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Ballistic Studies By SEM-EDX Analyses On The Surface Of A Tooth Of A Knight Of The Middle Age

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***Abstract*—In this study, the particles of interest in ballistic that are located on a surface of a tooth extracted from the cranium of the Middle Age knight Bayard were investigated. These particles were characterized in SEM-EDX, which permit both their visualizations and the semi-quantitative study of their elemental compositions. The particles so detected are of lead, of antimony (probably antimony trisulfide) and of barytine ; their morphological aspects, at least for some of them, indicate that they are a mixture of un-burnt and burnt material ; we observed also some micro-marbles of iron-oxide, that indicate fusion at very elevated temperatures. As particles of lead, of antimony and of barium are characteristics of the gunshot residues, we infer that the Bayard's mouth was in contact with combustion products of some firearms. As these conclusions are based on ballistic studies of products of modern firearms, we discuss about their validations concerning such an ancient material.**

Keywords—tooth of knight Bayard (1473?-1524) ; SEM-EDX of the tooth surface ; particles of lead, antimony, barium and iron ; ballistic.

1. Introduction

This knight is the famous French "Chevalier Bayard" (1473?-1524), who lived at the transition between the Middle Ages and the Renaissance. Through the centuries since his death, he has been known as "the knight without fear and beyond reproach" ; Bayard was considered at this period as the epitome of French chivalry [**1**].

His cranium is at present kept in the Dauphiné Museum of Grenoble (France). A molar tooth was extracted from his mandible. Genomic DNA obtained from this tooth permit us to study the mitochondrial DNA (mtDNA) of Bayard [**2**] ; his corresponding mtDNA haplogroup is that of a today living male, related (to 32 generations) to the Bayard matrilineal ascendance. The ^{14}C evidence dating from one of the root of this tooth provides a date of calendar 1430-1510 years (at 95.4% probability) interval, consistent with a mean date of 1486 for an individual who had started eruptions of his first molars.

We have previously studied [**3**] by SEM-EDX the dental plaque of the lateral lingual face of this tooth, with the aim of finding microscopic particles indicating the diet habits of Bayard. In the present study we concentrate on these particles involved in ballistic.

2. Material and Methods

Bayard's tooth extracted from one of us (G.L.) is the first molar, located at the left side of the mandible (the tooth number 36, according to the "Nomenclature dentaire internationale"). Both lateral faces of the extracted tooth (the exterior lateral face : labial, or jugal, and the interior lateral face : lingual) were examined *in situ* by SEM (Scanning Electron Microscopy). Metallic and mineral particles observed on the tooth surface that could be involved in ballistic were analysed by EDX (Energy Dispersive X-ray spectroscopy).

The SEM apparatus used is the FEI model Quanta FEG (an environmental electron microscope) of the Laboratory of Physico-Chemical Analyses of the Compiègne UTC (France). Both LFD (Large Field Detector) and CBS (Circular Back Scattering) procedures were used, the latter to better detect heavy elements. Elemental analyses of the structures observed with this apparatus were carried out, because it is equipped with a probe model X-flash 6/30.

Each elemental analysis is given in the form of a spectrum, with kiloelectrons/Volts (ke/V) on the abscissa and elemental peak heights (cps/ev) in ordinates. High resolution spectras are obtained by enhancing the ordinate values.

3. Results

Figure 1 shows both optic and electronic views of the jugal face of the tooth. Enamel regions of the tooth are clearly distinguished in the SEM photograph (taken in CBS) under the forms of sparkling zones, too white-to-electrons than the matter of the dental plaque.

The differential element compositions of the dental plaque and of the enamel are shown on Figure 2. Among the main elements of the dental plaque (upper spectrum of the figure) are the phosphorous and the calcium ; together they form calcium phosphate, the main constituent of the dental plaque [**3**]. The plaque contains also organic material (carbon and oxygen), a mineral component (of silicium, aluminium, magnesium, potassium and part of calcium), sulphur and iron.

The high resolution spectrum of the enamel (lower spectrum of the figure) shows the same elemental composition, but with tin and copper as supplementary metallic elements. Moreover there are three other supplementary metallic elements, of some importance in ballistic, that are :

. The **lead** (represented by its main peak ray in the spectrum).

. the **antimony** (represented by three peaks),

. the **barium** (two peaks).

3.1. Lead

The lower SEM photograph of Figure 3 shows seven (numbered 1-7) rounded sparkling micro-particles, located along the enamel external border of the tooth. There are very little metallic particles, of maximal lengths comprised between 0.5 and 3.5 µm.

The compositions of most of them (numbers 1,2,3,5 and 6) are of lead only (Figure 4 representing the SEM photograph and the spectrum of particle number 2, taken as an example). In particle number 4 (Figure 5) there are some traces of iron, representing supplementary metallic material ; in particle number 7 (Figure 6), there are some traces of copper and of iron as supplementary materials.

These particles located on the enamel are certainly residues of lead bullets. The corresponding molecule is lead sulphate, that is in accordance to the data on the bullet spectras (where sulphur is however masked by the abundance of the main lead peak). As it was the custom at the Bayard time and after, the lead of the bullets were hardened with iron and copper.

3.2. Antimony

Figure 7 shows , at two magnifications, SEM photographs (in CBS, 300x and 600x) of some part of the dental plaque of the jugal face of the tooth located just on the underside of some enamel zone. It contains one particle of antimony.

Figure 8 shows an enlarged view of this particle, together with its EDX analysis. The SEM photograph (in CBS, 20 000x) of the particle shows a sparkling quadrangular particle, of 1.3 µm of maximal length ; its angular outlines indicate that it is probably a granule of a manufactured powder. Its spectrum establishes that its main constituent is antimony (represented by five peaks). Presence of a sulphur peak on the spectrum shows that the corresponding molecule can be antimony trisulfide.

This particle is the only antimony remnant we have detected on the jugal face of the tooth. But the lingual face contains another particle of antimony (Figure 9) : it is a pentagonal particle, of 707 nm of maximal length on 63 nm of width, probably a crystal ; its composition is also mainly of antimony, with a little sulphur peak.

We know that antimony trisulfide is a main component of the powder used in firearms ; antimony acting as a fuel were known since the Middle Age**.**

The antimony crystal of figure 9 could be an indication that the residue on the knight ‘s tooth surface had been caused during the participation in an ‘arquebusade’, a violent scene of fight where numerous gunmen simultaneously used their firearms in a confined area.

3.3. Barium.

There is another mineral particle on the jugal tooth surface, showed on figure 7. Figure 10 summarizes its characterization : it is a little particle, of less than 2.5 µm of maximal length ; its outlines are angular, but with some part with a quasi-rounded shape that is characteristic of burnt material.

Its spectrum shows that it contains barium (two peaks) and a little peak of sulphur. So the corresponding molecule is the barium sulphate ($BaSO_4$) ; but it contains also traces of cerium , and consequently correspond to the mineral barytine.

This particle is the only barytine residue we detected on the jugal face of the tooth ; but numerous (up to 26) such particles were detected on the lingual face. The following figures show four examples of them. Figure 11 shows a first example of a barytine particle of 3.7µm of maximal length, whose outlines are both angular and rounded. The barytine particle of Figure 12 has angular outlines ; a smaller barytine particle, of similar brightness, is also visible on the SEM photograph. In SEM photograph of Figure 13 the third example of a detected barytine particle (of 970 mm of maximal length) is accompanied by several others, not located in the same observation field. In the SEM photograph of Figure 14, we can distinguish at least four barytine particles of a powder.

The outlines of these particles are angular (unburnt particles) or more or less partially rounded (burnt particles). These particles, as indicated by their similar sizes and with their angular outlines, are the factury components of an artificially manufactured powder.

4. Discussion.

The Table summarizes numbers, locations and characterisations of the thirty-six particles (of lead, antimony sulphide and barytine) identified on the tooth surface. Together, they establish that Bayard ‘s mouth was in close contact with products constituting firearms.

Firing a weapon produces combustion of both the primer and the powder. The residue of the combustion products, called “gunshot residue” (GSR)”, can consist of both burnt and unburnt primer and powder components, combined with additional residues from the surface of the bullet. Residues can be either inorganic or organic in nature ; inorganic residues consist of elemental chemicals, such as lead, barium and antimony. Less common elements include aluminium (Al), sulphur (S), tin (Sn), calcium (Ca), potassium (K), silicium (Si), copper (Cu) and zinc (Zn).

Early studies on GSR [**4,5**] established that the major primer elements are –in order-lead (Pb), barium (Ba) and antimony (Sb). Usually, all three are present. Scanning electron microscopy coupled with energy dispersive analysis by x-ray detector (SEM-EDX) is the method of choice used routinely today to identify the primer residues qualitatively and semi-quantitatively [**6**].

GSR may be found on the skin [**7**] or close to the person who fired the gun, on an entrance wound of a victim, or on other target materials at the scene.

We have also detected many particles containing iron, both on the jugal and lingual faces of the tooth. Figure 15 concerns particle O1 of the figure 7 : it is a particle of about 2.5 µm of maximal length, with angular outlines ; its composition of iron oxide, with a rich mineral component of silicium. Figure 16 concerns the O2 particle ; it is also an iron oxide particle , but with outlines more rounded.

Figure 17 shows a particle –or more exactly a group of micro-marbles-, also located on the jugal face, which is also mainly constituted of iron oxide (with some traces of zinc) ; this formation is relatively rich in minerals silicium, calcium and phosphorous. Remarkably, the metallic material is organized in numerous micro-marbles, each of perfect spherical forms and of diameters varying from about 350 to more than 600nm. Such a formation attests that the corresponding material was intensively heated at very elevated temperatures.

These two later observations on the jugal face of the tooth of an iron oxide particle with rounded outlines and of a group of iron oxide micro-marbles adds other arguments in favour to the mouth of Bayard at the end of his life was in contact to metallic materials in fusion.

5. Conclusion

In this study we find on the jugal surface of one of the teeth of the Bayard cranium many particles of lead, of antimony, of barium and of iron, which is proof that he participated in scenes where firearms were in action.

