Effects of the substrate on ToF-SIMS spectra of thin films of some fluorinated compounds deposited on calcarenite

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ABSTRACT

In this contribution we report on a Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) study of some fluorinated compounds that are possible candidates as protectives for stone artefacts.

Specimens of finely polished calcarenite stone were treated with diluted solutions of different fluorinated compounds of Zonyl™ family (DuPont) and analysed by ToF-SIMS. The results are compared with those obtained on gold surfaces treated with the same compounds.

The spectra of the compounds deposited on the calcarenite substrate display a more rapid decrease of the peak intensities with mass, compared with those obtained from the same compounds on gold, at least in the case of four (FSA, FSP, 9361, 9027) of the five compounds considered in this study. In fact, the overall dependence of ion intensities along the mass range for one of the investigated sample (Zonyl 8740) was not strongly affected by the substrate (gold or calcarenite). Moreover, the spectra of this compound on gold or calcarenite display very similar fragmentation patterns, especially the negative ones. On the contrary, the other substances deposited on calcarenite (particularly FSP, 9361 and 9027) show fragmentation patterns that significantly differ from those obtained on the gold substrates.

A detailed discussion of the fragmentation patterns will be given and the different (or similar) behaviour of the investigated compounds on the different surfaces will be interpreted in terms of interaction of some functional groups present in these compounds (phosphate, carboxylic, sulphate) with the calcium carbonate (calcarenite) surface, that strongly influence the fragmentation pattern. This interpretation is supported also by the results obtained on the calcarenite deposited samples by means of X-ray Photoelectron Spectroscopy.

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1. Introduction

In the evaluation of compounds intended to be used as protectives for surfaces (stone, marble, metals, etc.) it is important to follow the chemical modifications occurring due to interactions of these products with both the environment and the surface of the covered material. In order to gain a deeper insight on this complex phenomenology, the acquisition of detailed information on the composition of the surfaces, better if spatially resolved, is an important issue.

Among the analytical techniques giving useful information on the chemical composition of a solid surface, Secondary Ion Mass Spectrometry (SIMS) plays a very important role. This is due to its uncommon ability to provide spatially resolved chemical information with lateral resolution in the sub-micron range and with in-depth resolution in the nanometer range, joined with the high sensitivity typical of mass spectrometry techniques. Recently, the introduction of cluster ion primary beams has further increased the sensitivity of the technique, with detection limits located close to the femtomole, and still maintaining a spatial resolution of the order of 100 nm.

From the point of view of quantification, a drawback of the technique is that a change in secondary ion yield does not necessarily reflect an analogous change of the surface composition but, rather, a change in ionisation probability due to a different chemical environment (matrix effect). In the most unfavourable cases a matrix change can cause an increase (or decrease) of several orders of magnitude in the ion yield of a particular species and this can make difficult or even prevent a reliable quantification of SIMS data. In the particular instance of studies concerning surface treatments of artefacts, aimed to their preservation, it is important to monitor possible surface composition changes caused, for instance, by surface chemical reactions and/or physical rearrangements. Such changes can be masked by the matrix effect. In these studies, it is important to acquire information on the effects of the treatment, such as reactions/interactions of the protective compound with the substrate, possible degradation/ageing of the protecting agent due to the exposure to adverse external environment and so on. In order
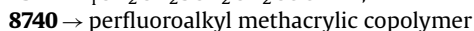
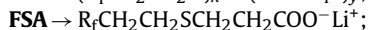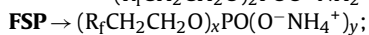to get benefit of the advantages of SIMS technique in this kind of studies, it is mandatory to be able to discriminate between ion yield changes caused by "real" effects such as those above described, from the intensity changes merely due to bare matrix effects.

In this work, we used Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) for studying thin films of oligomeric compounds – possible candidates as stone protectives – deposited on a real world substrate, a calcarenite stone. The same compounds deposited on a flat gold surface were used for comparison. ToF-SIMS is well known for its ability to supply rich chemical information from surfaces, basically due to the high transmission of ToF analyser that allows to minimise ion beam induced surface damage, so preserving the molecular information [1]. The investigated compounds pertain to Zonyl^{TM} family (DuPont) and all of them contain perfluorinated chains. The presence of a perfluoroalkyl chain is believed to cause a reduction of the surface free energy thus preventing water adsorption [2]. Indeed, the degradation phenomena of a stone are mostly due to pollutants and or/acid substances driven by atmospheric rain water; so reducing the moisture adsorption on the stone, by increasing the hydrorepellence of the surface, is the common practice in conservation science. On this respect, we have already evaluated the possibility of the use of these compounds as stone protectives (repellents) against the uptake and penetration of water and of water soluble pollutants [3]. We have also investigated, by means of XPS, the surface composition of Zonyl films deposited on calcarenite before [4] and after [5] an ageing treatment and shown the usefulness of ToF-SIMS in the study of films of these compounds on model gold surfaces [3,6]. However, the results obtained from these ToF-SIMS mass spectra are not in a complete agreement with those obtained from XPS spectra recorded from the same compounds deposited on calcarenite. It should be remarked, however, that these two techniques have different sampling depths: very sensitive to the last monolayer the ToF-SIMS, at least in the experimental conditions here used; 5–10 nm the typical depth explored by XPS, depending on the experimental set-up and on the material analysed. For instance, one might think to a preferential arrangement of long molecules that could also contribute to the differences found with the two techniques. Last but not the least one has to take into account the different nature of the substrate (calcium carbonate versus gold). Whatever is the reason, in order to discriminate among the different contributions to these different experimental findings, ToF-SIMS spectra, both in positive and in negative mode, were obtained also from thin films of the Zonyl compounds deposited on calcarenite samples. In this paper we report a systematic comparison between the mass spectra obtained from calcarenite deposited samples with those recorded on gold. The differences found are discussed in terms of interactions (or not) with calcarenite and gold substrates

2. Experimental

The Zonyl (Du Pont) products, namely FSA, FSP, 9361, 9027, 8740, were kindly provided by Garzanti Chimica S.p.A (Italy). The chemical formulae of these compounds, as supplied by the manufacturer [7], are reported below:

9361 → $(R_fCH_2CH_2O)_xPO(O^-NH_2{}^+[CH_2CH_2OH]_2)_y$;
9027 → $R_fCH_2CH_2OPO(O^-NH_2{}^+[CH_2CH_2OH]_2)_2$
$\qquad + (R_fCH_2CH_2O)_2POO^-NH_2{}^+(CH_2CH_2OH)_2$;
FSP → $(R_fCH_2CH_2O)_xPO(O^-NH_4{}^+)_y$;
FSA → $R_fCH_2CH_2SCH_2CH_2COO^-Li^+$;
8740 → perfluoroalkyl methacrylic copolymer
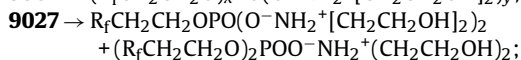
In all these formulae $R_f = CF_3CF_2(CF_2CF_2)_n$; $n = 2, 3, 4$; $x + y = 3$.

