MEASUREMENTS OF CHLORINE BY XPS AND SIMS IN NUCLEAR-GRADE GRAPHITE. EFFECT OF TREATMENT BY UV, HEAT AND MOISTURE

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Abstract

Pieces of historical nuclear-grade graphite from the same block were submitted to a treatment involving soft or hard UV and heating in moist air. XPS investigations before treatment have shown that – at the geometric surface at least – chlorine binds more commonly by covalent (30 to 100% depending on spots) than ionic bonds. After treatment, bond types are more balanced, though hardly more uniform. Shifts of the ionic peak indicating an oxidised bond were not found. Surface chlorine was measured up to 0.04% atomic. Treatment by hard UV and heating in moist air for 1 ½ hours up to 122°C led to a decrease of surface chlorine by a factor of 2 as measured by ToF and XPS, helped by an etching technique that ensured the accurate positioning of the spots under analysis. Treatment for 8 hours up to 151°C resulted in a decrease of the ToF $Cl/^{13}C$ signal for surface chlorine from 0.73 to 0.20 and of the atomic fraction from 0.02% to 0% as measured by XPS. SIMS investigations reveal that in the first 6 µm from the geometric surface, chlorine, hydrogen and oxygen have a decreasing profile suggestive of diffusion from the surface. In the vicinity to the surface the amounts of all three elements are much greater than in the bulk, possibly due to the availability of dangling bonds. It is speculated that when these are not saturated, back diffusion from the bulk under treatment may increase the quantity of surface chlorine. Treatment in moist air by hard UV for to 1 ½ hours has no marked effect on chlorine in the bulk, although it alters the quantities of hydrogen and oxygen. Treatment for 8 hours decreases chlorine by a factor of about 5 throughout the analysed depth of 6 µm and possibly farther to 15 µm, suggesting its diffusivity to be at least an order greater than 3.10^{-16} m²/s and possibly than 2.10^{-15} m²/s, although a range of values is expected owing to the diverse tortuosity and constrictivity of pores. Ratios of hydrogen to oxygen and of chlorine to hydrogen vary much less throughout the analysed depth than the quantities of these elements do separately, suggesting they exist as molecular species, likely to be H_2O and HCl. Yet under temperatures below 151°C, which do not allow graphite to be oxidised, the ratio of hydrogen to oxygen can change by a factor of about 2, indicative of hydrolysis either by UVs or by the moderate heating of graphite. The conclusion is that the covalent bonding of chlorine in graphite, which is prevalent, will not prevent it from being released and, if a non-labile form of chlorine exists at all, this cannot be identified to its being in a covalent bonding. It is proposed that chlorine swaps covalent and ionic (or halogenic) bondings quite readily. It is further proposed that hydrolysis plays a role in that process.

1. INTRODUCTION

In case irradiated graphite were destined for final disposal in geological repositories, the ensuing cost might reach in the order of 100 k€ per m^3 of unpackaged waste.

An alternative option would be to strip irradiated graphite of most of its activity in ^{36}Cl, a mobile radioelement with a long decay period present in irradiated graphite, for this would allow the latter to be disposed of in specially-built near-surface facilities for a fraction of the above cost.

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The basic idea underpinning this study was that, if enough hydrogen radicals could be generated in the immediate vicinity of unirradiated graphite, they would substitute to chlorine, thus accelerating a natural process. Photolysis was the chosen way to produce them, as it is readily available.

The photolysis of water can be achieved by class C ultra-violet rays emitted by a low-pressure mercury lamp with a peak at 183 nm. The 10.8×10^{-19} J energy of the photons is higher than that (6.08×10^{-19} J) of the H_2O molecule. They may also exert a direct action on surface C-Cl bonds. It was not expected that either photons or radicals would invade the porosity but instead, assuming an active equilibrium between shallow and deep impurities, that treating the surface would unlock the rest.

Investigations were carried out using XPS and SIMS techniques to probe how chlorine and other species behaved within the graphite matrix when submitted to UV radiolysis in a moist air atmosphere.

