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**HYDROGEN ISOTOPE ANALYSIS OF THICK LAYERS DEPOSITED IN
TOKAMAKS**

J P Coad, B G Skorodumov*, V G Ulanov* and C H Wu**

JET Joint Undertaking, Abingdon, Oxon OX14 3EA, UK

*Institute of Nuclear Physics, Academy of Science of Uzbekistan, 702132 Tashkent,
Uzbekistan

**The NET Team, Max-Planck-Institut für Plasmaphysik, D-85748 Garching, Germany

ABSTRACT

Predictions can be made of the tritium retention in future tokamaks such as ITER based on analyses of the D retention in redeposited films in existing tokamaks. However, although amounts of H+D up to the saturation level are frequently observed, measurement is invariably by Ion Beam methods such as NRA and ERDA which only analyse to a depth of the order of a micron, whilst it is only the total content of very thick layers that is of relevance to ITER. This paper compares these near-surface data with methods developed to determine the composition throughout thick C-H films (~100 microns) such as Neutron-induced Elastic Recoil Detection Analysis (n-ERDA) and SIMS and Nuclear Microprobe analysis of specially prepared cross-sections.

1 INTRODUCTION

The primary mechanism for hydrogen retention in large tokamaks is codeposition with (and/or implantation into) material eroded from areas of plasma-facing components (PFC) with high incident fluxes and redeposited in regions of lower fluxes. If the PFCs are made of carbon in the form of graphite the saturation level of H-isotope trapping in redeposited layers at <270C has been shown to be given by $H:C \approx 0.4:1$ (1). In a long pulse, high power machine such as the planned **I**nternational **T**hermonuclear **E**xperimental **R**eactor (ITER) redeposited films up to millimetres in thickness may accumulate at the deposition-dominated wall areas. If the machine is fuelled by a 50% deuterium (D)/50% tritium (T) mixture, then T may be trapped at up to 0.2 times the amount of C in these thick layers, and retention of this magnitude would be unacceptable both from radioactivity and cost considerations.

In the post-mortem analysis of PFCs from JET and other tokamaks, similar amounts of H and D are generally observed in the near-surface region: since JET is normally fuelled with D the reason for the prevalence of H is unclear (2). However, as a result a saturation level of H-isotopes in the near-surface region may correspond to an analysed retention of D of about 0.2 times the amount of C, and D at this level has frequently been observed in surveys of the PFCs in JET (3,4). Most of these measurements have been made using the **I**on **B**eam **A**nalysis (IBA) variant **N**uclear **R**eaction **A**nalysis (NRA), and with this technique usually only the outermost 1 micron (approximately) of the surface is analysed. Redeposited layers up to 130 microns thick have been measured in JET by sectioning the films on the flanks of the discrete limiters used until 1986 (5), and it is clearly important for the retained D inventory to know whether or not the D concentration throughout the film is the same as that seen by NRA in the outermost micron. A **S**econdary **I**on **M**ass **S**pectroscopy (SIMS) profile was made at a different point on the limiter where the film was 24 microns thick which showed that the D (and H) concentrations appeared to start high at the surface, but then fell by about an order of

magnitude within the bulk of the film (5). However, the SIMS technique, which consists of sputtering material from a surface using an ion gun and analysing the ion content of the sputtered material entering a mass spectrometer, cannot be considered to be quantitative except in certain well-defined situations. Firstly the sputtering yield for an impurity element in a surface can vary over orders of magnitude depending on the surface roughness, the composition of the substrate and the binding configuration of the impurity. Secondly the fraction of material sputtered as ions and detected by the spectrometer varies by many orders of magnitude for different elements, and thirdly the composition profiles into the surface can be severely distorted due to differential sputtering, knock-on and shadowing effects.

Thus JET data (which give a similar picture for H-isotope retention to other tokamaks) generally show high surface (~1 micron) concentrations of retained H and D, and provide an example of lower concentrations into the bulk of a thick redeposited film. This paper describes the assessment of techniques for determining the H-isotope content of thick (>10 micron) films and their application to the analysis of the same thick redeposited films from the 1986 JET limiters.

2 EXPERIMENTAL RESULTS

(a) Preparation of samples

The ideal situation would be to be able to make an analysis in situ, or at least on a complete component after removal from the tokamak. However, since the limiter tiles removed from JET after the 1986 operations were each 450 x 120 x 77 mm, the only technique able to analyse a complete tile was IBA using a large target chamber specially constructed for analysing JET components. In order to investigate other methods it was therefore necessary to prepare smaller samples: samples were cut from the flanks of one of the limiter tiles as shown in Figure 1. Samples cut from the same part of the profile of the tile (eg samples 3, 8 and 11) are assumed to be equivalent. Since the films are very thick, it is possible to profile through the film by analysing a cross-section of the film, if the spatial resolution of the technique is good enough, and this can be enhanced by producing a taper section which improves the resolution by up to an order of magnitude by increasing the apparent thickness of the film. Thus it can be seen that sections were prepared from samples cut adjacent to the conventional coupons. However it should be noted that preparation of sections may affect the results subsequently obtained by smearing material across the surface or leaching out certain components by reaction with the potting resin or polishing solution. (A possible method of preparing a section through a thick film without metallographic polishing is ion beam slope cutting (6,7). The area to be analysed is the side wall of a crater formed by ion bombardment, the line of the wall being defined by a sharp-edged screen. However development of the

technique from films a few microns thick (7) to films of the order of 100 microns has yet to be demonstrated.)

