Heavy Ion Radiolysis from Curie to Present

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Marie Skłodowska Curie

Nobel Prize in Chemistry 1911

Radium and Polonium (1898)

$^{210}Po \Rightarrow {}^{206}Pb + \alpha$ (5.4 MeV, $t_{1/2}$ = 138 days)

$^{226}Ra \Rightarrow {}^{222}Rn + \alpha$ (4.9 MeV, $t_{1/2}$ = 1601 years)

First heavy ion sources

Early Studies using Radium Sources

P. Curie and A. Debierne, Sur la radio-activité induite et les gas activés par le radium, Compt. Rend. 132, 768-70 (1901)

W. Ramsay and F. Soddy, Experiments in radioactivity, and the production of helium from radium, Proc. Roy. Soc. 72, 204-7 (1903)

W. Ramsay, The chemical action of the radium emanation. Part I. Action on distilled water, J. Chem. Soc. London 91, 931-42 (1907)

A. T. Cameron and W. Ramsay, The chemical action of radium emanation. Part III. On water and certain gases, J. Chem. Soc. London 93, 966-92 (1908)

M. Kernbaum, Sur la décomposition de l'eau par divers rayonnements, Radium, 7, 242 (1910)

W. Duane and O. Scheuer, Décomposition de l'eau par les rayons α Compt. Rend. 156, 466-467 (1913)

W. Duane and O. Scheuer, Recherches sur la décomposition de l'eau par les rayons α, Radium 10, 33-46 (1913)

Decomposition of Radium and Water

$$^{224}Ra \Rightarrow {}^{220}Rn + \alpha$$

$$^{224}Ra + H_2O \Rightarrow {}^{220}Rn + \alpha\ (He) + H_2 + ?$$

$2H_2O$ ^^^→ $H_2O_2 + H_2$

Observe only molecular products

Early Studies on Water Decomposition

O. Risse, On the radio-photolysis of hydroperoxide, Z. Physik. Chem. A140, 133 (1929)
H. Fricke and E. R. Brownscombe, Inability of x-rays to decompose water, Phys. Rev. 44, 240 (1933)