The fact that these metallic and mineral particles of interest are located on the Bayard's tooth does not imply that his was the gunman, or even the victim of a firearm. More probably these particles were deposited passively in the Bayard's mouth, who participated during his long life as a warrior to many manoeuvres and battles where firearms were involved [**1**]. Paradoxically for a knight who was one of the ultimate symbols of the traditional Middle Age chivalry, i.e. a swordman, he was mortally wounded on the 30th of April 1524 by a shooting of arquebus.

But all the results presented here are based on modern ballistic studies, concerning modern firearms. Particularly the argumentation about the presence of lead, antimony and barium concerns the chemical composition of primers of cartridges ; however, cartridges were not discovered at the Bayard time.

Detailed studies on metallic and mineral particles on all the surface of the lingual tooth surface are now in progress, with the goal to discover what precise sort of firearm Bayard was in contact with.

6. Acknowledgement

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Table : Numbers, locations and characterisations of the 36 particles studied.

Particles	Numbers found on the tooth		Characterization	Representative figures
	On or near enamel of the jugal face	On the lingual face		
Lead	7	0	Residues of bullets	Figures 4-6
Antimony sulfide	1	1	A manufactured particle and a crystal	Figures 8 and 9
Barytine	1	26	Mineral manufactured particles	Figures 10-14

Fig. 1 : Photographs of the jugal face of the tooth. *Above* : optical photograph (5x) of the tooth. PD : dental plaque ; **1** : basis of the sawed root ; **2** : basis of the broken root ; E1 : jugal enamel ; E2 : lingual enamel. *Below* : SEM photograph (in CBS, 19x) of the dental plaque. E are different parts of the jugal enamel (Cé : cement).

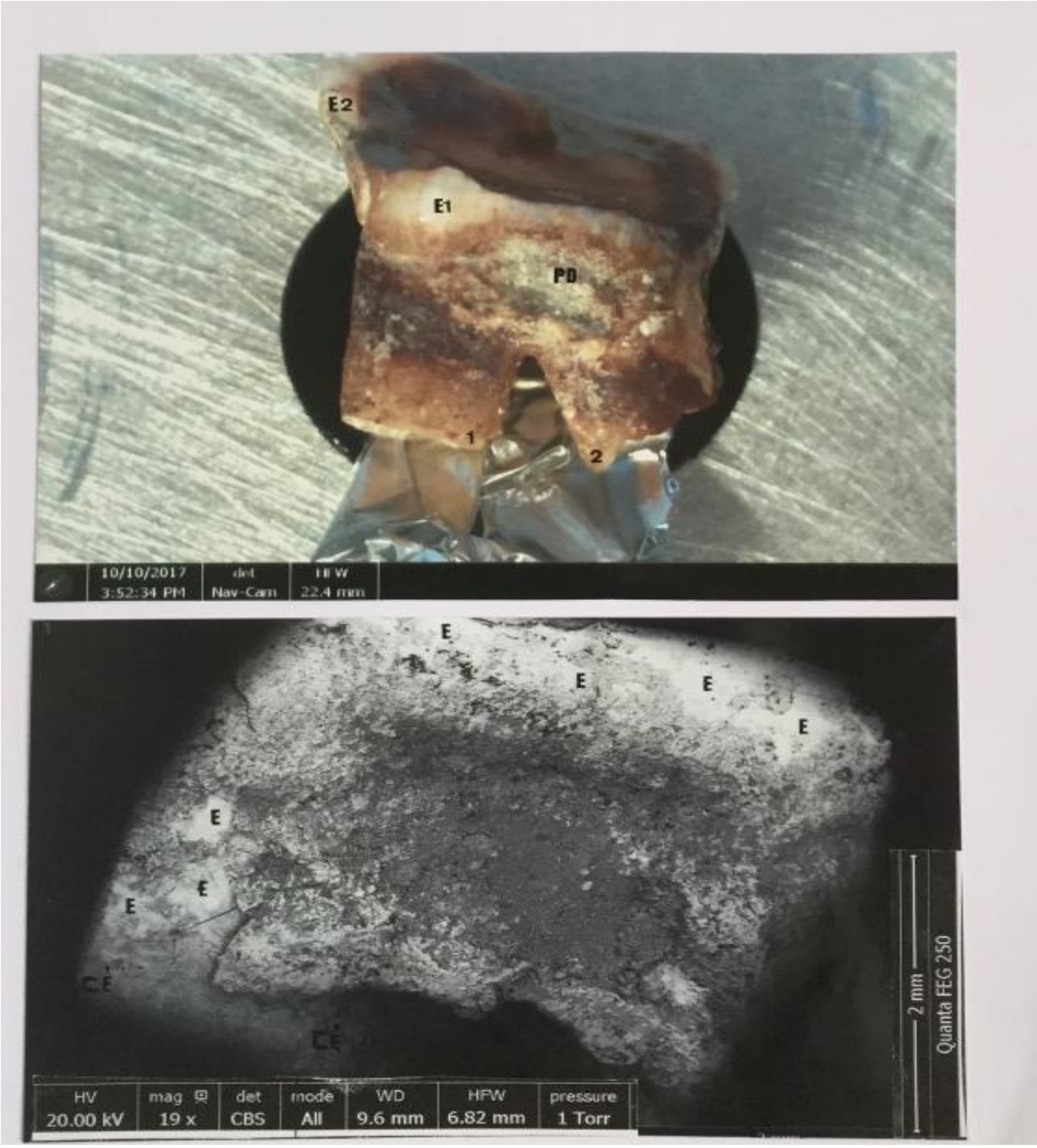

Fig. 2 : The dental plaque and the enamel. *Above* : SEM photograph (in CBS, 25x) of the dental plaque (PD) and the enamel (E) ; **1** and **2** indicate the roots. The big black point near PD and the little black point near E indicate regions where EDX analyses are realized. *Upper spectrum* : spectrum at the big black point. C : carbon ; O : oxygen ; Fe (three peaks) : iron ; Mg : magnesium ; Al : aluminium ; Si : silicium ; P : phosphorous ; S : sulphur ; K : potassium ; Ca (two peaks) : calcium. *Lower spectrum* : high resolution spectrum at the little black point. O : oxygen ; Fe (three peaks corresponding to rays Fe-Lα1, Fe-Kα1 and Fe-Kß1) : iron ; Cu (two peaks corresponding to Cu-Lα1 and Cu-Kα1) : copper ; Mg : magnesium ; Al : aluminium ; Si : silicium ; P : phosphorous ; P-Mα1 : main ray of the lead ; S :sulphur ; Sn-Lα1 : main ray of the tin ; K : potassium ; Sb (three peaks corresponding to Sb-Lα1, Sb-Lß1 and Sb-Lß2) : antimony ; Ca : calcium ; Ba (two peaks corresponding to Ba-Lα1 and Ba-Lß1) : barium.

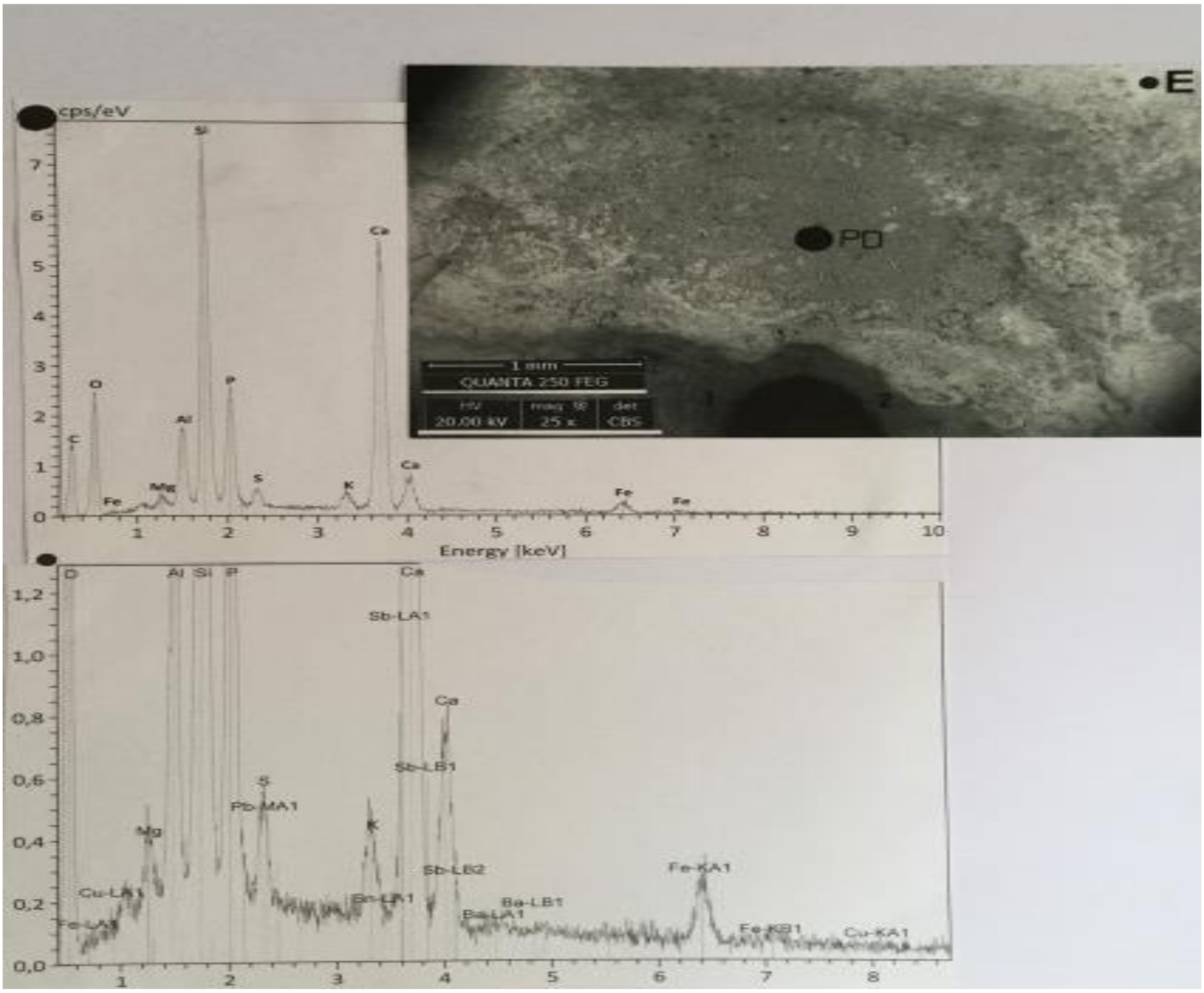

Fig. 3 : *Above* : SEM photograph (in CBS, 30x) of the superior part of the tooth. E : enamel ; PD : dental plaque ; L : limit line between E and PD ; **2** : basis of the broken root. *Below* : enlarged SEM photograph (in CBS, 300x) of the enamel, showing the seven particles (numbered 1-7) containing lead.