(b) NRA analyses of tile samples and an implanted standard

The samples cut from the JET limiter tile were analysed by NRA to obtain the surface (~1 micron) concentration of D using the $D(^3\text{He},p)^4\text{He}$ reaction. The results are given in the first column of Table 1. To check the quantification some graphite samples were also implanted to saturation with 5 keV deuterons over a 5 mm diameter region, which according to TRIM calculations should provide a surface containing 6.10^{17} deuterium atoms cm^{-2} within the outermost 0.15 microns. One of these standards analysed by NRA and by other techniques is included in Table 1 and the NRA result (which was duplicated in different laboratories) is shown to be in good agreement with the calculations.

(c) Heavy Ion Induced Elastic Recoil Detection Analysis

Another of the IBA family is **Elastic Recoil Detection Analysis (ERDA)** wherein an ion beam is incident at glancing angle and atoms may be ejected from the surface after an elastic collision with the incident ion (that is, most of the incident energy is transferred to a recoil in the collision). The detector for the ejected particles is placed at glancing angle in the forward direction. In the most common form of this technique a helium ion beam is employed at energies up to 3 MeV. Each of the H isotopes can be separately analysed by this method, and the depth of analysis is about 1 micron. The technique is much more dependent on surface roughness than NRA, but is usually the only way to obtain an idea of the H (ie protium) surface concentration. However, if very much higher incident energies are employed the analysable depth increases, and if ions of a heavier element are used the range of masses detected is also increased: this is the technique known as Heavy Ion ERDA (8,9). Ejected ions are detected using ionisation chambers wherein an ion from the sample passes through the chambers in series. The maximum value of the energy loss dE/dx , i.e. the Bragg peak height, of the detected particles in the detector gas depends on their atomic charge number Z . By suitable adjustment of the detectors, the atomic number and energy of each ion can be measured simultaneously. From the number of ions detected as a function of energy, for each element in the energy loss versus energy plots, can be calculated the depth distribution of that element into the surface.

Figure 2 shows depth distributions for the masses 1, 2, 12 and 16 (H, D, C and O, respectively) through the outermost 2 microns of the surface of sample 8 from the 1986 JET limiter tile. Profiles can be derived to about 10 microns for the H isotopes under these Heavy Ion ERDA conditions, but it can be seen in Fig. 2 that the H, D and O are mostly restricted to the outermost $1/2$ micron of the surface. Note, however, that the H continues at ~20% of its

peak value beyond 2 microns, whereas the D concentration falls to zero. Integrating under the D depth profile and using a surface density for graphite of 10^{19} atoms cm^{-2} gives a concentration of 3.10^{17} D atoms cm^{-2} on sample 8. As seen in Table 1 this is lower than the NRA value, but factors of two between these methods have been seen previously (10) and may be due to a difference in the calibration of the Heavy Ion ERDA technique.

(d) Neutron-induced Elastic Recoil Detection Analysis (n-ERDA)

ERDA with primary ions can be seen from the previous section to be potentially very powerful, but the depth attainable is limited by the need to use glancing angles (to approach the forward scattering conditions necessary for maximum momentum conservation, and which also imposes severe practical limitations on the sample) and by the penetration of the primary beam. These limitations are eased if **neutrons** incident on the rear of the sample are the primary source. Fast neutrons will pass through samples a few millimetres thick without significant energy loss or attenuation, and the maximum escape depth for the recoil particles (i.e. normal to the surface) can be utilised (11). For graphite samples total H isotope concentrations can be absolutely determined from comparison with $\text{TiH}_{1.87}$ and $\text{TiD}_{1.97}$ standard samples for films 300 - 400 microns thick using 14 MeV neutrons, with variations in concentration with depth visible with a resolution for D analysis of ~ 30 microns: using 2.5 MeV neutrons these figures become ~ 50 and ~ 5 microns, respectively. In these experiments a 14 MeV neutron source was employed, and a three detector telescope using silicon sensors was used to simultaneously measure energy loss and energy for each particle. One disadvantage of the method is that the neutron flux at the sample obtainable from an accelerator used as a neutron generator is much lower than the ion flux that can be achieved, so counting times are much longer (typically \sim an hour) for reasonable statistics and the absolute sensitivity of the technique is also lower than for the ion beam techniques.

