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ABSTRACT

This research relies on microscopy and digital microscopy observations and spectral analysis techniques: Raman spectroscopy, laser-induced breakdown spectroscopy (LIBS) and particle-induced X-ray emission (PIXE), to recover part of the lost identity of two pyrite (FeS_2) cones. Conserved in Paris, at the Muséum National d'Histoire Naturelle (MNHN), the first one is registered MIN000-3519 in the collection of the mineralogist René-Just Haüy, the second one, registered 105.504, is a stray object. All information related to its origin would have been lost during the move (1837–1841) of the collections from the former Cabinet du Jardin du Roy to the new earth science gallery of the MNHN. Our historical research (Gendron, 2022) revealed that the first one, described as an "Inca mirror", was shipped from Peru around 1760 by the botanist Joseph de Jussieu to his brothers Antoine and Bernard. They also confirmed that these two pyrite cones are archaeological objects of the Ecuadorian Cañari culture (500–1500 AD).

Raman analyses conducted on the MIN000-3519 specimen confirm that it was developed on a quartz paragenesis. While the faces observation of no.105.504 reveals that the crystal used for its cut was triglyph twinned, a crystal which must have been cubic or dodecahedral pentagonal. The observation of the technical traces in digital microscopy makes it possible to reconstruct a process of similar cut for the two "mirrors" and help to discover red mineral clusters in the bottom of the crystalline gaps. LIBS analyses were also applied to get complementary information on in-depth element distribution, such as Fe and Al, in order to understand the stratigraphy inside the cracks. Finally, PIXE measurements do not confirm that these two pyrites come from the same deposit. But, this analytical technique is hampered by the nature of the element Fe which offers multiple and random bonding possibilities during the crystallization of iron minerals and by the lack of a comparative sample in the Parisian mineralogic collections.

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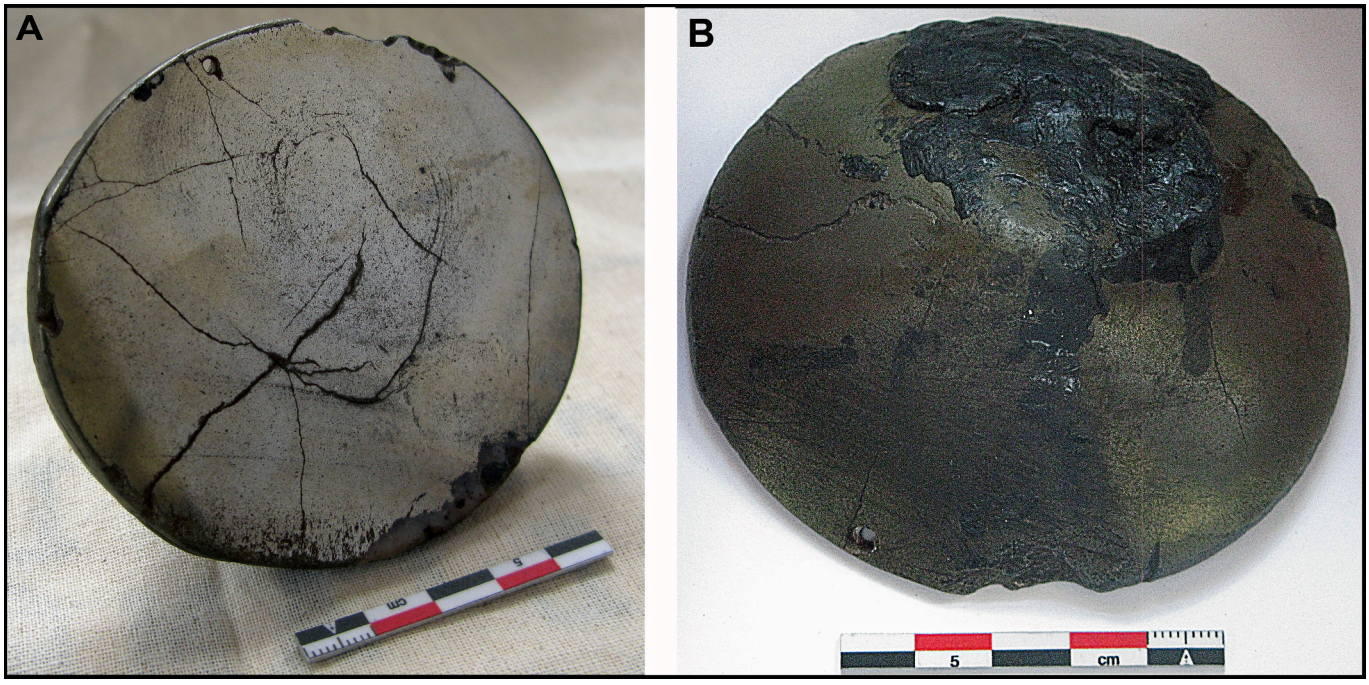

Fig. 1. A and b. A) Pyrite "Inca mirror" MIN000-3519 (no.1) preserved in the René-Just Haüy's collection seen from its basal reflective face (height: 26.8 mm; Ø: 87.5 x 77 mm; weight: 344.1 g). B) Conic side of the pyrite "Inca mirror" MIN000-3519 (no.1), the black substance on is Judean bitumen, which Haüy used to glue his mineralogical samples on their wooden base; (Photographs F. Gendron/MNHN).

1. "Mirrors of the Inca" conserved in the MNHN's collections

In the general mineralogical collection of the *Muséum National d'Histoire Naturelle* (MNHN) are conserved two pyrite (FeS_2) objects, registered as "mirrors of the Inca".[1] It is about two cones, one numbered MIN000-3519 (hereafter referred to as mirror no.1) and the second 105.504 (hereafter referred to as mirror no.2). Previously, the thorough re-examination of a third "Inca mirror" (ref.176.101) cut in obsidian allowed us to discover that it was one of the objects sent to France (1737) by Louis Godin (1704–1760) and Charles-Marie de La Condamine (1701–1774), two of the three French academicians of the famous royal geodesic expedition (1735–1743) over the equator (Bouguer 1744; Calligaro et al., 2019).

1.1. The pyrite "Inca mirrors"

The pyrite cone mirror no.1 is also registered under the number 5492 in René-Just Haüy's (1743–1822) catalog of his mineralogical working collection, with the mention "*fer sulfuré, miroir de l'Inca, Pérou, M. de Jussieu*"[2] (Fig. 1a and 1b). Its historical study (Gendron, 2022) revealed that it was shipped from the Vice-royalty of Peru to France, around 1760, by the botanist Joseph de Jussieu (1704–1779) to his brothers Antoine (1696–1758) and Bernard (1699–1777). Later, his nephew Antoine-Laurent de Jussieu (1748–1836) or his grand-nephew Laurent-Pierre de Jussieu (1792–1866) offered this object to the abbot Haüy, Father of the mineralogy science. This object also passed through the hands of Professor Paul Rivet (1876–1958), founder of the ethnographic *Musée de l'Homme* (MdH), who mentioned it in his writings on Ecuadorian archaeology (Verneau and Rivet, 1912: volume VI, fascicle 1, 214–217).

The story of the second "mirror" (mirror no.2), on the other hand, is less clear. It was discovered, without any mention of its origin, in the reserves of the Mineralogy-Geology Gallery of the MNHN by Professor Alfred Lacroix (1863–1948). This last recorded it in 1905 in the general catalog of the MNHN's mineralogy collections, adding in the margin this brief comment: "*stray*" (Fig. 2a and 2b).

