CHEMICAL EROSION OF GRAPHITE DUE TO SIMULTANEOUS H⁺ AND O⁺ IRRADIATION

by

Allen Y.K. Chen

A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy

Graduate Department of Aerospace Studies
University of Toronto

© Copyright by Allen Y.K. Chen (2001)
The author has granted a non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of this thesis in microform, paper or electronic formats.

The author retains ownership of the copyright in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author’s permission.

L’auteur a accordé une licence non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de cette thèse sous la forme de microfiche/film, de reproduction sur papier ou sur format électronique.

L’auteur conserve la propriété du droit d’auteur qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

0-612-58591-3
Chemical Erosion of Graphite Due to Simultaneous H⁺ and O⁺ Irradiation by Allen Y.K. Chen, Department of Aerospace Studies, University of Toronto submitted in conformity with the requirement for the degree of Ph.D. (2001)

ABSTRACT

Graphite is one of the prime candidates for first-wall use in fusion devices. Its main advantages are its low $Z$ and excellent thermomechanical properties, while its drawbacks are plasma-induced erosion and hydrogen retention. In addition to normal physical sputtering, graphite shows regimes of enhanced erosion at elevated temperatures. Exposure to hydrogen — the fusion fuel — in the temperature range 300 – 1000K leads to the formation of volatile hydrocarbons. Furthermore, since oxygen is often one of the main intrinsic impurities in the plasma of current fusion devices with carbon walls, the reaction of oxygen-containing ions with carbon materials also plays an important role in the complex process of plasma wall interaction. This thesis investigates the synergistic effect of H⁺ and O⁺ irradiation of graphite.

Experiments of simultaneous O⁺ and H⁺ irradiation on graphite showed that water is formed as the main synergistic product, along with reductions in the CO/O⁺, CO₂/O⁺ and CH₄/H⁺ yields. Similar to CH₄ yields, water yields (H₂O/O⁺) are temperature dependent with maximum yield occurring at ~ 800K. Beam range separation experiments of O⁺ and H⁺ irradiations indicated that water is produced at the end of the O⁺ ion range. Furthermore, water formation was shown to be dependent on the mobile hydrogen concentration on internal surfaces, and independent of ion range separation. Reduction of CO and CO₂ yields was found to depend on the reduction of oxygen supply due to water formation. CH₄ yield reduction was found to be dependent on the incident oxygen, and the “methane break-up” mechanism was postulated and confirmed by Ne⁺-H⁺→C experiments. Experiments of simultaneous O⁺ and H⁺ irradiation on boron-doped graphite showed that the methane yield reduction due to break-up may be more
than compensated for by the methane yield due to the combined presence of oxygen and boron. The reduction of methane yields from the $\text{H}^+ \to \text{C}/\text{B}$ reaction due to boron can also be partially nullified by the incident oxygen. Furthermore, $\text{O}^+ \cdot \text{H}^+ \to \text{C}/\text{B}$ irradiations showed that water formation was reduced when compared to $\text{O}^+ \cdot \text{H}^+ \to \text{C}$ irradiations. These observations provided additional details in the CH$_4$ and H$_2$O formation mechanisms. Finally, a semi-empirical mathematical model was formulated based on the emerging mechanisms.
ACKNOWLEDGMENTS

I would like to thank my supervisor, Professor A. A. Haasz, for his invaluable guidance and support throughout this project. In addition, I would like to thank Dr. J. W. Davis for his constant directions, insights and assistance, and Professor P. C. Stangeby for his comments and suggestions on the manuscript. I would like to give a special thanks to Charles Perez for his incomparable technical expertise that kept my experimental apparatus running. I would also like to give thanks to the other members of the Fusion Materials Research Group at UTIAS for their support and assistance. I am also very grateful for the inputs and suggestions received from Dr. E. Vietzke of the KFA Forschungszentrum, Jülich, Germany.

The financial supports provided by the National Sciences and Engineering Research Council, the Canadian Fusion Fuels Technology Project, ITER Canada, and the University of Toronto are also greatly appreciated.

Finally, I would like to thank my parents Mr. Nick Chen and Mrs. Misa Chen for their support, and all my friends (and ex-friends) for putting up with my anti-social behaviour in the duration of this project.
# TABLE OF CONTENTS

**ABSTRACT** .................................................................................................................. II

**ACKNOWLEDGMENTS** ................................................................................................. IV

**TABLE OF CONTENTS** .................................................................................................. V

1. **INTRODUCTION** ...................................................................................................... 1
   1.1 Nuclear Fusion ......................................................................................................... 1
   1.2 Magnetic Confinement and the Tokamak ................................................................. 2
   1.3 Plasma Surface Interactions .................................................................................... 3
   1.4 Objective of this Thesis .......................................................................................... 4
   1.5 Organization of this Thesis ..................................................................................... 5

2. **BACKGROUND OF FUSION-RELEVANT CARBON CHEMISTRY** ......................... 6
   2.1 Chemical Erosion of Graphite Due to Hydrogen Ions ............................................. 6
      2.1.1 Formation of H-Saturated Surface Layer ......................................................... 6
      2.1.2 Hydrogen Recombination and Re-emission ..................................................... 7
      2.1.3 Hydrocarbon Formation and Transport ......................................................... 9
   2.2 Previous Models for the Hydrogen-Carbon System ............................................... 11
      2.2.1 The Precursor Models of Hydrocarbon Formation in H\(^+\)\(\rightarrow\)C Reactions ...... 11
      2.2.2 Extensions of the Precursor Models to the H\(^+\)\(\rightarrow\)C Reactions .................. 12
      2.2.3 The Two-region Model of Hydrogen Transport .......................................... 13
      2.2.4 Application of the Two-Region Model to Include Hydrocarbon Formation ...... 17
   2.3 Chemical Erosion of Graphite Due to Oxygen Ions .............................................. 17
   2.4 Chemical Erosion of Carbon-based Material From Other Reaction Systems .......... 19
      2.4.1 Chemical Erosion of Graphite Due to Multispecies Impact ......................... 19
      2.4.2 Chemical Erosion of Boron-doped Graphite Due to H\(^+\) or O\(^+\) Impact .......... 19

3. **EXPERIMENTAL APPARATUS** ................................................................................. 21
   3.1 The Dual-Beam Accelerator Facility ....................................................................... 21
   3.2 Test Specimens ................................................................................................... 22
   3.3 Test Chamber and Diagnostics ............................................................................. 22

4. **EXPERIMENTAL PROCEDURES** ............................................................................ 25
   4.1 Determining the Reaction Products During H\(^+\)&O\(^+\) Irradiation of Graphite .......... 25
   4.2 Searching for the Mechanisms of Synergistic Effects .......................................... 26
      4.2.1 Sequential Implantation Experiments ......................................................... 27
      4.2.2 Simultaneous Implantation Experiments ..................................................... 27
      4.2.3 Flux/Range Dependencies of the Synergistic Effects: O\(^+\)-H\(^+\)\(\rightarrow\)C System ... 28
      4.2.4 Hydrogen Re-emission and Methane Break-up ........................................... 28
      4.2.5 Fluence and Microstructure ........................................................................ 29
   4.3 Flux/Range Dependencies of the Synergistic Effects: O\(^+\)-H\(^+\)\(\rightarrow\)C/B System .......... 29

5. **EXPERIMENTAL RESULTS AND DISCUSSIONS** ...................................................... 31
   5.1 Determining the Reaction Products During H\(^+\)&O\(^+\) Irradiation of Graphite .......... 31
      5.1.1 Consideration of Background Contributions to QMS signal in RGA Detection Mode .................................................................................................................. 31
      5.1.2 Temperature Dependence of Reaction Product Yields .................................. 32
   5.2 Searching for the Mechanisms of Synergistic Effects .......................................... 34
      5.2.1 Sequential Implantation Experiments .......................................................... 34
      5.2.2 Simultaneous Implantation Experiments ..................................................... 34
      5.2.3 Flux/Range Dependencies of the Synergistic Effects: O\(^+\)-H\(^+\)\(\rightarrow\)C System ... 35
      5.2.4 Hydrogen Re-emission and Methane Break-up ........................................... 37
      5.2.5 Fluence and Microstructure ........................................................................ 38
   5.3 Flux/Range Dependencies of the Synergistic Effects: O\(^+\)-H\(^+\)\(\rightarrow\)C/B system .......... 38
   5.4 Discussions of Mechanisms ................................................................................. 40
      5.4.1 The O\(^+\)-H\(^+\)\(\rightarrow\)C System ......................................................................... 40
1. INTRODUCTION

1.1 Nuclear Fusion

Nuclear fusion is a reaction where two light nuclei combine to form a heavier nucleus while releasing a large amount of energy. This is possible because of an interesting fact of nature. When free neutrons and protons combine to form a nucleus, the resulting nucleus is less massive than the sum of the mass of the original neutrons and protons! The missing mass is released in the form of energy, the amount of which can be calculated using Einstein’s famous $E=mc^2$ formula*. Conversely, it takes an equal amount of energy to reduce a nucleus to its constituents. The average amount of this “binding” energy per nucleon is usually less for the very light elements. Thus, when for example the nuclei of hydrogen isotopes are combined to form helium, which has relatively high binding energy compared to that of the reacting hydrogen isotopes, a considerable release of energy is accompanied by the reaction.

There are many types of fusion reactions involving light elements. A fusion reactor using only deuterium separated from water is ideal due to its abundance. Based on current energy consumption rates, the Earth’s water contains enough deuterium to supply the world’s energy demand for billions of years [1]. However, the D-T fusion reaction is easiest to achieve [2], hence it has been most extensively studied to date:

$$^3\text{D} + ^3\text{T} \rightarrow ^4\text{He}(3.52 \text{ MeV}) + n (14.06 \text{ MeV}).$$

This reaction has a high power density and natural energy exhaust via the 14.06 MeV neutrons (the 3.52 MeV alpha particles mainly contribute to self-heating of the fuel plasma for sustained reaction). However, D-T fusion uses the rare and radioactive tritium isotope and the resulting high-energy neutrons lead to the activation of most materials in the fusion reactor. The success of D-T fusion, however, may someday lead to other types of fusion reactions such as D-D fusion, which avoids much of the tritium problem.

There are several methods to provide D and T nuclei with enough energy to overcome the Coulomb barrier between the positively charged nuclei. One way is to heat the “fuel” to temperatures in excess of 100 million °C so that the tail of the Maxwellian velocity distribution coupled with quantum tunnelling effects will enable a sufficient number of the atoms to undergo fusion. This is the preferred method and is called thermonuclear fusion. The sun, like all stars, is the most spectacular example of this. In addition to the engineering challenges of achieving

* The formula was derived from Einstein’s special theory of Relativity published in 1905.
such a high temperature, there is another requirement. When atoms acquire high velocity, they
tend to disperse rapidly and escape in a very short time. In order to have enough atoms with high
enough velocity to stay long enough in the same region of space, some form of confinement is
required. The stars naturally rely on gravitational force to confine their "fuel". The hydrogen
bomb, a form of "uncontrolled" fusion reaction, uses the implosive force of a fission bomb to
both heat and confine the fusion material for a one-time-only ignition of fusion explosion.

To achieve controlled fusion, the two most commonly used techniques are inertial and
magnetic confinement. The former employs arrays of high-energy laser or particle beams to
uniformly implode pellets of fusion material, essentially setting off pulses of tiny hydrogen
bombs. For obvious reasons, such research has traditionally been tied to government military
programs. The magnetic confinement fusion, on the other hand, uses strong magnetic fields to
confine the plasma in a vacuum vessel, with the most extensively studied concept being the
tokamak.

1.2 Magnetic Confinement and the Tokamak

Magnetic confinement fusion utilizes the fact that when a gas is heated to a very high
temperature it becomes ionized forming ions and electrons, a state known as plasma. Unlike the
inertial confinement scheme, magnetic confinement fusion can, at least theoretically, ensure a
steady plasma state. Since charged particles will orbit a magnetic field line under the Lorentz
force with a cyclotron frequency of \( \omega_c = qB/m \), the motion of these fast-moving ions and
electrons can thus be controlled by externally applied magnetic fields. Along the field lines the
particles may move freely in a net helical motion. At present, the most successful magnetic
confinement technique is the toroidal "tokamak" configuration; see Fig. 1. Essentially, the
magnetic field lines are closed in a loop configuration by a set of toroidal field coils and a "twist"
is added to the donut-shaped toroidal field by a poloidal field. This poloidal field is generated
from a large current flow in the plasma produced by induction from transformer coils; the plasma
itself is the secondary winding of that transformer. Furthermore, external poloidal field coils are
sometimes employed for additional plasma shaping. The resulting helical magnetic field in the
tokamak configuration confines the plasma in a relatively stable configuration, and partial
plasma heating can be achieved by the ohmic heating from the induced plasma current.

**This is in contrast with the toroidal "stellarator" configuration in which the poloidal field is produced entirely from
external poloidal coils."
Even with the strongest magnetic field that we can manage today in tokamaks, perfect plasma confinement is still not possible. It is, in fact, theoretically impossible. There will always be particles leaving the plasma, and confining walls are required to supplement plasma confinement as well as for vacuum requirements. In a closed magnetic field configuration such as the tokamak configuration, the “end-losses” due to free plasma motion along the confinement field lines, experienced in open geometry configurations (such as the “mirror” devices), can be avoided. However, self-diffusion by Coulomb collisions or by turbulent (anomalous) transport processes lead to the appearance of particle drift motions that tend to make the plasma escape perpendicularly to the confining field lines. Furthermore, it is necessary to remove part of the helium ash continuously from the core plasma during fusion reactions; thus it is even necessary for the plasma confinement to be imperfect.

The ignition and subsequent steady-state operation of fusion reactors depend on the amount of energy generated via fusion reactions, the energy injected into the plasma, the loss of energy through the diffusion of plasma particles out of the core plasma, plus other energy-loss mechanisms such as conduction and radiation. The fuel plasma is said to achieve a self-sustaining reaction, or ignition, when the energy of the helium product equals the sum of all the energy loses. The criterion for the minimum amount of plasma confinement needed to achieve ignition can be calculated based on this equality, and is typically expressed in terms of a triple product of the plasma density, $n$, the plasma temperature, $T$, and the energy confinement time $\tau_E$ [2]:

$$nT\tau_E \approx 6 \times 10^{28} \text{m}^{-3} \cdot \text{s} \cdot K.$$

### 1.3 Plasma Surface Interactions

The escaped plasma from the never-perfect confinement field, consisting of hydrogen isotope “fuel” and impurities, will strike the material wall surrounding the plasma. The interaction of the high-energy plasma and the wall is expected to produce adverse effects on both the wall and the plasma. Depending on the nature of the fusion reactor operation, the confinement wall is subjected to high fluxes of energetic and thermal hydrogen and neutron bombardment, which may alter the composition and mechanical properties of the material. The eroded material can re-enter the plasma and make its way into the reactive core, causing fuel-dilution and radiation cooling — both of which reduces the probability of ignition in the fusion plasma.
Graphite is one of the prime candidates for use as a first wall material in the divertor* of future fusion devices such as the International Thermonuclear Experimental Reactor (ITER). Its excellent thermomechanical properties enable the material to withstand the high plasma heat loading on the divertor strike plate, and its low-Z reduces the effects of fuel-dilution and plasma cooling. Unfortunately, in addition to physical sputtering, graphite shows regimes of enhanced erosion at elevated temperatures: it can be eroded by radiation-enhanced sublimation (RES) and by chemical reactions due to hydrogen and oxygen impact. While physical sputtering and RES occur above a certain threshold energy for the incident ions (~20 - 30 eV for physical sputtering and ~50 - 100 eV for RES, for light ion impact on carbon [4]), chemical erosion can occur with low-energy ions or thermal atoms and cannot be avoided by lowering the plasma temperature near the plasma-facing material.

1.4 Objective of this Thesis

Chemical erosion in fusion reactors with carbon or carbon-based materials results mainly from reactions between carbon and the hydrogenic fuel or the oxygen plasma impurity, leading to the formation of hydrocarbons, carbon monoxide, and carbon dioxide. Water formation is also possible in the complex O⁺-H⁺→C system. These processes are further complicated by other multispecies impact phenomena involving the addition of the C impurity and He ash to the impacting species. Carbon atoms due to physical sputtering or RES, or hydrocarbon molecules due to chemical erosion from the carbon-containing first-wall may be ionized (and dissociated in the case of CₓHᵧ molecules) within the plasma and find their way back to the wall. We note that some of the implanted hydrogenic particles will be trapped and thus affect tritium inventory, fuel recycling, and microstructure. Comprehensive recent reviews of these topics are available: erosion [3-8], and hydrogen transport/retention/re-emission [9,10]. In addition to the plasma particles, neutrons are also present in D-T burning reactors. Via impact with materials, they can lead to changes in material characteristics, and consequently affect Plasma Surface Interaction (PSI) behaviour.

Most PSI phenomena have been extensively studied in the laboratory for single species, and in some cases for combined species impact. However, only few data exist currently on the

---

* Divertor configuration in the tokamak involves a diversion of the poloidal or toroidal magnetic field near the edge of the plasma confinement so that charged particles may be directed to impact on special target plates instead of on the surrounding walls [2,11].
effect of exposing graphite simultaneously to energetic oxygen and energetic hydrogen. With the dual-beam accelerator facility at UTIAS we are in a unique position to investigate such a reaction system and the new results presented here are based on such a study. The objectives of this thesis are:

(i) to study the formation of reaction products and synergistic effects in the $\text{H}^+-\text{O}^+\rightarrow\text{C}$ reaction system;

(ii) to study the underlying mechanism of the $\text{H}^+\text{-O}^+\rightarrow\text{C}$ reaction system, especially that of the formation of water; and

(iii) to develop a semi-empirical kinetic model of the $\text{H}^+-\text{O}^+\rightarrow\text{C}$ reaction system and perform computational analyses based on the model.

1.5 Organization of this Thesis

The present thesis is organized in six sections. Subsequent to the current introductory section (Sec. 1), background information on fusion relevant carbon chemistry will be presented in Section 2, with emphasis on hydrogen and oxygen ion irradiations on carbon materials. Section 3 then describes the apparatus and Section 4 the procedures for the experiments conducted in the present study. Section 5 presents the results of these experiments and their discussions. Based on the experimental results and discussions, Section 6 will present a semi-empirical kinetic model of the $\text{H}^+-\text{O}^+\rightarrow\text{C}$ reaction system and the results of the computational analyses based on the model. Final conclusions, with an outline of contributions, will be presented in Section 7.
2. BACKGROUND OF FUSION-RELEVANT CARBON CHEMISTRY

2.1 Chemical Erosion of Graphite Due to Hydrogen Ions

The flux of hydrogenic plasma particles striking plasma-facing components will primarily be in the form of ions, charge-exchange neutrals, and Frank-Condon neutrals, with energies ranging from a few eV to keV. From controlled laboratory experiments, a comprehensive database exists for chemical erosion involving sub-eV neutral hydrogen atoms, \( H^0 \), and energetic \( H^+ \) impacting on various forms of graphite; see Refs. [3-8]. Here, we shall concentrate on energetic hydrogen ion bombardment. More recently, the energy range with ion beams has been extended down to \( \sim 10 \text{eV} \) [12-14]. These low energies are characteristics of the gaseous divertors being developed in current tokamaks [2,11]. For the chemical reaction of graphite with hydrogen ions, the controlling reaction parameters are the energy and flux of the impacting hydrogen ions, and the temperature and microstructure of the graphite specimens. The process of hydrogen irradiation on graphite involves hydrogen trapping and hydrogen release via hydrogen re-emission and hydrocarbon formation. We will begin this discussion with mechanisms for hydrogen trapping in graphite, specifically the formation of the H-saturated surface layer under hydrogen ion bombardment.

2.1.1 Formation of H-Saturated Surface Layer

Currently, four mechanisms of hydrogen isotope retention in graphite are identified: (i) saturated surface layer, (ii) transgranular diffusion and trapping, (iii) chemisorption, and (iv) co-deposition of hydrogen and carbon. A detailed description of these mechanisms can be found in the review section of Ref. [10]. Here, we will concentrate on the formation of the H-saturated surface layer since it is the primary mechanism applicable to the \( H^+ / O^+ \) irradiation studies undertaken in this thesis.

Under energetic hydrogen ion bombardment, graphite is observed to retain all non-reflected hydrogen until a saturation concentration is reached (about 0.4 H/C at room temperature) [15-17]. The saturation concentration ratio does not appear to be affected by pre-implantation carbon microstructure or implantation energy [15,18-24], although it depends strongly on the graphite temperature.

Further implantation of hydrogen leads to a rapid release of hydrogen at virtually the implantation rate [16-19]. Experimental evidence, however, shows that some hydrogen atoms do
diffuse into the bulk of graphite beyond the saturated implantation layer [25-30]. Proton backscattering depth profiling of implanted 8 keV D\(^+\) shows that deuterium is retained at the end of its implantation range initially without any apparent post-implantation mobility [20], then the retained concentration extends towards the surface until saturation.

The nature of the H-saturated surface layer has also been studied. Thermal desorption measurements of graphite pre-implanted to saturation near room temperature exhibit a large release of hydrogen in the 900-1200K temperature range, indicating strong hydrogen-carbon bonds with energies of 2-3 eV [31-33,34,35]. Furthermore, direct studies\(^*\) of the chemical state of hydrogen bound in graphite [36-44] also indicate strong chemical bonding between implanted hydrogen and carbon atoms at radiation damage sites in the graphite lattice in the form of C-H bonds and C\(_2\)-H bridge bonds [41]. The preference of hydrogen trapping in the H-saturated surface layer as single C-H bonds will play a central role in the formation of precursor models of hydrocarbon formation and also the model proposed in this thesis (see Sec. 6.1.2).

As the concentration of damage sites increases from further ion bombardment, it leads to a reduction of the crystallite size. Although electron diffraction patterns indicate amorphicity [45], some crystallinity in graphite is still conserved even after an H\(^+\) dose as high as 10\(^{24}\) H\(^+\)/m\(^2\) at 10 keV [46-48]. The existence of a “local-order” in the form of “mini”-crystallites even at high H\(^+\) fluences leads to the basic assumption of the “Two-Region” model of hydrogen transport in graphite (see Sec. 2.2.3), which forms the basis of the chemical reaction product formation model developed in this thesis (see Sec. 6).

### 2.1.2 Hydrogen Recombination and Re-emission

During steady-state H\(^+\) irradiation of graphite (after saturation is reached), hydrogen may be released via re-emission. It was shown that detrapping is the controlling mechanism for hydrogen release at temperatures up to 2000K [31,49]. While the hydrogen-carbon bond in graphite is very strong, requiring temperatures in excess of 900K for thermal release, it can be easily exchanged by subsequent implantation with a different hydrogen isotope [17,19,50] or desorbed by implantation of other species such as He\(^+\) [15,51]. Ion-induced detrapping has been attributed to both electronic excitation [15] and atomic collisions [51] depending on the energy of the incoming ions.

---

\(^*\) These studies involved measurement by Raman spectroscopy, reflection high-energy electron diffraction (RHEED), x-ray photoelectron spectroscopy (XPS), and secondary ion mass spectrometry (SIMS).
Hydrogen atoms may recombine to form H$_2$ molecules before being released from graphite during implantation or thermal desorption. Above 900 K, however, hydrogen atom release is also observed during both H$^+$ or D$^+$ irradiation and post-implantation thermal desorption [52-56]. During steady-state irradiation, where all incident hydrogen is re-emitted, the fraction of hydrogen released in the form of atoms increases with increasing graphite temperature. Above 2000 K nearly all hydrogen is re-emitted in the form of atoms. For the temperature range considered here (the region where chemical erosion dominates, 300 – 1000 K), atomic hydrogen release will be deemed insignificant, and we will concentrate on hydrogen recombination.

An important question to consider is where the recombination occurs. The answer could provide information on the mechanisms of not only the hydrogen molecule formation and release processes, but also could lead to an understanding of the formation and release of hydrocarbons, or the chemical erosion processes in graphite. The first piece of the puzzle came from Möller et al. [57,58] when they performed thermal-desorption and irradiation of graphite sequentially implanted with different isotopes of hydrogen with different implantation depths, which showed very small amounts of isotope mixing in the released products. This suggests that molecules are not formed on the geometrical front surface but within the graphite, and that the respective isotope molecules are formed locally at the end of the ion range, where the ions thermalize, without any long-range atomic diffusion at low temperatures. The second piece came from Chiu and Haasz [59,60], who studied simultaneous implantation of isotopes with different energies, which showed a near-complete H isotope mixing in the recombined molecules independent of ion range separation. Furthermore, microstructure effects were observed from both the sequential and simultaneous implantation experiments with isotopes whose energies corresponded to completely separated ion ranges [59,60]. From their (Chiu) results of sequential implantation of 1 keV H$^+$ (pre-implanted) and 10 keV D$^+$, release of HD was observed immediately after switching on the D$^+$ beam for porous, pre-damaged, and pseudo-monocrystal graphites (when the incident D$^+$ was parallel to the graphite planes) [59,60]. For highly oriented pseudo-monocrystal graphite (with the incident D$^+$ perpendicular to the graphite planes), the release of HD was delayed until a certain fluence threshold was reached [59,60]. Similar microstructure effects were also observed for simultaneous implantation [59,60]. These results appear to directly contradict the findings of Möller et al. and suggest a fast transport of thermalized hydrogen atoms within the implantation zone in graphite and recombination on “inner surfaces” [59-61]. Diffusion channels, or micropaths, created by ion beam exposure can
enhance this process. The idea of long-range diffusion on inner surfaces, even at room temperature, is supported by the chemisorption experiments of Causey et al. [27,28] and Strehlow [62]. See the review section of Ref. [10].

The results of Chiu and Haasz [59-61] and Möller et al. [57,58] show that during sequential implantation, the pre-implanted hydrogen isotopes are trapped at the end of the ion range without post-implantation mobility. In their thermal desorption experiments of graphite simultaneously pre-implanted with isotopes at different depths [60,63], Chiu and Haasz observed that the isotope mixing was controlled by the range separation, and to some degree by the incident fluences. Clearly, a consistent picture is emerging: in steady-state irradiation, mobile hydrogen can freely and quickly diffuse along internal channels and recombine anywhere on the surfaces of these micro-channels, while hydrogen atoms at the trapping sites at the end of the ion range do not have post-irradiation mobility.

2.1.3 Hydrocarbon Formation and Transport

Hydrogen may also be released from graphite as hydrocarbons, which also implies the removal of carbon. This chemical erosion of carbon plays an important role in the engineering and physics aspects of the interaction of the fusion plasma with carbon-based first-wall materials. Again, an important question is where the hydrocarbons are formed in graphite. In addition, the mechanism of hydrocarbon formation and the transport of hydrocarbons out of graphite are also important topics of study.

As indicated in Sec. 2.1.1, when graphite is bombarded with energetic hydrogen ions, the formation of an H-saturated amorphous near-surface layer occurs, with a depth corresponding to the ion range. Essentially, the implanted hydrogen atoms are trapped near the end of their trajectory. As the hydrogen concentration becomes saturated in the implantation zone (reaching a value of 0.4 H/C at room temperature, and decreasing with increasing irradiation temperature [15-17]), re-emission of hydrogen and the formation of volatile hydrocarbons are observed. For H⁺ energies in the range 100 eV - 10 keV, the steady-state total hydrocarbon production rates are more than an order of magnitude larger than the thermal H⁰-C case. Furthermore, the C₁-containing molecule is the saturated methane CH₄ and not the CH₃ radical as observed for the H⁰-impact cases [64]. Furthermore, unlike the H⁰ case where the chemical erosion is dominated by heavy hydrocarbons, the H⁺-induced spectrum is dominated by methane, with only smaller amounts of C₂H₄ and C₃H₄ molecules being observed. At the temperature where maximum
methane erosion occurs ($T_m$), the contribution of the $C_2$ and $C_3$ groups to the total C erosion is relatively small for high $H^+$ energies (roughly 15% at 1 keV), but becomes more significant at low energies (roughly 45% at 100 eV) [65,66]. This leads to one of the assumptions in the model proposed in this thesis (see Sec. 6), i.e., we assume that CH$_4$ is the only hydrocarbon product in the $H^+\rightarrow C$ reaction case (for energies between 700 eV – 3 keV).

Experiments aimed at identifying the mechanisms of the hydrocarbon formation/release process came to the conclusion that hydrocarbons are formed in the graphite at the end of the incident-ion range [64,67-69]. Specifically, simultaneous $H^+/D^+$ isotope mixing experiments by Chiu and Haasz [60,69] showed that the amount of mixed methane molecules (in the form of CD$_3$H/CD$_4$ ratio) depends quite strongly on the overlap of the two ion beam ranges, *in contrast* to the HD formation (see previous section). This indicates that methane must form locally at the end of the ion range. This further implies that mobile back-diffusing hydrogen atoms near the geometrical surface of graphite do not participate in the production of hydrocarbons. However, some inconsistencies exist when viewing the fluence dependence of the mixed molecule yield (CD$_3$H/CD$_4$) [60,69]. Although at saturation fluences the CD$_3$H yield of the range-separated case is lower than that of the range-overlapping case (by a factor of more than two), below saturation fluences mixing does seem to increase (just like the HD formation) with fluence for the range-separated case by as much as a factor of 4 until saturation is reached [60,69]. This seems to suggest that as the “internal channels” are increased by ion irradiation, back-diffusing hydrogen atoms on the internal surfaces are able to participate in the formation of hydrocarbons. This possibility will be explored in Sec. 5.3 and Sec. 5.4.2 when we consider the O$^+\rightarrow H^+\rightarrow C/B$ reaction system.

As the detached hydrocarbon molecule diffuses towards the front surface of the material, it can undergo fragmentation due to incident ions [60,70,71]. The fact that lower-energy incident ions lead to hydrocarbon formation in a shallow surface layer (i.e., shorter range and hence shorter diffusion length for the molecule and less probability of fragmentation) is consistent with the observation that lower-energy ions lead to relatively more heavy-hydrocarbon release. This “methane break-up” effect will be a key element in our explanation of the behaviour of methane yield reduction when energetic oxygen ion is introduced to the $H^+\rightarrow C$ system (see Sec. 5.4).
2.2 Previous Models for the Hydrogen-Carbon System

Although irradiation of graphite by thermal hydrogen atoms is not the topic of this thesis, to understand the various mechanistic models proposed for hydrocarbon formation in graphite, it is necessary to begin with a very brief discussion of the $\text{H}^0 \rightarrow C$ reactions (Sec. 2.2.1). Extensions of the $\text{H}^0 \rightarrow C$ models to work with energetic $\text{H}^+ \rightarrow C$ reactions will also be discussed briefly (Sec. 2.2.2). The “two-region” model of hydrogen transport [10] will also be discussed in Sec. 2.2.3, followed by a brief discussion on the extension to the H-transport model to include hydrocarbon formation (Sec. 2.2.4). As the proposed model in this thesis is based on the differential equations developed in the “two-region” model of H-transport [10], more detailed description of the differential equations will be given in Sec. 2.2.3.

2.2.1 The Precursor Models of Hydrocarbon Formation in $\text{H}^0 \rightarrow C$ Reactions

It was first proposed by Vietzke et al. [64] that the formation of hydrocarbons due to exposure by atomic hydrogen occurs within the graphite, and not on the geometrical front surface. They suggested that increasing active sites (i.e., available carbon bonds for H attachment) in the graphite by pre-irradiating it with ions leads to the observed increase of hydrocarbon production [64]. Evidence of hydrocarbon precursor formation was first observed by Haasz et al. [72,73]. They suggested that the initial $\text{H}^0$ exposure might lead to the formation of bound unsaturated hydrocarbon precursors in graphite which, when exposed to $\text{H}^0$ at higher temperature, pick up additional H atoms, resulting in the formation of volatile molecules. Furthermore, due to the energetics, atomic H is unable to react with carbon atoms within the graphite basal plane, thus the $\text{H}^0$ attachment to C atoms and the subsequent formation of hydrocarbon precursors must take place at the edge plane, lattice defects, or damage sites [74,75].

This precursor model was further refined by the isotope exchange studies performed by Vietzke et al. [76-78]. Based on these studies, they proposed three mutually exclusive reaction branches for an incident $\text{H}^0$ atom in $\text{D}^+$ pre-irradiated graphite. First, an abstraction reaction between incident $\text{H}^0$ and bound D atoms can lead to the formation of HD molecules, which when desorbed, can leave dangling carbon bonds. Second, incident $\text{H}^0$ atoms can break up nearby C-C bonds by completely transferring their kinetic energy, again leaving dangling carbon bonds. These dangling carbon bonds are then available for attachment with other incident $\text{H}^0$ atoms to
form volatile hydrocarbons. The final reaction branch is the recombination of incident $H^0$ atoms into $H_2$ molecules on the inner surfaces. The $D^+$ pre-irradiation is assumed to lead to saturation of the dangling carbon bonds in trapping sites, where these D-saturated bonds can then be made available again by the first two reaction branches.

These reactions were not experimentally identified until detailed surface chemistry studies were made by Küppers et al. [79,80], using high-resolution electron energy loss spectroscopy (HREELS) to determine the type of C-hybridization state present in an a-C:H* surface during exposure to $H^0$ at various temperatures. Based on their results, they proposed a four-state cycling model [81,82]. Essentially, the key element of this model is the two competing reactions after the process of hydrogenation due to $H^0$ impact from the $sp^2$ state to the intermediate $sp^x$ state: (1) the formation of CH$_3$ from $sp^x$ to $sp^3$ and the thermally activated release of CH$_3$; (2) the reverse reaction from $sp^x$ to $sp^2$, and the accompanying thermal H release.

In the temperature range above 400K and below 600K, the steady-state hydrogenation and thermally activated release of CH$_3$ is dominant and the erosion rate increases. At temperatures exceeding 600K, the steady-state thermal H release is dominant and no $sp^3$-CH$_3$ erosion precursors can be formed because the H release process can start only from $sp^2$-CH bonds. The erosion rate thus decreases. The Küppers model successfully explained many of the observed results of $H^0$ reaction on graphite, including the observation of the release of heavier hydrocarbons (by the attachment of larger hydrocarbon chains instead of CH$_3$ in the $sp^3$ carbon of the fourth state). As we will see in the next section, it also serves as the foundation for modelling the reaction mechanisms for the case of energetic $H^+$ irradiation on graphite.

### 2.2.2 Extensions of the Precursor Models to the $H^+→C$ Reactions

Based on the evidence of precursor formation, Davis [83,84] first proposed a kinetic model for the synergistic methane formation due to hydrogenic fluxes (mainly $H^0$ and $H^+$) on carbon. Although the general form of the model consists of five reaction steps including both collisional and chemical processes, the hydrocarbon formation steps can be simplified to three-steps [83,84]:

---

*Amorphous hydrogenated carbon film (a-C:H) exhibit essentially the same features as the H-saturated surface layer of carbon irradiated by hydrogen ions, i.e., a carbon network partially terminated by hydrogen is considered to be appropriate models for the study of the interaction of H atoms and surfaces of partially or fully hydrogenated carbon materials.*
The production of chemically active sites, $C_a$, on the carbon surface, either thermally or by ion-induced damage: $C \leftrightarrow C_a$.

The formation of hydrocarbon precursors (CH): $C_a + H \rightarrow CH$.

The formation of volatile hydrocarbon (CH$_4$): $CH + 3H \rightarrow CH_4$.

As we will see in Sec. 6, aspects of this model of CH$_4$ formation will be combined with the “two-region” model of hydrogen transport (see the next section) to form the $H^+\rightarrow C$ side of the proposed new model for the current thesis (the other side, of course, is the $O^+\rightarrow C$ reaction, where the idea of a “CO precursor” will also be used).

