A combined XPS-SEM/EDX investigation on explanted UHMW polyethylene acetabular cups: possible role of silicon traces in the wear debris

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An investigation was started aimed at a better understanding of the complex phenomena leading to chemical degradation and morphological deterioration of UHMW polyethylene cups in total hip prostheses. Analysis was performed on retrieved implants which needed revision due to inflammation and pain problems. Preliminary results obtained by parallel XPS and SEM/EDX experiments gave evidence, for the first time, that silicon traces are involved in the process of particle formation and segregation onto the surface of the cups. The extent of modification of the surface chemical composition of cups and the process of particle segregation seem to be correlated to both the implant time and to some particular features of patient (age, activity, style of life, etc.). Investigation on a large number of samples is in progress in order to test this hypothesis. The results obtained so far confirmed the potential of surface spectroscopies (XPS) in biomaterial investigations.

1. Introduction

Osteolysis can occur around loose, as well as well fixed, cemented or cementless acetabular components in total hip arthroplasty. Histologic studies of tissues biopsied from osteolytic regions suggest an adverse foreign body response to polyethylene and other particulate debris from prosthetic materials. Phagocytosis of these particles by macrophages and giant cells stimulates the production of proteolytic enzymes and inflammatory mediators, all leading to tissue destruction. Anyway, this process occurs when the particle size is smaller than 10 μm [1–4]. The importance of polyethylene wear debris is now fully appreciated, and it is clear that this is the major source of particulate debris. Many studies are devoted to acquiring a deeper knowledge about the influence of polyethylene wear debris in relation to osteolysis and loosening. Several clinical studies [5–8] have shown a cause-effect relationship of polyethylene wear debris, found in the adjacent tissues, and failure of the implant.

Black *et al.* [1] have illustrated that in a clinical case involving cemented total hip prostheses made of titanium-based alloy and ultra high molecular weight polyethylene (UHMWPE), corrosion and wear debris were associated with pain and a need for revision, even though the prosthesis was seemingly well-fixed. The authors concluded that wear debris alone can produce clinically important pain.

Hailey *et al.* [9] have pointed out that the roughening of the femoral components is of major clinical significance in relation to osteolysis and loosening due to the greater numbers of sub-micron-sized particles formed.

Polyethylene wear debris are particularly harmful for the cementless prostheses [10, 11] and their quantity is proportional to the femoral component size [12], but it is not connected with its material [13]. Moreover, the number of wear particles greatly increases when other particles, metallic or non-metallic, were embedded in the bearing surface causing third-body wear [11].

In our laboratory a systematic investigation has been started, devoted to evaluate, by means of spectroscopic techniques, the degradation of concave surfaces of retrieved cups, implanted for different periods of time, on patients of different age, in order to get additional information on the mechanism of debris formation. Both X-ray photoelectron spectroscopy (XPS), whose potential in the chemical analysis of polymeric biomaterials surfaces has been already exploited by our group [14], and scanning electron microscopy/ energy dispersive X-ray analysis (SEM/EDX) have been used to examine UHMWPE acetabular cups taken from patients who underwent, after various implant times, revision operations for failed total hip replacements. Preliminary XPS results reported in this paper showed two main features:

the presence of oxygenated functionalities in the C 1s high-resolution spectra and of silicon species. In particular, the signal intensity of the latter (evaluated as Si/C peak area ratio) was found to be inversely correlated to the patient age, at the same time of implant, and directly correlated to the implant time when old-aged patients were considered. Moreover, SEM/EDX analysis of the same concave surfaces analyzed by XPS showed an increase in surface roughness with the extent of chemical degradation and the presence of sub-micron particles to which a silicon signal is associated.

Twelve samples have been analyzed at this first stage of the work; the results obtained, although preliminary, are encouraging and give an indication of some reasonable trends. A statistically significant number of samples of course are being collected and will be analyzed in order to test the hypothesis that silicon traces may be in some way responsible, beside other factors, for the debris formation from acetabular polyethylene cups. A possible correlation between this phenomenon and factors such as implant time, patient age and life-style will be investigated.