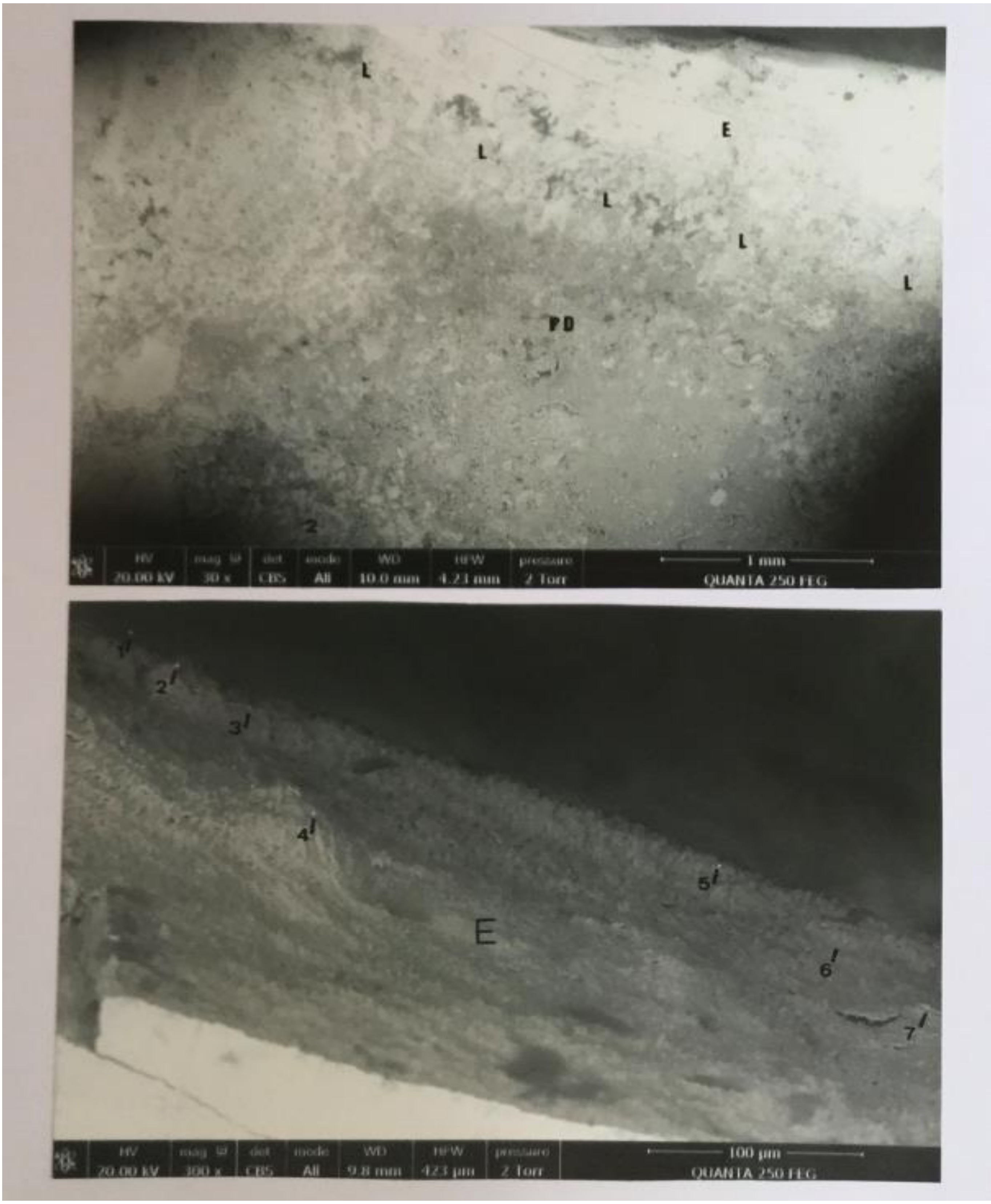

Fig. 4 : *Above* : SEM photograph (in CBS, 5000x) of the particle number 2 : dimension is in µm. *Below* : spectrum at the black point. C : carbon ; O : oxygen ; Na : sodium ; Mg : magnesium ; Al : aluminium ; Si : silicium ; P : phosphorous ; Pb (three peaks) : lead ; K : potassium ; Ca (two peaks) : calcium. *Note* : if the target is <1µm^2, EDX analyses of its concerns also that of the substratum where the target is deposited ; that explains, in the present case, while calcium phosphate of the enamel is also revealed.

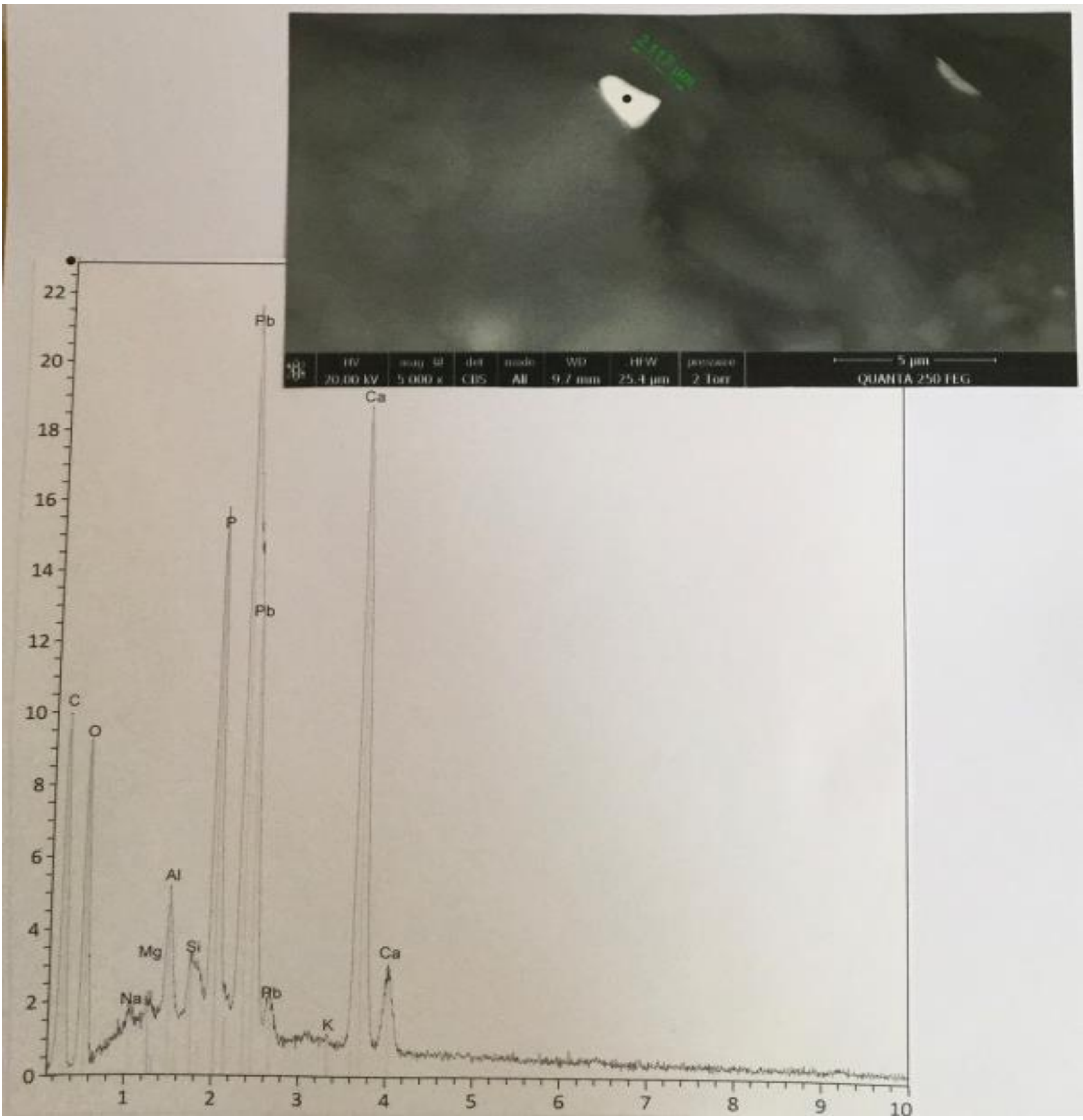

Fig. 5 : *Above* : SEM photograph (in CBS, 5000x) of particle number 4. *Below* : spectrum at the black point. C : carbon ; O : oxygen ; Na : sodium ; Mg : magnesium ; Al : aluminium ; Pb (three peaks) : lead ; K : potassium ; Ca (two peaks) : calcium ; Fe (traces) : iron .