2. CHEMISTRY AND THERMODYNAMICS

The impurities targeted by the treatment are ^{36}Cl atoms bonded to carbon by either covalent or ionic (halogenic) links [1]. Such atoms are the product of neutronic activation of ^{35}Cl. Although the recoil energy at the time of activation would allow them to cross graphene plans up to about a hundred nanometers, subsequent rearrangement of the graphite and short-distance diffusion have been shown to lead to their rapid expulsion to the nearest crystal boundary [2], thus lowering crystal energy. It is therefore the opinion of the authors that the location of ^{36}Cl atoms is not so much different from that of the original ^{35}Cl atoms as to preclude any relevance of tests carried out on un-irradiated graphite.

Sites for the stable location of chlorine and other atoms abound in the macro and nano-porosity of the graphite, the BET measure of which is in the order of 0,25 m²/g albeit with significant variations depending on the grade. Indeed, compared with the ambient thermal atomic energy ($1/2\ k_BT = 2.10^{-21}$ J at 300 K) covalent bond energy is quite high: $5{,}48\times10^{-19}$ J for C-Cl which is slightly less than that of hydrogen (6.89×10^{-19} J for C-H) and about the same as C-C (5.78×10^{-19} J).

Nevertheless the literature review suggests that such links can be overcome, most likely substituted by hydrogenated radicals. Vulpius [3] signalled that tritium undergoes a fast release by isotopic exchange in acid conditions. The same was reportedly observed in the presence of humidity [4]. Chlorine can be partially substituted by OH in the presence of alcaline hydroxides and by NH_2 in the presence of NH_3 [5]. In the presence of SO_2 the C-Cl link snaps at ambient temperature if it has been formed through reaction with gaseous HCl while it persists if it was through reaction with Cl_2 or aqueous HCl [6]. The chlorine-carbon reaction is reversible at 400°C in presence of H_2 and releases HCl [7]. ^{36}Cl has been reported to spontaneously, albeit slowly, leave from graphite powder exposed to air [8].

Water dissociates on graphite, releasing hydrogen. While this reaction is well known at elevated temperatures, it has also been observed with a low kinetics at ambient [9] [10].

Irradiation may accelerate the dissociation. Platonov et al. [11] report 19% hydrogen found upon submitting a graphite block from the Leningrad RBMK 3rd unit to vacuum degassing under gamma irradiation. Hydrogen is assumed to originate from water adsorbed on the porosity.

3. EXPERIMENTAL

As the source of photons a NIQ 60/35 XL lamp with a 6 w UV flux at 185 nm was bought from Heraeus. Assuming each photon is used, this flux amounts per hour to 0.6 g of water being radiolysed, or otherwise two photons for every carbon atom lining the porosity in a piece of graphite with a BET of 0.25 m²/g and a weight of 1 kg, or again one hundred times the amount of chlorine atoms with a concentration of 10 ppm in the same piece of graphite.

Radicals brought about by water photolysis recombine by collision. The free mean path of a free hydrogen atom, assuming the pressure of reacting radicals is the same as that of saturating water in air at 25°C, is about 30 µm, increasing to 1 cm when their pressure has dropped to 10 Pa. Shallow porosity is therefore readily accessible to radicals produced directly at its mouth and deep porosity inaccessible but to rare ones. Recombined hydrogen may reach every remote nanopore with some effect though.

The graphite was nuclear-grade, long kept by the owner and provided for the investigations in a polypropylene box (box material was determined using an IR spectrometer). Samples, with a weight of a few grams, were put directly under the UV flux and some liquid water kept on the bottom of the stainless steel irradiation vessel.

The UV lamp was switched on for either $1^{1/2}$ hour or 8 hours. Then, after allowing some time for the apparatus to cool down, the sample was investigated either by a PHI Quantera analyser for XPS measurements, or a Iontof TOF.SIMS 5 for SIMS measurements, both static (ToF) and dynamic (DSIMS).

Since the same measurements were also done before UV irradiation, the comparison yielded information on the effect of the treatment. The graphite piece was carefully replaced at the same position in the analyser, however this could not be done with a better precision than about a millimetre. For the later investigations the technique was refined.