H_2O	^^^→	H_2O^{act}
H_2O^{act}	→	H_2O
H_2O^{act} + reactant	→	product

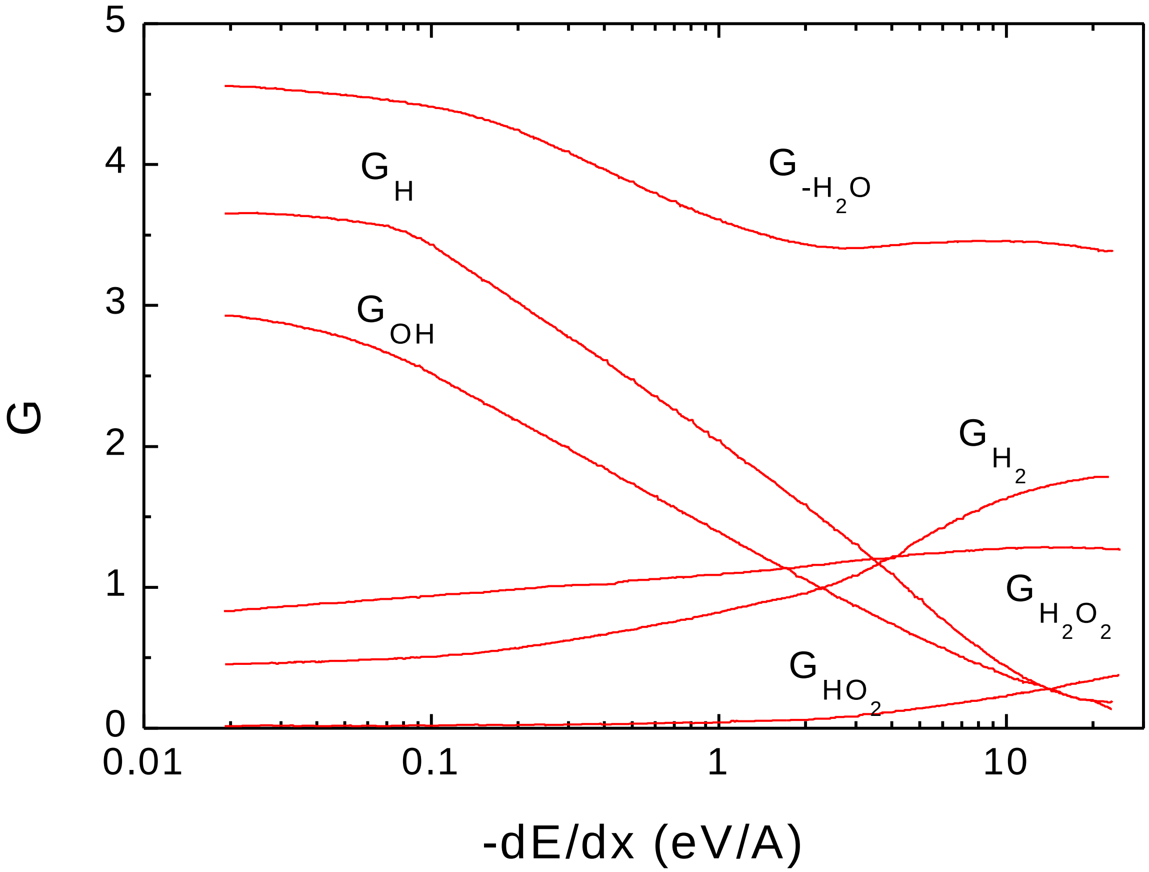
J. Weiss, Radiochemistry of aqueous solutions, Nature 153, 748 (1944)

