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Secondary ion mass spectrometry in art and archaeology

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Abstract

The continuous demand for new analytical methods for use in studies of relevance to art and archaeology has prompted researchers to investigate the possible applications of a variety of non-conventional and innovative analytical techniques. Secondary ion mass spectrometry was first used in this field in the 1980s and a number of applications have revealed its potential and limitations in the study of ancient materials. This paper presents an overview of its most relevant applications. Connections to the archaeological field are also discussed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The history of how analytical methods have been used to study archaeological remains and/or artistic objects goes back a long way. Since the 18th century scientists have devoted their attention to a variety of ancient materials with the basic double aim of shedding light on the past and finding ways of protecting such materials from degradation processes [1–3].¹ Since then archaeologists, museum curators, and more recently, conservators and archaeometrists have continued to look for analytical methods which can provide the widest range of information with the minimal degree of damage to the object under study. The balance between these requirements is of the utmost importance when the object under study is of special artistic and/or historical importance.

The last four decades have seen great developments in the availability of new analytical methods which

can be used in the investigation of remnants of the past, thus firmly establishing a fundamental link between science, art and archaeology. A number of analytical techniques have been consolidated as essential tools for the study of ancient materials. Others have clearly demonstrated their potential and their specific fields of application have been defined.

Surface analytical techniques have been used to study ancient materials since the 1970s. In the later years of that decade, Lambert and McLaughlin [4] and Leventhal and Thompson [5] analysed a variety of archaeological materials using X-ray photoelectron spectroscopy (XPS). In 1980, Cline Love et al. [6] used Auger electron spectroscopy (AES) to study ancient gold coins. Secondary ion mass spectrometry (SIMS) was first applied to studies of interest for art and archaeology later in the 1980s.

XPS and AES applications to art and archaeology have been reviewed by Lambert et al. [7] and Spoto and Ciliberto [8]. No further discussion of applications based on these specific techniques will be provided here. The role of SIMS in understanding ancient materials has been recently discussed by Adriaens [9], while Spoto et al. [1] have discussed the advan-

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¹ Brief overviews of the history of scientific examination of ancient material can be found in [1–3].

tages of the spatial resolution which these and other techniques are able to provide.

The many applications of surface analytical methods looked at so far have clearly shown their advantages and limitations in studies of relevance to art and archaeology. Surface sensitivity is severely limited when dealing with weathered or corroded materials. Altering processes modify the surface composition to such a degree that the information obtained may be considered representative of the top few monolayers of the altered surface only. On the other hand, studies aimed at identifying weathering processes in their early stages may greatly benefit from the use of a surface technique. However, surface sensitivity limitations may be partially overcome by using the depth profiles that most surface techniques can provide.

The SIMS is now well established as a surface technique which provides elemental data and a certain degree of molecular information whilst also allowing depth profiling, mapping or imaging to be carried out [10–15].² The wide elemental range that can be investigated (potentially from H to U), its excellent detection limits (in the range of 10^{13} – 10^{16} atoms cm^{-3}) and the quantitative information obtainable when using SIMS are just some of this technique's advantages. The use of time-of-flight (TOF) mass analysers has improved the performance of SIMS in terms of analysed mass range, surface sensitivity and mass resolution. The coupling of the static conditions allowed by the pulsed ion source used in TOF-SIMS with the above mentioned improved performances have expanded the application of SIMS to the study of a variety of organic, polymeric and biological materials [14,15]. Unfortunately, to the best of our knowledge, there are as yet very few applications of TOF-SIMS to the field discussed and no further mention to this technique will be done here. Papers showing the potential of SIMS in the scientific fields of archaeometry and conservation are relatively limited in number, but clearly show its advantages for specific applications. This paper will present an overview of SIMS applications to the general field of interest while

placing special emphasis on aspects of relevance from an archaeometric point of view.

2. Metals and alloys

Metals and alloys are in principle good materials for SIMS analysis. They are highly electrically conductive materials, can easily be handled so as to obtain clean, flat and smooth analyzable surfaces and they are also usually ultra-high-vacuum friendly. However, archaeological and/or artistic metal objects do not always possess all of these properties due to degradation processes which may chemically modify the external surface and deep regions of the samples. Non-conductive patinas and infiltrated compounds may often form as a result of long burial in soil or exposure to the atmosphere and these have very different characteristics compared to those observed for metal materials.

