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XRPD and SEM-EDS Identification of a Mineralogical Standards Kit Forming a 19th Century Collection for Educational Analysis

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Abstract

An historical collection of more than one hundred samples of minerals and ore, used in the second half of the XVIII century was found and acquired during Munich Mineralientage 2014. The samples contained in numbered glass vials but lacking description, were prepared for teaching purpose about determinative mineralogy and ore recognition. All samples were analysed and identified. The identification effort drove the authors along a historical excursus about the didactics of mineralogy and the dry method analysis, nowadays neglected.

Keywords

Blowpipe, XRPD, SEM-EDS, Historical Collection, Dry Analysis, Ore Identification

1. Introduction

During the 2014 edition of the most important European mineralogical exhibition-held in Munich every year—one of the authors, collector of mineralogical memorabilia, bought 19th century wooden box containing the 102 samples analysed in this study. The main objective of the acquisition and therefore of the present investigation has been the identification of each sample contained in its corresponding glass tube, as no historical list or label is anymore existing even if very probably it is, either for analytical or didactical purpose **Figure 1** and **Figure 2**.

A didactical collection of old samples has been rarely analysed with modern methods and instrumentations

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Figure 1. The wooden box with the three layered trays containing the probe-tube.

Figure 2. Three mineralogical samples.

and the results are of particular interest because they show what kind of mineral and substances are considered as industrial and scientific relevance at that time.

2. Determination of Mineralogical Samples by Means of the Dry Analysis

During the development of the industrial mineralogy, in the period starting from the late ‘700 to the beginning of the ‘900, there was a strong need for chemists and geologists of easy, quick and reliable analytical methods. Their essential requirement was to guarantee an analytical accuracy in determining the presence of major or relevant elements in a mineral or in an ore rock, so that the industrial exploitation could be justified.

The classical analysis through dissolution, precipitation and weighing, although already well established at the middle of ‘800 (at least for the most important elements) was a long, annoying and time consuming way to obtain chemical information about the composition of a generic mineralogical sample or of a specific ore sample, that is a mineral or an aggregate of minerals from which a valuable constituent, especially a metal, can be profitably mined or extracted. It needed a well-equipped laboratory, a number of chemical substances and a skilled chemist. All these conditions collided with the needs of obtaining, directly during the field search and in a short time, the information needed to prepare suitably the mining work and focus the research on the different field areas.

In order to satisfy the above request, different methods of analysis, which require no or little chemical manipulations, a minimal use of chemicals and laboratory tools, and only a simple training were developed. The most of them are practically using no water or acid for dissolution (and consequently no or very little glassware, as it is always problematic to be used in the field) and for this reason are called *dry analysis methods*. Essentially, these methods consist in observing the eventual modifications, reactions and transformations of the sample once heated, melted with simple chemicals, or placed in a flame.

The main methods are listed as follows:

-Heating on a platinum foil: the analyst could observe combustion (organic substance), possible formation of residual deposits, developing of volatile substances (some of them recognizable by their smell), fusion or resistance to heat. All of these characteristics could orient the researcher to different ways.

-Heating in close test tube: the observation of a small amount of unknown ore or mineral placed in a small test tube, heated on the base, can give useful information about the presence of water (condensation of droplets in the cold zone of the tube), sulphides (condensation of sulphur or developing of SO_2 or H_2S) and so on. The release of carbon monoxide—burning with blue flame at the top of the tube—can reveal the presence of formiate or oxalate groups. The release of red vapour of nitrous oxide suggests the presence of nitrates, whereas the ammonia smell suggests the presence of ammonia salts or nitrogen bearing organic substances.

Different sublimates can be deposited near the edge of the tube, such as red mercuric sulphide, or orange arsenic sulphide, thereby suggesting the presence of such so important industrial elements like mercury or arsenic.

-Heating in an open test tube: a small test tube, shaped as wide opened "U" arms, with a small amount of the sample placed in the lower part of the tube, is heated in a flame. Differently than the previous test, the air flowing in the tube from the open side can produce an oxidation of the unknown mineral developing different substances compared with those of the previous method.

-Heating on coal: a small amount of the substance, placed in a small pit carved in a coal brick, is heated directly by blowing the dart of a flame on it. The reaction with the coal can release small droplets or globules of reduced metals, such as lead, tin, zinc, bismuth, but also, in some cases, gold and silver, in revealing the interest for a mineral exploitation. Aside of these fortunate events, also the developing of a white or coloured halo on the coal can suggest the presence of some metals, and the variation of this method (heating in an oxidative or reductive flame and mixing with sodium carbonate) gives a lot of information to the chemist. In adopting such a method it would be very useful the use of an instrument called *blowpipe*.

-Flame test: this well know test even nowadays is based on the coloration assumed by the flame of a alcohol lamp (or better, if available on the field, a Bunsen lamp) which would reveal the presence of many different metals like copper, lithium, barium, potassium and so on. A skilled chemist can also notice the different colour obtained by using the substance as it is, or wetted with hydrochloric or nitric acid.

-Borate and phosphate pearls: this method also practiced by modern chemists, consists in obtaining a coloration in a vitreous mass of sodium borate or sodium ammonium phosphate (phosphate salt); it is a useful tool to suggest the presence of some metals in a substance. A small amount, sometimes a single grain of unknown substance is mixed with sodium borate (or phosphate salt), and heated until fusion. The developed colour, the difference of colour between the hot and the cold *pearl*, the tinge difference in oxidative or reductive flame are the distinctive features that could drive a chemist to the identify a specific metal in a mineral.

These are only the most important ways to test a substance without (or reducing to a very minimal amount) the use of acid, base and chemicals. Almost all these methods drive only to the identification of the metallic or semi-metallic element contained in an ore, because metals were (and still are) the base of the modern industry, and except in rare occasions, no relevance must be given to the oxidation state and/or to the coordination number of the metal within the crystal lattice. For example, there is no reason to know if chromium is in its trivalent or hexavalent form, or if copper carbonate is azurite or malachite. However, even if these methods of analysis look like quite simple, a training of the chemist or mineralogist is necessary. This is the reason why in the past many analytical kits producers organized didactical collections, containing samples of the most commons minerals, particularly interesting for the industrial exploitations.