Others have attempted to apply the atomistic Küppers model to ion irradiation. In applying the Küppers model to the chemical erosion yield of graphite in ASDEX upgrade, Wittmann and Küppers [85] calculated the effective flux of thermalized $H^0$ as a function of depth in the carbon substrate irradiated with energetic hydrogen ions, and applied the atom model to successive layers of the substrate. In applying the Küppers model to ion-beam experiments, Roth and García-Rosales [86] extended the model to include additional terms for radiation damage, low-energy erosion, and modified flux dependence, while still essentially retaining the atomic nature of the Küppers model. Basically, these “extensions” were external to the confines of the original model, and not internally consistent. An internally consistent semi-empirical model based on the Küppers model for $H^0$ was developed by Mech et al. for low-energy $H^+$ bombardment [14, 87]. In this model, atomistic processes resulting from low-energy $H^+$ bombardment were identified, and their effects on the populations of the four hybridized carbon states determined. Equations were set up to include the original atomistic terms from Küppers as well as the new terms associated with energetic impact. Predictions from the Mech et al. model [14, 87] generally agree quite well with experimental results from low-energy ion beam experiments. The model, however, does not describe well the flux dependence of the methane yields from low-energy impact, or the yields at high temperatures.

### 2.2.3 The Two-region Model of Hydrogen Transport

We will digress slightly from the hydrocarbon models to a comprehensive model explaining the hydrogen transport and retention in and release from graphite. Based on experimental evidence discussed in Sec. 2.1.1 and Sec. 2.1.2, Hassz et al. proposed a “two-region” model [10], which extended and improved over the “local hydrogen molecule formation” models such as the Möller and Scherzer model [88]. Essentially, a piece of graphite sample is
considered as being composed of two “regions” of distinct microstructures: the bulk region within a graphite crystallite*, and an inter-crystalline surface region, consisting of the crystallite surfaces. As mentioned in Sec. 2.1.1, this basic assumption of the model is valid since it is experimentally observed that some crystallinity in graphite still remains even after an H⁺ dose as high as \(10^{24}\) H⁺/m² at 10 keV H⁺ energy \([46-48]\). Even in amorphous a:C-H films, which have properties similar to the saturated surface layer of implanted graphite \([92]\), local order with a few graphitic planes—essentially a “mini”-crystallite—can still be expected to exist.

As the proposed model in this thesis is based on the differential equations developed in the two-region model \([10]\), we will devote a little more space here to describe the mathematics of the two-region model. Having differentiated the two basic regions within graphite, the model then assumes certain properties and behaviours of hydrogen associated with the two regions. The total concentration \(c\) of a hydrogen isotope \(i\) at a certain time \(t\) and at a depth \(x\) in graphite is expressed as the sum of the solute hydrogen concentration in the graphite crystallite, \(c_{si}\), the trapped hydrogen concentration in crystallites located at depth \(x\), \(c_{hi}\), and the solute hydrogen concentration on the inner surfaces, \(\gamma_{si}\) \([10]\):

\[
    c_i(x,t) = c_{si}(x,t) + c_{hi}(x,t) + \gamma_{si}(c,t).
\]

where the concentrations are given in ratios of hydrogen to carbon concentrations (i.e. H/C).

Incident hydrogen ions are then assumed to deposit only in the crystallite, initially with a depth distribution according to their range. Once deposited, a hydrogen atom will either diffuse within the crystallite until it is trapped in a C-H bond at a damage site or until it reaches a crystallite surface. It is assumed that only hydrogen atoms, not molecules, can move within the crystallite. This assumption can be justified by the small interlayer spacing within the graphite crystallite (\(\sim 0.3\)nm) that would restrict molecular motion, especially at low temperatures.

After reaching an internal surface, a hydrogen atom may diffuse along the surface until it recombines (if possible) or until it reaches the external surface through the internal surface structure, from where it can be released with a temperature-dependent probability. Furthermore it could be trapped in a C-H bond similar to that found in the crystallites. Since molecular diffusion within crystallite is not permitted in the model, all released hydrogen molecules are formed on internal surfaces. Diffusion of hydrogen molecules on the internal surfaces (gas phase diffusion or surface diffusion) is assumed to be infinitely fast, at least above room temperature.

---

* The term “crystallite” is used to describe a locally ordered, high-density region of graphite in accordance with usage in the literature \([46,89-91]\).
We can express the above behaviour mathematically, assuming two hydrogen isotopes (denoted by subscripts \(i\) and \(j\)) in the system, as [10]:

\[
\frac{\partial c_{si}}{\partial t} = S_{ri}(x) - k_i c_{si} \left( c_T - c_{si} - c_{sj} \right) + \left[ k_i + S_{ri}(x) + S_{ru}(x) \right] c_{si},
\]

\[
\text{Eq. 2-2}
\]

\[
\frac{\partial y_{si}}{\partial t} = -\frac{\partial}{\partial x} \left( \Delta_s \frac{\partial y_{si}}{\partial x} \right) + k_i c_{si} - k_{su} y_{si} (y_{si} + y_{sj}),
\]

\[
\text{Eq. 2-3}
\]

where \(k_i\) is the bulk transport rate coefficient; \(k_{si}\) is the trapping rate coefficient; \(k_i\) is the thermal detrapping rate coefficient; \(k_{su}\) is the surface recombination coefficient; and \(\Delta_s\) is the rate coefficient of surface diffusion. The implantation rate for isotopes \(i\) and \(j\) at depth \(x\) is \(S_{ri}\) and \(S_{rj}\), respectively. The ion-induced detrapping rate for isotopes \(i\) and \(j\) at depth \(x\) is \(S_{ri}\) and \(S_{rj}\). The total available trap concentration is denoted by \(c_T\). Note that at steady state, the sum of the incident H flux rate and the hydrogen detrapping rate within a graphite crystallite equals the sums of the rates of hydrogen trapping and hydrogen leaving the crystallite (Eq. 2-2). Similarly, in the internal surface region, at steady state, the rate of hydrogen entering the surface region balances out the rate of hydrogen leaving via recombination and surface diffusion (Eq. 2-3).

Let us now consider the trapped concentration. The rate of change of trapped hydrogen concentration is simply the difference of the rate of trapping and detrapping [10]:

\[
\frac{\partial c_{si}}{\partial t} = k_{si} c_{si} (c_T - c_{si} - c_{sj}) - \left[ k_i + S_{ri}(x) + S_{ru}(x) \right] c_{si}.
\]

\[
\text{Eq. 2-4}
\]

The rate of change of the total trap concentration \(c_T\) can be expressed as

\[
\frac{\partial c_T}{\partial t} = \left[ S_{ri}(x) + S_{ri}(x) \right] (1 - \nu_{orT} c_T)^2,
\]

\[
\text{Eq. 2-5}
\]

where \(S_{ri}\) and \(S_{ri}\) are the trap generation rates for incident isotope ions and \(\nu_{orT}\) is the atomic saturation volume of the traps \(\nu_{orT} = (c_T^{\text{max}})^{-1}, c_T^{\text{max}}\) being \(\sim 0.4\) traps/C. Note that during steady state, \(c_T\) reaches the maximum value and no more traps are generated. Also, trapping at the inner surface region is treated as part of the bulk trapping in the crystallite. This does not allow for trapping occurring beyond the implantation zone, even though diffusion of solute hydrogen atoms will occur on internal surfaces throughout the sample (see Sec. 2.1.2).

All rate coefficients have the unit \((1/s)\), and are assumed to obey Arrhenius equations of the form:
where $K$ is the pre-exponential factor, $E_{\text{act}}$ is the activation energy, $\kappa$ is Boltzmann's constant, and $T$ is the temperature. In fact, it was found that a simple Arrhenius relation cannot describe the temperature dependence of the diffusion coefficients for bulk transport, surface diffusion, and recombination. A better analytical representation was achieved by fitting two different Arrhenius relations for the temperatures below and above 500K [10].

Since surface molecular diffusion is assumed to be infinitely fast, the released flux of hydrogen molecules, for the single isotope case, is given by [10]

$$J_{H_2}(t) = k_{s1} \int_0^d \gamma_s^2(x,t) dx.$$  \hspace{1cm} \text{Eq. 2-7}

To account for both high temperature hydrogen atom re-emission and isotope mixing (see Sec. 2.1.2), mobile hydrogen atoms on the internal surfaces are assumed to undergo very fast surface diffusion. To disallow hydrogen atom re-emission at low temperatures, an energy barrier is assumed at the geometrical surface of the graphite allowing only hydrogen atoms with high enough energy to exit the sample. This energy barrier does not affect hydrogen molecules. For a single isotope case, the released flux of hydrogen atoms is thus given by [10]

$$J_H(t) = \kappa_s \gamma_s(x=0,t) \delta + \kappa_s \gamma_s(x=d,t) \delta,$$  \hspace{1cm} \text{Eq. 2-8}

where $\kappa_s$ is the rate coefficient for the atomic release that obeys an Arrhenius relation determined by the energy barrier, and $\delta$ is the "surface thickness", $N_c^{-1/3}$, where $N_c$ is the atomic density of the graphite crystallites. The fluxes $J_{H_2}$ and $J_H$ both have the unit of (m/s). Further multiplication by $N_c$ will yield the common flux density unit of (m$^2$/s$^{-1}$).

This model predicted the release of hydrogen atoms from graphite at high temperatures and the release of mixed hydrogen molecules for steady-state reemission during simultaneous and sequential ion bombardment and thermal desorption reasonably well [10]. The release of atoms is explained by a thermal process caused by a reduced recombination probability due to the small solute hydrogen concentrations and the fast atomic surface diffusion at high temperatures. The different amounts of mixing for simultaneous and sequential ion bombardment with separated ion ranges are explained by the differences in the solute H and D concentrations; only totally overlapping concentration profiles of solute atoms on the inner surfaces with equal concentrations lead to complete mixing. The "two-region" model developed in Ref. [10], however, does not take into account the formation of methane, and does not include
a separate treatment of surface trapping even though retention of hydrogen in graphite beyond the implantation range has been observed [27,28].

2.2.4 Application of the Two-Region Model to Include Hydrocarbon Formation

Although the comprehensive “two-region” model [10] applies only to hydrogen transport, retention in, and release from graphite, in fact the “two-region” concept arose from the necessity to explain the apparent contradictory results of the HD and \( \text{CH}_x\text{D}_y \) mixing during simultaneous \( \text{H}^+/\text{D}^+ \) irradiation with separated ion ranges (see Sec. 2.1.2 and Sec. 2.1.3) [60]. Incident hydrogen is initially deposited within the crystallite region where it may be trapped, or diffuse to the internal surface region. As indicated in the previous section, transport and recombination of mobile hydrogen atoms take place in the internal surface region, which allows HD mixing even when \( \text{H}^+/\text{D}^+ \) ranges are separated. The current understanding of the \( \text{CH}_4 \) formation for \( \text{H}^+ \)-induced erosion in graphite, as proposed by Chiu et al. [60,61,69], is that volatile methane molecules are formed at the end of the \( \text{H}^+ \) ion range at the edge of the crystallite, such that only hydrogen atoms implanted in the crystallites takes part in the C-H reactions. The “edge” is still considered to be within the crystallite, but allows the methane molecules to diffuse into the internal channel once they are released (thermally or induced by the incident energetic hydrogen). An energy barrier has been proposed to exist at the internal surfaces to prevent mobile hydrogen from re-entering the graphite crystallite [10,60]. As we shall see in Sec. 6, we will extend this “two-region” concept and combine it with the precursor concept described in Sec. 2.2.2, and present a detailed mechanism for methane formation in the \( \text{H}^+ \rightarrow \text{C} \) system.

2.3 Chemical Erosion of Graphite Due to Oxygen Ions

Now, let us examine what is currently known about carbon erosion due to oxygen, which is one of the main intrinsic impurities in the plasmas of current fusion devices, the other one being carbon. Some results on the interaction of oxygen with carbon materials have been compiled in Refs. [3,5]. Molecular-beam experiments with \( \text{O}_2 \rightarrow \text{graphite} \) at temperatures above 1000K have produced a maximum yield of about 2 to \( 5 \times 10^{-3} \) \( \text{CO} / \text{O}_2 \) at 1300K-1500K and at least an order of magnitude smaller \( \text{CO}_2 \) yield [93-95]. In comparison, the reactivity of atomic oxygen is much higher (a factor of \( \sim 40 \) at 1400 K) than that of \( \text{O}_2 \), even at low temperatures [96-98]. Here we will concentrate on ionic oxygen as it is more relevant to this thesis.
The interaction of energetic oxygen ions with graphite leads to a complex process of implantation, trapping, chemical reaction and re-emission — somewhat similar to the H⁺→C interaction discussed above. Implanted oxygen from bombarding O⁺ ions is trapped or re-emitted in the form of CO or CO₂, as in the case of thermal oxygen [93]. No re-emitted O or O₂ has been found [5]. For O⁺ energies above 500 eV, the adsorption and complex formation rate is near unity [93]. With increasing O⁺ fluence, the implanted oxygen is partly retained and the release of CO and CO₂ increases steadily until the trapped oxygen concentration in the carbon reaches a saturation value of ~ 0.25 O/C at room temperature [99-101]. The saturation level decreases with increasing carbon temperature, again similar to the case of hydrogen ion impact. After saturation is reached, all of the newly implanted oxygen ions react to form CO or CO₂. At room temperature, the CO molecules released were found to have an energy distribution with two components: about 60% of CO molecules are released with a thermal energy distribution characteristic of the target temperature, while the remaining 40% is released by an activated process (molecular sputtering) and have energies in the 0.25 eV range [101,102].

The CO formation yield, as well as the total chemical erosion yield, shows a slight temperature dependence with a minimum at ~ 600K [101,102]. The yield for CO₂, however, has a maximum at roughly the same temperature and vanishes for temperatures above 1400K. The total C erosion yield (sum of chemical erosion and physical sputtering) is nearly temperature-independent and has a value near unity for temperatures below 1000K and incident O⁺ energies above 500eV [93,103,104]. Above 1200K the contribution from RES becomes important. The energy dependence of the reaction yield for CO and CO₂ was observed to be weak in the O⁺ energy range of 50 eV to a few keV's [5,93]. Below 50 eV, however, a decreasing trend is observed [5].

Currently, there are no comprehensive models describing the O⁺-C reaction. However, based on the near-unity reaction probability for oxide formation during O⁺ impact on carbon, it is reasonable to consider the thermalized oxygen atom at the end of the ion range readily reacting with the carbon matrix to form volatile CO and CO₂. Black [105] suggested for the O₂→C system the existence of a carbon-oxygen complex which may lead to the release of CO or the further reaction with oxygen to form CO₂. A similar mechanism may exist for the O⁺-C system. We will consider such a mechanism in Sec. 6. This will also help to explain the trapping of oxygen in the carbon matrix. Unlike the hydrogen system, however, no free mobile oxygen is expected to exist within the carbon as no O or O₂ re-emission has been observed.
2.4 Chemical Erosion of Carbon-based Material From Other Reaction Systems

2.4.1 Chemical Erosion of Graphite Due to Multispecies Impact

We will now give a brief background on previous experiments on multispecies impact on carbon, concentrating in particular on simultaneous hydrogen and oxygen irradiation. In the case of the \( \text{O}^+\text{H}^0\rightarrow\text{C} \) system, in addition to hydrocarbon formation, CO is also generated, and the reaction yield for CO formation (CO/O\(^+\)) is near unity even at room temperature [106]. In an experiment with a mixed 5 keV \( \text{D}_2^+ \) and \( ^{18}\text{O}^+ \) ion beam, in addition to methane, CO, and CO\(_2\), water (D\(_2\)O) molecules were also formed [107]. The D\(_2\)O exhibits the same temperature dependence as methane, reaching a maximum at \( \sim 800 \) K. Other results, involving combined energetic H\(^+\) and thermal \( \text{O}_2 \) irradiation on graphite, show that the production of CO and H\(_2\)O does not affect the yield and temperature dependence of hydrocarbon formation [108].

We will see in Sec. 5 that similar results are found for the \( \text{O}^+\text{H}^+\rightarrow\text{C} \) system, although unlike the thermal \( \text{O}_2 \) case, energetic O\(^+\) impact does affect the hydrocarbon yield via the methane break-up process described in Sec. 2.1.3.

2.4.2 Chemical Erosion of Boron-doped Graphite Due to \( \text{H}^+ \) or \( \text{O}^+ \) Impact

Finally, doped graphite provides an interesting opportunity to further examine the mechanisms of the hydrogen-carbon, oxygen-carbon, and ultimately the combined hydrogen-oxygen-carbon systems (see Sec. 5.3 and Sec. 5.4.2). Here, we will present a very brief background on the chemical erosion of boron-doped graphite. From previous studies with doped graphites under hydrogen ion irradiation, it was observed that hydrocarbon yields could be reduced by the presence of dopants [109]. In particular, boron-doped graphite can lead to reductions as much as a factor of 5 for \( \text{CH}_4 \) yields; see Fig. 2 [109]. Other studies have shown similar dramatic reductions in chemical erosion yields through boron-doping of graphite; see Refs. [110-113]. It was speculated [3,109] that boron somehow enhances the recombination of mobile hydrogen atoms into hydrogen molecules, which in turn lowers \( \text{CH}_4 \) formation that competes with the available hydrogen supply. Alternatively, the presence of boron impurities in the graphite crystallite may alter the chemistry of hydrocarbon precursor formation. It has been suggested [5] that, with the presence of boron dopants, irradiation with energetic hydrogen leads to an increase of the \( sp^3 \)-hybridization states of the C atoms, resulting in reduced chemical erosion and a shift in the erosion maximum to lower temperatures (as is evident in Refs.
[109-113]). In later discussion in Sec. 5.4.2, we will see that the present results on methane formation during $O^+\cdot H^+$ irradiation of B-doped graphite cannot be fully explained by the change in the $sp^3$-hybridization states.

On the other hand, boron is a well-known gettering agent for oxygen [100]. Measurements using XPS in TEXTOR [114] also shows that $B_xO_y$ are formed during simultaneous $O^+\cdot H^-$ irradiation of boron-containing graphite. In ion beam experiments with energetic oxygen impact of B-containing carbon materials, the observed reaction products were $CO$, $BO$, $CO_2$, $BO_2$, $B_2O_2$, and $B_2O_3$; the same spectrum of reaction products are also observed during thermal desorption of B-containing carbon pre-implanted with oxygen [5,101,102]. The formation of boron-oxides in boron-doped graphite may have some impact on the transient behaviour of methane production, as we will speculate in the discussion in Sec. 5.4.2.
3. EXPERIMENTAL APPARATUS

3.1 The Dual-Beam Accelerator Facility

The dual-beam accelerator facility consists of two independently controlled low-energy, high-flux, mass-selected ion accelerators whose beam lines intersect in an ultra-high vacuum stainless-steel target chamber; see Fig. 3. A full description of the facility is available in Ref. [115].

Originally, both accelerators were supplied with identical hot-filament based duoplasmatron ion sources. The duoplasmatron sources have been used in our laboratory to successfully generate H+, H3+, D+, D3+, He+, Ne+, Ar+, and C+ ions in stable operation. Difficulties arose, however, in the generation of oxygen ions. The problems were threefold: (i) relatively lower ionization cross-section for oxygen, (ii) erosion of the cathode filament, the source chamber, and the tungsten exit-aperture and (iii) unstable accelerator operation. These problems are compounded when higher concentration of oxygen is required to produce reasonably high oxygen ion fluxes (due to the low ionization cross-section of oxygen). This, in turn, leads to unacceptably short filament and aperture lifetime, causing further instabilities in accelerator operations.

At the suggestion of Dr. E. Vietzke, a hollow-cathode ion source was installed in the heavy-ion line of the dual-beam facility, to avoid the use of hot-filaments and thus generate a stable high-current oxygen ion beam [116-118]. In the hollow-cathode geometry, electrons inside a narrow tube are trapped and undergo more ionizing collisions, creating denser plasma inside the tube compared to the outside. This dense plasma then releases the electrons required for the main discharge. The original duoplasmatron ion source on the heavy-ion line was modified to house a stainless-steel hollow cathode, replacing the hot filament cathode, while leaving the rest of the duoplasmatron source unmodified. This is essentially the same design as the hollow-cathode duoplasmatron source proposed by Roden [119] in 1974 and is widely used to generate ions from reactive gases. The supporting electronics were also modified, where the original 30A filament current supply was disabled and the original 200V/5A arc supply (between the cathode and anode) was replaced with a 1kV/200mA supply [115]. The source gas for the modified heavy-ion line was a 10%-oxygen/90%-helium mixture. Helium was chosen for its low ionization cross-section for the ease of starting the discharge in the hollow-cathode. Oxygen
content was reduced to 10% to reduce the erosion of the cathode and anode of the ion source while providing a reasonable oxygen ion flux from the ion source.

### 3.2 Test Specimens

The specimens used in most of the experiments were made of pyrolytic graphite (HPG99 from Union Carbide) with a density of ~2200 kg/m³, in strip form with approximate dimensions of 40 x 10 x 0.5 mm. For the experiment described in Sec. 4.1, the central portion of the specimen was sanded down to a thickness of ~0.1 mm to allow the central portion of the specimen to reach higher temperatures. Specimens with uniform thickness were used for all other experiments.

For the H⁺-O⁺→C/B experiments described in Sec. 4.3, two types of boron-doped carbon specimens were used, both were cut into 25 x 10 x 0.5 mm³ strips (with uniform thickness). The first specimen was cut from a block of doped graphite prepared by Ceramics Kingston Ceramique Inc. (CKC), manufactured from finely ground graphite (10-45 μm) mixed with an organic binder with boron added as B metal particulates of ~μm size. The specimen contains about 20 at. % B in the bulk (depth > 1 μm), and about 14 at. % B on the surface (depth < 1 μm) [109]. It has a measured density of 1970 kg/m³. This is the same material that was designated as CKC-B20-base in the experiment described in [109]. The second specimen (USB15) was a fine-grain (~0.01μm) boron-doped graphite manufactured by NII Grafit USSR with a density of ~2000 kg/m³ and a uniform distribution of 15 at. % boron [110].

### 3.3 Test Chamber and Diagnostics

The beams from the light- and heavy-ion lines are focused in the stainless-steel test chamber and intersect at an angle of 42 degrees, or 21 degrees from normal incidence. The test specimen is placed at the point of beam intersection. The beam spots, slightly elliptical in shape due to the off-normal incidence, were ~5 mm (for H⁺) and ~3 mm (for O⁺) in diameter. This allowed complete overlapping of the O⁺ beam spot by the H⁺ spot at the focus.

Independent turbomolecular pumping systems backed by mechanical pumps separate the target chamber and the beam lines, providing differential pumping and placing the test chamber under ultra-high vacuum (UHV), with pressure monitored by ionization gauges. An SAES USA
getter pump is also used to provide additional pumping. Before any experiment is performed, the test chamber is baked to a temperature of around 500K to degas the chamber walls. The test specimens were also heated to >1250 K for several minutes in order to eliminate intrinsic H and O impurities. The getter material in the getter pump is then recharged (by ohmic heating) to remove gases and water vapour taken up during test chamber baking. Typical pressure in the test chamber during the experiments was about 10^{-5} Pa consisting mainly of He and H_2 from the ion sources.

The specimen strip, held by stainless steel jaws to allow direct current heating, is biased at +30 V to suppress secondary electrons generated by incident ions. The temperature of the specimen is monitored by an E^2T Pulsar 11 optical pyrometer, where infrared light from the specimen is measured and the temperature is calculated based on the known emissivity of the specimen material. Reaction products from the specimen are monitored in-situ by a quadrupole mass spectrometer (QMS) made by Extranuclear Laboratories (now A.B.B. Extrel, Inc.). The QMS is placed in line of sight at 45 degrees above the plane of intersection by the two ion beams. See Fig. 4 for the schematics of the apparatus arrangement in the test chamber.

Because the QMS is placed in the line-of-sight of the test specimen, to avoid energetic ions reflected from the specimen from entering and damaging the channeltron multiplier of the QMS, an energy block was installed in the QMS lenses. This allowed us to filter out all the reflected ions while accepting only the non-energetic reaction products from the specimen and the background.

In residual gas analysis (RGA) mode, the signals from the multiplier are directly recorded. In line-of-sight (LOS) detection mode, a 50 Hz mechanical chopper is placed in front of the QMS and with a phase-locking amplifier the background signals are filtered out leaving only line-of-sight signals. A computer-controlled data acquisition system is used to collect the QMS data. For LOS measurements, CH_4, CO, and CO_2 yields were scaled to the calibrated RGA data, while water production was estimated from the CO data taking into account the different ionization cross-sections and quadrupole transmission sensitivities of CO and water. For RGA the absolute erosion yields of methane, carbon monoxide and carbon dioxide were obtained by using commercially produced calibrated leaks with an absolute error of 20%. The absolute value of water yield (from O^+ + H^+ → C reaction) is estimated from the difference of the oxygen balances between single-beam O^+ → C and simultaneous O^+ + H^+ → C cases, based on the CO and CO_2 yields, i.e.,
where $Y_{H_2O}$, $Y_{CO}$ and $Y_{CO_2}$ are the $H_2O/O^+$, $CO/O^+$, and $CO_2/O^+$ yields, respectively. For temperature dependence experiments (such as that described in Sec. 4.1), the absolute value of the highest water yield (which would be the water yield at 800 K, see Sec. 5.1.2) is estimated using the above oxygen balance method, and the water yields for all other temperatures are scaled based on the estimate at 800 K. For energy/flux dependence experiments (such as that described in Secs. 4.2.3 and 4.3), again the highest water yields for a particular set of flux/energy is estimated using the oxygen balance method, while all other yields are scaled accordingly.

\[
Y_{H_2O} = (Y_{CO} + 2 \cdot Y_{CO_2})^{\text{O-only}} - (Y_{CO} + 2 \cdot Y_{CO_2})^{\text{O-\&H}} ,
\]

Eq. 3-1
4. EXPERIMENTAL PROCEDURES

4.1 Determining the Reaction Products During H⁺&O⁺ Irradiation of Graphite

The experiments are divided into several stages, each a logical succession of the previous one. Given the possibility of a synergistic reaction in the H⁺-O⁺→C system that may be temperature dependent, it is logical to start by examining the temperature profiles of the dominant reaction products in the system. This will identify the temperature at which maximum synergistic effects, if any, will occur.

Beam energies were 10 keV O₂⁺ (5 keV/O⁺) and 3 keV H₃⁺ (1 keV/H⁺). From previous studies of methane formation form graphite under H⁺ and H₃⁺ irradiation, the H₃⁺ molecular ion was found to behave effectively as three hydrogen atoms with one-third of the H₃⁺ ion energy [120]. Thus, it is assumed that the incident O₂⁺ and H₃⁺ molecular ions break up immediately into atoms upon impact with the specimen. In the remainder of this work, H⁺ and O⁺ will be used to designate the incident atoms, even though not all of the atoms in the H₃⁺ and O₂⁺ molecular ions are charged. Beam fluxes were ~ 1 x 10¹⁹ O⁺/m²s, and ~ 5 x 10¹⁹ H⁺/m²s, with flux ratios being φO⁺/φH⁺ ~ 20%. Note that the beam fluxes are not precisely controlled in this stage of the experiments. Run-to-run variation in the O⁺ beam flux is about ± 4 x 10¹⁸ O⁺/m²s while H⁺ beam flux variation is about ± 8 x 10¹⁸ H⁺/m²s. Four reaction species were monitored via QMS in both RGA and LOS modes: CO, CO₂, CH₄, and H₂O.

The experiment consisted of four phases. Irradiations by the ion beams in each phase were performed until steady-state was reached, i.e., with the graphite target saturated. During phase I, only the O⁺ beam was turned on; the H⁺ beam was added in phase II; for phase III, the O⁺ beam was turned off, while the H⁺ beam remained on; finally, phase IV was a measure of the background with no beams on. No discernible differences were observed in the steady-state signal levels for the respective four phases when the sequence of the experiment was reversed. The CO, CO₂, and H₂O yields, corresponding to O⁺&H⁺ simultaneous exposures were obtained from the differences between the phase II and phase III signals, the latter being the effective background (reflected H⁺-induced signals coming from the chamber walls, etc.); i.e.,

\[ Y_{II}^i = K^i (S_{II}^i - S_{III}^i) / \phi_{O^+}, \]

Eq. 4-1
where $Y_i$ is the yield for species $i$, $K_i$ is the corresponding calibration factor, $S_i$ the measured QMS signal, and $\phi_{O^+}$ is the O$^+$ flux. Similarly, the yields corresponding to O$^+$-only exposure were obtained from

$$Y_i = K_i(S_i - S_{iO^+})/\phi_{O^+}.$$  \hspace{1cm} Eq. 4-2

For the evaluation of the CH$_4$ yield, an analogous procedure was followed, however, $S^{CH_4}$ is now the effective background (i.e., reflected O$^+$-induced signals coming from the chamber walls, etc.) for the simultaneous O$^+$/H$^+$ case, and the signals are normalized by the H$^+$ flux. The same procedures were followed for the experiments in the LOS and RGA modes (although the background contribution is mostly eliminated in the LOS mode) and all subsequent experiments where comparison of single-species impact and simultaneous H$^+$/O$^+$ impact are performed.

### 4.2 Searching for the Mechanisms of Synergistic Effects

As will be seen from the discussions of the results of the previous experiment described above (see Sec. 5.1), although the synergistic effect (namely the production of water) in the O$^+$/H$^+\rightarrow$C system is relatively small, it is nonetheless present. Searching for the mechanism underlying the production of H$_2$O becomes the next logical step in this investigation. This investigation is divided into two stages: sequential implantation and simultaneous implantation. In both stages, the main focus is on varying the ion depths of the two implanting species and observing the reaction products in order to deduce the exact location of the water formation within the ion implantation zone; hence, the experiments are qualitative in nature. As was the case in the study of hydrogen recombination and hydrocarbon formation (see discussion in Sec. 2.1.2 and Sec. 2.1.3), the manner in which the O$^+$ and H$^+$ are implanted (sequential vs. simultaneous at different ion ranges) may shed some light on the formation process of the reaction products.

In designing these experiments, the ion range distribution of the implanting species within the graphite specimen was calculated using a software package, TRIM (and the vectorized version TRVMMC), developed by W. Eckstein et al. [121]. Plots of the ion distributions of both O$^+$ and H$^+$ in graphite at various implantation energies are shown in Fig. 5. At 1 keV H$^+$ and 5 keV O$^+$ we have a fairly good partial overlapping of ion ranges; at 700 keV H$^+$ and 5 keV O$^+$ the ion ranges are completely overlapping; finally, at 3 keV H$^+$ and 5 keV O$^+$ the ion ranges are nearly completely separated. Note also that the oxygen range is quite shallow when compared to
the hydrogen ranges, even at 5 keV/O\textsuperscript{+} (which is the energy limit of our apparatus at 10 keV/O\textsubscript{2}\textsuperscript{+}). Based on the accelerator energy limit and the fact that lowering oxygen beam energy greatly reduces the beam flux, the oxygen beam energy was fixed at 5 keV/O\textsuperscript{+} for all subsequent experiments. Also, as will be discussed in Sec. 5.1.1, fixing the oxygen beam energy also allows us to control O\textsuperscript{+}-induced background contributions to the QMS signals.

\subsection{Sequential Implantation Experiments}

In this series of experiments, hydrogen ions with different energies (3 keV and 6 keV H\textsubscript{3}\textsuperscript{+}), but with identical flux density (~3 \times 10\textsuperscript{19} \text{H\textsuperscript{+}/m\textsuperscript{2}s}), were pre-implanted until saturation (specifically for fluences over 5 \times 10\textsuperscript{22} \text{H\textsuperscript{+}/m\textsuperscript{2}}) into the graphite specimen. The pre-implanted specimen was then irradiated with oxygen ions at a fixed energy (10 keV O\textsubscript{2}\textsuperscript{+}) and flux (~7 \times 10\textsuperscript{18} \text{H\textsuperscript{+}/m\textsuperscript{2}s}). Water signals were monitored via the QMS in the RGA mode. Due to the large time constant and noise-to-signal ratio, the LOS detection mode was not used here, as any transient effect is completely undetectable in this mode. Since the cycle of pre-implantation and implantation was performed on the same piece of graphite, the specimen was heated to >1400K before each cycle to ensure the removal of all the O\textsuperscript{+} and H\textsuperscript{+} from the specimen and that the specimen is annealed. The temperature dependence behaviour of the erosion yields, from the temperature dependence experiments (see discussion in Sec. 5.1), with relatively fixed energy and flux ratios, indicate that the greatest synergistic effects occur at a specimen temperature of ~800 K. Therefore, for this stage of the energy and flux-ratio dependence experiments, the specimen temperature was fixed at ~800 K. This temperature was maintained at both the pre-implantation stage and the subsequent irradiation stage.

\subsection{Simultaneous Implantation Experiments}

In this series of experiments, simultaneous irradiation of H\textsuperscript{+} ions (1.8 H\textsubscript{3}\textsuperscript{+} at ~ 1.5 \times 10\textsuperscript{19} \text{H\textsuperscript{+}/m\textsuperscript{2}s}, 3 keV H\textsubscript{3}\textsuperscript{+} at ~ 3.7 \times 10\textsuperscript{19} \text{H\textsuperscript{+}/m\textsuperscript{2}s}, and 6 keV H\textsubscript{3}\textsuperscript{+} at ~ 3.7 \times 10\textsuperscript{19} \text{H\textsuperscript{+}/m\textsuperscript{2}s}) and O\textsuperscript{+} ions (10 keV O\textsubscript{2}\textsuperscript{+} at ~ 7 \times 10\textsuperscript{18} \text{O\textsuperscript{+}/m\textsuperscript{2}s}) was performed on the same graphite specimen. Previous experiments have shown that the LOS detection mode was adequate to detect water production during simultaneous irradiation cases, so to completely eliminate the wall contribution, the water signal was monitored by the QMS in the LOS detection mode for these experiments. The specimen was heated to > 1400K prior to the series of simultaneous irradiations, and since here
we were only interested in the steady-state signals, the specimen was not reheated between each set. The specimen temperature was kept at ~ 800 K to ensure maximum water production.

### 4.2.3 Flux/Range Dependencies of the Synergistic Effects: O⁺-H⁺→C System

Having an initial indication of the mechanism of water formation (see discussions in Sec. 5.2.2), further detailed studies became necessary in order to obtain a more complete picture of the water production plus the resulting effect on the formation of CO, CO₂ and CH₄. The next step in the investigation involves studying the ion flux and range dependencies of the CO, CO₂, CH₄, and H₂O yields under simultaneous O⁺ and H⁺ irradiation of graphite.

Similar to the experiment described in Sec. 4.1, this set of experiments also consisted of four phases for every flux/energy combination: (I) O⁺-only, (II) simultaneous O⁺+H⁺ irradiation, (III) H⁺-only, and finally, (IV) background. The hydrogen beam energies were varied within the ranges 0.7 – 3 keV/H⁺ and the oxygen beam energy was fixed at 5 keV/O⁺. The energy ratio (E₀/E₇) was in the range 1.6 – 7.1. The hydrogen beam fluxes were varied within the range ~ 0.6 – 3.1 x 10¹⁹ H⁺/m²s, while the oxygen beam flux was fixed at ~ 3 x 10¹⁸ O⁺/m²s. The flux ratio (Φ₀/Φ₇) was in the range ~10%–50%. The graphite specimen temperature was kept at ~ 800 K to ensure maximum water production. Reaction products were measured by QMS in both the RGA and LOS modes, all in steady state.