The historical research carried out on these two historical "mirrors" has already allowed to conclude in their common archaeological origin: the Cañari culture. Southern archaeological populations of the current Republic of Ecuador, the Cañaris will be the only ones of the Andean Cultural Area, with the Chono (Milagro-Quevedo culture), to cut the pyrite[3] in way of "mirror".[4] This initial research also led us to

[1] In this article, we will systematically put the term "mirror" between quotation marks because the real function of these objects remains unknown to us. The qualification of "mirror" is imposed on them since their discovery in the 18th century but it does not mean that they were used for this function. The inventory that we have drawn up of these pyrite Cañaris artefacts reveals that there are quite a few of them and that, a priori, none of them come from a well-identified and well-dated archaeological context (Gendron, 2022: 263).

[2] The term "sulphured iron" was invented by René-Just Haüy while the physician Dioscorides in 50 BC already spoke of pyrite. The term pyrite refers to fire, firestone in Latin, because this mineral emits sparks when struck. Pyrite is an iron disulphur (FeS_2) which crystallizes in the cubic system, its hardness is from 6 to 6.5 on the Mohs scale and the species is recognized as valid by the International Mineralogical Association (IMA).

[3] The Quechua language uses the term *suruqch'i*, *suroqch'i* or *suruqchi* to designate alternatively mountain sickness and white to grey metallic minerals. In Ecuador, *suruqch'i* corresponds to pyrite (Boussingault 1849: 217), while in Chile and Peru it is galena (PbS; Barba 1817: 83). After the Conquest, the Quechua term was Spanishized into "*soroche*". One finds it under this form in the toponym *cerro* Soroche (alt. 4730 m). This mountain, located in the Ecuadorian provinces of Chimborazo and Morona-Santiago, has been visited since pre-hispanic times because its slopes are covered with pyrite crystals released by erosion.

[4] The Cañari culture is developed between 500 and 1500 AD, during the Integration Period, in the southern basins of Cuenca, Cañar and Alausí. It was wiped out at the end of the 15th century by the Incas (Meggers 1966: 151-154). The Chonos was populations of the Guayas basin integrated into the Milagro-Quevedo culture. A cultural phenomenon that also develops during the Integration Period. According to Meggers (1966: 133 and 137), the tombs of the Milagro culture contain as offerings objects of all kinds, including "*pyrite mirrors framed in silver*".

hypothesize that the wandering mirror no.2 could be, like the obsidian mirror ref. 176.101, one of the lost objects of the shipment made by Godin and La Condamine in 1737 (Ulloa de 1752: plate XVI; Calligaro et al., 2019: 426; Gendron 2022: 14-15). Associated with the mathematician-hydrographer Pierre Bouguer (1698–1758), these three academicians led the geodesic expedition sent in 1735 to measure a meridian arc on the South American equator (Bouguet 1744; La Condamine 1745; Mercier, 1969). According to de La Condamine (1751: 104, note) and Godin (1802), after its reception in Paris by the intendant Charles Cisternay du Fay (1698–1739), the shipment was dispersed in the Cabinet of the King's Garden.

In the present state of the research, the only links uniting these two mirrors are their material, their morphological similarity and their South American cultural origin. Also, in view of the tenuousness of these links, and their historical importance for the MNHN as well as for the History of sciences, we proposed to the management of the institution to extend their historical study by an archaeometric study. For this purpose, these pyrites were analyzed mineralogically and chemically, while their anthropized surfaces were observed and studied by digital microscopy.

2. Observations and analytical techniques

Initially, mineralogical indices were sought on the surface of the two "mirrors". A white translucent mineral vein differentiated from pyrite was observed on the edge of mirror no.1 (Fig. 1b). A series of parallel striations is noticed on the conical face of the "mirror" no.2 (Fig. 2b). In a second step, a search for micro-traces left by the cutting tooling on the surfaces of the two "mirrors" was conducted using digital microscopy. These observations revealed the presence of red mineral clusters at the bottom of the crystalline gaps revealed by the cutting. These were analyzed by LIBS spectroscopy to determine their nature. Finally, knowing that and depending on the deposit, pyrite (FeS_2) contains, trace amounts in variable proportions, why the two specimens were analyzed by PIXE.

All these observations and analyses are not-invasive, both for the mineral and for the objects. They were carried out, for some of them, at the Analytical Platform of the MdH and for the others, at the *Centre de Recherche et de Restauration des Musées de France* (C2RMF), with the kind permission of Mr. Cristiano Ferraris, in charge of the Earth Sciences collections at the MNHN.

2.1. Raman: Mineralogical analysis of the paragenesis

In order to determine the mineralogical nature of the white mineral vein observed on the edge of the "mirror" no.1, it was analyzed with a DeltaNu® laser Raman microprobe, RockHound model. This spectrometer is equipped with a red-NIR laser with a wavelength of 785 nm, analyzing a 35 μm diameter surface. The acquisition time of the spectra with the NuSpec 8.2.1 software is between 1 and 10 s, details about grating are not specified by manufacturer. These measurements are then processed with the LabSpec 4.18—–2006 software. The protocol for Raman analysis in archaeometry was established by Smith and Carabatos-Nedelec (2001) and Smith (2006).

2.2. Digital microscopy: A surface study of the "mirrors" faces

In order to observe and measure the micro-traces left by the cutting, polishing and shining of the two "mirrors'" faces, we reconstructed them in three dimensions using a digital microscope of the Hirox® Company, model RH-2000. This apparatus is equipped with MXB-2016Z (magnification of 6 to x320; FOV = 15.4 to 2.0 mm [H]; WD = 44 mm) and MXB-5000REZ (turret with three objectives:

1 - "Low range" magnification of 35 to x250; FOV = 8.71 to 1.22 mm [H]; WD = 10 mm;
2 - "Middle range" magnification of 140 to x1000; FOV = 2.18 to 0.31 mm [H]; WD = 10 mm;
3 - and "High range" magnification of 700 to x5000; FOV = 0.43 to 0.06 mm [H]; WD = 3.4 mm).

The best observation results of these surfaces were obtained by using simultaneously a partially coaxial and partially annular light, an option allowed by this microscope.

2.3. LIBS: Characterization of the red mineral clusters chemistry

In order to determine the mineralogical nature of the red clusters found at the bottom of the crystalline lacunae and size-cut cracks, we subjected them to an analysis by Laser-Induced Breakdown Spectroscopy (LIBS) technique. LIBS has been used for cultural heritage since 1997, analyzing the light emitted by plasma with characteristic wavelengths generated by a pulsed laser from the sample, allowing the elements or molecular fragments identification both on the surface and in the depths of the materials (Anglos et al., 1997; Detalle and Bai, 2022).

In this work, we used the fourth harmonic of Nd: YAG laser at 266 nm with a nominal pulse duration of 5.5 ns (FWHM), operating at 20 Hz. The laser beam was focalized by a lens with a focal length of 30 cm and the diameter of the laser spot on the surface was about 220 μm. The emission of plasma was collected by a lens (f = 15 cm) and transmitted through an optical fiber connected to a Czerny-Turner spectrometer (Shamrock 303i, Andor Technology®, UK) with three gratings of 600, 1200 and 1800 lines/mm. It was coupled to an ICCD camera (DH340T-18F-E3, Andor Technology®, UK). Each spectrum was acquired on a single-shot basis and a series of 60 spectra were recorded from the same point on the sample for one measurement.