2. Materials and methods

2.1. Materials

Twelve acetabular cups retrieved from patients whose hip prostheses were revised after various implant times, were examined. Table I lists age of patient and length of implantation time. All the acetabular cups were made of UHMWPE and all the femoral stem and head were of cobalt-chrome alloy. In order to perform XPS and SEM/EDX analysis pieces were cut from the concave surface of the cups $(1\,\text{cm} \times 1\,\text{cm}$ size) and were throughly cleaned with ethyl ether and then dried with a nitrogen stream. For each cup a blank sample was obtained from the inner part bulk of the cup, which had never been in contact with the femoral head (Blank Y). Moreover, a virgin cup was used to obtain a blank sample of the concave surface (Blank W). A visual inspection of the as-received cups revealed that the inner concave surfaces of the retrieved specimens were wrinkled and pale-yellow colored.

Sample preparation was of particular concern as a critical step with respect to possible sample contamination. A stainless steel cutting-saw was used to prepare samples. The cleanliness of the procedure was tested on standard polyethylene foils: silicon signals could be never detected by XPS/SEM analysis.

TABLE I Acetabular cup data

Cups	Patient age (years)	Duration of implant (years)	Si/C*
A	35	7	0.064
B	41	3	0.014
C	34	4	0.013
D	69	1	0.020
E	74	7	0.004
F	59	7	0.021
G	73	8	0.004
H	66	12	0.011
I	76	13	0.015
L	68	13	0.019
M	76	15	0.025
N	73	16	0.012
Blank W			0.005
Blank Y			absent (< detection limits)

Blank W: concave surface of a virgin cup.
Blank Y: sample obtained by cutting a piece of the internal bulk of the cup.
*A standard deviation of 10% has to be considered, as a typical figure for quantitative analysis in XPS.

2.2. XPS analysis

The XPS spectra were obtained using a Leybold LHS10 spectrometer equipped with a twin anode (MgKα/AlKα) source. Wide-scan (0–1500 eV, fixed retard ratio (FRR) mode, retarding ratio = 3) and high-resolution spectra (fixed analyzer transmission (FAT), pass energy = 50 eV) were recorded. Data analysis of high-resolution spectra was performed using two software packages, both running on a Compaq Deskpro 386. The first one [15] was employed in the preliminary stage of analysis, consisting of radiation satellite and non-linear background subtraction, peak area calculations and curve synthesis using Gaussian-Lorentzian peaks defined by the following parameters: centroid position, half-width at half maximum, peak height and Gaussian-Lorentzian ratio (0.85).

The outputs of this stage were used as initial estimates of peak parameters in the second software package, a non-linear least-squares fitting program [16].

Quantitation was performed by using peak areas, which were divided by empirically derived atomic sensitivity factors (uncertainty for atomic ratio around 10%) [16] to evaluate the ratios between species of different elements.

The correction for sample charging was accomplished by choosing the main component in the C 1s spectrum as a binding energy reference (284.8 eV).

2.3. SEM examination

SEM analysis was performed with a Leica Cambridge. Stereoscan 440 microscope equipped with an energy dispersive X-ray detector (EDXS) and a Link Analytical QX–2000 system for X-ray microanalysis. Two sets of samples were prepared and glued onto aluminum stubs. One set was sputter-coated with gold to observe the surface morphology and the other was carbon coated for chemical analysis. Samples were examined at 5–7 keV and 15 keV for morphology and chemistry, respectively.

