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Report

DEUTERIUM TRAPPING IN LOW Z COATINGS

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DEUTERIUM TRAPPING IN LOW Z COATINGS *

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(Euratom/UKAEA Fusion Association)

Abstract

Measurements of deuteron trapping in a series of low Z wall coatings, proposed for use in JET, are reported. Mass spectrometry has been used to study the re-emission of 100eV to 2keV D_2^+ ions during bombardment at implant temperatures of between 300 and 1100K. Titanium carbide coatings of 20 μm thickness are found to trap large quantities of deuterium at temperatures ≤ 800K. Other samples, including alumina, silicon and titanium dioxide all show a saturation behaviour following ion doses ≤ 10^{18} deuterons cm^{-2}. Under certain bombardment conditions an increase in trapping is recorded as the implant temperature is increased from 600K to 800K. The implications of these results for the tritium inventory when using D/T plasmas is discussed.

April 1982

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1. Introduction

Measurements are reported of deuteron trapping in a series of low Z coatings which have been proposed for use on the walls and limiter surfaces exposed to the JET plasma. Similar proposals and associated studies are underway for future use on TFTR (1) and JT-60 (2).

There are two major problems which arise from the plasma wall interaction. The first of these is the introduction into the plasma of wall materials with sufficiently high Z to cause unacceptable power loss by radiation. These impurities may be introduced by sputtering, arcing or evaporation; their abundance will be a strong function of the energy of the plasma particles in the near-wall region. The second problem, which will arise in the active phase, is hold up of tritium in the wall. On the grounds of cost and availability alone, the tritium inventory must be limited. A wall material into which tritium diffuses and is not readily recoverable, will be unacceptable.

The use of a cold gas blanket has been suggested to lower particle energies in the plasma edge region, and hence reduce the introduction of impurities. Bombardment with deuterium atoms and ions with energies ~ 100eV and higher would still be expected, however. In view of the dramatic reduction in radiation loss with decreasing Z, one possible solution is to coat the walls and limiter surfaces with a low Z material. JET has initiated several contracts to investigate the suitability of a selection of low Z coatings from the points of view of mechanical integrity, deuteron trapping and retention, and behaviour in a tokamak environment.

The object of this study is to investigate deuteron trapping and deuterium re-emission during bombardment with monoenergetic ion beams in the energy range 50eV to 1keV per deuteron. Sample temperatures in the range 20°C to 800°C suitably cover all expected wall temperatures, which should not exceed 500°C during operation. The results are relevant to deuterium re-cycling with the coated walls, and are of particular importance in the active phase in relation to tritium retention.

Since the start of this contract evidence has come to light which would suggest that most coatings studied are unsuitable for use on limiter surfaces. The problems are associated with conduction of heat away from the coating surface. To enable a sufficiently low surface temperature to be maintained to avoid loss by evaporation, a very thin coating must be used. This in turn puts a severe limit on the coating lifetime due to loss by

sputtering. Nevertheless, the data presented here is still very relevant in respect of coatings for the walls of the vacuum vessel, and indeed for limiters if in-situ coating is ever contemplated.

Samples were manufactured at AERE Harwell under a separate contract (3). Three deposition techniques were used: (1) plasma spraying; (2) co-sputter ion plating and (3) vapour deposition (PAVD). The substrate used in each case was 1mm thick Inconel 600. A summary of the sample materials, methods of deposition and resulting surface roughness are given in Table 1.1. The roughness figures are the average peak to valley height and peak to valley distance along a 3mm length of material using a "Sloan Dektak"* talystep.

Table 1.1

Summary of Sample Materials Used for Trapping Measurements

Material	Formula	Roughness	Colour	Method of Manufacture
Aluminium Oxide (Ref AO)	Al_2O_3	15/50μm	Off-White	Plasma spray 0.1 - 0.3mm thickness
Titanium Carbide (Ref TC)	TiC (+ added Ti)	1.5/25μm	Grey	Co-Sputtering of Ti and C 20μm thickness
Silicon (Ref S)	Si	15/30μm	Grey	Plasma Spray 0.1 - 0.3mm thickness
Spinel (Ref MA)	$MgAl_2O_4$	20/50μm	Off-White	Plasma Spray 0.1 - 0.3mm thickness
Alumina-Titania (Ref AT)	Al_2O_3 + 2.5% TiO_2	20/50μm	Off-White	Plasma Spray 0.1 - 0.3mm thickness
Titanium Dioxide (Ref TO)	TiO_2	20/30μm	Blue-Black	Plasma Spray 0.1 - 0.3mm thickness
Silicon Carbide (Ref SC)	SiC	0.5/25μm	Blue-Grey	Vapour Deposition (PAVD) 15μm thickness

Three sample materials are good insulators (Alumina, Alumina-titania and Spinel), and hence pose a charging problem during deuterium irradiation. They

* Santa Barbara CA

may, however, in a plasma environment afford a considerable reduction in arcing and associated impurity production (4), if made sufficiently thick to withstand breakdown.

2. Trapping and Re-Emission Measurements

2(i) Equipment used for Trapping Studies

Monoenergetic deuterium ion beams of between 100eV and 2keV D_2^+, (50 - 1000eV per deuteron), were produced in the Culham low energy, UHV ion accelerator. This apparatus has already been used for several earlier studies of deuterium ion trapping and re-emission from carbon (5) and stainless steel (6).

Ions are extracted from an electron impact source at 2keV, focussed and then passed through a Wien filter. This filter selects the ion of interest (D_2^+ for all measurements presented here), and removes any impurities which might be present. An electrostatic quadrupole doublet lens is used to focus and steer the beam through differential pumping apertures, and finally on to the target in the target chamber assembly.

Three stages of differential pumping allow pressures in the target chamber in the 10^{-9} torr range (typically 2×10^{-9} torr) to be maintained during bombardment. This background is mainly deuterium from the ion source, with small quantities of H_2O and CO. The use of mercury pumps throughout avoids the possibility of pump-oil contamination. Only during the highest temperature bombardment (800°C) did pressures reach an order of magnitude higher than this, due to outgassing within the target chamber.

The target chamber and associated target manipulation assembly was specially designed to cope with the difficult requirements imposed by the use of insulating samples and high target temperatures.

A schematic diagram of the arrangement is shown in Figure 2.1. Six targets can be incorporated in the chamber at any one time, each with its own heating system, grid assembly and beam defining apertures. Accurate positioning into the ion beam is made using a multi-motion goniometer. The technique used for ion trapping measurements requires a monitor of the re-emitted deuterium during ion bombardment. This is accomplished using a quadrupole mass spectrometer to monitor the partial pressure rise of deuterium in an inner target chamber, as it is released from the target due to backscattering, ion induced re-emission or diffusion. A second small

Figure 2.1

Schematic Diagram of Target Chamber Assembly

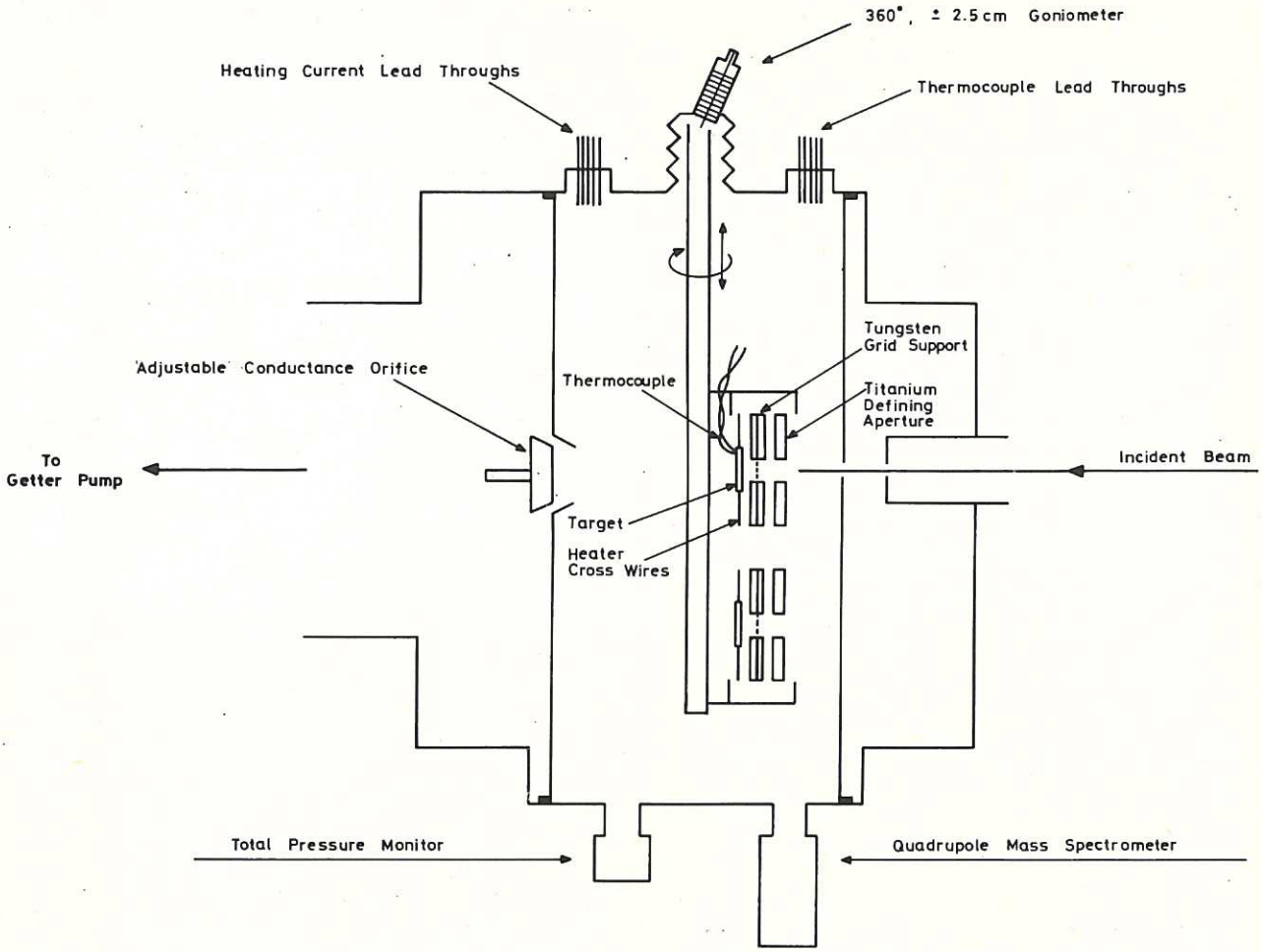
360°, ± 2.5 cm Goniometer
Heating Current Lead Throughs
Thermocouple Lead Throughs
Tungsten Grid Support
Adjustable Conductance Orifice
Thermocouple
Titanium Defining Aperture
To Getter Pump
Incident Beam
Target
Heater Cross Wires
Total Pressure Monitor
Quadrupole Mass Spectrometer

Fig. 2.1

quadrupole is used to record the partial pressures of other gases (H_2O, CO) in the chamber. The conductance of the pumping aperture from the inner target chamber defines the pressure rise and hence the sensitivity of the measurements. In order to achieve reasonable background pressures at high target temperatures (hence high outgassing rates) a variable conductance pumping aperture was incorporated.

A novel technique of using 0.15mm tungsten cross wires, spot welded to the Inconel back faces of the $1cm^2$ targets, has proved a very successful technique for conduction heating. The heating power requirement and resultant chamber outgassing is small compared with the more conventional ceramic oven technique (7), which was attempted early in the contract. Target temperature measurement was achieved using chromel-alumel thermocouples, spot-welded to the back of each sample.

The ion beam enters the target chamber with an energy of 2keV (D_2^+), and hence must be retarded to achieve bombardments at energies down to 100eV. This is accomplised by using a positive bias on a tungsten grid 3mm in front of the target which is biased to the same positive potential. During 2keV D_2^+ bombardments, a voltage of + 60V is applied to the grid and target structure to avoid loss of secondary electrons from the target. Tungsten is used for the grid and grid support structure, since it will reflect deuterium backscattered from the target, which might otherwise be trapped and lost before measurement by the mass spectrometer. A defining aperture is required to define the bombarded area of the target. A hole 1.25mm radius is used here, which is somewhat smaller than the beam radius of $\approx$ 1.5mm. Use of only the central portion of the beam aids fluence uniformity across the beam spot. The defining aperture has opposite requirements to the grid structure, i.e. it must trap the incident deuterons. Titanium has this property, and is used here. Using this arrangement, no loss of beam current was recorded down to incident energies < 100eV D_2^+.

Small tungsten filaments, also at the bias potential, were placed a few mm in front of the insulating targets to provide a source of electrons and hence prevent surface charging during ion bombardment. The technique was successful for 2keV and 1keV D_2^+ bombardments, but little electron current could be drawn at lower energies. An increase in grid current suggested that secondary electrons from the grid were neutralising the charge, however. In an attempt to overcome beam current uncertainty, frequent beam current measurements were made on a carbon (PAPYEX) sample during insulator bombardments at low ion energies.

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es were not heated.

each material, for different
. For this reason, samples
bombardments for each sample in
ed at 20°C, 100°C, 300°C, 500°C
0eV and 100eV (D_2^+), making a
addition, 2keV bombardments of
ract) were made at 20°C and
the same bombardments.

apyex) target, to a value
the carbon was monitored as
$_2$HD) amplitudes on the
ne carbon continued until the
nen it was assumed that the
e was re-emitted for each
ressure remained constant, a
mely that the walls of the
d not pumping re-emitted
the required temperature, and
conditions prior to turning
e re-emitted deuterium was
of $\approx 10^{18}$ deuterons cm^{-2} had
off to check background
d beam current due to
ardment the deuterium level
to monitor outward diffusion

Figures 3.1.1 to 3.1.4

Deuterium Re-emission during Bombardment at 20°C:
2 keV, 1 keV, 500 eV, 100 eV, D_2^+

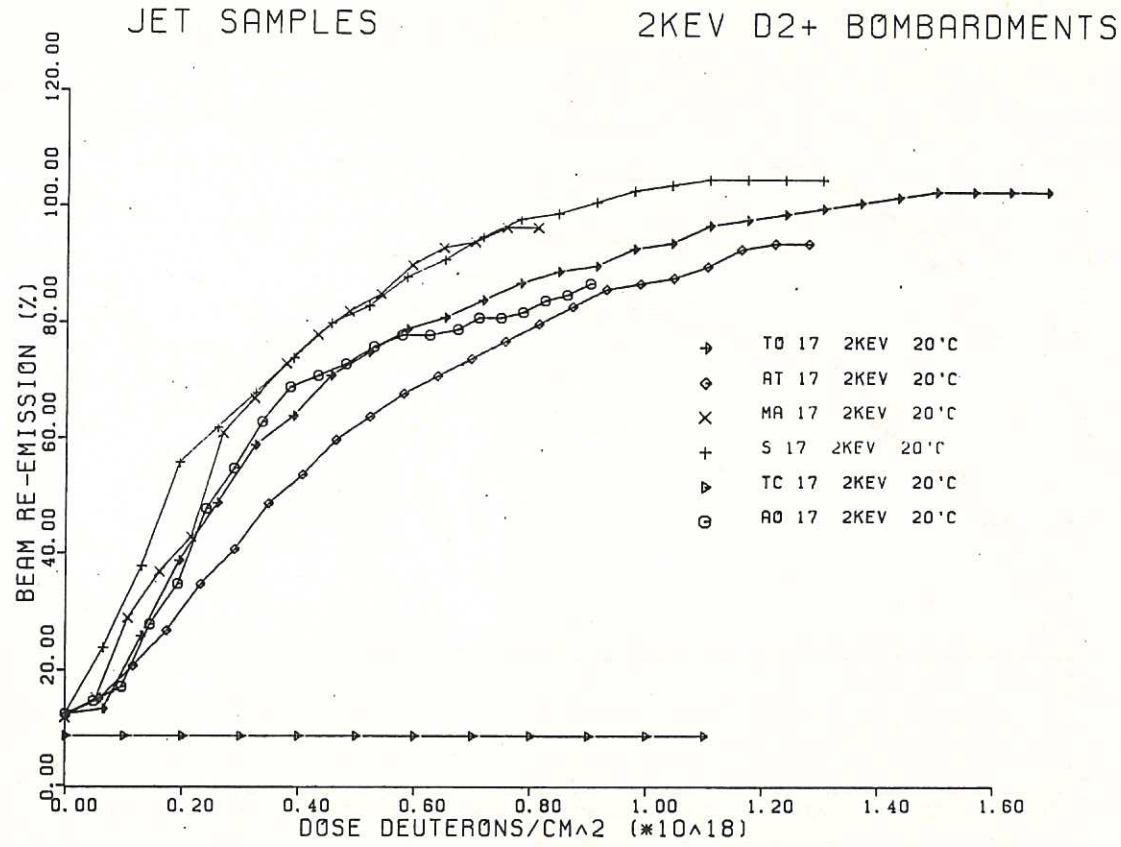

Fig. 3.1.1

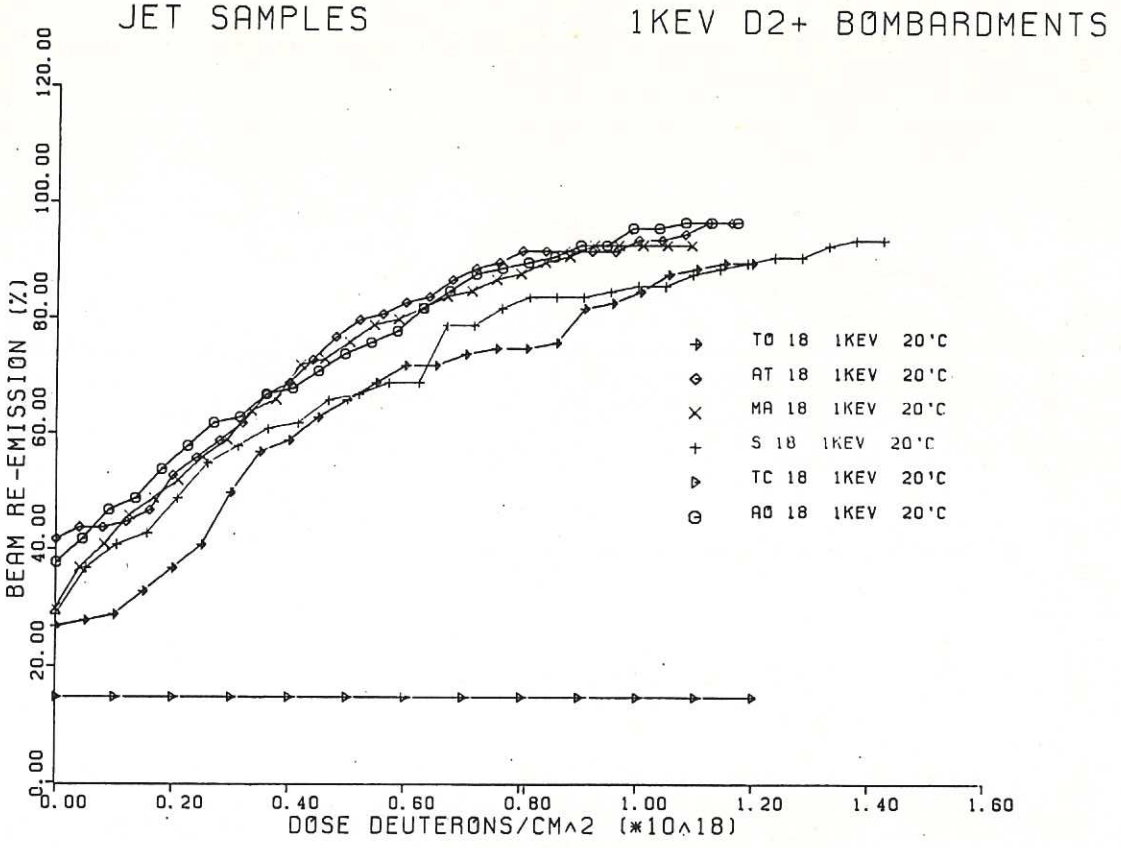

Fig. 3.1.2

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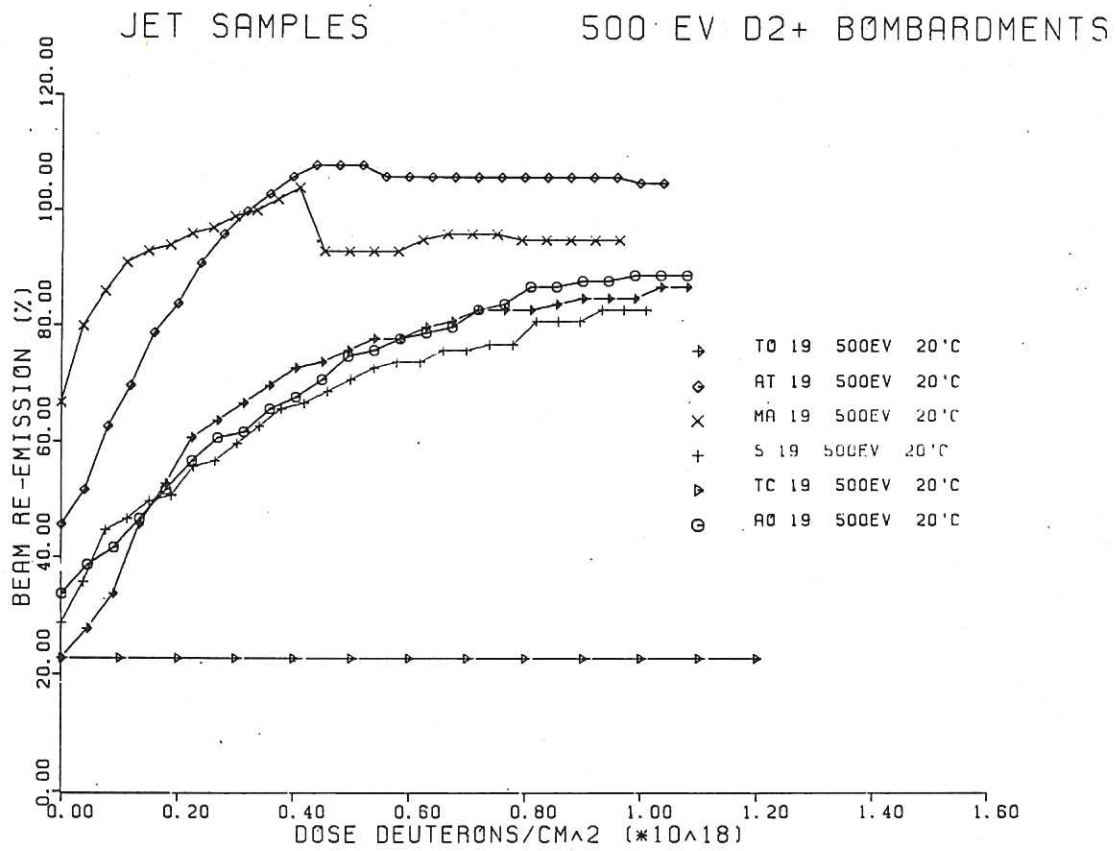

Fig. 3.1.3.