XPS readings are about their detection limit (see Figure 1). The depth of analysis is less than 10 nm, the diameter of analysed area about 200 µm and prolonged reading times allow the detection threshold to be put as low as 0.01 at%. Accuracy for chlorine is about 20%.

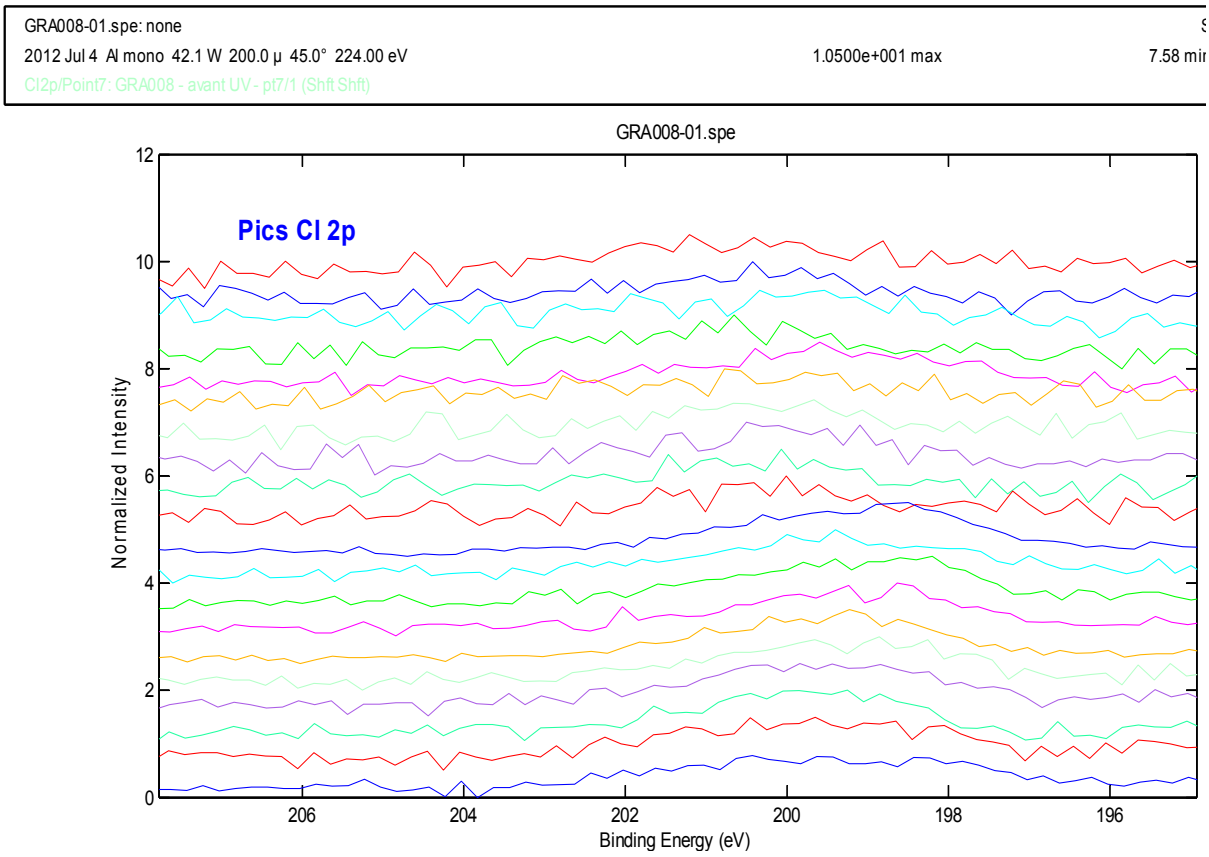


FIGURE 1: characteristic XPS readings

Blanks were carried out. No significant bias was identified from the ambience. Chlorine speciation may respond to moderate heating though (Table 1).