For each product, a 4% (v/v) solution was prepared in a 4:9 isopropanol/water solvent mixture. Some specimens of finely polished calcarenite were immersed for 1 min in the above solutions. For comparison, samples were prepared by deposition of few drops of these solutions onto a Si substrate covered by a thin layer of Au. After the evaporation of solvents under nitrogen flux, the samples were analysed by a TOFSIMS IV (ION-TOF, Muenster) equipped with a 25 keV gallium ion source. Spectra were acquired in static SIMS mode (primary ion dose <10^{12} ions cm^{-2}) in order to preserve the molecular information. In particular the conditions used are: 0.1 pA, 60 s, 200 μm × 200 μm for both positive and negative spectra on gold; 0.4 pA, 60 s, 200 μm × 200 μm for the positive spectra and 1.0 pA, 60 s, 200 μm × 200 μm for the negative ones on calcarenite. A low energy (~20 eV) pulse electron flood was used during the analysis of insulating calcarenite deposited samples, in order to achieve charge neutralisation of the surface. Charge neutralisation was not necessary for samples deposited on gold. The pressure in the analysis chamber was better than 5×10^{-9} mbar. For each sample eight spectra were acquired both in positive and negative mode. Peak assignment was accomplished by checking both the exact mass, within the available resolution, and the isotopic distribution, when the signal to noise ratio was adequate.

3. Results and discussion

Figs. 1–5 report the ToF-SIMS spectra of 8740, FSA, 9361, 9027, FSP compounds, respectively, deposited onto calcarenite, acquired both in positive (upper part of the figure) and negative (bottom part of the figure) mode. The corresponding spectra of the films deposited on gold are not shown here, since similar ones have been already reported [6]. However, in order to make easier the comparison with the spectra obtained from the samples deposited on calcarenite. The assignment of some of the main peaks found in the spectra of the films deposited on gold are reported in Table 1 (positive ones) and Table 2 (negative ones).

The observed resolution $M/\Delta M$ of about 800 at m/z 27 is at least one order of magnitude lower than that obtainable with the ToF-SIMS instrumentation used and actually obtained on thin films of the same compound on gold (>8000). This worsening is due to the roughness of the calcarenite that, even if finely polished and in spite of the levelling effect due to the spreading of the diluted film solution, prevents us to obtain better performances. With such a mass resolution we cannot easily distinguish – in the high mass portion of the spectrum (>m/z 100) – among –O- or –NH$_2$- containing fragments, due to the relatively small mass difference (0.123 Da) between the two functional groups.

We also note that, compared with the same compounds deposited on gold, the highest observed masses fall at about m/z 700, while the spectra of samples deposited on gold show the presence of peaks at mass as high as m/z 2000.

When deposited onto calcarenite, the compounds here investigated behave differently with respect to the films obtained on gold surfaces. The main differences are observed in the positive ToF-SIMS spectra, where the peak at m/z 18, attributable to ammonium ion (FSP), the peaks at m/z 6 and m/z 7, attributable to lithium ion (FSA), and the peak at m/z 106, attributable to $C_4H_{12}NO_2{}^+$ ion (9027 and 9361) are not detected with appreciable intensity. Such peaks are assigned to the counterions present in the above mentioned anionic compounds. These results are in agreement with the finding of the XPS measurements performed on similar samples [4]. More in detail, the XPS spectra of the compounds (FSP, 9361, 9027) with nitrogen-containing counterions do not show any detectable nitrogen peak. No comparison can be done in the case of FSA (with a lithium counterion) as lithium has a very low photoionisation cross section [8]. In addition, the mass spectra of all the above compounds

Table 1
Peak list of positive ToF–SIMS spectra obtained from FSP, 9361, 9027, FSA, 8740 compounds deposited on gold surface.

FSP		9027 and 9361		8740		FSA	
m/z	Formula	m/z	Formula	m/z	Formula	m/z	Formula
18	NH_4^+	31	CF^+	30	CH_4N^+	6, 7	Li^+
31	CF^+	50	CF_2^+	31	CF^+	31	CF^+
50	CF_2^+	69	CF_3^+	44	$C_2H_6N^+$	50	CF_2^+
69	CF_3^+	93	$(CF)_3^+$	50	CF_2^+	69	CF_3^+
93	$(CF)_3^+$	99	$H_4PO_4^+$	56	$C_3H_6N^+$	93	$(CF)_3^+$
99	$H_4PO_4^+$	100	$(CF_2)_2^+$	69	CF_3^+	100	$(CF_2)_2^+$
100	$(CF_2)_2^+$	106	$C_4H_{12}NO_2^+$	72	$C_4H_{10}N^+$	119	$CF_3CF_2^+$
119	$CF_3CF_2^+$	119	$CF_3CF_2^+$	86	$C_5H_{12}N^+$	131	$C_3F_5^+$
131	$C_3F_5^+$	131	$C_3F_5^+$	100	$(CF_2)_2^+ + C_6H_{14}N^+$	169	$C_3F_7^+$
169	$C_3F_7^+$	169	$C_3F_7^+$	113	$C_6H_9O_2^+$	181	$C_4F_7^+$
179	$H_5P_2O_7^+$	181	$C_4F_7^+$	119	$CF_3CF_2^+$	231	$C_5F_9^+$
181	$C_4F_7^+$	186	$PO_4C_4H_{13}NO^+$	131	$C_3F_5^+$	307	$F(CF_2)_4(CH_2)_2S(CH_2)_2^+$
361	$H_3P_2O_7\,(CH_2)_6(CF_2)_2^+$	291	$PO_4C_{12}H_{22}NO^+$	169	$C_3F_7^+$	393	$F(CF_2)_6(CH_2)_2SCH_2^+$
362	$H_4P_2O_7(CH_2)_6(CF_2)_2^+$	309	$PO_4C_{12}H_{24}NO_2^+$	181	$C_4F_7^+$	407	$F(CF_2)_6(CH_2)_2S(CH_2)_2^+$
445	$[H_2PO_3O(CH_2)_2(CF_2)_6F]H^+$	339	$PO_4C_7H_{13}CF_3N_2O_4$	184	$C_{10}H_{18}NO_2^+$ or $C_{11}H_{20}O_2^+$	465	$[F(CF_2)_6(CH_2)_2S(CH_2)_2COOLi]Li^+$
461	$H_3P_2O_7(CH_2)_6(CF_2)_4^+$	371	$PO_4C_9H_{19}NOC_2F_5^+$	186	$C_{10}H_{20}NO_2^+$ or $C_{11}H_{22}O_2^+$	493	$F(CF_2)_8(CH_2)_2SCH_2^+$
462	$H_4P_2O_7(CH_2)_6(CF_2)_4^+$	389	$PO_4C_9H_{21}NO_2C_2F_5^+$	202	$C_{10}H_{20}NO_3^+$ or $C_{11}H_{22}O_3^+$	507	$F(CF_2)_8(CH_2)_2S(CH_2)_2^+$
545	$[H_2PO_3O(CH_2)_2(CF_2)_8F]H^+$	445	$HPO_4CH_2NOC_6F_{13}^+$ or $[H_2PO_3O(CH_2)_2(CF_2)_6F]H^+$	231	$C_5F_9^+$	565	$[F(CF_2)_8(CH_2)_2S(CH_2)_2COOLi]Li^+$
791	${HOPO\,[O(CH_2)_2(CF_2)_6F]_2}H^+$ or $[(CF_3)_4(CF_2)_3(CH_2)_8P_3O_{10}]^+$	467	$(H_2PO_4C_7F_{15})H^+$	361	$C_3H_6(CF_2)_6F^+$	593	$F(CF_2)_{10}(CH_2)_2SCH_2^+$
891	${HOPO[O(CH_2)_2(CF_2)_6F][O(CH_2)_2(CF_2)_8F]}H^+$ or $[(CF_3)_4(CF_2)_5(CH_2)_8P_3O_{10}]^+$	532	$PO_4C_6H_{13}C_6F_{12}N$	461	$C_5H_8O_2C_3H_6(CF_2)_6F^+$	607	$F(CF_2)_{10}(CH_2)_2S(CH_2)_2^+$
991	${HOPO\,[O(CH_2)_2(CF_2)_8F]_2}H^+$ or $[(CF_3)_4(CF_2)_7(CH_2)_8P_3O_{10}]^+$			531	$C_{11}F_{21}^+$	665	$[F(CF_2)_{10}(CH_2)_2S(CH_2)_2COOLi]Li^+$