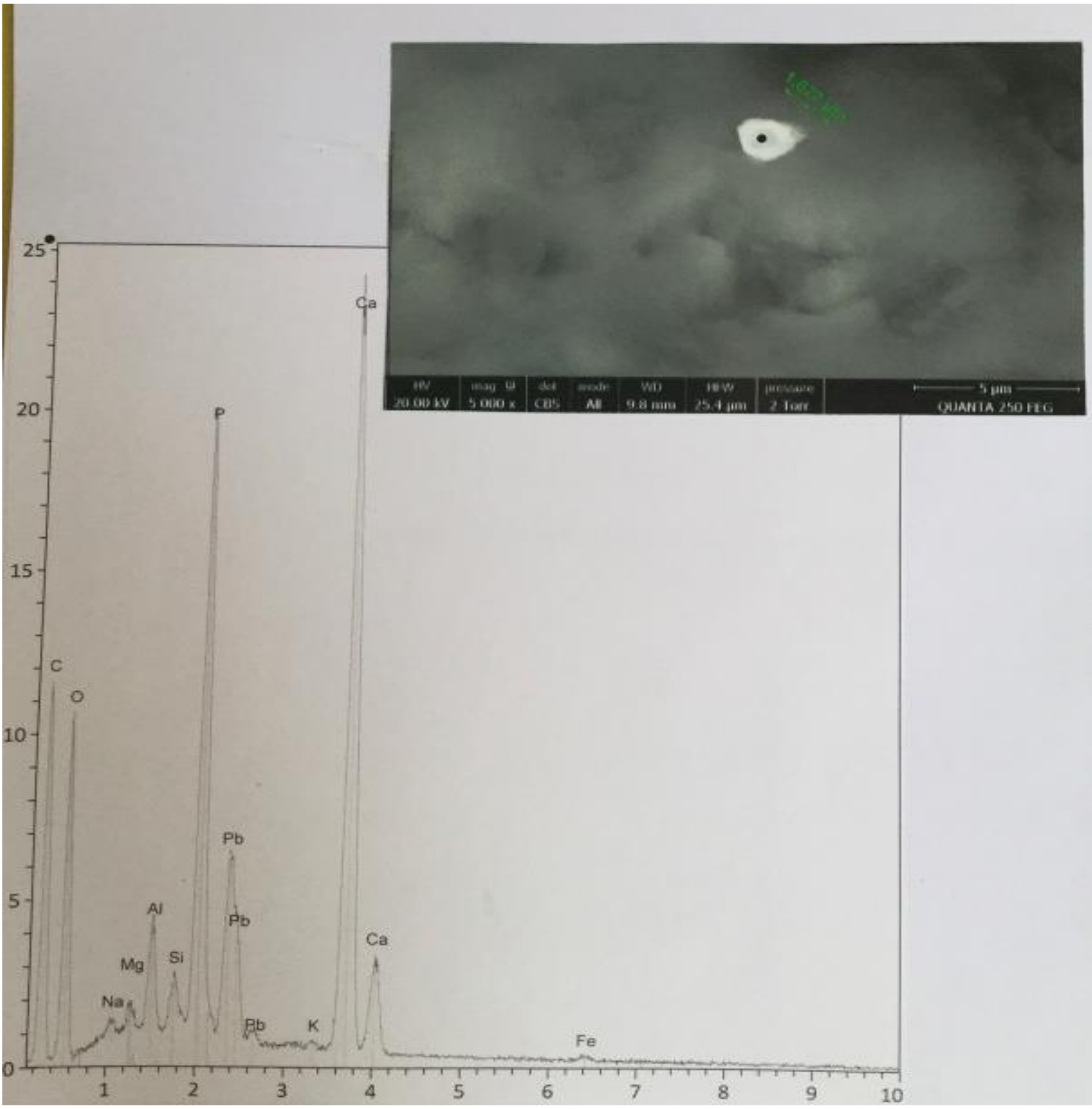

Fig. 6 : *Above* : SEM photograph (in CBS, 5000x) of particle number 7 (dimension is in nm). *Below* : spectrum at the black point. C : carbon ; O : oxygen ; Cu (two peaks) : copper ; Na : sodium ; Mg : magnesium ; Al : aluminium ; Si : silicium ; P : phosphorous ; Pb (three peaks) : lead ; K : potassium ; Ca (two peaks) : calcium ; Fe : iron.

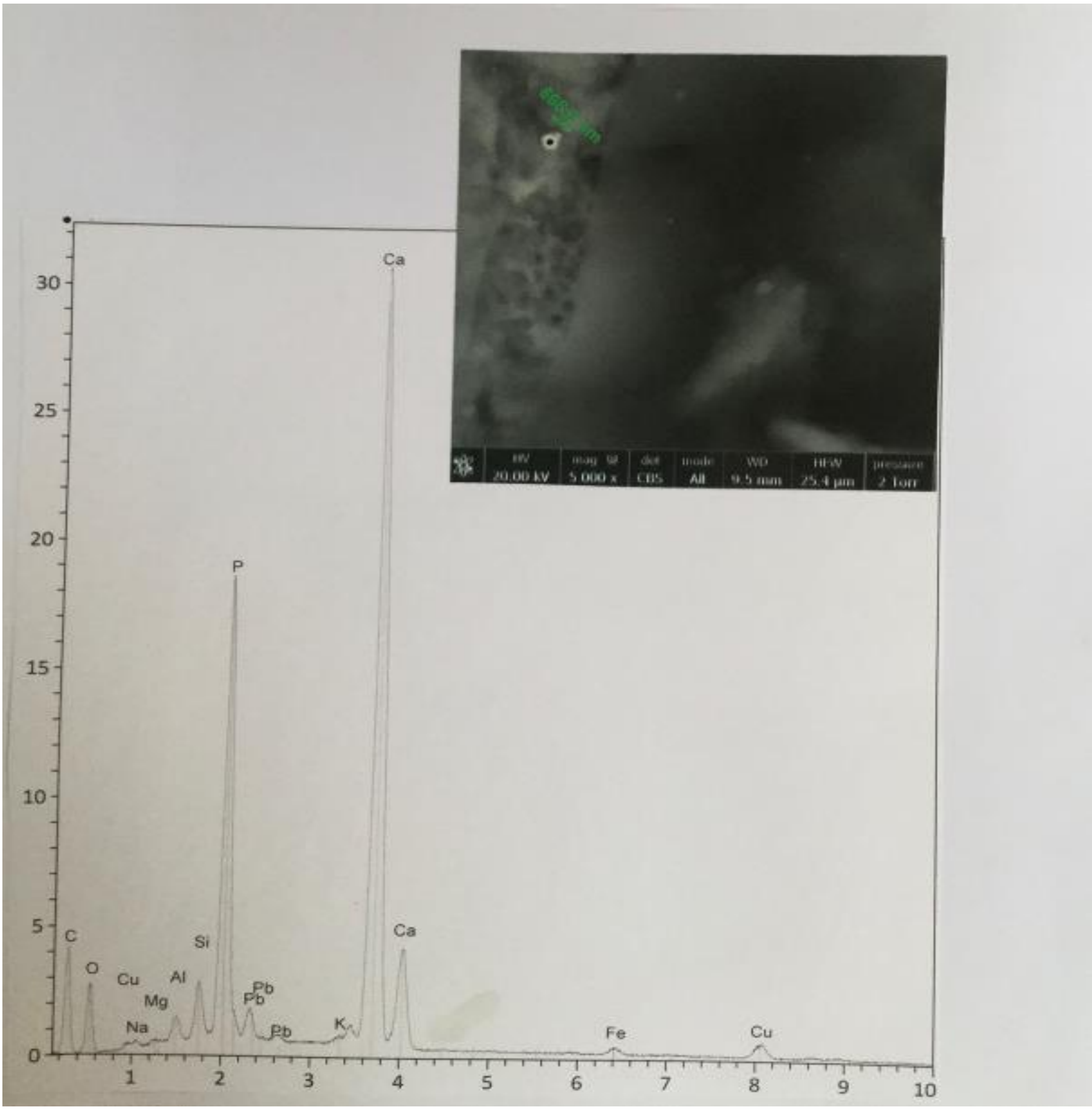

Fig. 7 : *Above* : SEM photograph (in CBS, 300x) of a region of the jugal face of the tooth, located just below the enamel (E). A : an antimony sulphide particle ; B : a barium sulphate particle ; O : two iron particles (O1 and O2). The squared area indicated is enhanced in the below photograph. *Below* : SEM photograph (in CBS, 600x) of the squared area. A : the antimony sulphide particle.