TABLE 1 – XPS BLANKS

XPS blanks	**spot**	**C**	**O**	**Cl**
Ratio of Nr of atoms - after 8 hours in the technical room - to before	1	1.00	1.03	1.5
	2	1.01	0.81	0.5
	3	0.98	1.36	3
Ratio of Nr of atoms - after 8 hours in switched-off UV vessel - to before	1 [i]	1.01	0.80	0.5
	2 [i]	1.00	1.03	1
	3 [i]	1.00	1.03	1
Ratio of Nr of atoms - after 8 hours in the meeting room - to before	1 [ii]	0.97	0.96	1
	2 [ii]	1.00	1.00	1
	3 [ii]	1.00	0.92	1
Ratio of Nr of atoms - after 8 hours in apparatus heated 40 w - to before	1 [iii]	1.00	1.08	-
	2 [iii]	0.99	1.35	1
	3 [iii]	1.00	1.21	-
Ratio of Nr of covalent Cl atoms - after one hour under 254 nm UVs (photons with this energy cannot break water molecules) - to before	1 [iv]	0.80		
	2 [iv]	0.85		
	3 [iv]	0.60		
	4 [iv]	0.73		
Ratio of Nr of covalent Cl atoms - after 1H30 under 183 nm UVs without water - to before	1 [v]	1.3		
	2 [v]	0.80		
	3 [v]	1		
	4 [v]	1.01		
Ratio of Nr of atoms - after 1H30 hours under 183 nm UVs without water - to before	1 [vi]	1.00	0.92	1.00
	2 [vi]	1.00	1.01	1.33
	3 [vi]	1.01	0.83	0.80
	4 [vi]	0.99	1.11	1.00

Typical atomic abundances before treatment are shown on Table 2. Surface Cl abundance is about 0.03% or 100 times higher than 10 wppm usually measured in bulk for this grade.

TABLE 2: TYPICAL XPS READINGS BEFORE TREATMENT (AT%)

spot	**C**	**O**	**Cl**	**others**
1	94.8	5.2	0.02	Si, N, Zn
2	92.9	7.0	0.06	-
3	93.5	6.5	0.05	-
4	94.5	5.4	0.04	-
5	94.8	5.2	0.02	-
6	95.5	4.5	0.01	-
7	93.4	6.6	0.02	-
8	96.7	3.2	0.01	-
9	91.4	8.6	0.04	-

Results of treatment by UV in humid ambience using de-ionized or tap water mostly did not exhibit any clear direction of change in the number of surface chlorine atoms, as shown in Table 3 and Table 4. Numbers suggest a slight statistical shift from covalent to ionic chlorine induced by the treatment.

Shifted XPS peaks attributed by Vaudey [1] to chloride with an oxidation number greater than 0 (oxychloride) were not seen in any of the series.

TABLE 3: TYPICAL RESULTS OF TREATMENT IN THE FIRST PHASE: ATOMIC NUMBERS

XPS measurements	**spot**	**C**	**O**	**Cl**
Ratio of Nr of atoms - after 1H30 above a splash of water on the bottom of the vessel - to before	1	1.01	0.90	0.50
	2	1.00	1.02	1.00
	3	1.00	1.05	1.00
	4	1.01	0.90	1.00

TABLE 4: TYPICAL RESULTS IN 1ST PHASE: SPECIATION, DE-IONISED WATER

XPS measurements	**spot**	**Above water**	
		Ionic	**Covalent**
% of Chlorine before treatment	1	46	54
	2	18	82
	3	0	100
	4	43	57
% of Chlorine after treatment $1^{1/2}$ hours using de-ionised water	1	0	100
	2	24	76
	3	67	33
	4	0	100

TABLE 5: TYPICAL RESULTS IN 1ST PHASE: SPECIATION.

XPS measurements	**spot**	**De-ionised water**		**Tap water**	
		Ionic	**Covalent**	**Ionic**	**Covalent**
% of Chlorine before treatment	1	46	54	0	100
	2	18	82	0	100
	3	0	100	0	100
	4	43	57	0	100
% of Chlorine after treatment $1^{1/2}$ hours using de-ionised water	1	0	100	15	85
	2	24	76	0	100
	3	67	33	0	100
	4	0	100	18	82

One exceptional series (Nr 4), results shown in Table 6 (for amounts) and Table 7 (for speciation), exhibited a big increase in surface chlorine coupled with a marked relative decrease in covalent chlorine. This has not been explained and might have been caused by pollution of the sample. If so,

some of the polluting chloride seems to have quickly formed covalent bondings, otherwise a 4-fold increase in total chlorine would have made chloride much more prevalent.