2.4. PIXE: Characterization of pyrites chemical composition

Particle Induced X-ray Emission (PIXE) analysis was carried out with the external beam of the AGLAE accelerator at the C2RMF (Dran et al., 2004). Whilst this analytical technique bears similarities with X-ray Fluorescence (XRF), it has four major advantages in archaeological artefacts analysing (Dran et al., 2000): non-invasive, non-destructive, it has high accuracy and high sensitivity.

The artefacts were subjected to a 3 MeV proton beam of 1nA intensity for a few minutes allowing the chemical composition of the samples made of pyrite to be derived from two PIXE spectra. The first spectrum was devoted to the measurement of major elements was recorded in a helium atmosphere allowing the measurement of Na, Al, Si, S, K, Ca, Ti and Cr, Mn and Fe. The second spectrum was devoted to the measurement of trace elements. It was recorded with two detectors screened with a 50-μm aluminum and 12 μm Cr absorbers to attenuate the strong X-ray emission of Fe. The analysis was recorded by scanning the 50 μm beam on a 1 x 1 mm^2 area yielding elemental maps of 60 x 40 pixels that allowed to check the homogeneity of the composition. The analysed areas were previously polished with abrasive disks to remove the surface layer which appeared to contain many spurious elements accumulated through time. The major element concentrations, mostly S and Fe, were determined from the low energy spectrum. The major composition determined in this step (matrix) was used in the processing of the high energy spectrum by scaling the trace elements concentrations to the iron concentration determined in the first spectrum.

The quantitative processing was achieved using the TRAUPIXE program (Pichon et al., 2015) developed at the C2RMF on the basis of GUPIXWIN software (Campbell et al., 2010). All in all, the measured elements comprised: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co,

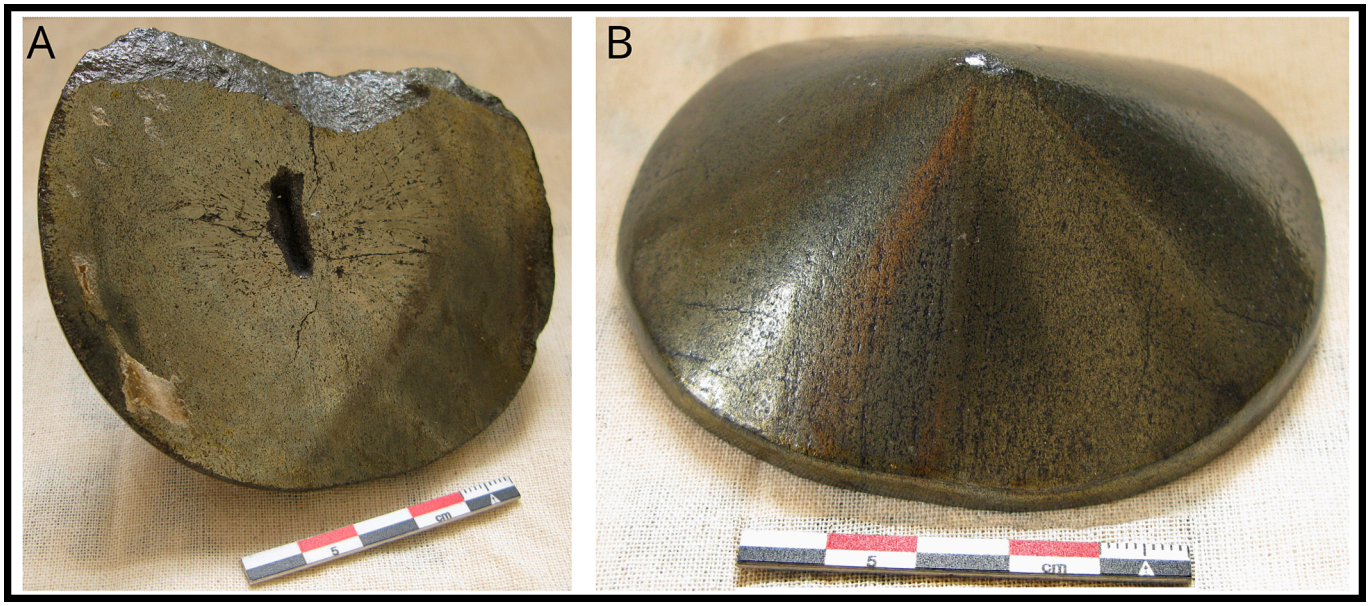

Fig. 2. A and b: a) Pyrite "Inca mirror" no. 105.504 (no.2) conserved in the Mineralogy's collections of the MNHN seen from its basal reflective face and conic side (height: 39.8 mm; Ø base: 95.3 x 75 mm; weight: 514 g). On the conic side, the parallel striations visible between the base and the top are due to the "triglyph" twin system (Photographs F. Gendron/MNHN).

Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ag, Sn, Sb, Ba and Pb. The quantitatively of the measurements was checked a pellet of reference geochemical standard (BX-N [Bauxite] from *Centre de Recherche Pétrographique et Géochimique* [CRPG]).

3. Results

The faces studies and observations of these two Cañaris "mirrors" and spectral analyses of their pyrite have produced many results. These bring new knowledges to their mineralogical, technical and archaeological histories. Useful results for researching their mineralogical origin.

3.1. A system of triglyph twins

The parallel striations observed on the conical face of "mirror" no.2 (Fig. 2b) cross the object at all its height. They are not traces left by the cutting but striations usually met on the faces of certain pyrite polyhedron[5] (Endo and Sunagawa, 1973). These are due to the so-called "triglyph" twin[6] which develops according to the $[100]_{90°}$ direction index. This one highlights the absence of an axis of order 4 in the hemihedral symmetry of pyrite (Bouillard, 2010: 106 and 212; Abreal, 2004: 172). According to Arrouvel and Eon (2019: 3, Figs. 3, 4, and 5), these striations are present only on:

- cubic crystals and always along the [100], [010] or [001] directions.
- And, the pyritohedron according to the directions [100], [010] or [001].

On the other hand, there can be no striation associated with triangular surfaces {111}. This excludes the possibility that the "mirror" no.2 was cut in an octahedral crystal.

3.2. A quartz vein

The two good Raman spectra obtained at different points of the white vein present on the edge of the "mirror" no.1 give wavenumber positions characteristic of vibrations within the SiO_4 tetrahedra of quartz-α (SiO_2; Fig. 3). The wavenumbers of comparison standards provided in catalogs of reference spectra (e.g., Bouchard and Smith, 2005) give peaks at positions close to:

- 128, 206, 263, 395 (weak) and 465 (strong) cm^{-1} for quartz-α.

The presence of this vein reveals that the "mirror" no.1 was cut from a pyrite single crystal with quartz paragenesis. This mineralogical association is indicative of high-temperature hydrothermal veins; quartz (SiO_2) was deposited first, followed by a suite of metallic minerals such as pyrite (FeS_2), chalcopyrite ($CuFeS_2$), galena (PbS), molybdenite (MoS_2), etc….

3.3. Digital microscopy: Surface studies of the two pyrite "mirrors"

The digital microscopic observations carried out on all the faces of the two "mirrors" reveal vestiges of an old technique of preventive conservation on specimen no.2. And, in both cases, traces were left by the tooling and red mineral clusters at the bottom of the crystalline gaps.