The total amounts of H and D present throughout the thickness of the films (since they are well within the detection range for 14 MeV neutrons) are listed in the right-hand columns of Table 1. It can be seen that according to n-ERDA the total amounts of D in films up to 120 microns thick are not much greater than those detected in the outermost micron by NRA, although there was good agreement in the analysis of the D standard. n-ERDA also showed larger quantities of H than D in the films. In order to shed light on these somewhat surprising results, the data were deconvoluted to provide depth profiles through the thickest film (sample 4), and these experimental profiles were compared with profiles simulated by Monte Carlo methods for a number of distribution scenarios. The results for D are shown in Figure 3. It can be seen in the figure that the data are a good match to a distribution with 33% of the D at the surface and the remainder tailing in approximately 70 microns into the film, but clearly do not match the other model distributions in the figure. Likewise Figure 4 shows the experimental

profile for H, and in this case there is a good match with a distribution with a constant level for 70 microns from the surface followed by a concentration decreasing from half that value to zero over the next 50 microns.

The distributions in Figs 3 and 4 are merely indicative and in reality there may be a wealth of fine structure, since the inherent resolution of the n-ERDA technique is rather poor. However, uniform concentrations of either H or D throughout the film are precluded, and there is a genuine difference between the distributions of the two isotopes: much more detailed information on the distribution in the outer part of the film would be obtained using 2.5 MeV neutrons. Assuming the best-fit profiles to be correct, the H and D contents of the outermost 1 micron would be 1.10^{17} and 2.7×10^{17} atoms cm^{-2} , respectively.

Thus the n-ERDA data suggest the D is concentrated at the surface, and are not inconsistent with the NRA results, although the expected amount in the outermost micron is about half the NRA amount (as was the Heavy Ion ERDA result). Note also that the H content of the outermost micron is ~ one-third of the D content (as indeed was shown by Heavy Ion ERDA on the adjacent sample), so that a more surface specific technique would suggest there is **more** D than H in the film whereas in fact there is almost an order of magnitude **less**.

(e) Nuclear Microprobe analysis of sections

The Nuclear Microprobe produces a focussed ion beam with a minimum diameter of about 5 microns. Thus in principle it is possible to produce NRA profiles through a thick film with a resolution of about 5 microns by analysing a section through the film in a Nuclear Microprobe. Indeed, this resolution can be improved to about 1 micron by producing a taper section through the film. At the maximum resolution the beam current becomes too low for analysis in a reasonable time, but since the film extends uniformly in one direction (supposedly) the beam can be extended parallel to the film surface without degrading depth resolution. In this investigation the bombarded area was thus oblong, 15 microns wide (which is thus the resolution across the section) and 100 microns long, allowing good statistics in about 60 secs. Figure 5 shows a plot of D peak intensity (in arbitrary units) versus distance across the redeposited film section. This section was a taper section of a 60 micron thick film polished at 5 degrees to the surface of the sample: the film appears 240 microns across, so the tapering improves resolution by a factor of 4. (The factor of 11 that might be expected geometrically does not appear to be realised). The sample was taken from a different part of the 1986 limiter, though from a similar section of tile to that shown in Fig.1.

The Nuclear Microprobe analysis shows a peak of D at the surface, the width of which is approximately equal to the beam width, so the actual width of the D-rich layer in this taper section must be $\ll 15$ microns, and therefore in normal section must be of the order of a micron or less. Integrating under the surface peak and under the rest of the depth distribution

suggests about half of the D is in the surface peak, a result similar to the n-ERDA analysis of another area of film.

(f) SIMS profiling and analysis of sections

As mentioned in the Introduction, a SIMS analysis of a similar limiter tile from 1986 showed lower H and D levels within than at the surface (5), but there are many possible errors associated with the measurement. However, many of the errors associated with sputter profiling disappear if SIMS is used to image the cross-section, as signal intensities from all points in the section should be directly comparable. Furthermore since the primary ion beam used can be focussed to $\ll 1$ micron the potential resolution makes the technique complementary to the Nuclear Microprobe. A number of sections, including sample 12, from limiter tiles were examined by SIMS, but the results were disappointing. When the whole cross-section was viewed good secondary electron images were obtained, and ions of impurity elements such as Cr and Ni could be mapped. However the D and H distributions were distorted and could not be used to compare the quantities of each isotope across the film. It was possible to see that there was generally an aggregation of H and D at the surface, and occasionally accumulations at defects within the film or at the film/substrate interface. It was also clear that on the micron scale the composition parallel to the surface, as well as through the film, was variable.