Table 2
Peak list of negative ToF-SIMS spectra obtained from FSP, 9361, 9027, FSA, 8740 compounds deposited on gold surface.

FSP		9361 and 9027		8740		FSA	
m/z	Formula	m/z	Formula	m/z	Formula	m/z	Formula
16	O^-	16	O^-	16	O^-	16	O^-
17	OH^-	17	OH^-	17	OH^-	17	OH^-
19	F^-	19	F^-	19	F^-	19	F^-
24	C_2^-	24	C_2^-	24	C_2^-	24	C_2^-
31	CF^-	31	CF^-	26	CN^-	31	CF^-
38	F_2^-	38	F_2^-	27	HCN^-		
69	CF_3^-	69	CF_3^-	31	CF^-	32	S^-
79	PO_3^-	79	PO_3^-	38	F_2^-	38	F_2^-
97	$H_2PO_4^-$	97	$H_2PO_4^-$	39	HF_2^-	69	CF_3^-
123	$C_2H_2OPO(OH)_2^-$	123	$C_2H_2OPO(OH)_2^-$	69	CF_3^-	105	$HS(CH_2)_2COO^-$
159	$C_2F_2OPO(OH)_2^-$	159	$C_2F_2OPO(OH)_2^-$	85	$CF_3O^- + C_4H_5O_2^-$	119	$CH_3S(CH_2)_2COO^-$
203	$FC_2F_2C_2H_2OPO(OH)O^-$	203	$FC_2F_2C_2H_2OPO(OH)O^-$	119	$CF_3CF_2^-$	293	$F(CF_2)_4(CH_2)_2S\,CH_2^-$
219	$FC_2F_2C_2H_4OPO(OH)OCH_2^-$	219	$FC_2F_2C_2H_4OPO(OH)OCH_2^-$	293	$^-CF_2(CF_2)_nC_3H_7\ n = 4$	393	$F(CF_2)_6(CH_2)_2S\,CH_2^-$
239	$FC_4F_4OPO(OH)O^-$	239	$FC_4F_4OPO(OH)O^-$	393	as 293, $n = 6$	493	$F(CF_2)_8(CH_2)_2S\,CH_2^-$
257	$F(CF_2)_2C_2H_4OPO(OH)OCH_2^-$	257	$F(CF_2)_2C_2H_4OPO(OH)OCH_2^-$	493	as 293, $n = 8$	907	$F(CF_2)_{16}(CH_2)_2S\,CH_2CH_2^-$
293	$F(CF_2)_3C_2H_4OPO(OH)O^-$	293	$F(CF_2)_3C_2H_4OPO(OH)O^-$	593	as 293, $n = 10$		
337	$F(CF_2)C_2H_4OPO(O\,C_2H_2CF_3)O^-$			693	as 293, $n = 12$		
393	$F(CF_2)_5C_2H_4OPO(OH)O^-$	393	$F(CF_2)_5C_2H_4OPO(OH)O^-$				
523	$(FC_2F_4C_2H_4O)_2P_2O_3OC_2H_3OC_2H_4^-$	523	$(FC_2F_4C_2H_4O)_2P_2O_3OC_2H_3OC_2H_4^-$	793	as 293, $n = 14$		
623	as 523 + CF_2CF_2	623	as 523 + CF_2CF_2				
723	as 623 + CF_2CF_2	723	as 623 + CF_2CF_2				
769	$(FC_2F_4C_2H_4O)_4P_3O_5(FCF_2C_2H_4O)_2OC_2H_4^-$	769	$(FC_2F_4C_2H_4O)_4P_3O_5(FCF_2C_2H_4O)_2OC_2H_4^-$				
		789	as 769 + HF				
823	as 723 + CF_2CF_2	823	as 723 + CF_2CF_2	127	I^{-a}		
869	$(FC_2F_4C_2H_4O)_4P_3O_5OC_2H_4^-$	869	$(FC_2F_4C_2H_4O)_4P_3O_5OC_2H_4^-$	451	AuI_2^{-a}		
		889	as 869 + HF				
923	as 823 + CF_2CF_2	923	as 823 + CF_2CF_2				
969	as 869 + CF_2CF_2	969	as 869 + CF_2CF_2				

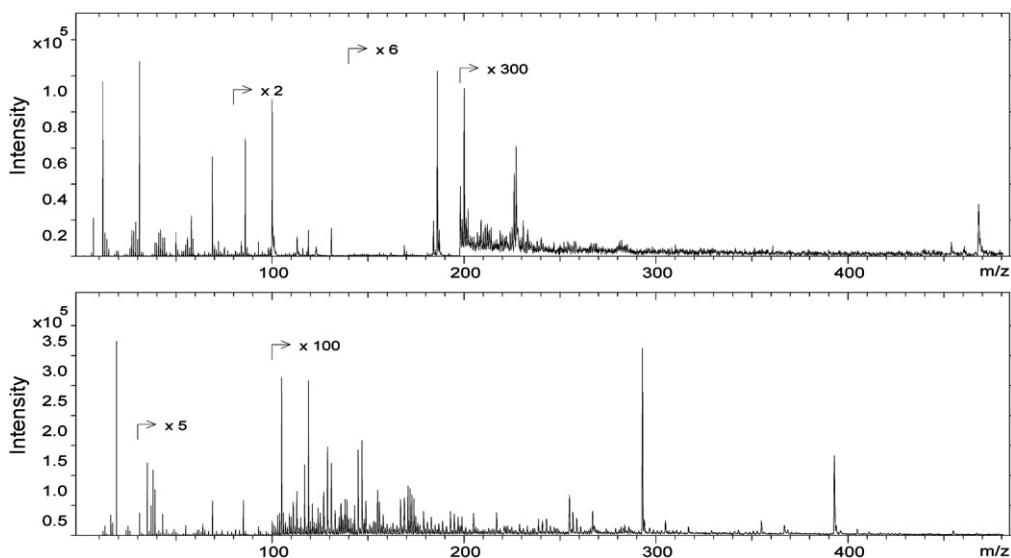[a] Iodine is a contaminant of the gold substrate.