The inconclusive results of this first phase of the investigations led to the assumption that the positioning of the graphite sample in the analyser had to be made more accurate. An etching technique was developed, using DSIMS, to mark the area where the successive analyses were to be made. Since the measurements destroy the matter under analysis, they could not be done on exactly the same spots, but it was reasonable to consider that locations a few tens of µm apart should have similar compositions. The etchings ensured that the position could be recognised through an optical microscope, and that the successively analysed spots were but a few tens of micrometers apart.

TABLE 6: EXCEPTIONAL 4TH SERIES WITH BIG CL INCREASE – % ATOMIC

XPS measurements	**spot**	**C**	**O**	**Cl**
Ratio of Nr of atoms - after $1^{1/2}$ hour above a splash of de-ionised water on the bottom of the vessel - to before	1	0.93	2.35	5.5
	2	0.97	1.64	3
	3	0.97	1.42	3
	4	0.96	2.38	4
	5	0.95	1.53	2.5
Ratio of Nr of atoms - after 1H30 immersed in de-ionised water below the UV lamp - to before	6	0.93	2.71	5
	7	0.84	4.14	3.5
	8	0.94	1.95	2.5
	9	0.94	2.36	3
	10	0.94	2.32	5

TABLE 7: EXCEPTIONAL 4TH SERIES. CHLORINE SPECIATION

XPS measurements	**spot**	**Above water**		**Immersed**	
		Ionic	**Covalent**	**Ionic**	**Covalent**
% of Chlorine before treatment	1	0	100	0	100
	2	0	100	0	100
	3	0	100	0	100
	4	0	100	0	100
	5	54	46	0	100
% of Chlorine after treatment $1^{1/2}$ hours, de-ionised water	6	76	24	60	40
	7	69	31	70	30
	8	72	28	38	63
	9	70	30	40	60
	10	41	59	48	52

Later measurements took advantage of the etching technique to accurately position the graphite sample in the analyser. The sample was UV-irradiated over de-ionized water.

XPS and static SIMS (time of flight) were concurrently used to compare surface chlorine on spots located within the same small area about 200 µm across. ToF reflects the first atomic layer (less than 1 nm) and XPS a depth about 5 nm (at most 10 nm or 3 layers).

While the XPS technique reveals actual atomic numbers in the target, the SIMS technique measures secondary ions emitted by it, which depend on each chemical element and on their environment. Since elements have different relative sensitivities[†] to the SIMS technique, either static (ToF) or dynamic (DSIMS), it does not directly allow quantifying them. Ratio to ^{13}C of known abundance (1.1%) provides a number that is more or less proportional to the absolute quantity of a given element at different stages of the treatment through a depth of matrix material.

Short (1H30) and long (8H) UV treatment were tested in this phase. Temperatures were measured: the short run had it go up to 122°C. It plateaued at 151°C from 4H in the long one. The treatment was shown to produce a very significant decrease in surface chlorine. This decrease is more pronounced when the treatment time is 8 hours than when it is only 1 hour and half (Table 9).

TABLE 8: COMPARISON OF XPS AND TOF READINGS OF TREATMENT EFFECT ON SPOTS MARKED WITH ETCHING

Spot ref.	Before treatment		Treatment time	After treatment	
	ToF Cl vs ^{13}C	XPS At%		ToF Cl vs ^{13}C	XPS At%
20-1	0.66	0.02	0	-	-
20-2	0.66	0.02	0	-	-
20-3	0.58	0.02	0	-	-
21-1	0.52	0.02	1H30	0.02	0.12
21-2	0.64	0.02	1H30	0.01	0.36
21-3	0.63	0.02	1H30	0.01	0.38
22-1	0.78	0.01	8H	0	0.21
22-2	0.62	0.01	8H	0	0.22
22-3	0.79	0.01	8H	0	0.16

It is therefore assumed that the inconclusive results shown in Tables 3 to 5 were due to the analysis being made before and after treatment in places of different initial chemical composition.