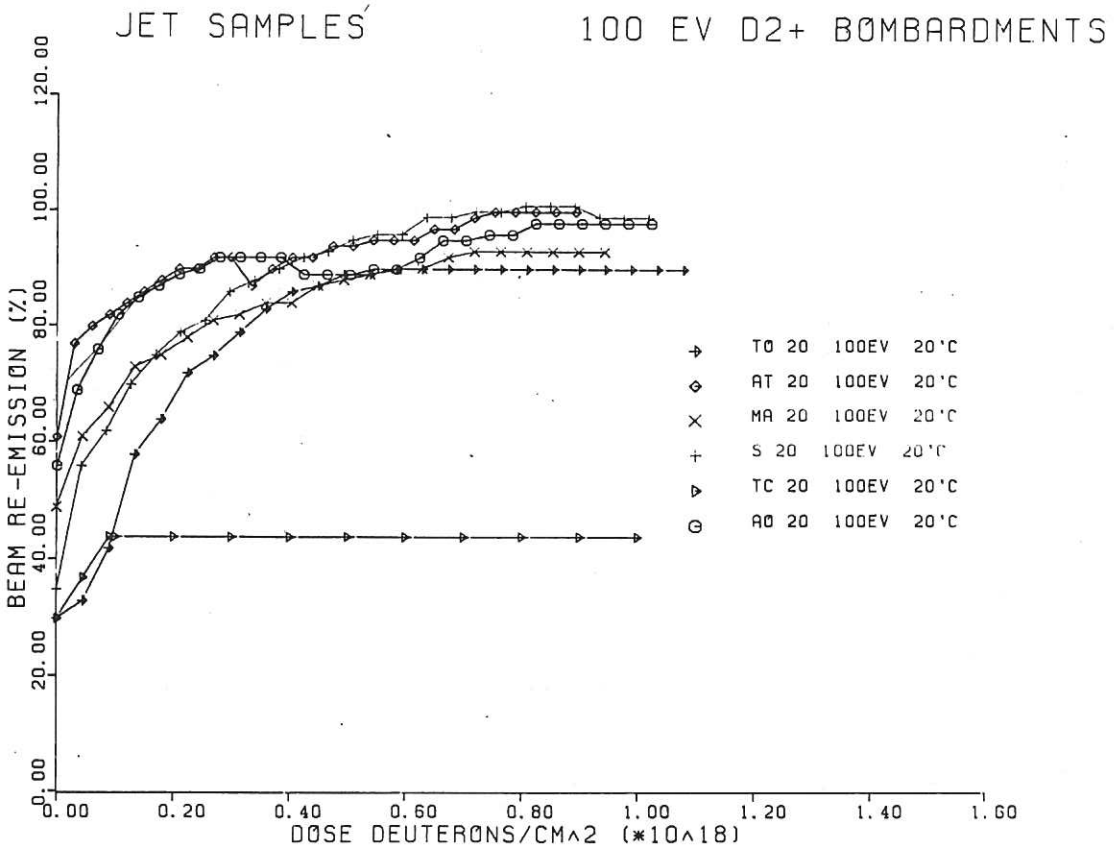

Fig. 3.1.4

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Figures 3.1.5 to 3.1.8

Deuterium Re-emission During Bombardment at 20°C:
2 keV, 1 keV, 500 eV, 100 eV, D_2^+; Normalised
to 100% Re-emission

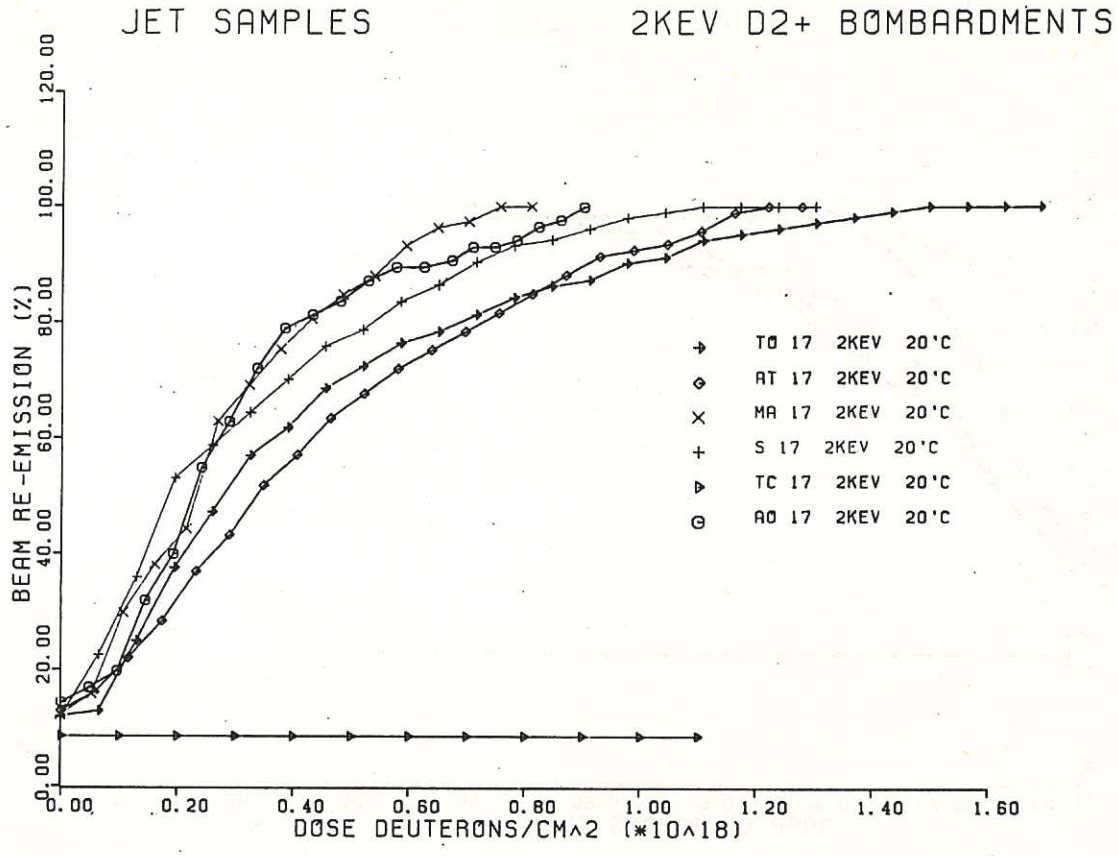

Fig. 3.1.5

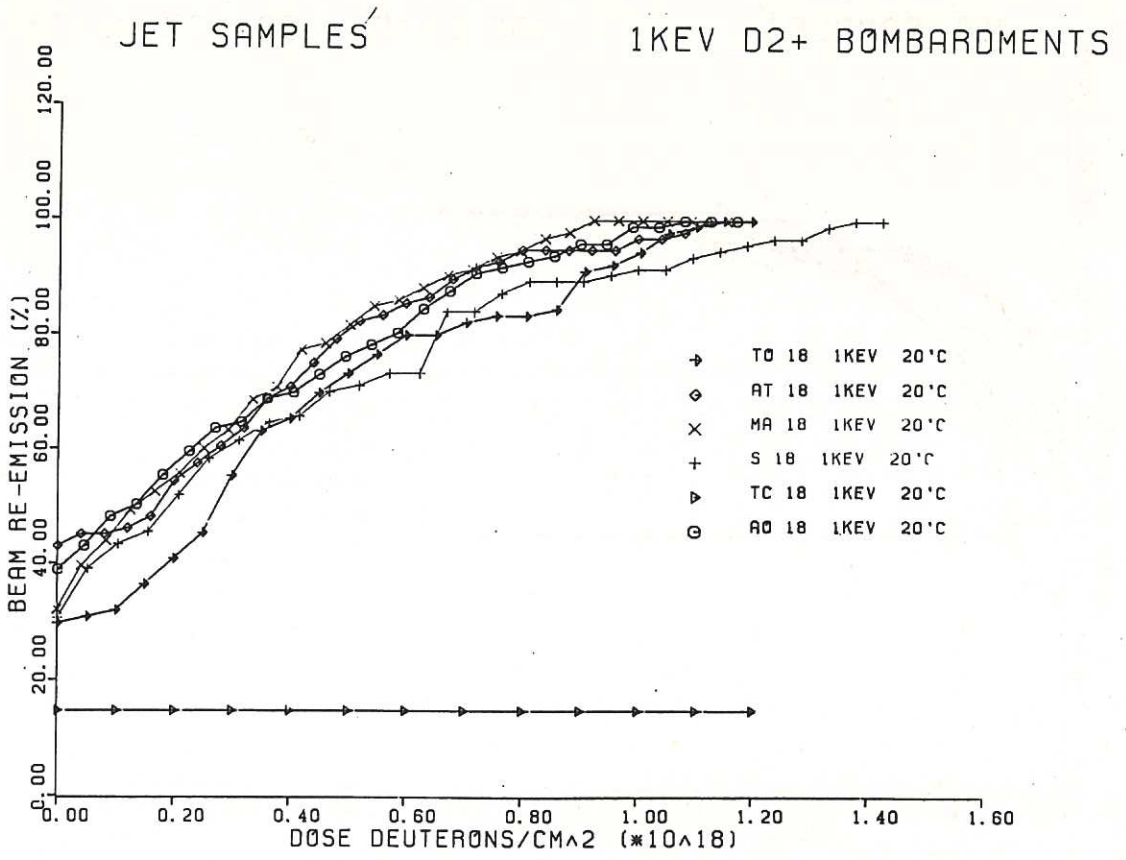

Fig. 3.1.6

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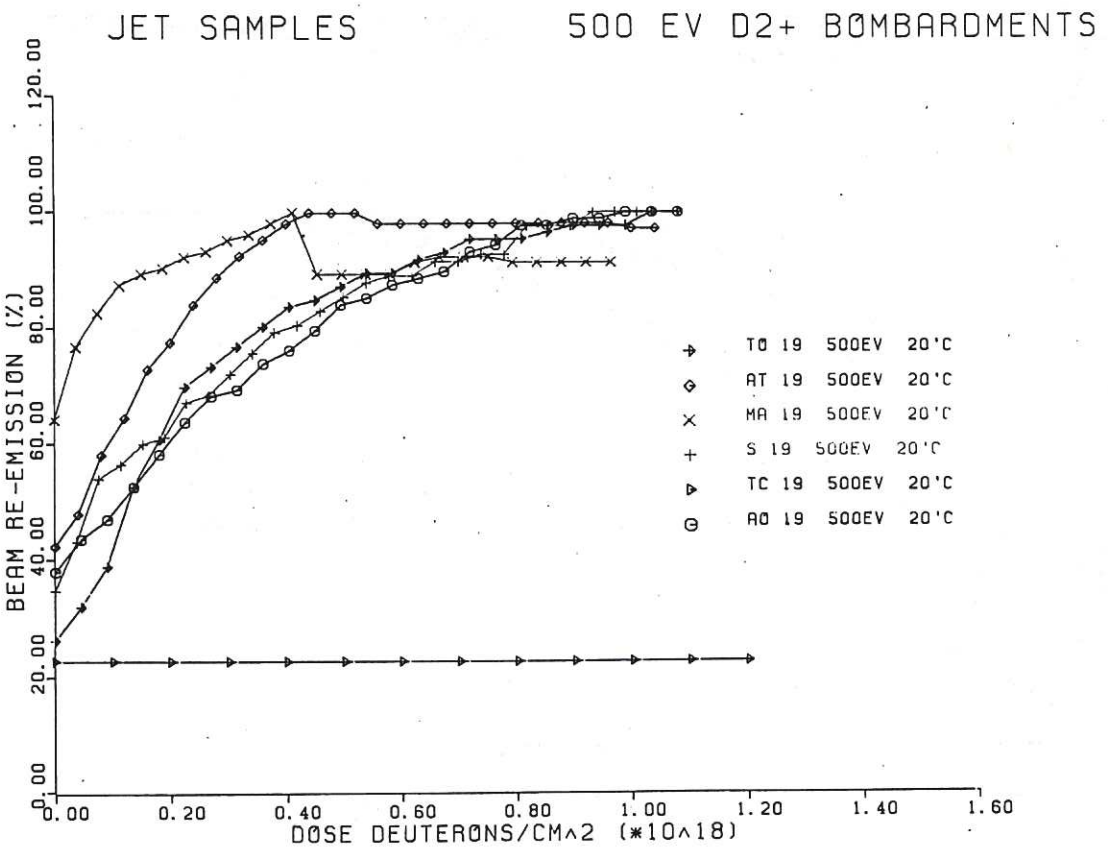