3. Blowpipe Analysis: An Historical Overview

In the modern day education of mineralogists and chemists, the study of blowpipe analysis becomes only a historical curiosity. On the other hand, by using this technique from the end of the 18th century to the middle of the

19th century, the qualitative composition of most minerals was identified and contributed to the discovery of over 15 elements [1].

In 1862, the German mineralogist Franz von Kobell (1803-1882) described the blowpipe as an instrument that "*in its way, served chemical mineralogy as much as the goniometer served crystallography*" [2]. In fact, the blowpipe was one of the most important analytical tools for identifying metallic elements by their different physical reactions like fusibility or colour change. The instrument consists of a small tube (more or less sophisticated in the various, advanced versions), an extremity of which was held in the mouth by the chemist, that gently blows a whisper of air in the flame through the other end, that was placed near, inside or at the middle of the flame itself. The air blow creates a so-called *dart*, directed with ability and skill on the substance (**Figure 3**). The different position in the flame generated an oxygen-rich or reductive environment, so modifying the reaction of the mineral. Old books [*i.e.* Bergman, Berzelius] devoted to this kind of analysis suggest the use of a candle flame, or an alcohol lamp flame, both inexpensive and easy to use in the field as well.

The reaction in the oxidizing or reducing zone of the flame can be easily observed with charcoal, clay, glass or platinum serving as a support. The sample, submitted to various tests with the blowpipe, can be analysed with the addition of fluxes and reagents. Most metals can be identified through the coloration of the flame. Much experience and talent is necessary for an efficient work with the blowpipe. Complicated modifications to the original blowpipe design were applied sometimes even including the use of oxygen or hydrogen to obtain the highest temperatures. The origin of the blowpipe is lost in antiquity but was probably an invention of the Egyptians whose goldsmiths were familiar with the use of metallic blowpipes as shown on wall tomb paintings dated around 2400 B.C. However, the very first description of a blowpipe experiment conducted on a fossil sample is due to the English physicist Robert Hooke (1635-1703). The Danish physician Erasmus Bartholin (1625-1698), in his famous work of 1669, not only was the first to recognize the crystal optics but was also the first to perform experiments in the field of crystal chemistry by decomposing a crystal of Iceland spar into lime by means of a blowpipe [3]. The best mine assayer and metallurgist of his time, the German Johann Andreas Cramer (1710-1777), recommended that a small quantity of ore be fused with borax on charcoal support. He first described in detail a copper blowpipe with a hollow ball to collect the saliva [4].

Particularly in Sweden the blowpipe was used by mineralogists and metallurgists for quick qualitative tests of ores, while in Germany at a later period, a school of blowpipe technique gradually evolved so that the teachers passed on their knowledge to their assistants. Among them, Andreas von Swab was the first to start using constantly the blowpipe for mineral analysis about the year 1738 [5]. Belonging to the same school, the chemist Carl Wilhelm Scheele (1742-1786) made experiments in which he first could discover the elements manganese, chlorine, barium, tungsten and molybdenum: he wrote that the inner flame of the blowpipe contains more phlogiston (oxygen) than outer and furthermore he recognized the reducing and the oxidizing zones of the flame. Meanwhile Axel Friedrich Cronstedt (1722-1765) was a first-rate mining expert and appointed director of all mines of Sweden in 1748 [6]. He employed soda and borax as fluxes and learnt how to use phosphorous salts in the quantitative analysis of characteristically coloured metallic oxides. In 1756, he examined minerals from Iceland and Lapland by discovering the existence of the important group of minerals called *zeolites*, a word de-

Figure 3. Some historical blowpipes.

rived from Greek meaning to effervesce. In 1770, Gustav von Engestrom (1738-1813) published very clear and illustrated instructions for the use of the blowpipe. This talented chemist invented not only a blowpipe, but also various other items for blowpipe experiments which all fit into a neat, small box which could comfortably be carried in a pocket—especially on travels—so that it could be called a pocket laboratory [7].

The Swedish chemical genius Torbern Olof Bergman (1735-1784) published many articles and treatises mentioning blowpipe experiments in passing. These were not limited to minerals but also extended into the fields of mineral waters and organic matter. In his main work of 1779, a modified 3-piece blowpipe made out of silver was described. In addition to charcoal, he also used a silver or gold spoon as a sample support; his portable kit also included an anvil, a hammer, some specimen pliers and a candle holder [8].

Bergman's most important student was Johann Gottlieb Gahn (1745-1818), who became his assistant at the chemical institute of Uppsala after 1767. Later he built his own laboratory in the mining town of Falun and became an unsurpassed master in the art of blowpipe analysis.

Jons Jakob Berzelius (1779-1848) was probably the most famous of the Swedish chemists. In 1803, he discovered cerium and later thorium and selenium (Bergman, 1779). Even if at his times he became famous for the blowpipe technique, he is the inventor of the chemical symbols in common use today and he proved the law of constant proportions. Also thanks to the invention of many types of laboratory equipment, he transformed the alchemical cellar into a modern laboratory. Among the many innovations, Berzelius introduced the practise of the analytical separation by using hydrogen sulphide to precipitate metallic sulphides, later on tested by means of the blowpipe. In his classic book of 1821, all aspects of the blowpipe analysis were clearly summarized and several different types of blowpipes as well as a special oil lamp designed by him are described in detail. In such a way, he was able to distinguish the four zones of the flame and used the key-words *oxidation* and *reduction* in this context [9].

Later on Edward Turner (1798-1837), a chemist, was one of the first to use the coloration of the flame as a diagnostic mean. He developed a technology to prove the existence of lithium in hardly fusible mineral species [10]. A mixture of the powdered sample was fused with fluorite and ammonium sulphate whereby a characteristic red colour of the blowpipe flame could be observed.