Conventional SIMS was performed (i.e. by bombarding the the outer surface) on samples 1 - 5 and the D standard. Figure 6 shows the signal intensities in the mass peaks 1, 2 and 12 (H, D and C, respectively) versus bombardment time for the D standard. The maximum D signal level is about a factor of 7 lower than the C signal, so this should correspond to the saturation ratio for D:C of 0.4:1 (1). The D level falls off after ~ 300 secs, which according to TRIM code predictions should correspond to a depth of ~ 150 nm. Figure 7 shows a similar spectrum recorded from the tile sample 4. Again the maximum D signal is about a factor of 7 lower than the C signal, so since the matrix is again essentially carbon, this should also indicate the saturation level for D in C. Note, however, that this is only for < 100 secs at the start of the profiling. The beam current density was about twice that used in Fig. 6 (hence the C signal is 10^4 rather than $4 \cdot 10^3$) so the amount sputtered away in this time (again assuming similar behaviour to the standard) is ~ 100 nm. The D concentration then stabilises at about a factor of 5 less than its earlier value.

The steps up and down in signal levels seen in Fig. 7 after ~ 600 and ~ 1000 secs are due to deliberately raising the beam current density by a factor of two and then returning it to the initial value. The signals from elements present in the substrate should also double, but impurities originating from the vacuum system should not respond in this manner. In particular H is always present in the system. From the behaviour of the H signal in Fig. 7 it

can be seen that about half of the H at that time is really part of the film whilst the rest may be contamination. By comparison with Fig. 7 and profiles from other samples analysed at that time, it seems probable that most if not all of the H seen in Fig. 6 comes from contamination. It should be noted that the relative intensities of the H and D signals cannot be taken as a measure of their relative quantities in the film, since the ion sputtering characteristics and detection efficiencies may differ.

3 DISCUSSION

All the analyses of these redeposited films on samples cut from the flank of one of the discrete limiters used in JET in 1986 agree that the D is peaked within the outermost micron (approximately) of the film, and that there is perhaps a similar amount in total in the remaining thickness of the film. Thus there is no serious discrepancy between any one technique and others. None of the techniques offers a non-destructive method of analysing the large components likely to be used as PFCs in ITER, and these data highlight the problem that **surface** analysis by NRA (which can be done non-destructively) cannot be used to predict **bulk** composition.

n-ERDA can provide a quantitative analysis simultaneously for each of the isotopes H, D and T through films up to some hundreds of microns thick (and would give the ratios H:D:T in the outer part of films in the millimetre range, should they occur). The method does rely on neutrons penetrating through the sample without significant losses, but the resulting limitations on sample composition and thickness have not been fully assessed. Samples of graphite a few millimetres thick as in this work present no problem, so it may be possible to analyse through certain first wall components, or to arrange for special components with the outer few millimetres detachable in areas where rapid film growth is expected. If samples have to be cut out for analysis, then cutting out samples to a rough thickness tolerance is all that is required for n-ERDA as well as the surface layer examination techniques like Heavy Ion ERDA and SIMS, whilst that is only the first step in the preparation of the sections necessary for Nuclear Microprobe analysis. There is also a risk that the polishing process may introduce anomalies into the film analysis, though there was no evidence of such problems in this investigation: ion beam slope cutting (6,7) may offer an alternative preparation method. Smearing effects during sectioning would, however, be expected to be too great to allow second order measurements such as bulk diffusion to be made using either technique. The Nuclear Microprobe could also measure T depth profiles for films deposited from D-T plasmas by using a different NRA reaction, but, like n-ERDA, does not have the sensitivity to measure the T in films deposited from D-D plasmas. Measurement of H by ERDA is also possible in principle, but would be very difficult in practice due to the glancing angle geometry required.

The samples used in this work are the only known examples of very thick (~100 microns or more) material redeposited in a tokamak, and it was hoped that they would contain significant D levels throughout the film to provide a better test for the analysis options. The fact that the SIMS analysis previously carried out on the tiles (5) showed reduced H and D levels within the film means that the localisation of the D to the surface in these analyses several years later is unlikely to have occurred merely with time. The discrete limiters regularly reached temperatures in excess of 1000C at the erosion zones to either side of the centre of the tile during plasma pulses, and temperatures in the redeposition zone must also have regularly exceeded the 400C at which the film starts to degas (12): a number of the plasma pulses also terminated in disruptions which can cause large transient heat loads. Thus thermal outgassing of the samples seems a plausible reason for the low total D content of these films, and it may be possible for high D levels to exist throughout a thick film provided the temperature is always kept low enough.

4 CONCLUSIONS

The H, D and T contents of films up to hundreds of microns thick can be simultaneously measured quantitatively by n-ERDA. For thick film analysis a source of 14 MeV neutrons is required, whilst better resolution in depth distributions is obtained using 2.5 MeV neutrons. It is intended to develop a n-ERDA analysis facility capable of providing both energies in the near future.

Metallographic sectioning can also be used to provide D depth profiles through thick films with the Nuclear Microprobe. These tests show that the depth resolution obtainable is a few microns using taper sections, which is equivalent to about 1 micron in a normal section through the film. Of course considerable effort is required to produce the sections, but the polishing process does not appear to have a deleterious effect on the profiles. T depth profiles could also be measured for films deposited from D-T plasmas.

