcophanite based on the bands at 570 and 669 cm-1. These authors also observed some weak bands in the region 500-700 cm-1, characteristic for manganese oxides. However, these were rather weak and exact characterization could not be obtained. Subsequently, samples were taken and analyzed in the laboratory using a micro-Raman system (785 nm laser, 20x and 50x objectives, < 3 mW), revealing ramsdellite and hausmannite as the manganese oxides16.

In this study we also wanted to discuss the ability of different mobile Raman systems to differentiate between manganese oxide phases. For this purpose, as these manganese oxide samples have been found in different archaeological contexts, the five natural manganese oxide samples described in this study were analyzed using different mobile Raman systems. Indeed, chalcophanite has been identified as a colorant in rock art paintings16, while birnessite has been identified as a pigment used in the clay embalmment of Chinchorro people11 and as colorant in rock paintings in rock shelters from the Western Sahara52 for example. Ranciéite was identified as one of the components of the dark color on the stones of Theploutonionat Hierapolisof Phrygiae in Turkey53. Romanechite was found in the patina of the Neang Khmau temple in Cambodia54 as well as in rock art in the Rouffignac cave (France)55. In Table 6, an overview of the mineral phases and ability of various Raman instrumentation (benchtop and mobile) to accurately characterize the specific compound is given. The micro-Raman system was able to identify and characterize each of the manganese oxides under investigation. However, except for chalcophanite (i.e. the mineral with the highest degree of crystallinity), the manganese oxide identification with the mobile instrumentation (Bruke Bravo system) was not straightforward. (Figure 7)

The different issues of ambiguous situations when trying to identify the precise manganese oxide phase using mobile instrumentation can be related to both the instrumentation and the samples. Instrumental reasons include; the larger spot size, higher laser power, lower spectral resolution, smaller spectral range, wavenumber instability, sensitivity of the detector and focusing optics16,31,56. The manganese oxides themselves impose additional challenges, the foremost is that they are weak Raman scatterers3,5 and that they have low crystallinity2,26. Moreover, focusing the analysis spot is critical to obtain a good quality spectrum of these minerals, as was evident when using the benchtop micro-Raman equipment (Senterra). In addition, considering the bigger spot sizes typically used in mobile equipment, sample inhomogeneity can influence the results as exact focusing cannot always be achieved. Indeed, during the analysis with the micro-Raman system (Senterra), other mineral components (such as haematite, muscovite, goethite, gypsum) present in these samples were also identified. The Raman spectra of these other species could dominate the spectrum obtained with the mobile equipment and even suppress the signal of the manganese oxide vibrations, which are typically already quite low in intensity. Manganese oxides (both layered and tunneled) often only differ in their chemical composition with respect to their most principal metal cation. For example, chalcophanite and jianshuiite both have the same structure but in jianshuiite, the main cation is Mg2+ while this is Zn2+ for chalcophanite. This results in only small differences in band positions2 and hence when the spectral resolution of the mobile equipment is insufficient, a differentiation between these species cannot be made effectively. Moreover, the higher laser powers that are often used in mobile Raman systems may also hamper the analysis of sensitive manganese oxides. At elevated power densities, manganese oxides are prone to degrade/transform into other species3. This was observed in the current study: when elevating the power output to 1.53 mW, the ranciéite sample degraded. In 2015, Burlet and Vanbrabant reported that the effect of the laser power on the Raman signal of asbolane can occur from as low as 0.2 mW with a 532 nm laser (50x objective, 3 acc of 30s)38. The specific thermal conduction also depends on the chemical composition as well as the crystallinity38, which is, as mentioned, low for most of the layered manganese oxides3,26. Hence, if the power cannot be kept sufficiently low, the manganese oxides might degrade under the influence of the laser power during data acquisition. It is clear that the identification of manganese oxides with mobile Raman equipment can thus be quite tricky and difficult. Lahil *et al.* encountered problems in their *in situ* measurements of prehistoric drawings in a cave in Rouffignac-Saint-Cernin, France43. They could not obtain a signal of manganese oxides, even after 1.5 days of measuring, and linked this to the high fluorescence background, the low density of manganese oxides on the drawing and their low crystallinity and scattering properties43. For future work, it might be very promising to test more instruments which combine the advantages of mobile instrumentation with the high-spatial resolution of micro-Raman spectroscopy. In the following paragraphs, the manganese oxide analysis using mobile instruments will be discussed.