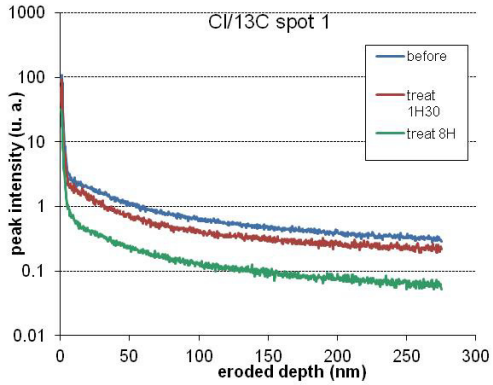
SIMS readings are shown on the graphs below.

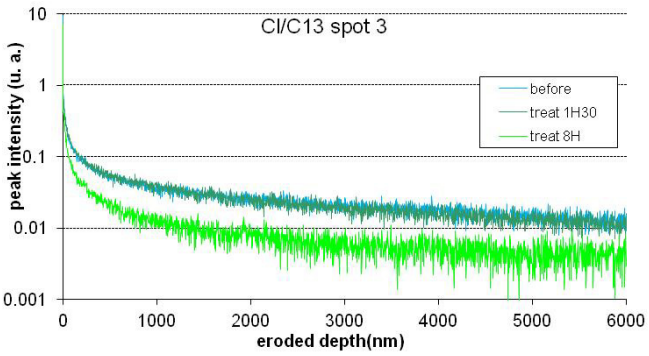
Concentrations of chlorine, hydrogen and oxygen in the bulk follow a decreasing curve, likely to be a diffusive pattern. Quantities of all three elements change mostly in the same direction under treatment.

The amount of chlorine remains stable or decreases only slightly during the 1st $1^{1/2}$ hour of treatment but is found lowered by a factor approaching 5 after the longer run.

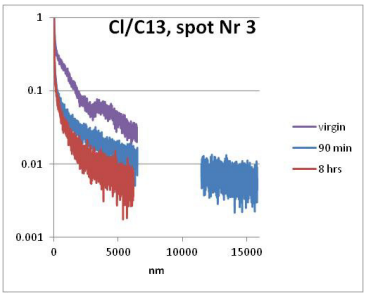
The uniformity of chlorine diminution from the surface to a depth d of 6000 nm in a time t of 8 hours indicates a diffusivity D greater than $d^2 / (4 \times t)$, or $D >> 3.10^{-16}$ m²/s.

[†] In a different context (glass matrix and primary source gallium) than the present study (graphite matrix and primary source bismuth) sensitivity to negative ions of chlorine and carbon are reckoned to be 23 000 [12]. This is key to chlorine being measured at such tiny concentrations as shown.





A deeper probing after the 1½-hour run, showing that the curve continues along the same line down to 15 000 nm (right) suggests the uniform diminution to reach at least that depth, which would indicate $D >> 2.10^{-15}$ m²/s.

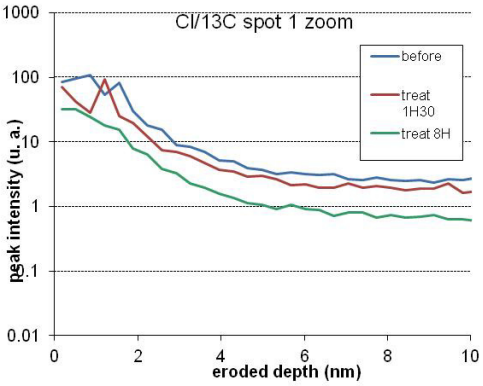


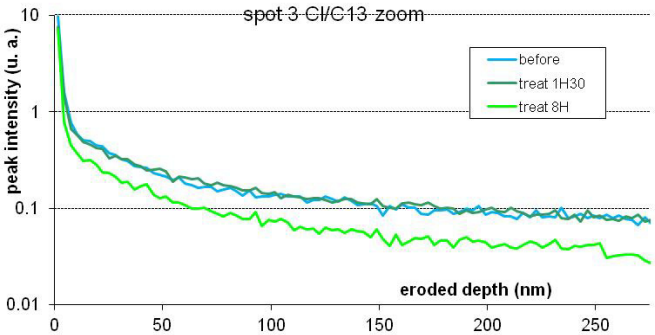
This would be in agreement with other findings [8].