Fig. 1. Positive (upper side) and negative (bottom side) ToF-SIMS spectrum of 8740 compound deposited on calcarenite.

(FSP, 9027, 9361 and FSA) show peaks attributable to fragments of the compounds under study and containing a calcium atom, clearly originated from calcarenite substrate.

In particular, a more detailed comparison of the spectra obtained from the above compounds deposited on calcarenite and on gold in the m/z interval 180–480 is useful in order to better outline the different behaviour of the fluorinated products with the two substrates.

For this purpose, Figs. 6–10 report the 180-480 mass interval of ToF-SIMS positive spectra of 8740, FSA, 9361, 9027, FSP respectively. The spectrum in the upper part of each figure refers to product deposited on calcarenite, while the spectrum in the bottom part refers to the same product deposited on gold.

The positive spectra of 8740 (Fig. 6) on calcarenite and on gold are similar to each other, if one excludes the obvious presence of peaks, in the portion of the mass spectrum not reported here, directly related to each substrate (such as the Ca$^+$ in the case of calcarenite as shown in Fig. 1). Some other differences are how-

ever present, such as changes in the relative intensity of some peaks (note, for instance, the intensity inversion of peaks at m/z 184 and m/z 186). Moreover, the spectrum from the calcarenite-supported sample shows an intense peak at m/z 468, not present on the sample deposited on gold, attributable to a 8740-related fragment containing four methacrylic moieties ($-C_5H_8O_2-$) and one $-(CH_2)_3-C\equiv N$ group. On the other hand in the spectrum of the gold-supported sample we observe peaks at m/z 361 and m/z 461, not present in the calcarenite-supported film, attributed, respectively, to $[C_3H_6(CF_2)_6F]^+$ (m/z 361) and to a co-polymeric unit containing both a methacrylic moiety and an alkyl-fluorinated chain $[C_5H_8O_2-C_3H_6(CF_2)_6F]^+$ (m/z 461). Both assignments are consistent with presence of a $-C_6F_{13}$ chain, in agreement with the XPS findings reported elsewhere [4]. As in the case of the peak at m/z 468 on the calcarenite-supported film, also the peaks at m/z 361 and m/z 461 are related to the structure of Zonyl 8740. The above described differences in the fragmentation pattern suggest a different arrangement of this compound on the two substrates, according
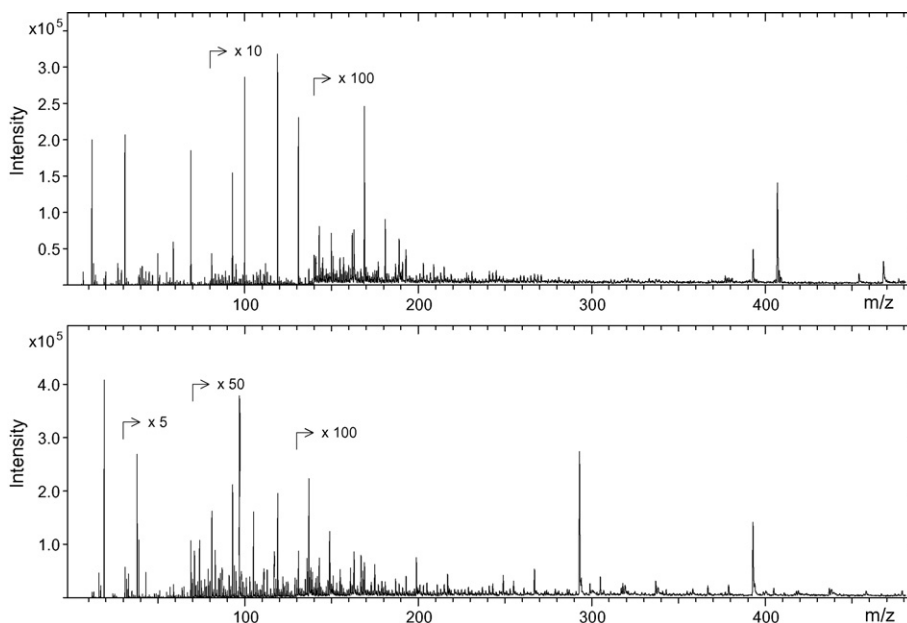

Fig. 2. Positive (upper side) and negative (bottom side) ToF-SIMS spectrum of FSA compound deposited on calcarenite.
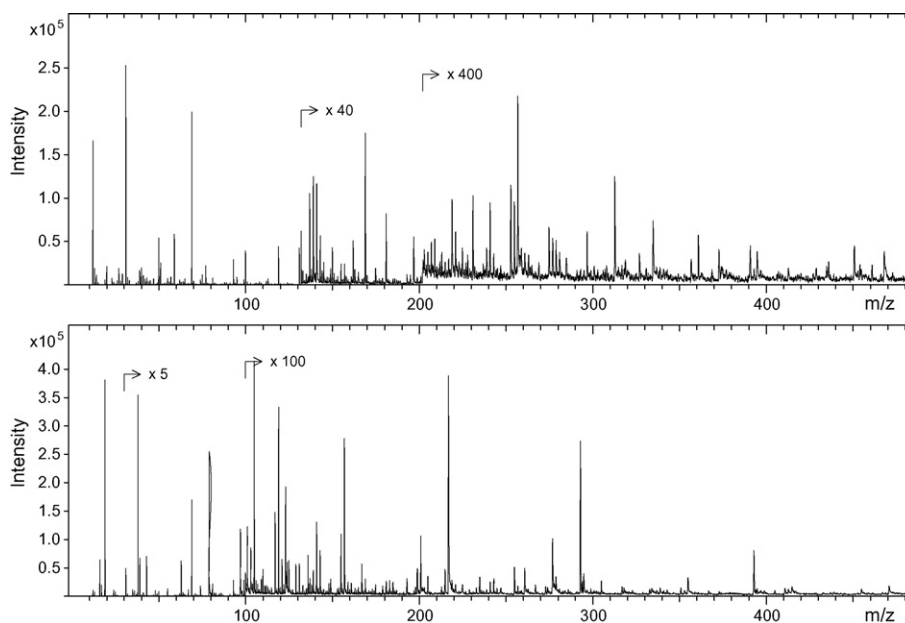
Fig. 3. Positive (upper side) and negative (bottom side) ToF-SIMS spectrum of 9361 compound deposited on calcarenite.

with the fact that one can expect a different interaction of the product with the two substrates.