Several metal objects of archaeological and artistic interest have been studied using SIMS. These include gold-plated pre-Columbian copper artifacts [16], antique iron music wires [17], bronze artifacts [18,19] and copper ingots [20].

2.1. Bronze

The production of copper and copper alloy objects evolved alongside technological developments for the extraction of this metal from ores, i.e. smelting, improved metal-working techniques, and lastly, the ability to form alloys [21]. Much of this evolution was a consequence of the metalworkers' ability to find and control processes which allowed them to heat the metal, either in its native state or in ores containing copper compounds, at increasingly high temperatures so as to reach the temperature necessary for the copper to melt (1083°C).

The shaping of native copper was a well-established custom in southwest Asia from around 10,000 BC onwards. This area was by far the most advanced in copper-work technology. Evidence for the smelting of copper-based ores dating back to 7000–6000 BC leads us to suppose that casting skills were already established at this time. (Çatal Hüyük, Anatolia).

The addition of elements other than copper to form alloys with better properties in terms of casting, hardness and appearance may originally have been accidental. Tin was the most important alloying element in

² Basic principles on SIMS will not be provided here. The reader is addressed to further readings for both basic and detailed information on SIMS.

the Old World from 4000 BC onwards, the resulting alloy being bronze.

The corrosion of copper and copper alloys has been studied since the 1800s [22]. Numerous studies have been carried out in order to analyze the formation of corrosion products, the influence of environmental and burial conditions, and the role of various copper-containing compounds resulting from the corrosion process. When exposed to the atmosphere, copper gradually develops a dull red patina which eventually turns a different color. For example, a green patina with malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$) as its main component is formed in most burial environments. The dark layer is mainly made up of cuprite (Cu_2O) but traces of copper hydroxy-sulfate and copper hydroxy-chloride may also develop.

The development of this patina on pure copper and copper alloys was first studied in the early 1930s [23] when the influence of atmosphere composition was established. Since then, the contribution of various pollutants in the development of copper patinas has been studied and various experiments have been performed in an attempt to understand the effect of typical pollutants such as SO_2 and chlorides. Surface sensitive analytical techniques have also been employed to observe the in-depth distribution of relevant elements across the patina profile.

Bronze is susceptible to corrosion processes similar to those seen for copper. Corrosion resistance may even in some cases be reduced. A polished cross-section of an archaeological bronze typically shows that corrosion extends into the metallic matrix along the grain joints [19,24]. This is coupled with a complex distribution of compounds within the copper alloy patina, especially when buried samples are taken into consideration [25,26].

The potential of SIMS in surface analysis and imaging has led to its use in a study of the distribution of S, Cl, Fe and Pb within the matrix of a bronze body-filled bracelet (*armilla*) [19]. The sample was found at the Chiavari Necropolis (Italy) and dated as coming from between the 8th and 6th century BC. The surface of a cross-section of the bracelet was scanned using SIMS to reveal chlorine segregation at the boundaries of the corroded α -bronze grains.

Chlorine preferentially diffuses from the burial environment into the bronze matrix along weakened areas of the grain boundaries as it is shown in the

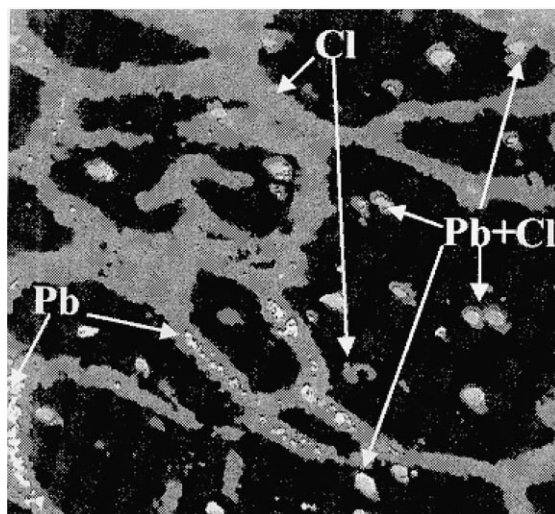


Fig. 1. Secondary ion image showing the $^{208}\text{Pb}^+$ and $^{35}\text{Cl}^-$ distribution within the corroded matrix of a bronze *armilla* dated between 8th and 6th BC. Reproduced with permission from [19].

secondary ion image reported in Fig. 1. Lead chloride inclusions may also contribute to the chlorine enrichment of the grain boundary area.