Fig. 3.1.7

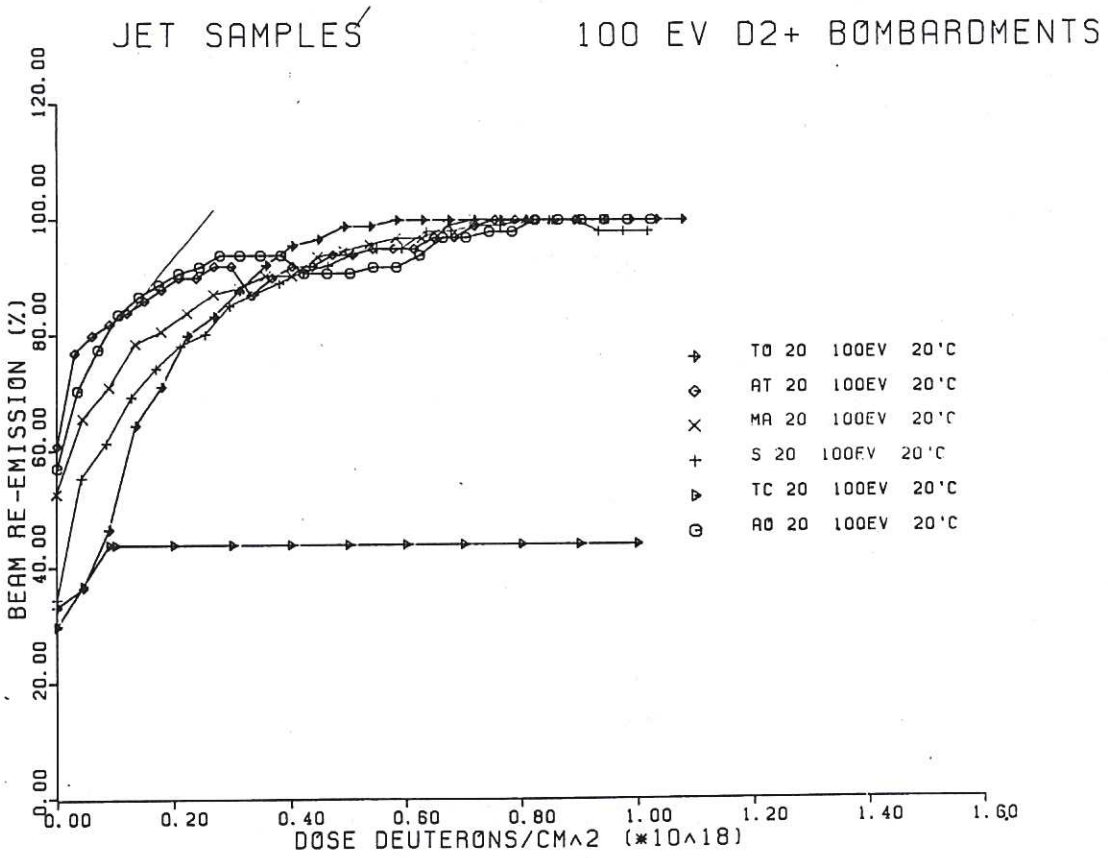

Fig. 3.1.8

Figures 3.1.9 to 3.1.14

Deuterium Re-emission During Bombardment
Effect of Ion Energy

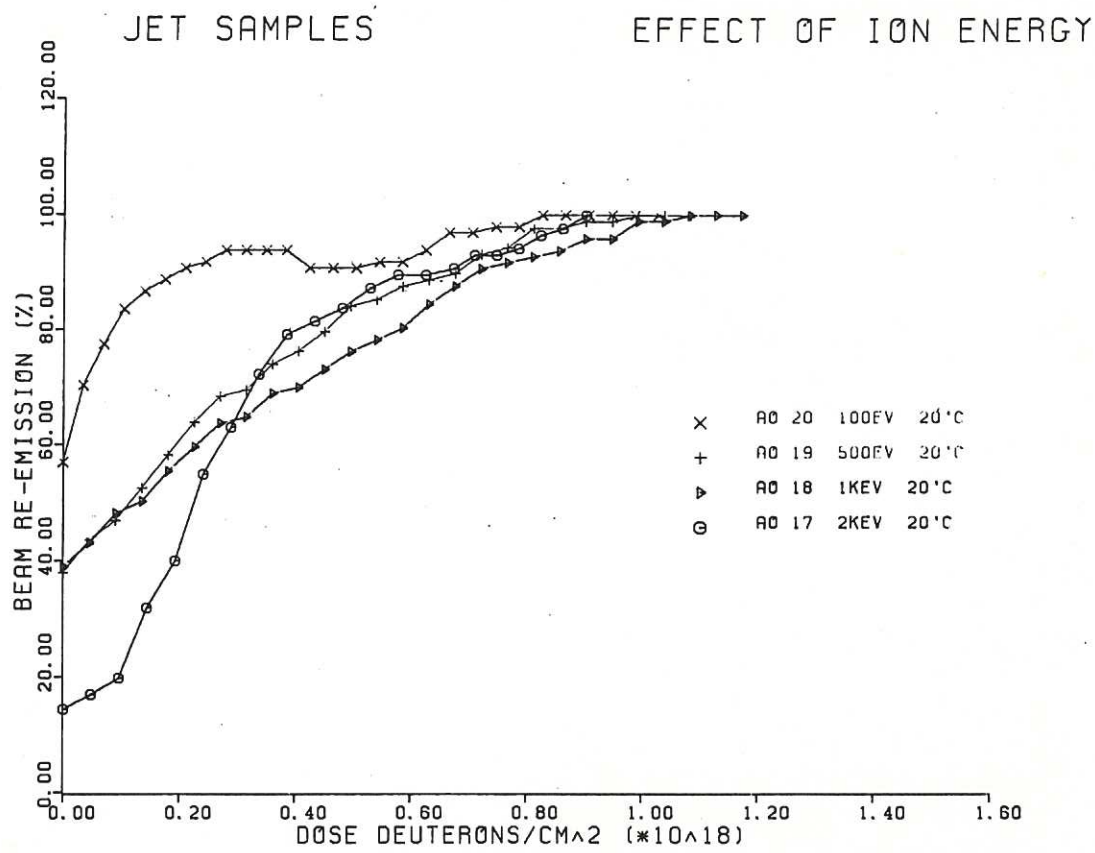

Fig. 3.1.9

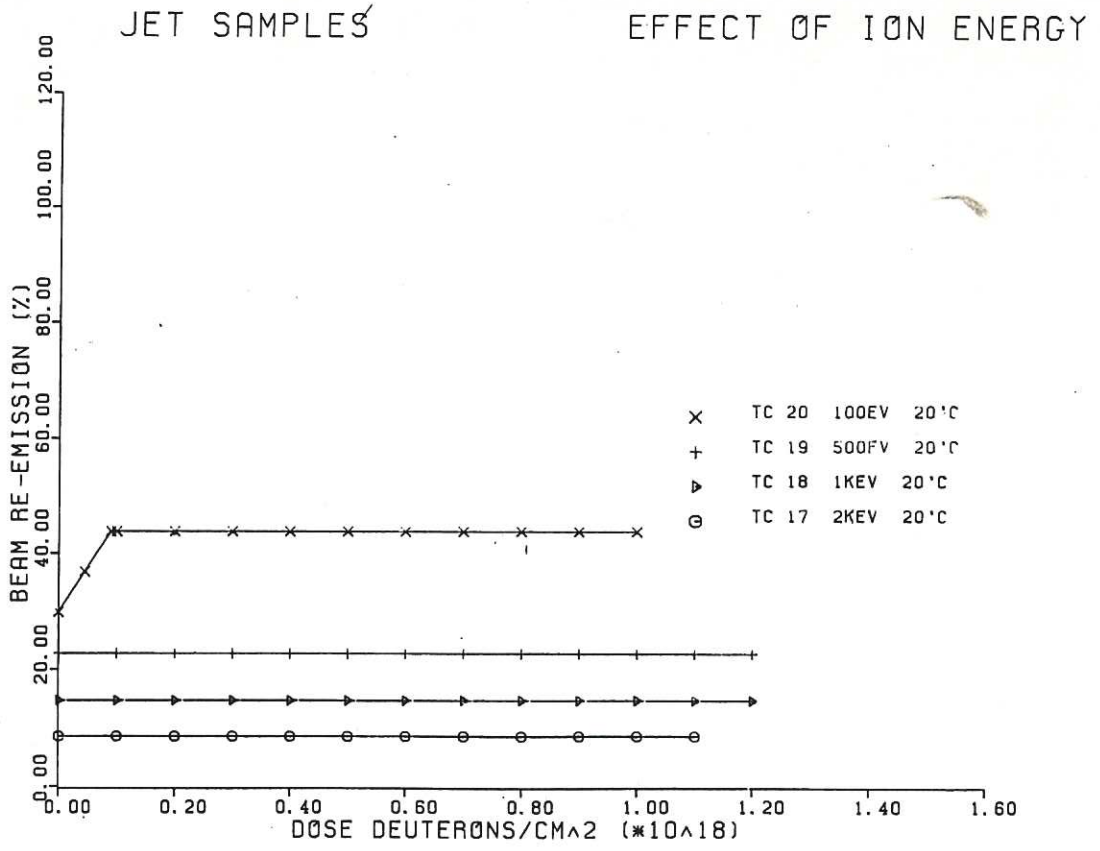

Fig. 3.1.10

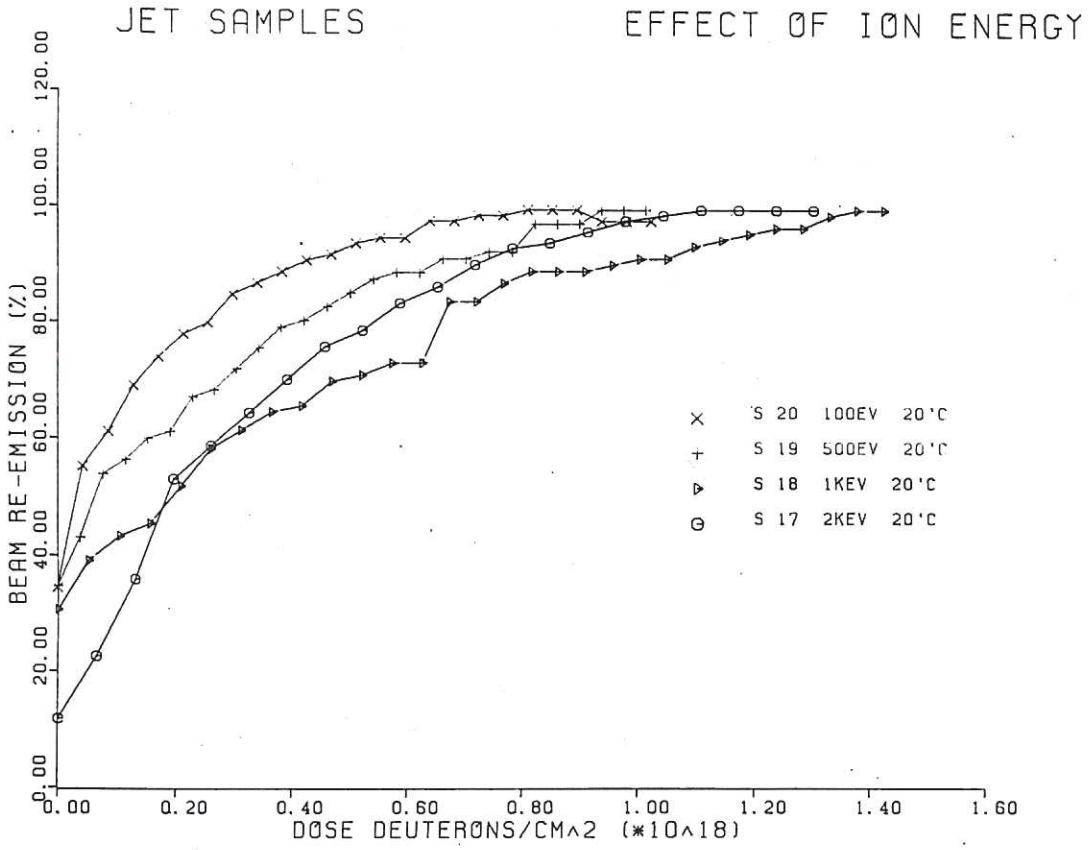

Fig. 3.1.11

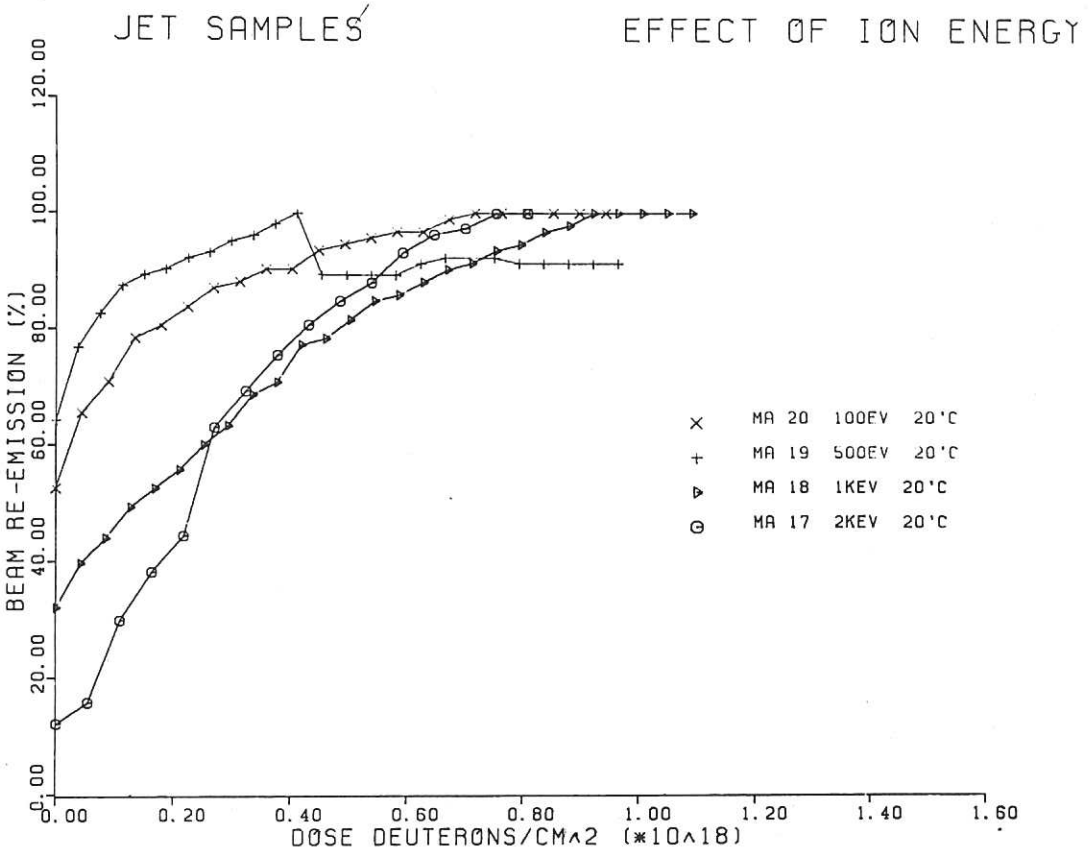

Fig. 3.1.12

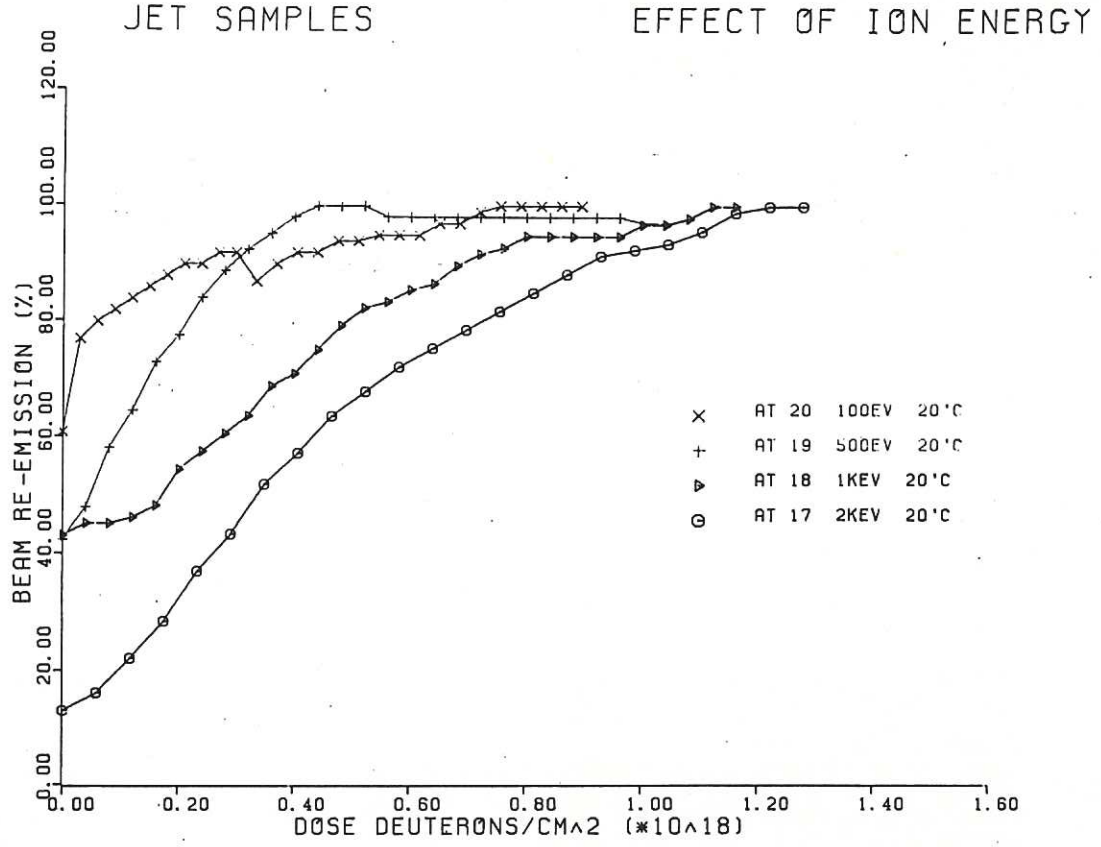

Fig. 3.1.13

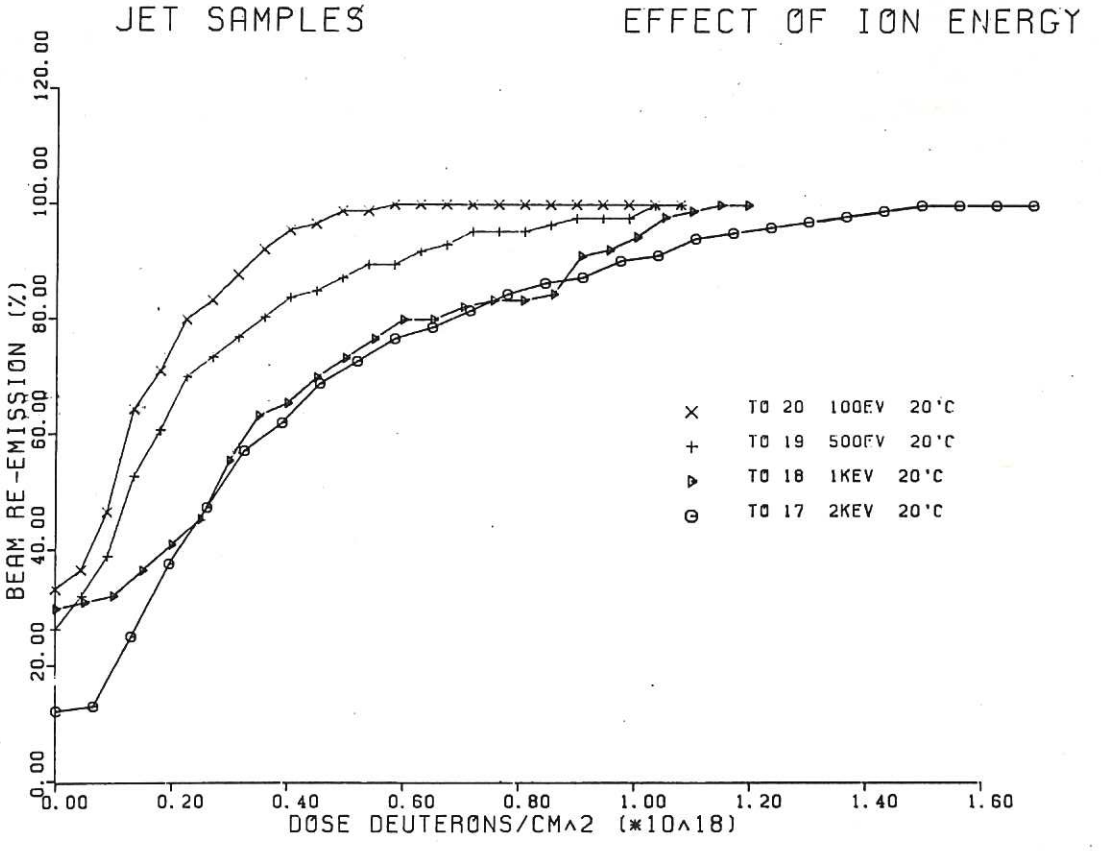

Fig. 3.1.14

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3(ii) Bombardments at elevated temperatures

Sample bombardment at elevated temperatures, in particular 500°C and 800°C, posed many problems. All plasma sprayed samples contained large amounts of hydrogen, some of which was re-emitted during heating to the bombardment temperature. During bombardment, the production of hydrogen deuteride (HD) was sometimes higher than the deuterium (D_2) re-emission. The HD production suggested that the amount of hydrogen in each sample varied considerably from one sample to the next even between samples from the same batch. In addition, the HD level did not fall appreciably with continuing D_2^+ bombardment suggesting a large reservoir of hydrogen within the samples.

A second problem was that of target chamber wall outgassing, particularly during 800°C bombardments, which necessitated long bombardments of the carbon standard target before equilibrium conditions could be reached.

Bombardments of each of the first six samples in Table 1.1 were made at 2keV, 1keV, 500eV and 100eV D_2^+ for sample temperatures of 100°C, 300°C, 500°C and 800°C. The results of deuterium re-emission measurements, again including the deuterium contribution from HD, are shown as a function of sample temperature in Figures 3.2.1 to 3.2.24. Figures 3.2.1 - 3.2.6 refer to 2keV bombardments, 3.2.7 to 3.2.12 to 1keV, 3.2.13 to 3.2.18 to 500eV and 3.2.19 to 3.2.24 to 100eV bombardments. The room temperature data is also included with each set of results for comparison purposes.

Again all the data has been normalised to 100% re-emission at the maximum deuterium re-emission rate (usually at high dose), when saturation is assumed. This is arguable since in a few cases the 100% re-emission as measured using the carbon standard target was higher by a factor of 2 over that depicted by the high temperature samples. Nevertheless, bombardment of the same sample type at the same temperature but at a different ion energy often resulted in excellent correlation between carbon and sample saturation levels. In view of this, the low saturation levels are thought to be artifacts due to pumping speed changes and not a result of inward diffusion of deuterium, for example.

Finally, the silicon carbide and Inconel samples were bombarded at room temperature and 500°C. Results from re-emission measurements on these samples are shown in Figures 3.2.25 and 3.2.26. The results are shown normalised to 100% re-emission as before, but in fact the actual level shows good agreement with the carbon standard data for these samples.

Figures 3.2.1 to 3.2.6

Deuterium Re-emission During Bombardment
Effect of Substrate Temperature 2 keV D_2^+

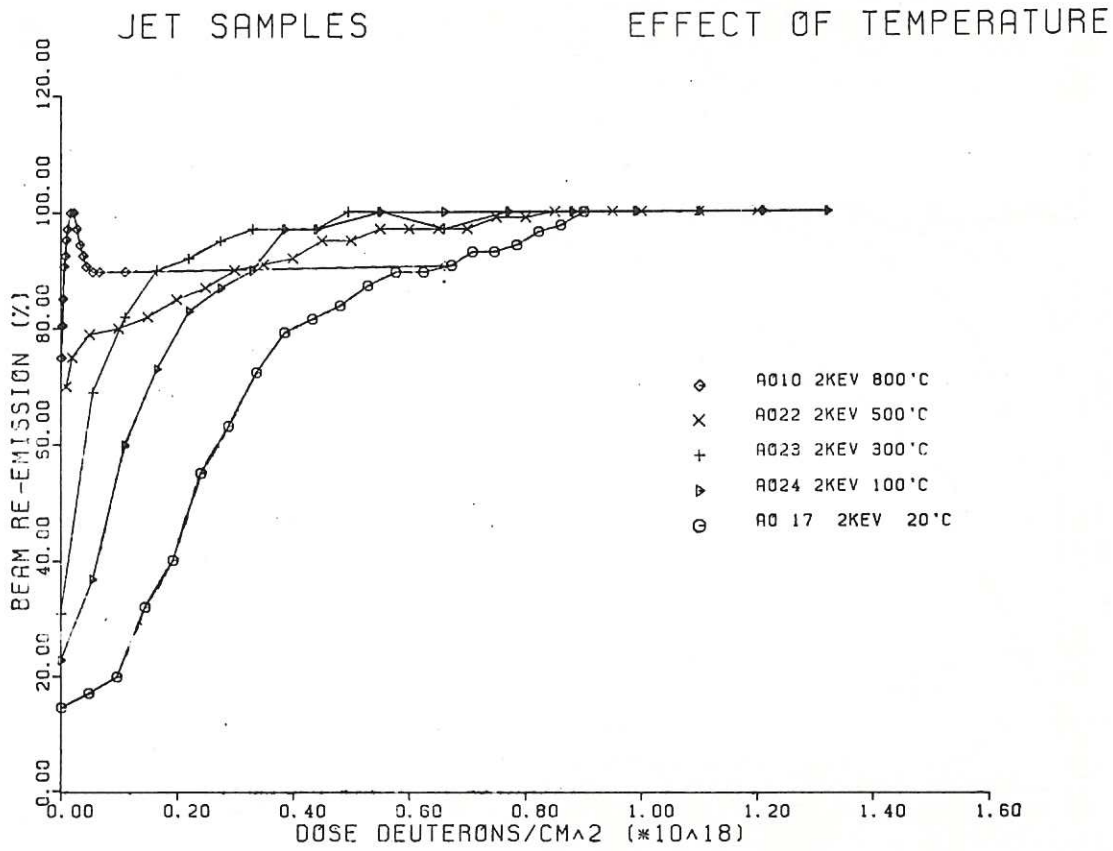

Fig. 3.2.1

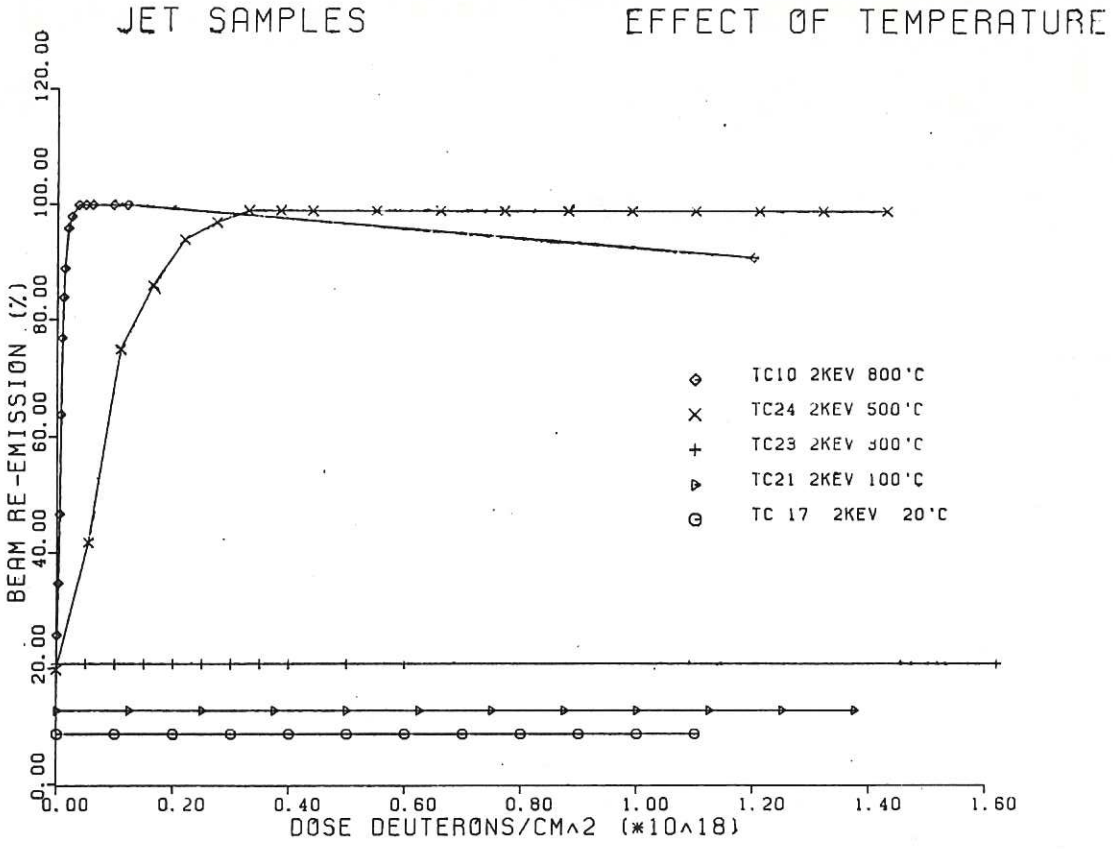

Fig. 3.2.2

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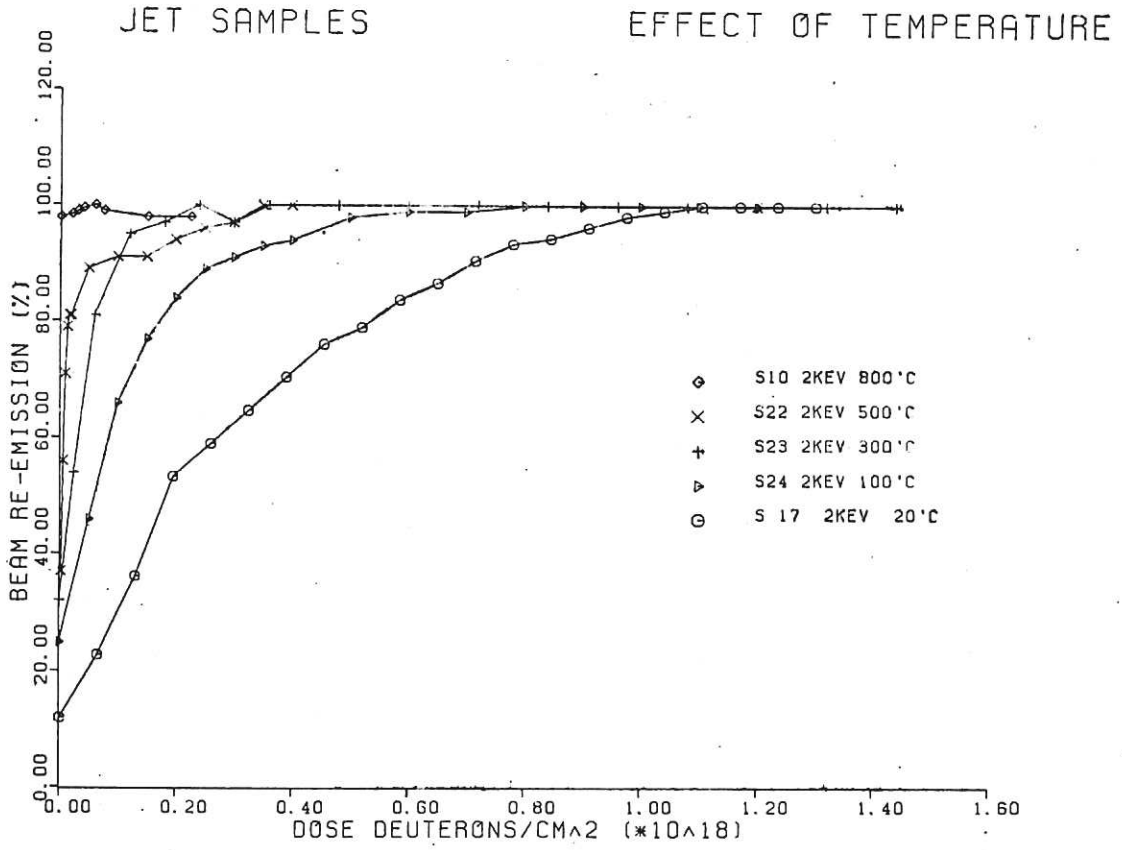

