Odyssey Papers 31

The Nature of Encrustation on Coins from the Wreck of the *Republic* (1865)

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During the excavation by Odyssey Marine Exploration of the SS *Republic*, an American sidewheel steamer lost in deep waters off Georgia, southeast USA, in 1865, a small selection of gold and silver coins was submitted to the Microscopy Core Labs at the University of South Florida, to analyze the nature of encrustation deposited on the artifacts. Analyses were conducted using an optical microscope with color camera and Scanning Electron Microscopes (SEM) with Energy Dispersive X-ray analyzers (EDS).

The coins displayed the presence of a matrix of black-colored iron sulfide and brown-colored iron oxide deposits formed through marine bacterial activity working on organic matter present in the shipwreck. This produced an environment that reacted with iron present in the vicinity of the coins. Coral growing on the outside of the encrustation indicated that the encrustation formed over a given period of time followed by cessation of growth. Thereafter, the coral grew over a stable mass of fused coins.

1. Introduction

In November 2003, four gold and four silver coins recovered from the wreck of the sidewheel steamer SS *Republic* were submitted to the Microscopy Core labs in the Department of Pathology at the University of South Florida's College of Medicine in Tampa, Florida, for optical and electron microscope evaluation. Follow-up work on selected samples from the initial group of samples was continued at the PITTCON Conference in Orlando, Florida, in March 2010. SEM and X-ray analysis was conducted on samples on both occasions. The *Republic* sank on 25 October 1865 en route from New York to New Orleans and was discovered by Odyssey Marine Exploration in 2003 at a depth of around 500m in the Atlantic Ocean, 150km off the coast of Georgia, USA.

Extensive excavations were conducted between October 2003 and February 2005 using the ROV Zeus, which led to the recording and recovery of a diverse range of cargo, including 51,404 coins, 4,135 of gold and 47,263 of silver (Bowers, 2010; Cunningham Dobson *et al.*, 2010; Cunningham Dobson and Gerth, 2010: 39). Upon recovery, some batches of the coins were washed and stored in deionized water, others in buckets of Agrosoak™ (Agrosoak, International, Inc., Dana Point, CA.), to help safely transport the artifacts. Some coins were placed in a jeweler's sonic cleaning bath. The majority were kept in saltwater. Prior to conservation and study, the coins were completely covered with an encrustation that colored the coins shades of dark brown and black. The objective of the current study was to analyze the source and nature of these encrustations. The coins used in this study were washed and stored in distilled water, which prevented sea salt deposition on the coins and were air-dried prior to being submitted for microscopy.

Fig. 1. Upper side of encrustation from a SS Republic *shipwreck gold coin examined under an optical microscope.*

2. Sample Preparation

The coins were larger in diameter than the ideal sample size for the scanning electron microscope intended to be used to examine the marine deposits coating the coins. All of the coins were covered with an encrustation, a biofilm produced by marine bacteria (McNeil and Little, 1999). The biofilm had dried onto the coins during transport to the laboratory. The film was the natural

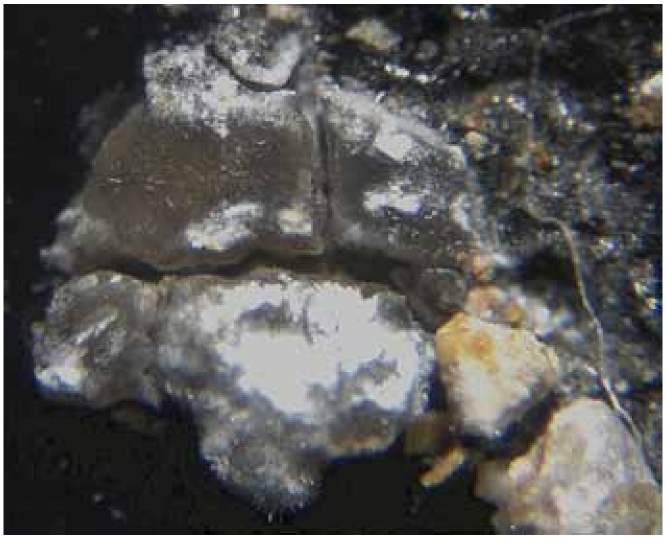


Fig. 2. Upper side of encrustation, crystalline in nature, from a silver coin examined under an optical microscope.

product of metabolism of marine bacteria feeding on the wood, coal and metal of the shipwreck. It served as a protective environment for the bacteria to live in while the artifacts were in the sea. In an effort not to damage the artifacts, yet to examine successfully the deposits contaminating the coins' surfaces, carbon-impregnated double-sided tape was used to gently lift the deposits from the surface of the coins. The tape was applied to the deposits, rubbed in place and pulled off the coins.

When the encrustation was pulled free from the surface of the gold coins, the beautifully polished surfaces below the deposits were revealed. The encrustation had formed such a tight bond on the surface of the coins that it produced a mirrored, bas-relief image of the entire coin surface. The underlying surface of the silver coins had oxidized and discolored from years of submersion in salt water. Some areas of the surface encrustation were mounted on the tape in such a way that the outer surface of the encrustation could be photographed, while other areas of the encrustation were mounted on the tape so the surface of the encrustation facing the coins could be examined.

Various areas of the encrustation were first photographed with an optical microscope (Carl Zeiss Microscopy, LLC, Thornwood, New York) and a color camera. The same areas photographed with the optical camera were also examined and photographed with a Philips 515 Scanning Electron Microscope (SEM), (FEI Corporation, Hillsboro, Oregon) equipped with an EDAX 9011 Energy Dispersive X-ray Analyzer (EDS) (EDAX, Inc., Mahwah, New Jersey) at similar magnifications.

Higher magnification photographs were also obtained with the SEM. The SEM was equipped with three different types of detectors. One detector gave general photographic information about the structure of the sample, the size and shape of objects in the sample at various areas (a secondary electron detector). Another detector provided information about the presence of lighter or denser materials, such as those composed of calcium or gold (a backscattered electron detector). A third detector yielded information about the presence of elements from the periodic table, in essence different types of atoms present in the sample, revealing what various parts of the sample were made from (Energy-Dispersive X-ray Analyzer, EDX). Scientific interpretation of the optical microscope photographs, in combination with the SEM information, would enable the materials producing the encrustation on the coins to be identified.

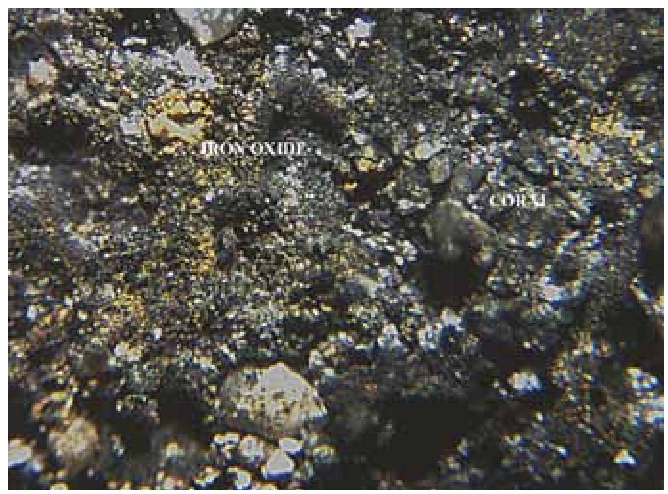


Fig. 3. Coral growing amongst iron oxide on the outer surface of a silver coin encrustation examined under an optical microscope (x 2.5).

Fig. 4. Coral growing on the outer surface of a gold coin encrustation examined under an optical microscope.

3. Analysis

A. Optical Microscope Evaluation

Using the optical microscope, many areas of encrustation on both gold and silver coins were observed to reflect light from their surface, indicating that these areas were either rich in metal (Fig. 1) or were crystalline in nature (Fig. 2). Deposits of coral could be identified growing in areas on the outer surface of the encrustation (Figs. 3-4). Brown deposits of iron oxide were also identified, formed in pockets on the outer surface of the black encrustation (Fig. 5). Small pieces of bright-colored metal were observed embedded in the overall black or dark brown colored matrix of the encrustation as well (Fig. 5). On the inside of the encrustation, facing one of the gold coins, a perfect mirror image of the letters 'TY' from the word 'LIBERTY' showed how tightly the encrustation was bonded to one of the gold coins (Fig. 6).

Following optical microscope examination of the samples, they were coated with a 20 nanometer-thick layer of carbon, applied by evaporation, to make the samples electrically conductive, preparing them for observation in the electron microscope. The same samples observed by optical microscopy were then observed and photographed in the SEM.

B. Coral Encrustation

Scanning electron microscopy began with the examination of the outer surface of the encrustation formed on the silver coins. At low magnification the skeletons of marine coral were observed on the surface of the encrustation, forming disc and spherical-shaped structures (Figs. 7-8). The coral colonies were easily observed at a higher magnification of x 300 (Fig. 9). Both iron oxide and iron sulfide deposits were identified on the silver and gold coins by X-ray analysis (Figs. 10-11). These deposits sometimes contained flakes of silver (Fig. 12).