3. Results and discussion

3.1. XPS analysis

Fig. 1a shows the XPS wide scan recorded on sample A, the most spoiled cup, compared with that recorded on the surface of the Blank Y (Fig. 1b) obtained from the internal part of the same cup that was never in contact with the femoral head. It can be seen that the most significant difference consists in the presence, in the 1a

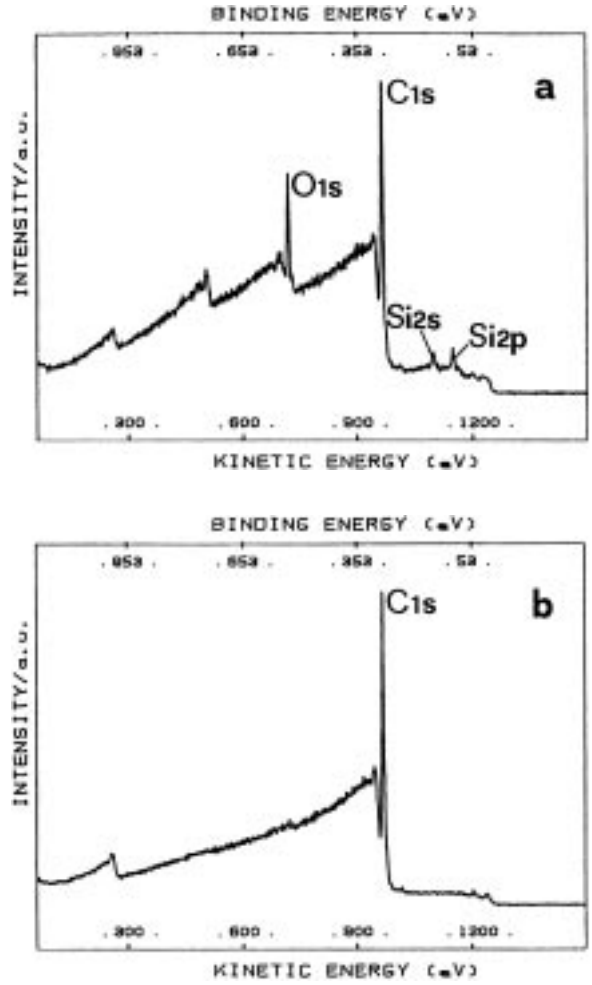

Figure 1 XPS wide-scan spectra recorded on: (a) the concave surface of the sample A; (b) Blank Y.

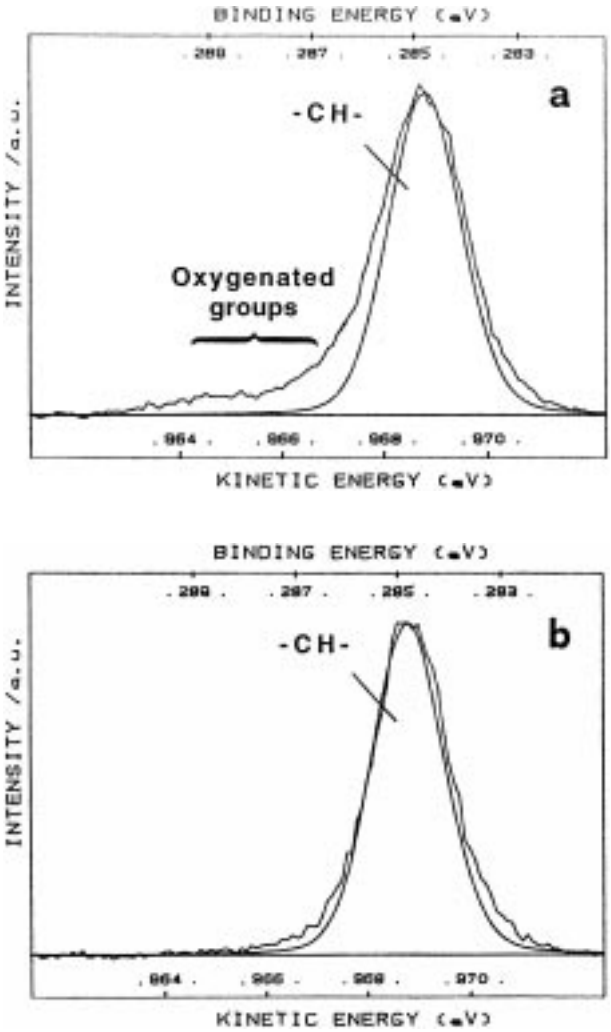

Figure 2 XPS high-resolution spectra of the C 1s region recorded on: (a) the concave surface of the sample A; (b) Blank Y.