The "Pope" of the blowpipe analysis was the German chemist Karl Friedrich Plattner (1800-1858) who studied in the Mining Academy of Freiberg and invented new procedures for quantitative blowpipe analysis for gold, copper, lead, tin and (at a later stage) for nickel, cobalt and bismuth [11]. He augmented the methods by adding wet chemical tests in combination with blowpipe experiments. Coming from the same school of Freiberg, Hyeronimus Theodor Richter (1824-1898) was appointed director of the Mining Academy in 1875 and by means of the blowpipe's methodology was able to discover the element thallium and indium from his studies on the mineral sphalerite. The blowpipe played an important role in the discovery of a new element for the last time in 1885 when Richter analysed a mineral sample of Argyrodite, which contains Germanium: the so-called *ekasilicium*, predicted by Mendeleev was therefore found and the validity of his Periodic table of the Elements was finally proven. At the end of his work, Richter also referred to some of the few extensions of the use of the blowpipe beyond the borders of mineralogy into the recognition and testing of organic substances.

In 1837, the above-mentioned Franz von Kobell proposed—in analogy to the well-known Mohs' hardness scale—a six-step fusibility scale and demonstrated how close-looking the mineral species could be differentiated by its application: he suggested that samples of the minerals in this scale should always be kept handy for comparative purposes.

The decline of the blowpipe began with the invention of gas burner by Robert Wilhelm Bunsen (1811-1899). Such an equipment was able to reach temperatures of more than 2300˚C and the research focused on the experiments with the indicative coloration that molten substances imparted to the flame [12]. He also developed the diagnostic methods for the determination of sodium in the presence of potassium and for better differentiating them he used a cobalt glass. A hollow prism filled with a solution of indigo allowed him to recognize the flame coloration of lithium in the presence of sodium and potassium. Bunsen's observations with the blowpipe and gas burner prompted him, in cooperation with Gustav Robert Kirchoff (1824-1887) to develop the spectral analysis in 1859. Flame spectroscopy and later absorption spectroscopy revolutionized chemical analysis and the chemical detection improved dramatically. With the aid of the spectral analysis, Bunsen discovered the two new elements caesium and rubidium [13] [14].

The 1912 discovery by Max von Laue (1879-1957) of diffraction of the X-rays passing through a crystal established the possibility of relating crystal structure to the chemical composition of a mineral. This new, revolu-

tionary method delivered the end to the use of the blowpipe, which had played such an important role during the century from ca. 1760 to 1860.

4. Materials and Methods

A multidisciplinary approach has been focused on studying the old samples. First, an elementary analysis has been accomplished by using a SEM-EDS, in order to identify the main constituents of the mineral phases. Subsequently, a XRPD identification has been carried out, by reducing the compositional range of the suitable mineral phases to what suggested by EDS.

The first check has been done by means of a SEM Stereoscan 360 (Cambridge Instrument), coupled with an EDS Link Pentafet (Oxford Instrument) equipped with a "thin window" detector, allowing qualitative/quantitative chemical analysis of light elements (down to carbon). Working parameters are as follows: acceleration voltage 15 kV, working distance 25 mm, probe current 1 nA and spectra acquisition time varying from 60 to 300 s. Daily standardization has been performed by using a pure Co specimen. Chemical data have been collected on coated carbon fragments of the samples, processed with the Inca 200 Microanalysis Suite Software, version 4.08 with main calibration on natural mineral standards by using the ZAF correction method. The instrument could not recognize hydrogen, lithium, beryllium and boron, therefore the presence of these elements has been often supposed during the following analytical step. The analysis, normally performed on unpolished samples, has been considered only as semi-quantitative and approximate.

XRPD characterization has been carried out on crushed sample using a Panalytical X'Pert PRO (Cu K_α radiation) diffractometer, with a PIXcel detector, a solid-state detector with rapid readout time and high dynamic range. Data collection has been performed between 5˚ and 90˚ 2θ, with a step of 0.02˚ 2θ. ICDD-PDF database has been used to interpret powder diffraction patterns.

5. Results and Discussion

The main goal (the identification of the mineral species contained in the historical wooden box) has been achieved with a high degree of confidence. Most identified minerals were interesting for industrial or technological purpose, as it can happen to a collection assembled on the behalf of teachers of quick mineralogical analysis and practical application.

A certain order in the distribution of the samples has been noticed: with some exception, the original sequence of numbers labelled on the tubes follows a chemical periodic order. At the beginning there are the mineralogical species containing cations of the first group (Li, Na, K and even ammonium). Then there are the samples containing the second group elements (Be, Mg, Ca, Sr and Ba). Afterwards, there is a group containing the most common transition metals (Mn, Zn, Fe, Ni, Co, Pb, Cr, Sn, Cu and Ag) in many cases as carbonate, oxide, sulphide, arsenide or antimonide, rarely as native element (like silver and arsenic, **Figure 4**). The mutual usage of both techniques has been fundamental either as the EDS, although necessary for screening the elements, is not able to detect some of them like B and Be, or as it can't distinguish among the different polymorphous phases.

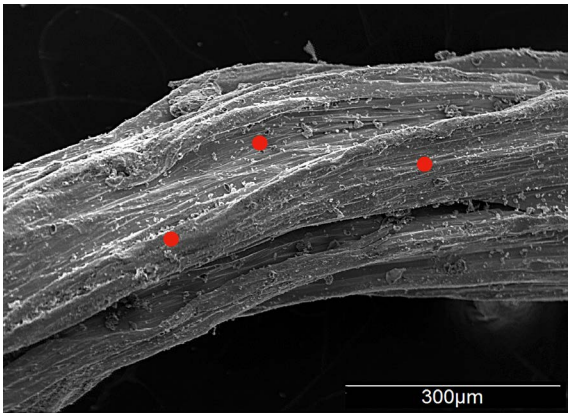
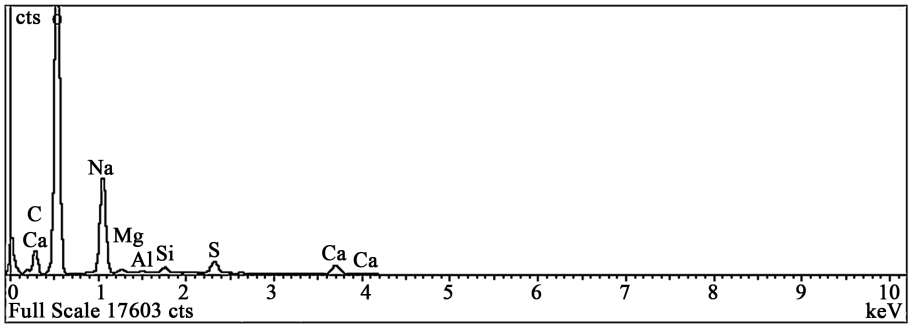