When using the iRaman-Ex system coupled to a 1064 nm laser, no viable signal was retrieved for any of the samples. The longer wavelength of the laser (near-IR) decreases the Raman scattering significantly, and the black manganese oxides absorb most of the laser light and/or Raman scattering. Various set-ups with the mobile equipment were tested. The first one included the probe together with a measuring cap, which was placed directly on the selected samples. This measuring cap ensures that the optimal focusing distance (7 mm) from the sample surface to the probe lens is obtained. A different set up with the probe fixed to the BAC150BXYZ microscope stage (BWTek) was also tested in order to find an optimal focusing distance relative to the sample surface. However, both set-ups failed to produce reproducible Raman spectra. Some samples even showed visual signs of degradation (i.e. crater formation) with the 1064 nm laser. A representative spectrum obtained in this manner is depicted in the supplementary data (Figure S4).

The Bruker Bravo system uses a two-laser operation system. Each laser is used to measure in a specific spectral range and the data is automatically merged, achieving a very broad spectral range (170-3200 cm-1). The system also relies on sequentially shifted excitation mode (SSE), a patented fluorescence mitigation method in which slight variations of the laser wavelength are obtained based on small temperature differences. In practice, three spectra are obtained using each laser with minor variations in laser wavelength. The system also performs an automatic background correction. The experimental conditions such as the laser power and the integration time are set by the instrument itself. However, the integration time can be chosen by the user when the instrument is placed on its docking stage. The use of the Bruker Bravo instrumentation has proven to be successful in identifying many different pigments in a laboratory setting as well as on the field31. However, it is evident that the pre-set experimental parameters are not helpful when characterizing manganese oxides due to their aforementioned challenges.

Chalcophanite was the only manganese oxide that was successfully analyzed in this part of the study. (Figure 7b) The mineral is highly crystalline and was easily measured by the two lasers of the micro-Raman system (Senterra, benchtop). By applying higher laser wavelengths (in this case 785 and 853 nm), the two bands around 381 and 296 cm-1 are clearly noticeable. The other samples did not yield acceptable spectra. In the lower wavenumber region of the unmerged spectra of birnessite and ranciéite, very minor bands around 580 cm-1 and 630 cm-1 could be found (Figure 7a4-6). The very low intensity of these bands, linked to $ν\_{sym}$(Mn-O), is most likely associated with the weak Raman scattering and the low crystallinity of these species. Unfortunately, characterization of the specific Mn oxide species cannot be performed solely based on these bands and in addition, the band around 630 cm-1 could also be the result of minor amounts of disordered haematite. A possibility further underscored by the presence of other haematite features around 225 and 300 cm-1 57. Due to the stitching and automatic background correction the possible Mn-O symmetric stretch bands somewhat disappear in the final spectrum (Figure 7a). This was also noticed in a spectrum obtained from the chalcophanite sample with the Raman bands of carbon black. On the other hand, the stitching and baseline correction procedures can also be beneficial in some cases, as indeed some haematite (α‑Fe2O3) was identified in a final spectrum of the asbolane sample.

An EnSpectr RaPort instrument was also used to analyze our samples. Again, the only spectrum that this system could provide was that of chalcophanite. However, when comparing the spectrum with those from the micro-Raman and the Bruker Bravo handheld spectrometers, the results were not comparable. The EnSpectr RaPort spectrum (Figure 8) shows a high background and a broad band around 650 cm-1 along with a band around 170 cm-1. The spectrum is comparable to the one reported by Fan *et al.* (2015) with broad bands around 606 and 650 cm-1 and a very weak one around 163 cm-1 40. The broad bands might indicate that the mineral degraded while measuring as the sample was characterized by well pronounced bands in the other Raman spectra obtained in this study (Figure 2 and Figure 7). Indeed, when the laser power was increased with the benchtop instrument (Senterra), some chalcophanite band shifting and broadening was observed (Figure S5). For the other samples, no signal was retrieved. This can be due to the larger spot size of the system (0.1 mm) and/or the increase in laser power. It is also noted that the power output of the EnSpectr spectrometer is controlled by an attenuation factor which is probably not linear and has to be checked independently. This may particularly cause problems when fine tuning of the laser energy is required as a minor increase in attenuation may result in disproportionately higher energy output than intended, which is highly unfavorable when trying to identify manganese oxides.