spectrum, of oxygen and silicon peaks in addition to the expected carbon peak.

The high-resolution scans of the C 1s region recorded on these samples are presented in Fig. 2. Oxygenated functionalities (C=O, C-O) are clearly evident in Fig. 2a while these are absent in the spectrum 2b, recorded on the Blank Y, which only showed a signal due to polyethylene -CH_2-. The presence of oxygenated functionalities is indicative of an oxidative degradation of the surface chemical composition.

The high-resolution scans of the Si2p region are reported in Fig. 3. It is important to point out that the silicon peak is detected at a binding energy (BE) value (ca 102.3 ± 0.3 eV) that is typical of a silicone-like compound. Parallel analysis performed on the other samples listed in Table I showed the same features. The amount of silicon, reported in the last column of the table, was evaluated as peak area ratio Si2p/C 1s, in order to compare data unaffected from differences in the sampled areas. A standard deviation of 10% has been reported as a typical figure for quantitative analysis in XPS. It is interesting to note that, at the same implant time, the intensity of silicon signal is higher in younger patients; on the other hand, it increases on increasing implant time in old-aged patients.

The silicon could originate either from the femoral head made of a Co-Cr-Mo alloy that contains silicon as impurity (< 1%) or from surface segregation of silicon species impurities introduced by peculiar treatments (abrasive paste) used for the smoothing of the concave surface of the cup. It must be pointed out, to this respect, that the XPS analysis of the Blank W (concave surface of a virgin cup) indicates the presence of silicon traces.

3.2. SEM/EDX analysis

The same samples analyzed by XPS were submitted to SEM/EDX investigation.

The bearing surface morphology of the Blank W sample (concave surface of a virgin cup) was rather heterogeneous, with smooth and rough areas adjacent to each other (Fig. 4). It was interesting to note the leaf-shape appearance of the rough zones attributable either to the manufacture technology or pre-implantation treatments. The concave surface of the most spoiled cup (sample A) showed a higher extent of surface roughness (Fig. 5): it showed numerous thin polymer sheets with notched edges, arranged in sheet sequences (series) with almost the same orientation. The presence of surface

