Erroneous attribution of Mn-oxides minerals in primary mineralogy collections

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ABSTRACT

The manganese oxides, hydro-oxides and closely related species form a group of minerals mainly resembling black or dark gray powder, black mammillons, black tiny crystals, black thin deposits within rock fissures and along veins. The distinction of the different species, based on the external appearance, is still difficult, although not as much as in the past, when knowledge and practice on the instrumental techniques were not available. In spite of the interest in the museum and mineral collecting community, detailed qualitative analyses and structural characterization have rarely been carried out on museum samples. In this study, we focus on the identification of a significant number of specimens from historic and modern collections. The analysis of 30 samples has revealed that in about half of the cases the original identification was not correct.

Key words:
mineralogy, Mn-oxides, museology, SEM-EDS, XRPD.

RIASSUNTO

Errata attribuzione dei minerali di ossidi di manganese nelle raccolte di mineralogia primaria

Gli ossidi di manganese, gli idrossidi e le specie strettamente correlate formano un gruppo di minerali che assomigliano principalmente a polvere nera o grigio scuro, mammelloni neri, piccoli cristalli neri, depositi sottili scuri o nerastri all'interno di fessure e vene nelle rocce. La distinzione delle diverse specie è ancora difficile, sebbene non tanto quanto in passato, quando la conoscenza e la pratica sulle tecniche strumentali non erano disponibili. Nonostante l'interesse per il museo e la comunità di collezionisti di minerali, raramente sono state condotte analisi qualitative dettagliate e caratterizzazioni strutturali su campioni museali. In questo studio ci concentriamo sull'identificazione di un numero significativo di esemplari da collezioni storiche e moderne. L'analisi di 30 campioni ha rivelato come in circa la metà dei casi l'identificazione originale non fosse corretta.

Parole chiave:
mineralogia, ossidi di manganese, museologia, SEM-EDS, XRPD.

Mn-oxides and related minerals form a large and complex group of minerals, which have been already investigated in the first decades of last century mainly for their importance as industrial source of manganese (Thiel, 1924; Orcel & Pavlovitch, 1932; Fleischer & Richmond, 1943; Gruner, 1943; McMurdie & Golovato, 1948; Kulp & Perfetti, 1950).

Many chemical and structural investigations have shown interesting differences among these minerals. Therefore, some studies pointed out some differences concerning the genesis environment and generating various interpretations on the ores' formation (Straczec et al., 1960; Fleischer et al., 1962; Zwicker et al., 1962; McKenzie, 1971; Potter & Rossman, 1979; Turner & Buseck, 1981; Ostwald, 1986; Golden et al., 1987; Krishnamurti & Huang, 1988; Post & Bish, 1988; Bish & Post, 1989; Manceau et al., 1992; DeGuzman et al., 1994; Post, 1999; Yang et al., 2006; Feng et al., 2007; Johnson et al., 2016).

Due to the importance of manganese deposits, several studies have been carried out on some specific geographic area, from local to regional scale (Hewett & Fleischer, 1960; Hariya, 1961; Finkelman et al., 1974; Hawker & Thompson, 1988; Nicholson, 1989; Carlos et al., 1990). Other authors have tried to apply the same methodology in individual mining districts (Ramdohr, 1956; Nimfopoulos & Pattrick, 1991; Nyame et al., 1995; Sorensen et al., 2010; Tan et al., 2010; Ali & Amankwah, 2013; Siddiquie et al., 2015; Dekoninck et al., 2016; Endo 2017; Vafeas et al., 2018a; Vafeas et al., 2018b; Sklyarov et al., 2019).

From mineral collectors and museology point of view, the peculiar characteristics of the manganese minerals (oxide, complex oxides and hydro-oxides with or without other metals rather than Mn) are not appreciated very much. Indeed, their appearance is not particularly appealing as they appear like black powdery crusts, black tiny crystals or thin deposits in rock fissures and vein or surfaces (Macholdt et al., 2019; Xiaoming et al., 2019). The differences among these oxides are not easily detectable as even minerochemical and diffractometric analysis are not effective enough to reveal the real nature of the investigated sample.

During the re-classification and reorganization process of some museum mineral samples, several of them were found without any label other than the generic ones "pyrolusite" or "psilomelane". Therefore, a preliminary chemical analysis of these samples has been performed. The results revealed that many specimens named "pyrolusite" or "psilomelane" correspond neither the one nor the other.