3.3.1. Remains of a preventive conservation technique

The surfaces study of the "mirror" no.2 was hampered by the presence of a thick layer of varnish that was partially flaked off. The combined presence of iron and sulfur in the crystalline structure of pyrite makes it an unstable mineral. If samples of this mineral are kept in a high-humidity environment, Sulphur in the crystal lattice interacts with the oxygen and moisture present in the air. Iron sulfide, sulfuric acid and sulfur dioxide are formed, a chemical reaction called "pyrite disease" leading to the formation of alteration compounds like jarosite ($(K^+Fe_3^{3+}(OH^-)_6(SO_4^{2-})_2)$). This causes the sample to swell and crack, leading to its shattering. Collectors have long sought ways to preserve their specimens, one of which is to varnish the faces of the specimens to isolate them from the air. The layer of varnish deposited on the faces of

[5] Pyrite crystallizes in the cubic system with very varied crystal forms. The most frequent are the cube, the octahedron and the pentagonal dodecahedron (12 faces with 5 sides) also called "pyritohedron".

[6] In crystallography, "macle" or "twin" is an oriented association of several crystals of the same species, joined and interpenetrated according to repetitive, precise and identifiable crystallographic laws.

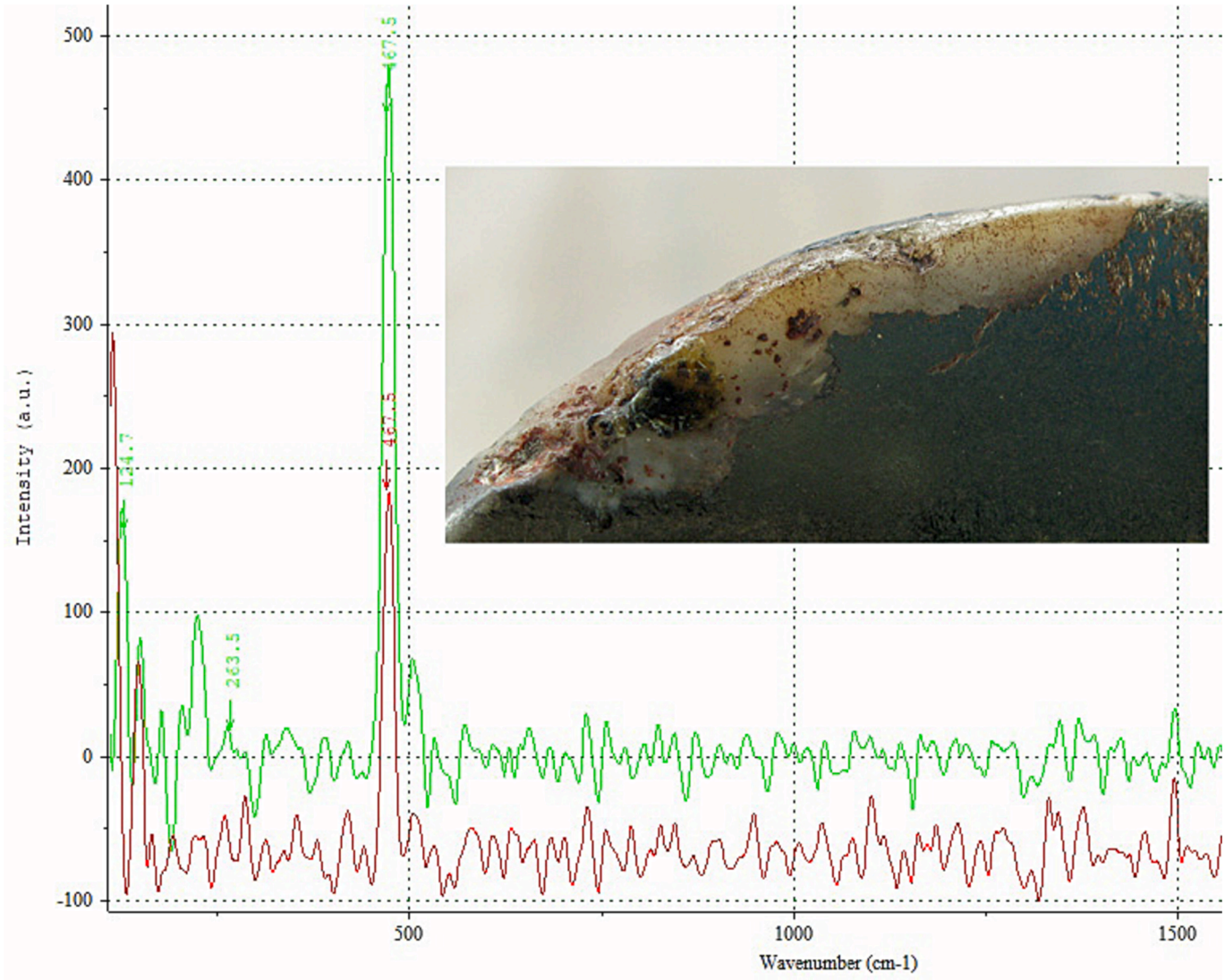

Fig. 3. Raman spectra obtained at different points of the white quartz vein cut and polished at the base of the "Inca mirror" MIN000-3519 (no.1). Peaks at 124 and 263 cm^{-1} as well as an intense peak at 467 cm^{-1} are characteristic of quartz-α; (Photography F. Gendron/MNHN).

the "mirror" no.2 indeed had the merit of preserving it but with the disadvantage of filling the micro-traces left by the cutting and polishing. This layer of varnish hinders the readability of the traces in reflected light, so we have concentrated our observations on the only areas cleared by its desquamation.

3.3.2. *Technical traces and cutting processes*

While Mesoamerican monolithic "mirrors" carved from metallic mineral species (pyrite, ilmenite [$FeTiO_3$], magnetite [$Fe^{2+}Fe_2^{3+}O_4$], hematite [Fe_2O_3], etc.) are generally circular and rather flat, the two Cañaris specimens from the MNHN are conical.[7] To carve this so particular shape and at the same time not very ergonomic to wear as a pendant, we pose the technical hypothesis that the lapidary Cañaris had to start by sawing a pyritohedron in two; thus, obtaining two hemi-dodecahedrons.

Our postulate is based on two clues found during the observation of the faces:

- the presence, in both cases (no.1 and 2 mirrors), of an apex located at the opposite of the center of the base and corresponding to the vestige of a vertex of the original crystal;
- on the beginning of a saw cut that cuts into the peripheral facet of the mirror no.1.

The further shaping of these cones must have consisted of the leveling of the edges, the vertices and the equalization of the faces of one or both hemi-crystals. This operation could only be carried out by direct polishing on a lithic grindstone because pyrite does not support cutting by percussion. As for the grindstone used, we assume it was made of sandstone because the main minerals of this kind of rock have Mohs hardness at least equal to that of pyrite (H: 6–6.5), and even higher than that of quartz (H: 7), a major constituent of the vein present on the edge of the specimen no.1 (Fig. 3). During this step of erasing the angularities,

[7] The MQB photo library holds the black and white print (management number: PV0064542) from a gelatin silver bromide positive on a glass plate, of a set of five Ecuadorian pyrite objects of the "mirror" type. This photograph was made between 1900 and 1924 at the *Musée d'Ethnographie du Trocadéro*'s photographic laboratory by Albert Cintract and at the request of Paul Rivet for the Museum's collection of projection plates. Of the five objects present on this print made in France, none is currently listed in the search engine of the MQB's "Collections" tab….