Fig. 3.2.3

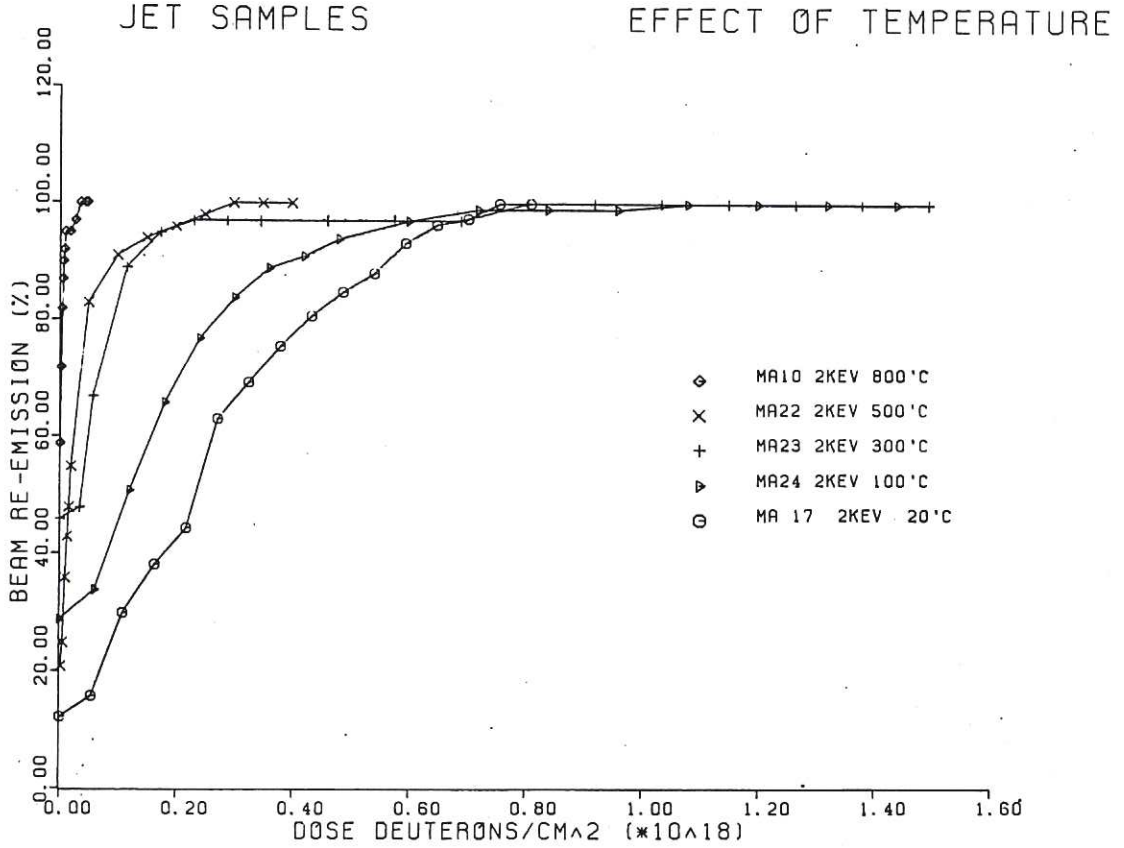

Fig. 3.2.4

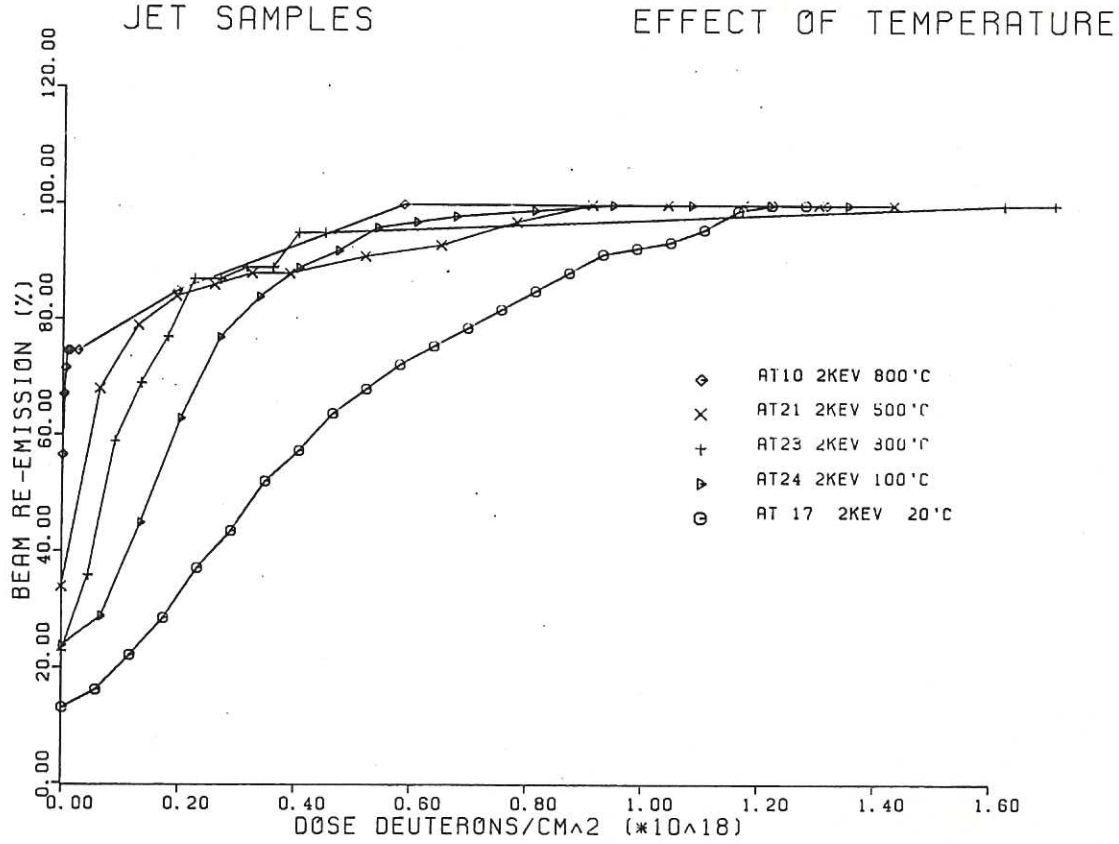

Fig. 3.2.5

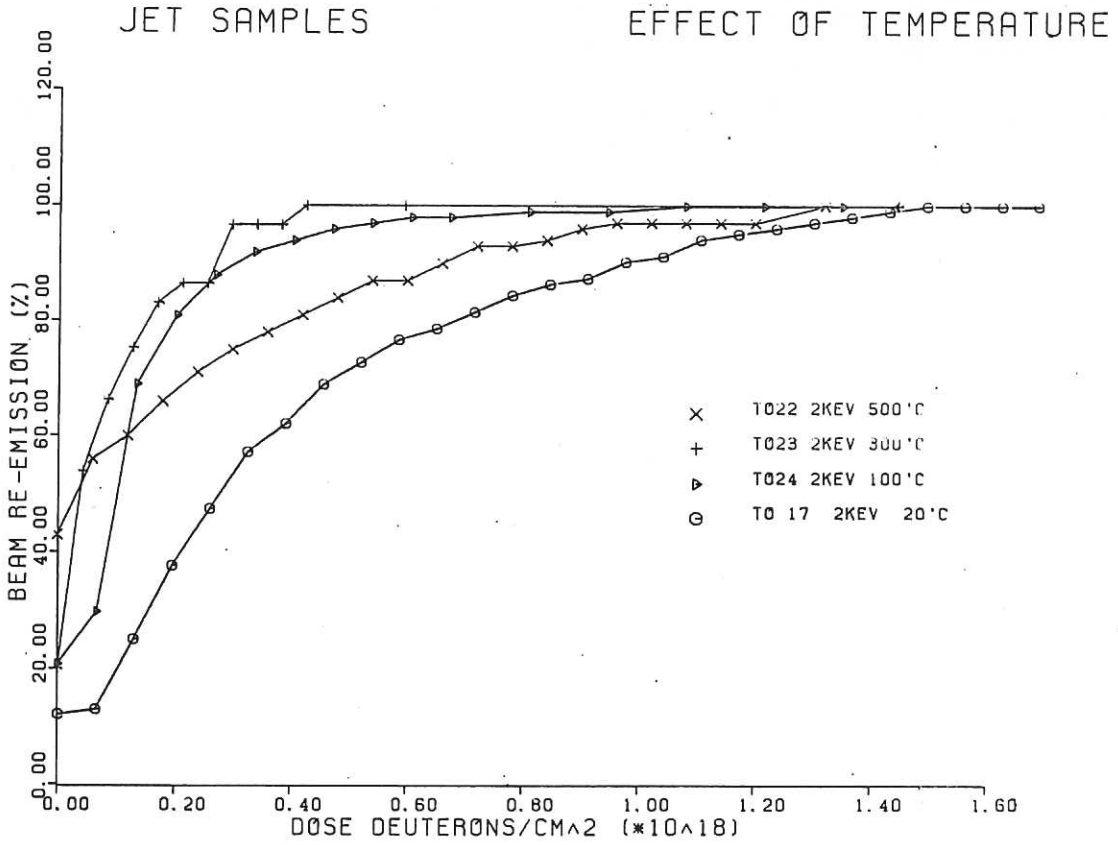

Fig. 3.2.6

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Figures 3.2.7 to 3.2.12

Deuterium Re-emission During Bombardment
Effect of Substrate Temperature 1 keV D_2^+

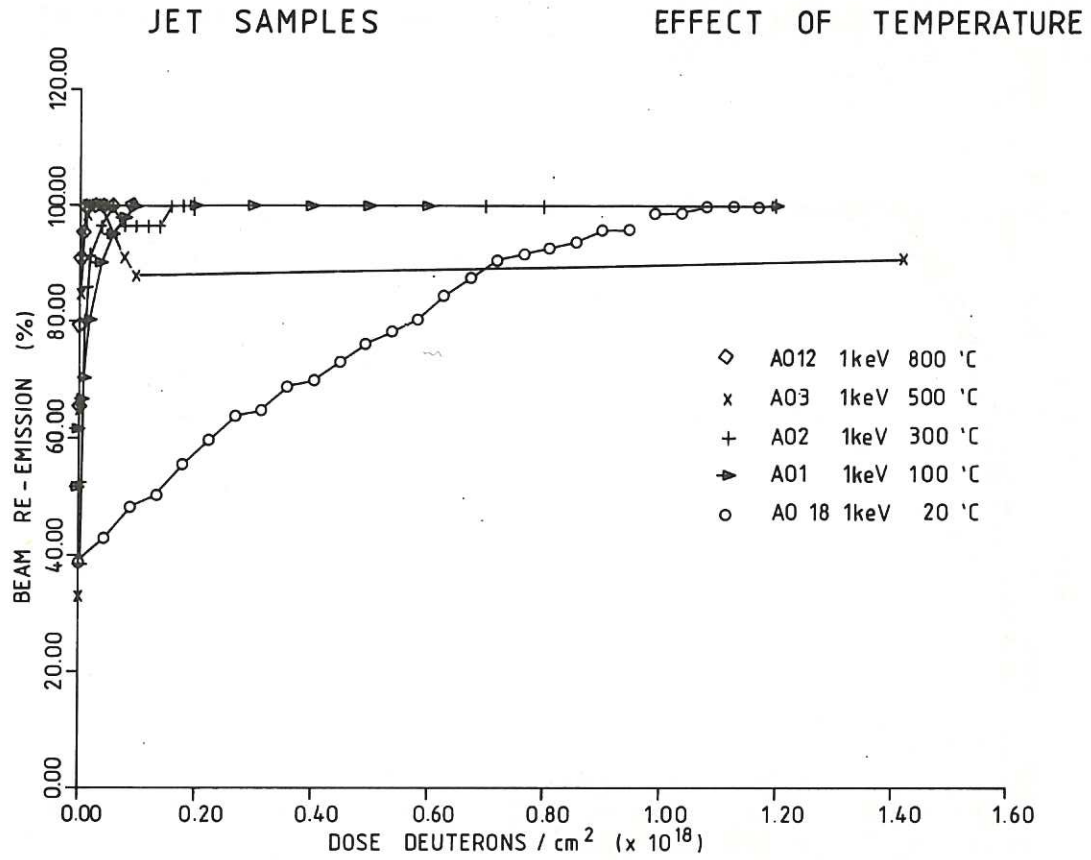

Fig. 3.2.7

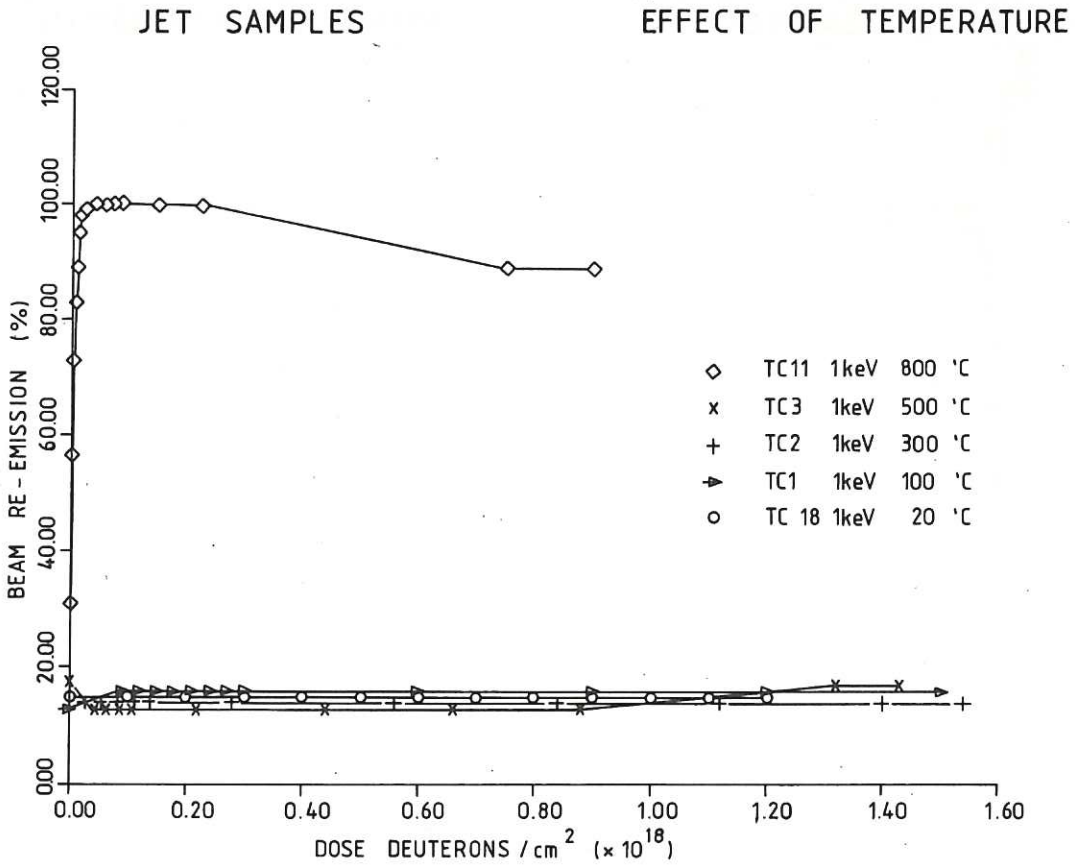

Fig. 3.2.8

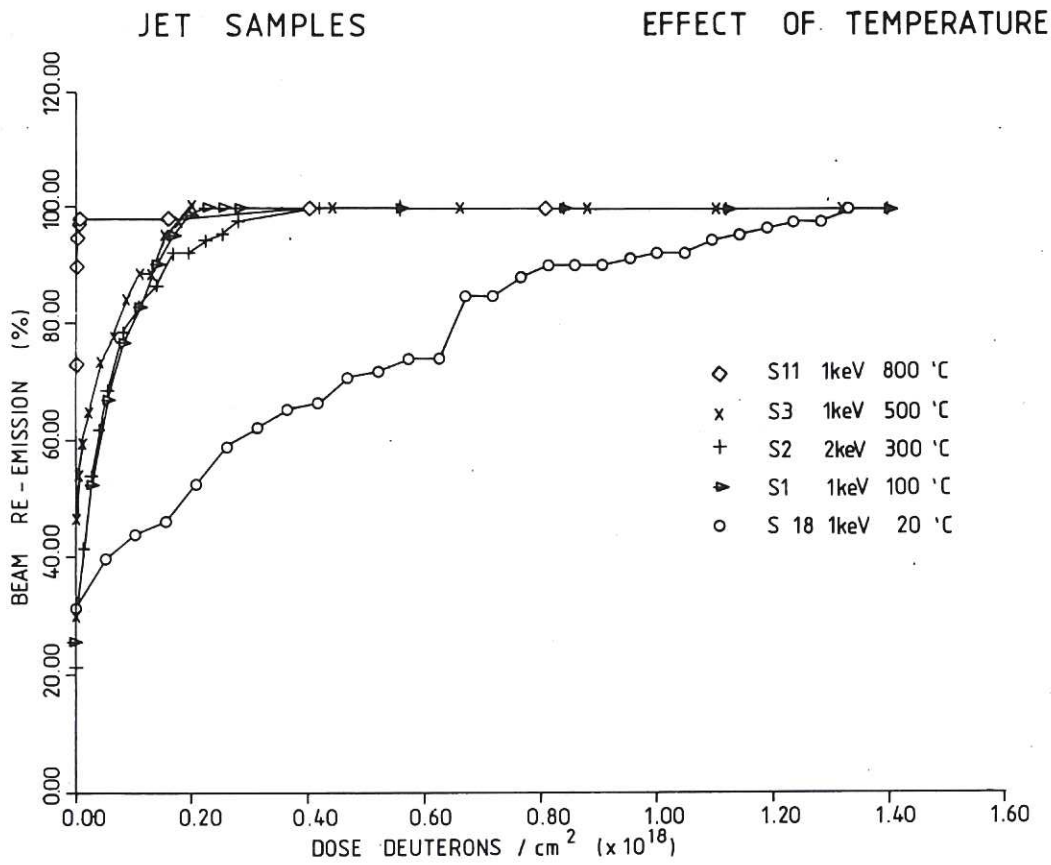

Fig. 3.2.9

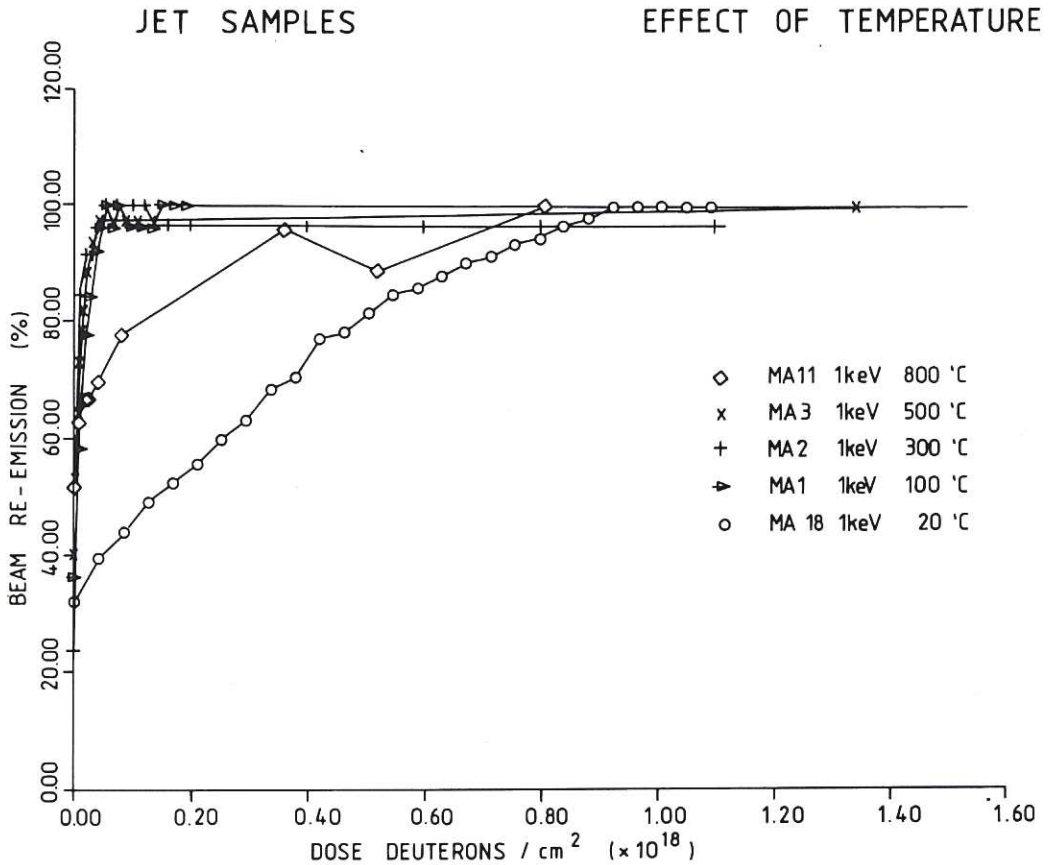

Fig. 3.2.10

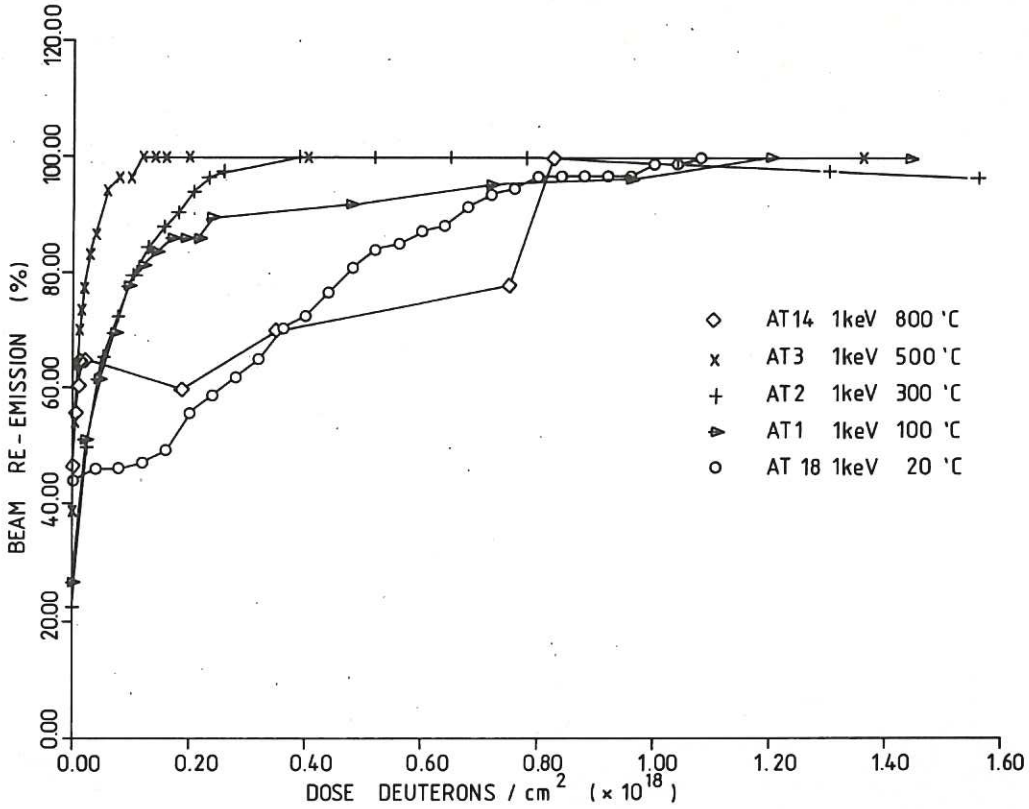

Fig. 3.2.11

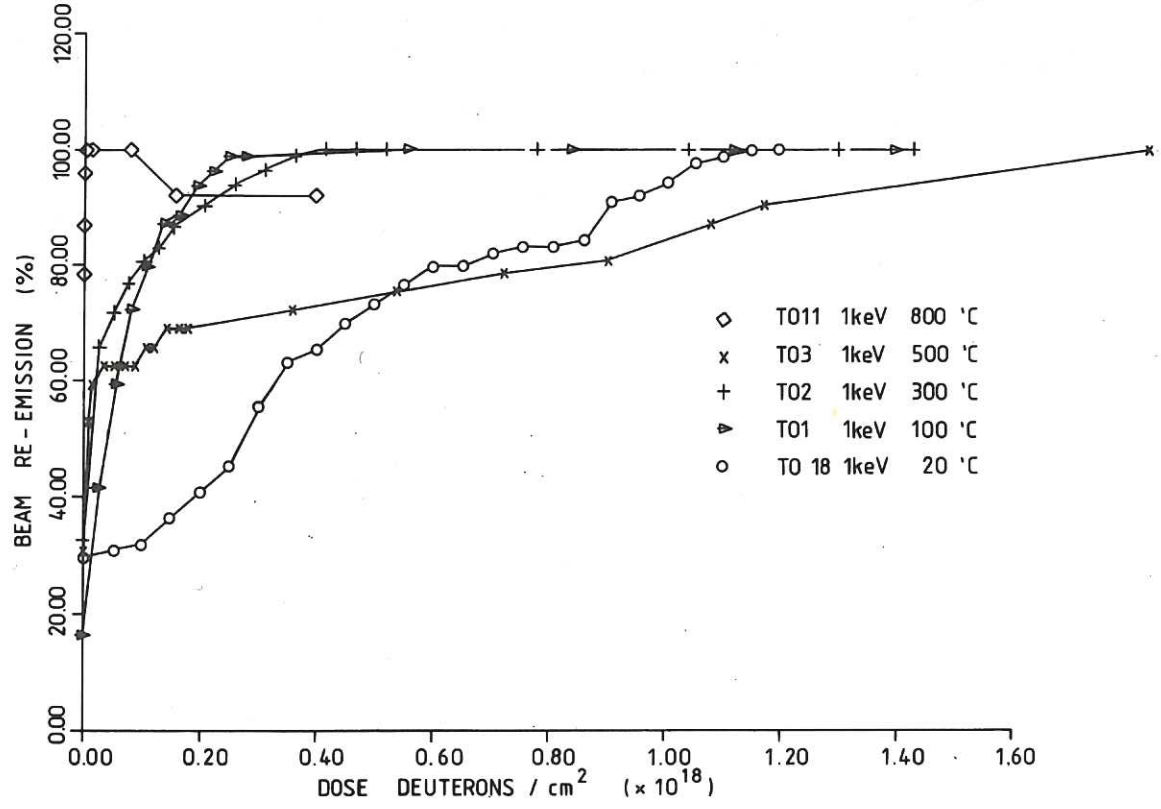

Fig. 3.2.12

Figures 3.2.13 to 3.2.18

Deuterium Re-emission During Bombardment
Effect of Substrate Temperature 500 eV D_2^+