It is to be expected though that the diffusivity of chlorine in graphite decreases as it nears exhaustion, since the remainder should be located in more tortuous and constricted pores.

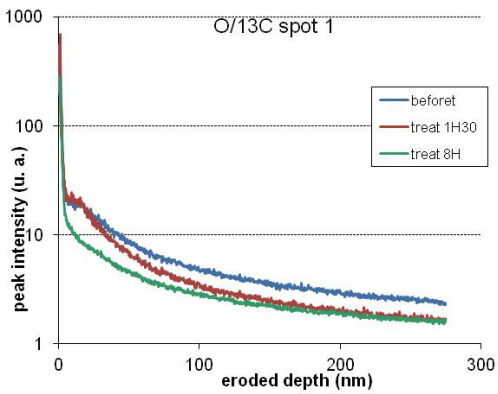
Chlorine, as well as hydrogen and oxygen, exhibits great variations in amount within the first 5 or so nanometers from the surface.

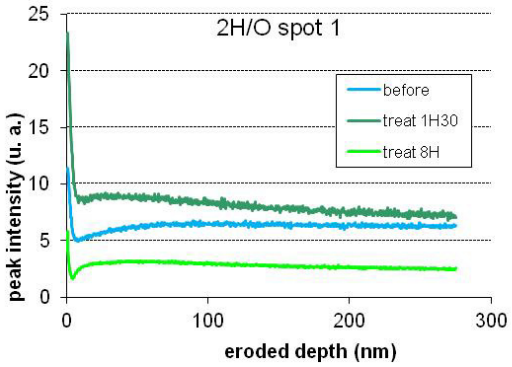
It is assumed that the higher concentration at the surface reflects the larger number of sites there due to roughness. This hypothesis is comforted by the continuity of curves in the shallow and deeper parts of the sample, strongly suggesting a communication exists. Surface abundance is therefore believed no to depart from the general diffusive behaviour of the species.





Graphs of ratios between amounts of different element may suggest correlations. With exception of the surface, variability of the 2H/O ratio is much lower than that of either elements considered independently, which suggests they exist mostly in the form of the H_2O molecule.





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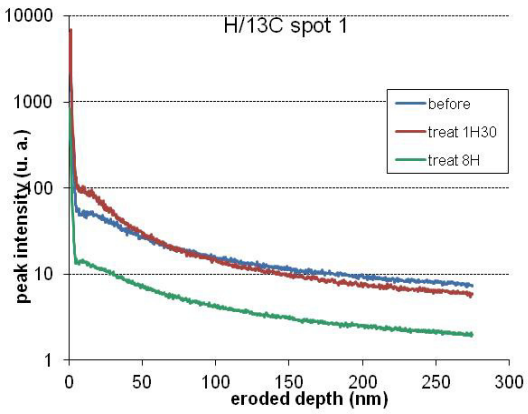
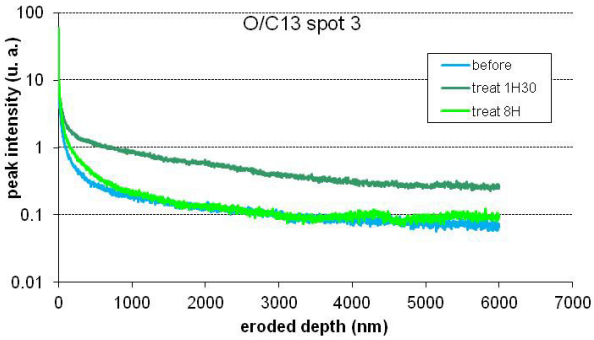
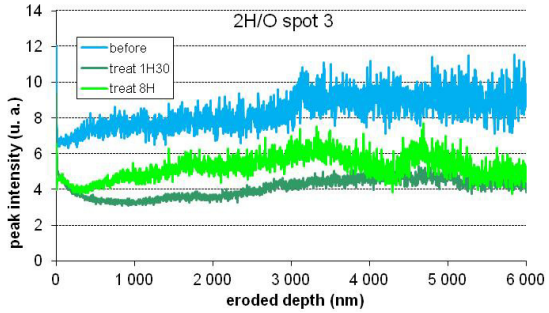
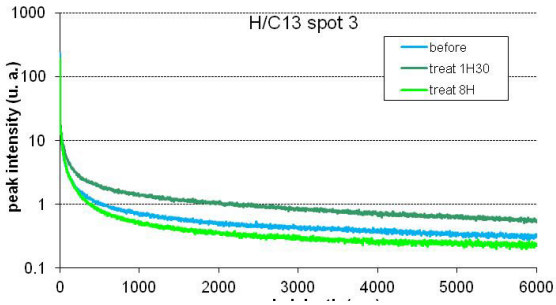