In addition, simultaneous irradiations by O⁺ and H⁺ were also performed on pyrolytic graphite in the temperature range 500 K – 1000 K for each beam energy and flux setting. Reaction products (CO, CO₂, CH₄ and H₂O) were monitored in the RGA mode, as the signal-to-noise ratio in the LOS mode was too small.

### 4.2.4 Hydrogen Re-emission and Methane Break-up

To examine the effect of CH₄ and H₂O formation on the hydrogen recombination, the H₂ QMS signal was monitored in the RGA and LOS detection modes during H⁺→C and O⁺-H⁺→C irradiations. To support the methane break-up theory to be discussed in Sec. 5.4 as the cause for the methane reduction during simultaneous O⁺-H⁺→C reactions, when compared to the H⁺→C reaction, the graphite specimen was subjected to simultaneous Ne⁺ and H⁺ irradiation with various beam energies and fluxes, and CH₄ was monitored in the LOS detection mode. Neon is an inert gas and its mass is similar to that of oxygen. Thus, any changes in the CH₄ yield during simultaneous Ne⁺ and H⁺ impact from H⁺-only impact should be purely due to the physical
break-up of methane molecules. TRVMC calculation of the range ratios, \( R_{H}/R_{Ne} \), for the beam separated case (5 keV Ne\(^+\) + 3 keV H\(^+\)) and the beam overlapping case (5 keV Ne\(^+\) + 1 keV H\(^+\)) are 3.5 and 1.5, respectively. The calculated implantation depth profiles for Ne\(^+\) and H\(^+\) in graphite are plotted in Fig. 6. The hydrogen beam fluxes range from \(3.5 \times 9 \times 10^{19} \text{H}^+ / \text{m}^2\text{s}\) while the neon beam fluxes range from \(5 - 9 \times 10^{18} \text{Ne}^+ / \text{m}^2\text{s}\). The elimination of H\(_2\)O production in the Ne\(^+\)-H\(^+\)→C system also enables us to study the effect of CH\(_4\) break-up on hydrogen recombination and release. For this purpose, the H\(_2\) QMS signal was monitored in the LOS detection mode during H\(^+\)→C and Ne\(^+\)-H\(^+\)→C reactions.

### 4.2.5 Fluence and Microstructure

To support the dependence of water production on mobile hydrogen concentration (see Sec. 5.4), a pyrolytic graphite specimen was annealed to 1800 K; this was followed by simultaneous H\(^+\) and O\(^+\) irradiation at various hydrogen implantation fluences to see if structural change from the annealed state has any effect on the transient behaviour of water production. The experiment was carried out with the specimen temperature held at 800 K (for maximum water yield), and the water signal was monitored in the LOS detection mode by the QMS.

To compare the transient H\(_2\)O production between the annealed and damaged graphite target when both O\(^+\) and H\(^+\) beams are turned on, we start the experiment with zero H\(^+\) fluence (i.e., the specimen having been freshly annealed). Then, both O\(^+\) and H\(^+\) beams are turned on for a period of time to (a) obtain the transient curve of the water yield, and (b) to induce structural changes in the annealed specimen; then both beams are turned off. After such a simultaneous O\(^+\)&H\(^+\) pre-implantation, the specimen is again exposed to simultaneous O\(^+\)&H\(^+\) impact, and a subsequent water yield transient is obtained.

### 4.3 Flux/Range Dependencies of the Synergistic Effects: O\(^+\)-H\(^+\)→C/B System

Doped graphite provides an interesting opportunity to further examine the mechanisms of the synergistic effect in the O\(^+\)-H\(^+\)→C system. It would be of interest to examine the result of introducing oxygen to the C/B-H\(^+\) system. Thus, the objective of the study described here is to investigate what happens during simultaneous O\(^+\)&H\(^+\) bombardment of B-doped carbon (i.e., the O\(^+\)-H\(^+\)→C/B reaction system). Boron-doped graphite may reveal further clues to the mechanisms leading to synergistic effects in the O\(^+\)-H\(^+\)→C reaction system. In turn, the addition
of O$^+$ to the C/B-H$^+$ reaction system may also add to the understanding of the CH$_4$ yield reduction mechanism due to boron.

Essentially, the same sets of flux/energy dependence experiments described in Sec. 4.2.3 are performed on two types of graphite specimens doped with boron (CKC-B20 and USB15, see Sec. 3.2). The estimated depth profiles of both O$^+$ and H$^+$ beams, based on the energies used, were calculated using the TRVMC program [121] assuming a graphite sample doped with 15 at.% boron with a density of ~2000 kg/m$^3$; see Fig. 7. The depth profiles are similar to the pure graphite calculations shown in Fig. 5.
5. EXPERIMENTAL RESULTS AND DISCUSSIONS

5.1 Determining the Reaction Products During H⁺&O⁺ Irradiation of Graphite

5.1.1 Consideration of Background Contributions to QMS signal in RGA Detection Mode

The raw trace of a typical experimental run in the RGA mode (at ~800 K) is presented in Fig. 8, showing the four experimental phases as described in Sec. 4.1. The method described in Sec. 4.1 effectively subtracts contributions from any O₂-ion-C and H₂-ion-C interactions (here 'ion' refers to either H⁺ or O⁺). It should further be noted that in the temperature range of the present experiments, contributions from O₂ and H₂ are expected to be very small. It is known that H₂ and O₂ do not react significantly with carbon at 800 K [5]. However, in order to get an upper limit of the effect of O₂ on the measured signals in the presence of ion irradiation, the published erosion yields for the O₂-Ar⁺(5keV) → C reaction at 800 K (~10⁻³ CO/O₂ and ~10⁻⁴ CO₂/O₂) was used [5]. We can expect the erosion enhancement due to Ar⁺ (5keV) to be at least as large as, and perhaps larger than, the enhancement due to H⁺ (≤3 keV) and/or O⁺ (≤5 keV).

With the typical O₂ background partial pressure at ~3×10⁻⁷ Pa during the experiments, the CO contribution to the QMS signal from the O₂-ion→C reaction at 800 K is expected to be about 5 orders of magnitude smaller than that obtained from the O⁺-C reaction, taking into account the differences in flux densities and reaction yields. In the case of H₂-O⁺→C reaction, it is evident from the CH₄ trace in Fig. 8 that the contribution of H₂ to the QMS signal is negligible (compare phases I and IV, the latter being the background). We also expect negligible contribution to the QMS signals in the H₂-H⁺→C reaction cases.

Furthermore, we note that the O⁺-induced wall effects for the CO and CO₂ signals cannot be eliminated from the four-phase experimental method. Similarly, the H⁺-induced wall effects for the CH₄ signals also cannot be eliminated. To address these issues, we compare results from experiments performed in LOS and RGA detection modes at 800K. Absolute calibration of the LOS signals was not possible in the current experimental set-up. However, by calculating the fraction of the yield changes of the O⁺-H⁺→C reactions with respect to the O⁺→C reactions, and matching this fraction to the corresponding RGA results, we can determine the contribution of wall effects to the RGA results for CO and CO₂. LOS experiments also show that the water signal drop during transition between phases II and III is equally sharp as those from other species. The corresponding slower drop observed during RGA experiments (see Fig. 8) is
mainly due to the much lower effective water pumping speed, which is caused by water molecules attaching to wall surfaces in the target chamber.

From the above analysis, we can ensure that the contribution of the O\textsuperscript{+}-induced wall effects is relatively small and constant by selecting a set of cases with a fixed O\textsuperscript{+} flux (3\times10^{18} O\textsuperscript{+}/m\textsuperscript{2}s) and a fixed O\textsuperscript{+} energy (5 keV). This is done for experiments described in Sec. 4.2 where precise control of the beam fluxes and energies are required. For the experiments described in Sec. 4.1 (the results of which will be discussed next in Sec. 5.1.2), larger fluxes will be required to produce a larger signal for obtaining the temperature dependence. In this case we will present the corresponding LOS results.

Finally, from the calculated depth profiles shown in Fig. 5, it is evident that the O\textsuperscript{+}-implantation depth is much shallower and localized than the depth for H\textsuperscript{+}. Hence, limiting the O\textsuperscript{+} beam to a fixed energy simplifies the analysis and interpretation of the results. We are, however, able to freely vary the energy and flux of the H\textsuperscript{+} beam since the wall effect produced in phase III of the experiments is always subtracted for CO and CO\textsubscript{2} analysis. Again, this is done for experiments described in Sec. 4.2. Furthermore, comparison between the LOS and RGA results in the manner described above confirmed that the H\textsuperscript{+}-induced background effect for CH\textsubscript{4} production with H\textsuperscript{+} ions in the energy range used here (0.7 – 3 keV/H\textsuperscript{+}) is negligible. The O\textsuperscript{+}-induced wall contribution also turns out to be negligible in the case of CO. For CO\textsubscript{2}, however, the O\textsuperscript{+}-induced background effect is \(-0.04\ CO_2/O^+\), or 20%–40% of the measured RGA signals.

### 5.1.2 Temperature Dependence of Reaction Product Yields

Fig. 9 shows the temperature dependence of CO, CO\textsubscript{2} and H\textsubscript{2}O yields measured in the RGA mode. The total oxygen released (CO + 2CO\textsubscript{2} in the O\textsuperscript{+}-only case and CO + 2CO\textsubscript{2} + H\textsubscript{2}O in the O\textsuperscript{+}&H\textsuperscript{+} case) is also plotted. For the O\textsuperscript{+}-only case, the CO yield temperature profile has a shallow minimum at \(~700\ K\), and the yields (present results) range from 0.6 to 0.9 CO/O\textsuperscript{+}. The temperature profile is similar to that of Refke's RGA results \([102]\), except our yield at the minimum is about a factor of 2 higher. The CO\textsubscript{2} profile has a shallow maximum at \(~700\ K\) and the agreement between the present results and those of Refke \([102]\) is quite good. The maximum CO\textsubscript{2} yield is smaller than the CO yield at the corresponding temperatures by about a factor of 5. With both the H\textsuperscript{+} and O\textsuperscript{+} beams turned on, a 10% – 20% drop in both the CO and CO\textsubscript{2} production is observed. In addition, water production is observed with a maximum yield of \(~0.15\ H_2O/O^+\), also at about 800K. The total oxygen released for both O\textsuperscript{+}-only and O\textsuperscript{+}&H\textsuperscript{+} cases
is near unity (within experimental uncertainties). Finally, only a small (~5% - 10%) reduction in the methane yield is seen when O\(^+\) is added to the H\(^+\) irradiation (less than 10% at 800 K); see Fig. 10.

The reason for performing the experiments in the line-of-sight QMS detection mode was to substantially suppress any non-beam related background signals (for example, the CO and CO\(_2\) signals observed during H\(^+\)-only bombardment) in RGA experiments. However, two important drawbacks of the LOS-QMS technique are (i) low signals, and (ii) not having in-situ absolute calibration. Nevertheless, low signal problems could be overcome by using longer detection times and absolute yields could be obtained by normalizing a particular data point (or the average of a set of points) to the corresponding absolute value on the RGA plot. For the LOS measurement presented in Fig. 11 the LOS yield curves were normalized to correspond to the RGA data at ~750 K. No re-emission of O or O\(_2\) was observed in the LOS detection mode for both the O\(^+\rightarrow\)C and O\(^+\)-H\(^+\rightarrow\)C irradiation cases. Due to the non-thermal nature of the energies of some of the released CO during irradiation [101,102], which is not taken into consideration in the present analysis, the actual shape of the LOS profiles will be slightly different from the plots in Fig. 11; at high temperatures, the yields shown in Fig. 11 might be too high.

Except for higher temperatures (>800 K), the temperature profiles of CO and CO\(_2\) yields for the O\(^+\)-only case are similar to the RGA data in Fig. 9. For T > 800 K, the yields for CO and CO\(_2\) in the LOS mode are higher. A possible cause might be related to the non-thermal energy of CO as noted above. In the simultaneous O\(^+\)&H\(^+\) case, smaller reductions in CO and CO\(_2\) yields (compared to the RGA results) is observed. This may be due to the intrinsic low signal-to-noise ratio in our LOS detection. Furthermore, as in the RGA mode, water is also observed in the O\(^+\)&H\(^+\) case. The maximum yield for water is slightly higher, likely due to a different method of estimating the absolute yield, but the temperature dependence is similar. Due to the uncertainty of the LOS data (possibly caused by the non-thermal CO release), we expect the RGA results – after applying appropriate background corrections – to be more reliable.

In conclusion, during simultaneous bombardment of graphite by 5 keV O\(^+\) and 1 keV H\(^+\), with H\(^+\) fluxes higher than O\(^+\) fluxes by factors of ~5-10, only ~10%-20% reduction is observed for both the CO and CO\(_2\) yields over the entire temperature range. Corresponding to the slightly reduced O\(^+\) \rightarrow C reactivity, a small amount of water production (~0.15 H\(_2\)O/O\(^+\) at 800 K) is observed with temperature dependence similar to that of CH\(_4\) formation. Finally, under the conditions of the present experiments, the O\(^+\) flux appears to have only a small influence on the production of CH\(_4\). Since the reduction of CO, CO\(_2\) and CH\(_4\) yields and the production of water
are all about one order of magnitude less than the actual CO and CO₂ yields, it is concluded that to first order, the mechanisms of O⁺ → C and H⁺ → C reactions appear to be largely independent. However, as we shall see later, more complex mechanisms for the synergistic effects will be revealed by flux/energy dependence studies.

5.2 Searching for the Mechanisms of Synergistic Effects

5.2.1 Sequential Implantation Experiments

Fig. 12a shows the raw RGA signal trace of water for graphite pre-implanted with 3 keV H₃⁺ (1 keV H⁺) to saturation and then irradiated with 10 keV O₂⁺ (5 keV O⁺). Implantation to saturation implies a "flat" target H concentration profile extending from the H⁺ ion range to the front surface. Fig. 12b shows the water signal trace for graphite pre-implanted with 6 keV H₃⁺ (2 keV H⁺) to saturation, then irradiated with 10 keV O₂⁺. The large water signal during the H⁺ pre-implantation stage is due completely to target chamber wall effects. The wall-effect induced water signal during O⁺ irradiation is much smaller, and can be eliminated by comparing with O⁺-only irradiation case without H⁺ pre-implantation (see Fig. 12c). All signal traces are plotted for 5 minutes.

Although the effect is small (due to a large noise-to-signal ratio), these traces indicate that in the near-overlapping case (1 keV H⁺ and 5 keV O⁺; see Fig. 12a) a water 'peak' was produced, while in the range-separated case (2 keV H⁺ and 5 keV O⁺; see Fig. 12b) no water spike was produced. Oxygen will only react with de-trapped hydrogen if the hydrogen ion range is overlapping the oxygen ion range. The 'peak' seen in Fig. 12a indicates a depletion of hydrogen supply in the oxygen ion range. By the same reasoning, we would also expect to see a water 'peak' in the range separated case (Fig. 12b), since the de-trapped H within the O⁺ implant zone should lead to water formation until this zone is depleted of H. However, the surface recession from the near-unity carbon erosion yield continuously moves the oxygen ion range towards the end of the hydrogen ion range, producing a flat H₂O signal as shown in Fig. 12b.

5.2.2 Simultaneous Implantation Experiments

Fig. 13 shows two raw LOS signal traces of water formation for graphite under simultaneous O⁺-H⁺→C irradiations. The first trace shows irradiations by (a) 1.8 keV H₃⁺ (0.6 keV H⁺) and 10 keV O₂⁺ (5 keV O⁺), and (b) 3 keV H₃⁺ (1 keV H⁺) and 10 keV O₂⁺. The second
trace shows irradiations by (c) 3 keV H$_{3}^{+}$ (1 keV H$^{+}$) and 10 keV O$_{2}^{+}$, and (d) 6 keV H$_{3}^{+}$ (2 keV H$^{+}$) and 10 keV O$_{2}^{+}$. The signals in (b) and (c) are of the same irradiation energies, and they show the relative signal strength in the two experimental traces.

As is evident, water signal is produced in all cases: beams completely overlapping in (a), beams nearly overlapping in (b) and (c), and beams separated in (d). Since the sequential experiments (see the previous section) suggest that during O$^{+}$ irradiation oxygen atoms do not move beyond the implantation zone to react with hydrogen, then during simultaneous irradiation there must only be mobile hydrogen (which was not present in the sequential experiments during O$^{+}$ irradiation) that can move from a separated H$^{+}$ implantation zone to the oxygen ion range to form water.

In summary, we have seen from the background review in Sec. 2.1.2 that the simultaneous experiments of Haasz and Chiu [59,60] lead to the conclusion that hydrogen recombination depends on the mobile hydrogen in the internal channels. The experimental results presented here also begin to suggest that mobile hydrogen during simultaneous implantation plays a major role in the production of water. Results from the next series of the experiments shall solidify this hypothesis.

5.2.3 Flux/Range Dependencies of the Synergistic Effects: O$^{+}$-H$^{+}$→C System

The RGA results of the experiments (at 800 K) aimed at studying flux and range dependence are shown in Fig. 14 - Fig. 17 for CO, CO$_{2}$, CH$_{4}$ and H$_{2}$O, respectively. The (a) parts of the figures show the yields for three different implantation depth ratios ($R_{H}/R_{O} = 1.2, 1.7, 4.4$) plotted against the flux ratio. Yields from both dual-beam and single-beam reactions are plotted for CO (Fig. 14), CO$_{2}$ (Fig. 15), and CH$_{4}$ (Fig. 16). For water production (Fig. 17), only the O$^{+}$-H$^{+}$→C reactions are plotted, and the LOS measurements for the case of $R_{H}/R_{O}=4.4$ are also plotted for verification. The single-beam yields are plotted for reference; variations in these yields indicate the run-to-run uncertainties in the measurements. Typically, one or two runs were performed in a day. The error bars indicate the relative error of the yield differences between the single- and dual-beam cases. The absolute error of the measurement, ~20%, is not included in the error bars. The CO, CO$_{2}$ and CH$_{4}$ yields drop during H$^{+}$ and O$^{+}$ co-bombardment, in comparison with the respective single species irradiation cases. These drops are accompanied by the formation of H$_{2}$O.
The percentage reductions of the CO, CO₂ and CH₄ yields in the O⁺-H⁺→C reactions, as compared with the O⁺→C reactions (in the cases of CO and CO₂) and the H⁺→C reactions (in the case of CH₄), are plotted separately in the (b) parts of Fig. 14 - Fig. 16, again as a function of flux ratios. A depth (or range) ratio of ~1.2 (RH/R₀) indicates a near-complete overlapping (as estimated by the TRVMC program; see Fig. 5) of the O⁺ and H⁺ ion ranges. [For 0.7 keV H⁺, RH ~ 13 nm and for 5 keV O⁺, R₀ ~ 11 nm]. On the other hand, a depth ratio of ~4.4 indicates a complete separation of O⁺ and H⁺ implantation; the estimated ranges (Fig. 5) for 3 keV H⁺ is ~50 nm. It is evident that within the uncertainty of the data, the depth ratio has almost no effect on the reductions of CO and CO₂ yields during the O⁺-H⁺→C reactions when compared to the O⁺→C reactions, and on the reduction of CH₄ yields during O⁺-H⁺→C reactions when compared to the H⁺→C reactions. Water production is also not significantly affected by the depth ratio.

The yield changes, however, do depend on the incident ion flux ratio. The reductions of CO yields range from ~10% (for Φₒ/Φₕ = 0.1) to ~5% (for Φₒ/Φₕ = 0.3–0.5), and are roughly similar for all depth ratios. The reductions of CO₂ yields range from ~45% (for Φₒ/Φₕ = 0.1) to ~15% (for Φₒ/Φₕ = 0.3–0.5), and again are similar for all depth ratios. Reductions of the CH₄ yields range from ~15% (for Φₒ/Φₕ = 0.1) to ~40% (for Φₒ/Φₕ = 0.5). A calibration for the H₂O yields was estimated using the oxygen balance method from the CO and CO₂ reductions for the case of 10% Φₒ/Φₕ flux ratio with complete ion-range overlap. All other cases were calculated relative to this value. Thus, the water production was found to be about 0.3 H₂O/O⁺ for Φₒ/Φₕ = 0.1, dropping to around 0.1 H₂O/O⁺ for larger flux ratios.

Finally, obtaining accurate temperature profile measurements for controlled flux ratio and energy is difficult due to the small oxygen flux involved (resulting in large experimental uncertainty). It was found that temperature profiles performed in the RGA detection mode were generally suspect due to the complexity of the background contribution from the test chamber walls. We may still obtain general shapes for selected cases in the LOS mode. These can be used to compare with results from the model calculations described in Sec. 6. Due to limitations in the ion source facility, the maximum hydrogen beam flux from the accelerator was limited and decreases roughly linearly with the beam energy. Thus in order to obtain the largest signals for the reaction products, it was necessary to increase the oxygen flux for experiments involving lower hydrogen beam energies. For example, for Rₕ/R₀ = 1.2 (H⁺ energy at 0.7 keV and O⁺ energy at 5 keV) the flux ratio Φₒ/Φₕ = 0.5 was used. Fig. 18 and Fig. 19 plot the temperature
profile of water production and methane production, respectively, in the O⁺-H⁺→C reaction system.

5.2.4 Hydrogen Re-emission and Methane Break-up

Since the observed reduction of CH₄ and the formation of H₂O in the O⁺-H⁺→C system may affect the supply of hydrogen in graphite, we could expect some change in the hydrogen re-emission signal in the form of H₂, as atomic hydrogen re-emission is insignificant until well above 900 K. We have discussed in Sec. 2.1.3 the effect of “methane break-up” and we can postulate that the reduction of CH₄ during simultaneous O⁺ and H⁺ irradiation when compared to the H⁺-only irradiation case may be due to the additional O⁺-induced methane break-up. This will have the effect of increasing hydrogen re-emission (due to the increase of hydrogen in the internal channels as a result of methane break-up). This was observed for He⁺-H⁺→C reactions [60,71]. On the other hand, the formation of H₂O during simultaneous O⁺-H⁺→C irradiation will decrease the available hydrogen supply, which in turn may decrease hydrogen re-emission. The two effects may cancel each other, and we may not see any change in the H₂ re-emission as a result. In hydrogen re-emission experiments monitored in the RGA detection mode, the high background hydrogen source gas from the light ion source causes the QMS to either overload when detecting H₂, or makes it unable to detect small changes over the large background signal. In experiments with LOS detection, the large H₂ background translates into large noise in the QMS, again causing small changes difficult to detect. A typical raw signal trace of H₂ re-emission in the LOS detection mode during H⁺→C and O⁺-H⁺→C reactions at 800 K is plotted in Fig. 20. As illustrated in the figure, the change in the H₂ signal during simultaneous O⁺ and H⁺ impact when compared to H⁺-only impact is essentially negligible within the experimental uncertainties.

To further confirm the “methane break-up” effect expected due to O⁺ impact, we replaced O⁺ with Ne⁺ and simultaneously irradiated graphite with H⁺. Fig. 21 plots the CH₄ yield as a function of ion range separation with two different beam flux ratios (Φ₁/Φ₂ ~ 0.1 and 0.25) for graphite under simultaneous Ne⁺ and H⁺ impact. Methane reduction during simultaneous Ne⁺ and H⁺ impact occurs for all cases shown in Fig. 21, and the effect of methane break-up is confirmed. For the range-separated case, the dependence on beam flux ratio follows the same trend observed in O⁺-H⁺→C system (i.e., higher O⁺ or Ne⁺ fluxes lead to higher methane break-up). For the range-overlapping cases, flux dependence seems to be negligible within the
experimental uncertainty. Furthermore, the overall reduction for CH₄ yield seems to be slightly higher for the range-overlapping cases. Since for the range-overlapping cases the methane precursor formation now coincides with the Ne⁺ range, it is very probable that Ne⁺-induced desorption will reduce the methane precursor formation thus decreasing the CH₄ yield. However, in the O⁺-H⁺→C system, when the O⁺ and H⁺ beam ranges are overlapping, water formation (which affects the supply of both oxygen and hydrogen) will add to the processes described above. The net result may be hard to predict.

Since the neon eliminates other chemical effects such as water production, we should expect an increase in the H₂ re-emission corresponding to the methane break-up similar to the results from the He⁺-H⁺→C experiment [60,71]. Fig. 22 plots a typical raw signal trace of H₂ re-emission during H⁺→C and Ne⁺-H⁺→C reactions at 800 K. The plot shows no significant change in the H₂ signal. Based on the RGA results of the He⁺-H⁺→C experiment [60,71], we expect the corresponding H₂ increase due to Ne⁺-induced methane break-up to be less than 20% of the total H₂ re-emission [60,71]. With the noise level at ~ 40% in the LOS detection mode, such change might not be discernible.

5.2.5 Fluence and Microstructure

As described in Sec. 4.2.5, a typical experiment starts out with zero H⁺ fluence, then both O⁺ and H⁺ beams are turned on for a period of time to (a) obtain the transient curve of the water yield and (b) creating structural change in the anneal specimen, after which both beams are then turned off. Fig. 23 plots a typical raw signal trace of water yield during this experiment. After the pre-implantation, O⁺ and H⁺ are again irradiated on the specimen, and a subsequent water yield transient is obtained; see Fig. 24. As is evident, on a newly annealed graphite specimen the water yield transient increases at a slower rate than on an ion-damaged graphite specimen. This seems to support the dependence of water production on the transport of mobile hydrogen via internal channels created by ion-damage.

5.3 Flux/Range Dependencies of the Synergistic Effects: O⁺-H⁺→C/B system

We will now examine the synergistic effects of the O⁺-H⁺→C/B reaction system. As with the O⁺-H⁺→C interaction, no re-emission of O or O₂ was observed in the LOS detection mode for both the O⁺→C/B and O⁺-H⁺→C/B irradiation of the CKC-B20 and USB15 specimens.
The single most obvious difference between the $\text{O}^+-\text{H}^+\rightarrow \text{C}$ and $\text{O}^+-\text{H}^+\rightarrow \text{C/B}$ systems is the $\text{CH}_4$ yield ($\text{CH}_4/\text{H}^+$) during simultaneous $\text{O}^+$ and $\text{H}^+$ impact. Fig. 25 shows the raw trace of a typical experimental run in the RGA mode (at ~800 K) for the $\text{O}^+-\text{H}^+\rightarrow \text{C/B}$ (CKC-B20) experiments. Two observations are immediately evident. First of all, compared to $\text{H}^+$-only irradiation, $\text{CH}_4$ yields increase during simultaneous $\text{O}^+$ and $\text{H}^+$ irradiation for the $\text{O}^+-\text{H}^+\rightarrow \text{C/B}$ (CKC-B20) case. For the $\text{O}^+-\text{H}^+\rightarrow \text{C}$ (HPG99) case, $\text{CH}_4$ yields decrease during simultaneous $\text{O}^+$ and $\text{H}^+$ irradiation (see Fig. 8). Secondly, comparing water signals from Phase II ($\text{O}^+&\text{H}^+$ impact) and phase III ($\text{H}^+$-only impact), there is very little water production in the $\text{O}^+-\text{H}^+\rightarrow \text{C/B}$ system. Similar results were observed for irradiation of the USB15 specimen.

To illustrate the effect of B on methane formation, $\text{CH}_4$ yields from both the $\text{O}^+-\text{H}^+\rightarrow \text{C}$ (see Sec. 5.2.3) and $\text{O}^+-\text{H}^+\rightarrow \text{C/B}$ systems are plotted in Fig. 26 as a function of beam flux ratio $\Phi_O/\Phi_H$ for two ion range separation cases: (a) beams are completely overlapping ($R_H/R_O \sim 1$), and (b) beams are completely separated ($R_H/R_O \sim 6$). It can be seen from the graph that the $\text{CH}_4$ yield increase during simultaneous $\text{O}^+$ and $\text{H}^+$ irradiation in $\text{O}^+-\text{H}^+\rightarrow \text{C/B}$ system is more prominent when the $\text{O}^+$ and $\text{H}^+$ beams are completely separated. Note that as suggested in Sec. 5.4, $\text{CH}_4$ molecules are broken up by the incident $\text{O}^+$ ions, which causes the $\text{CH}_4$ yield reduction during simultaneous $\text{O}^+$ and $\text{H}^+$ irradiation in the $\text{O}^+-\text{H}^+\rightarrow \text{C}$ case. Since this is a purely physical effect (depending entirely on the energy and cross-section of the collisions between $\text{O}^+$ and $\text{CH}_4$ molecules), this "methane break-up" effect must still be present in the $\text{O}^+-\text{H}^+\rightarrow \text{C/B}$ case. For the beam-overlapping case for the CKC-B20 specimen in Fig. 26a, $\text{CH}_4$ yields show an increase during simultaneous $\text{O}^+$ and $\text{H}^+$ irradiation, but the increase just barely offsets the $\text{CH}_4$ yield decrease due to $\text{O}^+$-induced methane break-up. By comparison, for both the overlapping and separated cases of USB-15 and the separated case of CKC-B20, the methane break-up effect is more than compensated for by whatever is causing the yield increase. We note the general trend of higher methane increase for the beam-separated case.

Now, let us examine what effect the addition of boron in the system will have on the water yields ($\text{H}_2\text{O}/\text{O}^+$), and the related CO/CO$_2$ and CO$_2$/O$_2$ yields. Fig. 27 plots the $\text{H}_2\text{O}$ yields from both $\text{O}^+-\text{H}^+\rightarrow \text{C}$ (see Sec. 5.2.3) and $\text{O}^+-\text{H}^+\rightarrow \text{C/B}$ systems as a function of beam flux ratio $\Phi_O/\Phi_H$ for two ion range separation cases: (a) beams are completely overlapping ($R_H/R_O \sim 1$), and (b) beams are completely separated ($R_H/R_O \sim 6$). The water yield is calibrated using the oxygen balance method based on the CO and CO$_2$ yields. We note that the water production at $\Phi_O/\Phi_H \sim 0.1$ is markedly smaller in the $\text{O}^+-\text{H}^+\rightarrow \text{C/B}$ system (both CKC-B20 and USB15)
compared to the $O^+\rightarrow C$ system. For other flux ratios, no consistent trend is seen. Results for the USB15 specimen are inconclusive due to the anomalous data observed for the cases (i) $\Phi_O/\Phi_H = 0.3$, $R_H/R_O \sim 1$, and (ii) $\Phi_O/\Phi_H = 0.5$, $R_H/R_O \sim 6$. However, for the $\Phi_O/\Phi_H = 0.1$ flux ratio for both the beam separated and overlapping cases, we note that the water yield is nearly completely suppressed for the USB15 specimen, even more than for the CKC-B20 specimen.

As in the $O^+\rightarrow C$ system, corresponding to the water production there will be a reduction of CO and CO$_2$ yields during simultaneous $O^+$ and H$^+$ irradiation compared to $O^+$-only impact. Fig. 28 and Fig. 29 show, respectively, the CO and CO$_2$ yields from both the $O^+\rightarrow C$ (see Sec. 5.2.3) and $O^+\rightarrow C/B$ systems as a function of beam flux ratio $\Phi_O/\Phi_H$ for two ion range separation cases: (a) beams are completely overlapping ($R_H/R_O \sim 1$), and (b) beams are completely separated ($R_H/R_O \sim 6$). In the $O^+\rightarrow C/B$ system, there seems to be a shift in the distribution of CO and CO$_2$ yields (i.e., generally higher CO yields and lower CO$_2$ yields, compared to the $O^+\rightarrow C$ system) while the overall oxygen balance is smaller than that for the $O^+\rightarrow C$ system, especially for the USB15 specimen. Since we have used the oxygen balance from the CO and CO$_2$ yields to estimate the absolute water yields, this leads to the small water yields for the $O^+\rightarrow C/B$ system. These findings will be addressed in Sec. 5.4.2.

5.4 Discussions of Mechanisms

5.4.1 The $O^+\rightarrow C$ System

We can now proceed to examine the physical mechanisms of the synergistic effect of simultaneous $O^+$ and H$^+$ irradiation and the resulting water production (as presented in Sec. 5.2). A pictorial illustration of the mechanisms discussed below is shown in Fig. 30. From the simultaneous irradiation experiments described in Sec. 4.2.2, we found that H$_2$O production occurs independent of ion depth separation. Further examination reveals that the H$_2$O production and the reduction of the other species are not significantly dependent on the depth ratio $R_H/R_O$. Based on these findings, plus the fact that O$_2$ re-emission is not observed and the oxygen balance for the $O^+\rightarrow C$ reactions is nearly unity, we propose the hypothesis that for the $O^+\rightarrow C$ case, all the oxygen participates in the reactions with carbon to form CO and CO$_2$ at the end of the $O^+$ ion-range. This suggests that there are no free O atoms that are mobile within the carbon matrix to form O$_2$ via recombination, or more importantly, in the case of $O^+$ and H$^+$ co-bombardment, to react with hydrogen elsewhere to form water molecules.
While oxygen mobility in the form of mobile O atoms is not likely, the volatile CO and CO₂ molecules are able to move freely via the internal channels (and leave graphite). However, CO and CO₂ molecules are not energetically probable to react further in the temperature range studied here (bond strength for the triple bond in the case of CO is \( \sim 11 \) eV and the double bond in the case of CO₂ is \( \sim 8 \) eV). Thus, the only way for the CO and CO₂ molecules to undergo further reactions beyond the O⁺ implantation range is by molecule break-up via ion-impact. However, it is more likely for the CO and CO₂ molecules to be broken up within the O⁺ implantation range, in which case the free oxygen atoms are likely to immediately return to the internal surfaces to react with carbon (since O₂ recombination is not observed). Therefore, as far as the synergistic reaction mechanisms are concerned, oxygen is not considered to be mobile within the carbon matrix either as free O atoms or as CO\&CO₂ molecules.

On the other hand, previous hydrogen isotope-mixing experiments show that some mobile H-atoms freely move through intercrystalline channels, or internal porosity, within the ion range (see Sec. 2.1.2). The microstructure experiment discussed in Sec. 5.2.5 also seems to suggest that water production transient is dependent on the amount of irradiation damage in the graphite target. Thus, during simultaneous H⁺ and O⁺ irradiation, the hydrogen atoms can readily react with oxygen even when the ion range for H⁺ is much greater than that of O⁺. Again, this property of the O⁺-H⁺→C system is evident from the results of both the sequential and simultaneous irradiation experiments (see Sec. 5.2.1 and Sec. 5.2.2). The reaction of hydrogen with available oxygen takes away a portion of the oxygen supply, resulting in the observed reductions of CO and CO₂ yields, compared to the O⁺→C reaction case.

We also observe from our results that the yields depend on the flux ratio. The smaller the oxygen flux compared to the hydrogen flux, the greater is the reduction of CO and CO₂ yields, and the greater is the H₂O yield. This might be explained by noting that when there is an over-abundance of available hydrogen, such as in the case when \( \Phi_O/\Phi_H \) is relatively low (e.g., \( \Phi_O/\Phi_H \sim 0.1 \)), relatively more hydrogen can go into the production of H₂O. We also observe that the reduction of CO₂ is much higher than that of CO when there is an over-abundance of available hydrogen. This can be explained by noting that since it takes twice as many oxygen atoms to form one CO₂ molecule than one CO, when the oxygen supply is reduced due to H₂O formation, it would show a greater effect on CO₂ production than on CO production.