These thick (up to 130 micron) redeposited films had a total D content no larger than thin films found elsewhere in JET, and the D concentration within the surface was at least an order of magnitude less than in the outermost 1 micron. It is believed that this is due to thermal outgassing of the films when the limiters were heated to ~1000C by the JET plasma during high power discharges and/or as the result of disruptions.

5 ACKNOWLEDGEMENTS

The help of Dr R Behrisch (Max-Planck Institut fur Plasmaphysik, Garching) and Dr W Assmann and H Huber (Ludwig Maximilians Universitaet Muenchen) with Heavy Ion ERDA analysis, Dr S Sugden (AEA Technology) and Dr A Clough (Surrey University) with Nuclear

Microprobe analysis, B Farmery (Sussex University) with NRA analysis and Dr A Chew (Loughborough Consultants) with SIMS analysis is gratefully acknowledged. This work was supported by NET in the context of the European Home Team contribution to ITER (ITER Task T62 of the 1994 Comprehensive Task Agreement).

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TABLE 1 Comparison of the analyses (all in units of 10^{17} atoms cm^{-2}) of H-isotopes in carbon samples by different techniques.

Sample Number	NRA	HIERD	NERD			
			Outer Micron		Total in Film	
			H	D	H	D
1 or 6	4.7					
2 or 7	5.4				19.0	6.2
3 or 8	5.0	3.0			72.0	8.0
4 or 9	4.8		1.0	2.7	65.0	8.5
5 or 10	2.6				87.0	5.3
D-standard 2	5.1 (5.3)				b/g	7.5

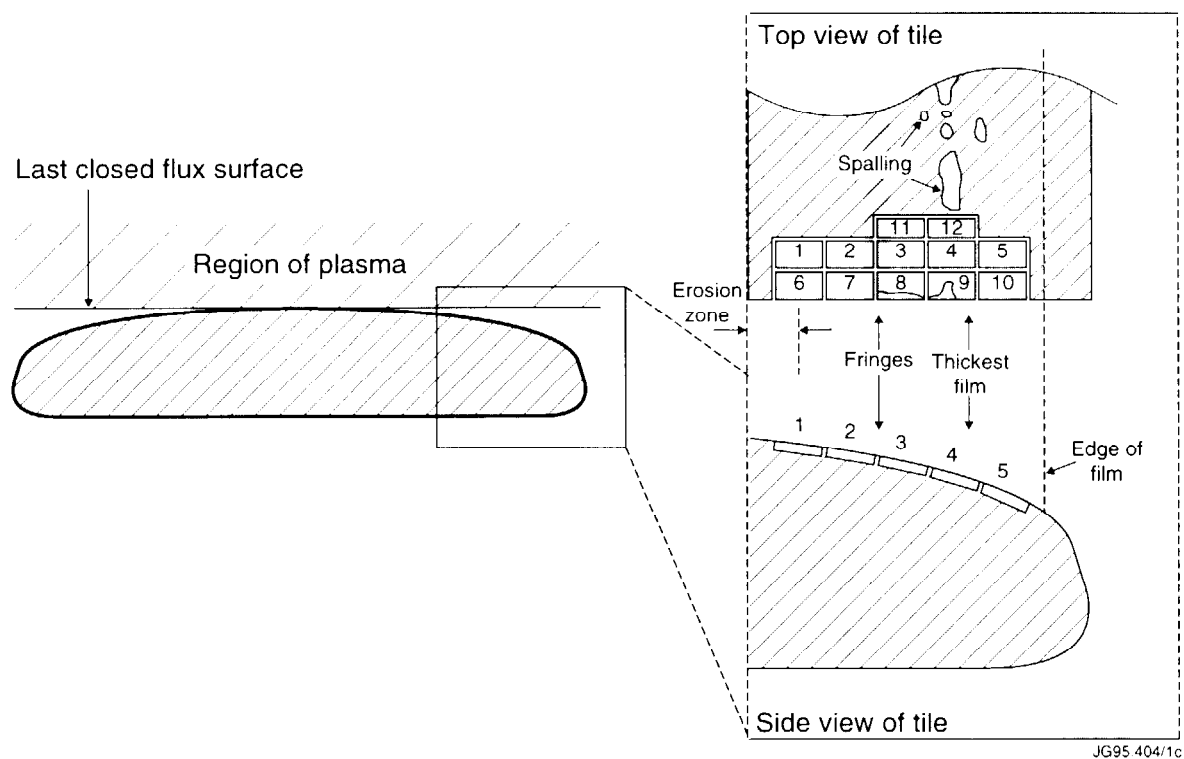


Fig.1: A diagram showing the original locations of the samples cut from a JET limiter tile used in this study, and the position of the tile relative to the JET plasma.