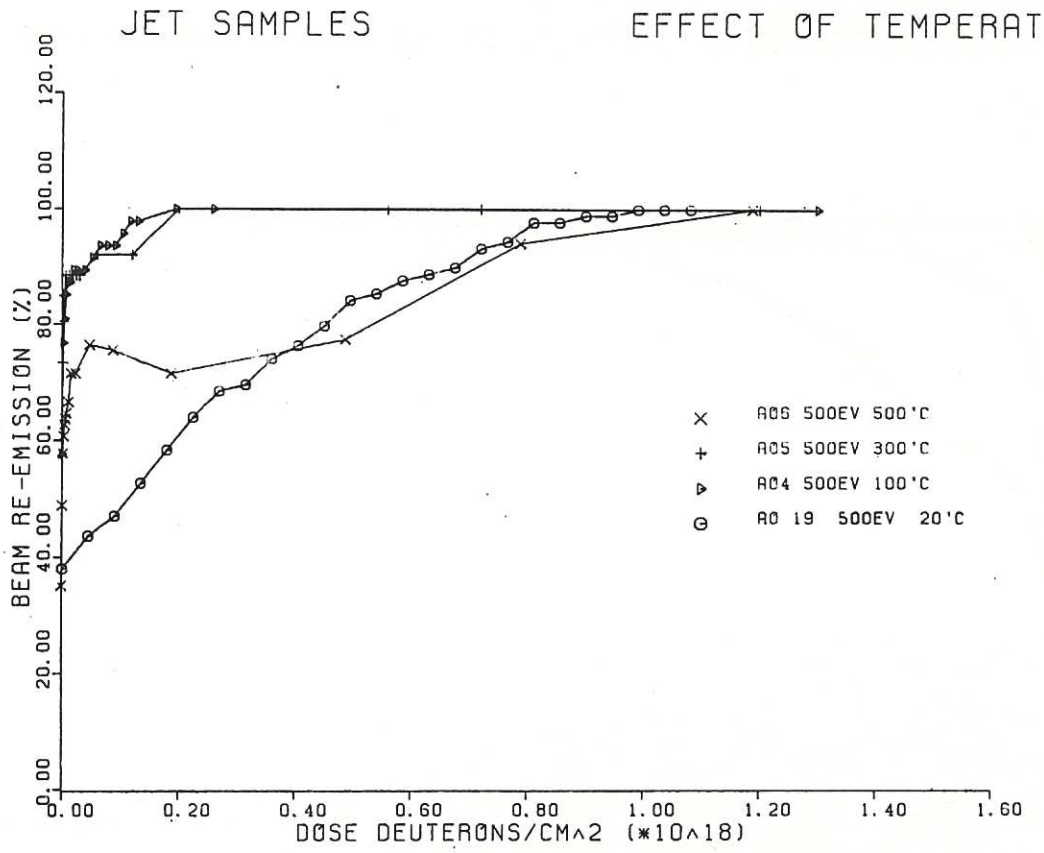

Fig. 3.2.13

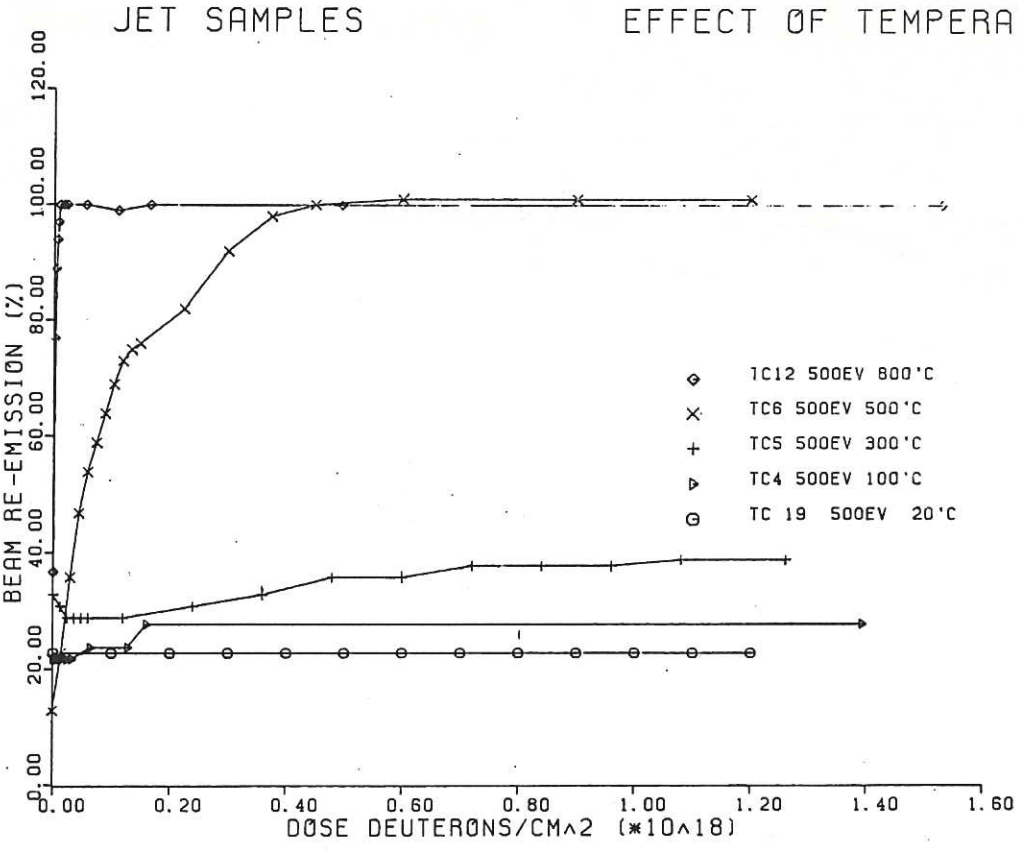

Fig. 3.2.14

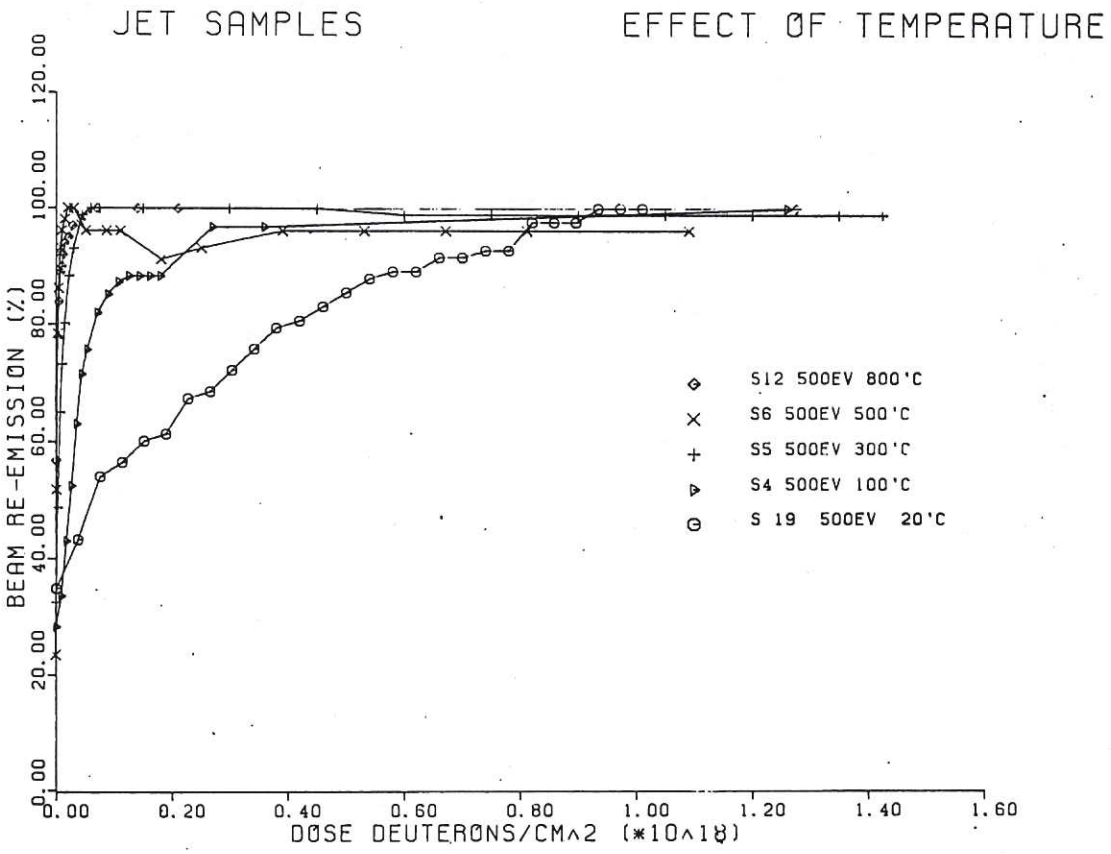

Fig. 3.2.15

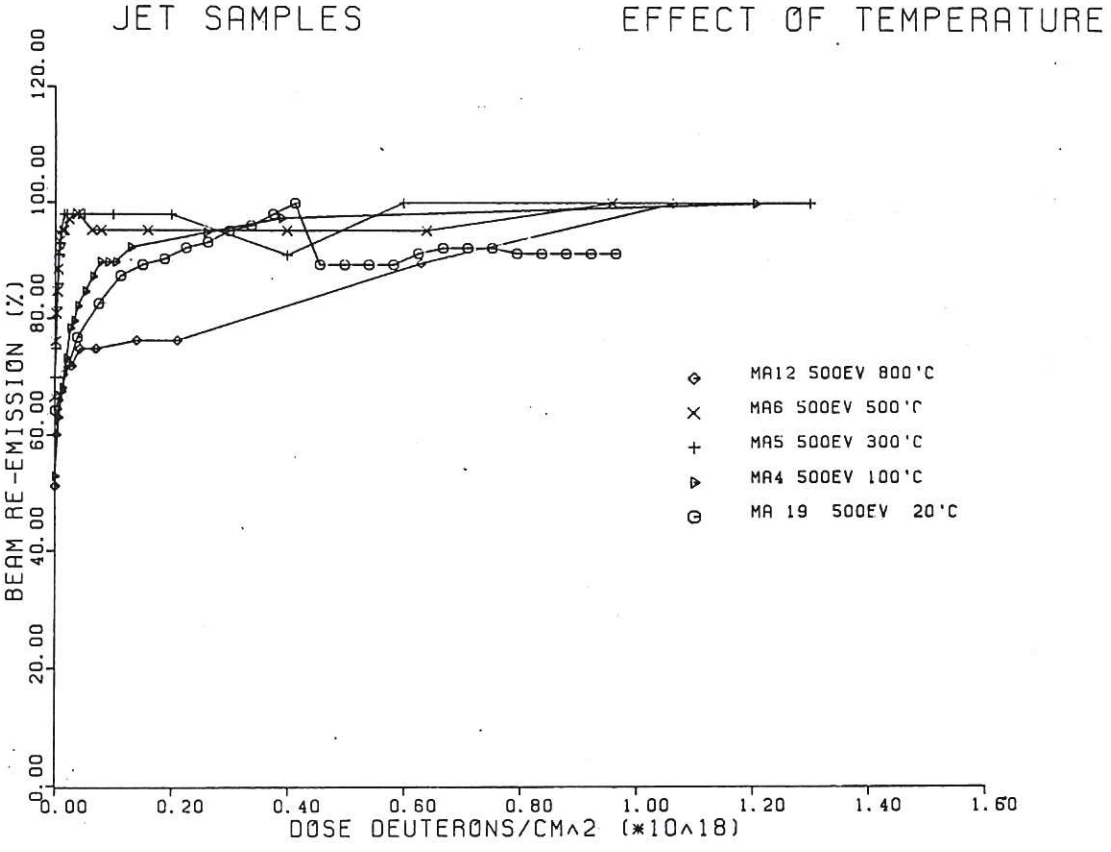

Fig. 3.2.16

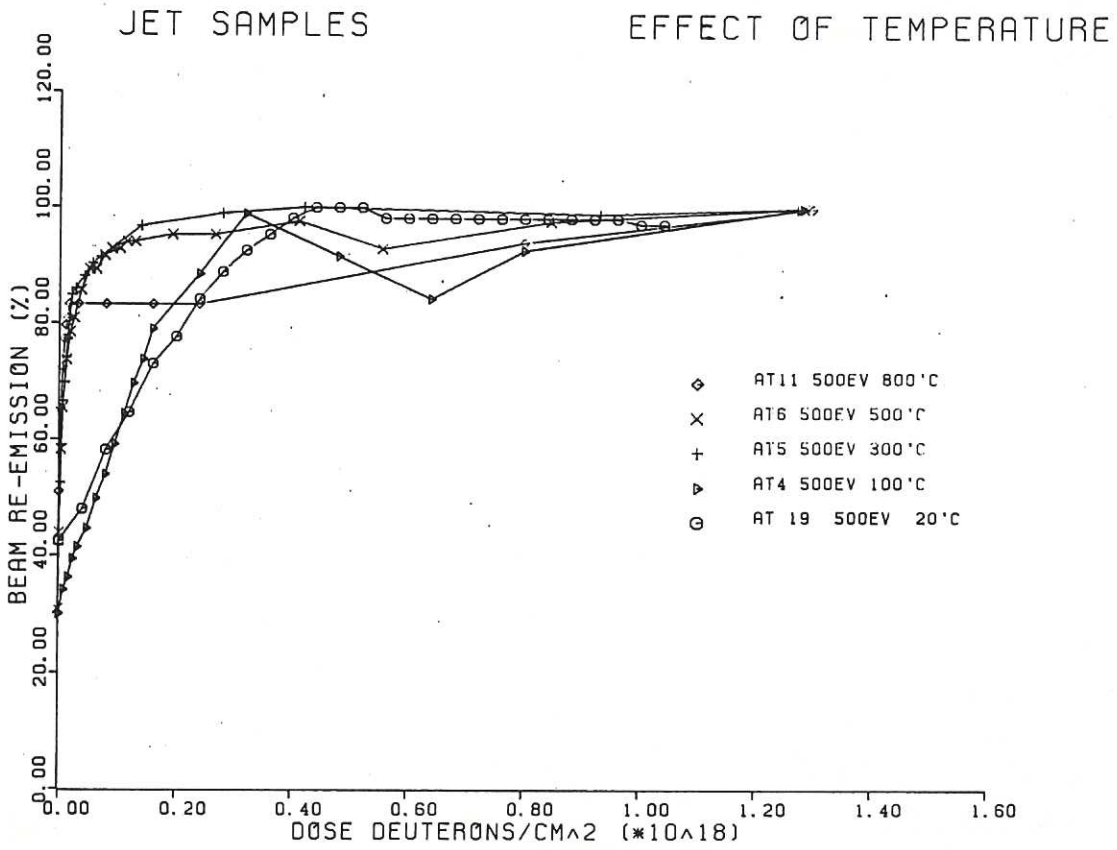

Fig. 3.2.17

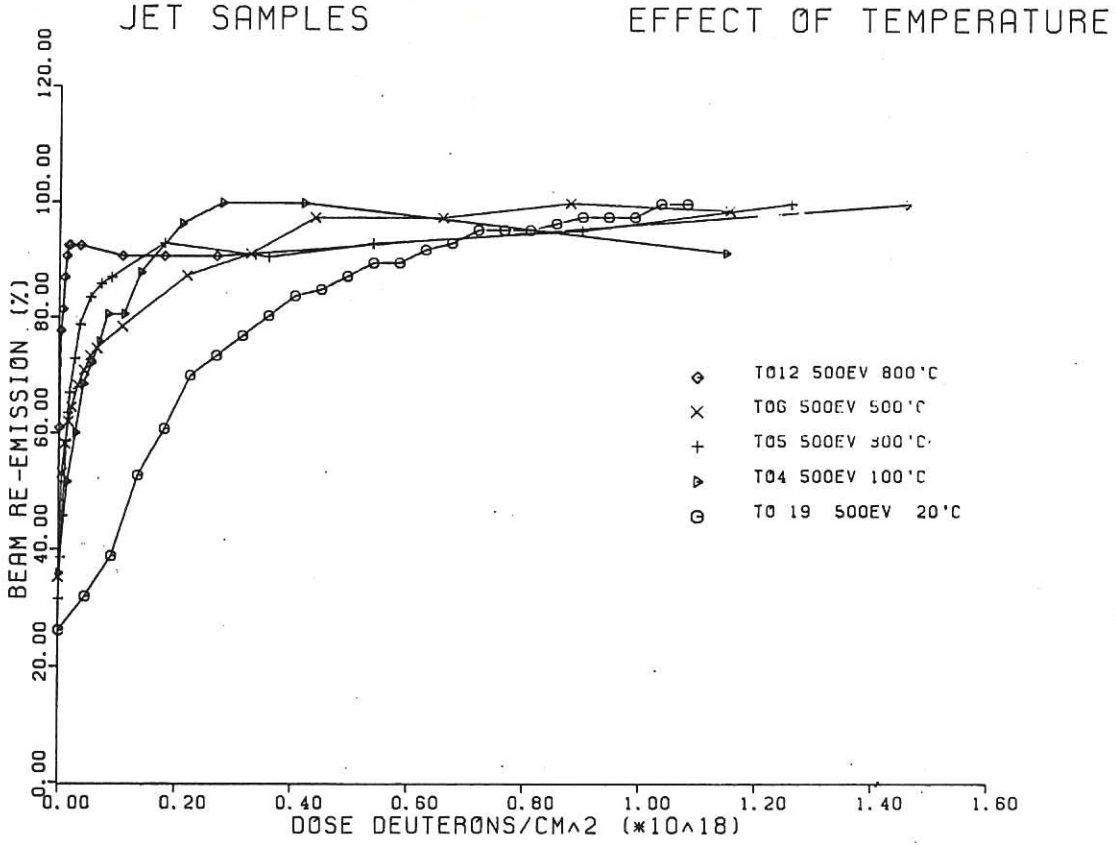

Fig. 3.2.18

CLM-R223

Figures 3.2.19 to 3.2.24

Deuterium Re-emission During Bombardment
Effect of Substrate Temperature 100 eV D_2^+