Figure 4. SEM image of native silver (sample n. 88). The red spots indicate the position of EDS analysis on the sample.

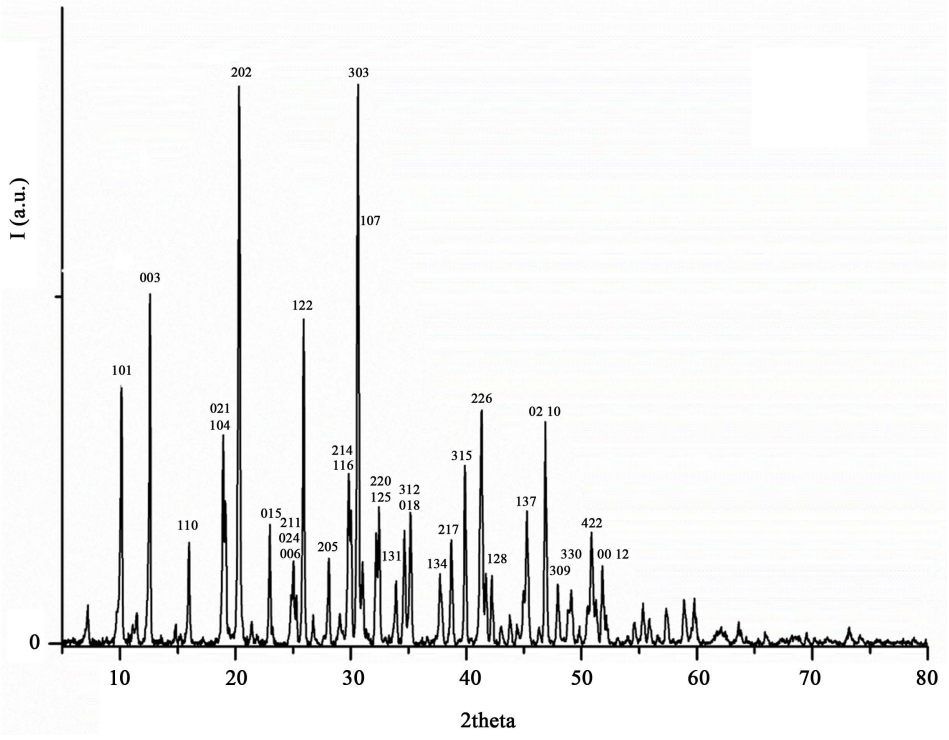
Uranium and REE belong to this group as well. The next group includes partly mixed and strictly correlated rarer species containing unusual or less useful—for that epoch!—elements (niobium, titanium, tungsten and molybdenum). The series of samples, besides some common silicates, finish with some organic substances as beeswax and amber, probably used to show the reactions of organics under the dry analysis (to be noticed the choice of the former, very fusible, and the latter almost infusible), and of a very fusible inorganic material (boric acid).

The last sample is quartz, one of the best examples of simple mineral without perceivable cations, and almost impossible to melt. On the opposite, the diffractometric technique allows a certain identification of each phase (**Figure 5(a)** and **Figure 5(b)**).

It is remarkable to notice that many of the samples are real ore fragments, containing different silicates as mother rocks or containing two or even three different species of the same cation, as it could be expected to be found during the normal field activity. The analytical work on the samples of the present study have allowed to identify the mineralogical species which were strategic from the industrial point of view of the time and interesting for representing the chemical reference terms. All the samples have been surely identified (**Table 1**).



(a)



(b)

Figure 5. (a) EDS spectrum of sample n. 11 showing the main peaks of C, O and Na, simulating a carbonate, (b) the XRPD of the same sample clearly identifies Tincalconite (ICDD-PDF 07-0277).

Table 1. Identification data of the samples. Samples 10, 25, 30 and 65 are missing.