C. Silver Coin Evaluation

Higher magnification studies of the silver coin encrustations were conducted to examine the samples for evidence of sulfur-fixing bacteria (SFB), a reported source of the iron sulfide deposits on marine archaeological remains (McNeil and Little, 1999). High magnification analysis at x 1,000 revealed areas of deposits with sulfur- and iron-rich particles that may have been formed by bacteria (Fig. 13). Some bacteria have been reported to form such shells and to live inside them, forming colonies. A nodule of spherical-shaped particles, the same size as encrusted sulfur-fixing bacteria, was observed at x 4,000 magnification

Fig. 5. Iron oxide and iron sulphide on the outer surface of a silver coin encrustation.

Fig. 6. Mirror image of the letters 'TY' from the word 'LIBERTY' preserved on the inside encrustation of a gold coin examined under an optical microscope.

(Fig. 14). A small deposit identified on one of the coins at x 2,000 magnification revealed a cluster of particles from a region of the iron sulfide deposits (Fig. 15), found to be silver sulfide, using both backscattered (L) and secondary electron detectors (Fig. 25).

Meanwhile areas of copper and iron sulfide were found on the surface of another coin, observed with the

Fig. 7. Skeletons of marine coral on the outer surface of a silver coin encrustation examined by Scanning Electron Microscopy (SEM) (x 50).

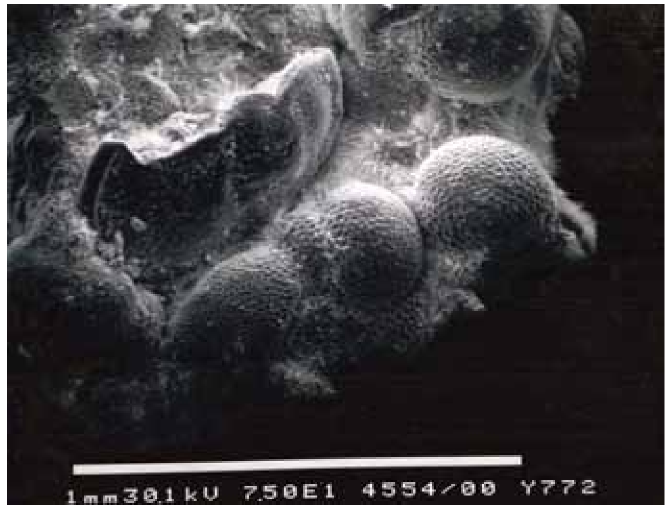


Fig. 8. Skeletons of marine coral on the outer surface of a silver coin encrustation examined by SEM (x 75).

secondary (Fig. 16-17) and backscattered electron detectors (Fig. 18), respectively. In some areas (Figs. 17-18), the encrustation on a silver coin was rich in iron oxide, the product of iron-oxidizing bacteria, coloring it brown, resulting in a change in the appearance of the crystal structure of the deposits in the encrustation. Some tubular iron oxide particles deposited on a silver coin were visible at high magnification (Fig. 24). Particles of this nature have been described in the literature as casts of deep-water bacteria, the iron being deposited as a shell surrounding the bacteria, resulting from their metabolic processes (Konhauser, 1997). An additional area of oxide deposits and silver particles taken from the surface of one of the silver coins was exposed (Fig. 25). A region of iron and copper sulfide deposits removed from a silver coin was again analyzed (Fig. 26).

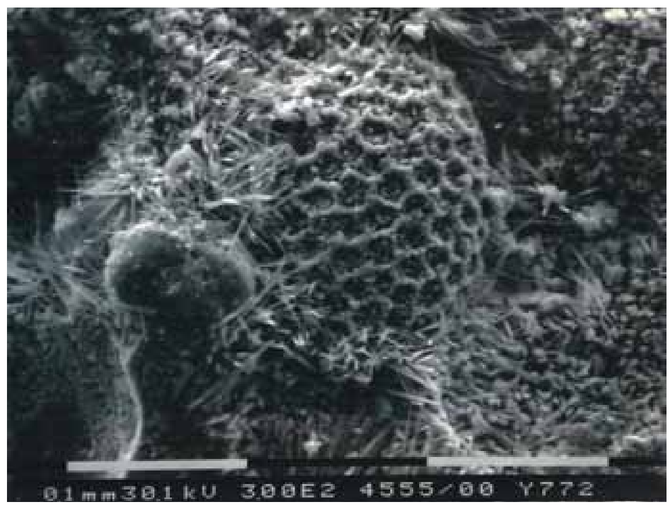


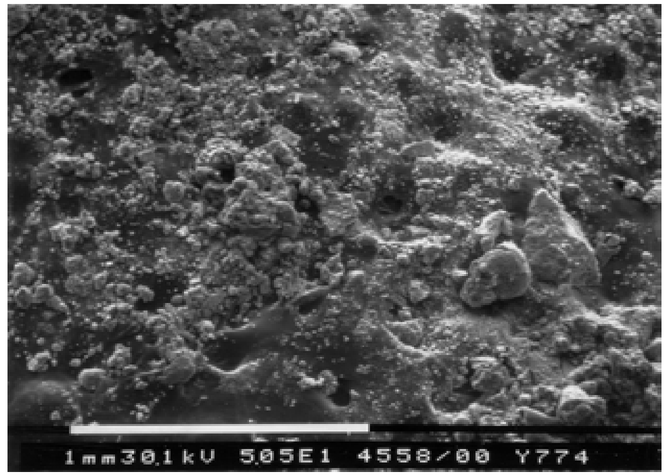
Fig. 9. Skeletons of marine coral on the outer surface of a silver coin encrustation, fractured open to reveal the walls of coral cell chambers inside. Examined by SEM (x 300).

D. Gold Coin Evaluation

Scanning Electron Microscope examination of the iron sulfide deposits on the gold coins revealed often-smooth surfaced deposits with small colonies of coral growing on their surface. These encrustations had adhered so tightly to the surface of the coins that the stamping marks of the coins were reproduced in mirror relief in the deposit undersurfaces (Figs. 19-20). Using a secondary electron detector and a backscattered electron detector, the same view was compared (Figs. 20-21). The secondary electron detector gives general topography of a sample, while the backscattered electron detector gives atomic number information of a sample. In this supplementary examination, using the backscattered detector, the higher the atomic number of an element present in an area of the sample, the brighter that area of the sample will appear.

The bright areas observed were attributable to gold particles that lifted off the coin when the encrustation was removed from the coin, while the darker areas show the presence of only the iron sulfide encrustation itself (Fig. 21). Higher magnification photography at x 200 magnification of some of the gold removed in the encrustation from this coin was viewed in both secondary and backscattered electron detector modes (backscattered mode is on the right; Fig. 22).

On 3 March 2010, the samples of encrustation removed from the gold coins recovered from the wreck of the



Figs. 10-11. Iron oxide and iron sulfide deposits identified on a silver coin encrustation examined by SEM (x 50).

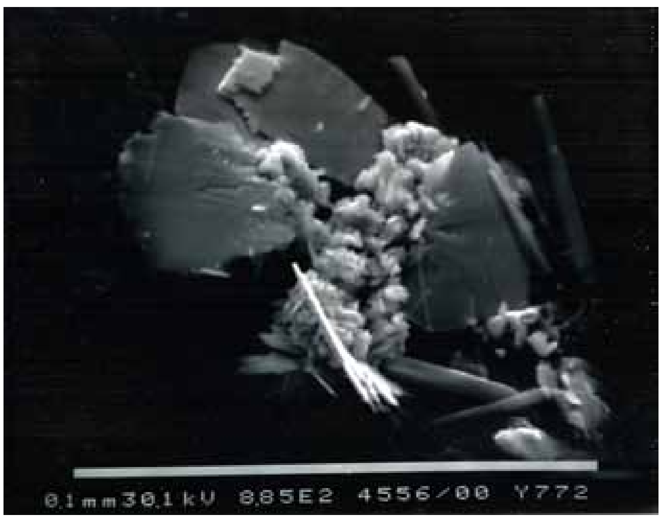


Fig. 12. Iron oxide and iron sulfide deposits identified alongside silver flakes on a silver coin encrustation examined by SEM (x 885).

Fig. 13. Deposits with sulfur- and iron-rich particles probably formed by bacteria on a silver coin encrustation examined by SEM (x 1,000).