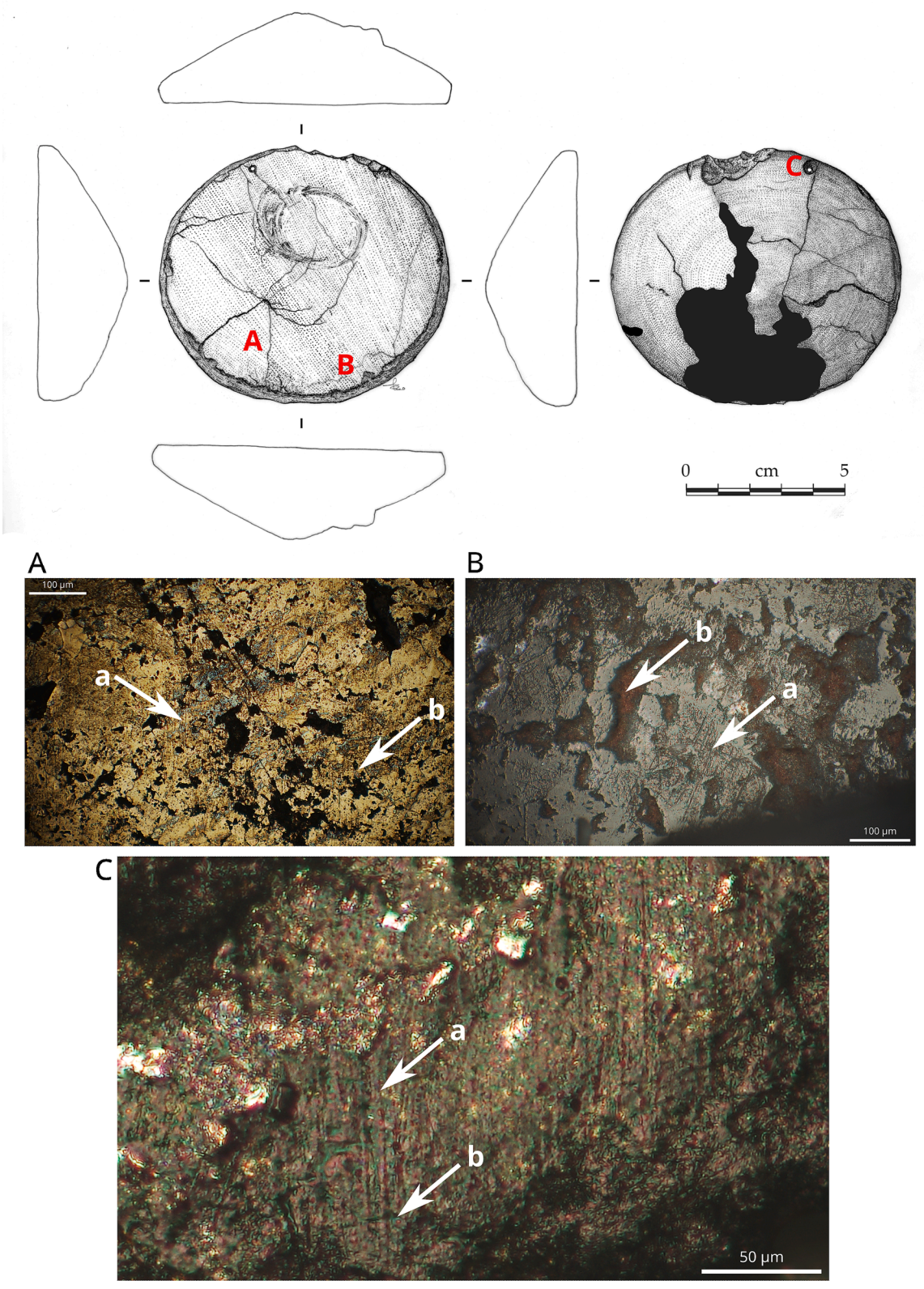

Fig. 4. Drawing of the faces and profiles of the "Inca mirror" MIN000-3519 (no.1) conserved in the René-Just Haüy's collection (Drawings É. Ahmed-Delacroix). A) image taken with the MXB-5000REZ lens Middle Range at x400, scale = 100 µm, a, b) multidirectional groups of parallel scratches and lustrous surfaces. B) image taken with the MXB-5000REZ lens Middle Range at x400, scale = 100 µm, a) crosshatch on the surface of pyrite islands, b) bottom of vacuoles filled with red powdery clusters and. C) image made with the MXB-5000REZ lens Middle Range at x1000, scale = 50 µm, a) group of vertical parallel striations (≈1 to 4 µm) and b) group of horizontal parallel striations (≈1 to 4 µm) remnants of shaping by direct polishing on a milling stone (sandstone?); (Photography A. Borel/MNHN). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