***Conclusion***

Micro-Raman spectroscopy has proven to be successful in the characterization and identification of the five selected (layered) manganese oxide samples in this study. By using both lasers (785 and 532 nm) on a benchtop spectrometer, a Raman spectrum could be obtained without degrading the manganese oxides, provided that the lowest laser power settings were used. When the power was increased, the manganese oxides displayed signs of decomposition/degradation. This was most apparent for our ranciéite sample. In general, the results presented in this work agree with published data. Unfortunately, the identification of layered manganese oxides with mobile instrumentation did not yield satisfactory results. Shortcomings in the identification of layered manganese oxides with mobile equipment are mainly linked to the low Raman scattering properties of manganese oxides and their sensibility with respect to the laser power. Due to the low crystallinity of phyllomanganates, precise focusing is required and this often cannot be obtained with mobile equipment. Only a chalcophanite sample, which is highly crystalline, gave satisfactory results using the mobile instrumentation. In the case of the Bruker Bravo mobile system, an identifiable spectrum was acquired, whereas with the EnSpectr RaPort a possible degraded spectrum was obtained. It can be concluded that typically, mobile Raman instrumentation cannot be used straightforwardly for the identification of layered manganese oxides.

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***Figure captions***

Figure 1 Photographs of the analyzed manganese oxides: a) asbolane (Ni,Co)xMn4+(O,OH)4·nH2O and chalcophanite Zn2+Mn3O7 · 3H2O.

Figure 2. Raman spectra of the mineral sample chalcophanite $Zn^{2+}Mn\_{3}O\_{7}∙3H\_{2}O$obtained with the benchtop equipment (Senterra). Measuring conditions were: 10 acc of 30 s, 50x, NA: 0.75 (4 µm spot size), 785 nm laser, 0.73 mW and 5 acc of 30 s, 50x, NA: 0.75 (4 µm spot size), 532 nm laser, 0.12 mW.

Figure 3 Raman spectra of asbolane (Ni,Co)xMn4+(O,OH)4·nH2O. The spectra were obtained with a 785 and 532 nm laser of the micro-Raman system (Senterra) with the parameters; 60 acc of 10 s, 50x, NA: 0.75 (4 µm spot) and 0.73 mW and 10 acc of 60 s, 50x, NA: 0.75 (4 µm spot), 0.12 mW, respectively.

Figure 4 Raman spectra of ranciéite (Ca,Mn2+,K,Ba)(Mn4+, Mn3+)4O9 · n H2O acquired with the benchtop instrumentation (Senterra). Experimental conditions were 30 acc of 10 s, NA: 0.75 (4 µm spot) and 0.73 mW or 0.12 mW for respectively the 785 or 532 nm laser.

Figure 5 Raman spectra of the manganese oxide birnessite (Na,Ca)(Mn4+,Mn3+)2O4 ·3/2 H2O. The experimental conditions for respectively the 532 and 785 nm laser of the benchtop system (Senterra) were; 10 acc of 30 s, 50x, NA: 0.75 (4 µm spot), 0.12 mW and 0.73 mW.

Figure 6 Raman spectra of romanéchite (Ba,H2O)2(Mn4+,Mn3+)5O10 acquired with the micro-Raman system (Senterra) with the following experimental conditions for respectively the 785 nm laser; 30 acc of 60 s, 50x, NA: 0.75 (4 µm spot), 0.73 mW and for the 532 nm laser; 60 acc of 30 s, 50x, NA: 0.75 (4 µm spot), 0.12 mW.

Figure 7 (A) Raman spectra of a birnessite obtained with the Bruker Bravo instrumentation. The unmerged and lower (4-6) and higher range (1-3) spectra are found at the top. The result (with merging and background correction) is found at the bottom. Note: Indicated with an asterisk are haematite bands (B) Raman spectra of chalcophanite obtained with Bruker Bravo instrumentation.

Figure 8 Raman spectrum of chalcophanite obtained with the EnSpectr RaPort. Measuring conditions were 3s and 30 accumulations, ± 15 mW, 532 nm laser.

***Table captions***

T1 Raman wavenumbers of the manganese oxide chalcophanite Zn2+Mn3O7 $∙$H2O in comparison with literature data.

T2 Raman wavenumbers of asbolane (Ni,Co)xMn4+(O,OH)4·nH2O in regard to published data.

T3 Raman wavenumbers of ranciéite (Ca,Mn2+,K,Ba)(Mn4+, Mn3+)4O9 · n H2O

, compared to published data.

T4 Raman wavenumbers of the manganese oxide birnessite (Na,Ca)(Mn4+,Mn3+)2O4 ·3/2 H2O in comparison with literature data. Note: indicated with H-Bir means hexagonal birnessite

T5 Raman wavenumbers of the tunnel manganese oxide romanechite (Ba,H2O)2(Mn4+,Mn3+)5O10, in comparison with published data.

T6 The ability to identify the different manganese oxide mineral samples in function of the Raman instrument.