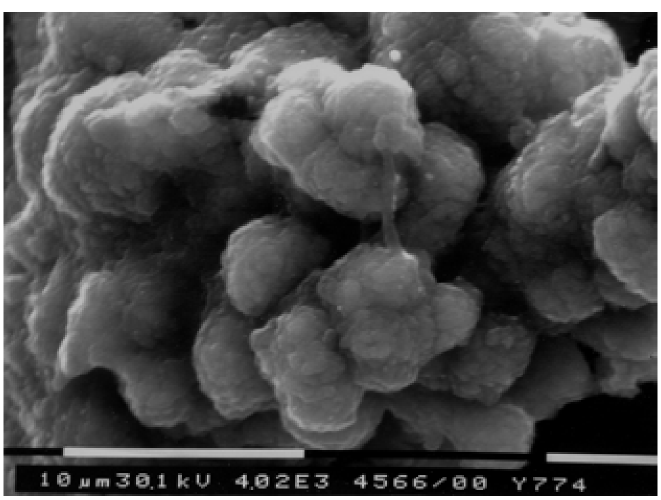


Fig. 14. Iron sulfide encrustation from a silver coin and a clump of probable sulfur-fixing bacteria particles examined by SEM (x 4,000).

Fig. 15. A small deposit of silver sulfide crystals identified on a silver coin concretion examined by SEM (x 2,500).

Republic were taken to the Pittcon Conference in Orlando, Florida. The Hitachi High Technologies America Company (Dallas, Texas) kindly allowed the author to view and analyze these samples in their instruments to demonstrate the capabilities of their TM 3000 desktop Scanning Electron Microscope and their S4800 Field Emission high resolution Scanning Electron Microscope with an Oxford Instruments (Concord, Massachusetts) INCA Energy-Dispersive X-ray Analyzer. The following results were obtained using photography and x-ray analysis. At x 60 magnification, encrustation taken from a gold coin showed a region of iron sulfide (Fig. 27). Photography was obtained using a backscattered electron detector, which is sensitive to element contrast. Gold, which has atoms of higher mass than iron or sulfur, therefore appears brighter. The extremely smooth surface of the encrustation, mirroring the surface of the coin, was noted (Fig. 28). Analysis at x 100 magnification revealed the letter 'R' in mirror relief and at x 500 magnification showed an area of iron sulfide encrustation in contact with the surface of a gold coin (Fig. 29). A thin foil of the gold from the coin (to the left of the photo) lifted off with the encrustation when it was removed from the coin.

Encrustation removed from a gold coin containing a flake of gold was observed on a second gold coin viewed at x 60 and x 100 magnification, and proved to be iron sulfide (Fig. 30). This area of encrustation faced away from the surface of a coin. At x 300 magnification some of the crystal structure of the iron sulfide deposits was examined (Fig. 31). Details of the iron sulfide crystals were visible at the higher magnification of x 1,000 (Fig. 32).

In relation to the Energy-dispersive X-ray Analysis spectra conducted in 2010, for the first sample (Fig. 33a) an area of encrustation was examined from one of the silver coins (corresponding to that photographed in optical microscope: Figs. 5, 30). This area had a silver flake on it. The first panel (Spectrum 1) examined was an area of iron oxide, or rust, from the encrustation. This area also contained some deposits of iron sulfide as well as calcium oxalate crystals (triangular-shaped structures). The iron oxide crystals were visible to the lower left of the sample. Spectrum 4 showed a region of encrustation with a silver flake (bright object to right of photo) embedded in the encrustation (Fig. 33b). The flake consists of silver sulfide (Fig. 33c), and is embedded in a matrix of iron sulfide (Fig. 33e). Calcium oxalate crystals are embedded in the iron sulfide matrix of the encrustation (Fig. 33d).

For the second sample (Fig. 34), an area of the iron sulfide encrustation facing the gold coin was examined and three x-ray spectra were generated, similar to the smooth region on the right side of the SEM photograph taken at

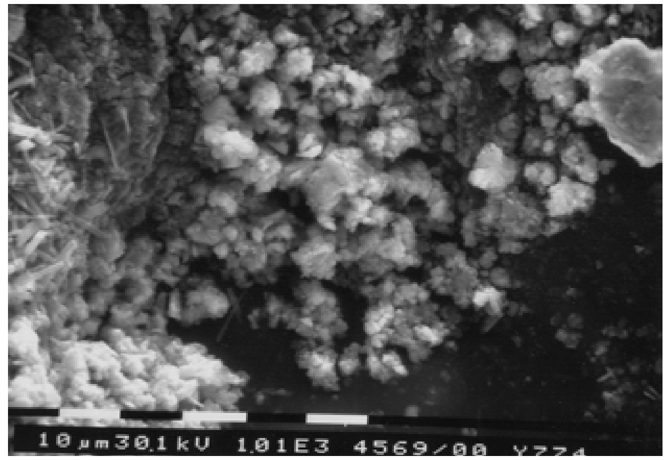


Fig. 16. Copper and iron sulphide deposits on a silver coin concretion examined by SEM (x 1,000).

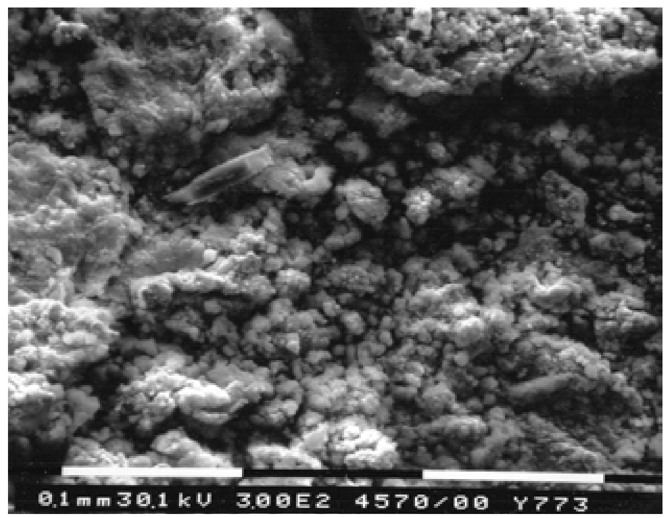


Fig. 17. Copper and iron sulphide deposits on a silver coin concretion examined by SEM (x 300).

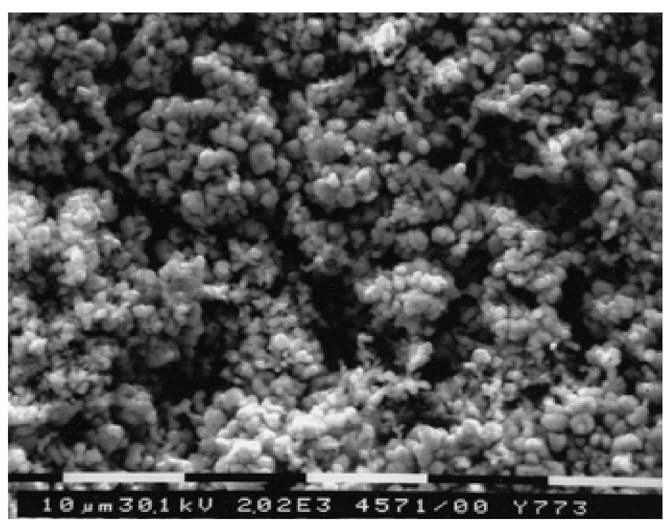


Fig. 18. Iron oxide and silver particles on a silver coin concretion examined by SEM (x 2,000).

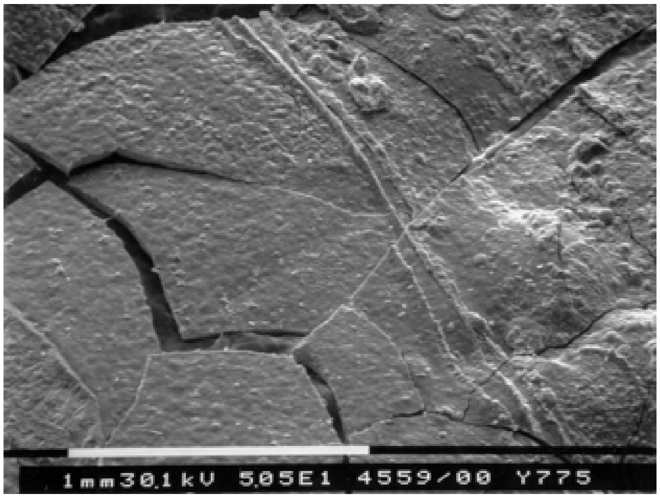


Fig. 19. Outer surface of a gold coin concretion with iron sulfide deposits examined by SEM (x 50).

Fig. 20. Inner surface of a gold coin concretion with engraving marks preserved in mirror relief, examined by secondary electron detector (x 15).

Fig. 21. Inner surface of a gold coin concretion with engraving marks preserved in mirror relief, examined using a backscattered electron detector (x15).