H_2O ^^^→ •H + •OH

Acceptance of radical chemistry

LET Effects in Water

A. O. Allen, "The Radiation Chemistry of Water and Aqueous Solutions",
Van Nostrand, Princeton, p. 58, 1961.

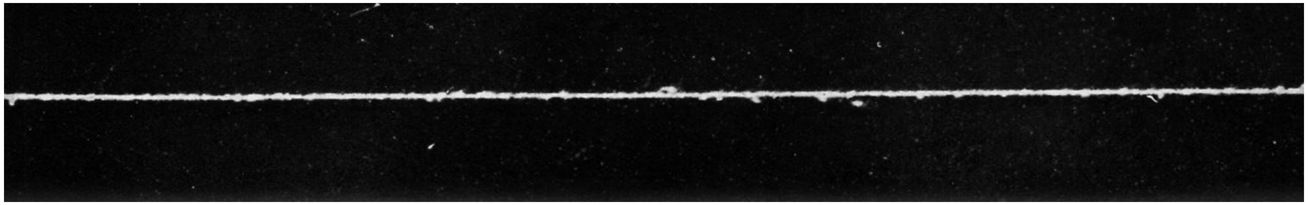


First summary of LET effects

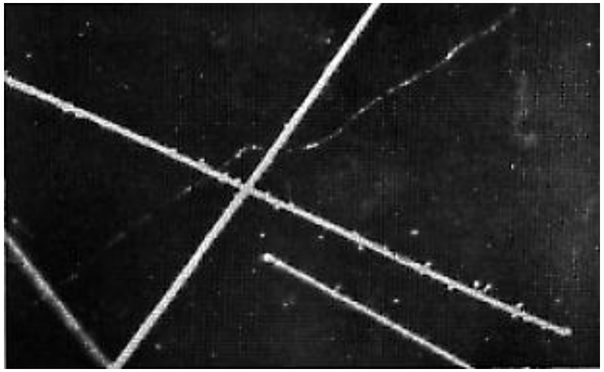
Cloud Chamber Tracks

β-particle: C. T. R. Wilson *Proc. Roy. Soc. A*, **1923**, *104*, 192

proton: P. I. Dee *Proc. Roy. Soc. A*, **1932**, *136*, 727



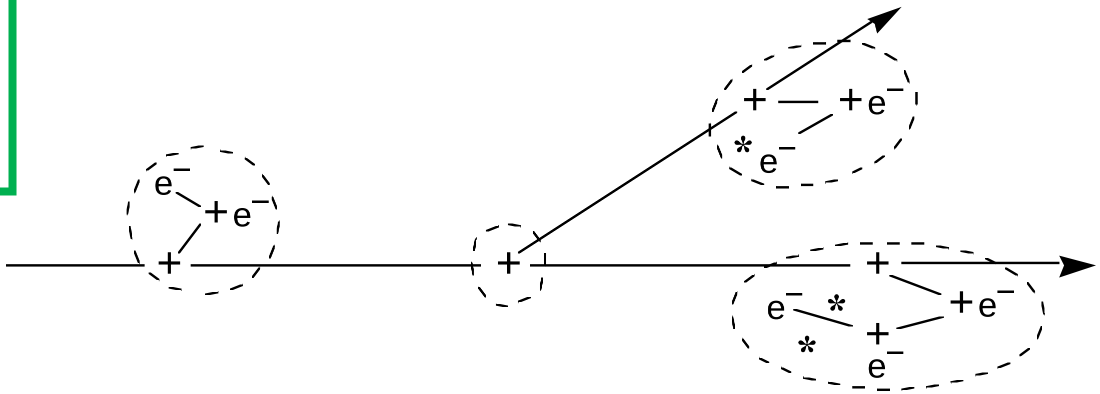
α-particle: C. T. R. Wilson *Proc. Cam. Phil. Soc. A*, **1922**, *21*, 405



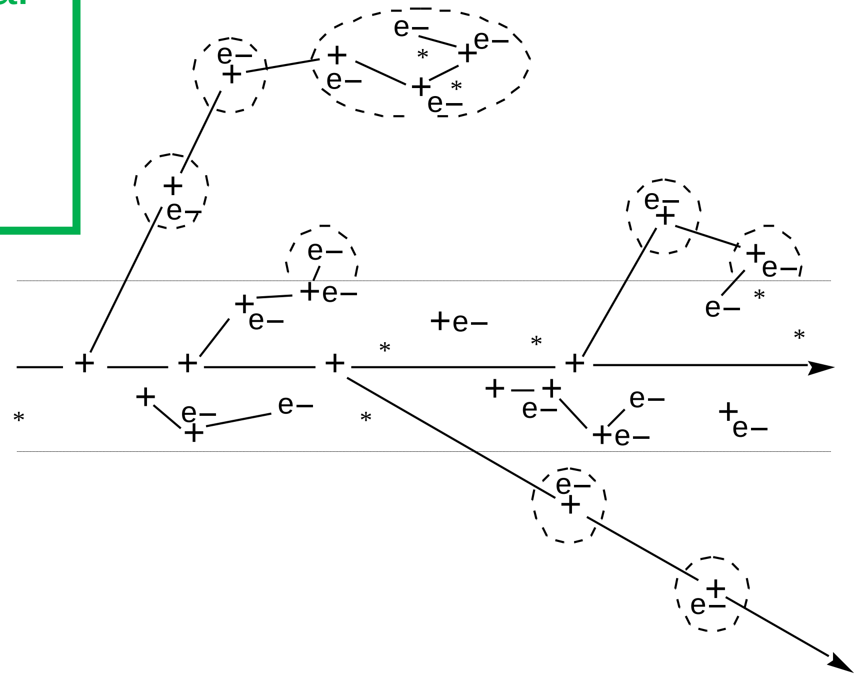
Various particles have tracks that look different.

Visualization of Tracks

Electron track made of isolated clusters with few reactive species in each.