***Tables***

*Table 1*

|  |  |  |  |
| --- | --- | --- | --- |
| ***Manganese oxide******mineral*** | ***Wavenumber/cm-1*** | ***Laser wavelength (nm)*** | ***Reference*** |
| Chalcophanite Zn2+Mn3O7 · 3H2O | 670, 570, 512, 484, 449, 392, 251, 219, 194, 179, 132 | 532 | This study |
|  | 670, 570, 511, 445, 379, 298, 250, 217, 192, 176, 130 | 785 | This study |
|  | 670 (s), 588 (sh), 570 (s), 511, 483, 448, 445, 379, 349, 298, 250, 218, 193, 177, 131 | 633 | 2 |
|  | 665, 566, 507, 479, 387, 215 | 532 | 58 |
|  | 667, 580, 556, 507, 478, 443, 299, 275, 250, 218 | 632.8 | 26 |

Table 2

|  |  |  |  |
| --- | --- | --- | --- |
| ***Manganese oxide******mineral*** | ***Wavenumber/cm-1*** | ***Laser wavelength (nm)*** | ***Reference*** |
| Asbolane (Ni,Co)xMn4+(O,OH)4·nH2O | 670 (sh), 620, 560 (sh), 500 | 532 | This study |
|  | 711 (sh), 633, 590, 558 (sh), 500 | 785 | This study |
|  | 630, 554, 497 | 532 | 59 |
|  | 654, 578, 516, 300, 142 | 785 | 2 |
|  | 677 (sh), 604, 492 | 632 | 60 |
|  | 627 (sh), 596, 553, 497, 456, 374 | 532 | 38 |
|  | 593, 550, 496, 385 | 532 | 39 |

Table 3

|  |  |  |  |
| --- | --- | --- | --- |
| ***Manganese oxide******mineral*** | ***Wavenumber/cm-1*** | ***Laser wavelength (nm)*** | ***Reference*** |
| Ranciéite (Ca,Mn2+,K,Ba)(Mn4+, Mn3+)4O9 · n H2O | 670, 584, 501 | 532 | This study |
|  | 656, 581, 501, 409, 280 | 785 | This study |
|  | 630, 575 (sh), 343, 292 | 632.8 | 26 |
|  | 667, 605, 578, 497, 408, 281, 195, 157 | 633 | 2 |
|  | 645, 370, 304 | 632 | 40 |

Table 4

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| ***Manganese oxide******mineral*** | ***Wavenumber/cm-1*** | ***Type*** | ***Laser wavelength (nm)*** | ***Reference*** |
| Birnessite (Na,Ca)(Mn4+,Mn3+)2O4 ·3/2 H2O | 654, 612, 577, 499, 388, 141 | Natural(H-Bir) | 532 | This study |
|  | 651, 581, 142 | Natural(H-Bir) | 785 | This study |
|  | 715 (sh), 635, 584, 513, 388, 288, 181 | Natural | 632.8 | 26 |
|  | 654, 578, 516, 300, 142 | Natural(H-Bir) | 785 | 2 |
|  | 730, 656, 575, 506, 303, 296 | Natural | 632 | 60 |
|  | 655, 636, 585, 560 (sh), 508, 477, 407, 281, 197 | Synthetic  | 532 | 4 |
|  | 645, 607, 573, 500, 407, 385,  | Synthetic (H-Bir) | 532 | 28 |
|  | 635, 587, 509, 485, 405, 279, 200 | Synthetic (T-Bir) | 532 | 42 |
|  | 650, 610, 575, 500, 387 | Synthetic (H-Bir) | 532 | 42 |

Table 5

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| ***Manganese oxide******mineral*** | ***Wavenumber/cm-1*** | ***Type*** | ***Laser wavelength (nm)*** | ***Reference*** |
| Romanéchite (Ba,H2O)2(Mn4+,Mn3+)5O10  | 738, 625, 584, 514, 476 (sh), 394, 280, 208, 182, 141 | Natural | 532 | This study |
|  | 730, 626, 583, 514, 396, 280, 182, 143 | Natural | 785 | This study |
|  | 720, 635, 580, 510 | Natural | 632.8 | 26 |
|  | 729, 635, 577, 510, 290, 200, 148 | Natural | 785 | 27 |
|  | 635, 577, 510, 385, 290, 148 | Natural | 532 | 27 |
|  | 721, 643, 578, 515, 372, 284 | Natural | 514.5 | 29 |

Table 6

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Senterra | Bravo | i-RAMAN® EX | EnSpectr RaPort |
|  | 785 nm | 532 nm | 785 and 853 nm | 1064 nm | 532 nm |
| Chalcophanite | ü | ü | ü | X | +/- |
| Asbolane | ü | ü | X | X | X |
| Ranciéite | ü | ü | X | X | X |
| Birnessite | ü | ü | X | X | X |
| Romanéchite | ü | ü | X | X | X |