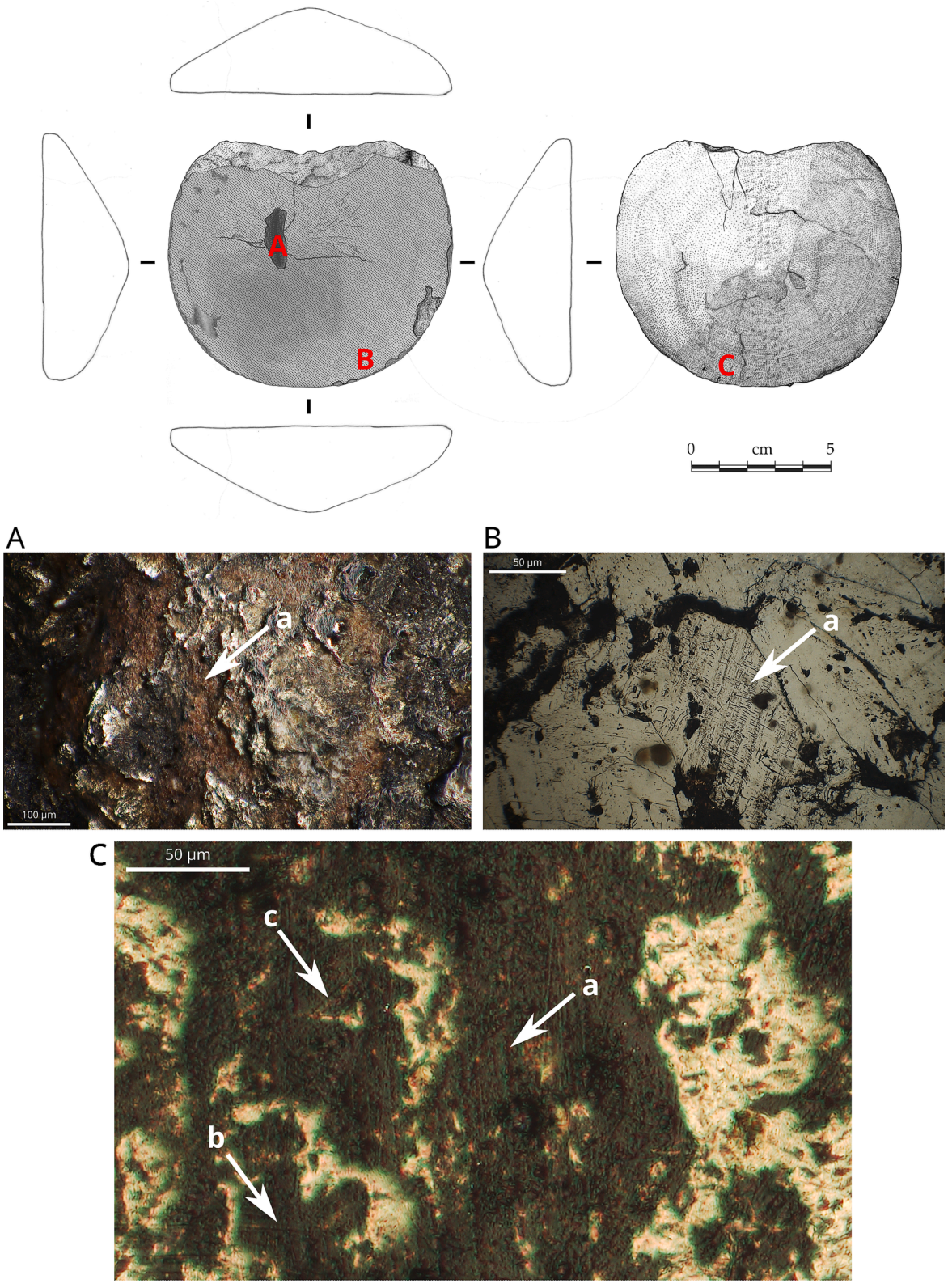

Fig. 5. Drawing of the faces and profiles of the « Inca mirror » 105.504 (no.2; Drawings É. Ahmed-Delacroix). A) image made with the MXB-5000REZ lens Middle Range at x400, scale = 100 µm, a) bottom of vacuoles filled with red powdery clusters. B) image made with MXB-5000REZ lens High Range at x1000, scale = 50 µm, unidirectional cluster of parallel glossy striations surrounded by lustrous surfaces. C) image made with the MXB-5000REZ lens Middle Range at x1000, scale = 50 µm, a) group of vertical parallel striations (≈1 to 4 µm), b) group of horizontal parallel striations and c) diagonal striations, remnants of shaping by direct polishing on a milling stone (sandstone?); (Photography A. Borel/MNHN). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the periphery of the base has been flattened to draw a peripheral facet of small width that we will call "rondiste".[8] The traces and micro-traces of these stages of cutting of the blanks have disappeared. Only the back of the "mirror" no.1 has a very smooth edge connecting the apex to the rondiste (Fig. 1).

The next technical step must have been a total polishing with fine to very fine abrasives of the one or two "mirror" blanks. It can be seen that in the two specimens studied, this polishing was less intense on the conical faces than on the basal faces because they reflect a duller image. The latter were polished with a very fine grain abrasive until a catoptric effect was obtained. This operation requires a much longer working time than simple polishing and a range of adapted abrasives. Our microscopic observations confirm that this polishing was carried out in a very relevant way, with the groups of very fine scratches observed being oriented in all directions (Fig. 4A**-ab, 4B-a, 4C-ab, 5B-a and 5C-abc**). This is a so-called "cross-stripe" polishing technique, which is used on large flat surfaces. The multi-directional micro-channels produced by this abrasion intersect, thus better capturing the light. And, in the case of an opaque material such as pyrite, these reflect the light without absorbing it, generating the desired catoptric effect. We therefore consider that the lapidary who cut, polished and glossed these "mirrors" was an authentic craftsman with real lapidary skills and appropriate tooling.

This digital microscopy campaign revealed the presence of red powdery clusters trapped at the bottom of the crystalline lacunae and cracks on the basal face of the two "mirrors" (Fig. 4B-b and 5A-a). The results of their LIBS analysis will be given in the next paragraph.

The final step in the technical chain of cut of these "mirrors" is their drilling. While this operation was successfully conducted on specimen no.1, it could be the cause of the breakage of part of the "mirror" no.2. According to Melgar et al., (2014: 45-46, Fig. 1 D), the perforation performed in the "mirror"[9] no.1 is of type 3. That is, it pierces it perpendicular to its diameter, from the back (conical face) to the front (basal or reflective face), without reworking or reaming the hole from the front face (Fig. 1). We can also observe that this perforation was made very close to the edge, which weakens the object. Indeed, only 2.8 mm of material remains between the hole and the edge of the object to support its weight (344.1 g). While many solutions of perforation exist so that a flat pendant remains oriented to the light, the "Inca mirror" no.1 is perforated in the worst possible way; almost contradicting the impression of ancestral know-how emitted to qualify the fineness of the glossing of its reflective face. Unless an intermediate piece of "clip" type is added, this "mirror" is at the very least painful to wear as a pendant. As we also observe that the perimeter of the perforation is not worn, it is almost certain that the "mirror" no.1 was never worn; unless it was part of a funeral trousseau as written by the Spanish officer Antonio de Ulloa in the 18th century (see note 1).

3.4. LIBS: Pyrite oxidation or polishing powder?

During the digital microscopy campaign, we have discovered that the bottom of the crystal gaps and cracks cut during the sawing of the crystal, was covered with powdery brick red clusters. These can be seen very well on the no.1 "mirror" (Fig. 4b). On the other hand, the partial flaking (Zone 4) of the old varnish layer covering the "mirror" no.2 causes them to be torn off (Fig. 5a). As the color and apparent fineness of the grain of these clusters could correspond to a "red polish" type abrasive, it was decided to analyze them by LIBS to identify their nature. The use of LIBS is also justified by the difficulty, or even the impossibility, of reaching the areas to be analyzed by other techniques.

The spectrum from each point analyzed by LIBS gives the information on elemental evolution in depth. Every ten spectra in depth were averaged and the averaged spectra from a3 area analyzed point on "mirror" no.2 as a function of the number of laser shots. The emission becomes stronger and the number of emission lines increased when the analyses occur to deeper in the "mirror", but no evident change of elemental composition has been observed.

All the analyzed locations are shown in Fig. 6 **a** to **c**. The main elements found in these "mirrors" from the averaged spectra (Fig. 6d) are Fe (pyrite) and the elements that can be found in quartz (SiO_2): Si, Mg, Ti and Al (the trace elements).

In order to compare the evolution of elemental distribution in depth for these two "mirrors", the emission intensity for the representative elements (Fe, Al, Mg and Ti) is normalized by the Si emission line intensity and it is shown in Fig. 7 as a function of laser shots number (in depth) on false color. From the surface (first laser shot) to the deep part of the "mirror", iron intensity increases, but it becomes stable after several laser shots. For the analyzed points a2 and a3, more laser shots were needed to obtain a Fe emission than other parts (shown in the red dashed square in Fig. 7), a varnish layer could be presented on "mirror" 105.504 (no.2).

So, the presence of silicon (Si) can be considered only located on the surface, and the main body has a constant quantity of iron. But the Al and Mg emissions gave a contrary behavior, which yields that these two elements are not from the body of the "mirrors" and they can be the evidence of the formation of quartz. Ti emission intensity rises slightly as the deeper analysis, it can be one of the elements both in the "mirror" body and the quartz.

According to the LIBS analysis results, the "mirror" no.1 contains more Al and Ti according to their stronger emission lines. The possible presence of quartz (SiO_2) is confirmed by the emission of Si and is located mostly at the mirror surface. All the elements found at the bottom of these gaps could correspond to bauxite, a sedimentary rock containing mainly aluminum oxides. Nowadays the main rock is used for the production of alumina (Al_2O_3), an abrasive employed to polish metal surfaces.