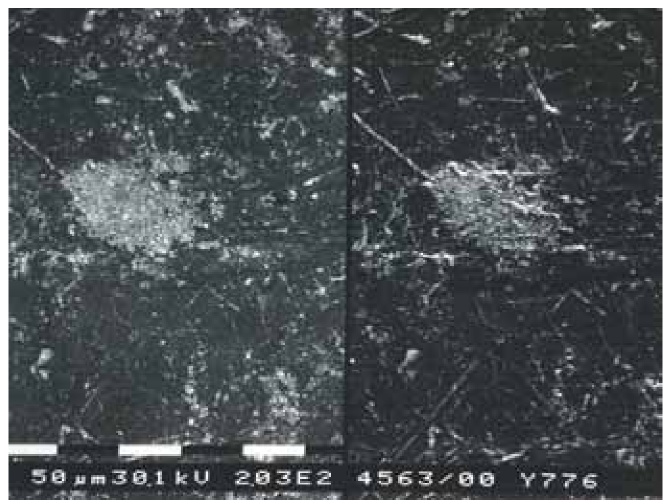


Fig. 22. Gold deposit on iron compared in a secondary electron detector (left) and backscattered electron detector (right) (x 200).

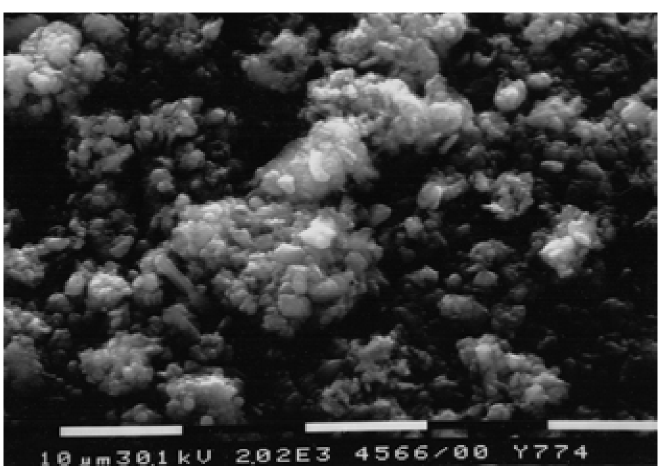


Fig. 23. An iron sulfide deposit on a silver coin encrustation examined by SEM (x 2,000).

Fig. 24. Tubular iron oxide particles deposited on a silver coin examined by SEM (x 4,000).

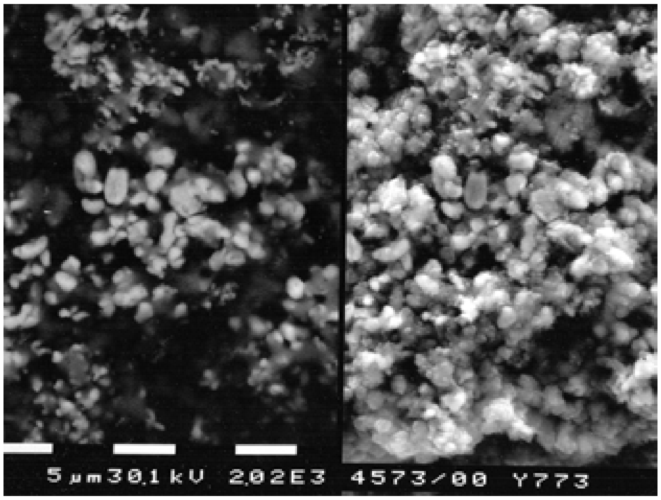


Fig. 25. Oxide deposits and silver particles on the surface of a silver coin encrustation examined by SEM (x 2,000).

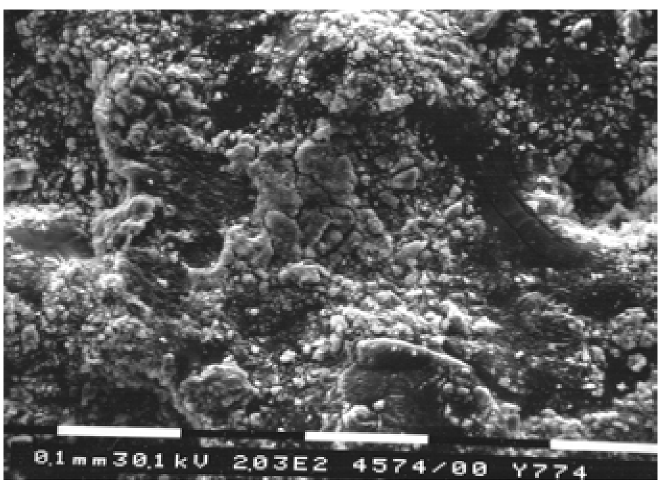


Fig. 26. Iron and copper sulfide deposits from a silver coin encrustation examined by SEM (x 200).

PITTCON of the gold foil on iron sulfide deposit (Fig. 29). All three spectra demonstrated the presence of gold in addition to iron in the encrustation. The smooth surface of the encrustation associated with the spectra was visible. The sulfur peaks associated with the iron sulfide are hidden in these spectra by the overwhelming gold.

4. Conclusion

In conclusion, the studies of the encrustation on the gold and silver coins recovered from the wreck of the sidewheel steamer the *Republic* show that the coins are covered with a matrix of both black-colored iron sulfide and brown-colored iron oxide deposits. The encrustation is predominately iron sulfide, a tightly adhering product that is difficult to remove from coins. According to published scientific research (McNeil and Little, 1999), the encrustation formed as the result of marine bacterial activity working on organic matter present in the shipwreck and sulfur in the seawater, producing an environment that reacted with the iron present in the vicinity of the coins.

The fact that coral was observed growing on the outside of the encrustation would indicate that the encrustation formed over a given period of time, and then the process stopped, allowing the coral to grow on top of a stable mass of fused coins. The silver coins exhibited some deterioration, their surfaces having converted to silver sulfide, which was indicated by x-ray analysis, whereas the gold had not deteriorated, which was to be expected since gold is generally a non-reactive metal. Some gold may have complexed as gold chloride, although this study was not able to determine that.

Acknowledgments

The author wishes to thank the Hitachi High Technologies Company for their generous assistance and donation of their time in analysis of our samples at the PITTCON Conference and the use of their excellent microscopes at the Conference.

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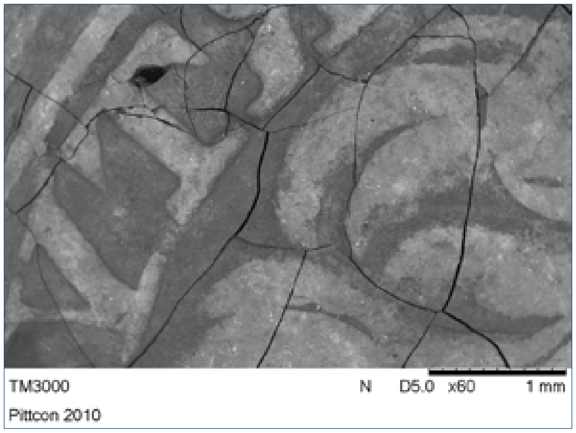


Fig. 27. A gold coin inner encrustation with iron sulfide and mirror image inscription examined by a Hitachi High Technologies America Company Scanning Electron Microscope (SEM) with a backscattered electron detector (x 60).

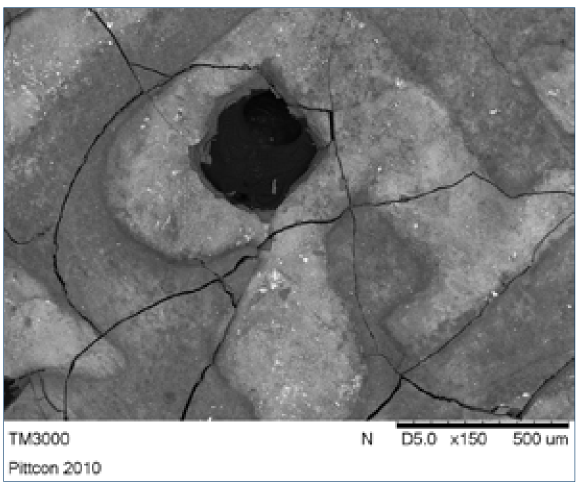


Fig. 28. Detail of an extremely smooth inner surface gold coin encrustation mirror-image 'R' from 'LIBERTY' examined by SEM (x 150).