#	Description at glance	SEM-EDS analysis	XRPD-analysis	Identification and notes
1	White crystalline powder	Oxygen, sulfur, aluminum and nitrogen	Ammonium aluminum sulfate hydrate **ICDD PDF 83-1933**	**Ammonium aluminum sulfate, dodecahydrate** $(NH_4)Al(SO_4)_2 \cdot 12H_2O$ The material, apparently synthetic, belongs to the collection probably to show the reactions of a very hydrate and heat-reacting substance
2	White crystalline powder, traces of natural plane faces and "cubic" aspect	Potassium and chlorine	Sylvite **ICDD PDF 41-1476**	**Sylvite,** KCl Could be either of natural or synthetic origin
3	White crystalline powder, no traces of cleavage	Silicon, potassium, aluminum and oxygen	Potassium feldspar (Adularia) **ICDD PDF 71-1543**	**Adularia,** $KAlSi_3O_8$
4	White crystalline powder, traces of cleavage and/or flat faces	Calcium, silicon, oxygen, fluorine, minor sodium and iron	Fluorapophillite **ICDD PDF 71-1778**	**Fluorapophillite** $KCa_4(Si_4O_{10})_2(F_{0.5}OH_{0.5})\ (H_2O)_8$
5	White smooth powder	Oxygen, sulfur, sodium, potassium, calcium	Sodium nitrate **ICDD PDF 89-2828** sodium potassium sulfate **ICDD PDF 74-0394**	Mixing of laboratory chemicals, mainly **potassium nitrate** (KNO_3) and **sodium potassium sulfate** ($KNaSO_4$) Probably synthetic, could have been included to show the reaction of nitrates and sulfates of alkali elements.
6	White granules	Fluorine, sodium and aluminum	Cryolite **ICDD PDF 25-0772**	**Cryolite,** Na_3AlF_6
7	White crystalline fragments	Oxygen, silicon, aluminum, sodium and minor amount of potassium	Albite **ICDD PDF 89-6423**	**Albite,** $NaAlSi_3O_8$ A plagioclase very close to albite composition
8	White crystalline fragments	Oxygen, silicon, aluminum, calcium, sodium and minor potassium	Albite **ICDD PDF 89-1939**	**Albite,** $NaAlSi_3O_8$ A plagioclase in the range of the albite-oligoclase composition
9	White crystalline powder	Oxygen, aluminum, sodium, silicon, small amount of calcium	Natrolite **ICDD PDF 45-1413**	**Natrolite,** $Na_2Al_2Si_3O_{10} \cdot 2H_2O$
10	Missing sample			
11	White powder	Oxygen, sodium and minor amount of magnesium, sulfur and chlorine	Tincalconite **ICDD PDF 07-0277**	**Borax or tincalconite** $Na_2(B_4O_5(OH)_4)\ (H_2O)_{2.668}$ It was probably Borax, but the long time altered it in a derivative of borax, Tincalconite.
12	Pale yellow crystalline powder, some fragments with cleavage	Oxygen, phosphor, iron and manganese	Lithiophilite **ICDD PDF 13-0336**	**Triphylite,** $Li(Mn,Fe)PO_4$ A sample of the Lithiofilite (Mn) and Triphylite (Fe) series, close to the Triphylite because of the iron content.
13	Pale whitish-yellowish fragments	Aluminum, silicon, oxygen	Spodumene **ICDD PDF 71-1063**	**Spodumene,** $LiAlSi_2O_6$
14	Withe powder	Aluminum, silicon, oxygen	Petalite **ICDD PDF 35-0463**	**Petalite,** $LiAlSi_4O_{10}$
15	White powder	Aluminum, silicon, iron, manganese, potassium and fluorine	Muscovite (fluor-muscovite) and/or celadonite **ICDD PDF 49-1840**	**Muscovite-Phlogopite series**
16	White crystalline powder	Aluminum, silicon, oxygen, manganese	Lithiophorite **ICDD PDF 41-1371**	**Lithiophorite,** $(Al,Li)MnO_2(OH)_2$ A mixture of Lithiophorite and Quartz
17	Greenish-blackish fragments	Oxygen, magnesium, silicon, calcium, iron and lesser amount of aluminum and chromium	Magnesium-hornblende **ICDD PDF 20-0481**	**Magnesio-hornblende** $(Ca,Na)_2(Mg,Fe,Al)_5(Si,Al)_8O_{22}(OH)_2$

Continued

18	White crystalline powder	Carbon, oxygen, barium	Witherite **ICDD PDF 71-2394**	**Witherite,** $BaCO_3$
19	White crystalline powder	Carbon, oxygen, barium, calcium	Cobaltocalcite **ICDD PDF 15-0285**	**Baritocalcite,** $BaCa(CO_3)_2$
20	White crystalline powder	Strontium, oxygen, sulfur	Celestine **ICDD PDF 05-0593**	**Celestine,** $SrSO_4$
21	White crystalline powder	Strontium, oxygen, carbon	Strontianite **ICDD PDF 71-2393**	**Strontianite,** $SrCO_3$
22	White crystalline powder with traces of cleavage	Fluorine and calcium	Fluorite **ICDD PDF 70-1469**	**Fluorite,** CaF_2
23	White fine powder	Calcium, oxygen and sulfur	Gypsum **ICDD PDF 70-1469**	**Gypsum,** $CaSO_4 \cdot 2H_2O$
24	Glassy yellowish and bluish fragments, conchoidal fracture	Phosphor, oxygen, calcium, fluorine, a small amount of chlorine	Fluoroapatite **ICDD PDF 71-0880**	**Fluorapatite,** $Ca_5(PO_4)_3F$
25	Missing sample			
26	White crystalline powder	Calcium, carbon, oxygen with minor amount of magnesium	Calcite **ICDD PDF 89-1304**	**Calcite,** $CaCO_3$ Composition is very close to pure calcite, with only 0.03% m/m of magnesium
27	White crystalline fragments	Silicon, calcium and oxygen, with minor iron and chromium	Wollastonite **ICDD PDF 42-0547**	**Wollastonite,** $CaSiO_3$
28	Green crystalline fragments	Silicon, calcium, aluminum, iron and oxygen, with minor amount of sodium	Clinozoisite **ICDD PDF 71-1539**	**Epidote,** $Ca_2(Fe,Al)_3(SiO_4)_3(OH)$ The sample is a mixed member of the series Clinozoisite-Epidote
29	White greenish scales	Magnesium, silicon, oxygen and minor iron	Talc **ICDD PDF 29-1493**	**Talc,** $Mg_3Si_4O_{10}(OH)_2$
30	Missing sample			
31	Creamy-white powder	Calcium, carbon, oxygen and little amount of iron and manganese	Ferroan Dolomite **ICDD PDF 41-0586**	**Ferroan Dolomite,** $Ca(Fe,Mg,Mn)(CO_3)_2$ Magnesium in dolomite is often replaced by a small amount of iron and manganese
32	Whitish powder	Carbon and oxygen	Phenolphthalein **ICDD PDF 51-2358**	**Phenolphthalein,** $C_{20}H_{14}O_4$ Phenolphthalein is an organic pH-indicator that does not match with minerals. Probably it was used as a replacement of a consumed sample
33	White powder	Manganese, sulfur, oxygen	Manganese sulfate hydrate **ICDD PDF 33-0906**	**Manganese sulfate monohydrate** $MnSO_4 \cdot H_2O$ May be a laboratory product
34	White powder	Sodium, sulfur, magnesium, oxygen	Magnesium sulfate hydrate and sodium magnesium sulfate hydrate **ICDD PDF 72-1068** **ICDD PDF 71-0307**	**Magnesium sulfate hydrate** $MgSO_4 \cdot 6H_2O$ **Sodium magnesium sulfate hydrate** $Na_2Mg(SO_4)_2 \cdot 4H_2O$ May be either a natural mineral or a laboratory product.
35	White crystalline powder	Aluminum, sulfur, potassium and oxygen	Alunite **ICDD PDF 73-1652**	**Alunite,** $K(Al_3(OH)_6(SO_4)_2$ May be either a natural mineral or a laboratory product.
36	Crystalline fragments, colorless, traces of natural faces, conchoidal fracture	Silicon, oxygen, aluminum and fluorine	Topaz, aluminum fluosilicate. **ICDD PDF 12-0765**	**Topaz,** $Al_2SiO_4(F,OH)_2$
37	Greyish fragments without particular features	Aluminum and oxygen with some impurities	Chrysoberyl **ICDD PDF 78-0958**	**Chrysoberyl,** Al_2BeO_4 EDS did not determine the presence of beryllium, due to its low atomic mass
38	Hyaline yellowish fragments	Aluminum and oxygen	Corundum **ICDD PDF 81-2267**	**Corundum,** Al_2O_3
39	A white-grayish powder of metallic appearance	Aluminum and oxygen with impurities of copper and iron	Aluminum **ICDD PDF 04-0787**	**Aluminum,** Al Impurities of Cu and Fe in the powder