3.5. Similar but different chemistries

Finally, to compare the bulk composition of the "mirrors", PIXE analyses were performed on refreshed micro-surface (a few mm^2) at the edge of the front face of both pyrite mirrors (Table 1). Not surprisingly, while the two pyrite crystals contain comparable concentrations in S and Fe, some trace elements appeared similar (Cu, Se) while some others markedly different. As can be seen in Fig. 8, specimen no.1 contains higher concentrations of Al, Si, Zn, Mo and Sb than specimen no.2. The higher Al concentration is consistent with LIPS measurement on specimen no.1. On the other hand, the higher Ti concentrations measured by LIBS on specimen no.1 could not be confirmed by PIXE due to the overlap with to the Fe escape peak. The differences in trace elements concentrations measured by PIXE on the two specimens discards to hypothesis that both "mirrors" were cut from the same raw crystal of pyrite. However, it not possible to tell if it they were extracted from the same occurrence, due to the lack of knowledge of the intrinsic variability of pyrite composition within a deposit and of comparative reference geochemical compositions on pyrite crystals.

4. Conclusion

The numerous results of this archaeometric study considerably enrich the knowledge related to these two MNHN objects issued from the collections of the *Cabinet du Jardin du Roy*. These "Inca mirrors" have a rich history that saw them pass from the hands of the academicians of the geodesic expedition on the equator line to those of the de Jussieu brothers, academicians and great French botanists of the 18th-19th

[8] "Rondiste" is a term used by diamond dealers to designate the peripheral and intermediate facet between the crown and the breech in the 57-facet brilliant cut diamond.

[9] Specimens 71.1936.25.298 and 300 from the MQB, as well as "mirror" No. 1985.49.134 from the Pitt Rivers Museum of Oxford University (UK; Engineer 2000), all have one or two suspension holes in its upper part.

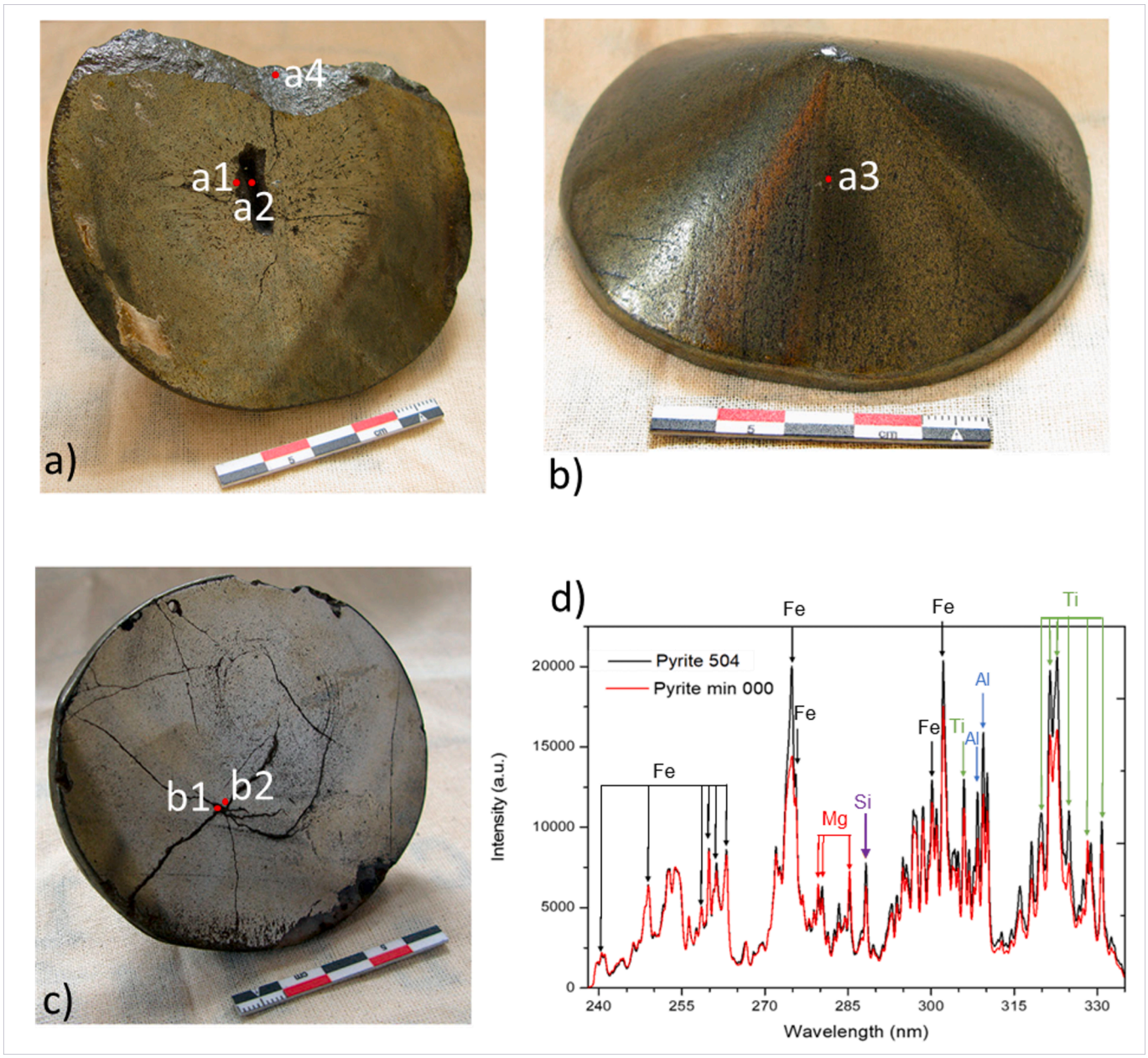

Fig. 6. Analyzed points by LIBS: A) and B) a1-a4 are four points analyzed on the mirror 105.504 (no.2). (C) b1 and b2 are two points analyzed on mirror MIN000-3519 (no.1). D) the typical averaged spectra for these two mirrors (a3 and b1); (Pictures X. Bai/C2RMF).

centuries. Then, at the end of the 18th century or later, specimen no.1 came into the possession of René-Just Haüy, the Father of mineralogy science. During the 20th century, the circulation of these two objects continued, through the writings of Dr Paul Rivet, founder of the MdH. While the mineralogist Alfred Lacroix gave a new existence to specimen no.2. Finally, it is in our humble hands and thanks to the most advanced analytical means of the archaeometry that these two Cañaris archaeological objects are recovering, at the beginning of the 21st century, large parts of their lost history.

Our archaeometric study thus brings several confirmations. Pyrite no.1 was extracted from a deposit with quartz paragenesis, a mineralogical cohabitation found in high temperature hydrothermal veins. As for the other "mirror" no.2, it was cut in a cubic single crystal or a triglyph twinned pyritohedron, as proven by the presence of visible striations on its conical face. The observations in digital microscopy of the traces and micro-traces present on the abraded surfaces, confirm that these two cones were cut according to the same technical process. A process starting with the sawing of a single crystal, followed by the direct polishing of its faces on a sandstone (?) milling stone. The basal face is then glossed with a very fine abrasive and by a mover which allows it to cross the lines until obtaining a catoptric effect. Finally, one of these "mirrors" is drilled near its upper edge. In addition to the reconstruction of a cutting process, surface observations led to the discovery of a protective varnish layer on specimen no.2 and of red pulverulent mineral clusters in the bottom of the crystalline lacunae opened by the cutting. The intriguing presence of these clusters on both objects motivated a LIBS analysis campaign to try to identify their nature. The results obtained are consistent with the presence of alumina (Al_2O_3) and therefore an abrasive. Still called "alumina oxide", this chemical compound can be obtained from alum, a double salt of hydrated aluminum sulphate ($Al[SO_4]_2$ $12H_2O$), but the presence of Si more certainly indicates bauxite. A lateritic sedimentary rock, bauxite tends to be red in color and contains minerals with high concentrations of hydrated aluminum oxides: bayerite and gibbsite (monoclinic alumina trihydrates