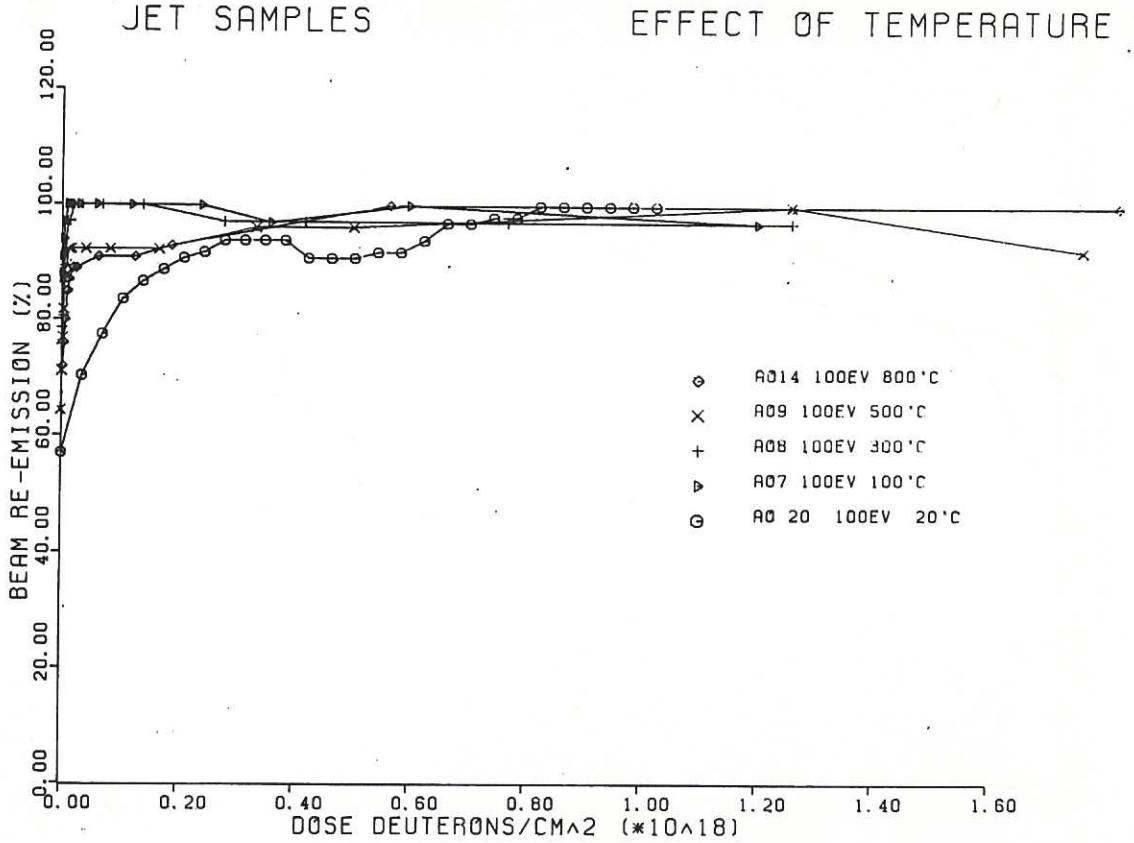

Fig. 3.2.19

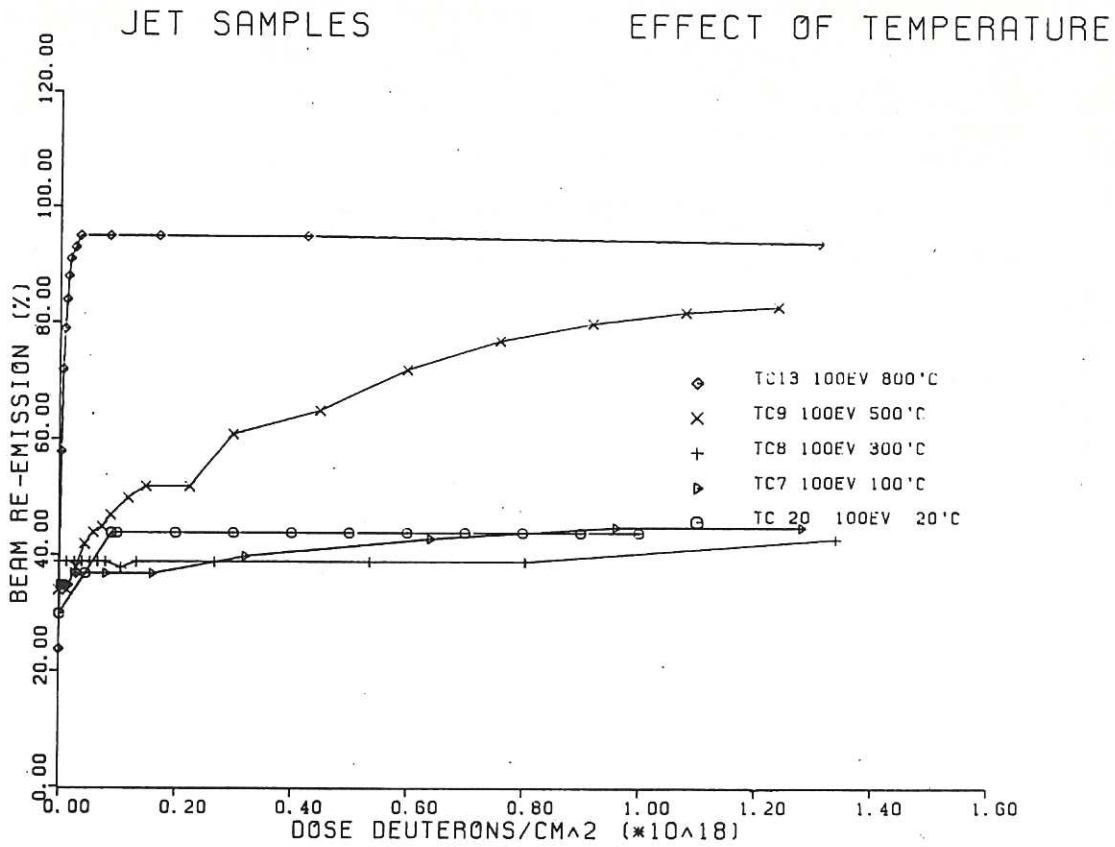

Fig. 3.2.20

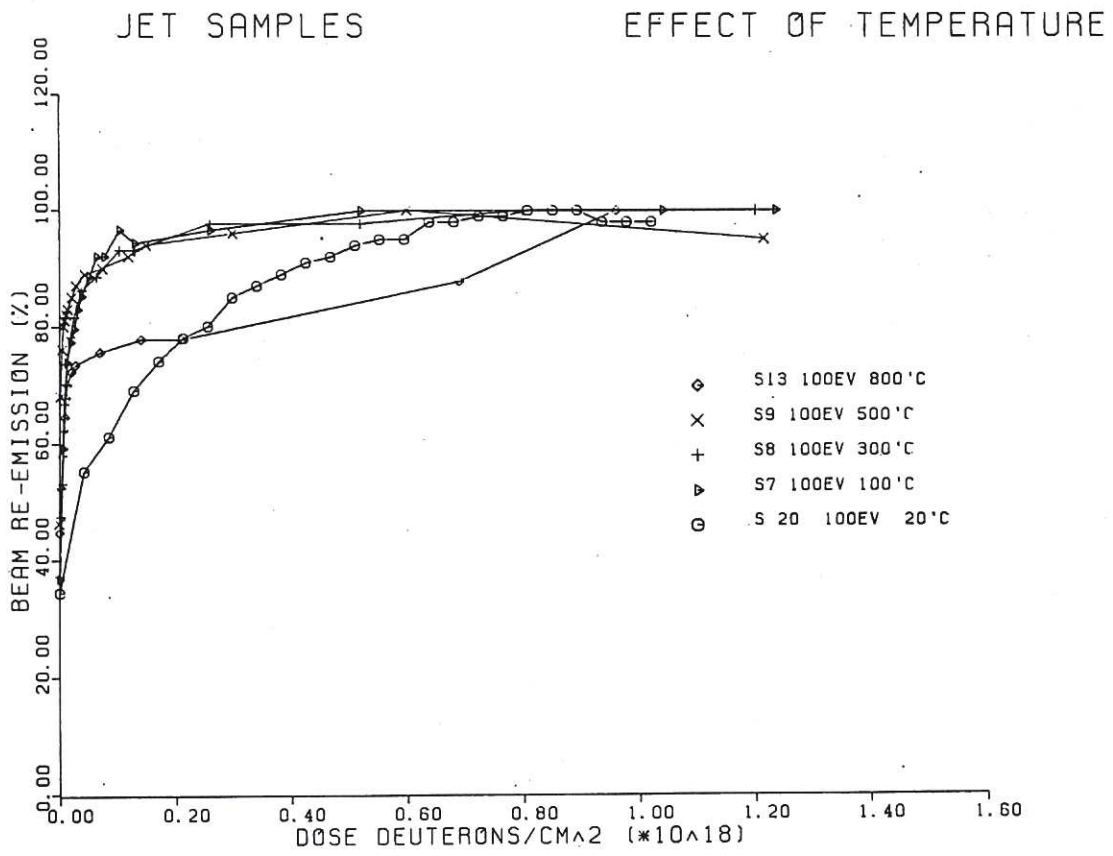

Fig. 3.2.21

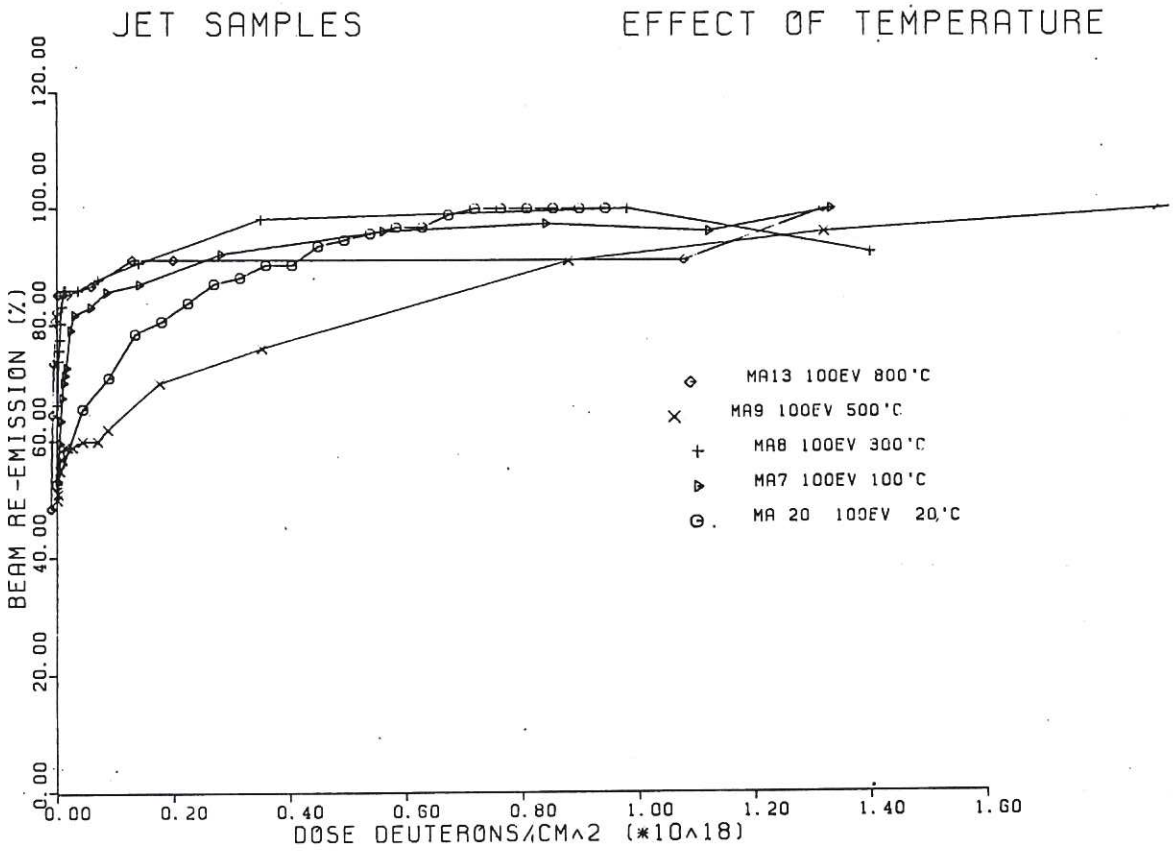

Fig. 3.2.22

CLM-R223

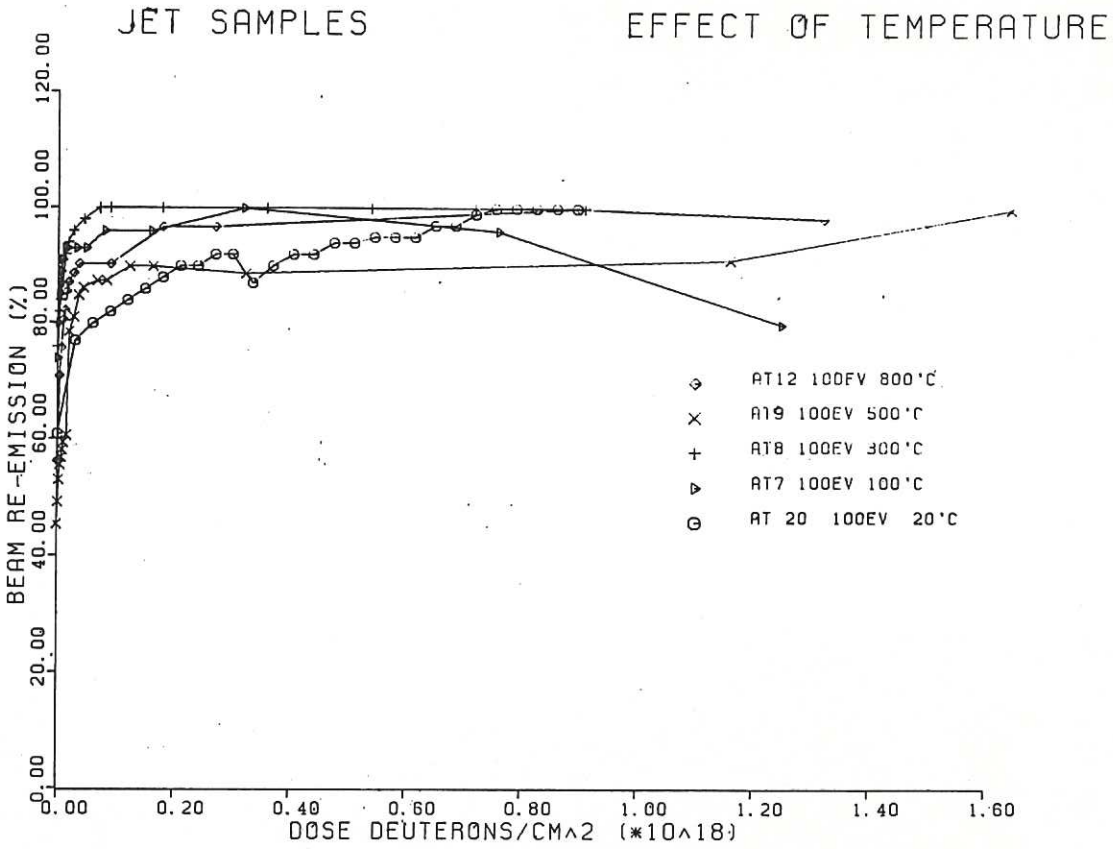

Fig. 3.2.23

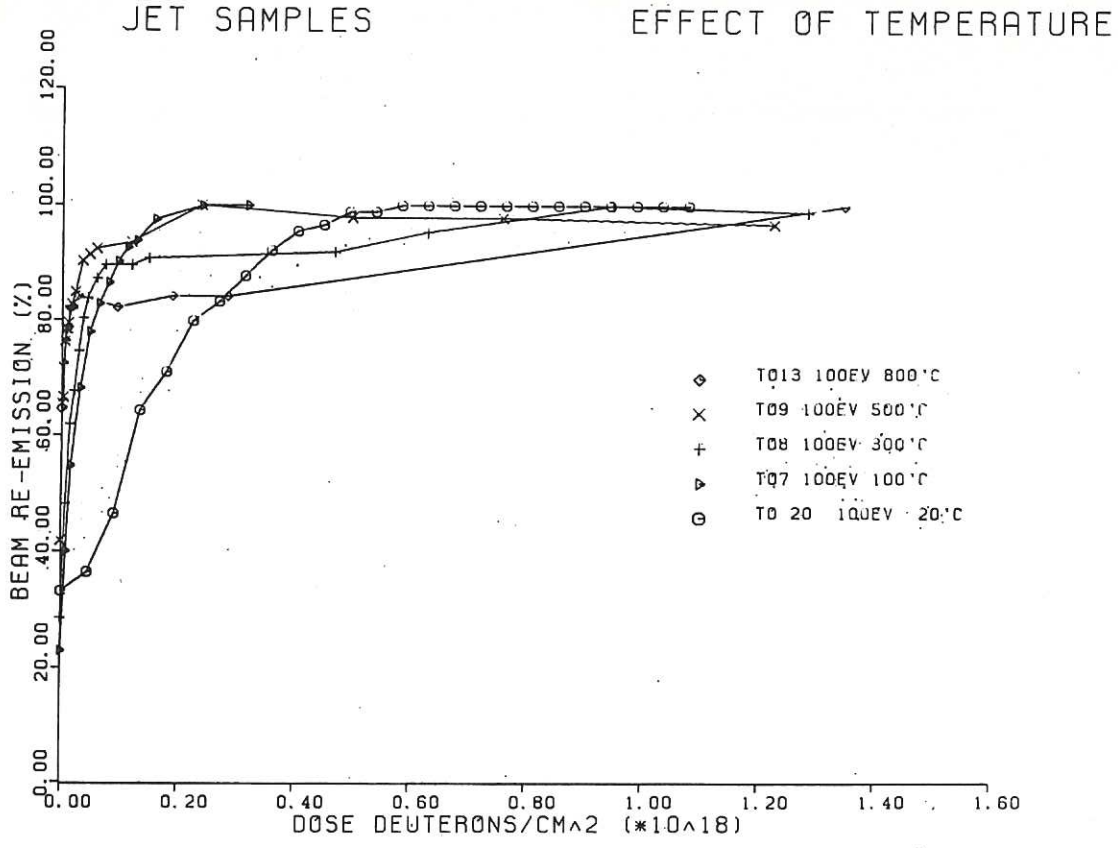

Fig. 3.2.24

CLM-R223

Figure 3.2.25

Deuterium Re-emission During Bombardment
Silicon Carbide at 20°C and 500°C 2 keV D_2^+

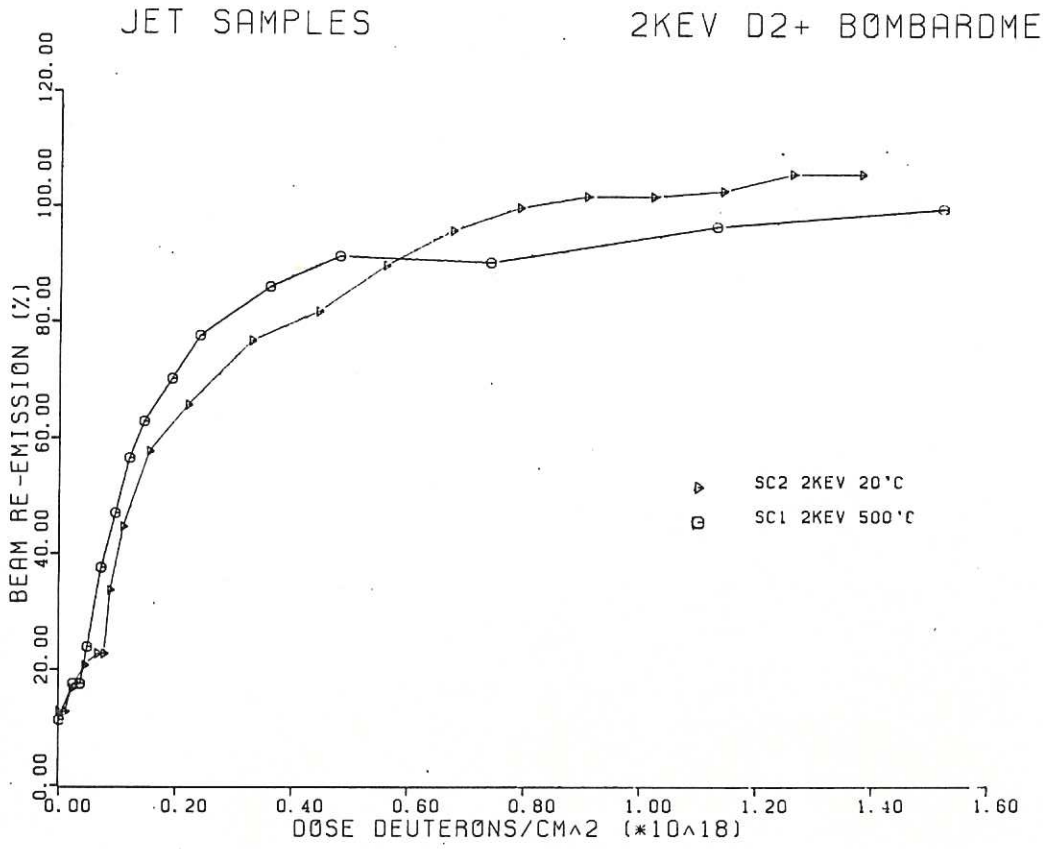
JET SAMPLES
2KEV D2+ BØMBARDMENTS
BEAM RE-EMISSION (%)
0.00
20.00
40.00
60.00
80.00
100.00
120.00
0.00
0.20
0.40
0.60
0.80
1.00
1.20
1.40
1.60
DØSE DEUTERØNS/CM^2 (*10^18)
SC2 2KEV 20°C
SC1 2KEV 500°C

Fig. 3.2.25

Figure 3.2.26

Deuterium Re-emission During Bombardment
Inconel at 20°C and 500°C 2 keV D_2^+

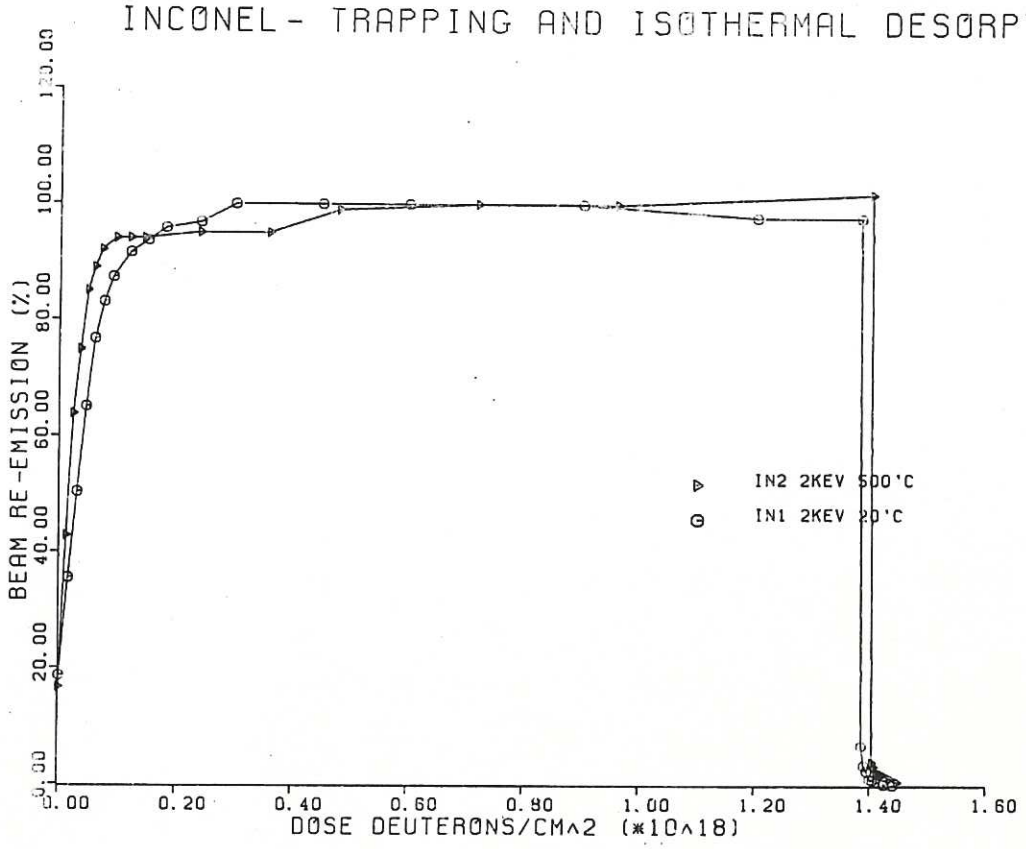
INCONEL- TRAPPING AND ISOTHERMAL DESORPTION
BEAM RE-EMISSION (%)
100.00
80.00
60.00
40.00
20.00
0.00
0.00
0.20
0.40
0.60
0.80
1.00
1.20
1.40
1.60
DOSE DEUTERONS/CM^2 (*10^18)
IN2 2KEV 500'C
IN1 2KEV 20'C

Fig. 3.2.26

4. Discussion of Results

4.1 Measurements at Ambient Temperatures

Two important results are immediately evident from a study of the data presented in Figures 3.1.5 to 3.1.8. These are:

(a) Titanium dioxide, Alumina-titania, Spinel and Alumina all behave in a similar manner at 20°C, that is a slow rise to 100% beam re-emission, at a dose dependent on the energy of the incident ion. Let us call these "saturable samples".

(b) Titanium carbide traps continuously with only a small constant re-emission, to doses in excess of 1 x 10^{18} deuterons cm^{-2}.

4.1(a) Saturable Samples

The five plasma-sprayed samples exhibit similar trapping characteristics to carbon (5,8). The re-emission process has been described in terms of ion induced re-emission of previously trapped gas - and not in terms of thermal diffusion. At the lowest doses only the backscattered fraction of the incident beam is measured, as the deuterium concentration builds up within the ion range. This can be seen as a plateau (particularly in the case of titanium dioxide, Figure 3.1.5) which continues to a dose of ~ 5 x 10^{16} ions cm^{-2}. Saturation of deuterium at a particular ion/target atom ratio within the ion range quickly ensues, and deuterium is re-emitted from the surface. Eventually all incident ions are re-emitted when the complete range distribution is saturated.

The fraction of beam re-emitted at any particular dose will, on the basis of the above model, be a function of the ion range and hence the ion energy. Ranges of 1keV deuterons in carbon, silicon and titanium carbide have been calculated by Doyle et al (1) using the TRIM code (Biersack, 9). The ion range should be roughly a linear function of ion energy below 1keV D^+. These results, and some calculated using LSS (10) for the other samples used in this study are shown in Table 4.1.

Table 4.1

Ion Ranges Calculated for 2keV D_2^+ Ions in low Z Coatings

Sample	Projected Range (TRIM)	Projected Range (LSS)
Titanium dioxide		202 Å
Alumina-Titania		212 Å
Spinel		212 Å
Silicon	220 Å	349 Å
Titanium carbide	122 Å	181 Å
Alumina		212 Å
Carbon	235 Å	267 Å

The LSS theory is quite inaccurate for these low energy ions, but the TRIM code has shown good agreement with experimental range measurements. Since TRIM is unavailable, LSS is simply included for comparison. As can be seen from the table, all samples studied have similar characteristics in respect of deuteron range. One would expect, therefore, similar trapping characteristics if ion-induced re-emission is the dominant release mechanism. This is indeed the case in Figures 3.1.5 - 3.1.8.

The trapping behaviour with ion energy, as shown in Figures 3.1.9 and 3.1.11 - 3.1.14, is also to be expected on the grounds of ion induced re-emission. The initial plateau disappears as the energy is reduced, a phenomenon observed previously in the case of carbon (8). The total amount of deuterium retained in a sample is calculated by integration above the re-emission vs dose curves and the results are presented for the saturable samples in Figure 4.1.1. Clearly the number of deuterons trapped increases with ion energy - the rate of increase falling somewhat at the higher energies. The scatter in data is to be expected in view of the nature of the targets. The fact that the data for silicon is higher than that for some of the other samples is consistent with the larger ion range in silicon (Table 4.1).