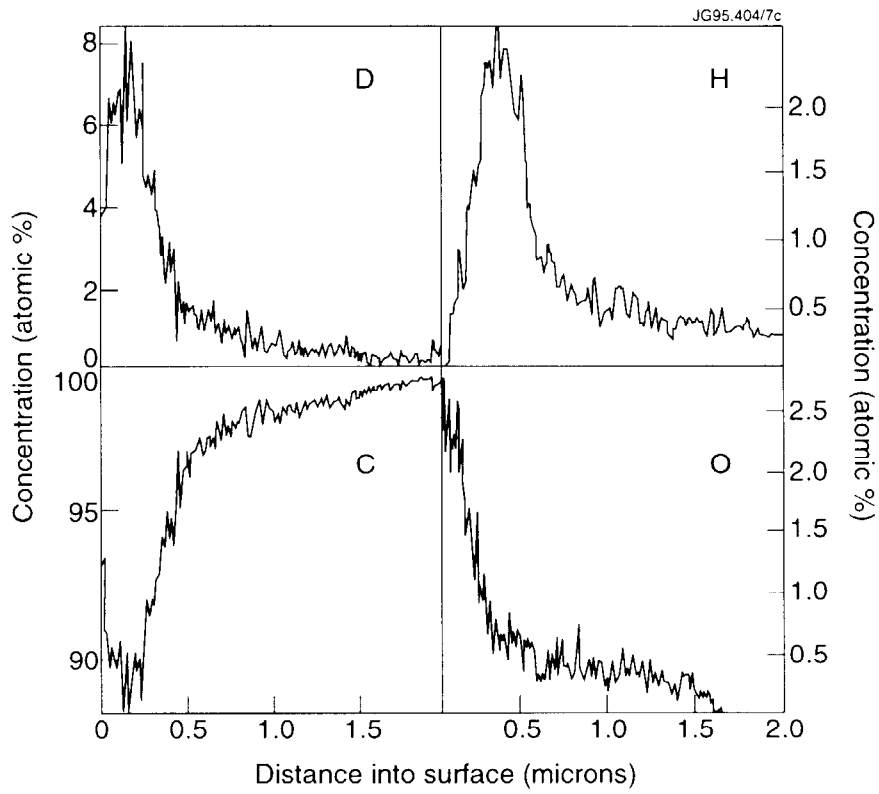


Fig.2: Depth distributions for masses 1, 2, 12 and 16 (H, D, C and O, respectively) determined by Heavy Ion ERDA in sample 8.

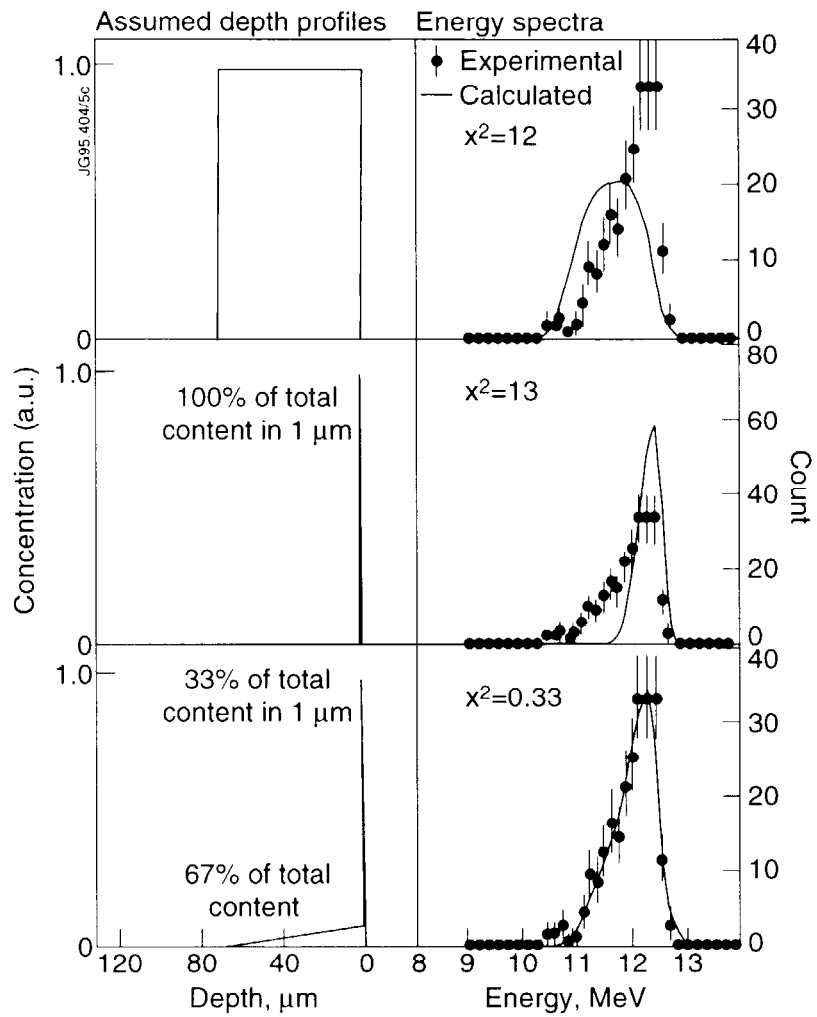


Fig.3: The n-ERDA spectrum for D from sample 4 compared with the calculated spectrum expected for each of three different D depth distributions in the film.