The behaviour of CH₄ shows the opposite effect in its flux ratio dependence: at a low \( \Phi_O/\Phi_H \) flux ratio, the synergistic reduction of the CH₄ production is smaller than that seen for the higher flux ratios. Previous studies indicate that the production of methane occurs at the end of
the H\(^+\) ion-range and that the methane molecules move through the internal porosity to be released from the surface (see Sec. 2.1.3). This suggests that in the simultaneous O\(^+\)-H\(^+\)→C reactions, methane production is not directly competing with CO and CO\(_2\) productions when the two ion ranges are completely separated (O atoms do not diffuse). The reduction of CH\(_4\) in this case comes mostly from a previously observed phenomenon known as "methane break-up" where methane molecules are formed at the end of ion-range, and while moving towards the surface via internal porosity they undergo fragmentation by incident ions (see Sec. 2.1.3). This effect is expected to increase with the addition of energetic O\(^+\) ions due to their greater mass. Furthermore, when more oxygen ions are present in the system relative to hydrogen ions, as in the case for the highest flux ratio (i.e., \(\Phi_O/\Phi_H = 0.5\)), methane break-up increases and we see a larger steady-state CH\(_4\) reduction. Using inert Ne\(^+\) to replace O\(^+\), the result of the Ne\(^+\)-H\(^+\)→C experiment discussed in Sec. 5.2.4 also confirms the methane break-up effect. The break-up effect might also be seen in the release of CO\(_2\) and H\(_2\)O, but we suspect that the effect is much less pronounced than it is on CH\(_4\). This is because the reactions that form CO\(_2\) and H\(_2\)O take place much closer to the surface, thus the molecules are less likely to encounter the incident ions during their transport out of the graphite. For the case where the two ion-ranges are overlapping, we cannot at this time separate the contributions of methane break-up and water-formation to the observed methane reduction.

As a final note, the intense ion bombardment employed in the current experiments will lead to the formation of a complex surface morphology. Although the surface does become amorphous, it does retain some of the microcrystalline structure (see Sec. 2.1.1). The associated variations in the microstructure of the surface may well affect the relative H\(^+\) and O\(^+\) ranges. However, TRVMC calculations of 21° incident beams with ±30° mosaic spread shows that the relative ranges are not greatly affected, assuming the modified surface retains a similar mosaic spread as the original specimen. This assumption is not totally unreasonable since the two beams incident at off-normal angles are expected to prevent the formation of any major surface features. Furthermore, the surface recession that occurs due to erosion also does not affect the reactions. As the target temperature in the present study is fixed at 800 K, almost no H trapping occurs at the end of the ion range. Therefore, all reactions are with dynamic or solute H, and recession of the surface will have no impact on the relative placement of solute H and the O\(^+\) range. It is possible, however, that for ion-range separation experiments performed at lower temperatures, the location of trapped H could be affected by surface recession, and this may have an impact on the erosion chemistry.
5.4.2 The \( O^+ - H^+ \rightarrow C/B \) System

Let us now examine the underlying mechanism that produces the marked difference between the \( O^+ - H^+ \rightarrow C \) and \( O^+ - H^+ \rightarrow C/B \) irradiation cases (see Sec. 5.3). First, let us consider the \( H^+ \rightarrow C/B \) case. We propose the hypothesis that the mobile hydrogen can be trapped at internal surfaces, where an abstraction reaction with another mobile hydrogen atom may form \( H_2 \) and release it into the internal channel [5]. The production of \( H_2 \) would then depend on the population of these trapping sites and the chemistry of the carbon bonds at these sites. The presence of boron on the internal surfaces may increase the number of traps for mobile hydrogen and may also change the chemistry of the bonds at these trapping sites, which could lead to an enhancement of hydrogen recombination and ultimately to the reduction of the \( CH_4 \) yield.

With this in mind, it is interesting to observe that the presence of oxygen ions in the \( O^+ - H^+ \rightarrow C/B \) case seems to reduce the \( CH_4 \) yield suppression effect of boron, causing the \( CH_4 \) yield to increase during simultaneous \( O^+ \) and \( H^+ \) irradiation, compared to \( H^+ \)-only impact. This increase is large enough that it more than compensates for the methane break-up effect due to energetic \( O^+ \) impact. The \( CH_3 \) precursor reduction theory of boron-induced methane yield reduction (see Sec. 2.4.2) does not clearly lead to this effect. Oxygen does not travel beyond the \( O^+ \) implantation range (see discussions in Sec. 5.4.1), and methane is produced at the end of the \( H^+ \) ion range (see Sec. 2.1.3). Therefore, \( O^+ \) should not be able to affect the production of \( CH_3 \) precursors in the deeper hydrogen range in any way. All of these observations point to the behaviour of the mobile hydrogen on the internal surfaces as the primary cause for the \( CH_4 \) yield suppression in boron-doped graphite.

How does the incident oxygen affect the hydrogen recombination at the end of the \( H^+ \) ion range? If we assume that the modification of the internal surfaces, by the presence of boron, enhances the hydrogen recombination by creating more inner surface recombination sites (this leads to the reduction of methane yield in boron-doped graphite under \( H^+ \)-only irradiation), then it is reasonable to postulate that the presence of oxygen combining with boron on the inner surfaces might "fill" these sites, thus nullifying the enhancement of hydrogen recombination.

The reduced hydrogen recombination due to the combined presence of \( B \) and \( O \), would lead to an increase of the mobile hydrogen supply — distributed uniformly [10] — throughout the \( H^+ / O^+ \) implantation zone. The increase of the observed methane yield for \( O^+ - H^+ \rightarrow C/B \) irradiation might thus be coupled to the mobile hydrogen supply, with the implication that the mobile hydrogen partakes in the formation of \( CH_4 \). The inclusion of mobile hydrogen in the
methane molecule formation is consistent with previous results obtained for H⁺-D⁺ co-bombardment of pure graphite where small amount of mixed-isotope methane was detected for depth-wise separated H⁺-D⁺ implantations and seem to increase as much as a factor of 4 until saturation is reached (see Sec. 2.1.3).

We have also noted in Sec. 5.3 the general trend of higher methane increase for the beam-separated case. This can be explained by noting that higher methane reduction in the O⁺-H⁺→C system is expected for the beam-overlapping case due to the interference of O⁺ to the formation of methane precursors, in addition to the O⁺-induced methane break-up (see the model discussion in Sec. 6). Thus, the resulting CH₄ increase in the O⁺-H⁺→C/B system is expected to be relatively less for the beam-overlapping case, consistent with the observed results.

Furthermore, we note that the BₓOᵧ formed from the above-mentioned combination of B and O during simultaneous O⁺&H⁺ irradiation of boron-containing graphite (see Sec. 2.4.2) may be slowly removed by energetic H⁺ when the oxygen is no longer in the system, i.e., after the O⁺ is turned off. This removal of BₓOᵧ molecules is largely due to physical sputtering below 1200 K, as observed in studies of the O⁺→BₓC system [101,102]. The presence of BₓOᵧ and its removal by H⁺ is likely to be the cause of the transient behaviour of CH₄ production seen in Fig. 25, where the CH₄ production decreases very slowly after the O⁺ beam is turned off. Although no attempt was made here to study the production of BₓOᵧ species, future studies should include the monitoring of BO to examine the relationship of its yield to the synergistic effects in the O⁺-H⁺→C/B system.

Finally, let us examine the mechanism that causes the water yield reduction for the O⁺-H⁺→C/B cases compared to the O⁺-H⁺→C cases. If we assume that during steady-state operation, the “oxygen-gettering” effect of boron reaches a state of saturation, then any effect of boron on the water production must be caused by the change of the chemistry of water production. We postulate the presence of hydrogen-oxygen-containing “complexes” at the end of the O⁺ range, created by attaching mobile hydrogen atoms and the implanted oxygen with either carbon or boron on the internal surfaces. The C-attached complexes form the “water precursor”, which during thermal or ion-induced desorption can release H₂O molecules into the internal channel and transport them out of graphite. The B-attached complex, on the other hand, have much less probability of releasing H₂O due to the higher stability of the B-O bond. (Instead, it may release BₓOᵧ and H/H₂ during thermal or ion-induced desorption). In other words, the presence of boron reduces the H and O supplies by providing competing reaction paths that do not produce water. This hypothesis is consistent with the observation of reduced
H$_2$O yield for the O$^+$-H$^+$→C/B cases when compared to the O$^+$-H$^+$→C cases. Furthermore, the concept of the "water precursor" is also consistent with the temperature dependence of water yield, which suggests the dissociation of the water precursors at higher temperatures.

The mechanism discussed in this section will next be incorporated into a model for reaction product formation during simultaneous irradiation of carbon by O$^+$ and H$^+$; see Sec. 6.
6. A SEMI-EMPIRICAL MODEL OF THE O⁺-H⁺→C REACTION SYSTEM

As a clear understanding of the reaction mechanisms in the O⁺-H⁺→C system began to emerge from the experimental investigations, it became necessary to translate the qualitative picture into a comprehensive mathematical model. The following outlines a semi-empirical model for CH₃/CH₄, CO, CO₂ and H₂O production in the O⁺-H⁺→C reaction system. The term "semi-empirical model" is used here to indicate the identification of the possible processes (both chemical and collisional) involved in the O⁺-H⁺→C reaction system and the development of a system of differential equations based on these processes. The majority of the rate coefficients and other parameters are determined by fitting with the single-species experimental results for one set of flux and energy. The rate coefficients and parameters unique to the dual-beam irradiation case (such as those for the formation of water and methane break-up) are also determined by fitting with the experimental results for one set of flux and energy. The mathematical model then utilizes these parameters to make predictions, where applicable, in the energy and flux dependences for both the single-beam (H⁺→C and O⁺→C) and the dual-beam (O⁺-H⁺→C) irradiation cases.

Before we introduce the equations, it is essential to outline some basic assumptions regarding the graphitic structure and reaction mechanisms. We will begin in Sec. 6.1.1 with assumptions made for the "two-region" model of hydrogen transport (as outlined in Sec. 2.2.3), followed by additional assumptions used specifically in the current model for hydrocarbon formation (Sec. 6.1.2), oxygen implantation (Sec. 6.1.3), and synergistic effects due to simultaneous O⁺ and H⁺ impact (Sec. 6.1.4).

6.1 The Model Assumptions

6.1.1 The Two-Region Model Assumptions

(1) Similar to the "two-region" model of hydrogen transport (Sec. 2.2.3), for the proposed model of the O⁺-H⁺→C reaction system, we again consider graphite to be composed of two regions: the bulk region within graphitic crystallites and the inner surface region consisting of the crystallite surfaces [10]. The presence of crystallites has been observed in hydrogen-irradiated graphite even at fluences as high as 10²⁴ H⁺/m² at 10keV H⁺.
energy [46-48], making this assumption reasonable. We will also assume here that a similar structure exists for oxygen irradiation.

(2) For the $\text{O}^+\text{H}^+\rightarrow\text{C}$ reaction system, the transport of molecules via these internal "channels" is considered to be near-instantaneous. A finite time is required for their release from the geometric graphite surface, allowing for ion-induced break-up.

(3) Transport of hydrogen atoms out of the hydrogen-saturated crystallites to the edge of crystallites is considered to be instantaneous, while transport of hydrogen atoms on the internal surfaces is assumed to obey the diffusion law until steady state is reached. At steady state, the concentration of mobile hydrogen atoms on the internal surfaces is assumed to be constant throughout the entire ion range. Transport of hydrogen atoms beyond the implantation zone into the unmodified graphite structure is not included in the model. Furthermore, re-entry of hydrogen atoms into the crystallite is inhibited by an energy barrier [10]. For the temperatures considered in the model ($< 1200$ K), it is also assumed that hydrogen is released only as molecules. An energy barrier at the geometric surface of the graphite is assumed to inhibit the release of hydrogen atoms [10]. Fig. 31 illustrates conceptually these energy barriers. The transport of hydrogen molecules within the internal channels is considered to be instantaneous.

6.1.2 Assumptions Regarding Hydrocarbon Formation

(1) For simplicity, methane is considered in this model to be the only hydrocarbon product in the $\text{O}^+\text{H}^+\rightarrow\text{C}$ reaction system. This is a reasonable assumption for energies $> \approx 1 \text{ keV/H}^+$ where heavy hydrocarbons represent about 15% of the total carbon yield [66].

(2) Incident hydrogen ions are assumed to thermalize at the end of the ion range and are assumed to be trapped within the graphite crystallite region and may be de-trapped thermally or by incident ions. There is strong evidence from various types of experiments (e.g. XPS, thermal desorption spectroscopy, and optical properties) that stable C-H bonds exist within the hydrogen-saturated region formed during $\text{H}^+$ bombardment of graphite [92]. This is the $\text{CH}^*$ precursor. It is also assumed that the $\text{CH}^*$ precursor can undergo dissociation (i.e., de-trapping of H) either thermally or via ion-impact. Hydrogen atoms de-trapped from the edge of the crystallite are assumed to
return to the crystallite from where they can again lead to CH* formation or enter the internal surfaces.

(3) The concentration of CH₂ as a precursor in the crystallite is assumed to be small, i.e., its rate of breaking up is assumed to be much larger than the rate of formation. At the edge of the crystallite volatile CH₃ may form, leaving the crystallite and entering the internal channels. From the CH* precursor stage, the addition of remaining hydrogen atoms to form CH₃ is thus assumed to be a one-step process, although its true nature may be quite complex. Thus, the process of CH₃ formation is assumed to be proportional to an arbitrary power of the concentration of the hydrogen in the crystallite. The power will be determined through empirical fitting. We will further assume that when the CH₃ radical enters the internal channel, it immediately strikes the internal surfaces and picks up an additional mobile hydrogen atom on the internal surfaces to form CH₄ [60,5]. The formation of CH₃ radical is supported by atomic H⁺C experiments where CH₃ is observed instead of CH₄ by line-of-sight QMS [64].

(4) As indicated in Sec. 2.2.4, we will assume that only hydrogen atoms implanted in the crystallites take part in the formation of CH₃ radical. An energy barrier has been proposed to exist at the edge to prevent mobile hydrogen from re-entering the graphite crystallite [10,60]; see Fig. 31. We will consider the “edge” region of the crystallite as part of the crystallite (i.e., it is at the same energy level as the rest of the crystallite; see Fig. 31), but allow the methyl radical to diffuse into the internal channel once they are released (thermally or induced by the incident energetic hydrogen). As discussed in Secs. 2.1.3 and 5.4.2, the assumption of coupling CH₃ radical with mobile hydrogen on the internal surfaces is consistent with previous results obtained for H⁺-D⁺ co-bombardment of pure graphite where small mixed-isotope methane was detected for depth-wise separated H⁺-D⁺ implantations and increase with fluence by as much as a factor of 4 until saturation is reached [60,69]. It is also consistent with the CD₃H/CD₄ ratio being near unity for depth-wise separated H⁺-D⁺ implantations at saturation [60,69], where the CD₃ radical formed at the deeper D⁺ range has equal probabilities to form CD₃H and CD₄ if the mobile D and H are completely mixed on the internal surfaces. Finally, it is consistent with the new findings presented here where the addition of oxygen in boron-doped graphite at a separated implantation range was seen to affect the production of methane. Refer to Secs. 5.3 and 5.4.2 on discussions regarding boron-doped experiments.
Recombination of hydrogen atoms into hydrogen molecules on the internal surfaces is assumed to involve trapping of hydrogen atoms on the internal surfaces and the subsequent abstraction via impact with another hydrogen atom. Since very little H-D mixing (in the form of HD molecules) is observed during sequential implantation on graphite with completely separated H⁺ and D⁺ ion ranges while complete H-D mixing is observed during simultaneous implantation experiments (see Sec. 2.1.2), it indicates that hydrogen recombination is mostly involved with the abstraction of trapped hydrogen atoms on the internal surfaces and not much with trapped hydrogen at the edge of the crystallite. Thus, the traps at the edge of the crystallite are considered to be separate and at a higher energy from the surface traps. This assumption then prevents mobile hydrogen atoms from being trapped at the edge and being involved in CH* precursor production (hence CH₃ radical formation); similarly, it prevents CH* precursors from being involved in the H₂ formation. Fig. 31 illustrates the potential energy barrier diagram discussed above. All traps are assumed to be identical in nature, but once a surface trap is filled with a mobile hydrogen atom its potential energy becomes positive for abstraction with another hydrogen atom on the surface. Further, since atomic hydrogen release is not modelled here, the actual surface trapping is not included in this model and the recombination process is simplified to a single step process involving the square of the mobile hydrogen concentration, as shown in (2) in the figure. Although it is beyond the scope of the present model, any change in the nature of the trapping-abstraction process (as when boron is involved) such as the chemistry and the mobility (as discussed in Sec. 5.4.2) may manifest itself in the activation energy and the pre-exponential factor, respectively, of the recombination rate.

6.1.3 Assumptions Regarding Oxygen Implantation

For the O⁺-H⁺→C reaction system, incident oxygen is assumed to react with carbon when it reaches the end of its trajectory, i.e., there are no mobile oxygen atoms within graphite and any transport beyond the oxygen ion range is not permitted. The supporting evidence for this assumption has been outlined in the previous sections. Like hydrogen, oxygen is assumed to be singly bonded to carbon to form CO* precursors. The CO* precursors can dissociate thermally or via ion-impact (as is the case with CH* precursors). They can also be released from the crystallite as a volatile CO molecule, or attach to another...
oxygen atom from the crystallite and release as CO₂, or react with mobile hydrogen atoms to form water precursors. Total carbon erosion yield due to incident O⁺ is assumed to be unity and independent of graphite temperature, see Sec. 2.3. Thus, for simplification this model will consider CO and CO₂ production as two branches of a single reaction system, i.e., they share the same CO* precursors.

(2) As a consequence of the assumptions described above: (i) mobile hydrogen can react with a CO* precursor to form water, and (ii) any atomic oxygen that is released into the internal channel is instantaneously re-trapped. This model also assumes that the CO* precursors involved in any reaction are located on the internal surfaces at a potential energy level similar to those of the mobile hydrogen, as opposed to being at the edge of the crystallite at a higher potential energy as in the case of CH* precursors; see Fig. 31.

6.1.4 Assumptions Regarding Synergistic Effects

(1) From the experiments of simultaneous H⁺/O⁺ irradiation of graphite described in the previous sections, it is evident that water formation is not affected greatly whether the H⁺ and O⁺ ranges are completely separated or not. This suggests that the mobile hydrogen on the internal surfaces plays a much greater role in the water formation than the hydrogen in the crystallite (see Sec. 5.4). In the present model, we assume that only mobile hydrogen atoms are involved with water production.

(2) In modelling the O⁺-H⁺→C reaction system, it is assumed that H₂O is the only significant synergistic reaction product. Due to the observed temperature profile of the water yield, dissociation of water molecules at higher temperatures is expected. This leads to the notion of a “water precursor” (CH₂O*) formed by mobile hydrogen on the internal surfaces reacting with CO* precursors. This is also consistent with the experimental results for the O⁺-H⁺→C/B reaction system (see discussions in Sec. 5.3). The form of the water precursor is chosen arbitrarily for simplicity. Before this water precursor is released into the internal channels for fast diffusion out of graphite, it may undergo dissociation and return to a CO* precursor and free-moving hydrogen atoms.

(3) As mentioned before (see Secs. 2.1.3 and 5.4), methane (CH₄) also undergoes break-up due to incident oxygen ions in the O⁺-H⁺→C reaction system. This is also supported by the present result obtained for Ne⁺-H⁺ co-bombardment of pure graphite (see Sec. 5.2.4).
At the $\text{H}^+$ energy used in the present experiments, break-up due to $\text{H}^+$ does not occur [60,70,71].

(4) Although CO, CO$_2$ and H$_2$O molecules are assumed to break up by energetic O$^+$, the released oxygen from the fragmented molecule is assumed to strike the inner surfaces and react instantly with the surrounding carbon. This is supported by the absence of “spikes” in the CO, CO$_2$ and H$_2$O signals when the O$^+$ beam is turned off, in addition to the absence of oxygen re-emission. For simplicity, the rate of break-up is assumed to be the same as the rate of re-formation and the ratios of CO, CO$_2$ and H$_2$O are assumed to be unchanged during the break-up and re-formation processes.

### 6.2 Differential Equations

For ease of analysis, all concentrations (and implantation rates) given below will be given in ratios of hydrogen to carbon concentrations (i.e., H/C). Thus, the rate coefficients all have the unit (1/s), as well as the hydrogen ion implantation profile $S_I^H(x)$ and the hydrogen ion-induced de-trapping profile $S_D^H(x)$. These rate profiles are respectively derived from ion depth profiles and ion damage profiles computed from the TRVMC code [121], and normalized to the incoming fluxes before being converted to hydrogen per carbon atom per second. The fluxes of the reaction products naturally have the unit (m/s). Multiplication by $N_c$, where $N_c$ is the atomic density of graphite, will yield the common unit (m$^{-2}$s$^{-1}$).

According to the assumptions stated in Sec. 6.1, a system of rate equations is formulated to describe the behaviour of various reaction products in the O$^+$-$\text{H}^+$→C system. The total hydrogen concentration $H$ at a certain time $t$ and depth $x$ in graphite is given by

$$H(x,t) = H_C(x,t) + H_P(x,t) + H_S(x,t), \quad \text{Eq. 6-1}$$

where $H_C$ is the hydrogen concentration in the graphite crystallite, $H_P$ is the trapped hydrogen concentration in the form of CH* precursors on the edge of the crystallites, and $H_S$ is the mobile or surface hydrogen concentration on the internal surfaces. The total concentration of oxygen $O$ at time $t$ and depth $x$ in graphite is given by

$$O(x,t) = O_C(x,t) + O_P(x,t) + W_P(x,t), \quad \text{Eq. 6-2}$$

where $O_C$ is the oxygen concentration in the crystallite, $O_P$ is the oxygen concentration in the CO* precursors (or to put it another way, it is simply the CO* precursor concentration) on the internal surfaces, and $W_P$ is the oxygen concentration in the CH$_2$O* precursors (again it is simply
the CH$_2$O* precursor concentration) on the internal surfaces. The total active carbon concentration for reaction with hydrogen, $C_a^H$, at the edge of the crystallite at time $t$ and depth $x$ is given by

$$C_a^H(x,t) = C_o^H(x,t) + C'_f(x,t),$$

Eq. 6-3

where $C_o^H$ and $C'_f$ are the concentration of occupied (with trapped hydrogen) and free (with available bonds) carbon sites at the edge of the crystallites, respectively. The total active carbon concentration for reaction with oxygen, $C_a^O$, on the internal surfaces at time $t$ and depth $x$ is given by

$$C_a^O(x,t) = C_o^O(x,t) + C'_f(x,t),$$

Eq. 6-4

where $C_o^O$ and $C'_f$ are the concentration of occupied (with trapped oxygen) and free (with available bonds) carbon sites on the internal surfaces, respectively.

### 6.2.1 Rate Coefficients

All rate coefficients are assumed to obey the Arrhenius equations of the form:

$$k = K \exp\left(-\frac{E_{act}}{\kappa T}\right),$$

Eq. 6-5

where $K$ is the pre-exponential factor, $E_{act}$ is the activation energy, $\kappa$ is Boltzman's constant, and $T$ is the temperature. For the dissociation rate coefficients $k_D$, $k_{DH_2O}$, $k_{CO}$, and $k_{dCO}$ ion desorption is accounted for by including an extra term:

$$k_i = (S_D^H(x) + S_D^O(x))\delta_i + K_i \exp\left(-\frac{E_{act}}{\kappa T}\right).$$

Eq. 6-6

where $S_D^H$ and $S_D^O$ are the ion-induced de-trapping rates for the incoming hydrogen and oxygen ions, respectively, and $\delta_i$ is the probability of an ion-induced desorption event and is assumed to be unity.

### 6.2.2 Hydrogen in the Crystallite

When oxygen and hydrogen ions are incident on a carbon target, the hydrogen concentration in the graphite crystallite varies with time and depth according to the following rate equation:
where $S_i^{H}$ is the incident hydrogen implantation rate; $k_{CH}$ is the rate coefficient for CH* precursor formation (i.e., H trapping), $k_D$ the rate coefficient for CH* precursor dissociation (i.e., H de-trapping), $k_S$ the rate coefficient for hydrogen transport out of the graphite crystallite, $k_{CH}$ the rate coefficient for volatile CH$_3$ radical formation due to hydrogen from the crystallite, and 'b' an arbitrary power factor for CH$_3$ formation. This equation is graphically illustrated in Fig. 32. Incident energetic hydrogen atoms after losing their energy via collisions, enter a crystallite at the end of their 'range', and are assumed to travel instantaneously to the crystallite edge, where they may undergo one of several reactions. (i) They may be trapped by free available carbon sites at the edge and form CH* precursors (shown as a solid circle), or (ii) they may leave the crystallite and enter the internal surfaces; and finally, (iii) two hydrogen atoms from the crystallite may react with a CH* precursor (shown as shaded circles) to form a CH$_3$ radical which is immediately released into the internal channel.

\[
\frac{\partial H_c(x,t)}{\partial t} = S_i^{H}(x) - k_{CH} H_c(C_a^{H} - H_p) - k_S H_c - 2(k_{CH}, H_p H_c^b) + k_D H_p, \quad \text{Eq. 6-7}
\]

6.2.3 Trapped Hydrogen

The trapped hydrogen concentration at the edge of the crystallite in the form of CH* precursors varies with time and depth according to the following rate equation:

\[
\frac{\partial H_p(x,t)}{\partial t} = k_{CH} H_c(C_a^{H} - H_p) - k_D H_p - (k_{CH}, H_p H_c^b), \quad \text{Eq. 6-8}
\]

where $k_{CH}$ is the rate coefficient for CH* precursor formation (i.e., H trapping) due to hydrogen in the crystallite. When one observes Fig. 32 from the point of view of the CH* precursors (illustrated by the shaded circles) at the edge of the crystallite, they may be populated by trapping hydrogen from the crystallite with an available carbon site (illustrated by a black circle). These precursors can depopulate by H de-trapping, releasing hydrogen back into edge of the crystallite. They can also depopulate by taking on two more hydrogen atoms from the crystallite and form volatile CH$_3$ radicals, which are released into the internal channels.

6.2.4 Mobile Hydrogen on the Internal Surfaces

The mobile hydrogen concentration on the internal surfaces varies with time and depth according to the following rate equation:
where $S_f^O$ is the incident oxygen implantation rate; $\Delta_s$ is the rate coefficient for internal surface diffusion, $k_{ss}$ the rate coefficient for hydrogen recombination, $k_{CH_2O}$ the rate coefficient for water precursor $CH_2O^*$ formation due to hydrogen from inner surfaces, and $k_{DH_2O}$ the rate coefficient for dissociation of the water precursor. The collisional term includes the probability $p_B$ for methane (CH$_4$) break-up due to incident O$^+$; breakup due to H is assumed not to occur. This term also includes the reaction probability $p_{CH_4}$ for the formation of CH$_4$ by H attachment to CH$_3$ volatiles. The value of $p_{CH_4}$ is assumed to be unity, while $p_B$ will be determined by parameter fitting. Fig. 33 illustrates the processes described in this rather complicated equation. Hydrogen atoms on the inner surfaces are populated by hydrogen leaving the crystallite and hydrogen atoms released from dissociated water precursors and CH$_4$ broken up via incident O$^+$ impact. They may be depopulated by several mechanisms: (i) they may undergo surface diffusion; (ii) they may form CH$_4$ by H attachment to CH$_3$ radicals; (iii) they may undergo recombination and form hydrogen molecules; and (v) they may form water precursors by combining with CO$^*$ precursors (illustrated by light shaded circles) on the inner surfaces, involving hydrogen purely from the inner surfaces.

### Eq. 6-9

\[
\frac{\partial H_s(x,t)}{\partial t} = k_s H_c \frac{\partial}{\partial x} \left[ \Delta_s \frac{\partial H_s}{\partial x} \right] - 2k_{ss} H_s^2 - \sigma_{CH_4} (k_{CH_3} H_p H_c^b) \]

\[+ 4 p_B \frac{S_f^O}{S_f^H} p_{CH_4} (k_{CH_3} H_p H_c^b) - 2k_{CH_2O} H_s^2 O_p + 2k_{DH_2O} W_p ,
\]

6.2.5 **Oxygen Concentrations**

Now let us examine the rate equations for the oxygen and carbon (in the form of CO$^*$) concentrations. These oxygen concentrations in the graphite crystallite vary with time and depth according to the following rate equations:

**Eq. 6-10**

\[
\frac{\partial O_c(x,t)}{\partial t} = S_f^O (x) - k_{CO_a} O_c (C_a - O_p) - k_{CO} O_c O_p + k_{dCO} O_p ,
\]

**Eq. 6-11**

\[
\frac{\partial O_p(x,t)}{\partial t} = k_{CO_a} O_c (C_a - O_p) - k_{CO} O_c O_p - k_{CO_2} O_c O_p - k_{dCO} O_p - k_{CH_2O} H_s^2 O_p + k_{DH_2O} W_p ,
\]

where $k_{CO_a}$ is the rate coefficient of CO$^*$ precursor formation at the edge of the crystallite, $k_{CO}$ the rate coefficient for the release of volatile CO molecules, $k_{CO_2}$ the rate coefficient for the
release of volatile CO₂ molecule, and \( k_{\text{dCO}} \) the rate coefficient for the dissociation of CO precursors. Essentially, implanted oxygen enters the graphite crystallite and is assumed to transport immediately to the edge and form CO* precursors, subject to the availability of the carbon sites. The CO* concentration is populated by oxygen atoms arriving from the crystallite. It can be depopulated by one of the several mechanisms: (i) dissociation of CO* by de-trapping the oxygen back into the crystallite; (ii) leaving the inner surfaces as volatile CO molecule, (ii) further reaction with oxygen to form volatile CO₂, and (iii) reacting with hydrogen from the inner surfaces to form water precursors, which will either become volatile and be released into the channel or will be dissociated. These processes are schematically shown in Fig. 34. The concentration of water precursors in the form of CH₂O* is given by the following rate equation:

\[
\frac{dW_p}{dt} = k_{\text{CH₂O}} H_s^2 O_p - k_{\text{H₂O}} W_p - k_w W_p,
\]

where \( k_w \) is the rate coefficient for the release of water molecules into the internal channels.

### 6.2.6 Active Carbon Sites

Explanation is required for the \((C_a^H - H_p)\) and \((C_a^O - O_p)\) terms. These are essentially \( C_f \) terms, the available active carbon sites, the free sites left after the formation of CH* and CO* precursors (represented by \( H_p \) and \( O_p \) concentrations). Any trapping of hydrogen or oxygen can only occur at these unoccupied or free sites. In reality, the number of CH* precursors will affect the number of active sites for CO* precursor formation, and vice versa. However, in order to simplify calculations, it is assumed that oxygen and hydrogen trapping sites are separate and independent based on the assumption that the oxygen and hydrogen trapping sites are at different energy levels (see Secs. 6.1.2 and 6.1.3). The occupied sites may become free again via de-trapping, or when the precursors become volatile (via further reactions with hydrogen or oxygen, forming CH₃, CO, CO₂, or H₂O) and leave the trapping site, freeing a carbon bond. This is implicitly described in the terms as the reduction of the \( H_p \) and \( O_p \) precursor concentrations, leading to increases of the \( C_f \) concentrations. The total active carbon site concentration \( C_a \) will increase from the initial intrinsic trapping site concentration in bulk graphite to a maximum value \( C_{a_{\text{max}}} = \frac{1}{v_0} \), where \( v_0 \) is the atomic saturation volume of the traps. The rate of trapping site generation will eventually become zero at steady state. This is given by the rate equation [10]:

\[
\frac{\partial C_a(x,t)}{\partial t} = (S_f^O(x) + S_f^H(x))(1 - v_0 C_a)^2,
\]
where $S^O_T$ and $S^H_T$ are the trap generation functions for incoming oxygen and hydrogen, and $C_{a}^{\text{max}}$ has a value of 0.42 traps/C for hydrogen and 0.25 traps/C for oxygen, corresponding to the saturation $H/C$ and $O/C$ concentrations at 300 K [5,10].

### 6.2.7 Steady-State Equations

We will make a simplifying assumption and consider the $O^\cdot-\text{H}^\cdot\rightarrow\text{C}$ reaction system only in steady state. This assumption is naturally valid as most experiments described previously have been performed in steady-state operation. Assuming steady state, all the time varying terms are zero and the rate equations reduce to the following system of non-linear equations:

\begin{align*}
0 &= S^H_I(x) - k_{CH} H_C (C_a^H - H_P) - k_s H_C - 2(k_{CH} H_p H_C^b) + k_p H_P, & \text{Eq. 6-14} \\
0 &= k_{CH} H_C (C_a^H - H_P) - k_{CH} H_P - (k_{CH} H_p H_C^b), & \text{Eq. 6-15} \\
0 &= k_s H_C - \frac{\partial}{\partial x} \left( \Delta_s \frac{\partial H_s}{\partial x} \right) - 2k_{ss} H_s^2 - \sigma_{CH_4} (k_{CH} H_p H_C^b) \\
&\quad + 4 p_b \frac{S^0_I}{S^H_I} P_{CH_4} (k_{CH} H_p H_C^b) - 2k_{CH_2O} H_s^2 O_p + 2k_{DH_2O} W_p, & \text{Eq. 6-16} \\
0 &= S^O_I(x) - k_{CO} O_C (C_a^O - O_P) - k_{CO_2} O_C O_P + k_{dCO} O_P, & \text{Eq. 6-17} \\
0 &= k_{CO} O_C (C_a^O - O_P) - k_{CO} O_P - k_{CO_2} O_C O_P - k_{dCO} O_P - k_{CH_2O} H_s^2 O_P + k_{DH_2O} W_p, & \text{Eq. 6-18} \\
0 &= k_{CH_2O} H_s^2 O_P - k_{DH_2O} W_P - k_{w} W_P. & \text{Eq. 6-19}
\end{align*}

The flux equations for the released products can be computed by integrating the appropriate terms from the above equations:

\begin{align*}
J_{H_2} &= k_{ss} \int_0^{R_H} H_s^2 dx, & \text{Eq. 6-20} \\
J_{CH_4} &= (1 - p_b S^O_I) P_{CH_4} k_{CH} H_p H_C^b dx, & \text{Eq. 6-21} \\
J_{CO} &= k_{CO} \int_0^{R_O} O_P dx, & \text{Eq. 6-22} \\
J_{CO_2} &= k_{CO_2} \int_0^{R_O} O_C O_P dx, & \text{Eq. 6-23} \\
J_{H_2O} &= k_{w} \int_0^{R_O} W_P dx, & \text{Eq. 6-24}
\end{align*}
where \( J_X \) is the flux for reaction product \( X \); \( R_H \) and \( R_O \) are the hydrogen and oxygen ion ranges, respectively. The formulation for the steady-state model of the \( O^+ - H^+ \rightarrow C \) reaction system is thus complete.

### 6.3 Model Calculations and Discussions

At this point, it will be necessary to apply the model to a few simpler special cases in which the parameter fitting process can be simplified. The full model will then utilize the parameters derived from the special cases in order to derive the remaining parameters. Two special cases are considered: (i) \( H^+ \)-only, and (ii) \( O^+ \)-only cases. By reducing the equations to apply to single-beam cases of single incident species, the number of parameters to be fitted with available experimental data becomes manageable. It turns out that equations for both cases can all be analytically solved. However, these seemingly simple equations have solutions that are much too complicated and lengthy to list here. In fact, it is much easier to solve them using numerical methods. This thesis uses the software package “Mathcad 7.0” by Mathsoft, Inc. to perform the necessary numerical analysis. Detailed programming and calculations are presented in the appendices.