In order to determine if the erroneous identification was limited to a specific collection or to a certain provenience or related to a specific historic period, we collected a representative amount of samples from primary museums and private collections.

The samples were selected from the museums listed here.

- The Mineralogical Museum of the Università di Torino (MU), which belongs to the Regional Museum of Natural Science of Torino. The MU dates back to the second half of the eighteenth century, and contains samples from various periods and from localities no more available for the collection and research of new specimens; in particular, some of the investigated samples were already studied and reported by Borson in his catalogue of 1830 (Borson, 1830; Costa & Trossarelli, 2003; Gallo, 2007).

Manganese oxides		
Akhtenskite	ε-$Mn^{4+}O_2$	(4/D.10-15, hexagonal)
Bixbyite	$Mn_2^{3+}O_3$	(4/C.03-10, cubic)
Feitknechtite	$Mn^{3+}O(OH)$	(4/F.06-90, trigonal)
Groutite	$Mn^{3+}O(OH)$	(4/F.06-80, orthorhombic)
Hausmannite	$Mn^{2+}Mn_2^{3+}O_4$	(4/B.05-10, tetragonal)
Manganite	$Mn^{3+}O(OH)$	(4/F.06-70, monoclinic)
Manganosite	MnO	(4/A.04-40, cubic)
Nsutite	$(Mn^{4+},Mn^{2+})(O,OH)_2$	(4/D.10-20, hexagonal)
Pyrochroite	$Mn(OH)_2$	(4/F.03-30, trigonal)
Pyrolusite	MnO_2	(4/D.02-20, tetragonal)
Ramsdellite	$Mn^{4+}O_2$	(4/D.10-10, orthorhombic)
Manganese oxides with other metals		
Asbolane	$(Ni,Co)_{2-x}Mn^{4+}(O,OH)_4 \cdot nH_2O$	(4/F.07-20, hexagonal)
Birnessite	$(Na,Ca)_{0.5}(Mn^{4+},Mn^{3+})_2O_4 \cdot 1.5H_2O$	(4/F.11-30, monoclinic)
Cesàrolite	$Pb(Mn^{4+})_3O_6(OH)_2$	(4/D.08-80, trigonal)
Coronadite	$Pb(Mn_6^{4+}Mn_2^{3+})O_{16}$	(4/D.08-70, monoclinic)
Cryptomelane	$K(Mn_7^{4+}Mn^{3+})O_{16}$	(4/D.08-20, monoclinic)
Hetaerolite	$ZnMn_2O_4$	(4/B.05-40, tetragonal)
Hollandite	$Ba(Mn^{4+}{}_6Mn^{3+}{}_2)O_{16}$	(4/D.08-60, monoclinic)
Manjiroite	$Na(Mn^{4+}{}_7Mn^{3+})O_{16}$	(4/D.08-10, tetragonal)
Quenselite	$PbMnO_2(OH)$	(4/F.14-10, monoclinic)
Ranciéite	$(Ca,Mn^{2+})_{0.2}(Mn^{4+},Mn^{3+})O_2 \cdot 0.6H_2O$	(4/D.12-10, trigonal)
Romanèchite	$(Ba,H_2O)_2(Mn^{4+},Mn^{3+})_5O_{10}$	(4/D.09-30, monoclinic)
Takanelite	$(Mn,Ca)Mn_4O_9 \cdot H_2O$	(4/D.12-20, hexagonal)
Todorokite	$(Na,Ca,K,Ba,Sr)_{1-x}(Mn,Mg,Al)_6O_{12} \cdot 3\text{-}4H_2O$	(4/D.09-10, monoclinic)
Vernadite	$(Mn^{4+},Fe^{3+},Ca,Na)(O,OH)_2 \cdot nH_2O$	(4/D.10-30, monoclinic)

Tab. 1. The list of the mineral species, with formula, class, subgroups classification and crystal system: manganese oxides and manganese oxides with other metals.