Bronze corrosion involves the formation of a variety of compounds, a few of these resulting from reactions between the bronze components and external species coming from the burial environment or from the atmosphere. Inclusions left or formed within the copper alloy matrix as a consequence of smelting and/or successive procedures may also contribute to the generation of altering reactions [27,28]. The formation of cuprous chloride (CuCl in the form of nantokite) generates an iterative sequence of reactions causing pits to form in the bronze matrix. This process is also known as *bronze disease* [28,29]. Wouters et al. [18] investigated a section of corroded bronze fragments taken from a middle Bronze Age sword and a late Bronze Age spearhead stored at the Vleeshuis Museum in Antwerp, Belgium (Hasse Collection). SIMS ion micrographs were used together with electron probe microanalysis (EPMA) data to identify pitting corrosion and the composition of the patina.

2.2. Antique music wire

The restoration of the original sound of ancient harpsichords and other wire-strung musical instru-

ments requires the selection of appropriate wire for each string. Ancient documents lack complete information concerning string material. The study of remnants of original material is, therefore, the only reliable way to reproduce original performance. Between the end of the 1500s and the beginning of the 1600s wire-strung instruments were made longer. This change was attributed to the introduction of steel wire since it is a demonstration of the availability of stronger wire to produce the same frequency with a longer string.

Blister steel was first produced at the beginning of the 1600s by introducing carbon into wrought iron. However, in one study the quantitative SIMS analysis of fragments of ancient wire samples dated as being from 1732, 1733 and 1782 unexpectedly showed a phosphorus content in the range of 0.1–0.2 wt.% coupled with a relatively low carbon content (<0.007 wt.%) [17]. The wires were not steel and contained an alloying element that was known to make steel brittle when cold-worked. The researchers' surprise at this result which can be understood if we consider that the presence of phosphorus in iron was discovered only in 1784 and that the earliest documented use of the technique of strengthening iron containing a small amount of carbon with phosphorus, a procedure commonly employed today, dates back no further than the 1800s. Longer music strings were probably a fortuitous discovery, possibly made in Nuremberg in 1601. Sulfur-free iron cleaned of inclusions by means of a special refining method simply made stronger wire. The unintentional combination of this and similar processes ensured a high phosphorus content in a low carbon-containing iron, thus enabling longer wire to be produced.

2.3. *The provenance of copper ingots*

Copper was commonly transported around regions in the European and Mediterranean areas in the form of copper ingots during the late Bronze Age (LBA, roughly between 1600 and 1200 BC). Studies which look at the provenance of copper ingots may, thus, help us to discover ancient trade routes. Most studies of this kind have involved considering the lead isotope data obtained using thermal ionisation mass spectrometry (TIMS) [30]. Adriaens and Adams [20] instead devoted their attention to the $^{78}\text{Se}^-/^{125}\text{Te}^-$ ratios

obtained with SIMS. LBA copper ingot samples taken from Rook Hall in Essex (UK) were analysed in order to calculate their $^{78}\text{Se}^-/^{125}\text{Te}^-$ ratios. Both elements, even at low concentrations (usually lower than 1%), were seen to concentrate in the sulphide inclusions formed in the copper matrix after the smelting process. The $^{78}\text{Se}^-/^{125}\text{Te}^-$ ratios found led the authors to suppose that the ingots contained copper from a variety of sources. It is, thus, possible to surmise that the principle function of such ingots was that of storing this metal as a source of wealth.

2.4. *Tin smelting*

The usual source of tin in antiquity was cassiterite (SnO_2). It was easily smelted using reducing techniques. Tin was mainly used in antiquity to make bronze and very few ancient objects made entirely of tin have been documented. In Egypt, a ring and a pilgrim bottle were discovered in an XVIII dynasty tomb (1580–1350 BC) and a bracelet dating from around 3000 BC was found in the Aegean island of Lesbos [31–33]. Prior to these periods, tin is known only as a component of bronze.

The question of the source of tin during the Aegean and Egyptian periods has opened up a debate between archaeologists [34]. It is currently supposed that tin arrived in those regions from the Erzgebirge mountains which lie between Germany and the Czech Republic. However, this source was certainly not the provider of tin for the southwest Asian region where bronze technology was born. The discovery of ancient tin mines in the Turkish region provided a significant contribution to the understanding of the tin ore source for southwest Asia [35]. The authors deduced that the smelting of tin had taken place in this region by studying a variety of crucibles and slag.