The comparison of ToF-SIMS spectra of FSA sample (Fig. 7) deposited on calcarenite or on gold reveals, as main difference, the presence on calcarenite of the peaks at m/z 189, 191, 193, 454 and 468 and the presence on gold of the m/z 465 peak. The peak at m/z 465, observed in the spectrum of the Au-supported sample, can be assigned, also on the basis of isotopic distribution, to the lithium cationised molecular peak of FSA $[F(CF_2)_6(CH_2)_2S(CH_2)_2COOLi]Li^+$, that basically contains a molecular unit of FSA compound (see the formula reported by the manufacturer in the Section 2). In the same spectrum two large fragments of the molecule are present at m/z 393 and 407, assigned to $[F(CF_2)_6(CH_2)_2SCH_2]^+$ and $[F(CF_2)_6(CH_2)_2S(CH_2)_2]^+$, respectively. These fragments are present also in the calcarenite-supported

sample, where the molecular peak is missing; however, due to scarce mass resolution and to the lower intensity, compared to the gold-supported sample, we cannot exclude with absolute certainty the assignment of the above fragments to calcium containing species, like $[F(CF_2)_4(CH_2)_2SOCH_2COOCa]^+$ (m/z 393) and $[F(CF_2)_4(CH_2)_2SO(CH_2)_2COOCa]^+$ (m/z 407). In the higher mass portion of the spectrum on gold, not shown here, peaks at m/z 493, 507, 565 and at m/z 593, 607, 665 are present. These peaks are clearly related to the previous at m/z 393, 407, 465 by adding respectively one or two $-(CF_2-CF_2)-$ moiety, according to the possible different length of the fluorinated chain in the formula reported by the manufacturer.

In the calcarenite-supported sample the peaks at m/z 189, 191, 193 – assigned to calcium-cationised species $[C_2H_5S(O)C_2H_4COOCa]^+$, $[CH_3S(O)_2C_2H_4COOCa]^+$ and $[CH_3S(OH)_2$
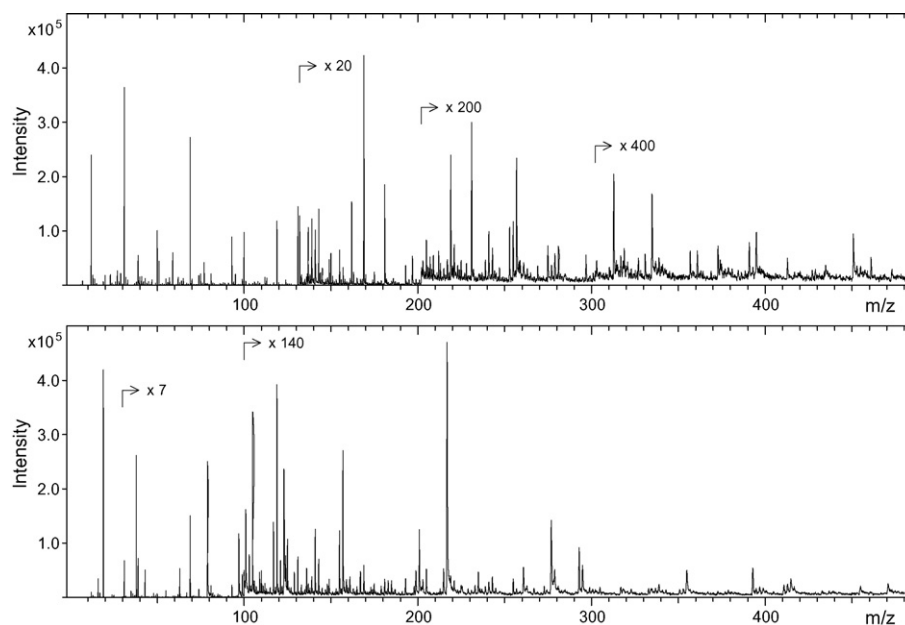

Fig. 4. Positive (upper side) and negative (bottom side) ToF-SIMS spectrum of 9027 compound deposited on calcarenite.
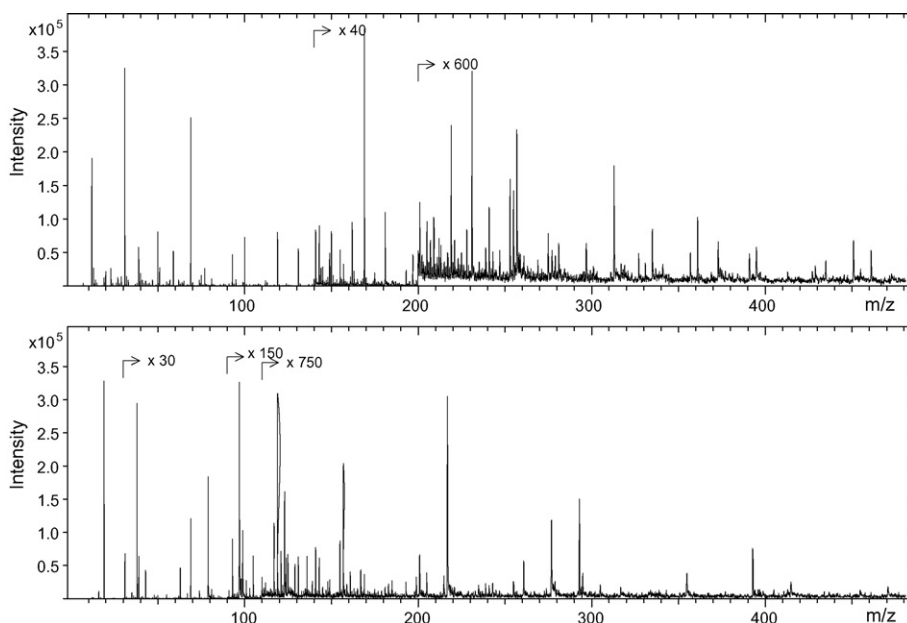
Fig. 5. Positive (upper side) and negative (bottom side) ToF–SIMS spectrum of FSP compound deposited on calcarenite.

$C_2H_4COOCa]^+$, respectively – could be related with oxidised forms of the thioether moiety present in the structure and clearly suggest an interaction of the carboxylate group with calcium atoms of the substrate. Those at m/z 468 $[F(CF_2)_6(CH_2)_2SO(CH_2)_2COOH]^+$ and m/z 454 $[F(CF_2)_6(CH_2)_2SOCH_2COOH]^+$ do not contain calcium atom, but oxidised sulphur atom is still present. The assignment of the above peaks to a structure containing an oxidised form of the thioether moiety, is done on the basis of XPS data [4,5] and in particular with the chemical shift observed on the S2p photoelectron peak. The negative spectra of this compound deposited on the two different substrates show a very close similarity.