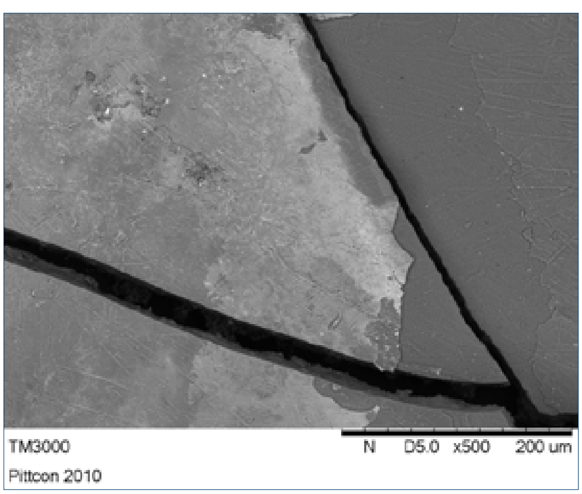
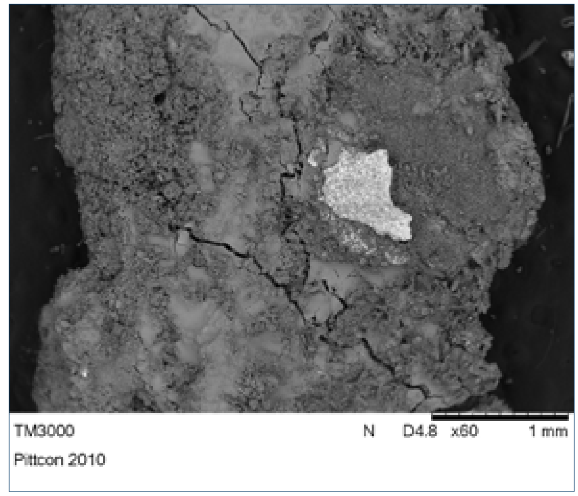
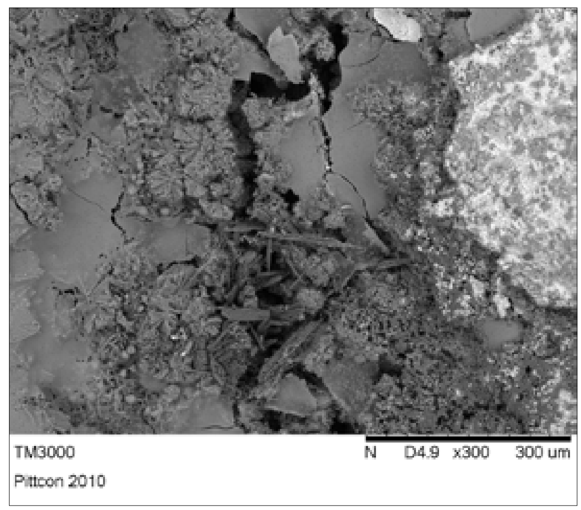


Fig. 29. Area of iron sulfide encrustation in contact with the inner surface of a gold coin, with thin gold foil lifted off at left, examined by SEM (x 500).





Figs. 30-31. Iron sulfide outer encrustation from a gold coin containing a flake of gold (x 60), with detail of its crystal structure (x 300), examined by SEM.

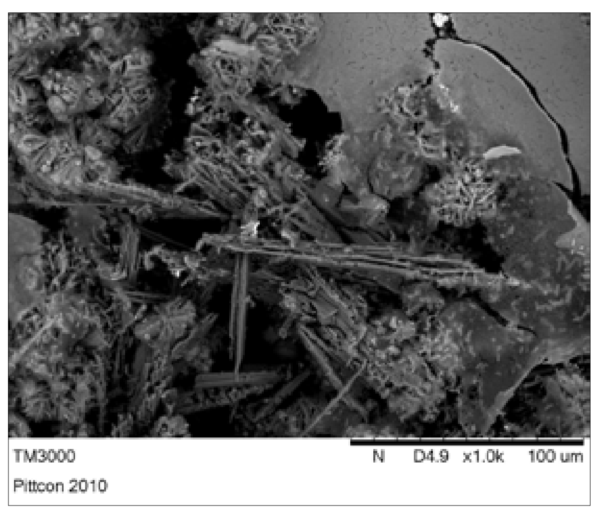


Fig. 32. Iron sulfide outer encrustation from a gold coin showing details of iron sulfide crystals, examined by SEM (x 1,000).

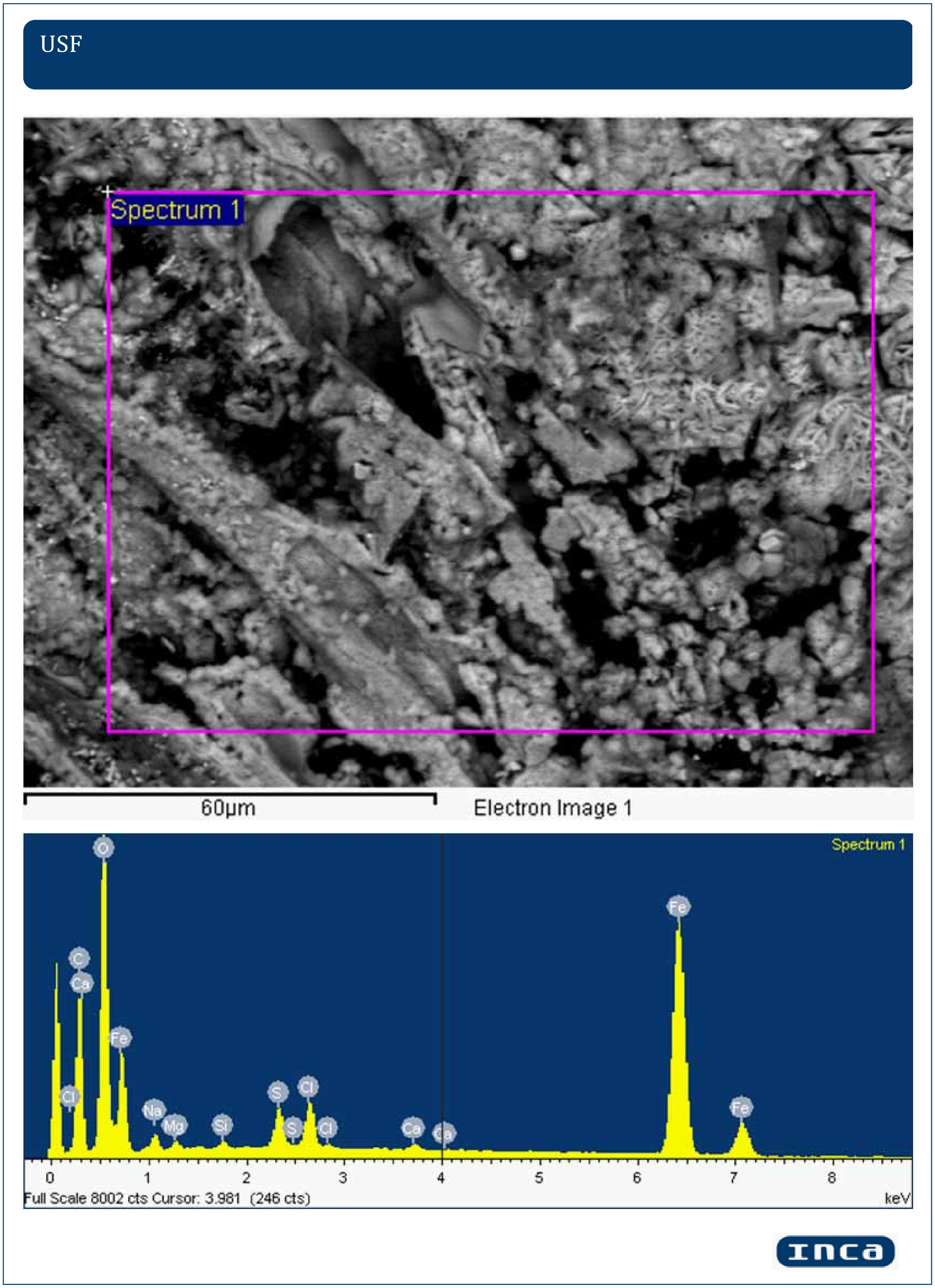


Fig. 33a. Silver coin iron oxide, iron sulfide and calcium chloride salt crystals examined by Energy-dispersive X-ray Analysis.