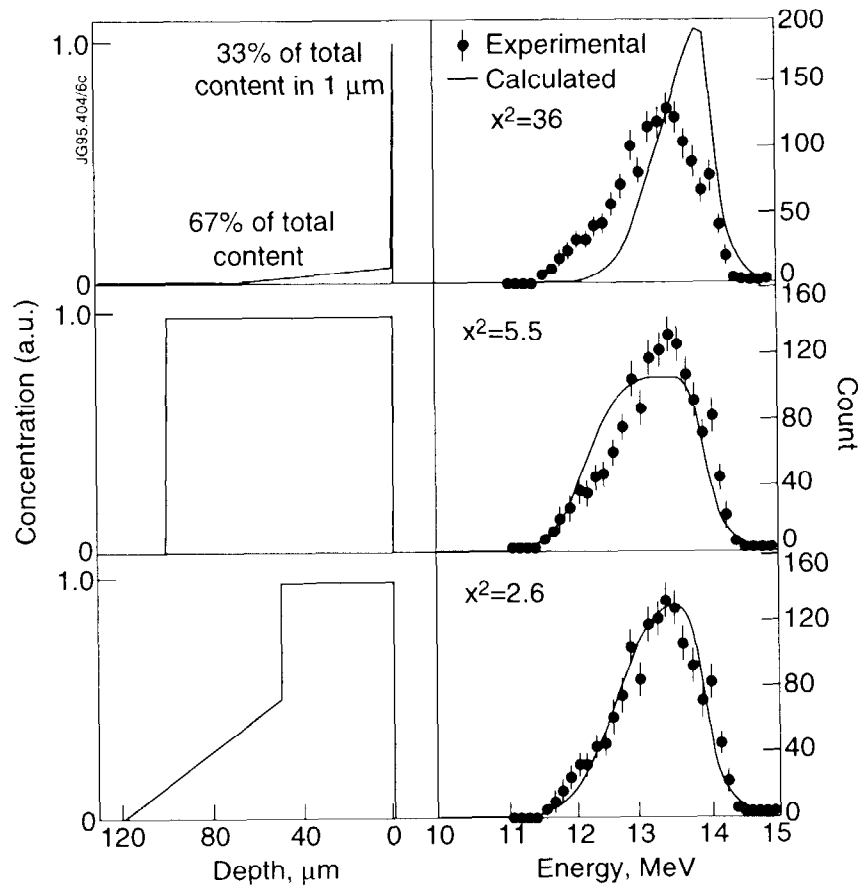


Fig.4: The n-ERDA spectrum for H from sample 4 compared with the calculated spectrum expected for each of three different H depth distributions in the film.

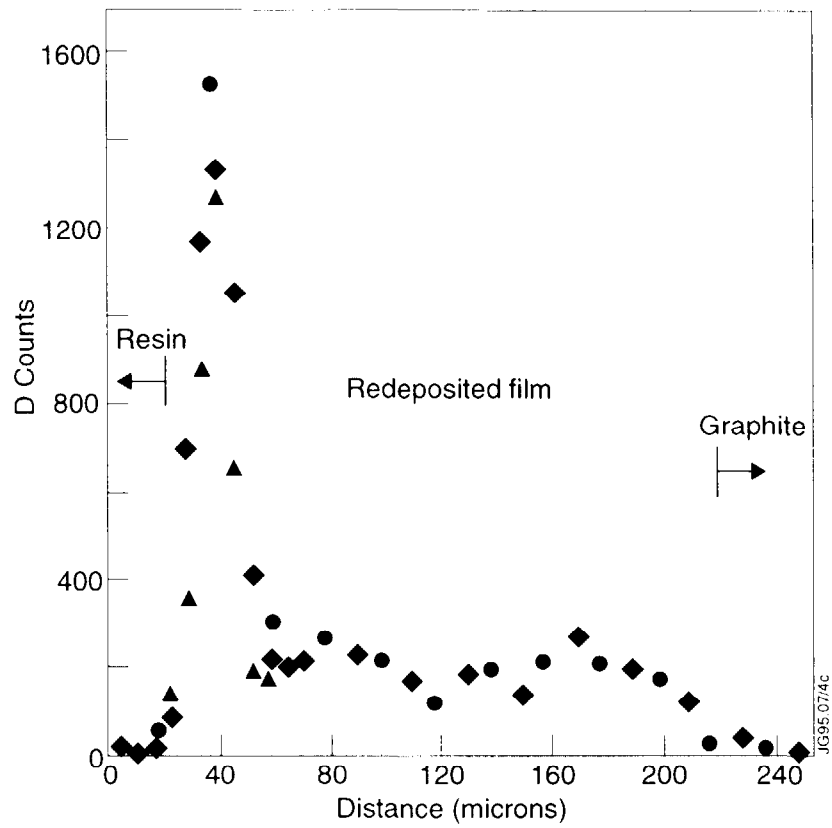


Fig.5: The D peak intensity versus distance across the taper section of a redeposited film obtained by NRA using a Nuclear Microprobe.