The comparison between the positive mass spectra of 9361, 9027, and FSP deposited on calcarenite with respect to the ones on gold, shows more pronounced differences than those found on the FSA sample. In particular, the peaks at m/z 197 $[C_2F_2PO_4Ca]^+$,

m/z 257 $[C_3H_5P_2O_7Ca]^+$, m/z 313 $[CF_3(CH_2)_2H_2P_2O_7Ca]^+$, m/z 335 $[F(CF_2)_2H_2P_2O_7Ca]^+$, m/z 373, m/z 391 $[F(CF_2)_2(CH_2)_4H_2P_2O_7Ca]^+$, m/z 451 $[(CF_3)_2(CF_2)_3(CH_2)_2PO_4Ca]^+$, observed in these spectra, could be attributed to fragments containing both the phosphate group (9361, 9027 and FSP are phosphoric esters) and the calcium atom from the substrate (calcarenite). In our opinion, these peaks suggest a chemical interaction of the phosphate group with the calcium atoms of calcarenite substrate. In the spectra obtained from the gold substrate, the peak at m/z 445 (FSP) and the ones at m/z 186, 291, 309 (9027 and 9361) are the main peaks and are not recognizable on the samples deposited on calcarenite. In addition, it should be noted that the mass spectra obtained from the above compounds deposited on calcarenite show a close similarity, while those obtained by using the gold substrate did not. This last finding is not surprising, since one of the obvious chemical differences among
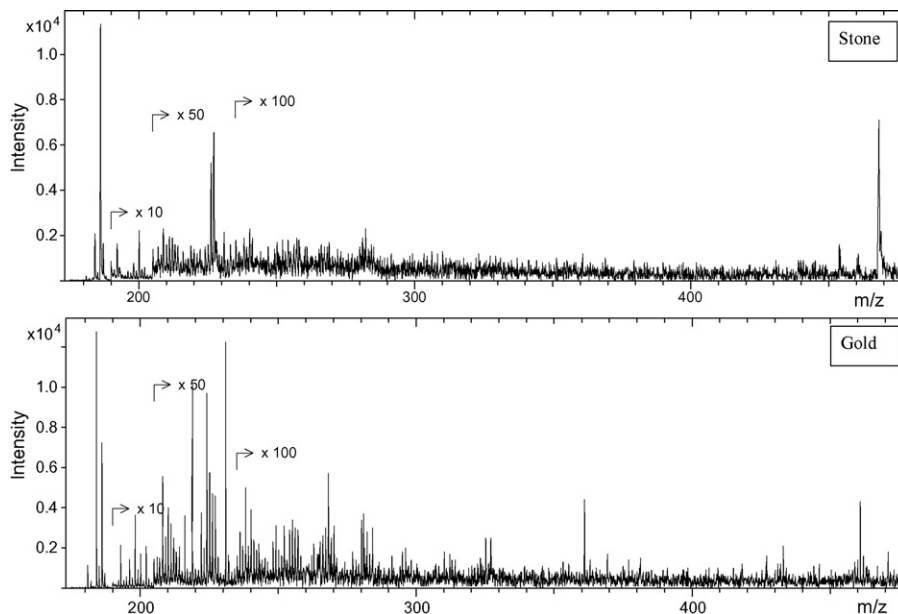

Fig. 6. Positive ToF–SIMS spectrum of 8740 compound deposited on calcarenite (upper side) and on gold (bottom side).
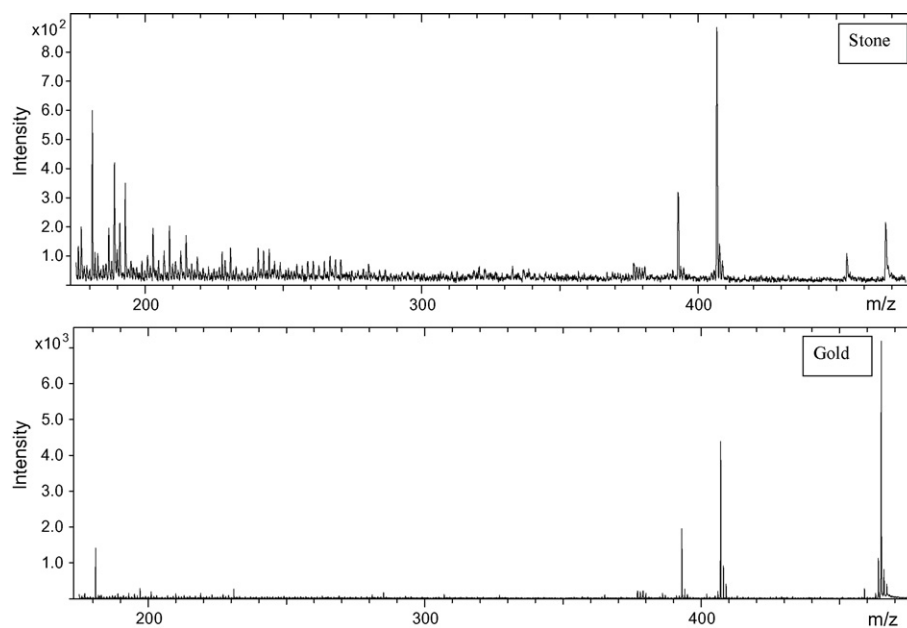
Fig. 7. Positive ToF-SIMS spectrum of FSA compound deposited on calcarenite (upper side) and on gold (bottom side).

these three compounds is just represented by the cationic part (see the chemical formulae reported in Section 2). Since these compounds deposited on calcarenite do not show a relevant amount of the cationic part, the remaining portion of the molecule of the three above mentioned compounds, being chemically similar each to other, giving rise to very close mass spectra. In addition, in the FSP sample deposited on calcarenite, the absence of the intense peak at m/z 445 found in the gold-deposited sample is noteworthy. This fragment is assigned to $[F(CF_2)_6(CH_2)_2OP(O)(OH)_2H]^+$ and contains one entire aliphatic fluorinated chain. This peak, together with the less intense peaks at m/z 545 $[F(CF_2)_8(CH_2)_2OP(O)(OH)_2H]^+$, m/z 791 $\{[F(CF_2)_6(CH_2)_2O]_2P(O)(OH)H\}^+$, m/z 891 $\{[F(CF_2)_7(CH_2)_2O]_2 P(O)(OH)H\}^+$, m/z 991 $\{[F(CF_2)_8(CH_2)_2O]_2P(O)(OH)H\}^+$, not shown here, is chemically representative of the FSP compound, according to the formula reported by the manufacturer and to the one derived

from the XPS spectra [4]. These peaks are not detectable in the positive spectrum obtained on calcarenite. In addition, the FSP mass spectrum obtained from the gold-deposited sample shows peaks at m/z 461, 462, 561 and 562 (the last two fragments are not shown in the spectrum here reported). The odd mass peaks show an intensity noticeably lower with respect to the even mass peaks. The peaks at m/z 462 and at m/z 562 can be assigned to $[H_4P_2O_7(CH_2)_6(CF_2)_4]^+$ and to $[H_4P_2O_7(CH_2)_6(CF_2)_6]^+$, respectively, while the remaining at m/z 461 and at m/z 561 can be obtained from the previous ones by the loss of one hydrogen atom. While the peaks at m/z 462 and at m/z 562 are not detectable on the mass spectrum obtained from the calcarenite support, the peaks at m/z 461 and at m/z 561 do.