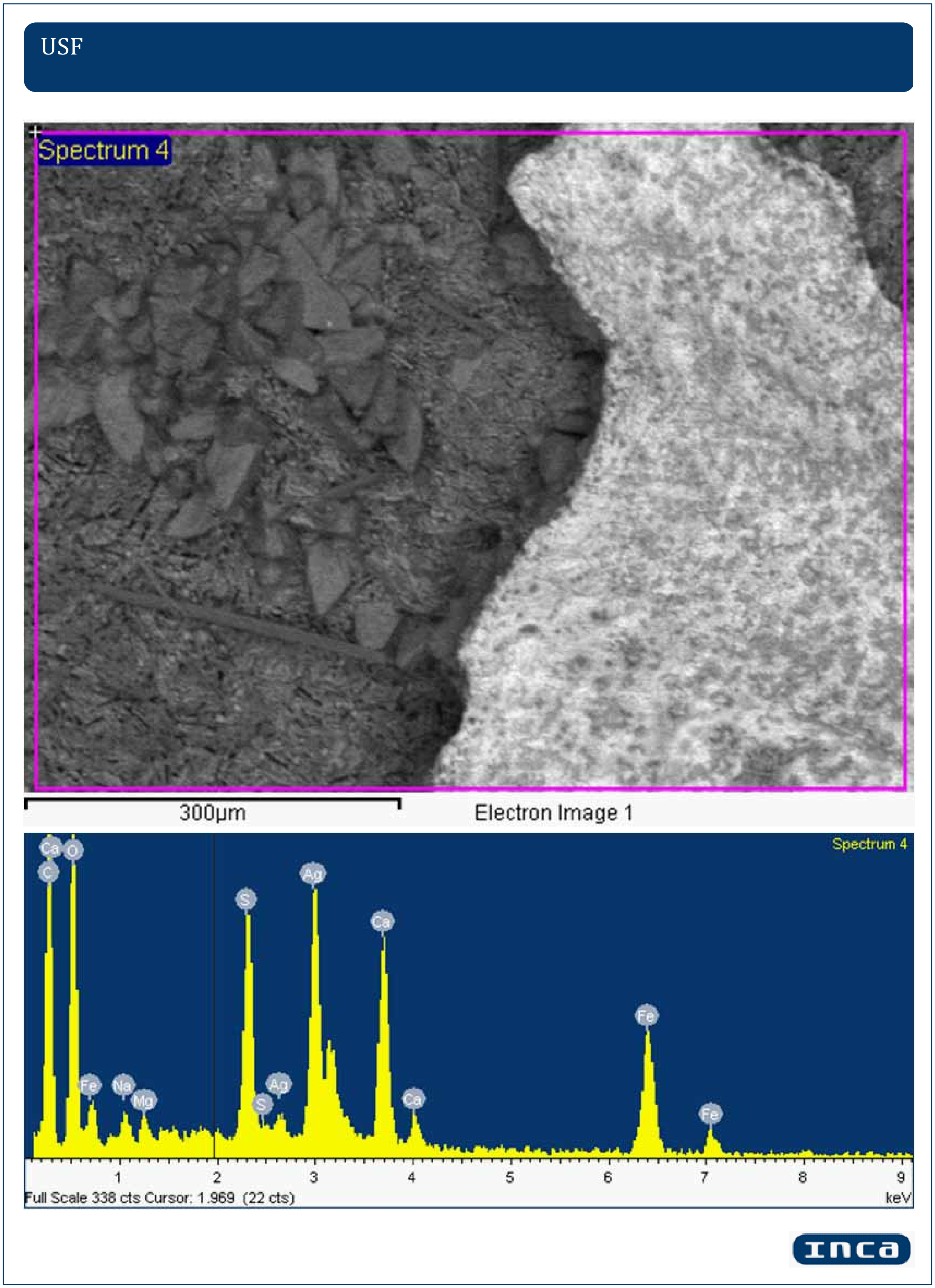


Fig. 33b. Silver coin with a silver flake embedded in the encrustation examined by Energy-dispersive X-ray Analysis.

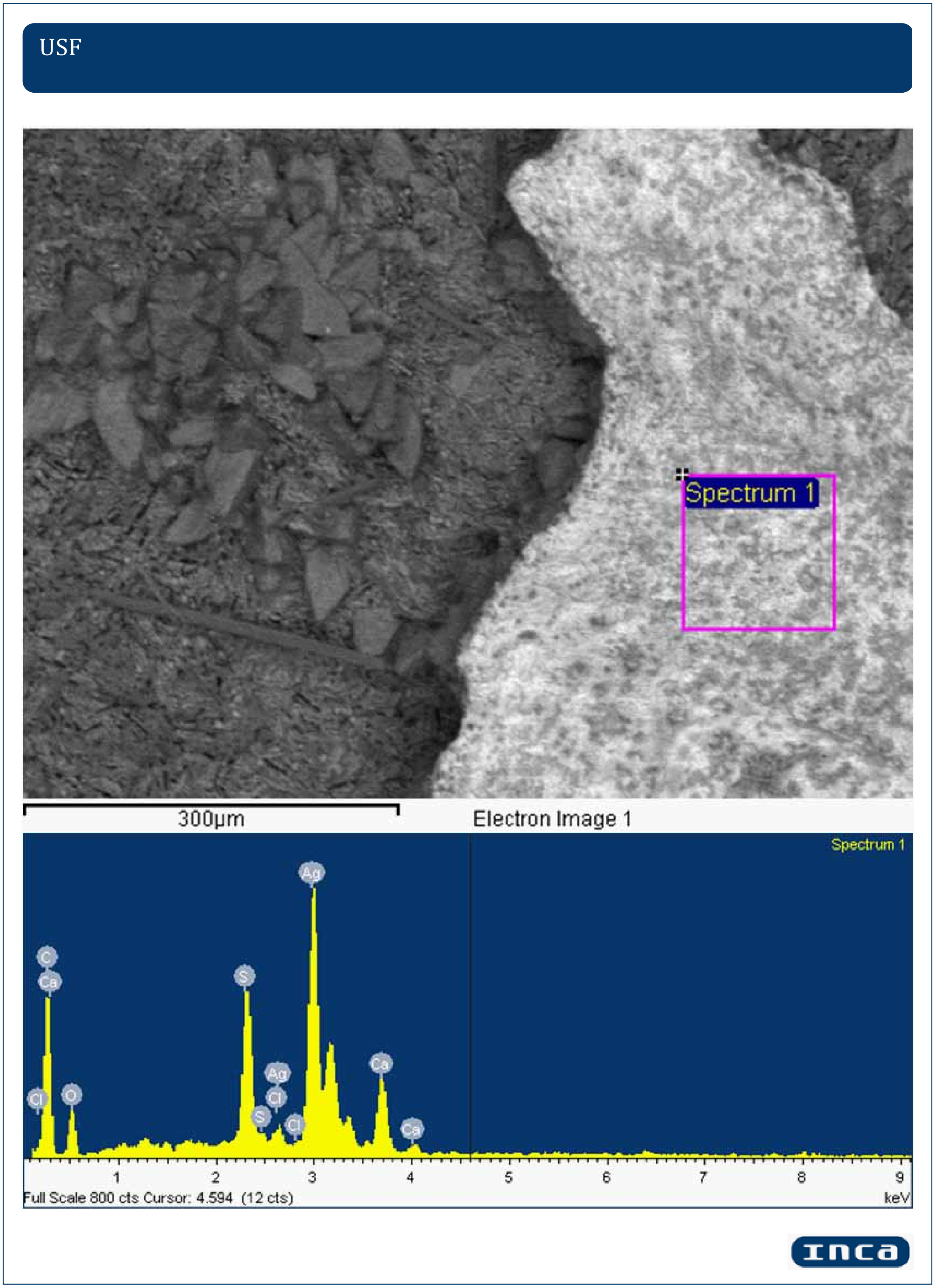


Fig. 33c. Silver coin with a silver sulfide flake embedded in the encrustation examined by Energy-dispersive X-ray Analysis.