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40	White porcelanaceous fragments, conchoidal fracture.	Silicon, aluminum and oxygen	Beryl **ICDD PDF 84-1141**	**Beryl,** $Be_3Al_2Si_6O_{18}$ EDS did not determine the presence of beryllium, due to its low atomic mass
41	Dark, blackish fragments with conchoidal fractures	Oxygen, aluminum, calcium, iron and silicon, REE elements (La, Ce, Nd)	The spectrum is probably matching the Allanite's one	**Allanite (epidote group)** $(Ca,REE)_2(Fe,Al)_3(SiO_4)_3(OH)$ XRPD spectrum shows a low crystallinity, probably due to a radiation damage (metamictization) of the crystalline structure
42	Yellow and dark yellow fragments, no cleavage, conchoidal fracture	Oxygen, silicon and zirconium	Zircon **ICDD PDF 83-1375**	**Zircon,** $ZrSiO_4$
43	Blackish, dark fragments with no distinctive features	Oxygen, carbon, fluorine and REE elements (La, Ce, Nd)	Parasite **ICDD PDF 47-1832** and Bastnaesite **ICDD PDF 11-0340**	**Bastnaesite,** $CeCO_3F$ **Parisite,** $Ca(Ce,La)_2F_2(CO_3)_3$ Probably a natural blend of the two minerals, used as standard for REE carbonates.
44	Greyish-green fragments	Phosphor, oxygen, thorium, calcium, REE elements (Ce, La, Nd)	Neodymium phosphate **ICDD PDF 83-0654**	**Monazite,** $(Ce,REE)PO_4$
45	Black fragments	Manganese, sulphur	Alabandite **ICDD PDF 88-2223**	**Alabandite, (**MnS**)**
46	Black fragments, with fibrous appearance. Black streak	Manganese and oxygen	Pyrolusite **ICDD PDF 72-1984**	**Pyrolusite,** MnO_2
47	Pink fragments with cleavage traces, low hardness	Manganese, oxygen, carbon and a minor amount of calcium	Rhodochrosite **ICDD PDF 44-1472**	**Rhodochrosite,** $MnCO_3$
48	Pink fragments without any cleavage	Silicon, oxygen, manganese and minor amount of calcium and magnesium	Rhodonite **ICDD PDF 83-2212** and Bustamite **ICDD PDF 85-1034**	**Rhodonite (magnesian),** $(Mn,Mg)SiO_3$ **Bustamite,** $(Ca,Mn)SiO_3$ Probably a natural mix of the two Mn-rich silicates Rhodonite and Bustamite
49	Sand	Oxygen, silicon, sodium, potassium and calcium	Quartz **ICDD PDF 86-1629** and Albite **ICDD PDF 09-0466**	**Quartz, sodic feldspar, potassic feldspar** Sand, mainly composed of Quartz and Feldspars.
50	Intense yellow fragments, vitreous, with some cleavage	Zinc, sulphur and iron	Pyrrothite **ICDD PDF 76-2308** and Sphalerite **ICDD PDF 77-2100**	**Pyrrothite (**Fe_7S_8**)** **Sphalerite (**ZnS**)** A mix of iron and zinc sulphides
51	Pale yellowish powder, with some metallic lustre	Iron, sulphur and oxygen	Pyrite **ICDD PDF 89-3057**	**Pyrite,** FeS_2 The sample was probably made of crushed Pyrite, strongly oxidized during a century.
52	Black fragments	Mainly iron and oxygen, some aluminum and calcium in small portions	Magnetite **ICDD PDF 88-0315**	**Magnetite,** Fe_3O_4 Impurities of silicates
53	Dark reddish fragments with fibrous appearance	Iron and oxygen, minor amount of aluminum and silicon	Hematite **ICDD PDF 89-0599**	**Hematite,** Fe_2O_3
54	Reddish-yellowish dark fragments, fibrous appearance	Oxygen and iron	Goethite **ICDD PDF 29-0713**	**Goethite,** FeO(OH)
55	Rhombohedrical shaped fragment, dark yellow	Iron, oxygen and carbon	Siderite **ICDD PDF 83-1764**	**Siderite,** $FeCO_3$
56	Grey-greenish fragments with conchoidal fracture	Iron, phosphor, oxygen and minor amount of sodium, aluminium.	Natrodufrenite **ICDD PDF 35-0570**	**Vivianite,** $Fe_3(PO_4)_2 \cdot 8H_2O$ The sample was probably vivianite, altered in Natrodufrenite