#### 6.3.1 Special Case (1): \( H^+ \rightarrow C \)

In this case, there is no \( O^+ \) implantation, and all terms containing \( O_C \) and \( O_P \) can be removed from the equations. For simplicity, the energy-dependent hydrogen implantation profile is assumed to have a square distribution using the average depth \( (x_H) \) and standard deviation \( (\sigma_H) \) of the penetration depth as calculated by TRVMC [121], i.e.,

\[
S_I^H(x) = \begin{cases} \frac{\Phi_H}{N_C 2\sigma_H}, & (x_H - \sigma_H) < x < (x_H + \sigma_H) \\ 0 & x < (x_H - \sigma_H) \text{ or } x > (x_H + \sigma_H) \end{cases}
\]

\[\text{Eq. 6-25}\]

where \( S_I^H(x) \) is the hydrogen implantation distribution (in the unit of \( s^2 \)); \( \Phi_H \) is the incident hydrogen flux (in the unit of \( m^{-2}s^{-1} \)); and \( N_C \) is the atomic density of graphite (in the unit of \( m^{-3} \)). The ion-induced de-trapping rate \( S_D^H(x) \) (used in the calculation of \( k_D \)) was estimated using the total DPA (displacements per atom) calculated by TRVMC. The DPA profile is slightly shallower than the implantation distribution, though here we assume the \( S_D^H(x) \) profile to be at the same depth as the \( S_I^H(x) \) profile. The steady-state equations, Eq. 6-14 to Eq. 6-16, reduce to:
We note that in regions where \( S_i^H(x) = 0 \), the hydrogen concentrations \( H_C \) and \( H_P \) are also zero. Thus, for regions with no \( H^+ \) implantation, the rate equation for hydrogen on the internal surfaces (Eq. 6-28) becomes,

\[
0 = k_s H_C \left[ C_a^H - H_P \right] - k_H H_C - 2(k_{CH_4} H_P H_C^b) + k_B H_P,
\]

\( \text{Eq. 6-26} \)

\[
0 = k_s H_C \left( C_a^H - H_P \right) - k_{d^s} H_P - (k_{CH_4} H_P H_C^b),
\]

\( \text{Eq. 6-27} \)

\[
0 = k_s H_C - \frac{\partial}{\partial x} \left( \Delta_s \frac{\partial H_S}{\partial x} \right) - 2k_{ss} H_S^2 - p_{CH_4} (k_{CH_4} H_P H_C^b).
\]

\( \text{Eq. 6-28} \)

This implies that the mobile hydrogen does extend into the region where \( S_i^H(x) = 0 \), leading to \( H_2 \) formation here even in the absence of implanted \( H \). For simplicity, we assume the mobile hydrogen concentration \( H_S \) to be uniform throughout the entire ion range. The ratio of the contribution to the total \( H_2 \) flux between the two regions equals the ratio of the depth range of the two regions. Thus, for the region where \( S_i^H(x) \neq 0 \), Eq. 6-28 becomes

\[
0 = k_s H_C - (1 + \theta_H) 2k_{ss} H_S^2 - p_{CH_4} (k_{CH_4} H_P H_C^b),
\]

\( \text{Eq. 6-30} \)

where \( \theta_H \) is the volumetric ratio of the region where \( S_i^H(x) = 0 \) over the region where \( S_i^H(x) \neq 0 \), which when normalized over the same beam spot area becomes

\[
\theta_H = \frac{x_H - \sigma_H}{2 \sigma_H}.
\]

\( \text{Eq. 6-31} \)

The total \( H_2 \) flux (converted back to the usual unit of \( m^2 s^{-1} \)) should be integrated over the entire ion range. Here it is simplified (and converted back to the usual unit of \( m^2 s^{-1} \)) to

\[
J_{H_2} = N_c k_{ss} H_S^2 \left( x_H + \sigma_H \right).
\]

\( \text{Eq. 6-32} \)

On the other hand, the total \( CH_4 \) flux should only be integrated over the region where \( S_i^H(x) \) is not zero,

\[
J_{CH_4} = N_c p_{CH_4} k_{CH_4} H_P H_C^b (2\sigma_H).
\]

\( \text{Eq. 6-33} \)

Finally, to test the internal consistency of the model, the equation below is verified for all calculations:

\[
2J_{H_2} + 4J_{CH_4} = \Phi_H.
\]

\( \text{Eq. 6-34} \)

The values of the parameters used for this special case (\( H^+ \rightarrow C \)) are listed in Table I. The calculated temperature profiles for three hydrogen ion energies (700 eV, 1000 eV, and 3000 eV)
normalized against the incoming H\(^+\) flux, are shown in Fig. 35. The parameters, \(k_5\) and \(k_{3S}\), are fixed parameters obtained from the original Two-Region Model [10]. The parameters, \(k_{CH}, k_D, k_{CH,t}\), and \(b\), are free parameters and are derived from fitting the experimental data for the H\(^+\)→C system described in Sec. 5.1 (HPG99 pyrolytic graphite exposed to 10000 eV/H\(^+\) with a flux density of \(5\times10^{19}\) H\(^+\)/m\(^2\)s, plotted in Fig. 35). See Appendix A for sample Mathcad calculations. An iterative process was employed for parameter fitting whereby the free parameters were varied in a systematic manner (by observing their interactions on an Arrhenius plot, see Appendix A) until the calculated CH\(_4\) yields are within a specified error for at least 70\% of the experimental data points (based on \(\chi^2\) distribution). The specified error was assumed to be ±0.004 CH\(_4\)/H\(^+\) (i.e., ~5\% of the maximum CH\(_4\) yield). The reduced \(\chi^2\) value of the fit to the 1000 eV/H\(^+\) data is 0.6, indicating a reasonable good fit. The calculated profiles for the 700 and 3000 eV cases are model predictions. For comparison, ion beam data from Refs. [83,84] are also plotted in Fig. 35 for 1000 eV/H\(^+\) and 3000 eV/H\(^+\) for a flux density of \(1\times10^{20}\) H\(^+\)/m\(^2\)s.

Although the experimental data from Refs. [83,84] shown in Fig. 35 are from a different experiment and the flux density is higher, we note that the trend agrees with the model prediction that the methane yield decreases with increasing incident H\(^+\) energy for H\(^+\) energies > 700 eV. This is also consistent with the present experimental results discussed in Sec. 5.2.3 and published data [65,66], which show that the methane yield, as a function energy, has a maximum at ~500 eV. However, the experimental data on the temperature dependence of methane yield show a slight shift in \(T_m\) (location of maximum on the temperature dependence profiles) to higher temperatures as the incident energy increases, while this model predicts the opposite, though the variations are very small (within 50 K). This may be due to the underestimation of \(S_D^H(x)\) from the DPA distribution calculated by TRVMC at 3 keV/H\(^+\) incident energy compared to the lower energies. This, in turn, may lead to a lower ion-induced de-trapping estimnation for \(k_D\) at the lower temperature region, which produces higher CH\(_4\) yields at the lower-temperature region leading to a decrease of \(T_m\).

The calculated flux density dependence at various temperatures (\(T = 750\) K, 800 K, 850 K, and \(T_m\)) are plotted in Fig. 36. For comparison, the methane formation yields due to 1 keV H\(^+\) impact on graphite from ion beam experiments [83] are also shown. The reduced \(\chi^2\) of the fit to the flux profile at \(T_m\) is 0.6, also indicating a reasonable fitting. The calculated flux profiles at all other temperatures are model predictions. As shown, the H\(^+\)-only model successfully generates
the profiles of the methane yield with flux density at various temperatures with good agreement
with experimental data.

The kinetic model proposed in Refs. [83,84] (described in Sec. 2.2.2) was also based on a
similar chemical reaction mechanism that is used in the current model. However, graphite was
treated as a homogeneous solid in Refs. [83,84]. On the other hand, the current model treats
graphite as two separate regions, crystallites and internal surfaces (see the model assumptions in
Sec. 6.1). Also, as mentioned in assumption #3 in Sec. 6.1.2, the rate of the intermediate
reaction step \( \text{CH} + 2\text{H} \rightarrow \text{CH}_3 \) in the current model is assumed to be proportional to the
hydrogen concentration to an arbitrary power,

\[
\frac{dn_{\text{CH}_3}}{dt} \propto H_p H_c^b,
\]

Eq. 6-35

while the model in Refs. [83,84] assumes first-order reaction kinetics, i.e., \( b=1.0 \). From the
result of empirical fitting from the flux-dependence experimental data using the current model,
the order of the reaction is found to be \( b=0.75 \). This allows the current model to generate a flux
dependence of the methane yield that agrees very well with the experimental data (see Fig. 36).
On the other hand, the first-order reaction kinetics used in [83] required separate fittings for the
high and low flux density cases. The non-integral order of the reaction indicates that from the
\( \text{CH}^* \) precursor stage, the addition of remaining hydrogen atoms (from the crystallite) to form
\( \text{CH}_3 \) may be a complex multi-step process, resulting in the observed non-linear flux dependence
of the methane yield. The true nature of this process, however, is not obvious from the arbitrary
reaction order \( b \), which is determined purely from experimental fitting.

In the current model, the activation energies in the rate coefficients are assumed to be
independent of the \( \text{H}^*-\text{implantation energy} \), which is what we would expect for thermally
activated chemical processes. Only ion-induced desorption, which was estimated using the
resulting DPA from implantation, was included in \( k_D \). Thus, all energy dependence on the
calculated \( \text{CH}_4 \) yield comes entirely from the average depth \( (x_H) \) and standard deviation \( (\sigma_H) \)
of the penetration depth and the DPA, which all vary with implantation energy according to
TRVMC simulations. Any inaccuracy in the TRVMC estimation on the energy dependence of
the implantation profile will influence the energy dependence of the magnitude of maximum
\( \text{CH}_4 \) yield \( (Y_m) \). Any inaccuracy in the estimation of the energy dependence of the DPA will
influence the shifting in the temperature where the maximum \( \text{CH}_4 \) yield occurs \( (T_m) \). As shown
above, TRVMC estimation of increasing \( x_H \) and \( \sigma_H \) with implantation energy (which translates to
a lower concentration of source hydrogen per carbon atom) results in the correct trend of
decreasing $Y_m$ with increasing implantation energy (for energies greater than 700 eV). On the other hand, the change of the magnitude of the DPA with implantation energy as estimated by TRVMC leads to a small ($\sim 50$ K) shift of $T_m$; the shift, however, is in a direction opposite to that observed in experiments [65,66].

Finally, a limitation of the current model is the simplifying assumption that volatile CH$_3^*$ radicals released into the internal channel instantly lead to the formation of CH$_4$ by picking up a mobile hydrogen from the internal surfaces, rather than allowing for another rate-determining step with an additional rate coefficient, i.e.,

$$\frac{dn_{CH_s}}{dt} = k_{CH_s} n_{CH_s} H_s.$$  \text{Eq. 6-36}

The consequence of this simplification is that the rate of CH$_4$ formation does not depend on the concentration of the mobile hydrogen. This, however, appears not to be the case in boron-doped graphite. According to the hypothesis discussed in Sec. 5.4.2, the inclusion of boron impurity in graphite enhances the recombination of hydrogen on the internal surfaces. In terms of the current model this may translate to a higher prefactor or higher activation energy in $k_{SS}$, resulting in an increase in H$_2$ production at temperatures greater than 800 K. This will then lead to a lower H$_S$ concentration, and consequently to a lower CH$_4$ production at higher temperatures, as evident from the experimental data in Fig. 2. For future studies, extension to the current model, with the inclusion of Eq. 6-36, may be used to model the behaviour of the H$^+\rightarrow$C/B and O$^+\rightarrow$H$^+\rightarrow$C/B reaction systems.

### 6.3.2 Special Case (2): O$^+\rightarrow$C

In this case, there is no H$^+$ implantation, and all terms containing $H_C$, $H_P$, and $H_S$ drop out. Again, for simplicity, the energy-dependent oxygen implantation profile is assumed to have a square distribution using the average depth ($x_0$) and standard deviation ($\sigma_0$) of the penetration depth as calculated by TRVMC [121], i.e.,

$$S^O_i(x) = \begin{cases} \frac{\Phi_o}{N_c 2\sigma_o}, & (x_0 - \sigma_0) < x < (x_0 + \sigma_0) \\ 0, & x < (x_0 - \sigma_0), x > (x_0 + \sigma_0) \end{cases}$$  \text{Eq. 6-37}

where $S^O_i(x)$ is the oxygen implantation profile, $\Phi_o$ is the incident oxygen flux, and $N_c$ is the atomic density of graphite. The ion-induced de-trapping rate $S^O_i(x)$ (used in the calculations for
The calculated temperature profiles for the CO and CO₂ yield at 5 keV/O⁺, normalized against the O⁺ flux, are shown in Fig. 37. The parameters, \( k_{CO}, k_{dCO}, k_{CO}, \) and \( k_{CO₂} \), are free parameters, derived from fitting the O⁺→C experimental results presented in Sec. 5.1 (HPG99 pyrolytic graphite exposed to 5 keV/O⁺ with a flux density of \( -10^{19} \) H⁺/m²s, plotted in Fig. 37). The same iterative parameter fitting procedure used for the H⁺→C case was employed. Due to the large scatter of the data, specified errors of ±0.135 CO/O⁺ (~20% of the average CO yield) and ±0.035 CO₂/O⁺ (~20% of the maximum CO₂ yield) were assumed. We note that the fit is reasonably good, considering the fact that the temperature dependence of both the CO and CO₂ yields needs to be accounted for. The reduced \( \chi^2 \) values for the fit are 0.6 for the CO yields and 0.7 for the CO₂ yields, both indicating reasonable fitting. Furthermore, due to the weak temperature dependence observed in the experiments, the activation energies found here for the coefficients are all very small compared to those obtained for the H⁺-only case. See Appendix B for sample Mathcad calculations.

The calculated flux density dependence at \( T = 800 \) K, based on the parameters in Table II, is shown in Fig. 38 for both CO and CO₂. No experimental flux dependence data are available for comparison. However, the model predicts little flux dependence in the carbon erosion yield, indicating a much higher reactivity of oxygen ions in graphite. Finally, as in the H⁺-only case, the internal consistency of the model is tested in all calculations by verifying the flux equation below:

\[
J_{CO} + 2J_{CO₂} = \Phi_o .
\]  

Eq. 6-42
6.3.3 Case (3): Simultaneous O\textsuperscript{+}-H\textsuperscript{+}→C

When both H\textsuperscript{+} and O\textsuperscript{+} implantations occur simultaneously, and again assuming square distributions for both \(S_I^H(x)\) and \(S_I^O(x)\), the steady-state equations, Eq. 6-14 to Eq. 6-19, become:

\[
0 = S_I^H(x) - k_{CH} H C (C_a^H - H_p) - k_s H C - 2(k_{CH}, H_p H C^b) + k_p H_p, \quad \text{Eq. 6-43}
\]

\[
0 = k_{CH} H C (C_a^H - H_p) - k_p H_p - (k_{CH}, H_p H C^b), \quad \text{Eq. 6-44}
\]

\[
0 = k_s H C - (1 + \theta_H) 2k_{sH} H S^2 - (1 - 4\theta_{dia} P_H \frac{S_I^O}{S_I^H}) p_{CH}^2 (k_{CH}, H_p H C^b) \nonumber \\
- \theta_{dia} \theta_{OH} (2k_{CH,O} H S^2 O_P - 2k_{DH,O} W_P), \quad \text{Eq. 6-45}
\]

\[
0 = S_I^O(x) - k_{CO} O C (C_a^O - O_P) - k_{CO} O C O_P + k_{dCO} O_P, \quad \text{Eq. 6-46}
\]

\[
0 = k_{CO} O C (C_a^O - O_P) - k_{CO} O C O_P - k_{dCO} O_P - k_{CH,O} H S^2 O_P + k_{DH,O} W_P, \quad \text{Eq. 6-47}
\]

\[
0 = k_{CH,O} H S^2 O_P - k_{DH,O} W_P - k_w W_P, \quad \text{Eq. 6-48}
\]

and the flux calculations Eq. 6-20 to Eq. 6-24 become:

\[
J_{H_3} = N_c k_{sH} H S^2 (x_H + \sigma_H) \quad \text{Eq. 6-49}
\]

\[
J_{CH_4} = (1 - \theta_{dia} P_H S_I^O) N_c p_{CH_4} k_{CH_4} H P H C^b (2\sigma_H), \quad \text{Eq. 6-50}
\]

\[
J_{CO} = N_c k_{CO} O_P (2\sigma_O), \quad \text{Eq. 6-51}
\]

\[
J_{CO_2} = N_c k_{CO_2} O C O_P (2\sigma_O), \quad \text{Eq. 6-52}
\]

\[
J_{H_2O} = N_c k_w W_P (2\sigma_O). \quad \text{Eq. 6-53}
\]

We can see that the equations for the H\textsuperscript{+}-only and O\textsuperscript{+}-only cases are linked together by the synergistic water production equation Eq. 6-48. The constant mobile hydrogen concentration \(H_S\) across the entire H\textsuperscript{+} ion range allows hydrogen to react with CO\textsuperscript{*} precursors to form water. As the water production occurs only in the region where CO\textsuperscript{*} is not zero (i.e., within the implantation width of \(2\sigma_O\) in the region where \(S_I^O(x) \neq 0\)), the amount of the mobile hydrogen atoms used for water production must be adjusted by the ratio \(\sigma_O/\sigma_H\) because the hydrogen balance calculation in Eq. 6-45 is based on the implantation width of \(2\sigma_H\) in the region where \(S_I^H(x) \neq 0\). Furthermore, the ratio of the O\textsuperscript{+} and H\textsuperscript{+} beam spots must be taken into account as well. Thus, the ratios \(\theta_{dia}\) and \(\theta_{OH}\) in Eq. 6-45 can be calculated as

\[
\theta_{OH} = \frac{\sigma_O}{\sigma_H}, \quad \text{Eq. 6-54}
\]
where $d_O$ and $d_H$ are the diameters of the beam spots for O\textsuperscript{+} and H\textsuperscript{+}, respectively. Essentially, the product $\theta_{dia} \theta_{OH}$ is the ratio of the implantation volumes of the incoming O\textsuperscript{+} and H\textsuperscript{+} beams.

Furthermore, it should be noted that when the H\textsuperscript{+} and O\textsuperscript{+} ion ranges overlap, the contribution of O\textsuperscript{+} to the collisional component of the coefficient $k_D$, and the contribution of H\textsuperscript{+} to the collisional components of the coefficients $k_{DH_2O}$, $k_{CO}$, and $k_{dCO}$ must be taken into account. This is estimated based on a simple volumetric ratio $\theta_{mix}^i$ of the overlapped region to the region where $S_H^i(x) \neq 0$, i.e., the coefficient $k_D$ has the form (assuming $R_H > R_O$ and both ion ranges have a square distribution):

$$k = (S_D^H + \theta_{mix}^O S_D^O) + K \exp\left(\frac{E_{acc}}{kT}\right),$$

Eq. 6-56

where

$$\theta_{mix}^O = \begin{cases} \frac{\theta_{dia} x_O + \sigma_O - (x_H - \sigma_H)}{2\sigma_H} & \text{if \ overlapping} \\ 0 & \text{if \ separated} \end{cases}$$

Eq. 6-57

similarly, $k_{DH_2O}$, $k_{CO}$, and $k_{dCO}$ have the form:

$$k = (S_D^O + \theta_{mix}^H S_D^H) + K \exp\left(\frac{E_{acc}}{kT}\right),$$

Eq. 6-58

where

$$\theta_{mix}^H = \begin{cases} \frac{1}{\theta_{dia}} \frac{x_O + \sigma_O - (x_H - \sigma_H)}{2\sigma_O} & \text{if \ overlapping} \\ 0 & \text{if \ separated} \end{cases}$$

Eq. 6-59

Finally, we note that the methane flux term in Eq. 6-50 now contains a break-up term in addition to the methane formation term for the H\textsuperscript{+}-only case (Eq. 6-33). To estimate the methane break-up due to O\textsuperscript{+} bombardment, it is assumed that the break-up is directly proportional to $S_H^O(x)$, normalized to $S_H^H(x)$, and adjusted for the beam spot area ratio and a break-up probability, $p_B$, which is determined by fitting.

As mentioned in the beginning of Sec. 6.3, the parameters determined from the H\textsuperscript{+}-only and O\textsuperscript{+}-only cases were applied to the simultaneous O\textsuperscript{+}-H\textsuperscript{+}→C case. However, additional parameters needed for the simultaneous O\textsuperscript{+}-H\textsuperscript{+}→C case were also derived by fitting to
synergistic experimental data for one set of energy and flux; these parameters are listed in Table III. See Appendix C for sample Mathcad calculations.

The calculated temperature dependence profiles for CO and CO$_2$ during O$^+$→C and simultaneous O$^+$-H$^+$→C cases are shown in Fig. 39, while H$_2$O yields during simultaneous O$^+$-H$^+$→C cases are shown in Fig. 40. The calculated temperature dependence profiles for CH$_4$ yields during H$^+$→C and simultaneous O$^+$-H$^+$→C cases are shown in Fig. 41. Model calculations were performed for $\sim 1 \times 10^{19}$ O$^+$/m$^2$s (5 keV/O$^+$) and $\sim 5 \times 10^{19}$ H$^+$/m$^2$s (1 keV/H$^+$). Experimental data for the same conditions from Sec. 5.1 are also plotted. The rate coefficients for the water precursor formation, water precursor dissociation, and water molecule release were chosen by fitting the H$_2$O yield data (see Fig. 40), while the resulting CO and CO$_2$ yield reductions are model predictions. The same iterative parameter fitting procedure was employed as before, with a specified error of ±0.03 H$_2$O/O$^+$ (~20% of the maximum water yield) assumed. The reduced $\chi^2$ for fitting the water temperature profile (at 1 keV/H$^+$ and 5 keV/O$^+$) is 0.6, indicating a reasonable fitting. From the figures, we can see that the model agrees reasonably well with the experimental data, except for CO yields in the O$^+$-H$^+$→C case.

To investigate further this discrepancy, the ratios of the CO$_2$ yields over CO yields (CO$_2$/CO), both experimental data and model calculations, are plotted in Fig. 42. Note the slight discrepancy between the experimental data and model calculations. The experimental data suggest that the yield ratios (CO$_2$/CO) for O$^+$→C and simultaneous O$^+$-H$^+$→C cases are very similar within the scatter of the data over the temperature range studied. This means that the proportions of the yield reductions for both CO and CO$_2$ yields are about the same. The model calculations, however, show a different trend. From Fig. 42 it is clear that the calculated yield ratio (CO$_2$/CO) for the simultaneous impact case is considerably lower than for the O$^+$→C case for most of the temperature range, except at high temperatures (> 1100K) where they are similar. For both the O$^+$-H$^+$→C and O$^+$→C cases, the calculated ratio curves have maxima at around 800 K, which coincide with the maximum for the water yields (Fig. 40). There are two possible reasons for this slight discrepancy. The treatment of the mechanisms in the model for the chemistry of CO, CO$_2$ and H$_2$O formation may have contributed to the discrepancy. For example, there may be an additional mechanism for CO and CO$_2$ production at lower temperatures, which was not taken into account in the present model. Secondly, the large scatter of the experimental data for the temperature dependence plot may not have sufficiently revealed the finer details as the model has done.
Fig. 43 shows the predicted dependence of the \( \text{H}_2\text{O} \) yield on the flux ratio \( \Phi_0/\Phi_H \) for the simultaneous \( \text{O}^+\text{-H}^+\rightarrow\text{C} \) case at 800 K for three range ratios \( R_H/R_O = 1.2, 1.7, \) and 4.4 for overlapping, partial overlapping, and complete separation cases. Experimental results from Sec. 5.2.3 are also plotted for comparison. As in the experiments, the \( \text{O}^+ \) energy and the flux were fixed while the \( \text{H}^+ \) energy and the flux were varied to produce different flux and range ratios. The predicted flux ratio dependence agrees reasonably well with the experimental data (within the experimental uncertainties), showing a trend of decreasing \( \text{H}_2\text{O} \) yield with increasing \( \text{O}^+/\text{H}^+ \) flux ratio. Model prediction shows that at low flux ratios \( (\Phi_0/\Phi_H \sim 1\%) \), most of the implanted oxygen takes part in water formation. Furthermore, although it is not evident in the experimental data due to the experimental uncertainties, the model also predicts range-separation dependence, i.e., overlapping cases result in slightly higher water yields for \( \Phi_0/\Phi_H > 5\% \). From the equations, it is evident that in the overlapping cases the shallower hydrogen implantation results in a higher concentration of mobile hydrogen atoms on the internal surfaces, as the mobile hydrogen atoms do not diffuse and extend over a relatively larger region associated with the separated case. This leads to a higher water production (which depends on the square of the mobile hydrogen concentration) in the overlapping cases. For \( \Phi_0/\Phi_H < 5\% \), the effect of water precursor dissociation due to \( \text{H}^+\)-impact begins to dominate when the ranges are overlapping and the relative supply of mobile hydrogen is higher, leading to a predicted lower water production and a reverse range-separation dependence.

The corresponding \( \text{CO} \) and \( \text{CO}_2 \) yield reductions due to water formation are compared with the experimental results (from Sec. 5.2.3) in Fig. 44 and Fig. 45, respectively. The percentage reduction is calculated as: \( R[\%] = 100 \times (Y_O - Y_{O+H})/Y_O \), where \( Y_O \) is the \( \text{CO} \) or \( \text{CO}_2 \) yield for the \( \text{O}^+\rightarrow\text{C} \) case and \( Y_{O+H} \) is the \( \text{CO} \) or \( \text{CO}_2 \) yield for the simultaneous \( \text{O}^+\text{-H}^+\rightarrow\text{C} \) case. Again, the calculated trend of decreasing \( \text{CO} \) and \( \text{CO}_2 \) yield reductions with increasing \( \text{O}^+/\text{H}^+ \) flux ratio is evident and the profiles agree reasonably well with experimental data, within experimental uncertainties. However, some discrepancy is noted in the \( \text{CO} \) and \( \text{CO}_2 \) yield reductions when compared with the experimental data. Furthermore, the predicted range separation dependence for both \( \text{CO} \) and \( \text{CO}_2 \) yield reductions seems to be more prominent, especially for \( \text{CO}_2 \). Possible explanations for the discrepancy were discussed above.

Finally, the predicted flux ratio dependence of the methane yield reduction at 800 K due to the methane break-up effect is plotted in Fig. 46. The percentage reduction is calculated according to the formula: \( R[\%] = 100 \times (Y_H - Y_{O+H})/Y_H \), where \( Y_H \) is the \( \text{CH}_4 \) yield for the \( \text{H}^+\rightarrow\text{C} \)
case and $Y_{O^+\textit{H}}$ is the CH$_4$ yield for the simultaneous O$^+$-H$^+$→C case. The experimental results from Sec. 5.2.3 are also plotted.

For all of the above calculations in the simultaneous O$^+$-H$^+$→C case, the methane break-up probability, $p_B$, was fixed to be 0.5. This choice produces a good agreement with the methane yield reduction from the experimental results. [Using $p_B=1$ increases the yield reduction by a factor of two]. In physical terms, $p_B=0.5$ means that only half of the incoming O$^+$ will encounter and break up methane molecules in the graphitic internal channels as they travel towards the geometric surface. The model predicts a trend of increasing CH$_4$ yield reduction with increasing O$^+$/H$^+$ flux ratio, which agrees well with experimental results. The model also predicts a dependence on range separation, where overlapping cases result in a slightly higher methane yield reduction. For flux ratios ($\Phi_O/\Phi_H$) at and below 30%, this trend seems to agree with the experimental results, although it is still inconclusive due to the large experimental uncertainties.

However, the same trend was also observed in simultaneous Ne$^+$-H$^+$→C reactions (see Sec. 5.2.4), where we also saw a higher CH$_4$ yield reduction for the beam-overlapping case. Furthermore, in simultaneous O$^+$-H$^+$→C/B reactions (see Sec. 5.3), we see that the resulting methane increase for the beam-overlapping case is smaller. Assuming the effect of boron is independent of beam-separation, this implies that the CH$_4$ yield reduction due to the presence of oxygen is higher for the beam-overlapping case. Since the present model applies the methane break-up (whether it is due to O$^+$ or Ne$^+$) uniformly for the methane molecules in the entire H$^+$ range, it is clear that the slight increase of methane yield reduction for the range overlapping cases is due to an increase in the hydrogen de-trapping rate coefficient, $k_D$ (see equations Eq. 6-56 to Eq. 6-59), owing to O$^+$-induced desorption. Therefore, the more the ranges overlap, the more the O$^+$-induced hydrogen de-trapping will occur, leading to more reduction of CH$_4$ yields.

### 6.4 Summary

In summary, a comprehensive kinetic model based on the two-region and precursor concepts was presented for the O$^+$-H$^+$→C reaction system. A detailed system of space-time-varying partial differential equations was formulated, including chemical and collisional processes for both H$^+$→C and O$^+$→C reactions, and synergistic effects such as methane break-up and water formation for the O$^+$-H$^+$→C reaction. A steady-state version was used for computation. The steady-state version was further simplified and reduced to single beam cases,
where some of the rate coefficients were determined via fitting to experimental data. With the derived coefficients, model predictions were made for flux and energy dependence, and generally good agreement with experimental results was seen for both \( \text{H}^+ \rightarrow \text{C} \) and \( \text{O}^+ \rightarrow \text{C} \) reactions. For \( \text{O}^+ - \text{H}^+ \rightarrow \text{C} \) reaction, the model agrees quite well with the flux ratio-dependence of \( \text{H}_2\text{O} \) yield, the resulting \( \text{CO} \) and \( \text{CO}_2 \) yield reduction, and the \( \text{CH}_4 \) yield reduction. However, the model predicts dependence on range-separation, which is unable to be conclusively verified by the experiment due to large experimental uncertainties.
7. CONCLUSIONS

This thesis was undertaken with the objective to investigate the interaction of energetic H$^+$ and O$^+$ with graphite. The work includes experimental studies and modelling of the reaction kinetics.

Reaction products and synergistic effects in the H$^+$-O$^+$→C reaction system were identified experimentally. H$_2$O is the main synergistic reaction product, which is temperature dependent with maximum yield at ~ 800K. Other main reaction products are CO, CO$_2$, CH$_4$, the yields of which all show a decrease during simultaneous H$^+$-O$^+$ irradiation when compared to single beam irradiation. Furthermore, hydrogen re-emission (in the form of H$_2$) was observed while no oxygen re-emission was seen.

Through ion range separation experiments of O$^+$ and H$^+$ irradiations, both sequentially and simultaneously, it has been demonstrated that the formation of water in graphite is largely independent of the range separation of the O$^+$ and H$^+$ ions. On the other hand, beam-flux variation experiments has shown that the formation of water is dependent on the ratio of the incident ion flux densities due to the availability of the H supply, i.e., relatively higher H supply will lead to a higher water yield.

Based on the observation that no oxygen re-emission was observed and the oxygen reactivity with graphite is near unity, we have concluded that there is no mobile oxygen in graphite. Furthermore, based on the observation that water production is independent of H$^+$ and O$^+$ range separation, we have concluded that water formation occurs at the end of the O$^+$ ion range in the H$^+$-O$^+$→C reaction system, and is dependent on the supply of mobile hydrogen atoms in the internal channels within graphite.

It was demonstrated experimentally that the addition of H$^+$ during the O$^+$→C irradiation leads to a reduction of the CO and CO$_2$ yields, corresponding to the formation of water. Similar to the water formation, the reduction of the CO and CO$_2$ yields is independent of the range separation of the O$^+$ and H$^+$ but is inversely dependent on the relative O$^+$ flux and the carbon temperature. It is suggested that the reduction is caused by the reduction of the oxygen supply due to the competing water formation.

It was also demonstrated that the addition of O$^+$ during the H$^+$→C irradiation leads to a reduction of the CH$_4$ yield. Based on previous studies, the cause of the CH$_4$ yield reduction is postulated to be the breaking up of the back-diffusing CH$_4$ molecules by the energetic incident O$^+$. Further experiments with adding inert Ne$^+$ with a 5 keV beam energy (same as the O$^+$
energy) during the $H^+ \rightarrow C$ bombardment confirmed the hypothesis. The $CH_4$ yield reduction was also independent of the range separation of the incident $O^+$ and $H^+$, but was dependent on the relative oxygen flux; i.e., higher $O^+$ flux led to higher $CH_4$ yield reduction. This is also consistent with the proposed methane break-up mechanism causing the $CH_4$ yield reduction.

To further examine the mechanism of the $H^+-O^+ \rightarrow C$ reaction system, studies of the $O^+ - H^+ \rightarrow C/B$ reaction system were also performed. Previous studies have shown that hydrocarbon yields from $H^+ \rightarrow C/B$ reactions could be greatly reduced, when compared with $H^+ \rightarrow C$ reactions. The first major discovery was that the addition of $O^+$ to the $H^+ \rightarrow C/B$ reaction leads to an increase of the $CH_4$ yield. This phenomenon is the opposite of what happens in the $H^+ - O^+ \rightarrow C$ reaction system. Based on the “abstraction” theory of hydrogen recombination, we have proposed that the presence of boron on the graphitic internal surfaces increases the recombination sites on the internal surfaces, leading to an increase of hydrogen recombination thus reducing the methane yield. The addition of oxygen then “fills” these recombination sites, leading to the observed increase in the $CH_4$ yields. As observed, in most cases, this increase more than compensates for the methane break-up effect due to incident $O^+$.

It was also demonstrated that the combined presence of B and O in the $O^+ - H^+ \rightarrow C/B$ system led to a reduction of water yield in comparison with the $O^+ - H^+ \rightarrow C$ case. Based on this observation we have suggested the presence of hydrogen-oxygen-containing “complexes” at the end of the $O^+$ ion range, attached to either carbon or boron. Due to higher stability in the B-O bonds, there may be less probability for the B-attached complexes to produce water, i.e., the presence of B reduces the H and O supplies by providing competing reaction paths that do not produce water. The C-attached complexes, on the other hand, do produce water. This concept of “water precursors” for the $O^+ - H^+ \rightarrow C$ system is consistent with the observed temperature dependence of water yields, which necessitates the dissociation of non-volatile complexes at high temperatures.

Based on the proposed mechanisms, a mathematical model of the $H^+ - O^+ \rightarrow C$ reaction system was formulated. The model is based on the two-region model of Haasz et al., with extensions such as $CH_4$ formation and the $O^+ \rightarrow C$ reaction branch. A detailed system of space-time-varying partial differential equations was formulated, including chemical and collisional processes for both $H^+ \rightarrow C$ and $O^+ \rightarrow C$ reactions, and synergistic effects such as methane break-up and water formation for the $O^+ - H^+ \rightarrow C$ reaction. A steady-state, simplified, version was used for computation. The steady-state version was further simplified and reduced to single beam cases,
where some of the rate coefficients were determined via fitting to experimental data. With the derived coefficients, model predictions were made for flux and energy dependence, and generally good agreement with experimental results was seen for both the H\(^+\)→C and O\(^+\)→C reactions. For the O\(^+\)-H\(^+\)→C reaction, the model agrees quite well with the flux ratio-dependence of H\(_2\)O yield, the resulting CO and CO\(_2\) yield reduction, and the CH\(_4\) yield reduction. However, the model predicts dependence on range-separation, which is unable to be conclusively verified by the experiment due to large experimental uncertainties.