A calculation of the deuteron concentration within the ion range can be made from the data presented in Figure 4.1.1 and Table 4.1. A figure of ≈ 1 deuteron/silicon atom is deduced from the 2keV D_2^+ data, assuming a range

Figure 4.1.1

Total Number of Deuterons Trapped in Each Coating
as a Function of Ion Energy
Incident Dose 1 x 10^{18} cm^{-2}

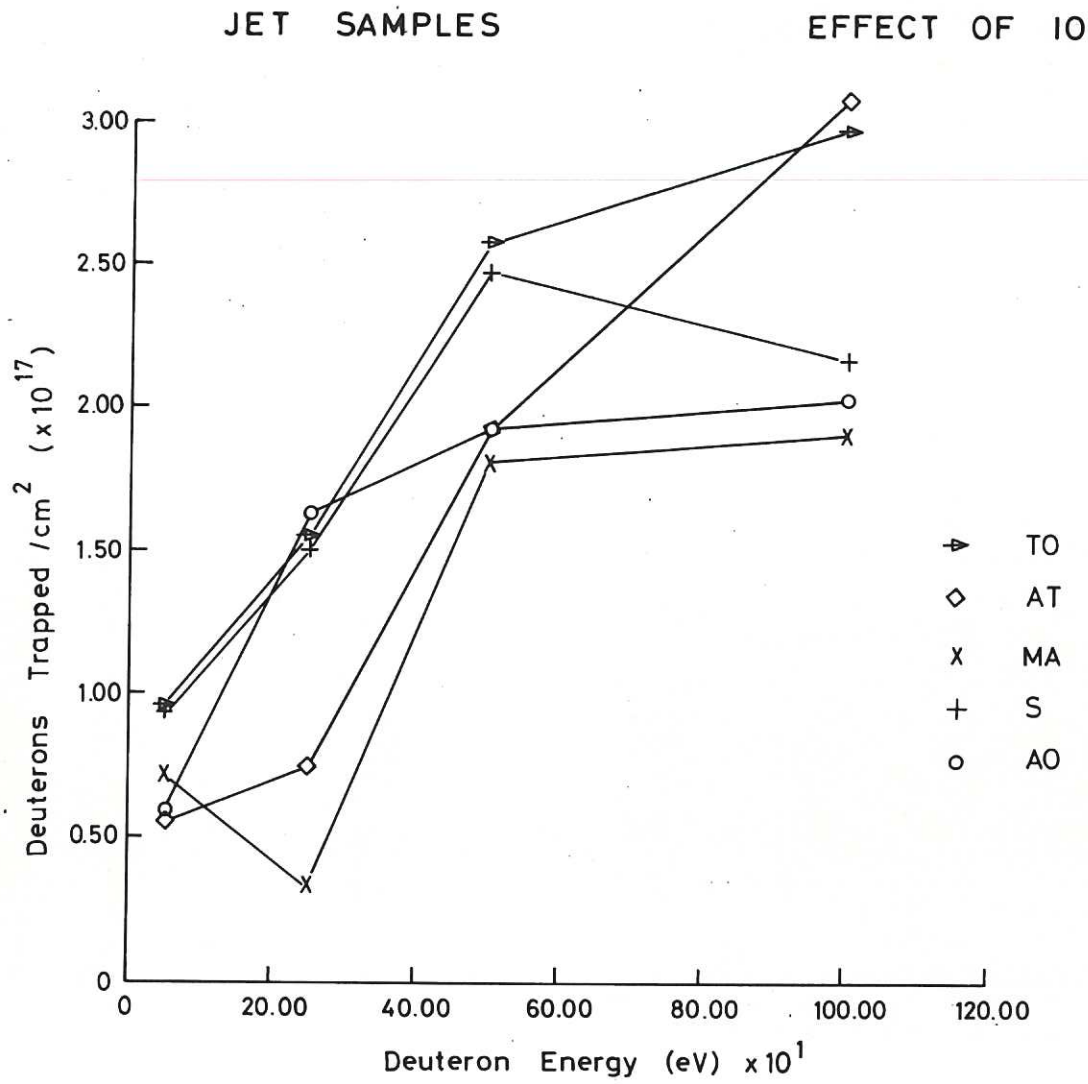
JET SAMPLES
EFFECT OF ION ENERGY
Deuterons Trapped /cm^2 (x10^{17})
3.00
2.50
2.00
1.50
1.00
0.50
0
0
20.00
40.00
60.00
80.00
100.00
120.00
Deuteron Energy (eV) x10^1
TO
AT
MA
S
AO

Fig 4.1.1

width at saturation of twice the projected range. In fact the range width is probably larger than this: it is for carbon (11). This would make the D/Si concentration somewhat less than unity, in closer agreement with the carefully measured carbon data of 0.44 ± 0.08 (11). Recent measurements on single crystal silicon by Doyle et al (1) show a saturation concentration of ≈ 0.5, but their value for the number of deuterons trapped for 1.5keV D^+ ions is 1.91 x 10^{17} cm^{-2}, which is not inconsistent with the data presented in Figure 4.1.1, in view of the different nature of the silicon surfaces.

4.1(b) Titanium Carbide

Trapping in titanium carbide samples is illustrated in Figure 3.1.10 as a function of deuteron (D^+) dose for different D_2^+ ion energies. The behaviour is similar to that seen previously for the reactive metals, titanium, niobium, zirconium and erbium (12). These materials trap continuously because of a rapid diffusion of deuterium away from the surface region into the bulk. The deuterium in fact dissolves in the lattice with a positive heat of solution - and this prevents escape from the surface.

The re-emission observed is constant with ion dose, and is simply the backscattered fraction. This fraction has been plotted on the universal curve for reflection coefficient vs. reduced energy (McCracken and Stott, (13)) and all points show good agreement with the curve. The agreement illustrates the accuracy of our experimental technique.

Measurements have been made of the trapping of deuterons in titanium carbide coatings by the Sandia group, in aid of the TFTR programme (1). They have not seen any continued trapping, in fact the behaviour of titanium carbide was similar to that of the saturable samples. The reason for the observation of titanium-like trapping in the present samples is probably due to the method of manufacture. A co-sputter technique was employed to deposit Ti and C on to the Inconel substrate. This could certainly lead to Ti-rich coatings (14). The Sandia group used a chemical vapour deposition technique.

Clearly if the walls of the JET torus were to be operated near room temperature, the present form of titanium carbide would be a bad choice in view of the large amounts of tritium which could be dissolved. On the other hand, recycling would be much reduced, and the material could be satisfactory since, as discussed later (section 4.2), the tritium could be recovered if the material is heated to ≥ 500°C.

4.2 Measurements at Elevated Temperatures

Trapping of deuterium in even simple elemental materials, for example nickel (15), is quite complex. The deuterium atoms are trapped in sites which are often created during bombardment, and these radiation damage sites can have a large number of discrete activation energies for deuterium re-emission. Gas is lost by a one step desorption process, rather than diffusion, and is released in bursts over a wide temperature range as the temperature is increased. This study does not include thermal desorption spectrometry, but a similar behaviour to nickel would be expected for many of the samples studied. This is evident from sets of curves such as Figure 3.2.1, for example, which show re-emission as a function of deuteron dose at temperatures up to 800°C. At 20°C, only the backscattered fraction is observed on beam switch on. At 100°C the re-emission rate is higher, presumably due to the instantaneous desorption of sites of low activation energy. More and more of these sites are quickly desorbed as the temperature is increased, when at 800°C > 70% of beam is immediately re-emitted. The titanium carbide data, an example of which is shown in Figure 3.2.2, again exhibits a different behaviour with temperature to the saturable samples. In general, trapping continues, with only the backscattered fraction re-emitted, to high doses for temperatures ≤ 300°C. At 500°C and above the TiC exhibits a saturation behaviour similar to the other samples studied - in a similar manner to titanium metal (12). The temperature of 500°C seems to be close to that required for the onset of thermal release since in one instance (1keV D_2^+ bombardments) re-emission was not observed at this temperature.

The data may be compared with that presented by Hotston and McCracken (12) for 18keV deuteron trapping in titanium metal. The trapping efficiency for deuterons in titanium carbide after an incident deuteron dose of 1 x $10^{18} cm^{-2}$ has been plotted in Figure 4.2.5, as a function of target temperature. Also included on this Figure is the Hotston and McCracken data, (solid curve).

It is clear that trapping in the present samples is very similar to that obtained previously for titanium - the lower trapping efficiency at low temperatures is simply due to backscattering of the 50eV - 1keV deuterons.

This result has important implications, since it suggests that tritium could be recovered between shots on JET by wall heating - whilst maintaining low wall re-cycling during the shot.

Figure 4.2.5

Trapping Efficiency of Titanium Carbide as a Function of Substrate Temperature 2 keV, 1 keV, 500 eV, 100 eV D_2^+ Solid Line is Result for 18 keV D^+ in Titanium Metal (12)

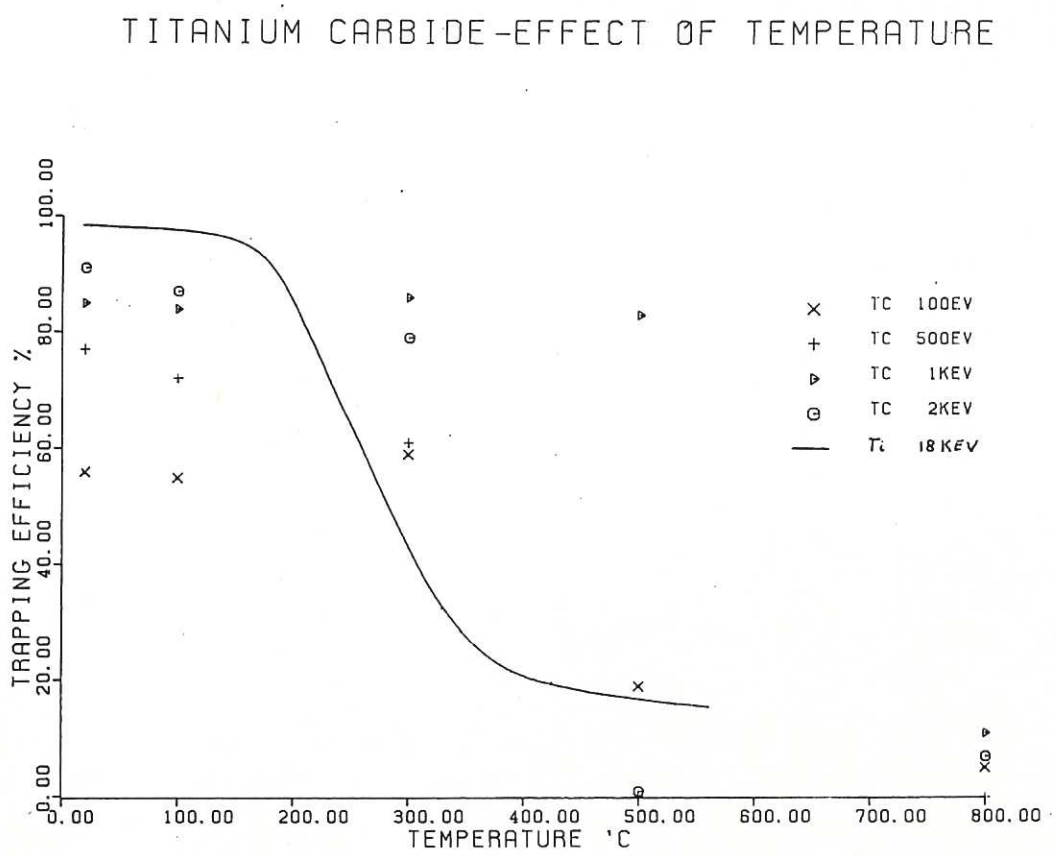
TITANIUM CARBIDE-EFFECT OF TEMPERATURE
TRAPPING EFFICIENCY %
100.00
80.00
60.00
40.00
20.00
0.00
0.00
100.00
200.00
300.00
400.00
500.00
600.00
700.00
800.00
TEMPERATURE 'C
TC 100EV
TC 500EV
TC 1KEV
TC 2KEV
Ti 18 KEV

Fig. 4.2.5

The outward thermal diffusion of deuterium from the samples was recorded by measuring the fall in re-emission rate with time after beam switch-off. With a few exceptions, the fall-off was dictated by the vacuum time constant of the target chamber - monitored by switching the beam off during bombardment of carbon at 20°C. The exceptions were titanium carbide at 500°C, Inconel at 20°C and 500°C, and at only one ion energy for titanium dioxide, at 500eV and 500°C. Since the effect was not observed for energies other than 500eV D_2^+, this latter result is thought to be erroneous. These measurements confirm the hypothesis that thermal diffusion is an unimportant re-emission mechanism, except for Inconel and titanium carbide.

The amount of deuterium trapped in each sample as a function of target temperature is of obvious importance from the point of view of tritium hold-up. Calculations of the trapped amount have been made from integration between the curves and the 100% beam re-emission level in Figures 3.2.1 to 3.2.24. This data is presented in Figure 4.2.1 to 4.2.4 for 2keV, 1keV, 500eV and 100eV D_2^+ bombardments.

At the higher ion energies of 2keV and 1keV the amount of deuterium retained in the samples falls with increasing target temperature - with very little retention at 800°C for alumina, silicon and titanium dioxide. This is to be expected on the grounds of trapping in sites of varying activation energy for re-emission. However certain exciting features are evident in the curves presented in figures 4.2.1 to 4.2.3. (On the grounds of Auger analysis, to be discussed later, the 100eV D_2^+ bombardments may not be representative of the bulk sample.) The main feature is a rise in trapping at a particular bombardment temperature. This is observed for titanium dioxide, for example, at 500°C in both 2keV and 1keV D_2^+ bombardments. One can only suggest a chemical binding (potential barrier) exists in a similar manner to that postulated for titanium (12), and that at 500°C some inward diffusion can occur within the sample. If this is indeed the case it could have serious consequences for use of many of these samples in the tritium phase of operation on JET.

The silicon carbide samples exhibit similar trapping features to the other saturable samples, although the data presented for 2keV D_2^+ bombardments in Figure 3.2.25 suggests only slightly lower trapping at 500°C to that measured at 20°C. The result would suggest high activation energies for deuterium release from silicon carbide. It would be useful if it were desired to leave the walls in a deuterium or tritium loaded state, even after baking to 500°C.

Figures 4.2.1 to 4.2.4

Total Number of Deuterons Trapped in Each Coating as a Function of Substrate Temperature
Incident Dose 1 x 10^{18} cm^{-2}
2 keV, 1 keV, 500 eV, 100 eV, D_2^+

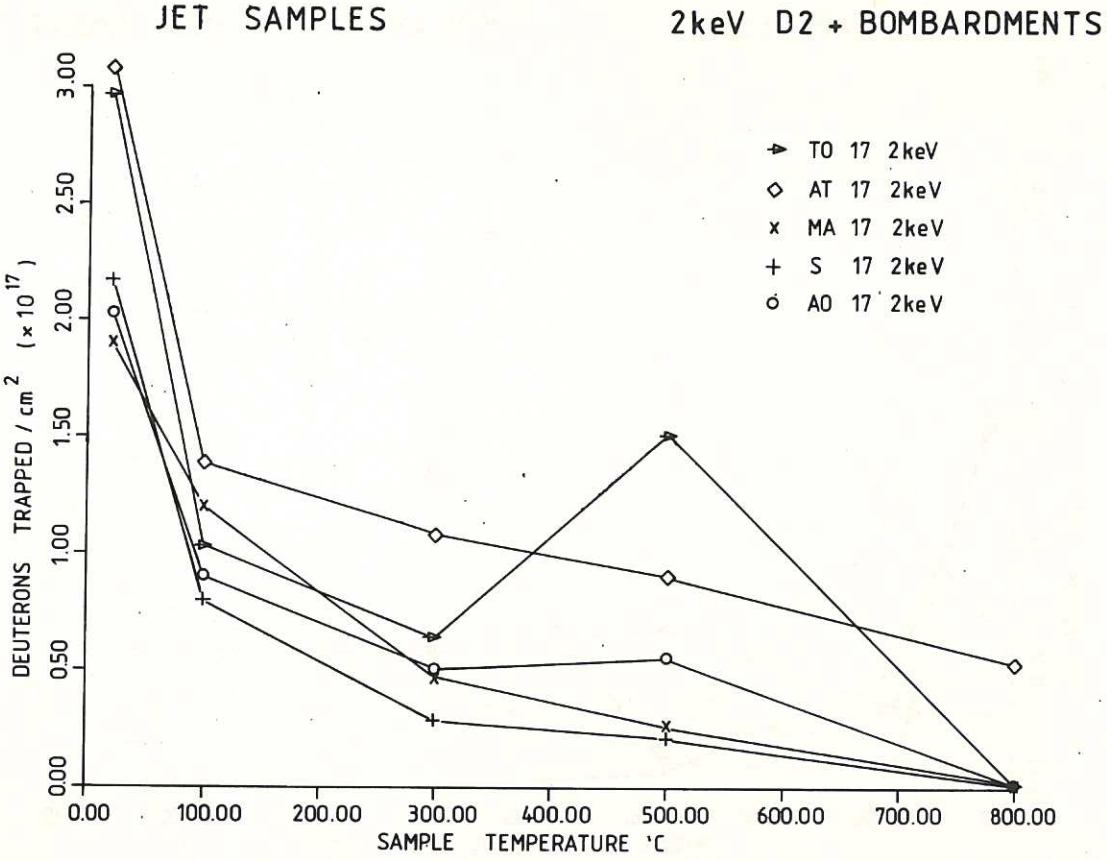

Fig. 4.2.1

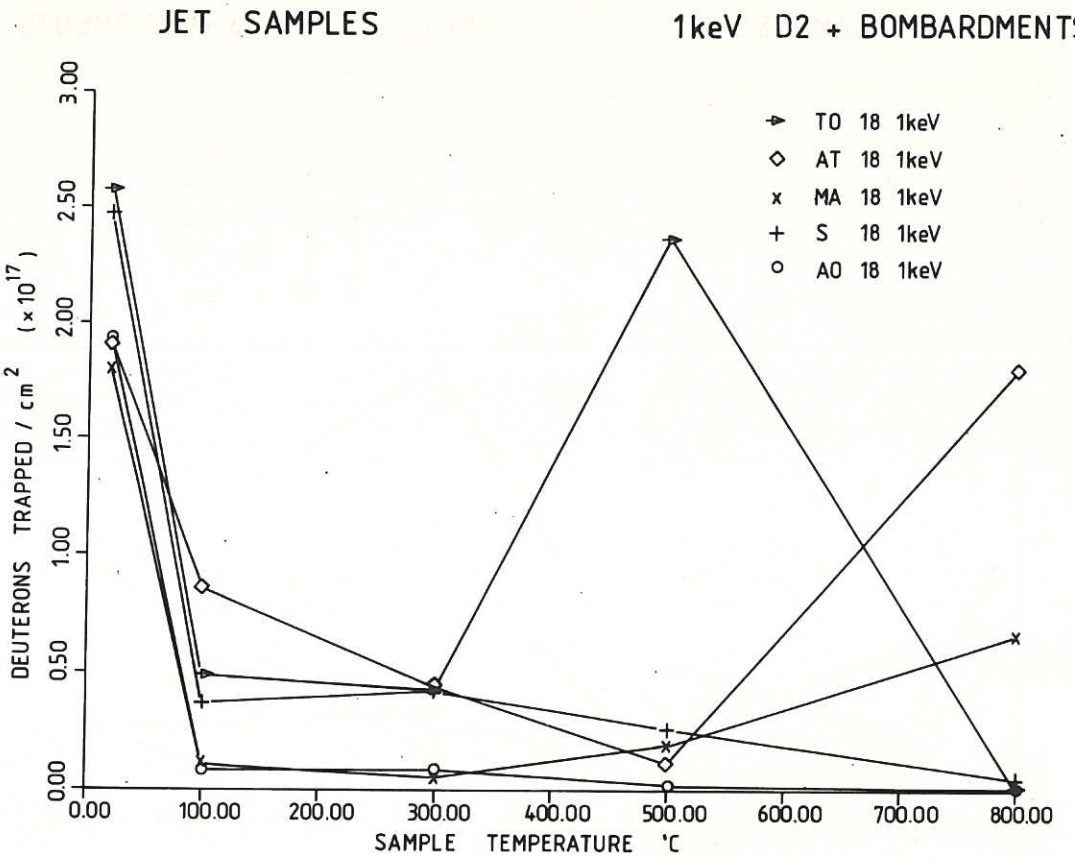

Fig. 4.2.2

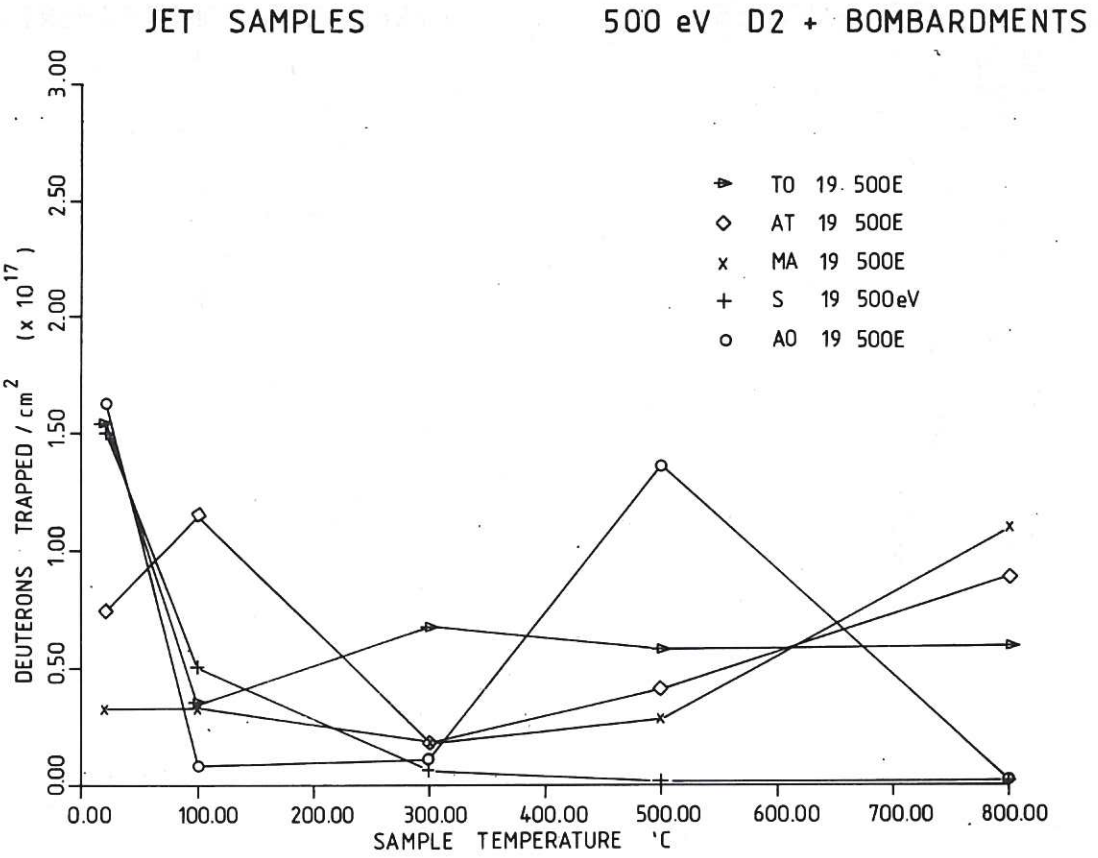

Fig. 4.2.3

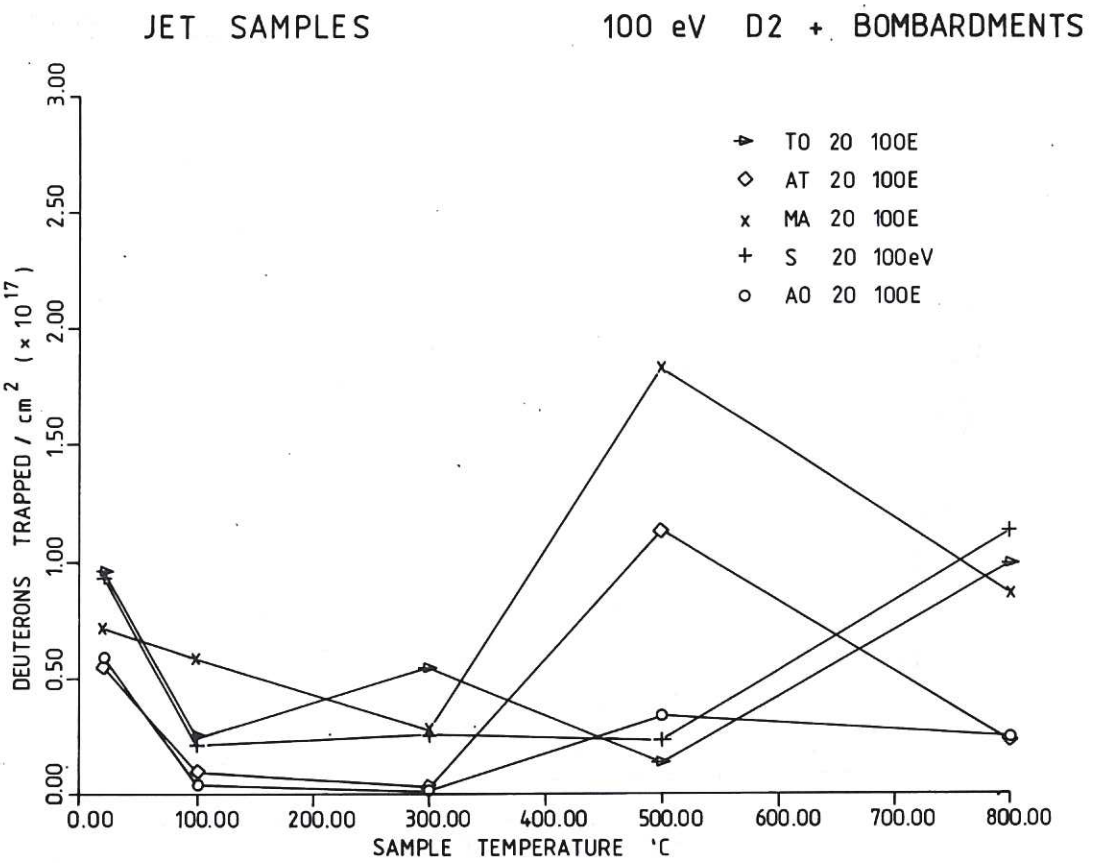

Fig. 4.2.4

CLM-R223

4.3 Trapping Measurements in Inconel

The Inconel data presented in Figure 3.2.26 has been set aside for separate discussion because firstly Inconel will be used in the initial phase of JET operation for both wall and limiter surfaces, and secondly the trapping behaviour is rather different from that discussed previously. The results are in fact comparable to those obtained previously for trapping in non-reactive metals, e.g. nickel (15) and stainless steel (6).