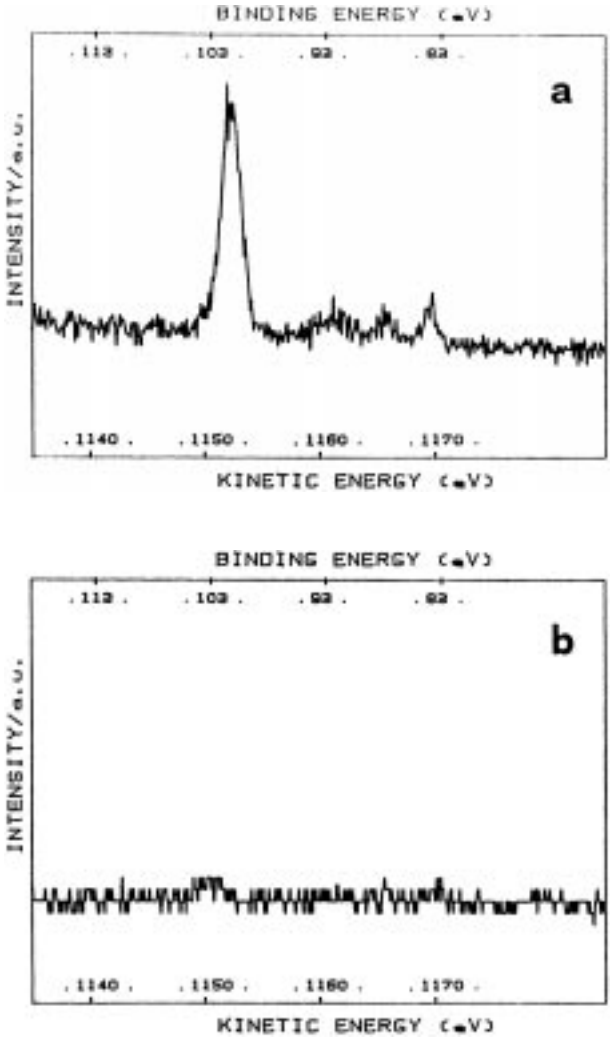

Figure 3 XPS high-resolution spectra of the Si2p region recorded on: (a) the concave surface of the sample A; (b) Blank Y.

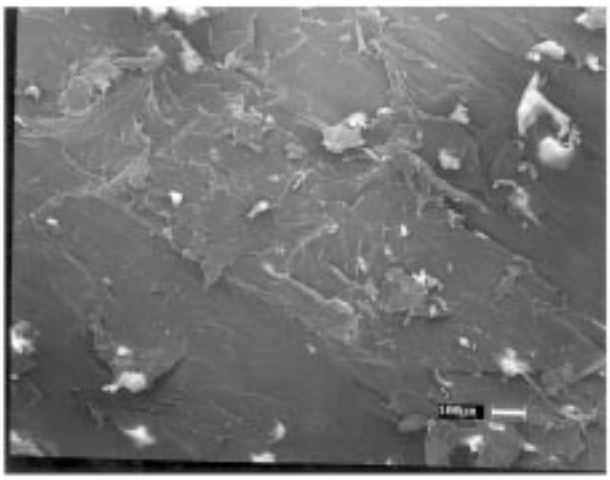

Figure 4 SEM analysis of the concave surface of a virgin cup (Blank W).

cracking often accompanied the above morphology. The shape of the polymer sheet edges suggested that small polymer particles might have been detached from the surface of the cup.

Sample I did not show a significant increase in surface roughness compared to the blank W sample; other types of morphological changes were observed, such as

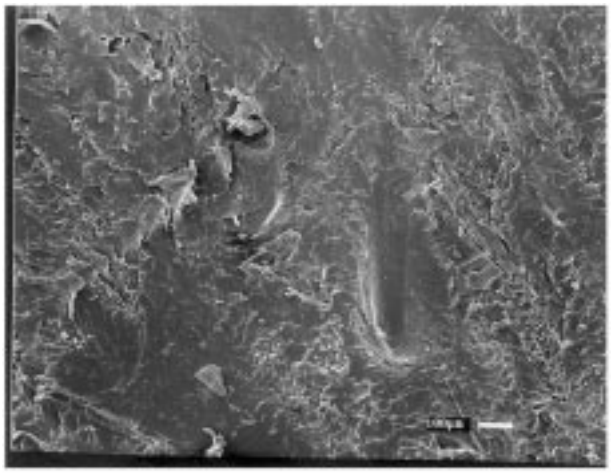

Figure 5 SEM analysis of the concave surface of the most spoiled cup (sample A).