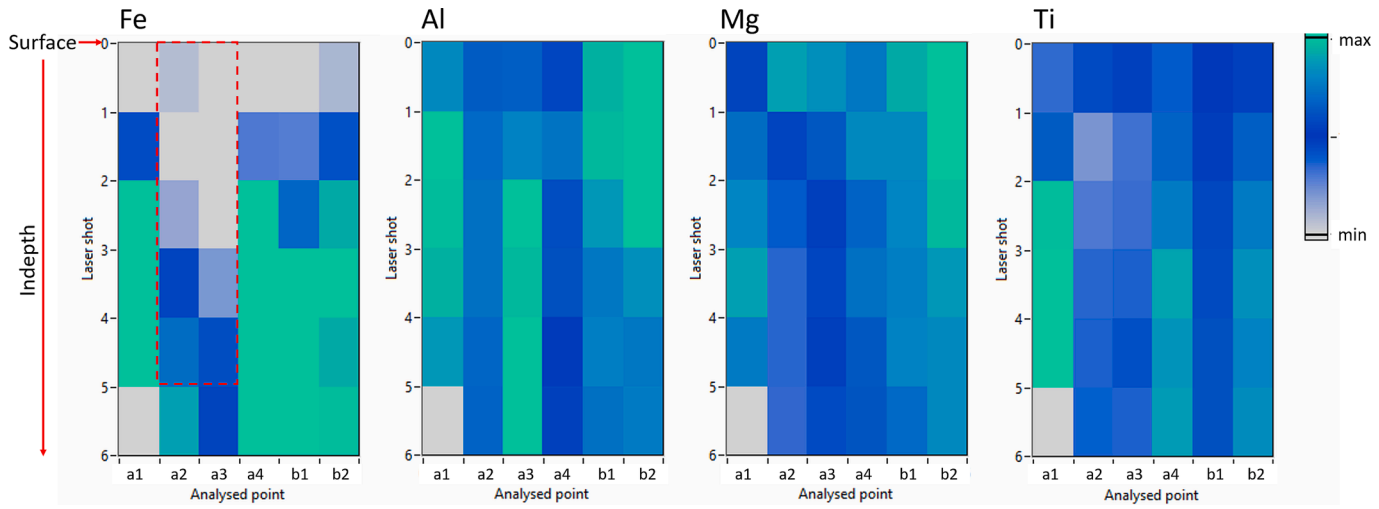

Fig. 7. The evolution of elemental emission intensity as a function of depth. For each element, the intensity is normalized by the Si emission and it is represented by false color. a1-a4 are four points analyzed on mirror 105.504 and b1- b2 are two points analyzed on mirror MIN000-3519. (Pictures X. Bai/C2RMF).

Table 1
Mean bulk composition obtained by PIXE method. Note the distinct trace element composition for the two mirrors, notably in Zn, As, Mo and Sb. Measurements were obtained on a fresh surface measuring 1 $mm^{2.}$

Catalogue number	Main elements in % weight						Trace elements in ppm weight					
	Al	Si	S	K	Ca	Fe	Cu	Zn	As	Se	Mo	Sb
Mirror no.1	0.6 ± 0.1	1.2 ± 0.1	50.0 ± 1	0.18 ± 0.01	0.07 ± 0.01	47.0 ± 1	182 ± 8	96 ± 6	416 ± 4	51 ± 4	70 ± 8	163 ± 50
Mirror no.2	0.3 ± 0.1	0.4 ± 0.1	50.5 ± 1	0.22 ± 0.01	0.17 ± 0.01	47.0 ± 1	198 ± 8	20 ± 4	52 ± 4	45 ± 4	<7	61 ± 30

$Al[OH]_3$), diaspore (AlO[OH]) and boehmite (AlO[OH], orthorhombic alumina monohydrates). This rock also contains iron oxides which give it its color and even a little beat of silica. Mainly present around the equator line, bauxite is found on or near the surface in the form of geologically thin strata (2 to 5 m thick).

Our archaeometric study concludes with a series of PIXE analyses which reveal that despite their morphological similarity, these two pyrites do not come from the same deposit.

The bibliographic and museographic researches we have carried out based on these results have not yet enabled us to find any mineralogic equivalents. Perhaps because published data on Peruvian and Ecuadorian pyrite deposits are scarce. Moreover, none of the Parisian

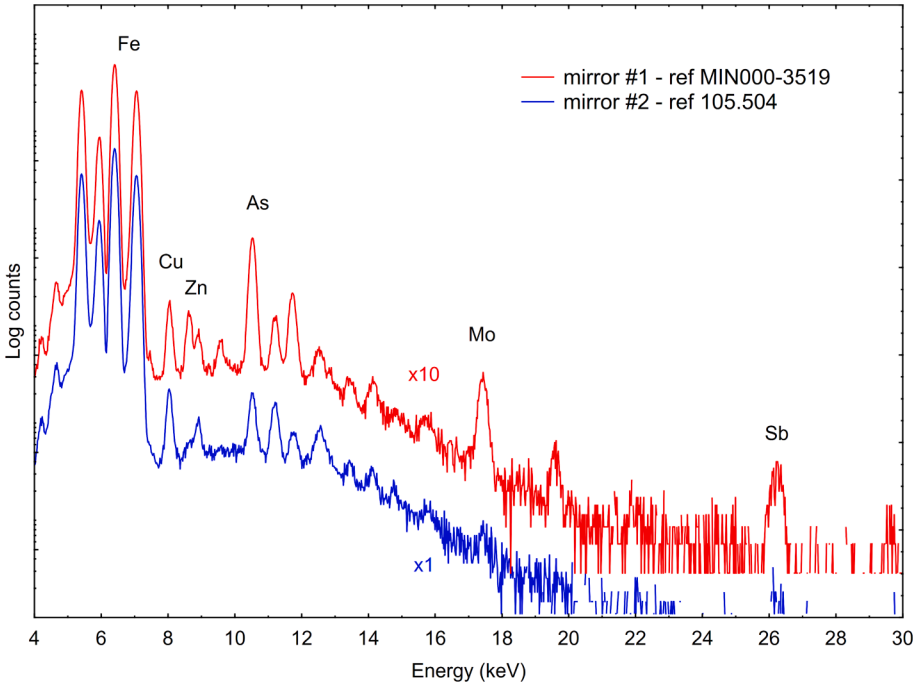

Fig. 8. Plot of the mean high energy PIXE spectrum of both “mirrors”. One can note the higher peaks of trace elements Zn, As, Mo and Sb. The two spectra were vertically shifted to ease the visualization.

mineralogical institutions (MNHN, mineralogic collections of the Sorbonne University and *Ecole des Mines*) keep Ecuadorian pyrite samples.

CRediT authorship contribution statement

François Gendron: Conceptualization, Writing – original draft, Funding acquisition. **Xueshi Bai:** Investigation, Writing – original draft, Validation. **Thomas Calligaro:** Investigation, Writing – original draft, Validation. **Antony Borel:** Investigation, Writing – original draft, Validation. **Vincent Detalle:** Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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