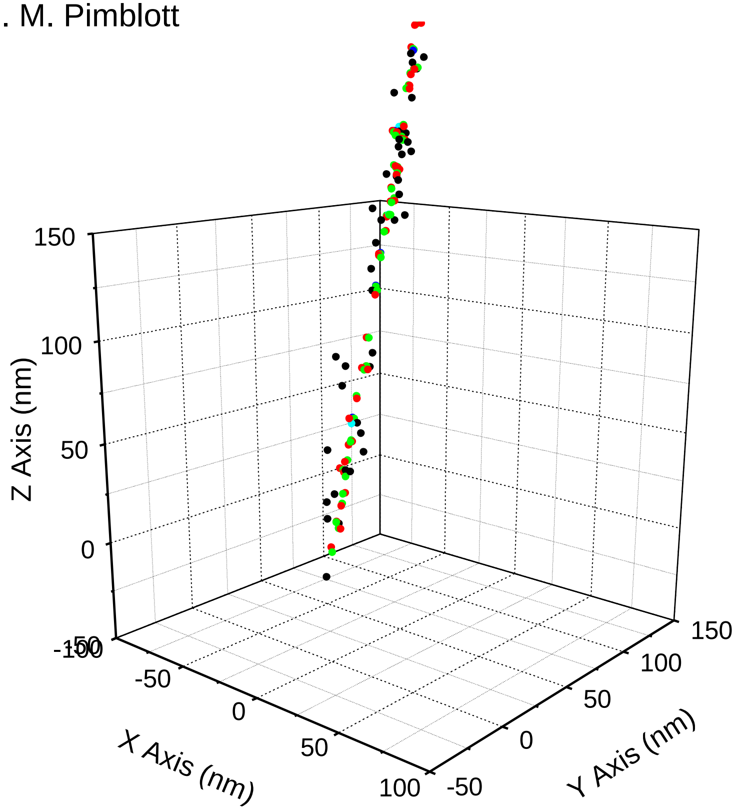


Heavy ion track has cylindrical structure with high concentration of reactive species.



Differences in 10 keV Track Segments at 1 ps

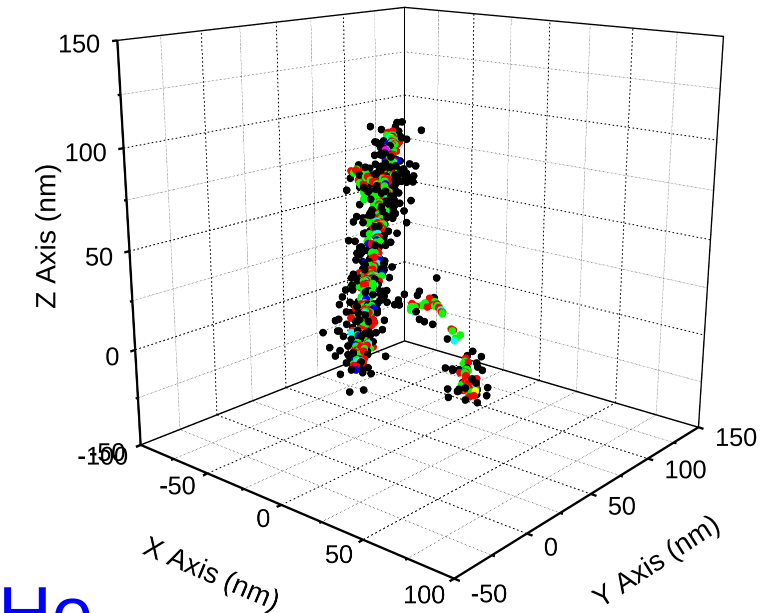
S. M. Pimblott



10 MeV ^{1}H

Black : e^-_{aq}
Red : H_3O^+
Green : OH
Blue : H
Cyan : H_2
Magenta : OH^-
Yellow : H_2O_2
Dark yellow : $O(^3P)$

Modern codes give “realistic” track structures.