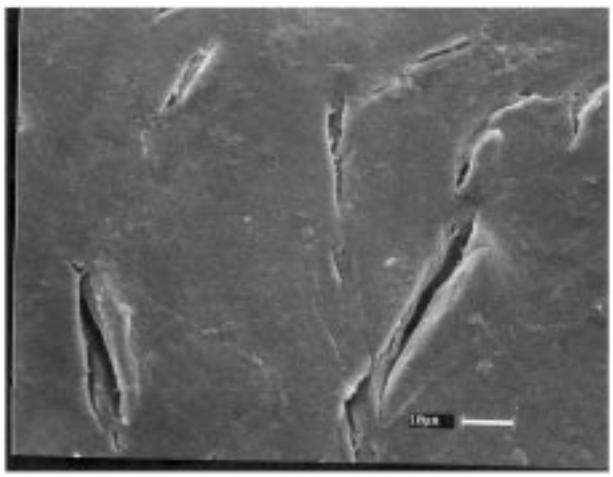

Figure 6 SEM analysis of the concave surface of sample 1.

superficial cracking (Fig. 6) and wave shape deformations.

By means of SEM/EDX analysis it has been possible to demonstrate that the Si signal (already evidenced by XPS analysis) was always associated with various particles present on the surface of the retrieved cups, while the bulk of the cups gave negative response.

Fig. 7 shows an example of Si-positive particle (see Fig. 8 spectrum (b) for the chemical analysis). The Si signal coincided with the globe-shape part of the particle (Fig. 7, see arrow). Positive response for Ca (see Fig. 8 spectrum (a)), as well as for other minor elements, was often detected.

4. Conclusions

XPS and SEM/EDX were used to examine the chemical and morphological status of the concave surface of retrieved femoral cups.

The comparison between XPS and SEM/EDX results suggested that some correlation existed between surface chemical composition and degradation and morphological deterioration. The latter was clearly associated with the presence of particles on which silicon was detected. Moreover, it was found that, as a general trend, the more

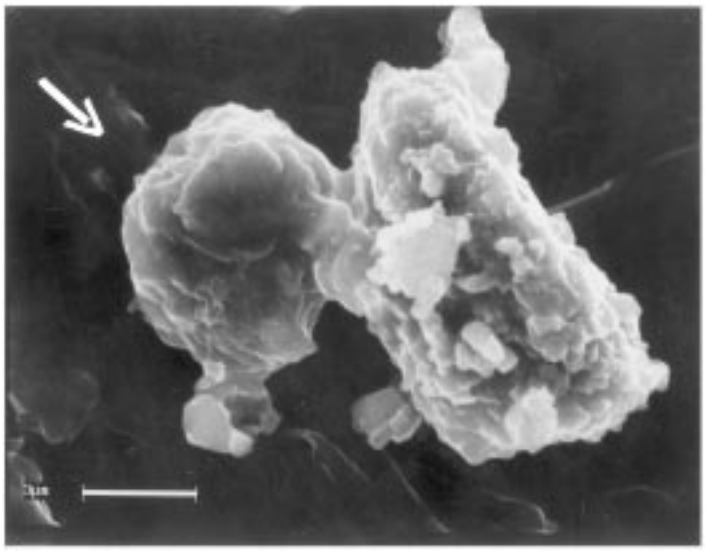

Figure 7 Example of a Si-positive particle (indicated by arrow).

intense the yellow color of the cup surfaces, the higher the amount of oxygen containing groups present on the polymer surface.

Interesting trends have been observed between the amount of silicon, the age of patient (which, in turn, reflects life-style) and implant time. In older patients, the silicon content increased with increased implant times. In the case of younger patients, higher silicon amounts were