Sample	Description	Provenance	Old museological attribution	EDS	XRPD	New attribution proposed
M/336	Brownish black to black, shiny little acicular crystals	Spain, Huelvas, Calañas	Pyrolusite	O, Mn (Fe)	Manganite - ICDD-PDF 88-0649	Manganite
M/595	Black brownish crust, dull	Italy, Sardinia, Carloforte, Capobecco mine	Pyrolusite	O, Mn, Ba (Ca, K)	Romanechite - ICDD-PDF 14-0627 Pyrolusite - ICDD-PDF 72-1984	Romanechite with Pyrolusite
M/766	Black brownish crust with iridescence	Hungary, Veszprén, Urkút	Manganite	O, Mn, Fe, K	Cryptomelane - ICDD-PDF 20-0908	Cryptomelane
M/771	Black shiny mass with scarce shiny crystals	Hungary, Veszprén, Urkút	Undeclared	Mn, O	Pyrolusite - ICDD-PDF 65-2821	Pyrolusite
M/2865	Black thin acicular crystals in brownish matrix	USA, Michigan, Baraga Co., Taylor Mine	Pyrolusite	Mn, O	Pyrolusite - ICDD-PDF 72-1984 Quartz SiO2 - ICDD-PDF 79-1906	Pyrolusite
M/4308	Black brownish mamelons, dull	Morocco, Ksar es Souk, Taouz	Goethite	O, Mn, Pb (Ba, K)	Pyrolusite - ICDD-PDF 65-2821	Pyrolusite
M/3734	Black brownish crust and tiny crystals with iridescence	Germany, Thuringia, Ilmenau	Pyrolusite		Pyrolusite - ICDD-PDF 72-1984	Pyrolusite
MU/2523.1	Botryoidal crust, black brownish	France, Saone-et-Loire, Romanèche-Thorins	Romanechite	O, Mn, Ba (Ca)	Romanechite - ICDD-PDF 14-0627	Romanechite
MU/2502.2	Very thin blackish crust on ocraceous matrix, dull	Belgium, Vielsalm, Bihain	Romanechite	O, Mn, Fe, (K, Na)	Pyrolusite - ICDD-PDF 12-0716 Quartz - ICDD-PDF 81-0066	Pyrolusite with Quartz and Hematite
MU/2507	Blackish mass, dull	Austria, Carinthia, Huttenberg	Wad	O, Fe, Mn	Goethite - ICDD-PDF 29-0713 Ramsdellite - ICDD-PDF 42-1316	Goethite with Ramsdellite
MU/2525	Black dull mass	France, Saône-et-Loire, Romanèche-Thorins (Romaniche)	Romanechite	O, Mn, Ba, (As, Ca)	Romanechite - ICDD-PDF 14-0627	Romanechite
MU/5615.1	Brownish earthy mass	Germany, Harz, Ilfeld	Wad	O, Mn, (Cu, Ca)		
MU/5615.2	Brownish earthy and fibrous mass	Germany, Harz	Asbolane	O, Mn, (Ca, K)		
MU/8081	Black, brownish, acicular portions with iridescence	Germany, Thuringia, Ilmenau	Pyrolusite	Mn, O	Pyrolusite - ICDD-PDF 72-1984	Pyrolusite
MU/9781	Blackish, dull crust mamelons-like	Great Britain, Cornwall, Redrouth	Romanechite	O, Mn, K (Ba, Co)	Cryptomelane - ICDD-PDF 12-0706 Hollandite - ICDD-PDF 13-0115	Cryptomelane with Hollandite
MU/13324	Gray blackish dull fragments, earthy	Brazil, Mato Grosso, Urucum	Pyrolusite	O, Mn, Fe, K (Ca, Na)	Cryptomelane - ICDD-PDF 12-0706 Hematite - 80-2377	Cryptomelane with Hematite
MU/17123	Mamelonary crust, black, with iridescence	Italy, Sardinia, S. Antioco island	Pyrolusite	O, Fe (Mn)	Goethite - ICDD-PDF 29-0713	Goethite
MP/A	Tiny acicular crystals, black, shiny	Spain	Pyrolusite	O, Mn	Pyrolusite - ICDD-PDF 81-2261	Pyrolusite
MP/B	Black tiny crust on matrix, earthy	Greece, Lavrion	Psilomelane	O, Mn	Pyrolusite - ICDD-PDF 81-2261 Hematite - ICDD-PDF 79-1741 Dolomite - ICDD-PDF 36-0426	Pyrolusite with Hematite and Dolomite
MP/C	Grayish black sub-acicular crystals	Germany, Harz, Ilfeld	Manganite	O, Mn	Manganite - ICDD-PDF 88-0649	Manganite
MP/391	Greyish black hard aggregate with very small shiny crystals	Germany, Thuringia, Ilmenau	Hausmannite	O, Mn, Fe, (Ba)	Hausmannite - ICDD-PDF 80-0382	Hausmannite
MP/392	Greyish black hard aggregate with very small shiny crystals	Germany, Thuringia, Ohrenstock	Hausmannite	O, Mn, (Ba)	Hausmannite - ICDD-PDF 80-0382	Hausmannite
MP/405	Blackish earthy aggregate	Germany, Rhineland-Palatinate, Platten	Pyrolusite	O, Mn	Pyrolusite - ICDD-PDF 72-1984	Pyrolusite
MP/418	Blackish tiny crust with small acicular crystals	Germany, Harz, Ilfeld	Pyrolusite	O, Mn	Pyrolusite - ICDD-PDF 72-1984	Pyrolusite
MP/420	Black powder	Portugal	Pyrolusite	O, Mn, Ba	Pyrolusite - ICDD-PDF 72-1984	Pyrolusite
MP/450	Black fragments, earthy	Germany, Bavaria, Schneeberg	Psilomelane	O, Mn, Ba	Hollandite - ICDD-PDF 13-0115 Pyrolusite - ICDD-PDF 72-1984	Hollandite with Pyrolusite
MP/451	Blackish small mamelons, earthy	France, Saône-et-Loire, Romanèche-Thorins (Romaniche)	Psilomelane	O, Mn, Fe, Ba, Ca, (K)	Romanechite - ICDD-PDF 31-0155 Hollandite - ICDD-PDF 13-0115	Romanechite with Hollandite
AD/713	Black brownish mamelons, dull	Italy, Sardinia, Carloforte, Capobecco mine	Pyrolusite	O, Mn, Fe, K (Ba, Pb)	Cryptomelane - ICDD-PDF 20-0908 Pyrolusite - ICDD-PDF 72-1984 (?)	Cryptomelane
AD/832	Brown blackish powder and fragments	Morocco, Ksar es Souk, Taouz	Goethite	O, Mn, Fe, Pb (Ba)	Coronadite - ICDD-PDF 41-0596 Goethite - ICDD-PDF 29-0713	Coronadite with Goethite
AD/1181	Blackish powder and fragments	Morocco, Ksar es Souk, Taouz	Romanechite	O, Mn, Fe, Ba (Pb)	Coronadite - ICDD-PDF 41-0596 Pyrolusite - ICDD-PDF 81-2661	Coronadite with Pyrolusite