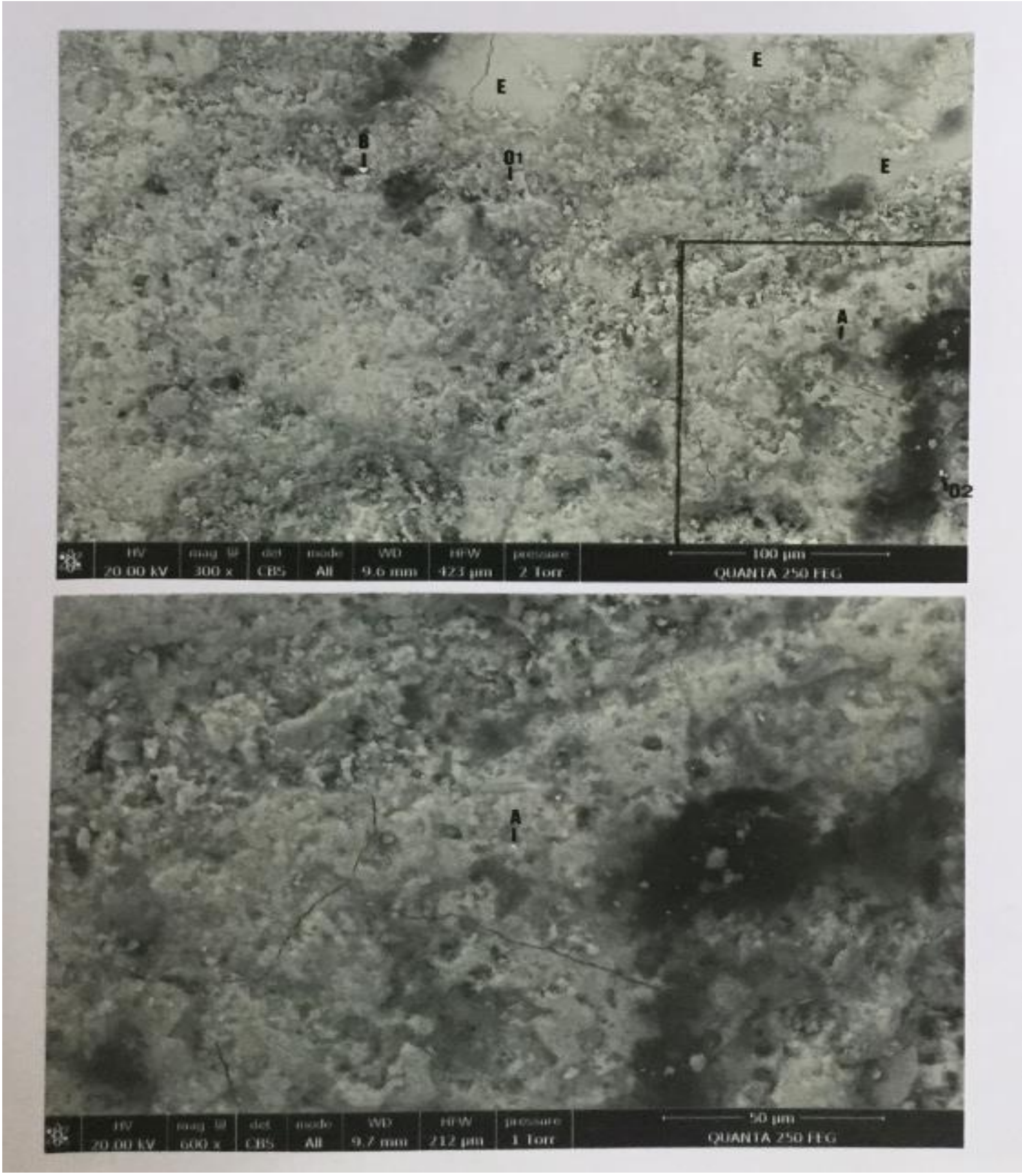

Fig. 8 : The antimony sulphide particle. *Above* : SEM photograph (in CBS, 20 000x) of the particle. *Below* : spectrum at the black point. S (two peaks) : sulphur ; C : carbon ; Fe (two peaks) : iron ; Na : sodium ; Mg : magnesium ; Al : aluminium ; Si : silicium ; P : phosphorous ; Pb (traces) : lead ; Sb (four peaks) : antimony ; Ca (two peaks) : calcium.

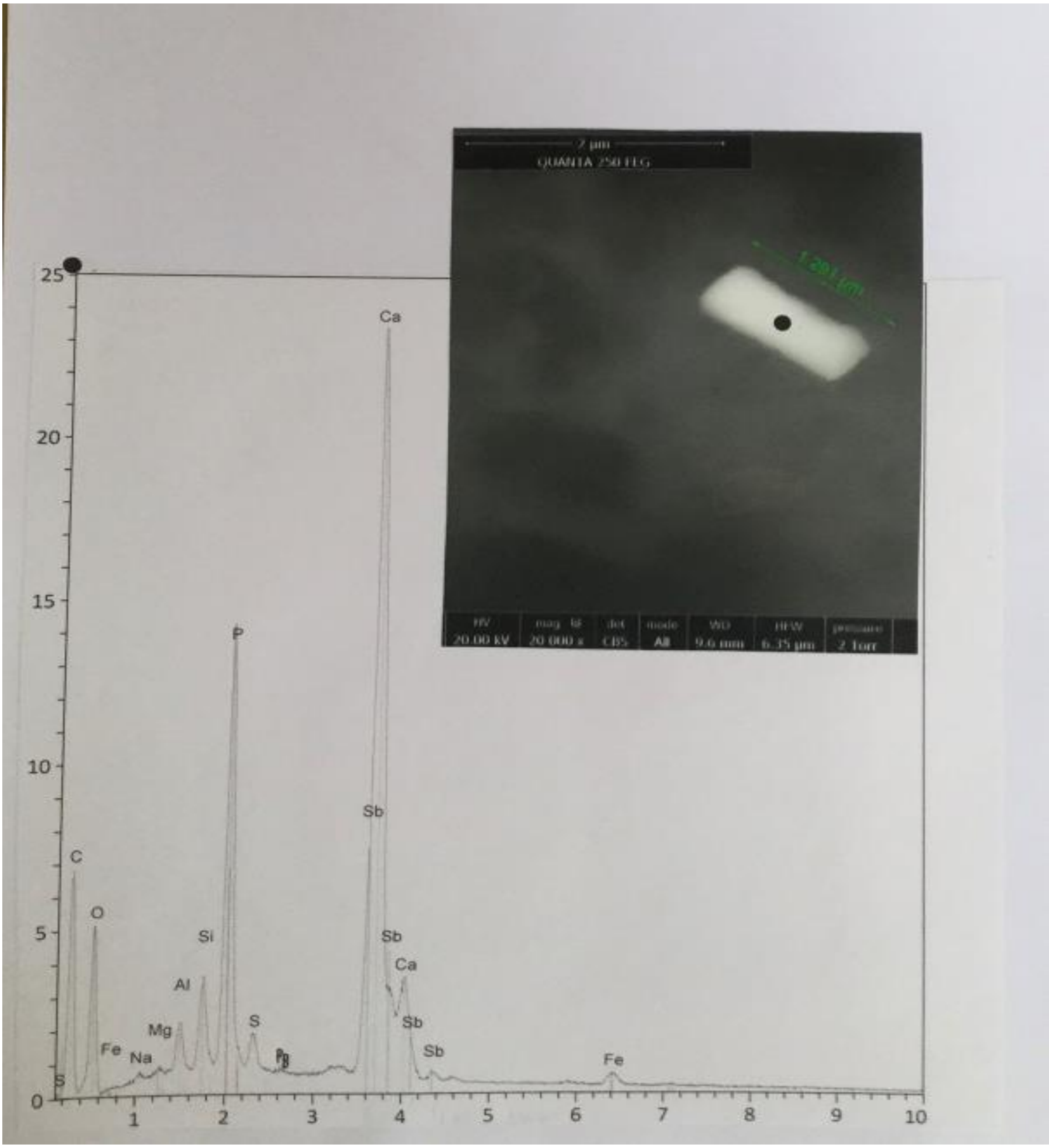

Fig. 9 : A crystal of antimony sulphide, located on the lingual face of the tooth. *Above* : SEM photograph (in CBS, 40 000x) of the crystal. *Below* : spectrum at the black point. C : carbon ; O : oxygen ; Fe (three peaks) : iron ; Na : sodium ; Mg : magnesium ; Al : aluminium ; Si : silicium ; P : phosphorous ; S : sulphur ; K : potassium ; Ca (two peaks) : calcium.

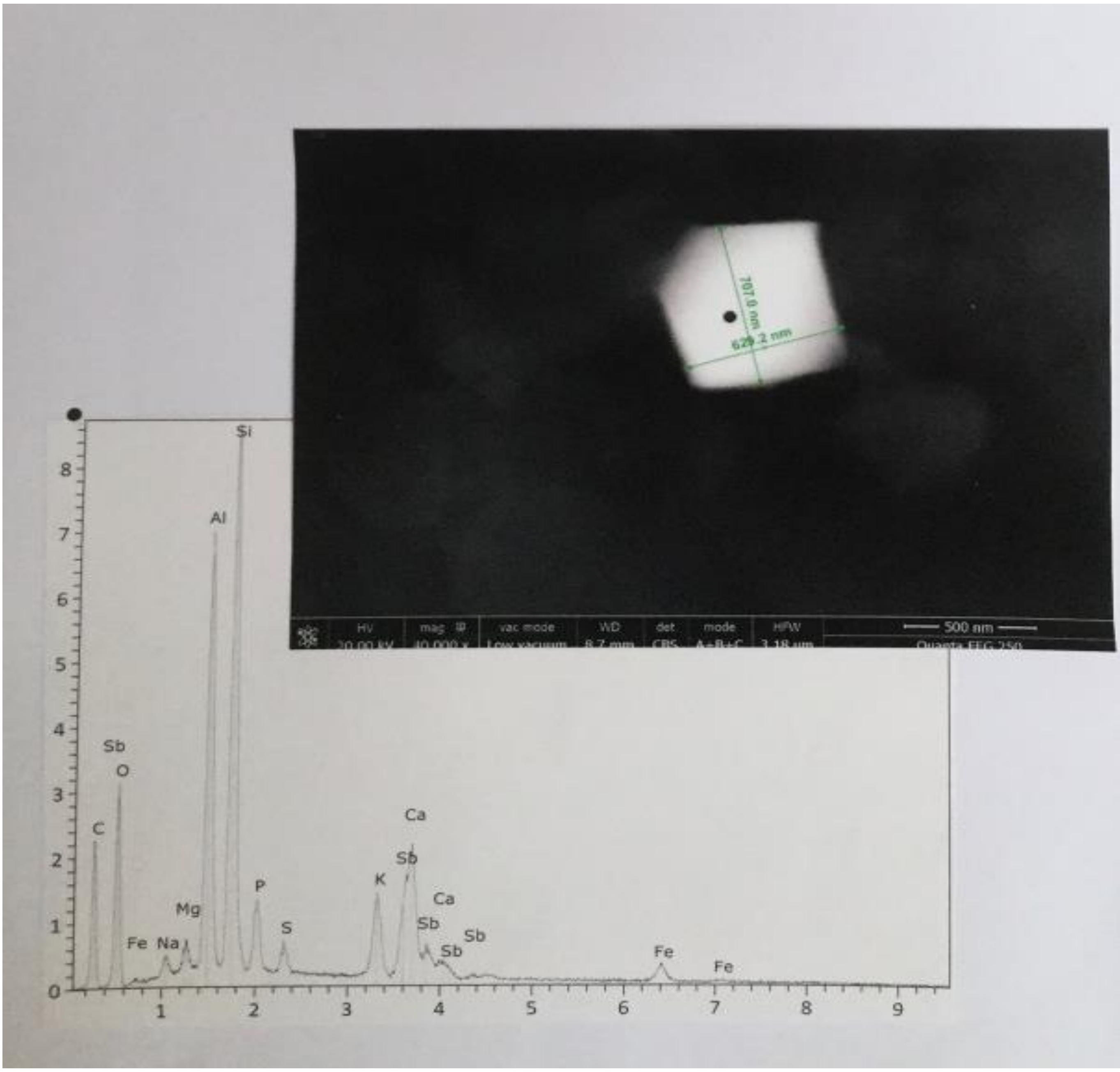

Fig. 10 : *Above* : SEM photograph (in CBS, 5000x) of the barium particle. *Below* : spectrum at the black point. C : carbon ; O : oxygen ; Fe (three peaks) : iron ; Na : sodium ; Mg : magnesium ; Al : aluminium ; Si : silicium ; P : phosphorous ; S : sulphur ; K : potassium ; Ca (two peaks) : calcium ; Ba (two peaks) : barium ; Ce (two peaks) : cerium.