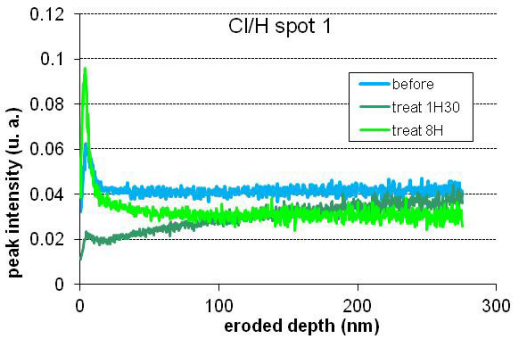
intake and release of moisture come nevertheless with some variations in the 2H/O ratio, which may be a sign of a hydrolytic activity even at these moderate temperatures, as oxidation is not likely to be significant. This can be the effect of UV radiation as well as that of catalysis by the graphite itself.

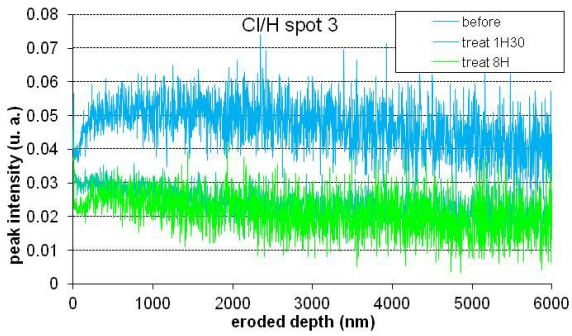




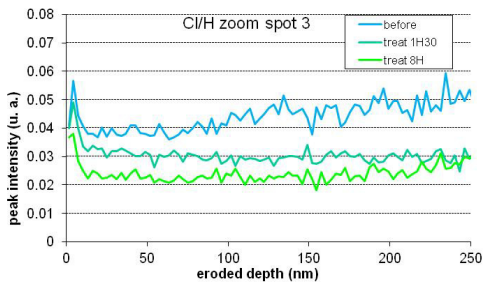


The Cl/H ratio varies very little, even considering the surface. This concurs with findings by Vaudey [1] that chlorine is mostly released as HCl and further indicates that this makes it the preponderant chlorine species also in the bulk.





A peak detected in both spots at about 10 nm below the surface is unexplained but might be related to accumulation in pores mouths or successive exchanges with the ambience in opposite directions.



4. CONCLUSION

Experimental observations may be summarized as follows.

- Treatment using hard-UV in humid air decreases the abundance of hydrogen and chlorine by a factor about 2 over $1^{1/2}$ hour and a factor about 3 to 5 over 8 hours, while that of oxygen is basically unaffected.

- Treatment appears effective at least throughout the first 15 µm from the surface of the graphite piece.

- Concentration profiles slope down from the surface for H, O and Cl. Gradient are sharp within the 5 first nanometers then look homogeneously diffusive in the bulk.

The main conclusion is that covalent bonding of chlorine in graphite, which is prevalent, will not prevent it from being released as hydrogen chloride. If a non-labile form of chlorine exists at all, as Vaudey [1] proposes, this cannot be identified to its being in a covalent bonding.

It is proposed that chlorine swaps covalent and ionic (or halogenic, a heavily lopsided covalent bonding) links quite readily. It is further proposed that hydrolysis plays a role in that process.

The apparatus

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