As can be seen from the Figure, both curves show an immediate beam re-emission of ~ 20%, which is not inconsistent with backscattering of 2keV D_2^+ from Inconel. However the ion dose required to saturate the Inconel at 20°C is much smaller than that required for the other saturable samples. In addition, release of deuterium, presumably via outward diffusion from the target, was recorded after beam switch-off. This result is in contrast to that obtained for the other saturable samples for which no outward diffusion could be measured - this could mean either a release too fast to be recorded in the time scale of the experiment, or a release too slow to show any measurable deuterium partial pressure signal.

The isothermal release of gas from a metal, assuming a diffusion process, has been analysed by Kelly (16). The solution to Fick's diffusion law for a planar source at the ion range is:

$$C\ (x,t) = \frac{Co}{2\sqrt{\pi Dt}} \quad \exp\ [-\frac{(x - p\lambda)^2}{4\ Dt}] - \exp\ [-\frac{(x + p\lambda)^2}{4\ Dt}] \qquad (1)$$

Where C is the concentration at a distance 'x' from the metal surface, Co is the initial concentration at a plane $p\lambda$ units from the surface, and D is the diffusion coefficient. The gas release rate from the surface, ρ is given by

$$\rho(t) = D \frac{dc}{dx}_{x\,=\,0} = \frac{C_o p\lambda}{2\sqrt{\pi Dt}.t} \quad \exp\ (-\frac{p^2\lambda^2}{4Dt}) \qquad (2)$$

Since D is a constant for any given target temperature, $D = D_o \exp\ (-\frac{Q}{RT})$, then $\rho(t) \alpha \quad t^{-\frac{3}{2}} \exp\ (-\frac{k}{t})$, where k is a constant.

Equation 2 in this analysis is only valid after long times, when the concentration distribution within the metal is established, (i.e. no longer a slab at $p\lambda$. Under these circumstances, $\exp\ (-\frac{k}{t}) \rightarrow 1$, and $\rho(t) \approx t^{-\frac{3}{2}}$. At short times, Lewin and Martin (17) have shown that $\rho(t) \approx t^{-\frac{1}{2}}$, for a semi-infinite slab of trapped gas in a solid, which should approximate to the

present situation. The time required for the transition from $t^{-\frac{1}{2}}$ to $t^{-\frac{3}{2}}$ dependence is a function of the rate of loss of gas from the solid, i.e. the diffusion coefficient.

In view of the above theoretical considerations, the isothermal release of deuterium from Inconel at 20°C and 500°C has been plotted as a function of time using logarithmic scales. This data is shown in Figure 4.3.1. The important conclusion from this figure is that the slope of the 500°C data is less than that of the 20°C, whereas on the grounds of diffusion with a single activation energy Q it should be much greater. This immediately implies more than one activation energy for gas releases, which unfortunately precludes any further useful analysis from the present limited data.

The total amount of deuterium retained in Inconel during bombardment may be compared with similar data obtained for stainless steel (6) at high ion doses. At 20°C, the equilibrium number of 2keV deuterons retained in Inconel is $\approx 3.5 \times 10^{16}$ ions cm^{-2}. At 500°C the trapping continues to slightly higher doses and the number is $\approx 5 \times 10^{16}$ ions cm^{-2}. This could be due to increased inward diffusion. In the case of 304 stainless steel, Thomas (6) has measured a room temperature retention of $\approx 4 \times 10^{16}$ deuterons cm^{-2} again for 2keV D_2^+ ions, in close agreement with the Inconel result. However, comparison of these results is difficult since it is known that trapping at low energies depends critically on the thickness of surface oxide present. Much more data could be obtained using thermal desorption spectrometry, and in view of the use of Inconel 625 on JET further studies are recommended.

4.4 Auger Analysis

Auger electron analysis was carried out on a few selected samples after bombardment in order to measure any stoichiometric changes which might have taken place on the surface. Samples were limited to those on which the bombarded area could be seen due to a surface colour change. For comparison, analysis of an unbombarded region on each sample was also made. The results of these studies are shown in Table 4.2.

Auger analysis is limited to 10 - 20Å of surface by the low energy of the escaping Auger electrons. The data presented in Table 4.2 indicates that the surfaces of all samples are covered in impurities, and little or nothing of the underlying bulk material can be seen. For instance, no aluminium could be recorded on alumina samples, and no silicon on silicon carbide samples.

Figure 4.3.1

Isothermal Desorption of Deuterium from Inconel Following 2 keV D_2^+ Bombardment at 20°C and 500°C

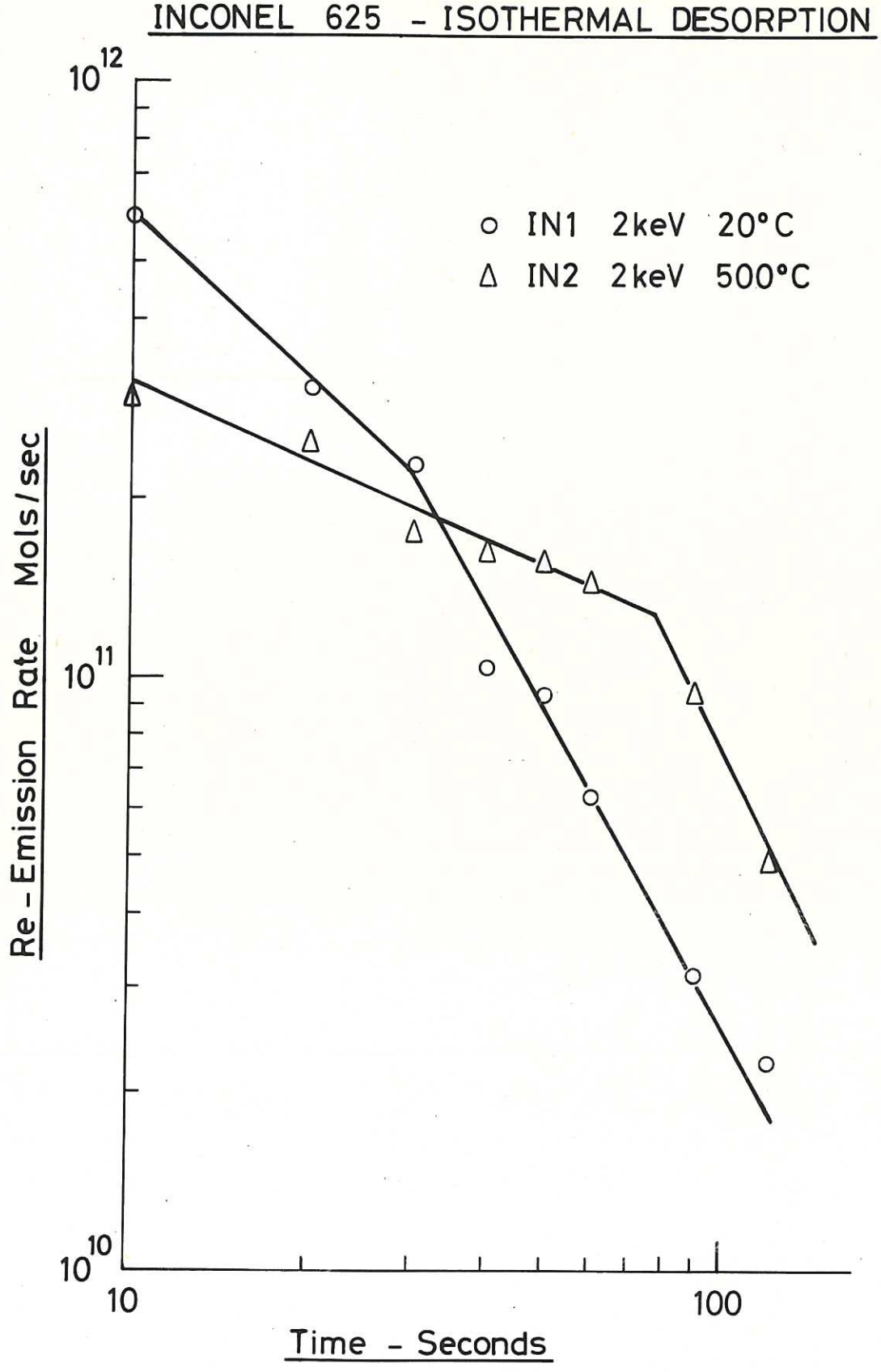
INCONEL 625 - ISOTHERMAL DESORPTION
10^12
10^11
10^10
10
100
Re-Emission Rate Mols/sec
Time - Seconds
IN1 2keV 20°C
IN2 2keV 500°C

Fig.4.3.1

Table 4.2

Auger Analysis of 2keV D_2^+ Bombarded Low Z Coatings

Element	Alumina		Silicon		Titanium Dioxide		Silicon Carbide	
	Virgin	Bombarded	Virgin	Bombarded	Virgin	Bombarded	Virgin	Bombarded
Carbon	84.84	89.37	51.56	63.81	85.06	86.58	75.76	85.44
Oxygen	4.04	2.85	7.49	8.59	5.14	3.85	6.17	4.42
Iron	2.67	2.28	1.74	2.25	2.62	2.30	2.73	2.21
Sulphur	0.53	0.91	0.28	0.78	0.80	0.78	5.66	1.62
Chlorine	6.54	3.16	2.74	3.91	4.76	4.81	4.04	4.95
Titanium	0.39	0.47	0.46	0.5	0.56	0.68	0.61	0.49
Aluminium	0	0	0	0	0	0	0	0
Silicon	0	0	35.1	19.28	0	0	0	0

Table 4.2 gives percentages of elements present in the first 10 - 20Å of surface. The results are an average of 2 measurements on separate samples.

Some pertinent points do emerge from Table 4.2. Firstly, at the lowest ion energy used in this study (100eV D_2^+) the re-emission data will be characteristic of the surface impurities and not the substrate - provided that these impurities are not desorbed at the bombardment temperature. Secondly, prolonged bombardments ($> 10^{18}$ ions cm^{-2}) of 2keV D_2^+ ions do not remove the surface impurities. This would be expected for a sputtering yield $< 10^{-2}$ atoms/ion. Thirdly, the presence of iron on all samples, including the vapour deposited silicon carbide, is surprising. In view of the different manufacturing techniques used to fabricate the samples, no explanation for its existence can be given.

Clearly Auger analysis cannot provide any evidence for stoichiometric changes on the sample surfaces. However, colour changes are useful indicators of chemical reaction, so these will be considered. The pre-bombardment colours of each sample are shown in Table 1.1.

The silicon samples change from a steel grey to blue-black during bombardment with 2keV D_2^+. This is probably a change of state from adamantine (crystalline) to amorphous. Any silane formed ($Si D_4$) would be desorbed from

the surface. Alumina turns white, from an off-white pre-bombarded state. This could simply be due to surface cleaning, although Table 4.2 does not suggest this. Reduction to aluminium would darken the surface. Again a change of state from crystalline to amorphous is probably responsible, giving rise to a change in refractive index of incident light. The violet-black colour of the unbombarded titanium dioxide suggests that it is, in fact, the sesqui-oxide, Ti_2O_3. This changes to a clear brown-black colour on bombardment, indicating TiO_2. Silicon carbide displays a bright purple-blue colouration on bombardment. Previous work by the author has indicated a loss of carbon during deuteron bombardment of silicon carbide (18). The colouration could therefore be due to silicon, or simply a change in the refractive index of the silicon carbide surface.

Finally the mechanical integrity of the samples during the bombardment experiments should be noted. All samples withstood the bombardments without visible signs of flaking or blistering. However two important results did emerge from annealing to 800°C. These were:

a) The titanium carbide samples blistered, possibly due to precipitation of dissolved gas. Argon was used during sputter deposition.

b) The plasma-sprayed silicon samples became detached from their Inconel substrates. This occurred for all silicon samples heated to 800°C.

4.5 Tritium Inventory

Certain elevated temperature data are somewhat disturbing in view of the possible large tritium inventory which may arise in the coatings due to operation at wall temperatures $\geq$ 500°C.

It was generally thought in the past that deuteron trapping in most materials decreased rapidly with increasing temperature. On the basis of simple diffusion, with no surface barrier to hinder escape, this would be expected. The high concentration gradient towards the surface, compared to the almost zero gradient into the bulk, should ensure that virtually all incident ions escape and that there is little inward diffusion. Exceptions to this model have been identified and include those materials into which deuterium dissolves with a positive heat of solution - such as titanium and niobium for example.

Deuteron trapping measurements are (historically) made in three types of experiment.

(1) Re-emission of deuterium during deuteron bombardment.
(2) Thermal desorption of trapped deuterium following bombardment.
(3) The D (^{3}He, α)H nuclear reaction, following implantation.

Unfortunately all these techniques fail to identify inward diffusion of deuterium following modest doses of deuterons ($1 \times 10^{18} cm^{-2}$). (1) suffers from a calibration uncertainty of $\pm$ 10%. (2) suffers from errors due to desorption of deuterium from chamber walls at the high temperatures required to release deuterium from deep within the targets. (3) suffers from limitations in sensitivity, and short probing depths of the incident MeV ^{3}He ions.

Evidence <u>for</u> inward diffusion of deuterium in low Z coatings has been obtained in this study during measurement of trapping as a function of target temperature. The surprising feature of these results, which can be explained in terms of inward diffusion, is an <u>increase</u> in trapping in many instances for a temperature increase from 300°C to 500°C, or 800°C.

A tabulation of the coatings which show the effect is given below;

Titanium dioxide:	1keV deuterons:	1.5×10^{17} trapped at 500°C
Alumina :	1keV deuterons:	6×10^{16} trapped at 500°C
Titanium dioxide:	500eV deuterons:	2.5×10^{17} trapped at 500°C
Alumina titania :	500eV deuterons:	1.8×10^{17} trapped at 800°C
Spinel :	500eV deuterons:	7×10^{16} trapped at 800°C
Alumina :	250eV deuterons:	1.4×10^{17} trapped at 500°C
Spinel :	250eV deuterons:	1.2×10^{17} trapped at 800°C
Alumina titania :	250eV deuterons:	9×10^{16} trapped at 800°C
Titanium dioxide:	250eV deuterons:	6×10^{16} trapped at 800°C

Similar increases have been observed for 50eV deuterons - although these measurements are probably not representative of the bulk material, but rather of the surface contaminants, (such as carbon and oxygen).

Very similar data have recently been obtained by Wilson and Pontau[19] for deuteron trapping in vapour-deposited boron films. They attribute the "barrier" which prevents deuterium escape from the bombarded surface as simply the lack of deuterium atoms to supply the surface recombination reaction D +

$D \rightarrow D_2\uparrow$. The release rate J for deuterium molecules from the surface is written:

$J = K.C^2_{(0)}$ where $C_{(0)}$ is the concentration of deuterium near the surface. When the temperature gets sufficiently high, diffusion occurs and reduces $C_{(0)}$. The reaction governing release from the surface thus becomes small compared with the diffusion rate into the bulk. The situation has been studied theoretically by Ali-Khan et al[20]; Baskes[21] and Hotston et al[12].

It can be easily seen that a critical condition is met when the release rate from the bombarded surface is comparable to the diffusion rate into the bulk. If diffusion is higher, then the deuterium concentration will build up in the bulk, until the overall concentration is comparable to the surface concentration required to allow total incident beam release from the recombination reaction $D + D \rightarrow D_2\uparrow$.

Hotston and McCracken[12] have plotted the hydrogen trapping efficiency in a sample as a function of the parameter $\{Q/Q_c\}$, where Q is the incident dose ($J_o t$), $Q_c = D\pi/K.T^{-\frac{1}{2}}.\exp(-2Q_1/RT)$, D is the diffusion coefficient and Q_1 the heat of solution. It is shown that even for high values of $\{Q/Q_c\}$ the trapping efficiency is still quite large ($\sim 10\%$).

Let us consider the case of a target with a small heat of solution (Q_1 = 0.1 eV), and an incident dose of 10^{18} cm^{-2}. We will assume a value for D of 1.3×10^{-9} cm^2 sec, as per the thin boron films of Wilson and Pontau[19]. Under these conditions Wilson's calculations show that for a dose of 10^{18} deuterons cm^{-2}, 5×10^{17} $D.cm^{-2}$ i.e. 50% are trapped at $\sim 500^oC$. The trapping behaviour at even higher doses has not been calculated, but on the basis of the Hotston and McCracken model one would expect $\sim$ 10% effective trapping efficiency: i.e. for an incident dose of 10^{21} cm^{-2}, $\sim 10^{20}$ cm^{-2} would be retained.

The JET wall has an area of $\sim 500m^2$, thus an inventory of 5×10^{26} tritium atoms (2.5kg) would be built up. This is to be compared with an allowable inventory of 3 - 10g. Clearly materials which trap in this manner, and cannot be fully outgassed at much lower incident fluxes, cannot be used on JET.

This argument probably limits the choice of tested materials to titanium carbide, silicon and possibly silicon carbide. Of these three, titanium carbide appears to be the best choice, for although trapping well at temperatures $< 500^oC$, gas release appears possible by heating to $> 500^oC$. Typical incident fluxes of $\sim 10^{16}$ cm^{-2} sec^{-1} are observed near to the wall on

DITE. Assuming that 10^{16} gas atoms cm^{-2} are trapped in the walls of JET in a single discharge, then the gas inventory in titanium carbide/discharge would be 0.25 g - about $\frac{1}{10}$ of the the allowable inventory for a 1:1 D-T mixture. This situation will not arise, of course, if the walls are run at 500°C during each discharge. However any useful reduction in recycling obtainable by using titanium carbide at lower temperatures will then be lost.

Probably of more importance is the loss of tritium by wall pumping during each discharge - due to recycling with previously trapped deuterium in the wall and resulting in a tritium-weak mixture. Assuming 10^{-4} torr fill pressure, and a 1:1 initial D-T mixture, then only ~ 3.5 mg of tritium will be used, (~ 10 torr litres). At a gas atom loss rate of 5×10^{22} sec^{-1} to the wall, the density will fall to unacceptable levels in a few tens of ms without extra gas feed, (c.f. particle containment time). Careful considerations will have to be given to this problem to ensure that the required ratios are maintained.

Finally results from both silicon carbide and carbon indicate low inward diffusion of deuterium at 500°C, and for ions of 100 eV maximum energy this would result in a total inventory of ~ 10^{17} gas atoms cm^{-2}, or 2.5 g of tritium at saturation. Any small inward diffusion would result in "lost tritium", since recovery by heating alone is impossible. Use of these materials may therefore result in an unacceptable tritium inventory after several discharges. Replacement of the wall coating at this stage may be required.

5. Conclusions

The re-emission of deuterium from a variety of low Z coatings has been measured during bombardment with 2keV, 1keV, 500eV and 100eV D_2^+ ions. Measurements were repeated at sample temperatures of between 20°C and 800°C.

In terms of their trapping behaviour, samples can be divided into two categories. These are:

(a) Samples which saturate, i.e. re-emit all incident deuterons, at doses $\leq 10^{18}$ cm^{-2} for 2keV ions and

(b) Samples in which the incident deuterium diffuses into the bulk of the material and shows no signs of gas re-emission, other than the backscattered fraction, for doses well in excess of $10^{18} cm^{-2}$.

Alumina, silicon, spinel, alumina-titania, titanium dioxide and silicon carbide all fall into category (a). Titanium carbide exhibits properties of category (b) at temperatures < 500°C. This behaviour is like that of titanium metal, and has not been found for titanium carbide samples prepared by chemical vapour deposition (1). It is thought that the present samples could have a surface which is titanium-rich, which would explain our result.

In view of the absence of any measurable outward diffusion of deuterium after beam switch off, at any target temperature for the category (a) samples, ion induced re-emission of previously trapped gas appears to be the primary re-emission mechanism. Prompt desorption from sites of low activation energy, via a single step desorption rather than a diffusion process, is suggested to explain the decrease in trapping with increase in target temperature for these samples. Confirmation of this suggestion and quantitative measurements of activation energies for desorption could be obtained by thermal desorption spectrometry.

One disadvantage of the present technique is the difficulty in measuring accurately the 100% beam re-emission value. An error of even a few percent could mask a continuous inward diffusion of a small fraction of beam, which in JET could lead eventually to a large tritium inventory. Evidence for such an inward diffusion has been obtained for some samples at particular temperatures in the present study. Titanium dioxide, for example, appears to trap much more deuterium at 500°C, for both 2keV D_2^+ and 1keV D_2^+ bombardments, than it does at 300°C. A trend towards category (b) behaviour therefore seems possible at certain temperatures which will allow deuterium to go into solution, but which are sufficiently low to inhibit deuterium escape from the

Inconel falls into what could be described as a third trapping category, similar to other metals like nickel and molybdenum which do not react chemically with hydrogen. Beam re-emission from Inconel occurs very rapidly even at 20°C, and the total number of deuterons trapped following an incident dose of 10^{18} cm^{-2}, 1keV deuterons is $\approx 3.5 \times 10^{16} cm^{-2}$, almost an order of magnitude less than that trapped in the other low Z saturable samples. Although deuterium re-emission after beam switch-off suggests an outward diffusion of gas, measurements at 20°C and 500°C show that if diffusion is indeed the release mechanism then at least two activation energies for the process exist. This is consistent with data on other metals such as nickel (15). A further more detailed study, possibly including thermal desorption spectrometry, is recommended to a obtain better understanding of deuteron trapping in Inconel.

Finally, Auger analysis of bombarded and unbombarded samples suggests that an impurity layer of at least 10 - 20Å of carbon and oxygen exists on all samples at room temperature. This implies that our 100eV D_2^+ (and possibly 500eV D_2^+) data is representative of the impurity layer rather than the low Z coating. This will possibly be the case in JET if carbon monoxide or water vapour adsorb in any quantity between discharges.

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