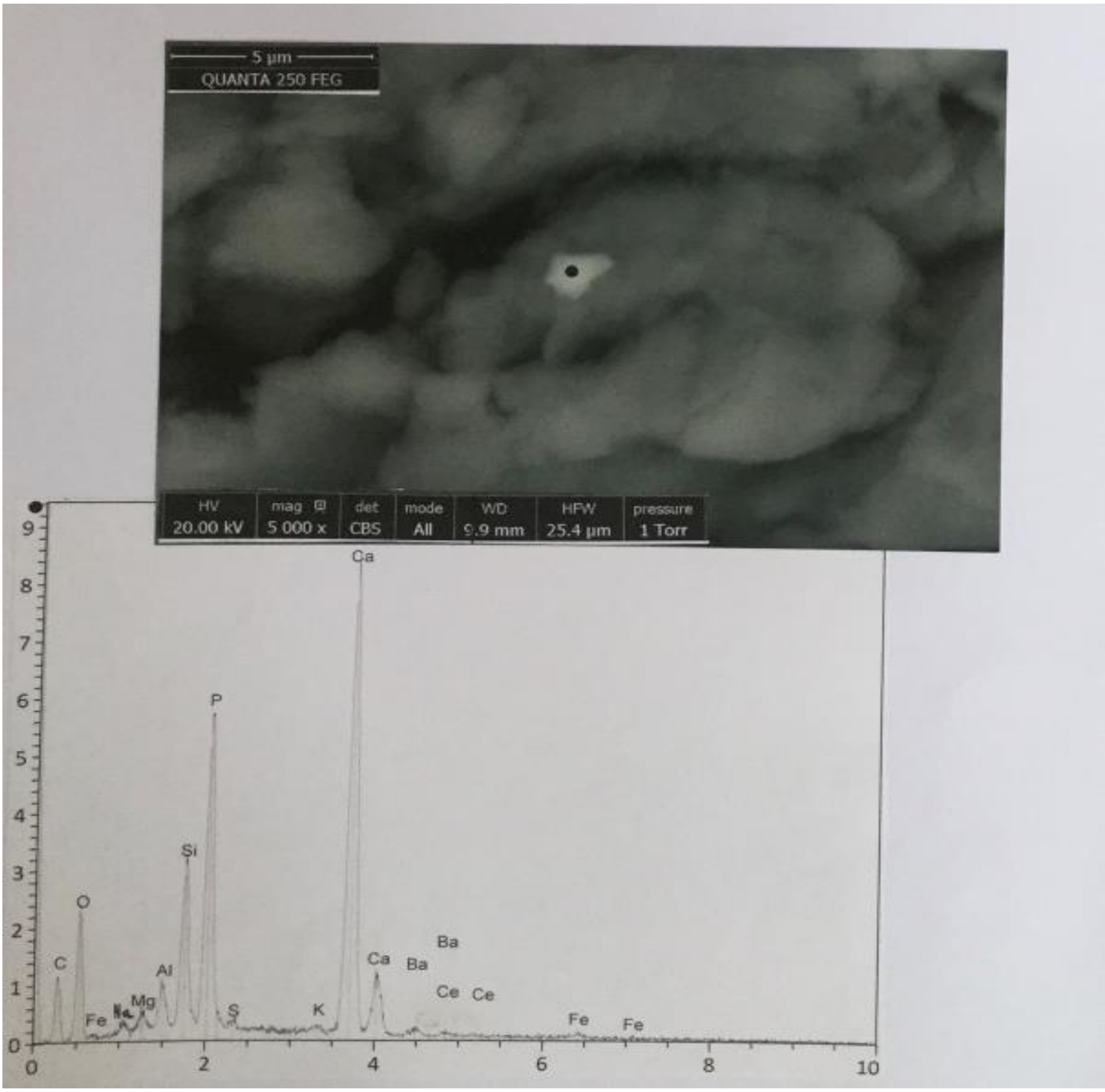

Fig. 11 : A first example of a barytine particle, located on the lingual face of the tooth. *Above* : SEM photograph (in CBS, 6000x)of the particle. *Below* : spectrum at the black point. C : carbon ; O : oxygen ; Fe (two peaks) : iron ; Na : sodium ; Mg : magnesium ; Al : aluminium ; Si : silicium ; P : phosphorous ; S : sulphur ; K : potassium ; Ca (two peaks) : calcium ; Ba (three peaks) : barium.

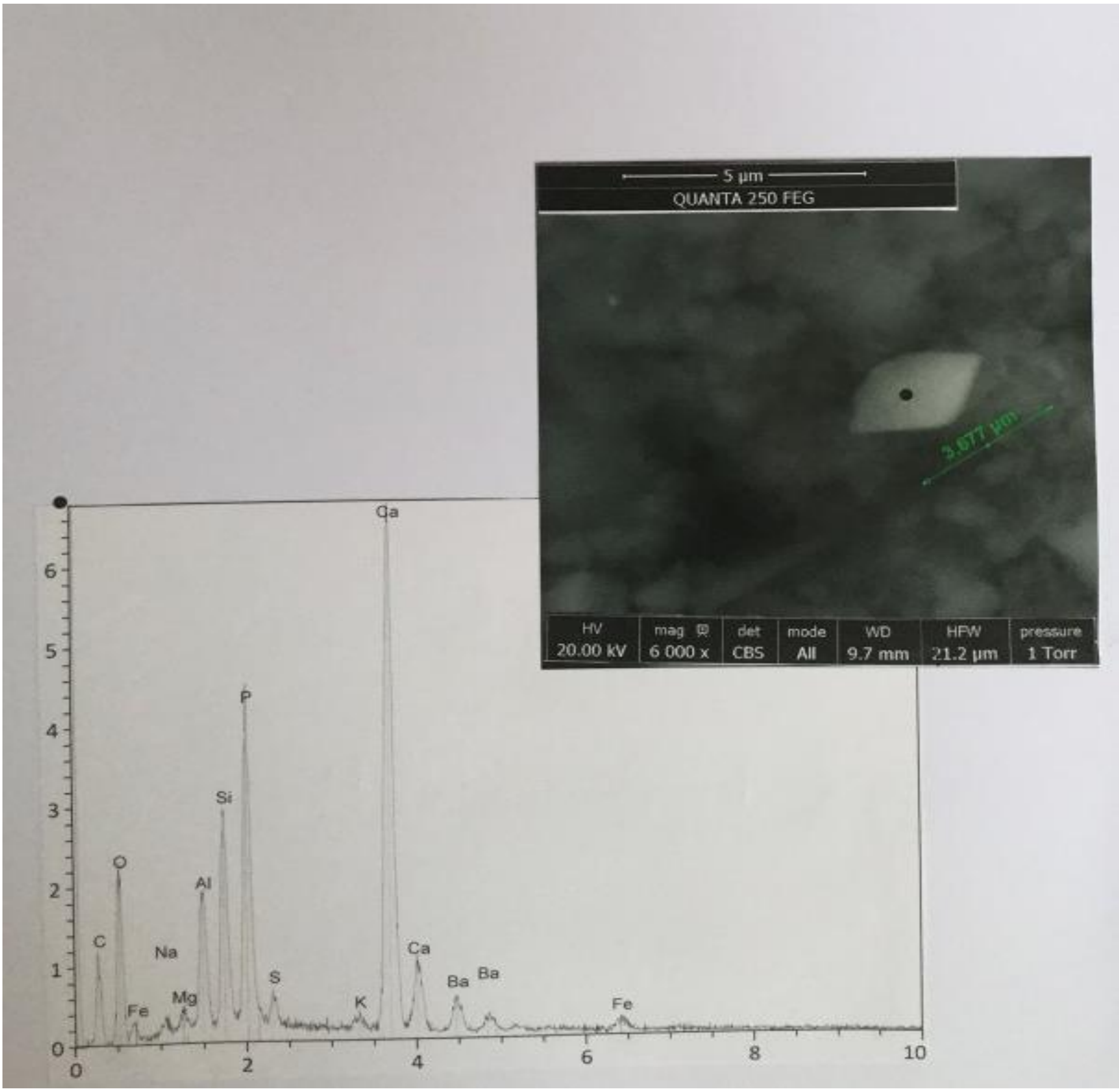

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Fig. 12 : A second example of barytine particle (**1**) – with another one (**2**) , of more little size. *Above* : SEM photograph (in CBS, 6000x) of the particles **1** and **2**. *Below* : spectrum at the black point. C : carbon ; O : oxygen ; Fe (two peaks) : iron ; Na : sodium ; Mg : magnesium ; Al : aluminium ; Si : silicium ; P : phosphorous ; S : sulphur ; K : potassium ; Ca (two peaks) : calcium ; Ba (two peaks) : barium.