Reasonably, these peaks might be assigned to the same formulae as proposed above for the corresponding peaks found on the mass
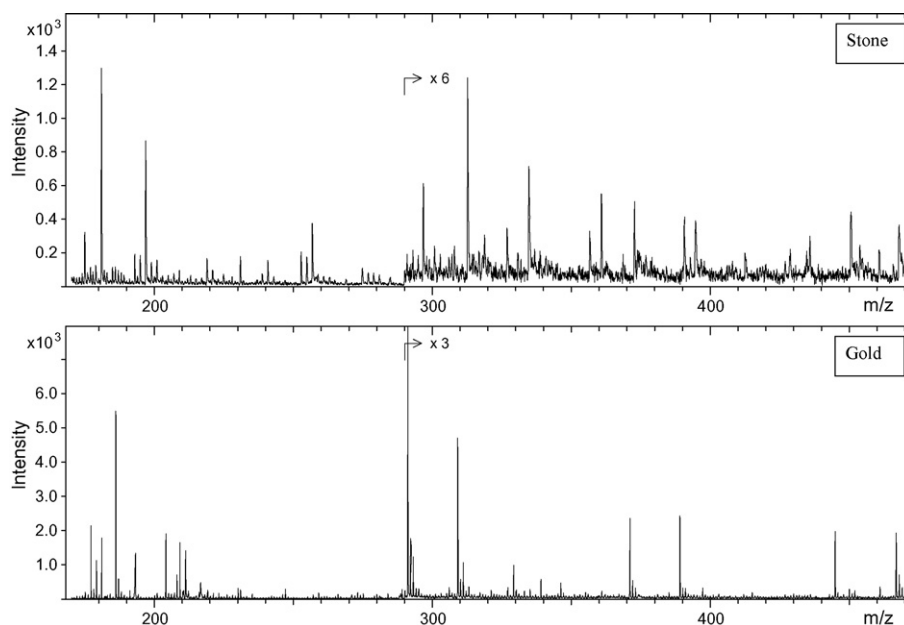

Fig. 8. Positive ToF-SIMS spectrum of 9361 compound deposited on calcarenite (upper side) and on gold (bottom side).
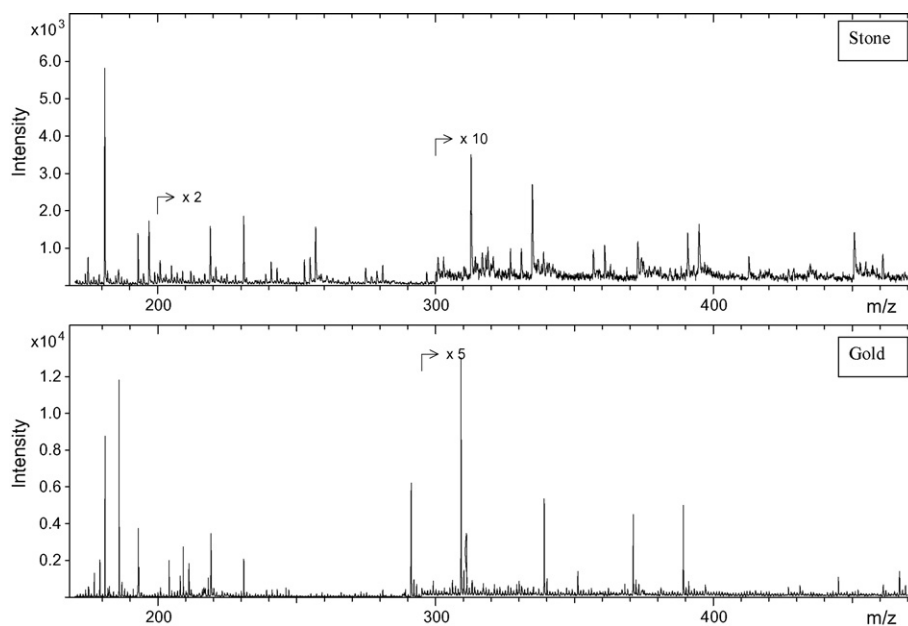
Fig. 9. Positive ToF-SIMS spectrum of 9027 compound deposited on calcarenite (upper side) and on gold (bottom side).

spectrum of the gold deposited samples. However, the poor mass resolution in the calcarenite deposited samples, do not allow us to exclude the assignment of the peaks at m/z 461 and at m/z 561 to isobaric fragments such as $[F(CF_2)_5(CH_2)_4O(OH)P(O)OCa]^+$ (m/z 461) and $[F(CF_2)_7(CH_2)_4O(OH)P(O)OCa]^+$ (m/z 561), both containing Ca atoms. Moreover, the peak at m/z 511, observed on the spectrum of calcarenite-supported FSP sample and not detectable on the gold-supported one, can be assigned to a $[F(CF_2)_6(CH_2)_4O(OH)P(O)OCa]^+$ fragment. This fact, together with the absence of the m/z 462 and 562 peaks in the calcarenite-supported FSP sample, induces us to believe that peaks at m/z 461 and m/z 561 must be assigned to Ca-containing structures, as proposed above.

As to the 9361 and 9027 compounds, it should be noted that also the peaks at m/z 186 $[PO_4C_4H_{13}NO]^+$, m/z 291 $[PO_4C_{12}H_{22}NO]^+$, m/z 309 $[PO_4C_{12}H_{24}NO_2]^+$, m/z 339 or $[PO_4C_7H_{13}CF_3N_2O_4]^+$, m/z 371 $[PO_4C_9H_{19}C_2F_5NO]^+$, all containing the $OC_4H_{12}NO^+$ group (m/z

106) and found in the positive mass spectra obtained on gold, are not detectable on the spectra obtained on calcarenite.