SIMS has also been employed to illustrate how early Bronze Age crucibles (3000–2000 BC) from Göltepe in the southern regions of central Turkey were used to smelt tin [36–39]. Line scans were used to profile the Ca^+ , SiO^+ and Sn^+ signals across sections of fired and unfired crucibles. Tin was observed on the inner surface of the fired crucible samples and was seen to be confined to an area more than 20 μm thick within the silicate matrix that had formed after the smelting of the ore. No tin signal was, instead, observed in the analyses of the unfired

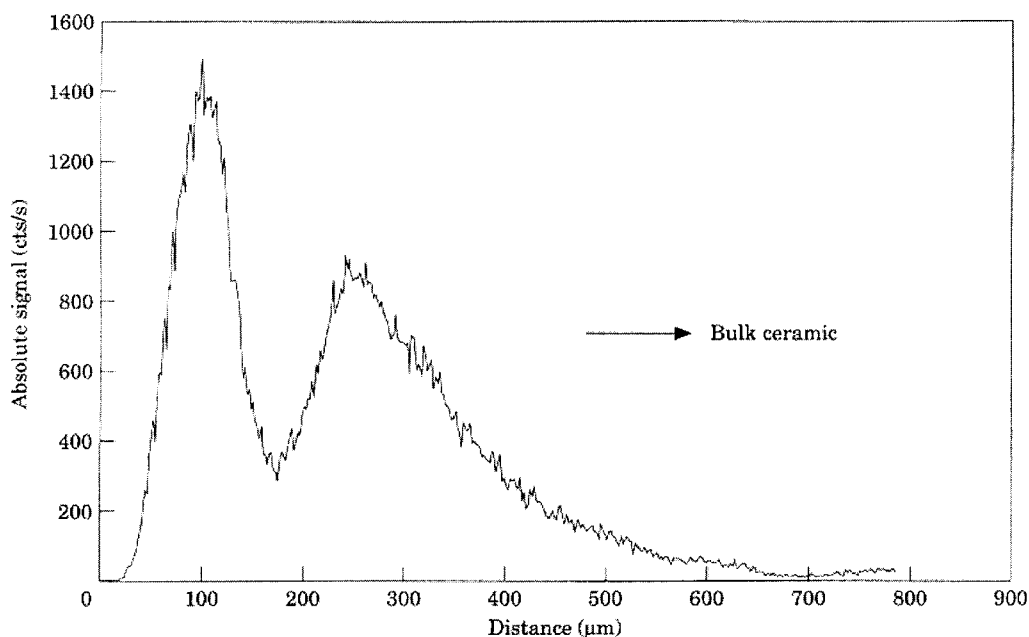


Fig. 2. SIMS line scan obtained from the section of a fired crucible. The intensity of the Sn^+ signal is plotted as a function of the distance. Reproduced with permission from [36].

crucible sections, thus making it possible to exclude the use of tin in the manufacturing of the crucibles themselves. A SIMS line scan carried out across the inner cross-section of a crucible sample (see Fig. 2) showed a double tin peak. The latter might be an indication that the crucible was used more than once.

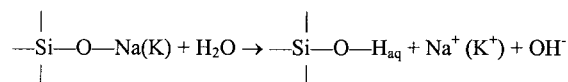
It was, therefore, deduced that crucibles were most likely used for tin smelting, thus further supporting the theory of the Turkish tin ore source.

3. Glass and glassy material

The technological developments necessary for obtaining glass may be linked either to the smelting of metal ores or to the manufacturing of glazed pottery. The earliest known glass materials are supposed as being linked to smelting technology and go back as far as around 2000 BC [40,41]. Glazing technology may, however, have preceded the origin of glass [33]. Mesopotamia was probably the region where glass production was first established but it was in Egypt after 1500 BC during the XVIII dynasty that glass production found its first landmark.