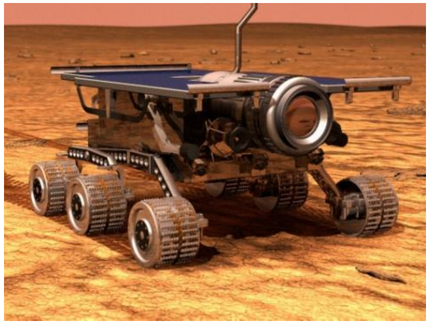
5 MeV ^{4}He

Radiation Effects due to Nuclear Power

Transuranics are α-particle emitters.
Must deal with legacy of weapons and reactors.

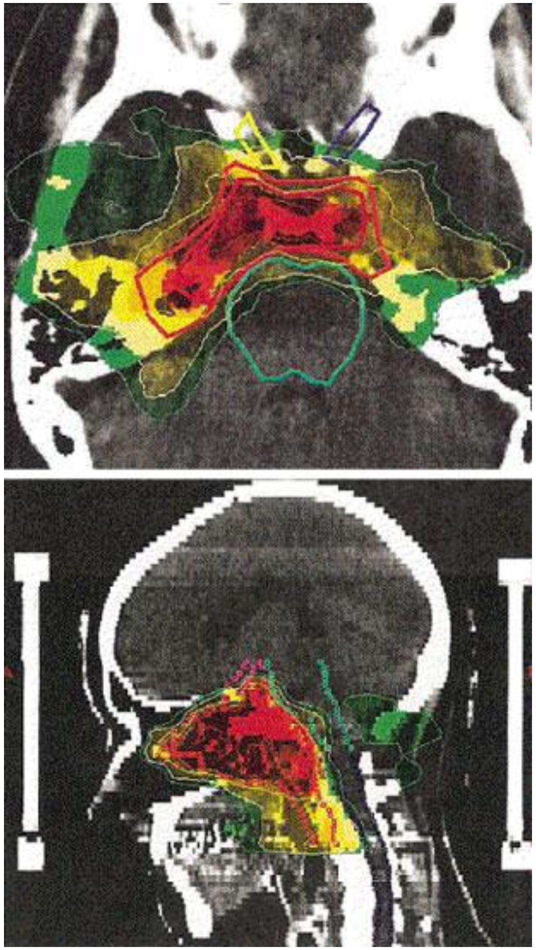
Heavy Ion Radiolysis in Space

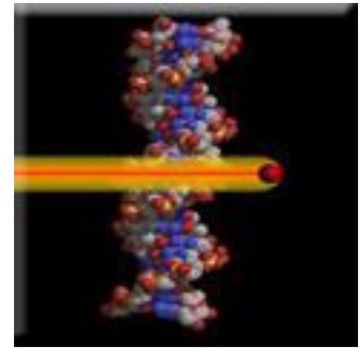
solar/cosmic radiation: H, He, etc.
planetary particles

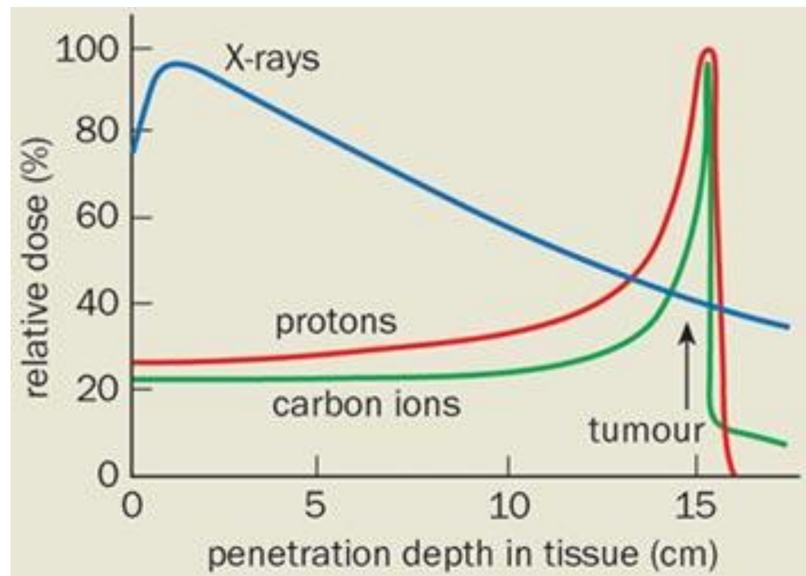


Applications in space exploration and origin of life.