Based on the experimental results and the model predictions of this thesis, water formation is expected in tokamaks using pure graphite, regardless of the implantation energies of the hydrogen and oxygen. The fraction of the oxygen involved in water production increases as the flux ratio (\(\Phi_O/\Phi_H\)) decreases. What is the implication of this finding for tokamaks? At flux ratios typical in tokamaks (i.e., \(\Phi_O/\Phi_H \sim 1\%\)), most of the implanted oxygen will participate in water formation, leaving little oxygen to participate in carbon erosion (i.e., CO and CO\(_2\) formation). Furthermore, the methane break-up effect due to O\(^+\) at this flux ratio is expected to be very small. Therefore, while the synergistic effect of combined oxygen and hydrogen irradiation in tokamaks is helpful in reducing carbon erosion by O\(^+\)-impact, it has little effect on carbon erosion by H\(^+\)-impact.

On the other hand, one reason for achieving very small relative oxygen fluxes in tokamaks is the addition of oxygen-gettering agents such as boron in the plasma-facing carbon materials. Previously published experimental results show that boron reduces oxygen-impurity and hydrocarbon formation. Based on the experimental results of this thesis, for small flux ratios, boron also suppresses water formation, which in turn leads to an increase of carbon erosion by O\(^+\)-impact.

Publication resulting from this thesis:
(1) “Carbon Chemistry due to combined H\(^+\) and O\(^+\) irradiation” [6]
(2) “Chemical Erosion of graphite under simultaneous O\(^+\) and H\(^+\) irradiation” [122]
(3) “Methane formation in graphite and boron-doped graphite under simultaneous O\(^+\) and H\(^+\) irradiation” [123]
(4) “Water formation in graphite and boron-doped graphite under simultaneous O\(^+\) and H\(^+\) irradiation” [124]
(5) “Two-region model for the O\(^+\)-H\(^+\)→C reaction system” [125]
REFERENCES


Table I Parameters for the C-H⁺ only case.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transport out of crystallite (kₜ)</td>
<td>8.73×10³ exp(-0.42 eV / kT) s⁻¹</td>
<td>See Ref. 10 (T &gt; 500 K)</td>
</tr>
<tr>
<td>Recombination (kₛₛ)</td>
<td>8×10¹⁶ exp(-0.56 eV / kT) s⁻¹</td>
<td>See Ref. 10 (T &gt; 500 K)</td>
</tr>
<tr>
<td>CH⁺ formation (kₕₜ)</td>
<td>1.0×10³ s⁻¹</td>
<td>Fit for 5×10¹⁹ H⁺/m²s @ 1 keV/H⁺</td>
</tr>
<tr>
<td>CH⁺ dissociation (kₒ) **</td>
<td>6.0×10¹¹ exp(-2.20 eV / kT) s⁻¹</td>
<td>Fit for 5×10¹⁹ H⁺/m²s @ 1 keV/H⁺</td>
</tr>
<tr>
<td>CH₃ formation (kₕₜ₃)</td>
<td>9.0×10¹¹ exp(-1.50 eV / kT) s⁻¹</td>
<td>Fit for 5×10¹⁹ H⁺/m²s @ 1 keV/H⁺</td>
</tr>
<tr>
<td>Maximum active site Cₙ [H]</td>
<td>0.42</td>
<td>See Sec. 6.2.6</td>
</tr>
<tr>
<td>CH₄ formation probability pₜₜ₄</td>
<td>1</td>
<td>Assumed unity for simplicity</td>
</tr>
<tr>
<td>CH₄ formation parameter b</td>
<td>0.75</td>
<td>Fit for 1 keV/H⁺</td>
</tr>
<tr>
<td>Atomic density of graphite Nₖ</td>
<td>1.1×10²⁹ m⁻³</td>
<td>Based on density of 2200 kg/m³</td>
</tr>
<tr>
<td>Average penetration depth xₚ</td>
<td>13.5/18.2/47.7 nm</td>
<td>TRVMC values for 0.7/1/3 keV/H⁺</td>
</tr>
<tr>
<td>Penetration standard deviation σₚ</td>
<td>6.52/8.65/18.1 nm</td>
<td>TRVMC values for 0.7/1/3 keV/H⁺</td>
</tr>
</tbody>
</table>

** Ion-induced desorption term is not shown

Table II Parameters for the C-O⁺ only case.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO* precursor formation (kₜₒ)</td>
<td>1.0×10³ s⁻¹</td>
<td>Fit for 1×10¹⁹ O⁺/m²s @ 5 keV/O⁺</td>
</tr>
<tr>
<td>CO* precursor dissociation (kₒₜₒ)</td>
<td>0.2×10¹ exp(-0.25 eV / kT) s⁻¹</td>
<td>Fit for 1×10¹⁹ O⁺/m²s @ 5 keV/O⁺</td>
</tr>
<tr>
<td>CO release (kₜₒ)</td>
<td>4×10¹ exp(-0.5 eV / kT) s⁻¹</td>
<td>Fit for 1×10¹⁹ O⁺/m²s @ 5 keV/O⁺</td>
</tr>
<tr>
<td>CO₂ formation (kₒₐ)</td>
<td>8×10¹⁴ exp(-0.02 eV / kT) s⁻¹</td>
<td>Fit for 1×10¹⁹ O⁺/m²s @ 5 keV/O⁺</td>
</tr>
<tr>
<td>Maximum active site Cₙ [O]</td>
<td>0.25</td>
<td>See Sec. 6.2.6</td>
</tr>
<tr>
<td>Average penetration depth xₚ</td>
<td>10.7 nm</td>
<td>TRVMC value for 5 keV/O⁺</td>
</tr>
<tr>
<td>Penetration standard deviation σₚ</td>
<td>4.79 nm</td>
<td>TRVMC value for 5 keV/O⁺</td>
</tr>
</tbody>
</table>

** Ion-induced desorption terms are not shown

Table III Parameters for the simultaneous O⁺-H⁺→C case.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃O⁺ precursor formation (kₜₒₜ)</td>
<td>1.0×10²¹ exp(-1.0 eV / kT) s⁻¹</td>
<td>Fit for 1 keV/H⁺ &amp; 5 keV/O⁺</td>
</tr>
<tr>
<td>CH₃O⁺ precursor dissociation (kₒₜₒ)</td>
<td>1.2×10¹⁸ exp(-1.9 eV / kT) s⁻¹</td>
<td>Fit for 1 keV/H⁺ &amp; 5 keV/O⁺</td>
</tr>
<tr>
<td>H₂O molecule release (kₜₜₕ)</td>
<td>4×10¹² exp(-1.0 eV / kT) s⁻¹</td>
<td>Fit for 1 keV/H⁺ &amp; 5 keV/O⁺</td>
</tr>
<tr>
<td>Beam spot area ratio Eq. 6-55 (θₒₛ)</td>
<td>0.36</td>
<td>For dₒ=0.003m, dₛ=0.005m</td>
</tr>
<tr>
<td>Adjustment factor in Eq. 6-54 (θₒₖ)</td>
<td>0.733/0.553/0.265</td>
<td>For 0.7/1/3 keV/H⁺ &amp; 5 keV/O⁺</td>
</tr>
<tr>
<td>Ion-desorption mixing in Eq. 6-57 (θₒₜₒ)</td>
<td>0.236/0.123/0</td>
<td>For 0.7/1/3 keV/H⁺ &amp; 5 keV/O⁺</td>
</tr>
<tr>
<td>Ion-desorption mixing in Eq. 6-59 (θₒₜₒ)</td>
<td>2.485/1.718/0</td>
<td>For 0.7/1/3 keV/H⁺ &amp; 5 keV/O⁺</td>
</tr>
<tr>
<td>Methane break-up probability (pₚ)</td>
<td>0.5</td>
<td>See Sec. 6.3.3</td>
</tr>
</tbody>
</table>

** Ion-induced desorption term is not shown
Fig. 1. Schematics of the Tokamak configuration [from Atom 369, July 1987]

Fig. 2. Temperature dependence of the methane yields for 3 keV $H_3^+$ bombardment of CKC B-doped specimens [109]. *The HPG99 yield [66] is shown for comparison.
Fig. 3. Photographs of the dual-beam accelerator facility
Quadrupole Mass Spectrometer in LOS and RGA detection modes

50 Hz Chopper

Pyrolytic Graphite Specimen

Fig. 4. Schematics of the apparatus arrangement in the test chamber

Fig. 5. Ion implantation depth profile of O$^+$ and H$^+$ in graphite as calculated by TRVMC. Incident angle is 21° from the normal.
Fig. 6. Ion implantation depth profile of Ne$^+$ and H$^+$ in graphite as calculated by TRVMC. Incident angle is 21° from the normal.

Fig. 7. Ion implantation depth profile of O$^+$ and H$^+$ in boron-doped graphite as calculated by TRVMC. Incident angle is 21° from the normal.
Fig. 8. Raw signal trace in RGA detection mode for O⁺-H⁺→C system at 800K.
Fig. 9. Temperature dependence of CO, CO₂ and H₂O yields measured in the RGA mode.

Fig. 10. Temperature dependence of CH₄ yields measured in the RGA mode.
Fig. 11. Temperature dependence of CO, CO₂ and H₂O yields measured in the LOS mode.
no \( H^+ \) pre-implantation before \( O^+ \) implantation.

After \( H^+ \) pre-implantation for the range separated case; in (c), there is
(a) \( \nabla \) indicates the water signal increases with the \( O^+ \) beam limited on
pre-implantation of \( H^+ \). Graphite specimen temperature is 800 K. In
pre-implantation after \( C \) implantation after

\( \text{FIG. 12. Raw RGA H}_2O \) signal trace during \( O^+ \) C implantation after

(a) 2 Key O \( \leftrightarrow \) C (without pre-implanted \( H^+ \))

(c) 5 Key O \( \leftrightarrow \) C (without pre-implanted \( H^+ \))

(\( H^+ \) and then 5 Key C)

(\( H^+ \) and then 5 Key C)

(\( H^+ \) and then 5 Key C)

(\( H^+ \) and then 5 Key C)
(a) 0.6 keV H⁺ + 5 keV O⁺  →  C
(b) 1 keV H⁺ + 5 keV O⁺  →  C

H⁺&O⁺ ranges overlap

H⁺&O⁺ ranges nearly overlap

(c) 1 keV H⁺ + 5 keV O⁺  →  C
(d) 2 keV H⁺ + 5 keV O⁺  →  C

H⁺&O⁺ ranges nearly overlap

H⁺&O⁺ ranges are separated

Fig. 13. Raw H₂O signal trace in LOS detection mode during simultaneous implantation of H⁺ and O⁺ in graphite; graphite specimen temperature is 800 K.
Fig. 14. CO Yields at 800 K, measured by RGA; (a) actual production yields as a function of the flux ratio $\Phi_0/\Phi_H$ for various implantation depth ratios $R_H/R_O$, (b) yield reduction, in percentage, as a function of the flux ratio for the implantation ratios shown in (a). The O$^+$ energy is fixed at 5 keV/O$^+$ ($R_O \sim 11$ nm), while the H$^+$ energy varies from 0.7 – 3 keV/H$^+$ ($R_H \sim 13 – 50$ nm). The O$^+$ flux $\Phi_0$ is fixed at $\sim 3 \times 10^{18}$ O$^+/m^2s$, while the H$^+$ flux $\Phi_H$ varies from 0.6 – 3.1 $\times 10^{19}$ H$^+/m^2s$. Error bars indicate the relative error of the yield differences between the single- and dual-beam cases. The absolute error of the measurement, $\sim 20\%$, is not included in the error bars.
Fig. 15. CO₂ Yields at 800 K, measured by RGA; (a) actual production yields as a function of the flux ratio \( \Phi_O/\Phi_H \) for various implantation depth ratios \( R_H/R_O \), (b) yield reduction, in percentage, as a function of the flux ratio for the implantation ratios shown in (a). The O⁺ energy is fixed at 5 keV/O⁺ (\( R_O \sim 11 \text{ nm} \)), while the H⁺ energy varies from 0.7 – 3 keV/H⁺ (\( R_H \sim 13 – 50 \text{ nm} \)). The O⁺ flux \( \Phi_O \) is fixed at \( \sim 3 \times 10^{18} \) O⁺/m²s, while the H⁺ flux \( \Phi_H \) varies from 0.6 – 3.1 \( \times 10^{19} \) H⁺/m²s. Error bars indicate the relative error of the yield differences between the single- and dual-beam cases. The absolute error of the measurement, \( \sim 20\% \), is not included in the error bars.
Fig. 16. CH$_4$ Yields at 800 K, measured by RGA; (a) actual production yields as a function of the flux ratio ratio $\Phi_O/\Phi_H$ for various implantation depth ratios $R_H/R_O$, (b) yield reduction, in percentage, as a function of the flux ratio for the implantation ratios shown in (a). The O$^+$ energy is fixed at 5 keV/O$^+$ ($R_O \sim 11$ nm), while the H$^+$ energy varies from 0.7 – 3 keV/H$^+$ ($R_H \sim 13 - 50$ nm). The O$^+$ flux $\Phi_O$ is fixed at $\sim 3 \times 10^{18}$ O$^+/m^2s$, while the H$^+$ flux $\Phi_H$ varies from $0.6 - 3.1 \times 10^{19}$ H$^+/m^2s$. Error bars indicate the relative error of the yield differences between the single- and dual-beam cases. The absolute error of the measurement, $\sim 20\%$, is not included in the error bars.
Fig. 17. H₂O Yields at 800 K, measured by RGA and LOS. The O⁺ energy is fixed at 5 keV/O⁺ (R₀ ~ 11 nm), while the H⁺ energy varies from 0.7 – 3 keV/H⁺ (Rₜ ~ 13 – 50 nm). The O⁺ flux Φ₀ is fixed at ~ 3 x 10¹⁸ O⁺/m²s, while the H⁺ flux Φₜ varies from 0.6 – 3.1 x 10¹⁹ H⁺/m²s. Error bars indicate the relative error of the water yield. The absolute error of the measurement, ~20%, is not included in the error bars.

Fig. 18. Temperature profile of water yields (H₂O/O⁺) in the O⁺-H⁺→C reaction system for selected flux/energy ratio cases.
Fig. 19. Temperature profile of methane yields (CH₄/H⁺) in the O⁺-H⁺→C system for selected flux/energy ratio cases.

Fig. 20. Typical raw LOS signal trace obtained in an experiment aimed at detecting hydrogen recombination for the O⁺-H⁺→C reaction; specimen temperature is at 800K.
Fig. 21. Methane yield as a function of ion range separation with two different beam flux ratios $\Phi_{\text{Ne}}/\Phi_{\text{H}}$ for graphite at $T \sim 800\text{K}$ under simultaneous $\text{Ne}^+$ and $\text{H}^+$ impact. The yield reduction (in percentage) is also plotted. Error bars indicate the relative error of the yield differences between the single- and dual-beam cases. The absolute error of the measurement, $\sim 20\%$, is not included in the error bars.

Fig. 22. Typical LOS raw signal trace of $\text{H}_2$ re-emission for the $\text{Ne}^+-\text{H}^+\rightarrow \text{C}$ reaction; specimen temperature is $800\text{K}$

94
Fig. 23. Typical raw LOS signal trace of water yield for the O\(^+\)-H\(^+\)→C reaction performed on a newly annealed graphite specimen.

Fluences:
\[ H^+: 2.5 \times 10^{19} \text{ H}^+/\text{cm}^2 \]

\[ O^+: 2.4 \times 10^{18} \text{ O}^+/\text{cm}^2 \]

5 keV/O\(^+\) @ \sim 6 \times 10^{18} \text{ O}^+/\text{m}^2\text{s}

3 keV/H\(^+\) @ \sim 1 \times 10^{19} \text{ H}^+/\text{m}^2\text{s}

Fig. 24. Typical raw LOS signal trace of water yield for the O\(^+\)-H\(^+\)→C reaction performed on an ion-damaged graphite specimen.
Fig. 25. Raw signal trace in RGA detection mode for the O\(^+\)-H\(^+\)→C/B system at 800K. Beam ranges are overlapping (5 keV/O\(^+\) and 0.7 keV/H\(^+\)) and the flux ratio \(\Phi_{O}/\Phi_{H} \sim 0.1\).
Fig. 26. CH₄ yields for both O⁺-H⁺→C and O⁺-H⁺→C/B irradiations as a function of beam flux ratio $\Phi_O/\Phi_H$ for two ion range separation cases: (a) beams are completely overlapping ($E_0 = 5$ keV, $E_H = 0.7$ keV, $R_H/R_O \sim 1$), and (b) beams are completely separated ($E_0 = 5$ keV, $E_H = 3$ keV, $R_H/R_O \sim 6$). The oxygen flux $\Phi_O$ is fixed at $\sim 3 \times 10^{18}$ O⁺/m²s, while the hydrogen flux $\Phi_H$ varies from $0.6 - 3.1 \times 10^{19}$ H⁺/m²s. Results for both CKC-B20 and USB15 are plotted for O⁺-H⁺→C/B. Error bars indicate the relative error of the yield differences between the single- and dual-beam cases. The absolute error of the measurement, $\sim 20\%$, is not included in the error bars.
Fig. 27. H₂O yields for both O⁺-H⁺→C and O⁺-H⁺→C/B irradiations as a function of beam flux ratio Φₒ/Φₜ for two ion range separation cases: (a) beams are completely overlapping (Eₒ = 5 keV, Eₜ = 0.7 keV, Rₜ/Rₒ = 1), and (b) beams are completely separated (Eₒ = 5 keV, Eₜ = 3 keV, Rₜ/Rₒ = 6). The oxygen flux Φₒ is fixed at ~ 3 × 10¹⁸ O⁺/m²s, while the hydrogen flux Φₜ varies from 0.6 – 3.1 × 10¹⁹ H⁺/m²s. Results for both CKC-B20 and USB15 are plotted for O⁺-H⁺→C/B. Error bars indicate the relative error of the water yield. The absolute error of the measurement, ~20%, is not included in the error bars.
Fig. 28. CO yields for both $O^+\rightarrow C$ and $O^+\rightarrow C/B$ irradiations as a function of beam flux ratio $\Phi_O/\Phi_H$ for two ion range separation cases: (a) beams are completely overlapping ($E_O = 5$ keV, $E_H = 0.7$ keV, $R_H/R_O \sim 1$), and (b) beams are completely separated ($E_O = 5$ keV, $E_H = 3$ keV, $R_H/R_O \sim 6$). The oxygen flux $\Phi_O$ is fixed at $\sim 3 \times 10^{18}$ $O^+/m^2s$, while the hydrogen flux $\Phi_H$ varies from $0.6 - 3.1 \times 10^{19}$ $H^+/m^2s$. Results for both CKC-B20 and USB15 are plotted for $O^+\rightarrow C/B$. Error bars indicate the relative error of the yield differences between the single- and dual-beam cases. The absolute error of the measurement, $\sim 20\%$, is not included in the error bars.
Fig. 29. CO₂ yield of both O⁺-H⁺→C and O⁺-H⁺→C/B systems as a function of beam flux ratio \( \Phi_O/\Phi_H \) for two ion range separation cases: (a) beams are completely overlapping (\( E_O = 5 \) keV, \( E_H = 0.7 \) keV, \( R_H/R_O \approx 1 \)), and (b) beams are completely separated (\( E_O = 5 \) keV, \( E_H = 3 \) keV, \( R_H/R_O \approx 6 \)). The oxygen flux \( \Phi_O \) is fixed at \( \approx 3 \times 10^{18} \) O⁺/m²s, while the hydrogen flux \( \Phi_H \) varies from \( 0.6 - 3.1 \times 10^{19} \) H⁺/m²s. Results for both CKC-B20 and USB15 are plotted for O⁺-H⁺→C/B. Error bars indicate the relative error of the yield differences between the single- and dual-beam cases. The absolute error of the measurement, \( \approx 20\% \), is not included in the error bars.
Fig. 30. Illustration of the reaction mechanisms representing the case of total implantation depth separation of simultaneous O\(^+\) and H\(^+\) implantation
Fig. 31. Potential energy diagram of hydrogen and oxygen in graphite, based on the activation energies in Table I, Table II, and Ref. [10] with oxygen added to the system: (1) bulk diffusion of H; (2) surface diffusion and recombination of H; (3) potential energy barrier for H atom release; (4) dissociation energy of molecular hydrogen; (5) trap energy for hydrogen; (6) trap energy for oxygen. Surface traps for hydrogen are drawn, although they are not included in the model. The absolute energy scale is not valid for the H traps in the edge of the crystallite region and the O traps in the internal surface region.

Fig. 32. Hydrogen in the crystallite
Fig. 33. Hydrogen on the inner surfaces

Fig. 34. Oxygen on the inner surfaces
Fig. 35. Calculated temperature profiles of the methane yields in the $\text{H}^+\rightarrow\text{C}$ reaction. Experimental data (1 keV/$\text{H}^+$, $\sim5\times10^{19}$ H$^+/\text{m}^2\text{s}$ from Sec. 5.1 and $1\&3$ keV/$\text{H}^+$, $\sim1\times10^{20}$ H$^+/\text{m}^2\text{s}$ from [83,84]) are also plotted.

Fig. 36. Calculated flux density dependence of the methane yield in the $\text{H}^+\rightarrow\text{C}$ reaction. Experimental data are taken from [83,84].
Fig. 37. Calculated temperature profiles of the CO and CO$_2$ yields in O$^+\rightarrow$C reaction. Experimental data from Sec. 5.1 are also plotted.

Fig. 38. Calculated flux density dependence of the CO and CO$_2$ yields in the O$^+\rightarrow$C reaction, T = 800 K.
Fig. 39. Calculated temperature dependence of CO and CO$_2$ yields during O$^+\rightarrow$C and simultaneous O$^+\cdot$H$^+$\rightarrow$C cases. Experimental data from Sec. 5.1 are also plotted.

Fig. 40. Calculated temperature dependence of H$_2$O yields during simultaneous O$^+\cdot$H$^+$\rightarrow$C bombardment. Experimental data from Sec. 5.1 are also plotted.
Fig. 41. Calculated temperature dependence of CH₄ yields for the \( \text{H}^+ \rightarrow \text{C} \) and simultaneous \( \text{O}^+ \cdot \text{H}^+ \rightarrow \text{C} \) cases. Experimental data from Sec. 5.1 are also plotted.

Fig. 42. Calculated temperature dependence of the \( \text{CO}_2/\text{CO} \) yield ratios for the \( \text{O}^+ \rightarrow \text{C} \) and simultaneous \( \text{O}^+ \cdot \text{H}^+ \rightarrow \text{C} \) cases. Experimental data from Sec. 5.1 are also plotted.
Φ₀ fixed at ~ 1 x 10¹⁹ H⁺/m²s
Φ_H is varied

T ~ 800 K

Data (R_R₀ = 1.2)
Data (R_R₀ = 1.7)
Data (R_R₀ = 4.4)
Model (R_R₀ = 1.2)
Model (R_R₀ = 1.7)
Model (R_R₀ = 4.4)

Fig. 43. Model predictions for the flux ratio dependence of the H₂O yields for the simultaneous O⁺-H⁺→C case at 800 K. Experimental data from Sec. 5.2.3 are also plotted.

Φ₀ fixed at ~ 1 x 10¹⁹ H⁺/m²s
Φ_H is varied

T ~ 800 K

Data (R_R₀ = 1.2)
Data (R_R₀ = 1.7)
Data (R_R₀ = 4.4)
Model (R_R₀ = 1.2)
Model (R_R₀ = 1.7)
Model (R_R₀ = 4.4)

Fig. 44. Model predictions for the flux ratio dependence of percent CO yield reduction for the simultaneous O⁺-H⁺→C case at 800 K, as compared with the O⁺→C case. Experimental data from Sec. 5.2.3 are also plotted.
Fig. 45. Model predictions for the flux ratio dependence of the percent CO₂ yield reductions for the simultaneous O⁺-H⁺→C case at 800K, as compared with the O⁺→C case. Experimental data from Sec. 5.2.3 are also plotted.

Fig. 46. Model predictions for the flux ratio dependence of the percent CH₄ yield reductions for the simultaneous O⁺-H⁺→C case at 800 K, as compared with the H⁺→C case. Experimental data from Sec. 5.2.3 are also plotted.
APPENDIX A: Sample Mathcad Calculations for the H⁺ → C Case

\[ eV = 1.602 \cdot 10^{-19} \text{J} \quad \text{nm} = 10^{-9} \text{m} \]

Average Carbon Density

\[ C_D = \frac{2200 \text{kg m}^{-3} \cdot (6.0221367 \cdot 10^{23} \text{mole}^{-1})}{12.011 \text{ kg mol}^{-1}} = 1.103 \cdot 10^{29} \text{ m}^{-3} \]

\[ c = 1 \quad \text{active carbon site} \quad h = 1 \quad \text{hydrogen atoms} \]

\[ C_{\text{max}} = 0.42 \cdot c \quad \text{Max. available surface carbon sites} \quad R_H = 100 \text{ nm} \]

\[ b = 0.75 \quad \text{CH}_4 \text{ power dependence} \]

\[ k = 1.380658 \cdot 10^{-23} \text{ joule K}^{-1} \]

Sample Temperatures

\[ T = 300 \cdot \text{K}, 310 \cdot \text{K} \ldots 1800 \cdot \text{K} \quad I_{\text{max}} = 56 \quad i = 0 \ldots I_{\text{max}} \]

\[ T_i = 500 \cdot \text{K} + i \cdot 125 \cdot \text{K} \]

\[ t_s = 24 \quad T_S = T_{t_s} \]

\[ T_S = 800 \cdot \text{K} \quad \text{Fixed sample temperature for flux dependence calculation} \]

Beam Fluxes

\[ J_{\text{max}} = 20 \quad j = 0 \ldots J_{\text{max}} \quad h = 17 \quad \Phi_{J_j} = 10^{18+j} \cdot 10^{-2} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \]

\[ \Phi_H := \Phi_{J_h} \]

\[ \Phi_H = 5.012 \cdot 10^{19} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \quad \text{Fixed flux density for temperature dependence calculation} \]

Rate Coefficients

Rate coefficient equation

\[ k_g(T_g, K_g, E_g) := K_g \cdot \exp \left( \frac{-E_g}{k \cdot T_g} \right) \quad S := 0.05 \text{ s}^{-1} \]

\[ k_{gl}(T_g, S_g, \sigma_g, K_g, E_g) := S_g \cdot \sigma_g + K_g \cdot \exp \left( \frac{-E_g}{k \cdot T_g} \right) \]
transport out of crystallite

\[ K_S := 8.73 \times 10^{-5} \text{s}^{-1} \quad E_S := 0.42 \text{eV} \]

\[ k_S(T_g) := k_g(T_g, K_S, E_S) \]

\[ k_S(T) \]

\[ 10^5 \quad 10^4 \quad 10^3 \]

\[ 100 \quad 10 \quad 1 \]

\[ 0.1 \quad 0.01 \quad 0.001 \quad 0.0015 \]

recombination

\[ K_{SS} := 8 \times 10^{16} \text{s}^{-1} \quad E_{SS} := 0.56 \text{eV} \]

\[ k_{SS}(T_g) := k_g(T_g, K_{SS}, E_{SS}) \]

\[ k_{SS}(T) \]

\[ 10^{16} \quad 10^{15} \quad 10^{14} \]

\[ 10^{13} \quad 10^{12} \quad 10^{11} \]

\[ 10^{10} \quad 10^{9} \quad 10^{8} \]

\[ 10^{7} \quad 10^{6} \quad 10^{5} \]

\[ 0.001 \quad 0.0015 \]

CH precursor formation (trapping)

\[ K_{CH} := 1.0 \times 10^3 \text{s}^{-1} \quad E_{CH} := 0.0 \text{eV} \]

\[ k_{CH}(T_g) := k_g(T_g, K_{CH}, E_{CH}) \]

\[ k_{CH}(T) \]

\[ 10^4 \quad 10^3 \]

\[ 100 \quad 10 \quad 1 \]

\[ 0.1 \quad 0.01 \quad 0.001 \quad 0.0015 \]

volatile CH$_3$ formation

\[ K_{MP} := 9.0 \times 10^{11} \text{s}^{-1} \quad E_{MP} := 1.5 \text{eV} \]

\[ k_{MP}(T_g) := k_g(T_g, K_{MP}, E_{MP}) \]

\[ k_{MP}(T) \]

\[ 10^{16} \quad 10^{15} \quad 10^{14} \]

\[ 10^{13} \quad 10^{12} \quad 10^{11} \]

\[ 10^{10} \quad 10^{9} \quad 10^{8} \]

\[ 10^{7} \quad 10^{6} \quad 10^{5} \]

\[ 0.001 \quad 0.0015 \]

CH precursor dissociation (detrapping)

\[ \delta_D := 1 \quad K_D := 6 \times 10^{11} \text{s}^{-1} \quad E_D := 2.2 \text{eV} \]

\[ k_D(T_g, S_g) := k_g(T_g, S_g, \delta_D, K_D, E_D) \]

\[ k_D(T, S) \]

\[ 10^6 \quad 10^5 \quad 10^4 \]

\[ 10^3 \quad 10^2 \quad 10^1 \]

\[ 1 \quad 0.1 \quad 0.01 \]

\[ 0.001 \quad 0.0015 \]

\[ \sigma_M := 1 \]
Hydrogen Ion Range Depth Profiles

\[ D_H := \begin{array}{c|c|c|c|c|c|c|c|c} \hline \text{H} & 0.486 & 0.541 & 0.541 & 0.582 & 0.582 & 0.582 & 0.582 & 0.582 \\
0.3 & 1.605 & 1.65 & 1.65 & 1.702 & 1.702 & 1.702 & 1.702 & 1.702 \\
0.4 & 1.605 & 1.65 & 1.65 & 1.702 & 1.702 & 1.702 & 1.702 & 1.702 \\
0.6 & 1.605 & 1.65 & 1.65 & 1.702 & 1.702 & 1.702 & 1.702 & 1.702 \\
0.8 & 1.605 & 1.65 & 1.65 & 1.702 & 1.702 & 1.702 & 1.702 & 1.702 \\
1.0 & 1.605 & 1.65 & 1.65 & 1.702 & 1.702 & 1.702 & 1.702 & 1.702 \\
\hline \end{array} \]

\[ D_{DPA} := \begin{array}{c|c|c|c|c|c|c|c} \hline \text{H} & 0.00 & 0.364 & 0.00 & 0.323 & 0.00 & 0.323 \\
0.3 & 0.20 & 0.434 & 0.00 & 0.323 & 0.00 & 0.323 \\
0.6 & 0.30 & 0.434 & 0.00 & 0.323 & 0.00 & 0.323 \\
0.9 & 0.40 & 0.434 & 0.00 & 0.323 & 0.00 & 0.323 \\
1.2 & 0.50 & 0.434 & 0.00 & 0.323 & 0.00 & 0.323 \\
1.5 & 0.60 & 0.434 & 0.00 & 0.323 & 0.00 & 0.323 \\
\hline \end{array} \]

\[ x_H(e_i) := D_H^{<e_i>}, \quad \text{extract } x \text{ ranges} \]

\[ \Delta x := 0.6 \text{-nm} \]

\[ R_1(e_i) := \begin{cases} 6.94 \text{-nm if } e_i = 0 \\ 9.58 \text{-nm if } e_i = 1 \\ 29.6 \text{-nm if } e_i = 2 \\ 3.12 \text{-nm if } e_i = 3 \\ 5.93 \text{-nm if } e_i = 4 \end{cases}, \quad R_2(e_i) := \begin{cases} 20.0 \text{-nm if } e_i = 0 \\ 26.9 \text{-nm if } e_i = 1 \\ 65.7 \text{-nm if } e_i = 2 \\ 8.45 \text{-nm if } e_i = 3 \\ 15.5 \text{-nm if } e_i = 4 \end{cases} \]

\[ c_H := \Delta x \cdot C_D \]

\[ S_H(\Phi, e_i) := \frac{D_H^{<e_i >} \cdot \Phi}{c_H \cdot I_X(e_i)} \]

\[ S_{DPA}(\Phi, e_i) := \frac{D_{DPA}^{<e_i + 1 >} \cdot \Phi}{c_H \cdot I_X(e_i)} \]

\[ S_{H2}(\Phi, e_i, i) := \frac{\Phi}{C_D \cdot R_H(e_i)} \begin{cases} 0 \text{-s}^{-1} \text{ otherwise} \\ \text{otherwise} \end{cases} \]

\[ S_{D2}(\Phi, e_i, i) := S_{H2}(\Phi, e_i, i) \frac{I_{DPA}(e_i)}{I_X(e_i)} \]

\[ S_{H3}(\Phi, e_i) := \frac{\Phi}{C_D \cdot R_H(e_i)} S_{D3}(\Phi, e_i) := S_{H3}(\Phi, e_i) \frac{I_{DPA}(e_i)}{I_X(e_i)} \]

\[ l := 0, 1, \ldots, 166 \]
Below is the simplified steady-state rate equation for H-only case

Given

\[ 0 = S_{\text{HI}} - k \, C_{\text{H}} \cdot H \cdot C \cdot (C_{\text{max}} - H_P) - k \, S \cdot H \cdot C - 2 \cdot k_{MP} \cdot H \cdot P \cdot H \cdot C + k_{D} \cdot H \cdot P \]

\[ 0 = k \, C_{\text{H}} \cdot H \cdot C \cdot (C_{\text{max}} - H_P) - k_{MP} \cdot H \cdot P \cdot H \cdot C - k_{D} \cdot H \cdot P \]

\[ 0 = k \, S \cdot H \cdot C - \left( i + \theta \right) \cdot 2 \cdot k \, SS \cdot H \cdot S \cdot 2 - \sigma \cdot k_{MP} \cdot H \cdot P \cdot H \cdot C \]

\[ f_H(H, C, H, S, P, S, H, S, k, S, k, SS, k, C, H, k, MP, k, D, \theta_H) := \text{find}(H, C, H, S, P) \]

\[ G_H(\Phi, T, e) := f_H(0, 0, 0, S_{H3}(\Phi, e), k, S(T), k, SS(T), k, C_H(T), k, MP(T), k, D, T, S_D3(\Phi, e), \theta_H(e)) \]