Tab. 2. Attributions, macroscopic descriptions and minerochemical features of the samples analyzed.

- The collection of the Regional Museum of Natural Science of Torino (M). The museum, founded in 1978, not only preserves the old University collection with the aim of keeping, using and enhancing them, but also it has acquired samples from famous dealers and private collections of international reputation (Costa & Gallo, 2010).
- The Mineralogical Museum of the Politecnico di Torino (MP). As for the Museum University, it collects samples dating back to the beginning of the 19th century, when the precursor of the Polytechnic School of Torino was founded (the Royal School of Application for Engineers) (Delmastro, 2002; Barresi et al., 2012).
- The private collection of one of the authors, Alessandro Delmastro (AD), curator of the Mineralogical Museum of the Politecnico di Torino and honorary curator of the Regional Museum of Natural Science of Torino.

The study focused on minerals of the subgroups 4/A to 4/F according to Strunz's classification (Strunz & Nickel, 2001), i.e. oxides having a variable metal-oxygen ratio with oxydriles and water in their formula. Many of these minerals contain metals different from Mn like potassium or barium, and sometimes a partial substitution of Mn with Mn-related metals can be observed. Vanadates, arsenites, antimonites, bismuthites, sulfites, selenites, tellurites, and iodates were not included. The list of the mineral species, with formula, class, subgroups classification and crystal system, is shown in table 1.

Asbolane should be ideally considered a Mn bearing nickel-cobalt oxide, but traditionally in many collections it is classified as a manganese oxide or a Mn mineral so that it has been included within the list.

None of the investigated samples was in dendritic form, although Mn-dendrites are a very common form of manganese mineralization. Nowadays the dendrites pose so complex analytical questions that they are not yet included in the present paper, but they will be considered in a future investigation.

Regarding the experimental setup, the sampling process, except for the private collection, is subject to the rule of the Cultural Heritage goods, so that only a very tiny amount of the samples has been removed. These fragments were investigated with SEM and EDS microprobe in order to have a semi-quantitative analysis of their composition. Therefore, XRD analyses were performed to confirm the species on the basis of the chemical data. The complete list of the analyzed samples is reported in table 2.