3.1. Glass corrosion

Glass is commonly susceptible to a variety of reactions that affect its durability. Ancient glasses most clearly show the consequences of the relatively limited resistance of this material to attack by water, acid and alkaline aqueous solutions, steam, or atmospheric agents. Long exposure to altering agents worsens the consequences of degradation phenomena which are also seen to affect modern glasses. Glass weathering specifically involves attack by water combined with atmospheric agents. An overview of the chemistry and corrosion processes seen in archaeological finds made of glass can be found in the work of Pollard and Heron [42]. Water corrosion is sparked off by an ion exchange mechanism involving the alkali ions in the glass and hydrogen from the environment. The mechanism may be represented as follows:



The initial phase of attack involves the non-bridging oxygen sites. The hydrogen ions released in the glass

then attack the otherwise stable silica network, converting bridging oxygen sites into non-bridging sites, thus disrupting the glass network. Following this reaction a hydrated layer forms on the surface during the leaching process. Species may also form on the surface of the leached glass as a result of reactions with atmospheric gasses (e.g. CO_2 , SO_2 , NO_x), thus, giving rise to solid crusts made up of salts such as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) or calcite (CaCO_3).

Medieval glass is particularly susceptible to degradation due to its low silica and high potassium content. However, painted medieval glass with a significant lead and phosphorous oxide content shows higher stability.

SIMS has been used to study a variety of Austrian painted medieval window glasses [43–45]. In Schreiner et al.'s experiments depth profile analyses were carried out in order to see how the composition of the leached layer differed from that of the glass bulk (Fig. 3).

The sputtering time scale was converted into a depth scale by measuring the depth of the sputter crater. The alkali depletion layer was estimated as being in the range of 1–1.5 μm thick. A relative sensitivity factor (RSF) method was used for quantitative calculations. The reliability of this method for the SIMS quantification of glass composition was discussed after comparison with measurements obtained using Rutherford

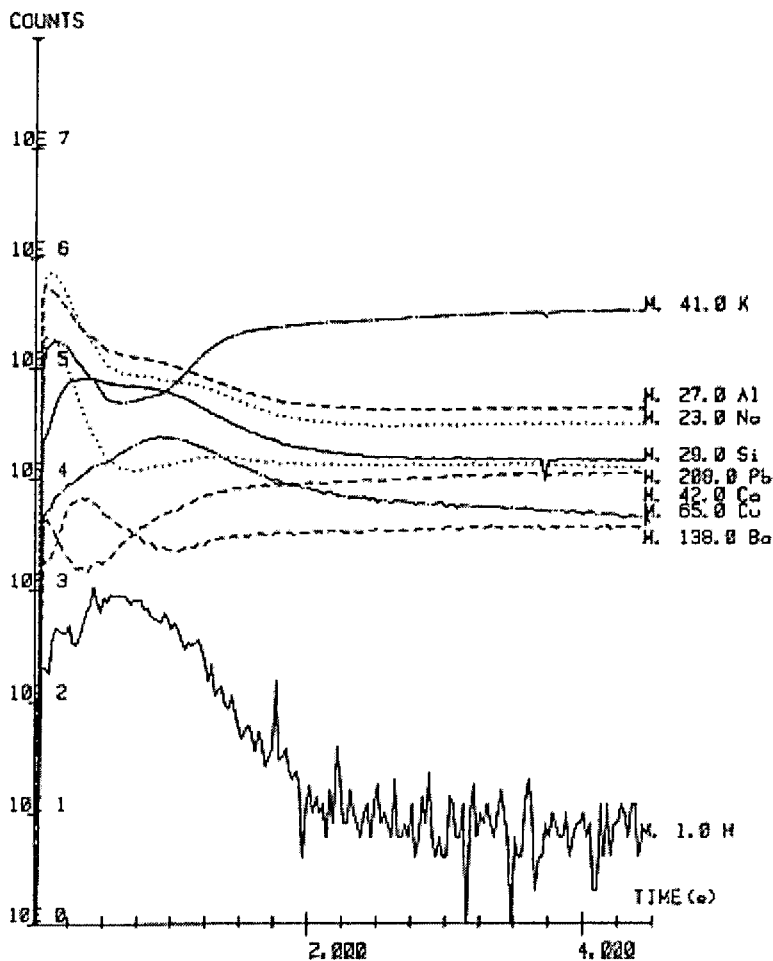


Fig. 3. SIMS depth profile of a medieval Austrian glass. Reproduced with permission from [44].

backscattering spectroscopy (RBS) [46]. While a fairly constant representative bulk composition was revealed beyond the depletion layer, alkali, lead, calcium and barium depletion coupled with silicon enrichment was generally observed in the leached layer. Another of the important features of SIMS, i.e. its ability to detect hydrogen, was also demonstrated by profiling the hydrogen content of the medieval glass. Hydrogen accumulation in the leached layer was confirmed. More recent studies of weathered glass with a composition similar to that of medieval glass have confirmed similar trends by comparing SIMS data with information extracted using atomic force microscopy (AFM) [47–49].