The Solution

\[ T_H(a) := \begin{cases} \text{for } j \in 0..J_{\text{max}} \\ \text{for } i \in 0..I_{\text{max}} \\ Y \leftarrow G_H(\Phi_j, T_j, e) \\ X^{<j>} \leftarrow Y \\ Z \leftarrow X^T \\ M^{<j>3} \leftarrow Z^{<0>} \\ M^{<j>3+1} \leftarrow Z^{<1>} \\ M^{<j>3+2} \leftarrow Z^{<2>} \end{cases} \]

\[ T_{700eV} := T_H(0) \quad T_{1000eV} := T_H(1) \quad T_{3000eV} := T_H(2) \]

\[ H_{C, 7} := T_{700eV}^{<h3+0>} \quad H_{S, 7} := T_{700eV}^{<h3+1>} \quad H_{P, 7} := T_{700eV}^{<h3+2>} \]

\[ H_{C, 10} := T_{1000eV}^{<h3+0>} \quad H_{S, 10} := T_{1000eV}^{<h3+1>} \quad H_{P, 10} := T_{1000eV}^{<h3+2>} \]

\[ H_{C, 30} := T_{3000eV}^{<h3+0>} \quad H_{S, 30} := T_{3000eV}^{<h3+1>} \quad H_{P, 30} := T_{3000eV}^{<h3+2>} \]
Plotting the solution for $\Phi_h = 5.012 \times 10^{19} \text{ m}^{-2} \text{s}^{-1}$
And now calculating flux by integration using trapezoid method

\[ f_{\text{H}_2-700eV(a,c)} := \left( k \mathrm{SS} \left( T_{T_a} \right) \right) \left( T_{700eV} \right)^{<\epsilon+1>} \int_{T_{T_a}}^{C\Phi J_c} R_2(0) \frac{C_{D}}{\Phi J_c} \]

\[ f_{\text{CH}_4-700eV(a,c)} := \left( k \mathrm{MP} \left( T_{T_a} \right) \right) \left( T_{700eV} \right)^{<\epsilon+2>} \int_{T_{T_a}}^{C\Phi J_c} R_2(1) \frac{C_{D}}{\Phi J_c} \]

\[ J_{\text{H}_2,7_{i,j}} := f_{\text{H}_2-700eV(i,j)} \]

\[ J_{\text{CH}_4,7_{i,j}} := f_{\text{CH}_4-700eV(i,j)} \]

\[ f_{\text{H}_2-1000eV(a,c)} := \left( k \mathrm{SS} \left( T_{T_a} \right) \right) \left( T_{1000eV} \right)^{<\epsilon+1>} \int_{T_{T_a}}^{C\Phi J_c} R_2(1) \frac{C_{D}}{\Phi J_c} \]

\[ J_{\text{CH}_4,10_{i,j}} := f_{\text{CH}_4-1000eV(i,j)} \]

\[ f_{\text{H}_2-3000eV(a,c)} := \left( k \mathrm{SS} \left( T_{T_a} \right) \right) \left( T_{3000eV} \right)^{<\epsilon+1>} \int_{T_{T_a}}^{C\Phi J_c} R_2(2) \frac{C_{D}}{\Phi J_c} \]

\[ J_{\text{CH}_4,30_{i,j}} := f_{\text{CH}_4-3000eV(i,j)} \]

For Temperature Profile, input flux fixed at: \( \Phi J_h = 5.012 \times 10^{19} \ m^{-2} \ s^{-1} \)

\[ J_{\text{H}_2,7} := J_{\text{H}_2,7}^{<\epsilon>} \]

\[ J_{\text{CH}_4,7} := J_{\text{CH}_4,7}^{<\epsilon>} \]

\[ J_{\text{H}_2,10} := J_{\text{H}_2,10}^{<\epsilon>} \]

\[ J_{\text{CH}_4,10} := J_{\text{CH}_4,10}^{<\epsilon>} \]

\[ J_{\text{H}_2,30} := J_{\text{H}_2,30}^{<\epsilon>} \]

\[ J_{\text{CH}_4,30} := J_{\text{CH}_4,30}^{<\epsilon>} \]

For Flux Dependence, sample temperature fixed at: \( T_s = 800 \ K \)

\[ J_{1} \text{H}_2,7_{j} := J_{1} \text{H}_2,7_{b,j} \]

\[ J_{1} \text{CH}_4,7_{j} := J_{1} \text{CH}_4,7_{b,j} \]

\[ J_{1} \text{H}_2,10_{j} := J_{1} \text{H}_2,10_{b,j} \]

\[ J_{1} \text{CH}_4,10_{j} := J_{1} \text{CH}_4,10_{b,j} \]

\[ J_{1} \text{H}_2,30_{j} := J_{1} \text{H}_2,30_{b,j} \]

\[ J_{1} \text{CH}_4,30_{j} := J_{1} \text{CH}_4,30_{b,j} \]

For Flux Dependence, sample temperature fixed at \( T = T_m \)

\[ J_{m} \text{CH}_4,7_{j} := \max \left( J_{\text{CH}_4,7}^{<\epsilon>} \right) \]

\[ J_{m} \text{CH}_4,10_{j} := \max \left( J_{\text{CH}_4,10}^{<\epsilon>} \right) \]

\[ J_{m} \text{CH}_4,30_{j} := \max \left( J_{\text{CH}_4,30}^{<\epsilon>} \right) \]
### Data Points

#### CH₄ Temperature profile from Chen et al

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>443.000</td>
<td>8.738e-4</td>
</tr>
<tr>
<td>473.000</td>
<td>9.175e-4</td>
</tr>
<tr>
<td>513.000</td>
<td>0.001</td>
</tr>
<tr>
<td>543.000</td>
<td>0.002</td>
</tr>
<tr>
<td>573.000</td>
<td>0.002</td>
</tr>
<tr>
<td>623.000</td>
<td>0.008</td>
</tr>
<tr>
<td>643.000</td>
<td>0.010</td>
</tr>
<tr>
<td>673.000</td>
<td>0.014</td>
</tr>
<tr>
<td>723.000</td>
<td>0.038</td>
</tr>
<tr>
<td>823.000</td>
<td>0.072</td>
</tr>
</tbody>
</table>

#### CH₄ Flux profile from Davis, et al

**T = 750 K**

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Fᵦ₇₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.150e20</td>
<td>0.042</td>
</tr>
<tr>
<td>1.060e20</td>
<td>0.048</td>
</tr>
<tr>
<td>9.790e19</td>
<td>0.075</td>
</tr>
<tr>
<td>2.810e19</td>
<td>0.064</td>
</tr>
<tr>
<td>2.100e18</td>
<td>0.078</td>
</tr>
<tr>
<td>9.690e19</td>
<td>0.047</td>
</tr>
<tr>
<td>1.500e19</td>
<td>0.074</td>
</tr>
<tr>
<td>3.750e19</td>
<td>0.063</td>
</tr>
<tr>
<td>6.110e18</td>
<td>0.079</td>
</tr>
<tr>
<td>7.240e19</td>
<td>0.051</td>
</tr>
</tbody>
</table>

**T = 800 K**

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Fᵦ₈</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.150e20</td>
<td>0.064</td>
</tr>
<tr>
<td>1.060e20</td>
<td>0.066</td>
</tr>
<tr>
<td>9.700e19</td>
<td>0.065</td>
</tr>
<tr>
<td>7.300e19</td>
<td>0.069</td>
</tr>
<tr>
<td>5.200e19</td>
<td>0.073</td>
</tr>
<tr>
<td>3.700e19</td>
<td>0.074</td>
</tr>
<tr>
<td>2.800e19</td>
<td>0.077</td>
</tr>
<tr>
<td>1.900e19</td>
<td>0.075</td>
</tr>
<tr>
<td>1.500e19</td>
<td>0.079</td>
</tr>
<tr>
<td>9.900e18</td>
<td>0.075</td>
</tr>
</tbody>
</table>

#### CH₄ Temperature profile from Davis et al

**6x10¹⁹ H⁺/m²s @ 1 keV/H⁺**

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>800.000</td>
<td>0.066</td>
</tr>
<tr>
<td>800.000</td>
<td>0.065</td>
</tr>
<tr>
<td>775.000</td>
<td>0.061</td>
</tr>
<tr>
<td>750.000</td>
<td>0.054</td>
</tr>
<tr>
<td>725.000</td>
<td>0.043</td>
</tr>
<tr>
<td>700.000</td>
<td>0.032</td>
</tr>
<tr>
<td>685.000</td>
<td>0.030</td>
</tr>
<tr>
<td>675.000</td>
<td>0.021</td>
</tr>
<tr>
<td>650.000</td>
<td>0.014</td>
</tr>
</tbody>
</table>

#### CH₄ Temperature profile from Davis et al

**1x10²⁰ H⁺/m²s @ 3 keV/H⁺**

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>800.000</td>
<td>0.054</td>
</tr>
<tr>
<td>775.000</td>
<td>0.049</td>
</tr>
<tr>
<td>750.000</td>
<td>0.040</td>
</tr>
<tr>
<td>700.000</td>
<td>0.022</td>
</tr>
<tr>
<td>700.000</td>
<td>0.021</td>
</tr>
<tr>
<td>650.000</td>
<td>0.009</td>
</tr>
<tr>
<td>600.000</td>
<td>0.004</td>
</tr>
<tr>
<td>600.000</td>
<td>0.004</td>
</tr>
<tr>
<td>650.000</td>
<td>0.010</td>
</tr>
<tr>
<td>700.000</td>
<td>0.026</td>
</tr>
</tbody>
</table>
Chi-squared test for temperature dependence

\[ N_{\text{Data}} = 14 \quad \text{Number of data points} \]
\[ N_{\text{Free}} = 4 \quad \text{Number of free parameters} \]
\[ df := N_{\text{Data}} - N_{\text{Free}} \quad \text{Degrees of freedom} \]

\[ \chi^2 := \sum_{i=0}^{N_{\text{Data}}-1} \left( a_i \left( T_{C_i}^{<1>} + J_{\text{CH}_4-1000} a_i \right) - \log \left( F_{\text{TM}}^{<0>} \right) - 18 \right)^2 \left( \frac{0.1}{0.5} \right) \]
\[ \chi^2 = 5.502 \quad \chi^2_v = 0.55 \quad \text{reduced chi-squared value} \]

\[ \text{pchisq}(\chi^2, df) = 0.145 \]

Chi-squared test for flux dependence

\[ N_{\text{Data}} := \text{length}(F_{\text{TM}}^{<0>}) \quad \text{Number of data points} \]
\[ df := N_{\text{Data}} - N_{\text{Free}} \quad \text{Degrees of freedom} \]

\[ \chi^2 := \sum_{i=0}^{N_{\text{Data}}-1} \left( a_i \left( F_{\text{TM}}^{<1>} - J_{\text{CH}_4-1000} a_i \right) - \log \left( F_{\text{TM}}^{<0>} \right) - 18 \right)^2 \left( \frac{0.1}{0.5} \right) \]
\[ \chi^2 = 6.931 \quad \chi^2_v = 0.578 \quad \text{reduced chi-squared value} \]

\[ \text{pchisq}(\chi^2, df) = 0.138 \]
H2 and total C Yield

Temperature [K]

Methane Temperature Profile

Temperature [K]

700 eV/H+
1000 eV/H+
3000 eV/H+
1 keV/H+ (Chen)
Output Tables for graphing

\[ T_{\text{profiles}_{i,0}} := T_{J_i \cdot K^{-1}} \quad T_{\text{profiles}_{i,1}} := J\text{CH}_4_{-700i} \quad T_{\text{profiles}_{i,2}} := J\text{CH}_4_{-1000i} \quad T_{\text{profiles}_{i,3}} := J\text{CH}_4_{-3000i} \]

\[ F_{\text{profiles}_{j,0}} := \Phi_{J_j \cdot m^2 \cdot s} \quad F_{\text{profiles}_{j,1}} := J1\text{CH}_4_{-700j} \quad F_{\text{profiles}_{j,2}} := J1\text{CH}_4_{-1000j} \quad F_{\text{profiles}_{j,3}} := J1\text{CH}_4_{-3000j} \]

\[ F_{\text{profiles}_{j,4}} := J2\text{CH}_4_{-1000j} \quad F_{\text{profiles}_{j,5}} := J3\text{CH}_4_{-1000j} \quad F_{\text{profiles}_{j,6}} := Jm\text{CH}_4_{-1000j} \]

\[
\begin{array}{|c|c|c|c|}
\hline
500.0000 & 3.2171e-5 & 3.8282e-5 & 3.8425e-5 \\
512.5000 & 6.1595e-5 & 6.4452e-5 & 7.2237e-5 \\
525.0000 & 1.1398e-4 & 1.1842e-4 & 1.3094e-4 \\
537.5000 & 2.0376e-4 & 2.1026e-4 & 2.2881e-4 \\
550.0000 & 3.5155e-4 & 3.6115e-4 & 3.8652e-4 \\
562.5000 & 5.5013e-4 & 6.0158e-4 & 6.3241e-4 \\
575.0000 & 9.6208e-4 & 9.7306e-4 & 1.0040e-3 \\
587.5000 & 1.5257e-3 & 1.5320e-3 & 1.5452e-3 \\
600.0000 & 2.3555e-3 & 2.3427e-3 & 2.3272e-3 \\
612.5000 & 3.5458e-3 & 3.4954e-3 & 3.4072e-3 \\
625.0000 & 5.2047e-3 & 5.0866e-3 & 4.6699e-3 \\
637.5000 & 7.4593e-3 & 7.2234e-3 & 6.7979e-3 \\
650.0000 & 0.0104 & 0.0100 & 9.2752e-3 \\
662.5000 & 0.0142 & 0.0135 & 0.0124 \\
675.0000 & 0.0189 & 0.0179 & 0.0161 \\
687.5000 & 0.0244 & 0.0230 & 0.0206 \\
700.0000 & 0.0308 & 0.0290 & 0.0257 \\
712.5000 & 0.0378 & 0.0355 & 0.0313 \\
725.0000 & 0.0452 & 0.0423 & 0.0373 \\
737.5000 & 0.0525 & 0.0492 & 0.0434 \\
750.0000 & 0.0595 & 0.0558 & 0.0494 \\
762.5000 & 0.0671 & 0.0618 & 0.0548 \\
775.0000 & 0.0708 & 0.0669 & 0.0595 \\
787.5000 & 0.0746 & 0.0707 & 0.0630 \\
800.0000 & 0.0769 & 0.0731 & 0.0653 \\
812.5000 & 0.0777 & 0.0740 & 0.0660 \\
825.0000 & 0.0771 & 0.0735 & 0.0652 \\
837.5000 & 0.0751 & 0.0716 & 0.0630 \\
850.0000 & 0.0721 & 0.0686 & 0.0597 \\
862.5000 & 0.0682 & 0.0647 & 0.0555 \\
875.0000 & 0.0637 & 0.0602 & 0.0507 \\
887.5000 & 0.0588 & 0.0552 & 0.0456 \\
900.0000 & 0.0537 & 0.0502 & 0.0406 \\
\hline
\end{array}
\]

\[ T_{\text{profiles}} \]

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
1.0000e+18 & 0.0526 & 0.0469 & 0.0338 & 0.0726 & 0.0209 & 0.0734 \\
1.2589e+18 & 0.0583 & 0.0508 & 0.0373 & 0.0737 & 0.0239 & 0.0737 \\
1.6849e+18 & 0.0603 & 0.0546 & 0.0409 & 0.0744 & 0.0268 & 0.0744 \\
1.9953e+18 & 0.0638 & 0.0582 & 0.0445 & 0.0747 & 0.0298 & 0.0747 \\
2.5119e+18 & 0.0670 & 0.0615 & 0.0479 & 0.0748 & 0.0332 & 0.0749 \\
3.1693e+18 & 0.0699 & 0.0645 & 0.0512 & 0.0741 & 0.0366 & 0.0752 \\
3.9811e+18 & 0.0724 & 0.0672 & 0.0543 & 0.0734 & 0.0401 & 0.0754 \\
5.0119e+18 & 0.0746 & 0.0695 & 0.0571 & 0.0724 & 0.0437 & 0.0755 \\
6.3098e+18 & 0.0763 & 0.0714 & 0.0599 & 0.0712 & 0.0471 & 0.0758 \\
7.9432e+18 & 0.0776 & 0.0729 & 0.0616 & 0.0688 & 0.0503 & 0.0756 \\
1.0000e+19 & 0.0785 & 0.0740 & 0.0633 & 0.0663 & 0.0537 & 0.0757 \\
1.2589e+19 & 0.0791 & 0.0748 & 0.0646 & 0.0667 & 0.0567 & 0.0757 \\
1.5849e+19 & 0.0794 & 0.0752 & 0.0659 & 0.0650 & 0.0594 & 0.0754 \\
\hline
\end{array}
\]

\[ F_{\text{profiles}} \]
APPENDIX B: Sample Mathcad Calculations for the O\(^+\) \(\rightarrow\) C Case

\[ eV := 1.602 \times 10^{-19} \text{ J} \quad \text{m} := 10^{-9} \text{ m} \]

\[ \text{Average Carbon Density} \quad C_D := \frac{2200 \text{ kg m}^{-3}}{1000 \text{ mol}} = 1.103 \times 10^{29} \text{ m}^{-3} \]

\[ c := 1 \text{ active carbon site} \quad h := 1 \text{ hydrogen atoms} \]

\[ C_{\text{max}} := 0.25 \text{ cm}^{-1} \quad \text{Max. available surface carbon sites} \quad R_H := 100 \text{ nm} \]

\[ k := 1.380658 \times 10^{-23} \text{ joule K}^{-1} \]

**Sample Temperatures**

\[ T := 300 \text{ K, 310 K, 1800 K} \quad I_{\text{max}} := 55 \quad i := 0 \ldots I_{\text{max}} \quad T_{J_i} := 300 \text{ K} + i \times 20 \text{ K} \]

\[ T_S := 800 \text{ K} \quad \text{Fixed sample temperature for flux dependence calculation} \]

**Beam Fluxes**

\[ J_{\text{max}} := 10 \quad j := 0 \ldots J_{\text{max}} \quad \Phi_{J_i} := 10^{(18 + 0.2 j)} \text{ m}^{-2} \text{ s}^{-1} \]

\[ \Phi_O := 1 \times 10^{19} \text{ m}^{-2} \text{ s}^{-1} \quad \text{Fixed flux density for temperature dependence calculation} \]

**Rate Coefficients**

**Rate coefficient equation**

\[ k_{g1} [T_g, K_g, E_g] := K_g \exp \left( \frac{-E_g}{kT_g} \right) \quad s := 0.1 \text{ s}^{-1} \]

\[ k_{g1} [T_g, S_g, g, K_g, E_g] := S_g g + K_g \exp \left( \frac{-E_g}{kT_g} \right) \]
-CO precursor formation

\[ K_{bCO} = 10^5 \text{s}^{-1}, \quad E_{bCO} = 0.0 \text{eV} \]

\[ k_{bCO}(T,g) = k_g(T,g,K_{bCO},E_{bCO}) \]

\[ k_{bCO}(T) = 1 \times 10^5 \]

\[ 0.001 \quad 0.002 \quad 0.003 \quad \frac{1}{T} \]

CO release

\[ \delta_{CO} = 1, \quad K_{CO} = 4 \times 10^4 \text{s}^{-1}, \quad E_{CO} = 0.5 \text{eV} \]

\[ k_{CO}(T,g,S,g) = k_g(T,g,S,g,\delta_{CO},K_{CO},E_{CO}) \]

\[ k_{CO}(T,S) \]

\[ 0.001 \quad 0.002 \quad 0.003 \quad \frac{1}{T} \]

CO₂ formation and release

\[ K_{CO₂} = 8 \times 10^4 \text{s}^{-1}, \quad E_{CO₂} = 0.02 \text{eV} \]

\[ k_{CO₂}(T,g) = k_g(T,g,K_{CO₂},E_{CO₂}) \]

\[ k_{CO₂}(T) = 1 \times 10^5 \]

\[ 0.001 \quad 0.002 \quad 0.003 \quad \frac{1}{T} \]

- CO Dissociation

\[ \delta_{DCO} = 1, \quad K_{DCO} = 0.2 \times 10^4 \text{s}^{-1}, \quad E_{DCO} = 0.25 \text{eV} \]

\[ k_{DCO}(T,g,S,g) = k_g(T,g,S,g,\delta_{DCO},K_{DCO},E_{DCO}) \]

\[ k_{DCO}(T,S) \]

\[ 0.001 \quad 0.002 \quad 0.003 \quad \frac{1}{T} \]
Hydrogen Ion Range Depth Profiles

\[ D_0 := \begin{array}{cccccccc}
0.00 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \\
0.00 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \\
1.00 & 1.25 & 1.25 & 1.25 & 1.25 & 1.25 & 1.25 & 1.25 \\
2.00 & 2.00 & 2.00 & 2.00 & 2.00 & 2.00 & 2.00 & 2.00 \\
3.00 & 3.00 & 3.00 & 3.00 & 3.00 & 3.00 & 3.00 & 3.00 \\
4.00 & 4.00 & 4.00 & 4.00 & 4.00 & 4.00 & 4.00 & 4.00 \\
5.00 & 5.00 & 5.00 & 5.00 & 5.00 & 5.00 & 5.00 & 5.00 \\
6.00 & 6.00 & 6.00 & 6.00 & 6.00 & 6.00 & 6.00 & 6.00 \\
7.00 & 7.00 & 7.00 & 7.00 & 7.00 & 7.00 & 7.00 & 7.00 \\
8.00 & 8.00 & 8.00 & 8.00 & 8.00 & 8.00 & 8.00 & 8.00 \\
9.00 & 9.00 & 9.00 & 9.00 & 9.00 & 9.00 & 9.00 & 9.00 \\
10.00 & 10.00 & 10.00 & 10.00 & 10.00 & 10.00 & 10.00 & 10.00 \\
\end{array} \]

\[ D_{DPA} := \begin{array}{cccccccc}
0.00 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \\
0.00 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \\
1.00 & 1.00 & 1.00 & 1.00 & 1.00 & 1.00 & 1.00 & 1.00 \\
2.00 & 2.00 & 2.00 & 2.00 & 2.00 & 2.00 & 2.00 & 2.00 \\
3.00 & 3.00 & 3.00 & 3.00 & 3.00 & 3.00 & 3.00 & 3.00 \\
4.00 & 4.00 & 4.00 & 4.00 & 4.00 & 4.00 & 4.00 & 4.00 \\
5.00 & 5.00 & 5.00 & 5.00 & 5.00 & 5.00 & 5.00 & 5.00 \\
6.00 & 6.00 & 6.00 & 6.00 & 6.00 & 6.00 & 6.00 & 6.00 \\
7.00 & 7.00 & 7.00 & 7.00 & 7.00 & 7.00 & 7.00 & 7.00 \\
8.00 & 8.00 & 8.00 & 8.00 & 8.00 & 8.00 & 8.00 & 8.00 \\
9.00 & 9.00 & 9.00 & 9.00 & 9.00 & 9.00 & 9.00 & 9.00 \\
10.00 & 10.00 & 10.00 & 10.00 & 10.00 & 10.00 & 10.00 & 10.00 \\
\end{array} \]

Hydrogen Ion Range Depth Profiles

more...

\[ x_O(ei) := D_0 \begin{array}{c}
<2<e_i>
\end{array} \]

extract x ranges

beam spot slice thick

\[ \Delta x := 0.6 \text{ nm} \]

\[ I_x(ei) := \sum_{i=0}^{166} |D_0|^{<2<e_i + 1>} \]

\[ I_{DPA}(ei) := \sum_{i=0}^{166} |D_{DPA}|^{<2<e_i + 1>} \]

average carbon atoms in a beam spot slice [per unit area]

extract source distribution [per carbon atom, normalized]

\[ S_O(\Phi, ei) := \frac{D_0^{<2<e_i + 1>} \Phi}{c_O I_x(ei)} \]

extract source distribution [per carbon atom, normalized]

\[ S_{DPA}(\Phi, ei) := \frac{D_{DPA}^{<2<e_i + 1>} \Phi}{c_O I_x(ei)} \]

\[ S_{O2}(\Phi, ei, i) := \begin{cases} 
\Phi \frac{C_D R(ei)}{R_O(ei)} & \text{if } (x_O(ei) - \text{nm}2R(ei)) \leq x_O(ei) \text{-nm} \leq \text{R}_2(ei) \\
0 \text{ s}^{-1} & \text{otherwise} 
\end{cases} \]

\[ S_{D2}(\Phi, ei, i) := S_{O2}(\Phi, ei, i) \frac{I_{DPA}(ei)}{I_x(ei)} \]

\[ S_O(\Phi, ei) := \frac{\Phi}{C_D R_O(ei)} \]

\[ S_{D3}(\Phi, ei) := S_O(\Phi, ei) \frac{I_{DPA}(ei)}{I_x(ei)} \]

more...

126
Below is the simplified steady-state rate equation for O-only case

Given

\[ 0 = S_{\text{Ol}} - k_{b\text{CO}} O_C (C_{\max} - O_P) - k_{\text{CO}_2} O_P O_C + k_{\text{DCO}} O_P \quad \text{O}_C \]

\[ 0 = k_{b\text{CO}} O_C (C_{\max} - O_P) - :k_{\text{CO}} + k_{\text{CO}_2} - 1 C + k_{\text{DCO}} \quad \text{O}_P \]

\[ f_O(O_C, O_P, S_{\text{Ol}}, k_{b\text{CO}}, k_{\text{CO}}, k_{\text{CO}_2}, k_{\text{DCO}}) := \text{find}(O_C, O_P) \]

\[ G_{\text{O}_2}(\Phi, T, e) := f_O(0, 0, S_{\text{O}_3}(\Phi, e), k_{b\text{CO}}(T), k_{\text{CO}}(T, S_{\text{D}_3}(\Phi, e)), k_{\text{CO}_2}(T), k_{\text{DCO}}(T, S_{\text{D}_3}(\Phi, e))) \]

The Solution

\[ T_{O}(a) := \begin{cases} \text{for } i \in 0..I_{\max} & Y \leftarrow G_{\text{O}_2}(\Phi, T_{I_1}, a) \\ X^T & \end{cases} \]

\[ X^{<2+x>} \leftarrow T_{2500eV} \]

\[ T_{5000eV} := T_{O}(3) \]

\[ T_{2500eV} := T_{O}(3) \]

\[ F_{2500eV} := F_{O}(3) \]

\[ F_{5000eV} := F_{O}(4) \]

\[ T_{\text{extract1}(x)} := \begin{cases} \text{for } i \in 0..I_{\max} & X^{<2+x>} \leftarrow T_{2500eV} \\ X & \end{cases} \]

\[ F_{\text{extract1}(x)} := \begin{cases} \text{for } i \in 0..J_{\max} & X^{<2+x>} \leftarrow F_{2500eV} \\ X & \end{cases} \]

\[ T_{\text{extract2}(x)} := \begin{cases} \text{for } i \in 0..I_{\max} & X^{<2+x>} \leftarrow T_{5000eV} \\ X & \end{cases} \]

\[ F_{\text{extract2}(x)} := \begin{cases} \text{for } i \in 0..J_{\max} & X^{<2+x>} \leftarrow F_{5000eV} \\ X & \end{cases} \]

\[ O_{C,2500eV} := T_{2500eV} <^@> \]

\[ O_{P,2500eV} := T_{2500eV} <^\uparrow> \]

\[ O_{C,5000eV} := T_{5000eV} <^@> \]

\[ O_{P,5000eV} := T_{5000eV} <^\uparrow> \]

\[ O_{C,F25} := F_{2500eV} <^@> \]

\[ O_{P,F25} := F_{2500eV} <^\uparrow> \]

\[ O_{C,F50} := F_{5000eV} <^@> \]

\[ O_{P,F50} := F_{5000eV} <^\uparrow> \]
Plotting the solution

\[ \text{Concentrations [carbon]} \]

\[ T_J \quad \text{Temperature [K]} \]

\[ \text{O}_C_{2500\text{eV}} \]
\[ \text{O}_P_{2500\text{eV}} \]

\[ \text{O}_C_{5000\text{eV}} \]
\[ \text{O}_P_{5000\text{eV}} \]
And now calculating flux by integration using trapezoid method

For Temperature Profile, input flux fixed at: \( \Phi_O = 1 \times 10^{19} \text{ m}^{-2} \text{ s}^{-1} \)

\[
\int_{\text{CO}_25000eV(j)} = k_{\text{CO}}(T_j \cdot S \cdot D_3(\Phi_o, 3)) \cdot O_{P, 25000eV_j} \cdot R \cdot O(3) \frac{C_D}{\Phi_O}
\]

\[
\int_{\text{CO}_22500eV(j)} = k_{\text{CO}_2}(T_j \cdot S \cdot D_3(\Phi_o, 3)) \cdot O_{P, 25000eV_j} \cdot R \cdot O(3) \frac{C_D}{\Phi_O}
\]

\[
J_{\text{CO}_225000eV(j)} = f_{\text{CO}_225000eV(i)} \quad J_{\text{CO}_225000eV(j)} = f_{\text{CO}_225000eV(i)}
\]

\[
\int_{\text{CO}_50000eV(j)} = k_{\text{CO}_2}(T_j \cdot S \cdot D_3(\Phi_o, 4)) \cdot O_{P, 50000eV_j} \cdot R \cdot O(4) \frac{C_D}{\Phi_O}
\]

\[
\int_{\text{CO}_25000eV(j)} = k_{\text{CO}_2}(T_j \cdot S \cdot D_3(\Phi_o, 4)) \cdot O_{P, 50000eV_j} \cdot R \cdot O(4) \frac{C_D}{\Phi_O}
\]

\[
J_{\text{CO}_250000eV(j)} = f_{\text{CO}_250000eV(i)} \quad J_{\text{CO}_250000eV(j)} = f_{\text{CO}_250000eV(i)}
\]

For Flux Dependence, sample temperature fixed at: \( T_s = 800 \text{ K} \)

\[
\int_{\text{CO}_25000eV(j)} = k_{\text{CO}_2}(T_s \cdot S \cdot D_3(\Phi_j, 3)) \cdot O_{P, F250j} \cdot R \cdot O(3) \frac{C_D}{\Phi_j}
\]

\[
\int_{\text{CO}_25000eV(j)} = k_{\text{CO}_2}(T_s \cdot S \cdot D_3(\Phi_j, 4)) \cdot O_{P, F250j} \cdot R \cdot O(4) \frac{C_D}{\Phi_j}
\]

\[
J_{\text{CO}_225000eV(j)} = f_{\text{CO}_225000eV(j)} \quad J_{\text{CO}_225000eV(j)} = f_{\text{CO}_225000eV(j)}
\]

\[
\int_{\text{CO}_50000eV(j)} = k_{\text{CO}_2}(T_s \cdot S \cdot D_3(\Phi_j, 4)) \cdot O_{P, F500j} \cdot R \cdot O(4) \frac{C_D}{\Phi_j}
\]

\[
\int_{\text{CO}_25000eV(j)} = k_{\text{CO}_2}(T_s \cdot S \cdot D_3(\Phi_j, 4)) \cdot O_{P, F500j} \cdot R \cdot O(4) \frac{C_D}{\Phi_j}
\]

\[
J_{\text{CO}_250000eV(j)} = f_{\text{CO}_250000eV(j)} \quad J_{\text{CO}_250000eV(j)} = f_{\text{CO}_250000eV(j)}
\]
### Chi-squared test for temperature dependence

- **$N_{\text{Data}} := \text{length}(T_{\text{c}})$** Number of data points
- **$N_{\text{Free}} := 4$** Number of free parameters
- **$df := N_{\text{Data}} - N_{\text{Free}}$** Degrees of freedom

#### CO

- $\chi^2_{\text{CO}} := \sum_{i=0,1, \ldots, N_{\text{Data}} - 1} \left( \frac{T_{\text{c}, i} - 300}{\sigma} - 0.5 \right)^2$
- $\sigma := \text{mean}(CO_{c}) - 0.2$
- $S := S + \frac{\chi^2_{\text{CO}}}{\sigma^2}$

#### CO$_2$

- $\chi^2_{\text{CO}_2} := \sum_{i=0,1, \ldots, N_{\text{Data}} - 1} \left( \frac{T_{\text{c}, i} - 300}{\sigma} - 0.5 \right)^2$
- $\sigma := \max(CO2_{c}) - 0.2$
- $S := S + \frac{\chi^2_{\text{CO}_2}}{\sigma^2}$

- $\chi^2_{v,\text{CO}} := \frac{\chi^2_{\text{CO}}}{df}$
- $\chi^2_{v,\text{CO}} = 8.008$ reduced chi-squared value for CO fit
- $p\text{chisq}(\chi^2_{\text{CO}}, df) = 0.157$

- $\chi^2_{v,\text{CO}_2} := \frac{\chi^2_{\text{CO}_2}}{df}$
- $\chi^2_{v,\text{CO}_2} = 9.604$ reduced chi-squared value for CO$_2$ fit
- $p\text{chisq}(\chi^2_{\text{CO}_2}, df) = 0.274$
TEMPERATURE DEPENDENCE OF CO

TEMPERATURE DEPENDENCE OF CO2

Temperature [K]

CO Yield (CO2/CO)

CO2 Yield (CO2/CO)

T_J, T_J, T_{c_i}, K, T_{v_i}, K, T_{r_i}, K, T_J, T_J
Output Tables for graphing

\[ T_{\text{profiles}_{i,0}} := T_{j_i} \cdot K^{-1} \quad T_{\text{profiles}_{i,1}} := J \cdot CO_{2500_i} \quad T_{\text{profiles}_{i,2}} := J \cdot CO_{2500_i} \]

\[ F_{\text{profiles}_{j,0}} := \Phi_j \cdot m^{-2} \quad F_{\text{profiles}_{j,1}} := J_1 \cdot CO_{2500_j} \quad F_{\text{profiles}_{j,2}} := J_1 \cdot CO_{2500_j} \]

\[ T_{\text{profiles}_{i,3}} := J \cdot CO_{5000_i} \quad T_{\text{profiles}_{i,4}} := J \cdot CO_{5000_i} \]

\[ F_{\text{profiles}_{j,3}} := J_1 \cdot CO_{5000_j} \quad F_{\text{profiles}_{j,4}} := J_1 \cdot CO_{5000_j} \]

<table>
<thead>
<tr>
<th>( T )</th>
<th>( 300.00 )</th>
<th>( 320.00 )</th>
<th>( 340.00 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_{\text{profiles}} )</td>
<td>0.67</td>
<td>0.66</td>
<td>0.65</td>
</tr>
<tr>
<td>( 0.17 )</td>
<td>( 0.17 )</td>
<td>( 0.17 )</td>
<td></td>
</tr>
<tr>
<td>( 0.75 )</td>
<td>( 0.75 )</td>
<td>( 0.74 )</td>
<td></td>
</tr>
<tr>
<td>( 0.12 )</td>
<td>( 0.13 )</td>
<td>( 0.13 )</td>
<td></td>
</tr>
</tbody>
</table>

\[ \begin{array}{cccc}
1.00 \times 10^{18} & 0.73 & 0.14 & 0.81 \\
1.59 \times 10^{18} & 0.69 & 0.16 & 0.78 \\
2.51 \times 10^{18} & 0.66 & 0.17 & 0.75 \\
\end{array} \]

\[ F_{\text{profiles}} \]

\[ \begin{array}{cccc}
443.00 & 0.63 & 0.16 \\
473.00 & 0.60 & 0.17 \\
513.00 & 0.63 & 0.16 \\
543.00 & 0.65 & 0.17 \\
\end{array} \]

Chen

\[ \begin{array}{cccc}
443.00 & 0.63 & 0.16 \\
473.00 & 0.60 & 0.17 \\
513.00 & 0.63 & 0.16 \\
543.00 & 0.65 & 0.17 \\
\end{array} \]

\[ \begin{array}{cccc}
300.00 & 0.53 & 0.10 \\
493.00 & 0.40 & 0.14 \\
596.00 & 0.39 & 0.15 \\
695.00 & 0.47 & 0.14 \\
\end{array} \]

Vietzke

\[ \begin{array}{cccc}
300.00 & 0.46 & 0.10 \\
500.00 & 0.36 & 0.12 \\
700.00 & 0.31 & 0.13 \\
900.00 & 0.38 & 0.11 \\
\end{array} \]

Refke
APPENDIX C: Sample Mathcad Calculations for the O⁺-H⁺ → C Case

eV := 1.602 \cdot 10^{-19} \text{ J} \quad \text{nm} := 10^{-9} \text{ m}

\text{Average Carbon Density} \quad C_D := \frac{2200 \text{ kg/m}^3 \cdot 6.0221367 \cdot 10^{23} \text{ mole}^{-1}}{12.011 \text{ kg/1000 mol}} = 1.103 \cdot 10^{29} \text{ m}^{-3}

c := 1 \quad \text{active carbon site} \quad h := 1 \quad \text{hydrogen atoms}

C_{H\text{max}} := 0.42 \text{ e}^{-1} \quad \text{Max. available surface carbon sites for H-trapping} \quad R_H := 100 - \text{nm}

C_{O\text{max}} := 0.25 \text{ e}^{-1} \quad \text{Max. available surface carbon sites for O-trapping}

b := 0.75 \quad \text{CH}_4 \text{ power dependence}

k := 1.380658 \cdot 10^{-23} \text{ m}^2 \text{ mole} \cdot \text{K}^{-1}

\text{Sample Temperatures}

T := 300 \cdot \text{K, 310 K, 1800 K} \quad I := 50 \quad i := 0 \ldots 1 \text{ max} \quad T_j := 500 \cdot \text{K} + i \cdot 20 \cdot \text{K}

T_S := 800 \cdot \text{K} \quad \text{Fixed sample temperature for flux dependence calculation}

\text{Beam Fluxes}

J_{\text{max}} := 20 \quad j := 0 \ldots J_{\text{max}} \quad \Phi_{j} := 10^{(19 + 0.1j)} \text{ m}^{-2} \text{ s}^{-1}

\Phi_{H} := 5 \cdot 10^{19} \text{ m}^{-2} \text{ s}^{-1} \quad \text{Fixed flux density for temperature dependence calculation}

\Phi_{O} := 1 \cdot 10^{19} \text{ m}^{-2} \text{ s}^{-1} \quad \text{Fixed flux density for temperature dependence calculation} \quad \frac{\Phi_O}{\Phi_H} = 0.2

\text{Rate Coefficients}

\text{Rate coefficient equation}

k_g(T_g, K_g, E_g) := K_g \exp \left( \frac{-E_g}{k \cdot T_g} \right)

S_H := 0.025 \text{ s}^{-1}

S_O := 0.15 \text{ s}^{-1}
transport out of crystallite

\[ k_S := 8.73 \times 10^5 \text{ s}^{-1}, \quad E_S := 0.42 \text{ eV} \]

\[ k_S(T_g) := k_S(T) e^{E_S/T} \]

recombination

\[ k_{SS} := 8 \times 10^{16} \text{ s}^{-1}, \quad E_{SS} := 0.56 \text{ eV} \]

\[ k_{SS}(T_g) := k_S(T) e^{E_{SS}/T} \]

CH precursor dissociation (detrapping)

\[ \delta_D := 1, \quad K_D := 6.0 \times 10^{11} \text{ s}^{-1}, \quad E_D := 2.2 \text{ eV} \]

\[ k_D(T_g, S_g) := k_D(T) e^{E_D/T} \]

CH precursor formation (trapping)

\[ k_{CH} := 1.0 \times 10^3 \text{ s}^{-1}, \quad E_{CH} := 0.0 \text{ eV} \]

\[ k_{CH}(T_g) := k_S(T) e^{E_CH/T} \]

volatile CH$_3$ formation

\[ k_{MP} := 9.0 \times 10^{11} \text{ s}^{-1}, \quad E_{MP} := 1.5 \text{ eV} \]

\[ k_{MP}(T_g) := k_S(T) e^{E_{MP}/T} \]

Water Release

\[ k_W := 4.0 \times 10^{12} \text{ s}^{-1}, \quad E_W := 1.0 \text{ eV} \]

\[ k_W(T_g) := k_S(T) e^{E_W/T} \]
### Ion Range Depth Profiles

<table>
<thead>
<tr>
<th>$D_{ac}$</th>
<th>0.00</th>
<th>0.00</th>
<th>0.00</th>
<th>0.00</th>
<th>0.00</th>
<th>0.00</th>
<th>0.00</th>
<th>0.00</th>
<th>0.00</th>
<th>0.00</th>
<th>0.00</th>
<th>0.00</th>
<th>0.00</th>
<th>0.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_{H}$</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c_{O}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Hydrogen and Oxygen beam energy indexes for 1000 eV/H$^+$ and 5000 eV/O$^+$

<table>
<thead>
<tr>
<th>$E_{D_{PA}}$</th>
<th>$E_{D_{PA}}$</th>
<th>$E_{D_{PA}}$</th>
<th>$E_{D_{PA}}$</th>
<th>$E_{D_{PA}}$</th>
<th>$E_{D_{PA}}$</th>
<th>$E_{D_{PA}}$</th>
<th>$E_{D_{PA}}$</th>
<th>$E_{D_{PA}}$</th>
<th>$E_{D_{PA}}$</th>
<th>$E_{D_{PA}}$</th>
<th>$E_{D_{PA}}$</th>
<th>$E_{D_{PA}}$</th>
<th>$E_{D_{PA}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1000$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$5000$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### More...