Dealing with the EDS analysis, the samples were untreated and investigated by means of an Environmental SEM to avoid the use of any coating. For the XRD analysis, very small representative pieces were grinded until a fine powder was obtained.

EDS analyses were performed in the SEM-EDS Laboratory in the Earth Science Department of the Università di Torino, employing an LV300 Jeol SEM with Oxford ISIS Pentafet Inca Analitical setup and using thin window condition, an acceleration voltage of 15 kV and probe current of 1 nA.

As mentioned before, the analyses were not quantitative for different reasons. First of all, the samples portions were not in thin section form, so alteration of EDS data should be expected because of the different orientations of the mineral's surfaces. Secondly, most of the samples were exposed to environmental dust and contaminants deposition for many decades. Furthermore, many organic substances and soot adhere on the surface of the sample and can determine an overestimation of carbon content as well as an underestimation of lighter elements due to the absorption of X-photons. For this reason, the amount of carbon suggested by EDS data was not taken into account unless the carbon amount was so high to suggest clearly the presence of a carbonate phase.

The EDS data were used mainly to check the presence of potassium, lead or barium that constitute the significant difference between simple manganese oxides and more complex phases like cryptomelane, containing potassium, or lead-bearing coronadite. The fine-tuning of the mineralogical species determination was conducted by means of XRD.

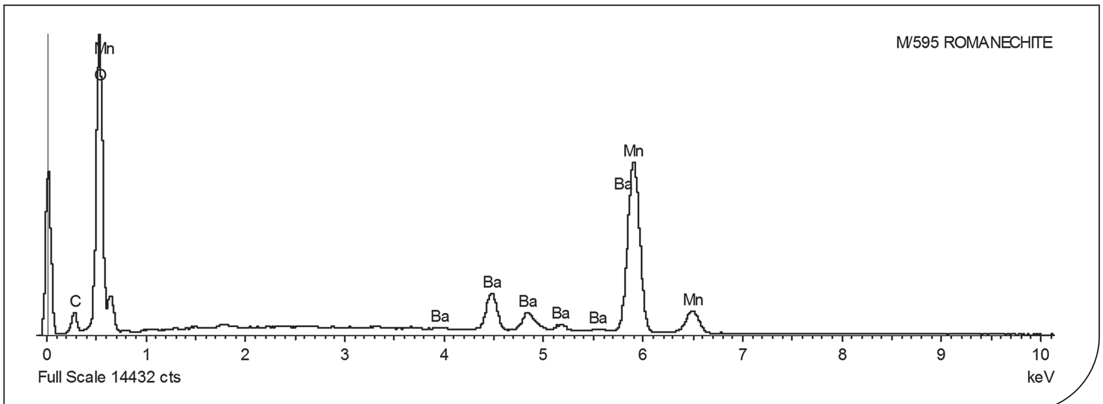

Fig. 1. EDS spectrum of M/595 sample.

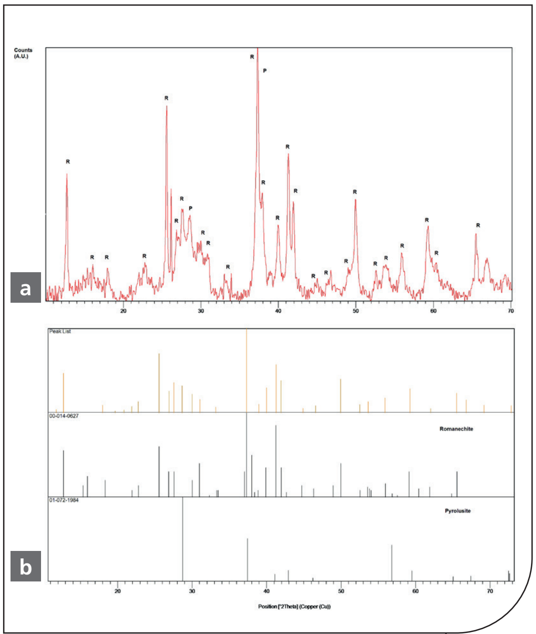

Fig. 2. XRD pattern (a) and peak list (b) of M/595 sample. Abbreviations: R, Romanechite; P, Pyrolusite.