Health / Therapy Effects due to Track Structure

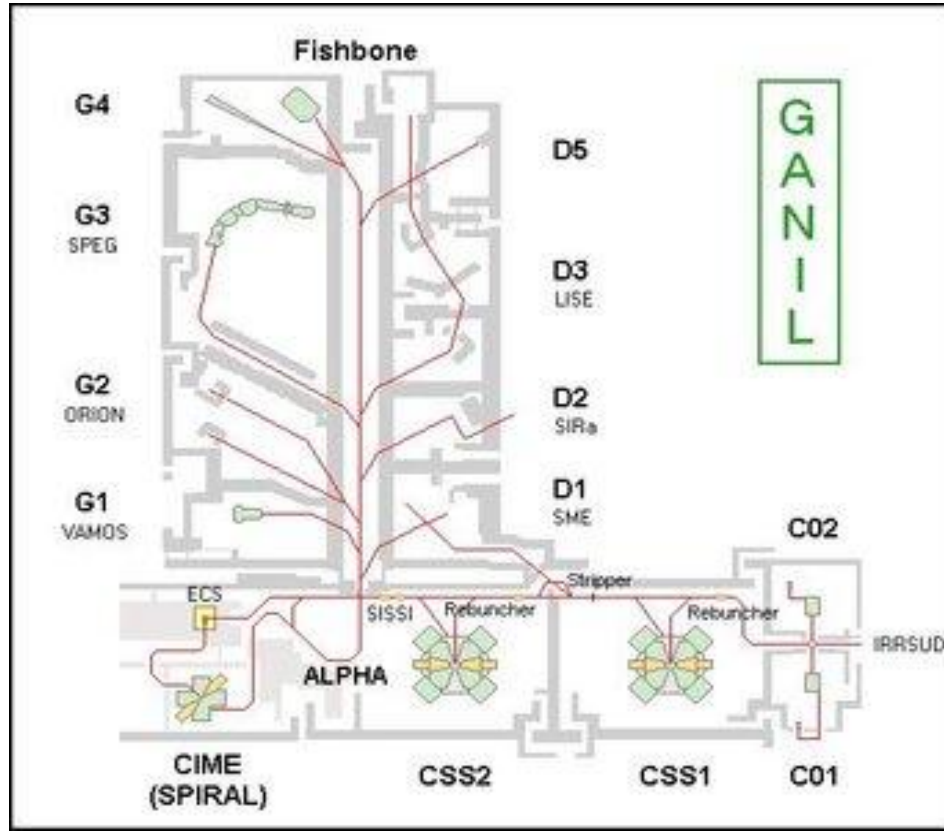






Precise dose delivery with heavy ions

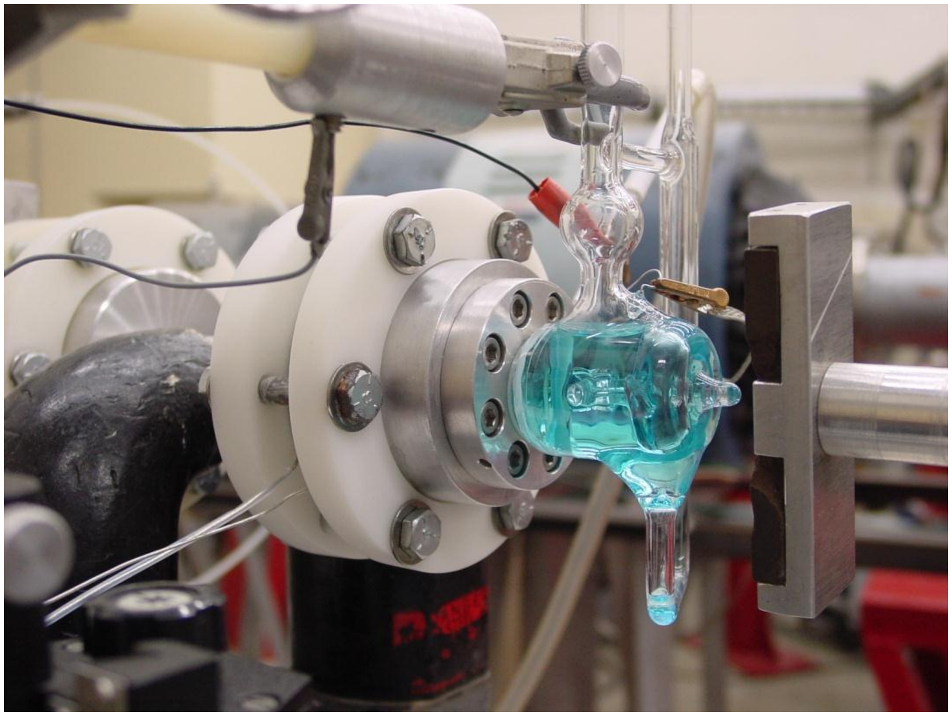
Advancement of Heavy Ion Radiolysis



Progression from radium salts to advanced accelerators

Radiolysis of Water and Aqueous Solutions

$$H_2O \rightarrow e_{aq}^-,\ H_3O^+,\ OH,\ H,\ H_2,\ H_2O_2$$



e_{aq}^- : electron transfer reactions