#### Extract $x$ ranges

- $x_{R(ci)} := D_{2} - c_{i} >$

#### Beam spot slice thickness

- $\Delta x := 0.6 \, mm$

#### Average carbon atoms in a beam spot slice [per unit area]

- $c_{A} := \Delta x \cdot C_{D}$

#### More...

- $RI(ci) := \frac{R_{R}(ci)}{R_{R}^{(ci)}}$
- $RI_{2}(ci) := \frac{R_{R}(ci)}{R_{R}^{(ci)}}$
- $RI_{3}(ci) := \frac{R_{R}(ci)}{R_{R}^{(ci)}}$
- $RI_{4}(ci) := \frac{R_{R}(ci)}{R_{R}^{(ci)}}$

- $\theta_{H} := \frac{RI(ci)}{RI_{2}(ci)}$
- $\theta_{H} := \frac{RI(ci)}{RI_{2}(ci)}$
- $\theta_{H} := \frac{RI(ci)}{RI_{2}(ci)}$
- $\theta_{H} := \frac{RI(ci)}{RI_{2}(ci)}$

- $S_{H}(\Phi, ci) := \frac{D_{2} - c_{i} >}{c_{A} \cdot \Delta x_{(ci)}}$
- $S_{H}(\Phi, ci) := \frac{D_{2} - c_{i} >}{c_{A} \cdot \Delta x_{(ci)}}$
- $S_{H}(\Phi, ci) := \frac{D_{2} - c_{i} >}{c_{A} \cdot \Delta x_{(ci)}}$
- $S_{H}(\Phi, ci) := \frac{D_{2} - c_{i} >}{c_{A} \cdot \Delta x_{(ci)}}$

- $S_{H}(\Phi, ci) := \frac{D_{2} - c_{i} >}{c_{A} \cdot \Delta x_{(ci)}}$
- $S_{H}(\Phi, ci) := \frac{D_{2} - c_{i} >}{c_{A} \cdot \Delta x_{(ci)}}$
- $S_{H}(\Phi, ci) := \frac{D_{2} - c_{i} >}{c_{A} \cdot \Delta x_{(ci)}}$
- $S_{H}(\Phi, ci) := \frac{D_{2} - c_{i} >}{c_{A} \cdot \Delta x_{(ci)}}$

- $\phi := \frac{C_{B} \cdot R_{R}(ci)}{R_{R}(ci)}$
- $\phi := \frac{C_{B} \cdot R_{R}(ci)}{R_{R}(ci)}$
- $\phi := \frac{C_{B} \cdot R_{R}(ci)}{R_{R}(ci)}$
- $\phi := \frac{C_{B} \cdot R_{R}(ci)}{R_{R}(ci)}$

- $0 < 1$
- $0 < 1$
- $0 < 1$
- $0 < 1$

#### 3000 eV H$^+$ and 5000 eV O$^+$

- $S_{H} := S_{H}(\Phi, ci, H_{i}, 11)$
- $S_{O} := S_{O}(\Phi, O_{i}, O_{i})$
- $X_{H} := S_{D_{3}} \Phi_{H_{i}, c_{i}} + \text{mix}_{O} S_{D_{3}}(\Phi_{O_{i}, c_{i}})$
- $X_{O} := S_{D_{3}} \Phi_{O_{i}, c_{i}} + \text{mix}_{H} S_{D_{3}}(\Phi_{H_{i}, c_{i}})$
Below is the simplified steady-state rate equation for H+O case

**Given**

\[ H_C = 0 = S_{HI} - k_{CH} H_C \cdot C_{H_{max}} - H_P - k_S H_C - 2 k_{MP} H_P \cdot H_C + k_D H_P \]

\[ H_P = 0 = k_{CH} H_C \cdot C_{H_{max}} - H_P - k_{MP} H_P \cdot H_C - k_D H_P \]

\[ H_S = 0 = k_S H_C \cdot (1 + \theta) \cdot 2 k_{SS} H_S \cdot S_{HI} - \sigma_{M} k_{MP} H_P \cdot H_C + \theta_{di,0} H_O H_P \cdot H_S^2 + k_{DOH} H_P + 4 \sigma_{b,0} \frac{S_{OI}}{S_{HI}} \sigma_{M} k_{MP} H_P \cdot H_C^b \]

\[ O_C = 0 = S_{OI} - k_{bCO} O_C \cdot C_{O_{max}} - O_P - k_{CO2} O_P O_C + k_{DCO} O_P \]

\[ O_P = 0 = k_{bCO} O_C \cdot C_{O_{max}} - O_P - k_{CO} + k_{CO2} O_C + k_{DCO} + k_{OH} H_S^2 + O_P + k_{DOH} H_P \]

\[ W_P = 0 = k_{OH} H_S^2 + O_P - k_{DOH} H_P - k_{W} H_P \]

\[ f_{OH} = H_C, H_S, H_P, O_C, O_P, W_P, S_{HI}, S_{OI}, S_{SS}, k_{CH}, k_{MP}, k_{D}, k_{bCO}, k_{CO}, k_{CO2}, k_{DCO}, k_{OH}, k_{DOH}, k_{W}, \theta_{H}, \theta_1, \theta_2, \sigma_b \]

**The Solution**

\[ T_{OH} := T_{OH} \]

\[ \sigma_{H} := \sigma_{b} \]

\[ v := f_{OH}(0, 0, 0, 0, 0, 0, S_{HI}, S_{OI}, S_{SS}, T), k_{CH}(T), k_{MP}(T), k_{D}(T), T, X_{HI}, k_{bCO}(T), k_{CO}(T), X_{O}, k_{CO2}(T), k_{DCO}(T), X_{O}, k_{OH}(T), k_{DOH}(T), T, X_{O}, k_{W}(T), \theta_{H}, \sigma_{b} \]

\[ X^{i,0} := v \]

for \( i \in 1..l_{max} \)

\[ T_{OH} := T_{OH} \]

\[ v := f_{OH}(v_1, v_2, v_3, v_4, v_5, S_{HI}, S_{OI}, S_{SS}, T), k_{CH}(T), k_{MP}(T), k_{D}(T), T, X_{HI}, k_{bCO}(T), k_{CO}(T), X_{O}, k_{CO2}(T), k_{DCO}(T), X_{O}, k_{OH}(T), k_{DOH}(T), T, X_{O}, k_{W}(T), \theta_{H}, \sigma_{b} \]

\[ X^{i,1} := v \]

\[ X^T \]

\[ H_{C,T} := T_{OH} \]

\[ H_{S,T} := T_{OH} \]

\[ H_{P,T} := T_{OH} \]

\[ O_{C,T} := T_{OH} \]

\[ O_{P,T} := T_{OH} \]

\[ W_{P,T} := T_{OH} \]
\[ F_O = T - T_S \]
\[ \sigma_h = 0 \]
\[ v_T = T^{<15>} \]
\[ s_h = 0 \text{ s}^{-1} \]
\[ s_o = S_D / \Phi_{O, eO} \]
\[ x_h = 0 \text{ s}^{-1} \]
\[ x_o = S_D / \Phi_{O, eO} \]
\[ v = f(y_0, y_1, y_2, y_3, y_4, y_5, S_h, S_o, k_s(T), k_{SS}(T), k_{CH}(T), k_{MP}(T), k_D(T), k_CO(T), k_CO_2(T), k_{DCO}(T), k_{OH}(T), k_{DOH}(T), k_{W}(T), \theta, H, \sigma_h) \]
\[ x^{<0>} \leftarrow v \]
\[ \text{for } i = 1 \text{ to } J_{MAX} \]
\[ v = f(y_0, y_1, y_2, y_3, y_4, y_5, S_h, S_o, k_s(T), k_{SS}(T), k_{CH}(T), k_{MP}(T), k_D(T), k_CO(T), k_CO_2(T), k_{DCO}(T), k_{OH}(T), k_{DOH}(T), k_{W}(T), \theta, H, \sigma_h) \]
\[ x^{<i>} \leftarrow v \]

\[ H_{C, FO} = F_O^{<0>} \]
\[ H_{S, FO} = F_O^{<1>} \]
\[ H_{P, FO} = F_O^{<2>} \]
\[ O_{C, FO} = F_O^{<3>} \]
\[ O_{P, FO} = F_O^{<4>} \]
\[ W_{P, FO} = F_O^{<5>} \]
And now calculating flux by integration using trapezoid method

For Temperature Profile, input flux fixed at: \( \Phi_{\text{H}} = 5 \cdot 10^{19} \text{ m}^{-2} \text{s}^{-1} \quad \Phi_{\text{O}} = 1 \cdot 10^{19} \text{ m}^{-2} \text{s}^{-1} \)

\[
\begin{align*}
\phi_{\text{H}_{2}(a)} &= k_{\text{SS}} \left( \frac{\Phi_{\text{H}}}{C_{\text{D}}} \right)^{2} \text{R}_{\text{2H}}(\text{eH}) \\
\phi_{\text{H}_{2}(a)} &= k_{\text{SS}} \left( \frac{\Phi_{\text{H}}}{C_{\text{D}}} \right)^{2} \text{R}_{\text{2H}}(\text{eH}) \\
\phi_{\text{CH}_{4}(a)} &= 1 - \alpha_{B} \frac{S_{\text{O}}}{S_{\text{H}}} \frac{k_{\text{MP}}(T_{J_a})}{k_{\text{PM}}(T_{J_a})} \frac{1}{\Phi_{\text{H}}} \frac{H_{\text{T}}}{H_{\text{T}_{a}}} \frac{1}{H_{\text{T}}_{a}} \text{R}_{\text{H}}(\text{eH}) \frac{C_{\text{D}}}{\Phi_{\text{H}}} \\
\phi_{\text{CH}_{4}(a)} &= 1 - \alpha_{B} \frac{S_{\text{O}}}{S_{\text{H}}} \frac{k_{\text{MP}}(T_{J_a})}{k_{\text{PM}}(T_{J_a})} \frac{1}{\Phi_{\text{H}}} \frac{H_{\text{T}}}{H_{\text{T}_{a}}} \frac{1}{H_{\text{T}}_{a}} \text{R}_{\text{H}}(\text{eH}) \frac{C_{\text{D}}}{\Phi_{\text{H}}} \\
J_{\text{H}_{2}(a)} &= \phi_{\text{H}_{2}(a)} \quad J_{\text{H}_{2}(a)} = \phi_{\text{H}_{2}(a)} \\
J_{\text{H}_{2}(a)} &= \phi_{\text{H}_{2}(a)} \quad J_{\text{H}_{2}(a)} = \phi_{\text{H}_{2}(a)} \\
J_{\text{CH}_{4}(a)} &= \phi_{\text{CH}_{4}(a)} \quad J_{\text{CH}_{4}(a)} = \phi_{\text{CH}_{4}(a)} \\
J_{\text{CH}_{4}(a)} &= \phi_{\text{CH}_{4}(a)} \quad J_{\text{CH}_{4}(a)} = \phi_{\text{CH}_{4}(a)} \\
J_{\text{CO}(a)} &= \phi_{\text{CO}(a)} \quad J_{\text{CO}(a)} = \phi_{\text{CO}(a)} \\
J_{\text{CO}(a)} &= \phi_{\text{CO}(a)} \quad J_{\text{CO}(a)} = \phi_{\text{CO}(a)} \\
J_{\text{CO}_{2}(a)} &= \phi_{\text{CO}_{2}(a)} \quad J_{\text{CO}_{2}(a)} = \phi_{\text{CO}_{2}(a)} \\
J_{\text{CO}_{2}(a)} &= \phi_{\text{CO}_{2}(a)} \quad J_{\text{CO}_{2}(a)} = \phi_{\text{CO}_{2}(a)} \\
J_{\text{W}(a)} &= \phi_{\text{W}(a)} \quad J_{\text{W}(a)} = \phi_{\text{W}(a)} \\
J_{\text{W}(a)} &= \phi_{\text{W}(a)} \quad J_{\text{W}(a)} = \phi_{\text{W}(a)}
\end{align*}
\]

0 DPA(0) = 1.692 0 DPA(3) = 11.588 0 DPA(1) = 2.13 0 DPA(4) = 17.734
For Flux Profile, sample temperature fixed at: $T_S = 800\cdot K$

$g_{H_2(a)} := k_{SS}^T(S_s;1^T_{S,J} a_2 \cdot R_2(cH)) \frac{C_D}{\phi_{J_a}}$

$g_{CH_4(a)} := \left[ 1 - \sigma_{H} \theta \text{dia} \frac{S_O}{S_{13}(\phi_{J_a}, cH)} \right] k_{MP}^T(S_s;1^T_{P,F_a} b \cdot R(cH) \frac{C_D}{\phi_{J_a}}$

$g_{H_2(a)} := k_{SS}^T(S_s;1^T_{S,FH_a} 2^T_{2} \cdot R_2(cH)) \frac{C_D}{\phi_{J_a}}$

$g_{CH_4(a)} := k_{MP}^T(S_s;1^T_{P,FH_a} b \cdot R(cH) \frac{C_D}{\phi_{J_a}}$

$J_2 H_2 := g_{H_2}(j)$

$J_2 CH_4 := g_{CH_4}(j)$

$J_3 H_2 := g_{H_2}(j)$

$J_3 CH_4 := g_{CH_4}(j)$

$g_{CO(a)} := k_{CO}^T(S_s, S_{D3} \cdot \phi_{CO}, cO) + \frac{mix}{H} S_{D3} \cdot \phi_{J_a} \cdot cH \cdot O_{P,F_a} \cdot R(cO) \frac{C_D}{\phi_{O}}$

$g_{CO_2(a)} := k_{CO_2}^T(S_s;1^T_{O,F_a} b \cdot O_{P,F_a} \cdot R(cO) \frac{C_D}{\phi_{O}}$

$g_{CO(a)} := k_{CO}^T(S_s, S_{D3} \cdot \phi_{CO}, cO) + \frac{mix}{H} S_{D3} \cdot \phi_{J_a} \cdot cH \cdot O_{P,F_a} \cdot R(cO) \frac{C_D}{\phi_{O}}$

$g_{CO_2(a)} := k_{CO_2}^T(S_s;1^T_{O,F_a} b \cdot O_{P,F_a} \cdot R(cO) \frac{C_D}{\phi_{O}}$

$J_2 CO := g_{CO}(j)$

$J_2 CO_2 := g_{CO_2}(j)$

$J_3 CO := g_{CO}(j)$

$J_3 CO_2 := g_{CO_2}(j)$

$g_{W(a)} := k_{W}^T(S_s, W_{P,F_a} \cdot R(cO) \frac{C_D}{\phi_{O}}$

$g_{W(a)} := \theta \text{dia} k_{W}^T(S_s, W_{P,F_a} \cdot R(cO) \frac{C_D}{\phi_{J_a}}$

$J_2 W := g_{W}(j)$

$J_3 W := g_{W}(j)$
### Chen Results

<table>
<thead>
<tr>
<th>( T_e )</th>
<th>( \text{CO}_e )</th>
<th>( \text{CO}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>443</td>
<td>0.625</td>
<td>0.16</td>
</tr>
<tr>
<td>473</td>
<td>0.597</td>
<td>0.167</td>
</tr>
<tr>
<td>513</td>
<td>0.63</td>
<td>0.164</td>
</tr>
<tr>
<td>543</td>
<td>0.654</td>
<td>0.166</td>
</tr>
<tr>
<td>573</td>
<td>0.615</td>
<td>0.164</td>
</tr>
<tr>
<td>623</td>
<td>0.563</td>
<td>0.117</td>
</tr>
<tr>
<td>643</td>
<td>0.726</td>
<td>0.174</td>
</tr>
<tr>
<td>673</td>
<td>0.637</td>
<td>0.169</td>
</tr>
</tbody>
</table>

### Vietzke Results

<table>
<thead>
<tr>
<th>( T_e )</th>
<th>( \text{CO}_e )</th>
<th>( \text{CO}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.53</td>
<td>0.14</td>
</tr>
<tr>
<td>493</td>
<td>0.4</td>
<td>0.15</td>
</tr>
<tr>
<td>596</td>
<td>0.385</td>
<td>0.14</td>
</tr>
<tr>
<td>695</td>
<td>0.465</td>
<td>0.14</td>
</tr>
<tr>
<td>880</td>
<td>0.55</td>
<td>0.11</td>
</tr>
<tr>
<td>1130</td>
<td>0.66</td>
<td>0.07</td>
</tr>
<tr>
<td>1280</td>
<td>0.67</td>
<td>0.04</td>
</tr>
<tr>
<td>1375</td>
<td>0.71</td>
<td>0.02</td>
</tr>
<tr>
<td>1580</td>
<td>0.69</td>
<td>0.004</td>
</tr>
<tr>
<td>1770</td>
<td>0.67</td>
<td>0</td>
</tr>
</tbody>
</table>

### CH\(_4\) Temperature profile from Chen et al

<table>
<thead>
<tr>
<th>( C )</th>
<th>( T_{WL} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>443,000</td>
<td>0.0009</td>
</tr>
<tr>
<td>473,000</td>
<td>0.0009</td>
</tr>
<tr>
<td>513,000</td>
<td>0.0011</td>
</tr>
<tr>
<td>543,000</td>
<td>0.0016</td>
</tr>
<tr>
<td>573,000</td>
<td>0.0017</td>
</tr>
<tr>
<td>623,000</td>
<td>0.0077</td>
</tr>
<tr>
<td>643,000</td>
<td>0.0096</td>
</tr>
<tr>
<td>673,000</td>
<td>0.0138</td>
</tr>
<tr>
<td>723,000</td>
<td>0.0379</td>
</tr>
<tr>
<td>823,000</td>
<td>0.0717</td>
</tr>
</tbody>
</table>

### H\(_2\)O Temperature profile from Chen et al

<table>
<thead>
<tr>
<th>( T_{WR} )</th>
<th>( \text{H}<em>2\text{O}</em>{WR} )</th>
<th>( \text{H}<em>2\text{O}</em>{WL} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>513</td>
<td>0.015</td>
<td>0.006</td>
</tr>
<tr>
<td>543</td>
<td>0.038</td>
<td>0.006</td>
</tr>
<tr>
<td>573</td>
<td>0.011</td>
<td>0.085</td>
</tr>
<tr>
<td>623</td>
<td>0.121</td>
<td>0.158</td>
</tr>
<tr>
<td>643</td>
<td>0.104</td>
<td>0.195</td>
</tr>
<tr>
<td>673</td>
<td>0.106</td>
<td>0.218</td>
</tr>
<tr>
<td>723</td>
<td>0.14</td>
<td>0.139</td>
</tr>
<tr>
<td>823</td>
<td>0.137</td>
<td>0.116</td>
</tr>
<tr>
<td>873</td>
<td>0.15</td>
<td>0.035</td>
</tr>
<tr>
<td>973</td>
<td>0.1</td>
<td>0.03</td>
</tr>
<tr>
<td>1133</td>
<td>0.057</td>
<td>0.03</td>
</tr>
<tr>
<td>1303</td>
<td>0.023</td>
<td>0.03</td>
</tr>
</tbody>
</table>

### Flux Ratio dependence from Chen et al

<table>
<thead>
<tr>
<th>( F_{\text{DAT}} )</th>
<th>( F_{\text{R}} = F_{\text{DAT}} )</th>
<th>( F_{\text{CO}<em>0} = F</em>{\text{DAT}} )</th>
<th>( F_{\text{CO}<em>1} = F</em>{\text{DAT}} )</th>
<th>( F_{\text{CO}<em>2} = F</em>{\text{DAT}} )</th>
<th>( F_{\text{CO}<em>2} = F</em>{\text{DAT}} )</th>
<th>( F_{\text{CO}<em>2} = F</em>{\text{DAT}} )</th>
<th>( F_{\text{CO}<em>2} = F</em>{\text{DAT}} )</th>
<th>( F_{\text{CO}<em>2} = F</em>{\text{DAT}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>10.00</td>
<td>10.00</td>
<td>10.00</td>
<td>10.00</td>
<td>10.00</td>
<td>10.00</td>
<td>10.00</td>
<td>10.00</td>
<td>10.00</td>
</tr>
<tr>
<td>0.70</td>
<td>0.70</td>
<td>0.70</td>
<td>0.70</td>
<td>0.70</td>
<td>0.70</td>
<td>0.70</td>
<td>0.70</td>
<td>0.70</td>
</tr>
<tr>
<td>0.63</td>
<td>0.63</td>
<td>0.63</td>
<td>0.63</td>
<td>0.63</td>
<td>0.63</td>
<td>0.63</td>
<td>0.63</td>
<td>0.63</td>
</tr>
<tr>
<td>0.69</td>
<td>0.69</td>
<td>0.69</td>
<td>0.69</td>
<td>0.69</td>
<td>0.69</td>
<td>0.69</td>
<td>0.69</td>
<td>0.69</td>
</tr>
<tr>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
</tr>
<tr>
<td>0.59</td>
<td>0.59</td>
<td>0.59</td>
<td>0.59</td>
<td>0.59</td>
<td>0.59</td>
<td>0.59</td>
<td>0.59</td>
<td>0.59</td>
</tr>
<tr>
<td>0.64</td>
<td>0.64</td>
<td>0.64</td>
<td>0.64</td>
<td>0.64</td>
<td>0.64</td>
<td>0.64</td>
<td>0.64</td>
<td>0.64</td>
</tr>
<tr>
<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
</tr>
<tr>
<td>0.16</td>
<td>0.16</td>
<td>0.16</td>
<td>0.16</td>
<td>0.16</td>
<td>0.16</td>
<td>0.16</td>
<td>0.16</td>
<td>0.16</td>
</tr>
<tr>
<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
</tr>
<tr>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
</tr>
</tbody>
</table>
Temperature Dependence of H₂

Temperature Dependence of CH₄
Chi-squared test for 
\(\text{H}_2\text{O} \) temperature dependence

\[ \chi^2 := \frac{S}{\sigma^2} \]
for \( i = 0, 1 \ldots N_{\text{Data}} - 1 \)

- \( \alpha_i = \frac{T_{WR_i} - 5000}{20} + 0.5 \)
- \( \nu_i = T_{WR_i} - J_{W_{\alpha_i}} \)
- \( \sigma_i = \max(T_{WR_i}) 0.2 \)
- \( S_i = S + \frac{\nu_i^2}{\sigma_i^2} \)

Reduced chi-squared value

\[ \chi^2_v := \frac{\chi^2}{df} \]
where \( \chi^2 = 5.674 \) and \( \chi^2_v = 0.63 \)

\( p \chi^2 (\chi^2_v, df) = 0.228 \)
### Output Tables for graphing

<table>
<thead>
<tr>
<th>Value</th>
<th>0.50</th>
<th>0.50</th>
<th>3.38e-5</th>
<th>3.05e-5</th>
<th>0.70</th>
<th>0.78</th>
<th>0.15</th>
<th>0.11</th>
<th>0.01</th>
</tr>
</thead>
<tbody>
<tr>
<td>500.00</td>
<td>0.50</td>
<td>0.50</td>
<td>9.33e-5</td>
<td>8.30e-5</td>
<td>0.70</td>
<td>0.77</td>
<td>0.15</td>
<td>0.11</td>
<td>0.02</td>
</tr>
<tr>
<td>520.00</td>
<td>0.50</td>
<td>0.50</td>
<td>0.00</td>
<td>0.00</td>
<td>0.70</td>
<td>0.76</td>
<td>0.15</td>
<td>0.11</td>
<td>0.02</td>
</tr>
<tr>
<td>540.00</td>
<td>0.50</td>
<td>0.50</td>
<td>0.00</td>
<td>0.00</td>
<td>0.69</td>
<td>0.75</td>
<td>0.15</td>
<td>0.11</td>
<td>0.03</td>
</tr>
<tr>
<td>560.00</td>
<td>0.50</td>
<td>0.50</td>
<td>0.00</td>
<td>0.00</td>
<td>0.69</td>
<td>0.74</td>
<td>0.15</td>
<td>0.11</td>
<td>0.04</td>
</tr>
<tr>
<td>580.00</td>
<td>0.50</td>
<td>0.49</td>
<td>0.00</td>
<td>0.00</td>
<td>0.68</td>
<td>0.73</td>
<td>0.15</td>
<td>0.11</td>
<td>0.06</td>
</tr>
<tr>
<td>600.00</td>
<td>0.50</td>
<td>0.49</td>
<td>0.00</td>
<td>0.00</td>
<td>0.68</td>
<td>0.72</td>
<td>0.15</td>
<td>0.11</td>
<td>0.08</td>
</tr>
<tr>
<td>629.00</td>
<td>0.49</td>
<td>0.49</td>
<td>0.00</td>
<td>0.00</td>
<td>0.68</td>
<td>0.72</td>
<td>0.15</td>
<td>0.11</td>
<td>0.10</td>
</tr>
<tr>
<td>640.00</td>
<td>0.49</td>
<td>0.48</td>
<td>0.01</td>
<td>0.00</td>
<td>0.68</td>
<td>0.71</td>
<td>0.16</td>
<td>0.10</td>
<td>0.09</td>
</tr>
<tr>
<td>660.00</td>
<td>0.47</td>
<td>0.47</td>
<td>0.01</td>
<td>0.01</td>
<td>0.69</td>
<td>0.70</td>
<td>0.15</td>
<td>0.10</td>
<td>0.11</td>
</tr>
<tr>
<td>680.00</td>
<td>0.46</td>
<td>0.46</td>
<td>0.02</td>
<td>0.01</td>
<td>0.68</td>
<td>0.69</td>
<td>0.15</td>
<td>0.10</td>
<td>0.13</td>
</tr>
<tr>
<td>700.00</td>
<td>0.44</td>
<td>0.44</td>
<td>0.03</td>
<td>0.02</td>
<td>0.68</td>
<td>0.68</td>
<td>0.16</td>
<td>0.10</td>
<td>0.14</td>
</tr>
<tr>
<td>720.00</td>
<td>0.42</td>
<td>0.42</td>
<td>0.04</td>
<td>0.03</td>
<td>0.69</td>
<td>0.68</td>
<td>0.16</td>
<td>0.10</td>
<td>0.15</td>
</tr>
<tr>
<td>740.00</td>
<td>0.41</td>
<td>0.41</td>
<td>0.05</td>
<td>0.04</td>
<td>0.69</td>
<td>0.67</td>
<td>0.16</td>
<td>0.10</td>
<td>0.16</td>
</tr>
<tr>
<td>760.00</td>
<td>0.38</td>
<td>0.39</td>
<td>0.06</td>
<td>0.05</td>
<td>0.69</td>
<td>0.67</td>
<td>0.16</td>
<td>0.10</td>
<td>0.17</td>
</tr>
<tr>
<td>780.00</td>
<td>0.36</td>
<td>0.37</td>
<td>0.07</td>
<td>0.06</td>
<td>0.69</td>
<td>0.66</td>
<td>0.16</td>
<td>0.10</td>
<td>0.17</td>
</tr>
<tr>
<td>800.00</td>
<td>0.35</td>
<td>0.36</td>
<td>0.07</td>
<td>0.07</td>
<td>0.70</td>
<td>0.65</td>
<td>0.15</td>
<td>0.10</td>
<td>0.18</td>
</tr>
<tr>
<td>820.00</td>
<td>0.35</td>
<td>0.36</td>
<td>0.07</td>
<td>0.06</td>
<td>0.70</td>
<td>0.65</td>
<td>0.15</td>
<td>0.10</td>
<td>0.17</td>
</tr>
<tr>
<td>840.00</td>
<td>0.35</td>
<td>0.36</td>
<td>0.07</td>
<td>0.06</td>
<td>0.70</td>
<td>0.65</td>
<td>0.15</td>
<td>0.10</td>
<td>0.17</td>
</tr>
<tr>
<td>860.00</td>
<td>0.37</td>
<td>0.37</td>
<td>0.07</td>
<td>0.06</td>
<td>0.71</td>
<td>0.65</td>
<td>0.15</td>
<td>0.10</td>
<td>0.17</td>
</tr>
<tr>
<td>880.00</td>
<td>0.38</td>
<td>0.38</td>
<td>0.07</td>
<td>0.06</td>
<td>0.71</td>
<td>0.64</td>
<td>0.15</td>
<td>0.10</td>
<td>0.17</td>
</tr>
<tr>
<td>900.00</td>
<td>0.40</td>
<td>0.40</td>
<td>0.05</td>
<td>0.05</td>
<td>0.73</td>
<td>0.67</td>
<td>0.14</td>
<td>0.10</td>
<td>0.17</td>
</tr>
<tr>
<td>920.00</td>
<td>0.42</td>
<td>0.42</td>
<td>0.05</td>
<td>0.05</td>
<td>0.73</td>
<td>0.67</td>
<td>0.14</td>
<td>0.10</td>
<td>0.17</td>
</tr>
<tr>
<td>940.00</td>
<td>0.43</td>
<td>0.43</td>
<td>0.04</td>
<td>0.04</td>
<td>0.74</td>
<td>0.68</td>
<td>0.13</td>
<td>0.10</td>
<td>0.15</td>
</tr>
<tr>
<td>960.00</td>
<td>0.44</td>
<td>0.44</td>
<td>0.03</td>
<td>0.03</td>
<td>0.75</td>
<td>0.70</td>
<td>0.12</td>
<td>0.10</td>
<td>0.13</td>
</tr>
<tr>
<td>980.00</td>
<td>0.46</td>
<td>0.45</td>
<td>0.02</td>
<td>0.02</td>
<td>0.76</td>
<td>0.71</td>
<td>0.12</td>
<td>0.10</td>
<td>0.12</td>
</tr>
</tbody>
</table>

### T Profiles

<table>
<thead>
<tr>
<th>Value</th>
<th>50.78</th>
<th>2.37</th>
<th>12.91</th>
<th>0.06</th>
</tr>
</thead>
<tbody>
<tr>
<td>79.43</td>
<td>43.68</td>
<td>2.77</td>
<td>15.57</td>
<td>0.07</td>
</tr>
<tr>
<td>63.10</td>
<td>37.39</td>
<td>3.24</td>
<td>18.68</td>
<td>0.08</td>
</tr>
<tr>
<td>50.12</td>
<td>31.83</td>
<td>3.79</td>
<td>22.30</td>
<td>0.08</td>
</tr>
<tr>
<td>39.81</td>
<td>26.95</td>
<td>4.43</td>
<td>26.43</td>
<td>0.11</td>
</tr>
<tr>
<td>31.62</td>
<td>22.70</td>
<td>5.18</td>
<td>31.07</td>
<td>0.13</td>
</tr>
<tr>
<td>25.12</td>
<td>19.03</td>
<td>6.05</td>
<td>36.19</td>
<td>0.15</td>
</tr>
<tr>
<td>19.95</td>
<td>15.87</td>
<td>7.04</td>
<td>41.69</td>
<td>0.18</td>
</tr>
<tr>
<td>15.85</td>
<td>13.19</td>
<td>8.14</td>
<td>47.45</td>
<td>0.20</td>
</tr>
<tr>
<td>12.50</td>
<td>10.91</td>
<td>9.34</td>
<td>53.32</td>
<td>0.23</td>
</tr>
<tr>
<td>10.00</td>
<td>8.99</td>
<td>10.63</td>
<td>59.14</td>
<td>0.25</td>
</tr>
</tbody>
</table>

### F Profiles