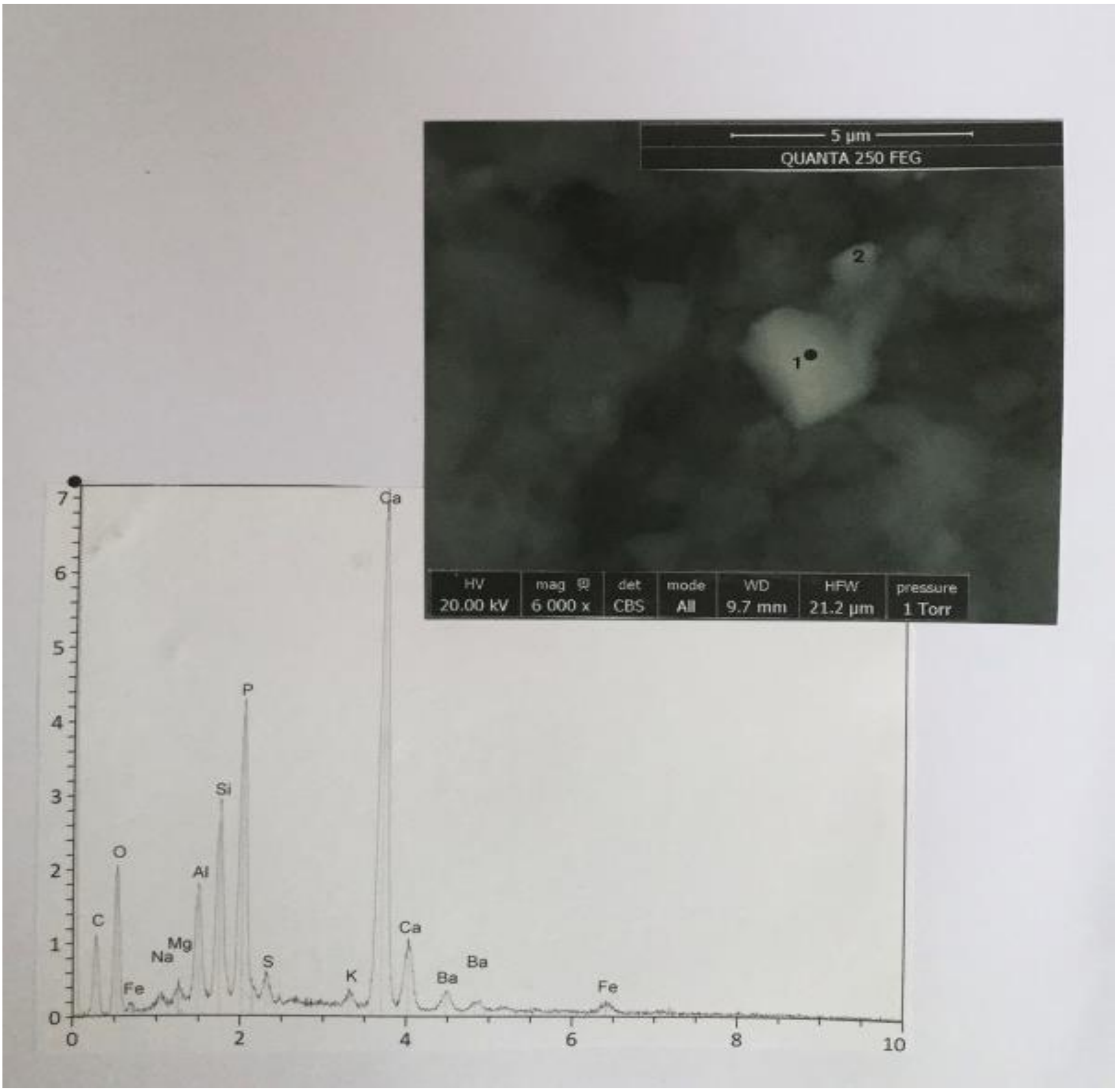

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Fig. 13 : A third example of barytine particle. *Above* : SEM photograph (in CBS, 12 000x) of the particle. *Below* : spectrum at the black point. C : carbon ; O : oxygen ; Fe (three peaks) : iron ; Na : sodium ; Mg : magnesium ; Al : aluminium ; Si : silicium ; P : phosphorous ; S : sulphur ; K : potassium ; Ca (two peaks) : calcium ; Ba (two peaks) : barium.

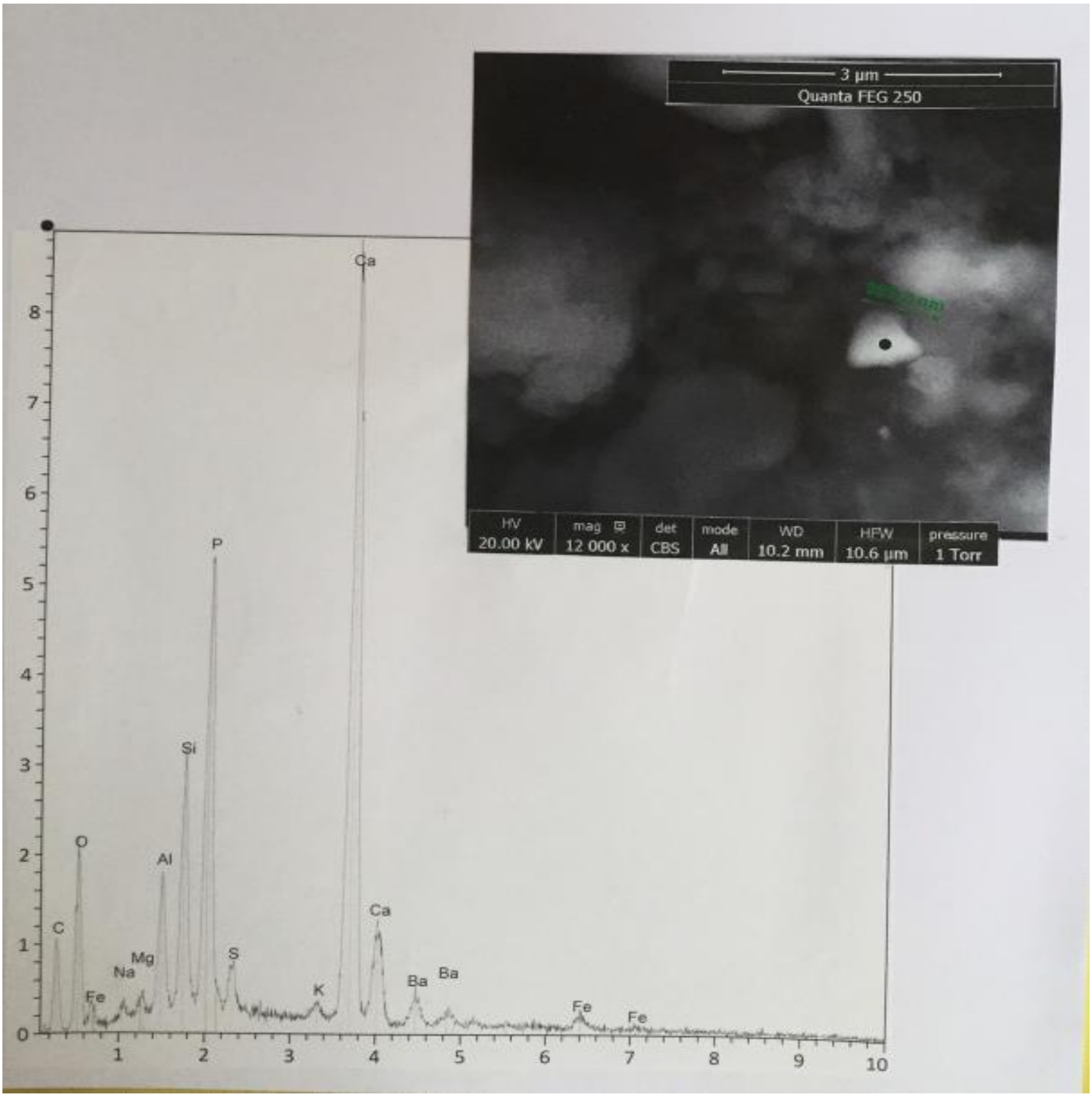

Fig. 14 : A group of barytine particles of a powder . *Above* : SEM photograph (in CBS, 6 000x) of the group. *Below* : spectrum at the black point. C : carbon ; O : oxygen ; Fe (two peaks) : iron ; Na : sodium ; Mg : magnesium ; Al : aluminium ; Si : silicium ; P : phosphorous ; S : sulphur ; K : potassium ; Ca (two peaks) : calcium ; Ba (four peaks) : barium. The main ray of cerium is indicated.