XRPD (X-Ray Powder Diffraction) investigation was carried out on powdered sample by employing a Panalytical X'Pert PRO (Cu Kα radiation) diffractometer. The PIXcel detector is a solid-state detector with a rapid readout time and a high dynamic range. The X-ray diffractometer has worked with a generator voltage of 40 kV and a current of 40 mA. Data collection has been performed between 5° and 90° 2θ, with a step of 0.02° 2θ. Minerals identification has been obtained with the PANalytical X'Pert HighScore Plus software. After the background noise subtraction from the pattern, full profile ICDD-PDF database has been used to interpret the powder diffraction patterns.

In table 2, the column "sample" refers to the original inventory number given to the specimen by the Museum's curator. The column "provenience" refers to the locality reported on the Museum's records, if existing. "Museological attribution" refers to the identification stated at the time of acquisition by the Museum. The elements detected by EDS analysis are shown in terms of increasing atomic abundance. The elements of minor relevance (below 1%) are also reported in brackets. The results of the diffractometric investigation and the reference file data used for the identification of the specific phases are also indicated. In two samples (MU/5615.1 and MU/5615.2) the mix of various poorly crystallized phases does not permit to attribute a reliable diffractometric pattern. The last column reports the identification obtained by means of the carried out analysis. If a mismatch is observed between the old and the new identification, the name of the sample is highlighted in bold.

By comparing the old mineralogical attribution with the new identification, 14 samples show that their original attribution was not correct. In some cases the mistake affects the main composition as in the case of the iron oxide identified as a manganese mineral (MU/17123) or vice-versa (AD/832).

In other cases, the determination of minor elements, which couldn't be recognized in the past, allows to assign the correct identity to some "pyrolusites" by identifying them as rarer mineralogical species like cryptomelane (MU/13324) or romanechite (M/595). As an example, the composition of M/595 sample is shown in the EDS spectra (fig. 1) and the romanechite species is confirmed by XRD pattern, as reported in figure 2.

It is interesting to remark that the SEM investigation has generated some nice pictures of uncommon species of manganese minerals, as shown in figure 3. In these photographs, showing the surface of another romanechite sample (M/U 2523.1), the typical botryoidal surfaces created by the radial acicular crystals are clearly visible. Another amazing aspect involves some samples coming from well-known localities around the world. This is the case of samples coming from the Moroccan mine of Ksar es Souk (Taouz), where most of the specimens bearing a so-called goethite, indeed correspond to coronadite (AD/832, AD/ 1181).

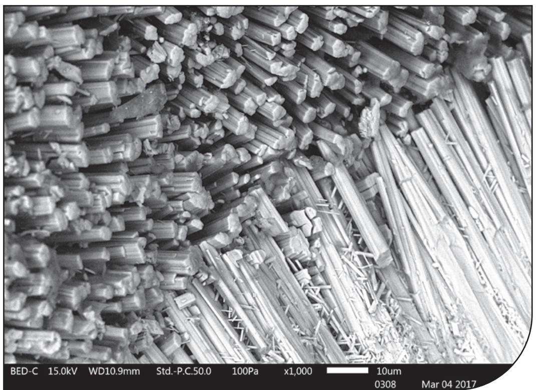

Fig. 3. SEM image of M/U2523.1 (romanechite) sample. Scale bar is 10 µm.

Fig. 4. Sample AD/713 (Cryptomelane, once attributed as pyrolusite). Field of view 15 cm.

Moreover, samples coming from the Italian mine of Capo Becco and Capo Rosso (Carloforte, Isola di San Pietro, Sardinia, Italy) also reserved some surprise. In fact, two specimens declared as pyrolusite, in reality correspond to cryptomelane (AD/713) (fig. 4) and romanechite (M/595), both species not yet included in the minerals list of this locality (Conti-Vecchi & Stara, 1991; Fadda, 1997).

In conclusion, the correct attribution of the mineral species is very important both for scientific and museological purposes. It has been demonstrated that either the visual determination or the old analytical data of manganese oxides and related minerals are no longer reliable, while modern instrumental techniques allow to achieve a much more correct identification.

Considering these preliminary results, it is worth performing new analysis on the samples acquired before the second half of the last century and in particular on the samples identified in the past as "manganese oxides", "pyrolusite" or "wad".

It is also worth remembering, on this occasion, that the storage conditions of the samples are not always optimal in museums, and that therefore some samples, over time, may have at least partially changed their nature due to oxidation, hydration or dehydration consequent to to the environment in which they have been stored for many years. So some of the old attributions, which could have been exact, could have changed over time.

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