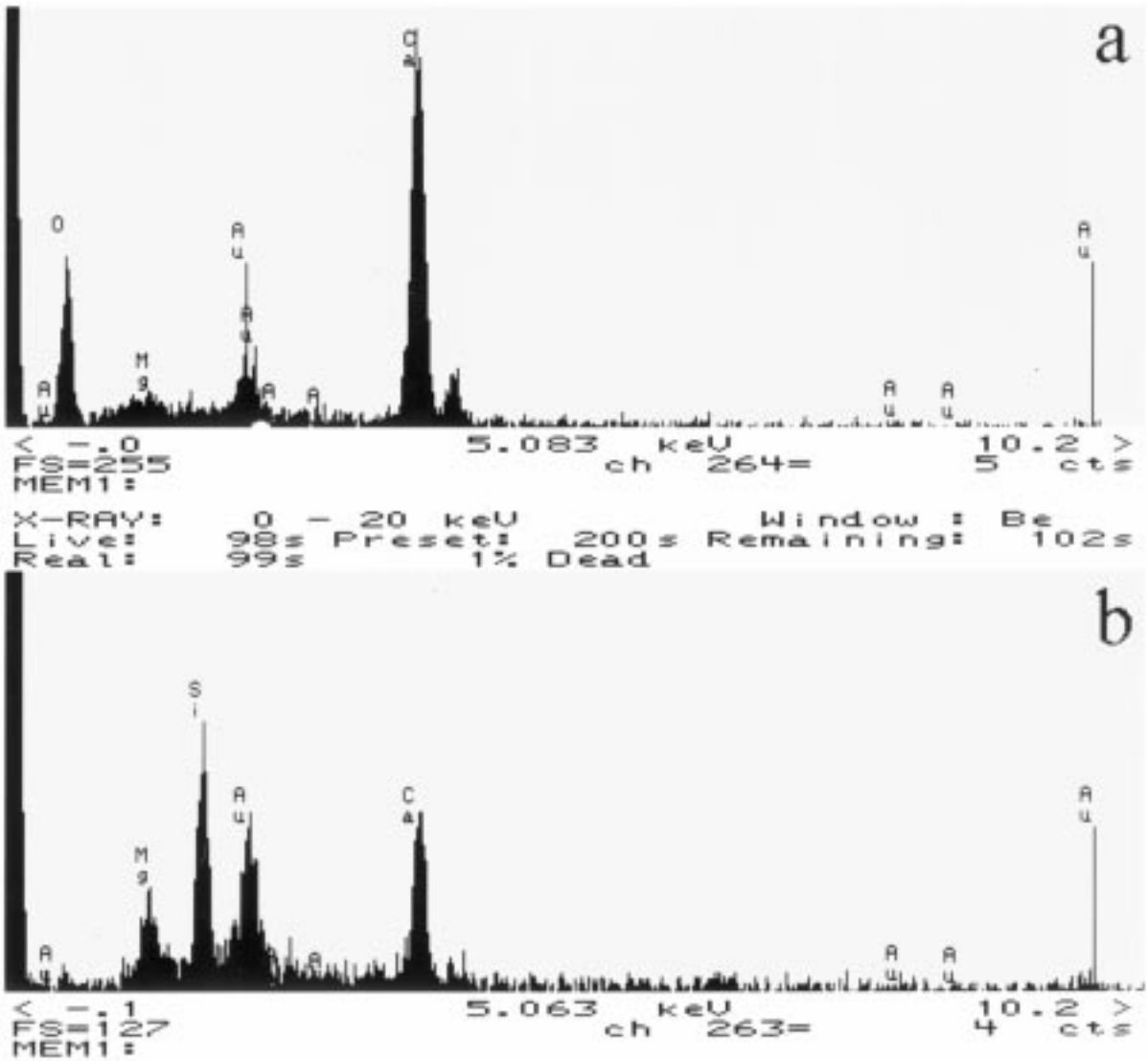

Figure 8 SEM/EDX spectra for: (a) a Ca-positive particle; (b) a Si-positive particle (shown in Fig. 7).

present after only two-three years of implantation. This faster degradation could probably be due to the more active life-style of young and healthy men compared to older patients. As a further support to this trend the maximum value of silicon was found on the sample which was implanted for a relatively long time (7 years) on a young patient. These particles could break off from the concave surface of the cup promoting a negative response of the close tissues.

The results seem to be encouraging; work is in progress to confirm and support by a statistically significant number of examinations the observed trends between wear, host patient activity/implantation time, surface composition and morphology.

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