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57	White, dusty fragments	Iron, arsenic and oxygen.	Scorodite **ICDD PDF 37-0468**	**Scorodite,** $FeAsO_4 \cdot 2H_2O$
58	Greenish fragments	Iron, sulphur and oxygen, with sodium as minor element	Copiapite **ICDD PDF 71-1546** and sodium iron sulfate **ICDD PDF 29-1218**	**Copiapite,** $Fe_5(SO_4)_6(OH)_2 \cdot 20H_2O$ **sodium iron sulphate,** $Na_6Fe(SO_4)_4$ Original sample was Copiapite, slightly altered with formation of iron sulphates
59	Dark grey fragments of metallic lustre	Sulphur and antimony	Stibnite **ICDD PDF 74-1046**	**Stibnite,** Sb_2S_3
60	Light grey fragments with metallic lustre	Arsenic, nickel, cobalt and minor amount of sulphur and iron	Skutterudite **ICDD PDF 25-0118**	**Ni-Skutterudite,** (Co, Ni, Fe)As_3
61	A very dark, black powder and fragments	Manganese and oxygen, small amount of calcium and magnesium	The spectrum shows a very low degree of crystallinity.	**WAD ("Psilomelane")** A mix of manganese oxide
62	Apple green fragments with crusty appearance	**Nickel and oxygen, with small amount of arsenic**	The spectrum shows a very low degree of crystallinity.	**Nepouite** The sample is the Ni homologous of Chrysocolla, a mix of various Ni-silicate with different hydration degree and low crystallinity, deriving from Ni-sulphide alteration
63	Greyish-metallic fragments	Nickel and arsenic	Nickeline **ICDD PDF 75-0603**	**Nickeline,** NiAs
64	Greyish-black fragment, crystalline	Nickel, antimony, sulphur, arsenic	Ulmannite **ICDD PDF 83-1221**	**As-Ulmannite,** NiSbS
65	Missing sample			
66	Angular gold-yellow vitreous fragments	Sulphur and zinc	Sphalerite **ICDD PDF 65-0309**	**Sphalerite,** ZnS
67	Angular blackish fragments with submetallic lustre	Sulphur, zinc and minor iron	Ferroan Sphalerite **ICDD PDF 89-4938**	**Iron-rich sphalerite,** (Zn,Fe)S The iron rich variety of sphalerite often known as "marmatite"
68	White sub-hyaline fragments with traces of cleavage	Zinc, oxygen and carbon	Smithsonite **ICDD PDF 83-1765**	**Smithsonite,** $ZnCO_3$
69	Blackish crystalline fragments with good pseudo-cubic cleavage	Lead and sulphur	Galena **ICDD PDF 65-0135**	**Galena,** PbS
70	Black fragments without cleavage	Sulphur, antimony and minor iron	Berthierite **ICDD PDF 24-0509** Iron sulphide **ICDD PDF 65-1211** Iron sulfate **ICDD PDF 73-1057**	**Berthierite,** $FeSb_2S_4$ A mixing of Berthierite and minor Pyrite, oxidized during time
71	Hyaline whitish fragments with cleavage traces and natural flat surfaces	Lead, phosphor, oxygen and minor amount of calcium,	Pyromorphite **ICDD PDF 73-1729**	**Pyromorphite,** $Pb_5(PO_4)_3Cl$
72	White fragments	Lead, oxygen and carbon	Cerussite **ICDD PDF 76-2056**	**Cerussite,** $PbCO_3$
73	Orange crystalline fragments	Lead, chromium and oxygen	Crocoite **ICDD PDF 73-1332**	**Crocoite,** $PbCrO_4$
75	Brown-reddish crystalline fragments	Tin and oxygen	Cassiterite **ICDD PDF 77-0447**	**Cassiterite,** SnO
76	Elongated steel-greyish fragments	Bismuth and sulphur	Bismutinite **ICDD PDF 65-3884**	**Bismutinite,** Sb_2S_3