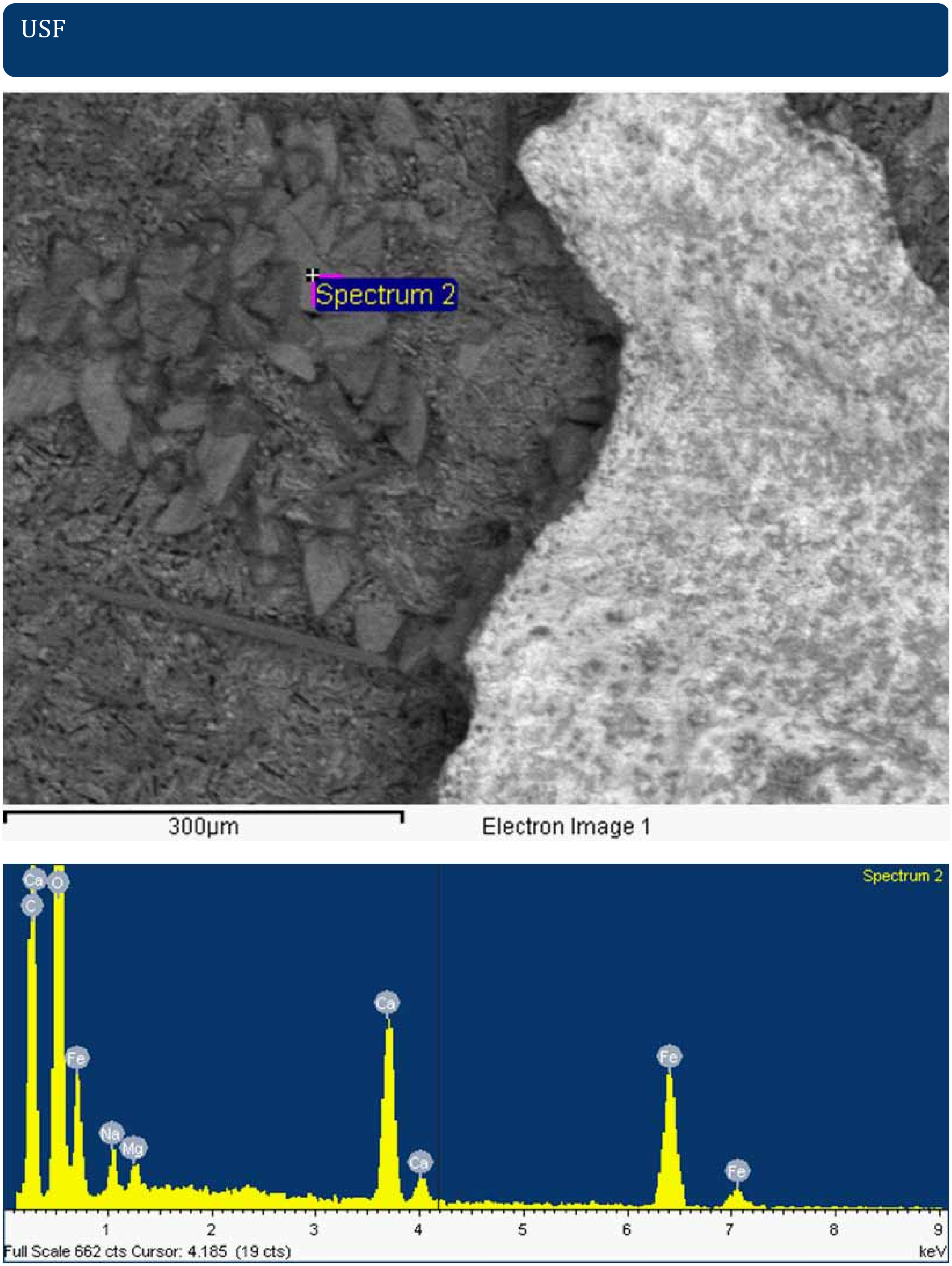


Fig. 33d. Calcium oxalate crystals embedded in iron sulfide matrix of silver coin encrustation examined by Energy-dispersive X-ray Analysis.

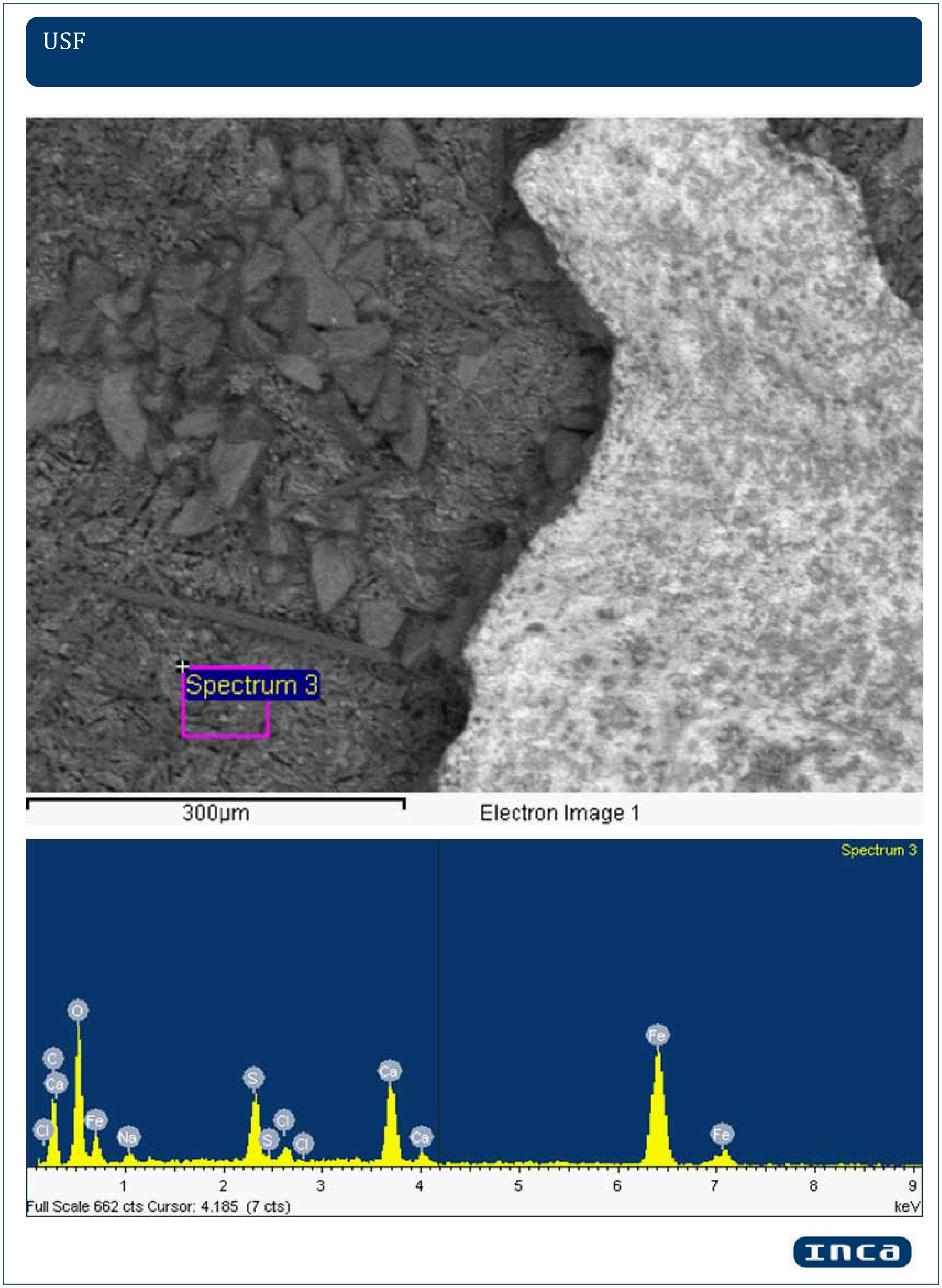


Fig. 33e. Silver coin encrustation with a silver sulfide flake embedded in a matrix of iron sulfide examined by Energy-dispersive X-ray Analysis.

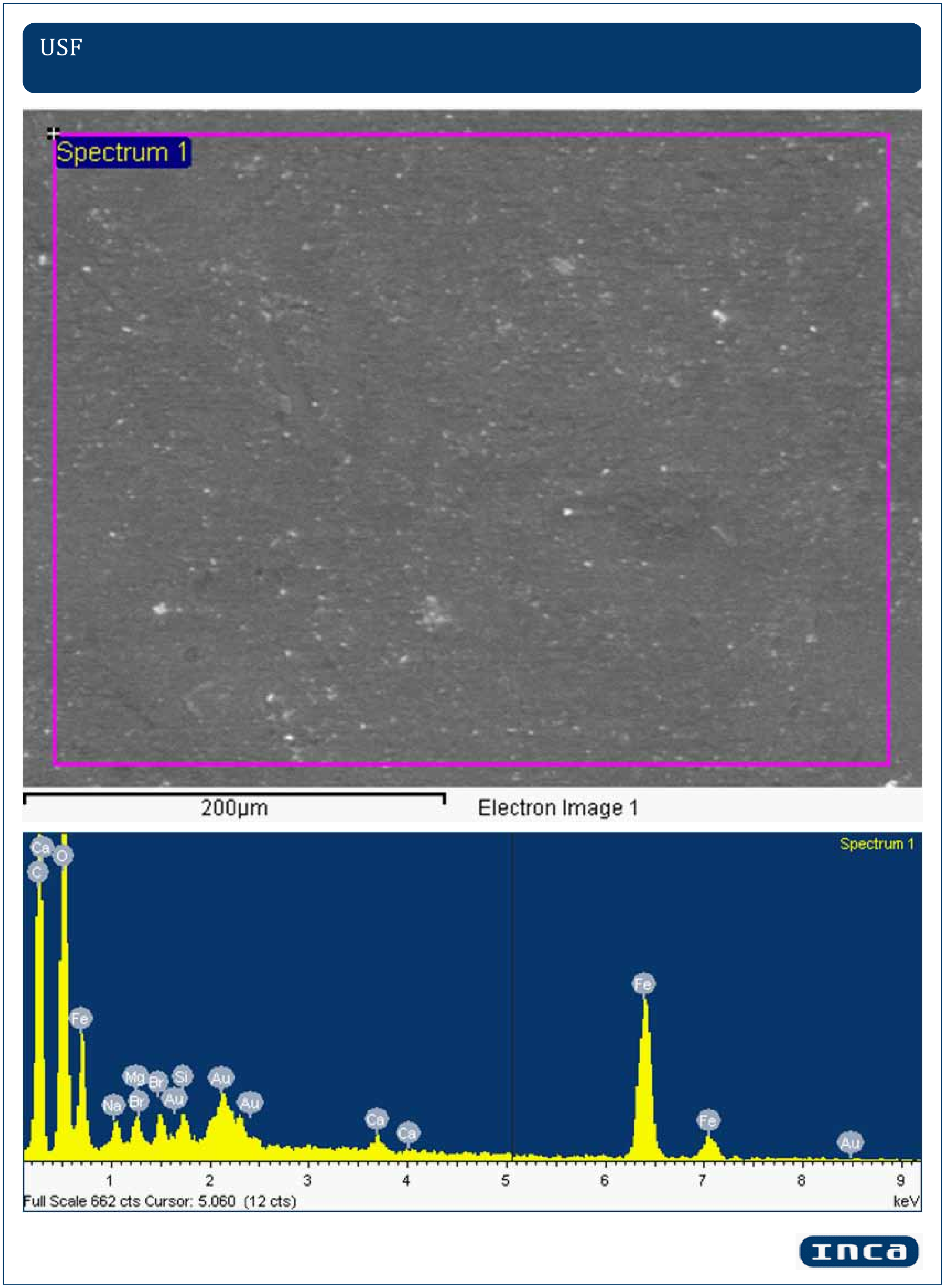


Fig. 34a. Gold and iron sulfide in the inner smooth surface encrustation of a gold coin examined by Energy-dispersive X-ray Analysis.