3.2. The smalt case-study

Smalt is a blue coloured pigment obtained by grinding down cobalt-containing glass into a fine powder. It has been used in Europe since 1493 [50]. Its earliest use in Italy is currently believed to have been in Sicily in 1506. In experiments conducted by Ciliberto et al. [51,52] fragments of the blue pigment were extracted from the coloured reliefs of the *lunetta* in the Sicilian Renaissance church of S. Maria la Vetere. X-ray fluorescence (EDX) studies were compared with SIMS analyses carried out on particles of the glassy pigment (average dimensions $50\ \mu\text{m} \times 50\ \mu\text{m} \times 25\ \mu\text{m}$). Both Co and As were revealed to be present in the potash glass. The colouring starting mineral was assumed to belong to the smaltite family (CoAs_3). The presence of As in the glass was presumed to be a consequence of a relatively low temperature and a reduced air stream during the heating of the starting cobalt mineral to produce blue cobalt oxide (zaffera).

3.3. Obsidian

Obsidian is a volcanic glass formed by rapidly cooling lava. The resulting conchoidal fracturing is a feature which led to this material being used for the manufacturing of a variety of stone tools in ancient times. The significant role played by obsidian in the manufacturing of ancient stone artefacts and tools and the wide availability of documented examples are factors which have prompted researchers to optimise the procedures used for dating this glass material in

particular. Most methods investigate the nature and cause of environmentally-induced modifications in the near surface region of the glassy stone.³ A hydration layer, whose thickness depends on how long the obsidian is exposed to the atmosphere, is formed following the diffusion of ambient water through the stone surface. SIMS has also been used in the dating of obsidian by measuring the penetration depth of nitrogen in the hydrated surface [53]. The authors profiled the nitrogen concentration by following the intensity of the $^{28}\text{Si}^{14}\text{N}^-$ signal obtained by bombarding the surface with a Cs^+ primary beam. Procedures were optimised on an obsidian sample implanted with nitrogen. Depth profiles showed different trends from sample to sample but also varied from position to position within the same sample. Having excluded charging and edge effects checkerboard ion images were acquired during depth profiling. These images provided a $16\ \text{pixel} \times 16\ \text{pixel}$ view of the analysed area. Each individual pixel is recorded during each scanned frame. By combining all of the measured frames it was possible to construct the 3D ion image of the area investigated shown in Fig. 4. Slices taken at specific x or y values show the lateral variation of the nitrogen penetration depth.

The combined images showed that nitrogen was mainly confined to pits with diameters ranging from 40 to $120\ \mu\text{m}$. The presence of pits introduced artefacts in the SIMS depth profile analysis. Profiles of this kind were, thus, excluded as a source for dating obsidian due to the non-uniform distribution of the nitrogen in the obsidian matrix.

4. Human residues

The study of human remains plays a significant role in the scientific study of our past. Body residues provide information about diet and lifestyle and remains themselves can be dated by looking at diagenetic modifications due to interaction with the burial environment. An example of a method established for dating human remains consists quantifying the racemization of amino acids present in the collagen component of human parts such as bone and tooth enamel [42]. Electron spin resonance (ESR) is also an estab-

³ A wider discussion on obsidian can be found in [42].