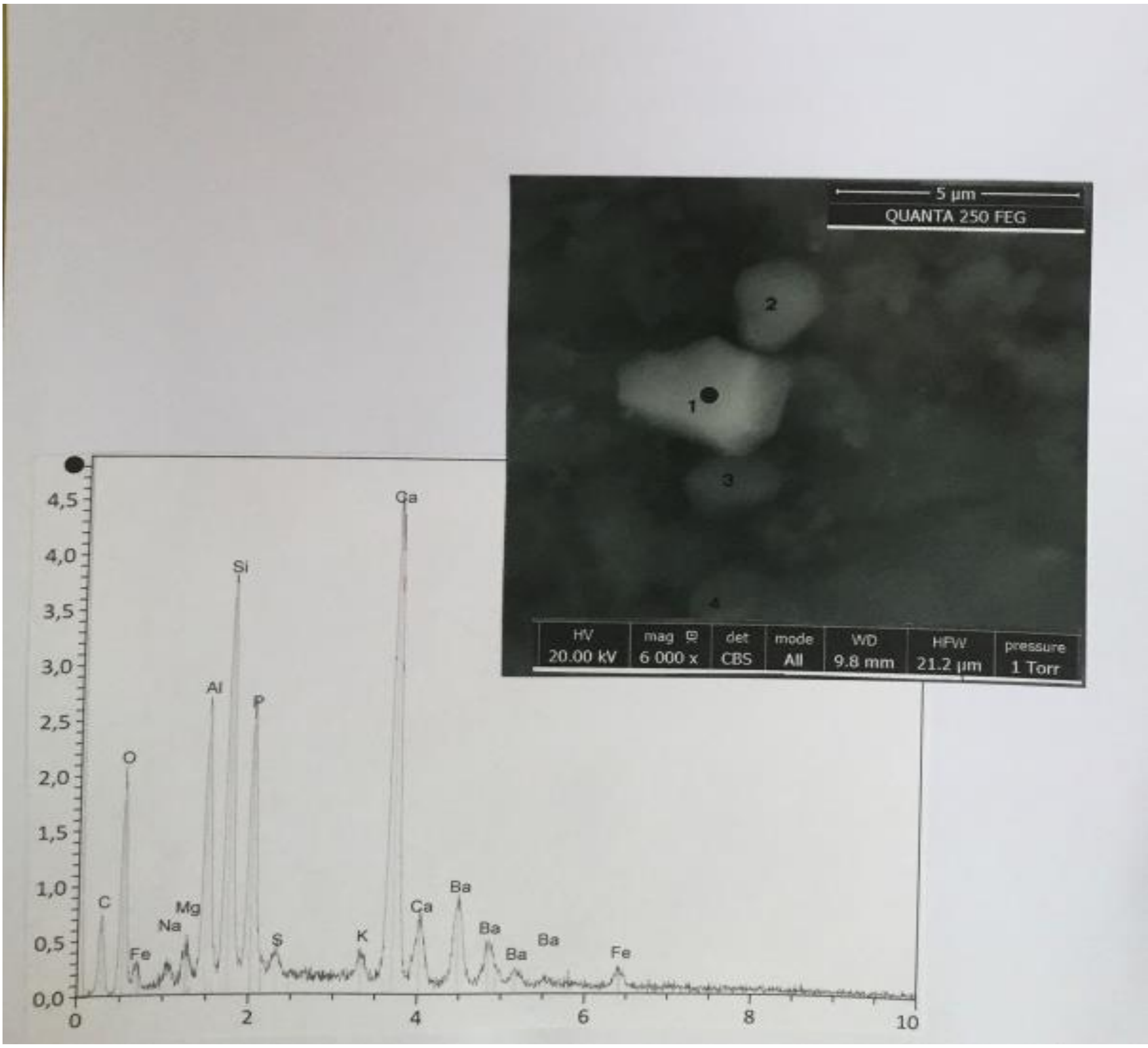

Fig. 15 : The O1 particle. *Above* : SEM photograph (in CBS, 12000x) of the particle *Below* : spectrum at the black point. C : carbon ; O : oxygen ; Fe (three peaks) : iron ; Na : sodium ; Mg : magnesium ; Al : aluminium ; Si : silicium ; P : phosphorous ; S : sulphur ; K : potassium ; Ca (two peaks) : calcium.

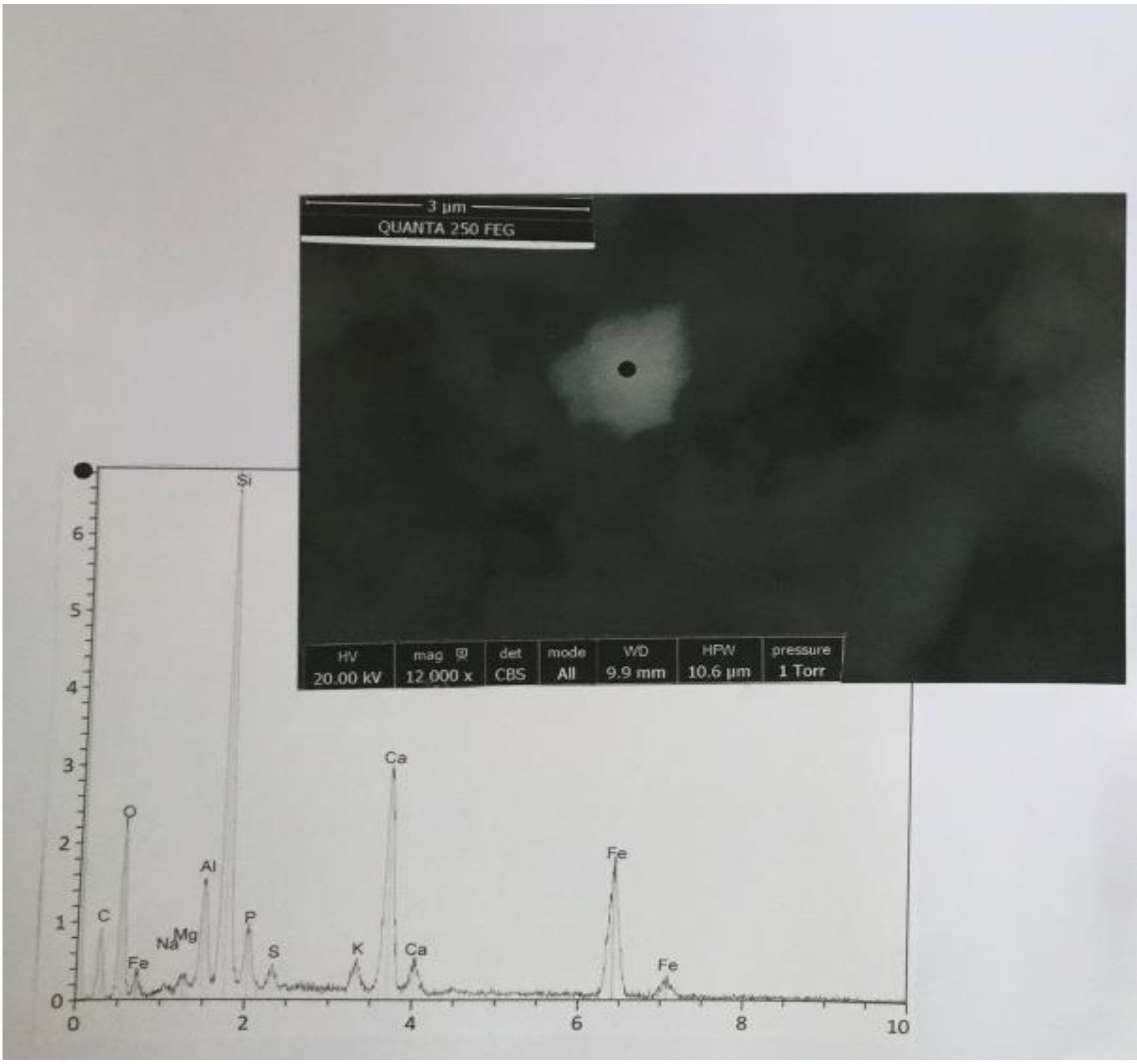

Fig. 16 : The O2 particle. *Above* : SEM photograph (in CBS, 25000x) of the particle. *Below* : spectrum at the black point. C : carbon ; O : oxygen ; Al : aluminium ; Si : silicium ; P : phosphorous ; S : sulphur ; K : potassium ; Ca (two peaks) : calcium ; Fe : iron.

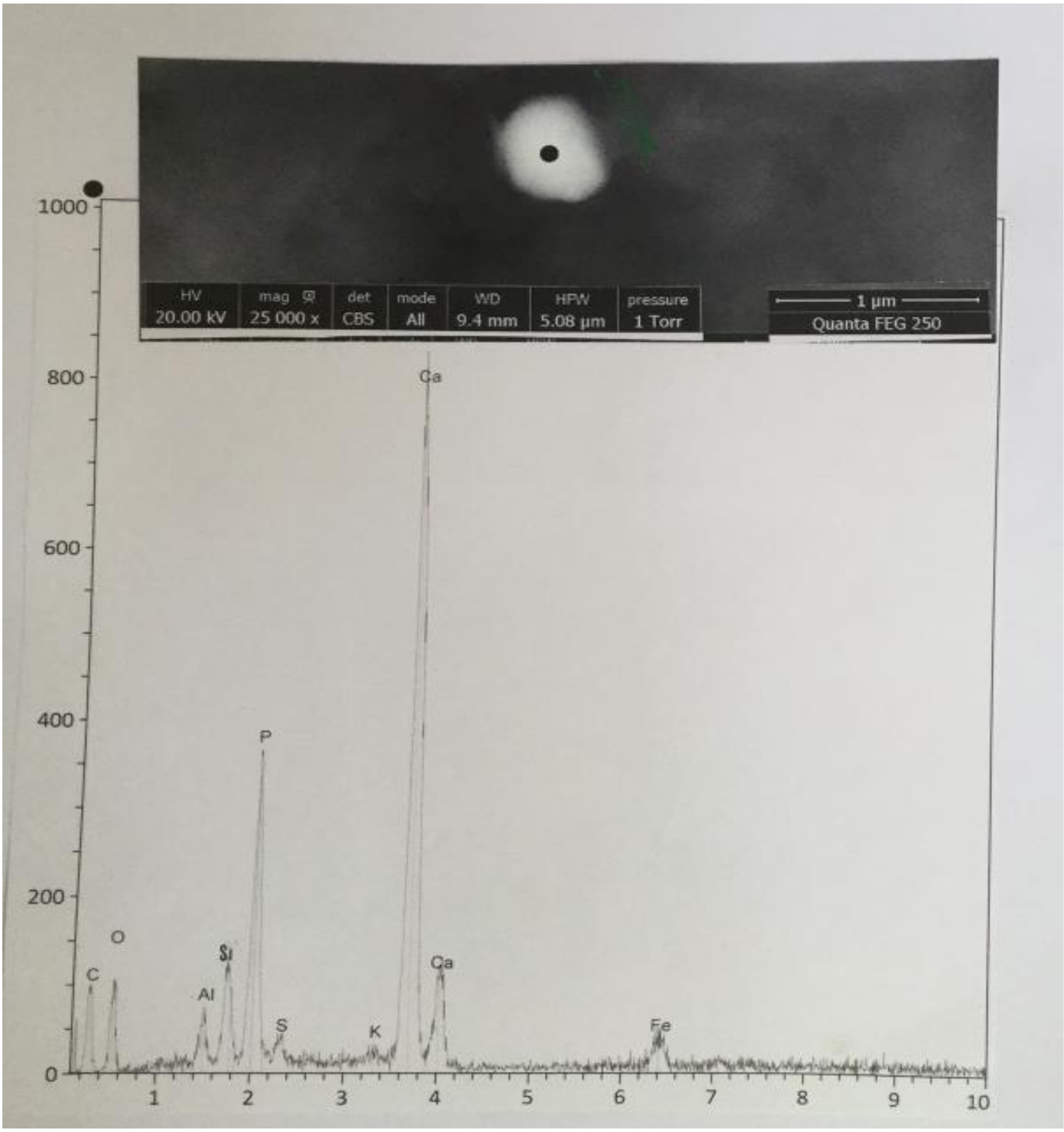

Fig. 17 : Micro-marbles of iron oxide. *Above* : SEM photograph (in CBS, 10000x) of the micro-marbles. *Below* : spectrum at the black point. C : carbon ; O : oxygen ; Fe (three peaks) : iron ; Na : sodium ; Mg : magnesium ; Al : aluminium ; Si : silicium ; P : phosphorous ; S : sulphur ; K : potassium ; Ca (two peaks) : calcium. Zn : zinc.