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77	Blackish fragments	Uranium, oxygen, and minor calcium, silicon and iron	Uraninite **ICDD PDF 47-1879**	**Uraninite,** UO_2
78	Black lustre fragments	Copper and sulphur	Chalcocite **ICDD PDF 33-0490**	**Chalcocite,** Cu_2S Quartz-impure chalcocite
79	Blackish fragments	Copper, antimony and sulphur	Tetrahedrite **ICDD PDF 42-0561**	**Tetrahedryte,** $Cu_{12}Sb_4S_{13}$ The sample also contains pyrite and iron/copper oxides
80	Greenish black fragments with alterations	Copper, sulphur, iron and oxygen	Chalcopyrite **ICDD PDF 83-0983**	**Chalcopyrite,** $CuFeS_2$ The sample shows alteration and oxidation of the surface
81	Dark, reddish fragments	Copper and oxygen	Cuprite **ICDD PDF 78-2076**	**Cuprite,** Cu_2O
82	Reddish fragments with deep green little crystals	Sulphur, oxygen and copper	Brochantite **ICDD PDF 43-1458**	**Brochantite,** $Cu_4(SO_4)_2(OH)_6$
83	Green earthy fragments with traces of cleavage	Copper, oxygen and carbon	Malachite **ICDD PDF 41-1390**	**Malachite,** $Cu_2(CO_3)(OH)_2$
84	Earthy light blue fragments	Silicon, oxygen, copper and calcium as trace element	Malachite **ICDD PDF 41-1390**	**Malachite,** $Cu_2(CO_3)(OH)_2$ **Chrysocolla**
85	Red globular fragments	Mercury and sulphur	Cinnabar **ICDD PDF 89-0438**	**Cinnabar,** HgS Small globular aggregates of Cinnabar in clay matrix
86	Blackish, earthy mass with no cleavage	Sulphur, antimony, copper and zinc, minor arsenic and iron	Tetrahedrite **ICDD PDF 88-0282**	**Tetrahedrite,** $Cu_{12}Sb_4S_{13}$ Tetrahedryte with a little amount of S and Zn as vicariant of Sb and Cu respectively
87	Whitish-green ductile fragments	Silver and chlorine	Chlorargirite **ICDD PDF 01-1031**	**Chlorargirite,** AgCl
88	Small silvery filamentous fragments	Silver and small amount of oxygen.	Silver **ICDD PDF 03-0921**	**Silver,** Ag
89	Ductile steel-grey fragments	Silver and sulphur, with a small amount of oxygen	Acanthite **ICDD PDF 14-0072**	**Acanthite,** Ag_2S The small amount of identified oxygen is probably due to surface oxidation
90	Blackish fragments with deep red tinge	Silver, sulphur and antimony	Pyrargiryte **ICDD PDF 77-0329**	**Pyrargyrite,** Ag_3SbS_3
91	Pitch black fragments with conchoidal fracture	Niobium, oxygen, iron, manganese and minor tantalum, uranium and titanium	Columbite **ICDD PDF 84-1020**	**Columbite,** $FeNb_2O_6$
92	Blackish-brownish fragments	Oxygen and titanium	Rutile **ICDD PDF 87-0710**	**Rutile,** TiO_2
93	Black pitchy fragments	Iron, titanium and oxygen	Ilmenite **ICDD PDF 75-1210**	**Ilmenite,** $FeTiO_3$
94	Steel grey fragments with traces of cleavage	Sulphur and antimony	Stibnite **ICDD PDF 74-1046**	**Stibnite,** Sb_2S_3
95	Steel grey fragments with good cleavage	Calcium, oxygen, tungsten and iron	Hubnerite **ICDD PDF 12-0727**	**Hubnerite,** $(Fe,Mn)WO_4$ **Scheelite,** $CaWO_4$ Mn-poor Hubnerite and traces of Scheelite
96	Pale yellow fragments with good cleavage	Calcium, oxygen, tungsten	Scheelite **ICDD PDF 41-1431**	**Scheelite,** $CaWO_4$
97	Silvery plates, flexible	Molybdenum and sulphur	Molybdenite **ICDD PDF 65-3656**	**Molybdenite,** MoS_2
98	Yellow orange small crystals	Lead, molybdenum and oxygen	Wulfenite **ICDD PDF 74-1075**	**Wulfenite,** $PbMoO_4$

Continued

99	Greenish black fragments, no trace of cleavage	Chromium, oxygen, magnesium, aluminium and iron	Ferroan-magnesiochromite spinel **ICDD PDF 09-0353**	**Spinel** (magnesiochromite, ferroan) **$(Mg,Fe)(Cr,Al)_2O_4$**
100	Grey dusty fragments	Arsenic, with small amount of oxygen and antimony	Arsenic **ICDD PDF 72-1048**	**Arsenic,** As Probably altered on surface with formation of trivalent arsenic oxide (Arsenolite)
101	Orange reddish crystals, with vivid lustre	Sulphur and arsenic	Realgar **ICDD PDF 71-2434**	**Realgar,** AsS
102	Yellow brownish light fragments, rounded aspect	Carbon	Amorphous	**Amber** The identification was obtained also by mean of combustion test
103	Yellowish-brownish granules, very soft	Carbon, oxygen	Amorphous	**Beeswax** Final identification has been obtained with combustion and fusion test. The mass was contaminated by different substances (Feldspar, Galena and others)
104	White small scales	Oxygen	Boric acid **ICDD PDF 30-0199**	**Boric acid (sassolite),** H_3BO_3 May be either a natural mineral or a laboratory product.
105	Vitreous greenish black fragment with conchoidal fracture	Silicon, aluminium, oxygen, magnesium, sodium, iron with some titanium	Dravite (tourmaline group) **ICDD PDF 85-1816**	**Dravite (tourmaline group)** $NaMg_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$
106	Vitreous greenish **grey fragments**	Silicon, aluminium, calcium, magnesium, iron and manganese	Axinite **ICDD PDF 29-0344**	**Mg-axinite** $Ca_2(Fe^{2+}, Mg, Mn^{2+})Al_2BO_3Si_4O_{12}(OH)$
107	White powder	Magnesium, chlorine and oxygen	Magnesium chloroborate **ICDD PDF 85-0899**	**Magnesium chloroborate** $ClMg_3B_7O_{13}$ Probably a laboratory product
108	Transparent, colourless vitreous fragments	Silicon, oxygen	Quartz **ICDD PDF 86-1629**	**Quartz,** SiO_2

6. Conclusions

On the other hand, it has not been possible to determine the manufacturing date and origin even if the probe-tubes' type, the box design and its wood kind suggest a German builder and a period around the second half of XIX century.

The general features of the wooden box show that it is designed either for being carried out during mineralogical missions or for didactic purposes. These didactic-scientific collections have played in their time a fundamental role for largely improving the chemical, geological and mineralogical level of knowledge just before and during the important period of the so-called *industrial revolution*. Many data are going to be collected about similar collections (private and public) in order to characterize the importance of some mineralogical species, which can be considered as reference terms for the industrial development.

The whole set shows a good correspondence with the description of mineralogical and didactical collections and kits described in several old advertising brochures and catalogues, issued by companies who, since the mid '800, started designing and selling scientific and technological tools and equipment: the German Krantz, based in Bonn and Hugershoff, based in Leipzig or Gregory & Bottley, based in London. In particular, most these companies built up and supplied their educational collections, like the wooden box, examined in this study, consisting of a minimum of 50 to a maximum of about 170/200 different mineralogical and/or chemical samples each. Just to get an economical evaluation of the wooden box of the present study, a similar one containing 105 samples arranged according Kobell system was costing around 30.00 D.M. after having been quoted by the Franz Hugershoff's catalogue of 1911.

A countertype of the same box (104 fragments of minerals in neat case for blowpipe analysis) was offered in 1936 by the firm Gregory & Bottley at a price of around 1.5 £. Today, the approximate and estimated current prize of both boxes would be between 450 and 750€.

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