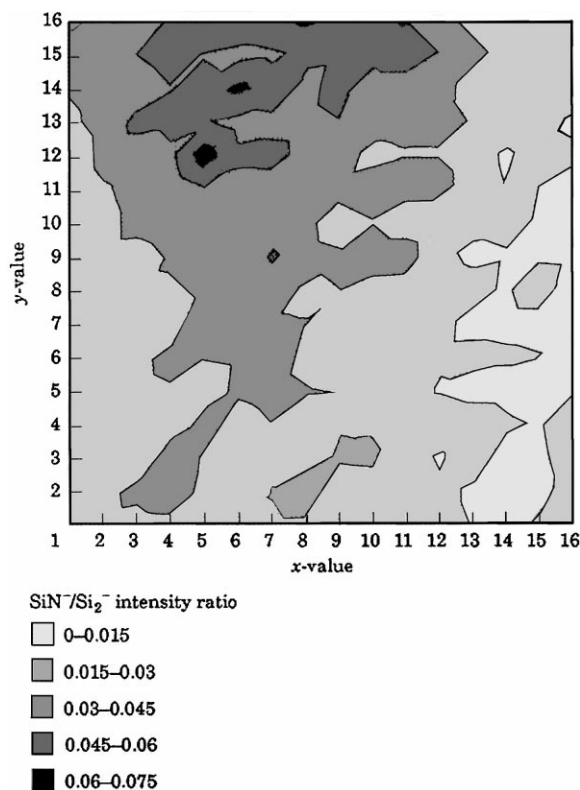


Fig. 4. A checkerboard ion image of the $\text{SiN}^-/\text{Si}_2^-$ ratio obtained from an obsidian surface. Reproduced with permission from [53].

lished technique for dating tooth enamel [54]. The principal inorganic components of both bones and teeth are based on the structure of hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$). The mineral phases are poorly crystallised and relatively un-stoichiometric compared with the hydroxyapatite formula [55–57]. Hydroxyapatite-based mineral phases are highly susceptible to substitutions [58]. Carbonate groups may be seen to replace phosphate units, while F^- ions may substitute OH^- groups, thus, rendering the resulting mineral phase less soluble. Other ions such as Ba^{2+} or Sr^{2+} may substitute Ca^{2+} ions. As a result of substitutions such as these a variety of inorganic species are “fixed” in the inorganic components of human remains. Some of these modifications follow a time dependent law.

Using SIMS a variety of elements such as Mg, C, F, Ba, and Pb, were line-scanned across sections of a variety of archaeological tooth material coming from sites in Greece, Israel and Cyprus [59,60]. SIMS line

scans were compared with those obtained from freshly extracted tooth. Systematic differences were observed between the distribution of elements such as Mg, F, Ba, Pb. In particular, F was absorbed by both the enamel and dentine regions of the tooth. The amount absorbed in the inner enamel region was apparently dependent on burial time. Other elements such as Li, Sr, Ba, Si, and Zn were also absorbed in both the enamel and dentine regions. Both Pb and Sn were preferentially absorbed in the internal enamel region alone while B was seen to have been absorbed in the central dentine region. The lower amount of Mg observed in the archaeological samples in comparison with modern teeth suggested that this element had leached out. Elements such as Na and Cl were instead seen to be almost unaffected by burial time. When considering the F concentration in six differently dated teeth, the plateau concentration of this element in the internal enamel region was also seen to vary in accordance with Fick’s law.

A bluish-black discoloration which cannot be scraped off often affects the crowns of archaeological teeth. Its origin has been discussed with regard to understanding its possible correlation with oral habits during lifetime. In order to find an answer to this question sections of crowns of teeth from 51 skulls found in the medieval church of St. Olav in Trondheim, Norway, were line-scanned using SIMS [61]. Manganese, barium and strontium were seen to be correlated with discoloration patterns. However, manganese oxides were most likely specifically responsible for the bluish-black discoloration of the crowns due to the widespread presence of the two main manganese ores (pyrolusite and psilomelane) in the soil. The in terra staining theory was, thus supported by the SIMS findings.

Uranium is also absorbed by buried fossil bones and teeth from the surrounding soil. This uranium uptake has been seen as a problem since it clearly interferes with ESR annual dose rate evaluation [54]. Grün et al. [62] proposed a one-parameter equation to describe uranium accumulation in tooth enamel as follows:

$$U(t) = U_m \left(\frac{t}{T} \right)^{p+1} \quad (1)$$

where $U(t)$ is the uranium concentration at time t , U_m the measured uranium concentration, T the age, and p the diffusion parameter. SIMS was also used to study

the distribution of U within 14 different fossil bones and teeth samples [63]. A semi-quantitative calculation amount of U showed concentrations ranging from 4.5 ± 1.1 to 1300 ± 260 ppm. The uranium concentration differed from sample to sample and was presumed to be time dependent. Uranium was also found to be unevenly distributed within the fossil.

5. Conclusions

The continuous demand for new and up-to-date analytical techniques for applications in studies of interest for art and archaeology constantly requires new efforts. So far SIMS has not been used as widely as other more conventional analytical techniques. Nevertheless, the applications made to date have clearly demonstrated the advantages that this technique can provide in the study of our past. The high level of elemental sensitivity and the imaging and depth profile potential of SIMS have already resulted in a certain number of questions being solved and this technique promises to continue to be of use for a long time to come.

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