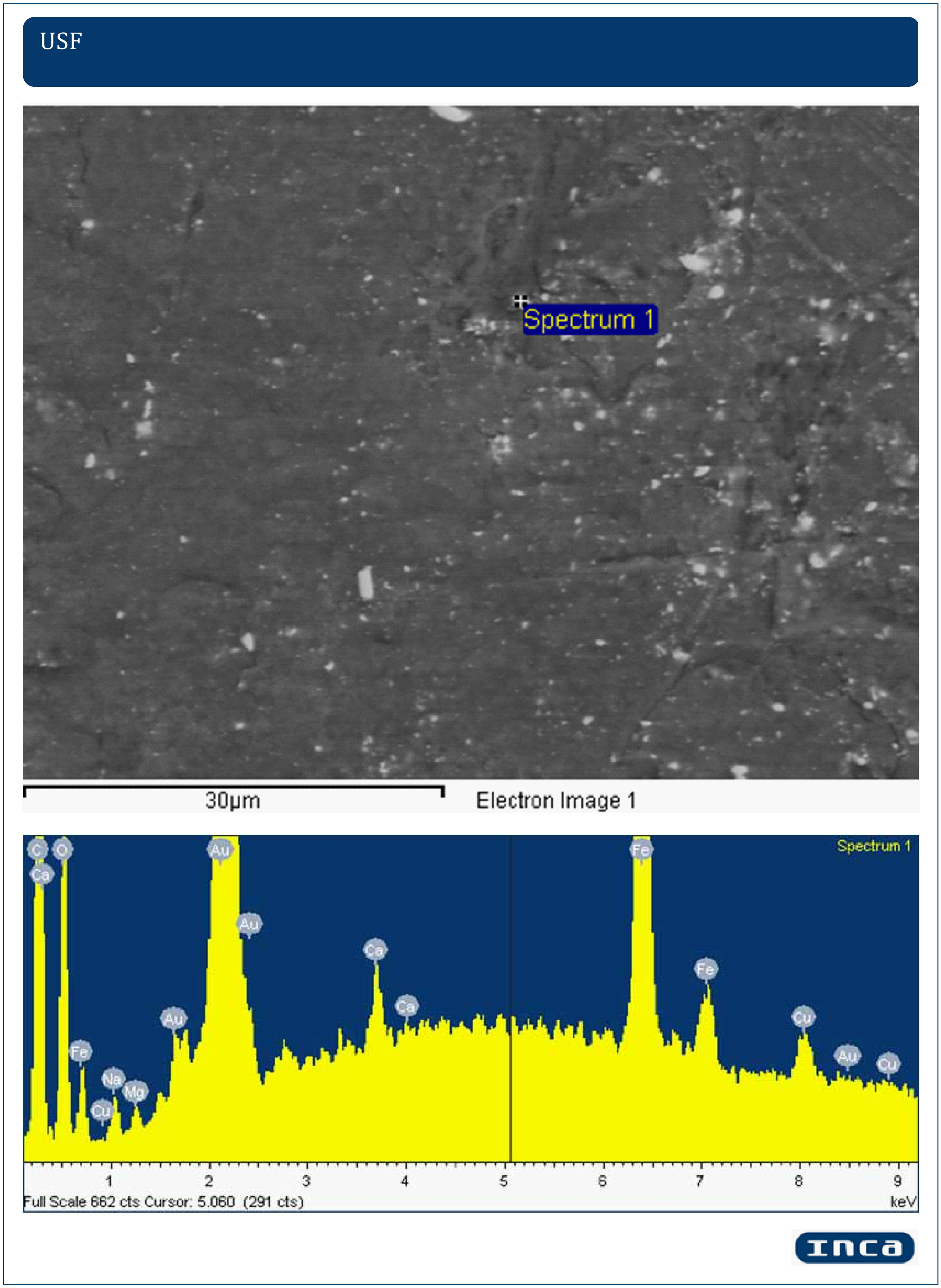


Fig. 34b. Gold and iron sulfide in the inner smooth surface encrustation of a gold coin examined by Energy-dispersive X-ray Analysis.

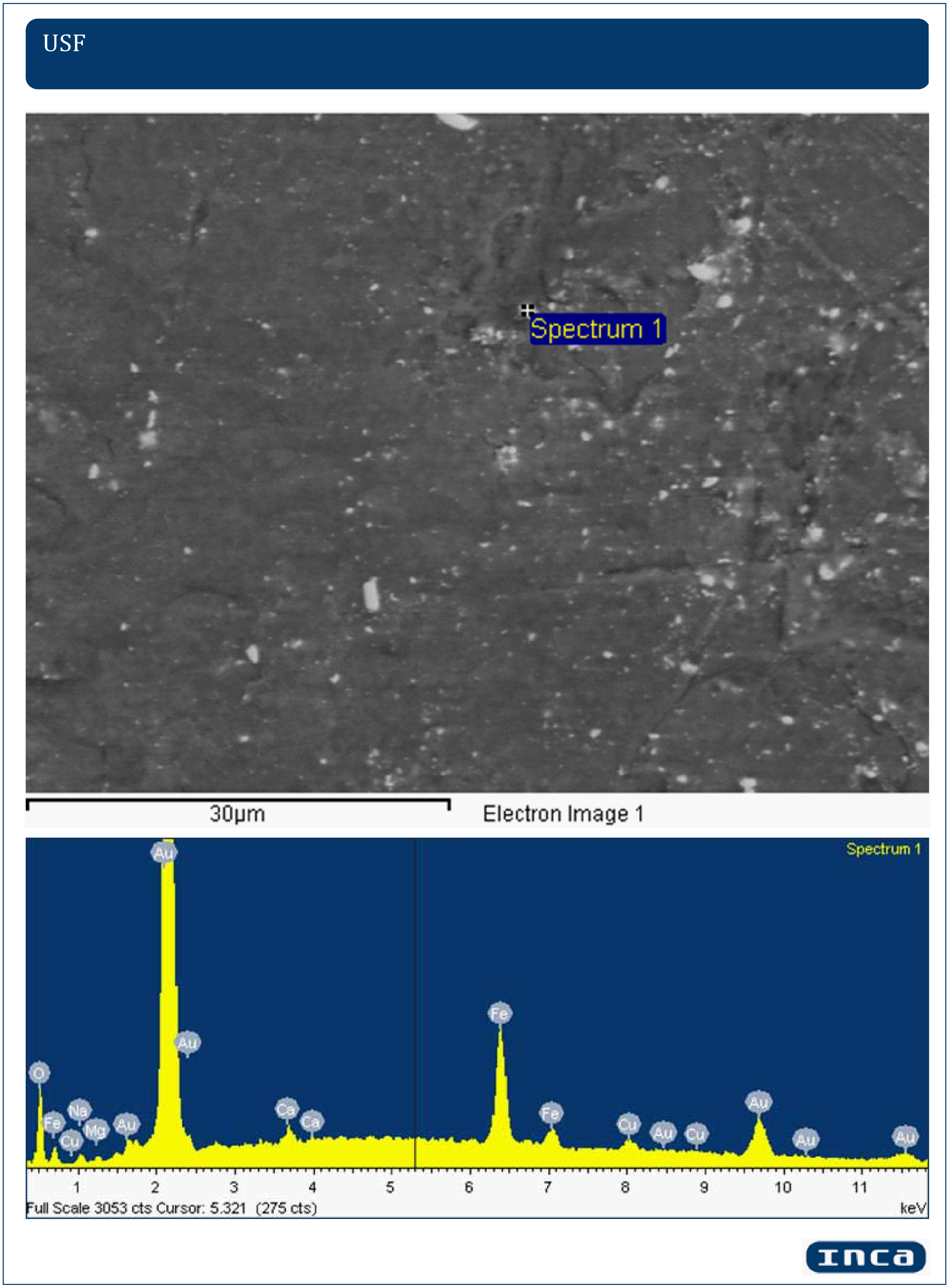


Fig. 34c. Gold and iron sulfide in the inner smooth surface encrustation of a gold coin examined by Energy-dispersive X-ray Analysis.