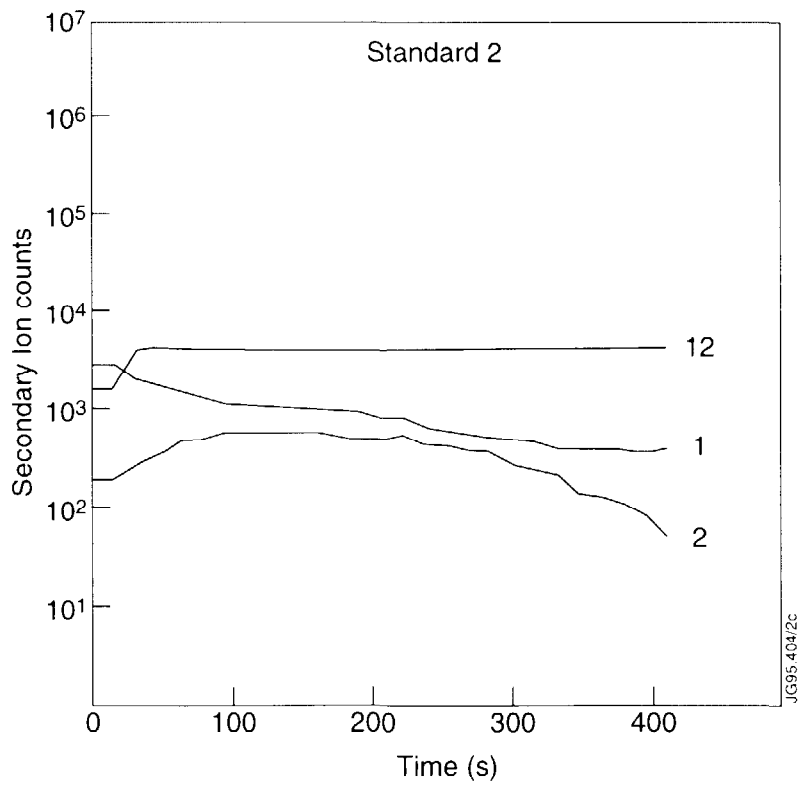


Fig.6: Signal intensities for masses 1, 2 and 12 (H, D and C, respectively) versus sputtering time (i.e. depth) into a D-implanted graphite standard.

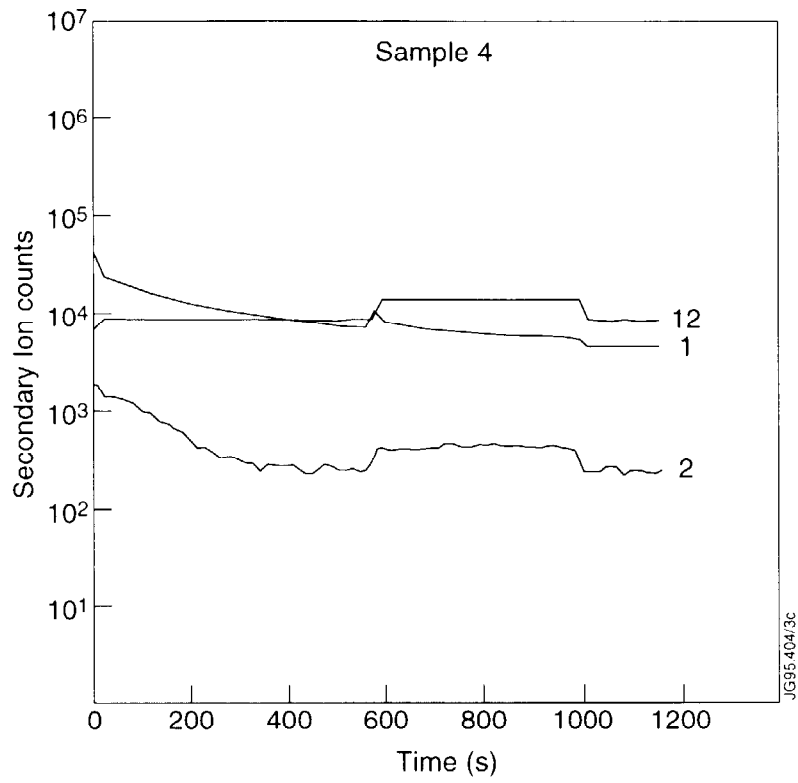


Fig.7: Signal intensities for masses 1, 2 and 12 (H, D and C, respectively) versus sputtering time (i.e. depth) into sample 4.