The details of the similar comparison between the negative mass spectra obtained on the two substrates are not reported here. This is because in the case of 8740 and FSA compounds, the mass spectra obtained on calcarenite (low part of Figs. 1 and 2, respectively) and gold (Fig. 2 of reference [6]) show very close fragmentation patterns. As to the 9361, 9027 and FSP compounds, the negative spectra obtained on calcarenite substrate show peaks (low part of Figs. 3–5, respectively) at m/z 157 $[CaF_2 \cdot PO_3]^-$, m/z 201 $[CaH_3P_2O_6]^-$ or $[CaF \cdot P_2O_5]^-$ (the resolution being not enough to choose among these two attributions), m/z 217 $[CaH_3P_2O_7]^-$, m/z 261 $[CaP_3O_8]^-$, m/z 277 $[CaP_3O_9]^-$, not observable on the samples deposited on gold (Fig. 2 of reference [6]). A further note is that also the negative mass spectra on calcarenite of FSP, 9027, 9361 are very similar to each other as already observed for the positive ones.
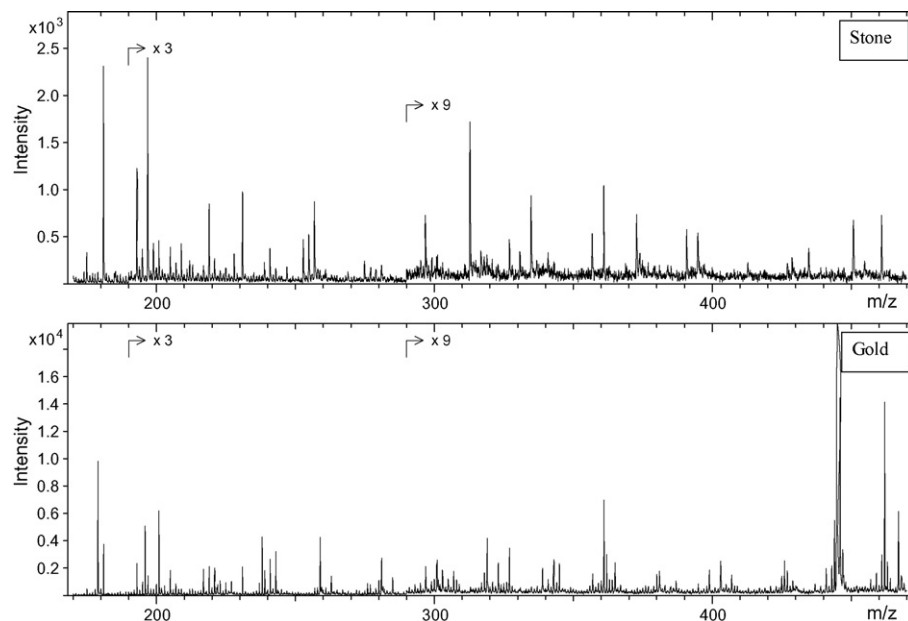

Fig. 10. Positive ToF-SIMS spectrum of FSP compound deposited on calcarenite (upper side) and on gold (bottom side).

The strong decrease of the peaks related to the cations and the presence, in the positive and negative mass spectra of 9361, 9027 and FSP compounds deposited on stone substrate, of Ca-containing fragments, gives further support to the hypothesised interaction of these compounds with calcarenite. The existence of an interaction between the three phosphoric ester compounds with the calcarenite substrate has been previously hypothesised [4,5] on the basis of the relevant increase of the difference between the Ca2p and the C1s carbonate component binding energies (BE), observed in the XPS spectra of the FSP, 9027, 9361. This fact suggests the formation of a true chemical bond between the surficial Ca atoms and the phosphate groups. Also the positive mass spectrum of FSA compound on calcarenite showed some not negligible difference with respect to the one on gold (as above reported). This, together with the XPS findings, suggests also for this compound some chemical interaction with the calcarenite substrate, perhaps through the carboxylate group.

The interaction of some of these compounds with the calcarenite substrate leads to a different fragmentation with respect to that observed on gold deposited samples, hindering, for instance, the emission of high mass molecular fragments. The occurrence of a chemical interaction, between the substrate and the compounds deposited on it, is not trivial, since it concerns the possible utilisation of these compounds, or similar ones, as protection of the stone surface, for instance as water repellent and against water penetration. On this respect, these compounds have been previously evaluated by means of static contact angle and water absorption by capillary tests [3] and it was found that the FSP compounds gave the better performances.

In the above depicted framework, the 8740 compound seems to show an anomalous behaviour. Indeed our data, although indicating a different arrangement on the two substrates, do not suggest a strong interaction with the calcarenite surface. This might be quite surprising because the 8740 compound is a perfluoroalkyl methacrylic copolymer. The acrylic polymers indeed, have been used since long time for restoration and preservation purposes, especially for marble [9,10] stones. Perhaps the interaction of this compound with the substrate is based on short range interactions (for instance van der Waals) and do not give rise to a true chemical bond. However, the differences found in ToF-SIMS mass spectra of this products deposited onto gold with respect to those obtained from calcarenite and above discussed, could be related with the behaviour of thin films of this compound deposited on calcarenite with static contact angle and with water absorption by capillary tests, previously reported [3]. Indeed, this product showed by far the lowest static contact angle among the five compounds tested, while at the water absorption by capillary test it gave satisfactory results. The 8740 compound, in spite of a relative long fluorinated single chain $[F(CF_2)_6-]$, when deposited on calcarenite, shows only smaller fluorine-containing fragments, while on gold the entire copolymeric unit is detectable (m/z 461). This suggests a different arrangement of 8740 compound on calcarenite with respect

to that on gold. In particular this gives rise to relative large surface areas mainly covered by the acrylic groups (m/z 468) that prevent to obtain good contact angle values, due to the less hydrophobic degree of the acrylic group with respect to the fluorinated one. On the other hand, the complete covering of the calcarenite surface, as revealed by the XPS measurements, and the compactness of the film allows a quite good behaviour against the penetration of water by capillarity, perhaps justifying the wide use of this kind of product in the preservation of stone.

Finally, it should be considered that the absence of strong interaction (i.e., a chemical bond) between the stone and the protective compound, could constitute an advantage if one takes into account the possibility to take out the protective. Indeed, the reversibility of the treatment is coming to be one of the fundamental aspects to be taken into account in the project of a protection of a surface (stone, metal, etc.) of artefacts in the cultural heritage field.

4. Conclusions

The comparison between the ToF-SIMS mass spectra of the fluorinated compounds here studied, obtained on gold and on calcarenite, shows differences in the fragmentation pattern among films of the same compound deposited on different substrates. These differences could be related with the nature of the substrate. In particular, the interpretation of the mass spectra has shown numerous Ca-containing peaks in the samples deposited on calcarenite and the absence, or the drastic lowering, of peaks related to the cationic part of some of these compounds. This constitutes a reasonable support to the hypothesis advanced on the basis of previous XPS studies of the existence of a quite strong interaction of some of these compounds with the calcarenite substrate giving rise to a true chemical bond. The high sensitivity of Tof-SIMS technique can reveal the modifications of the organization of the molecules at the surface of a film, in spite of the problem related to the change of the ionisation yield due to matrix effects. This renders the ToF-SIMS technique a very powerful analytical tool also in the study of chemical interaction between different materials.

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