H_2 : explosive, flammable

H_2O_2 : corrosive

OH : biological

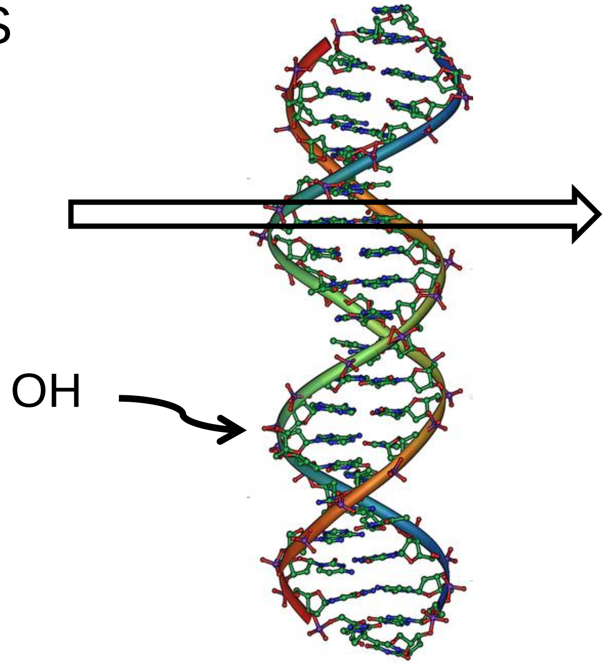
DNA Radiation Damage

Direct Effects

DNA → single strand breaks, SSB

double strand breaks, DSB

multiply damaged sites, MDS



Indirect Effects

$H_2O \rightarrow OH$

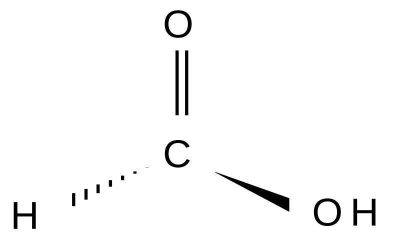
$n(OH) + DNA \rightarrow SSB, DSB, MDS$

OH Radical Scavenging

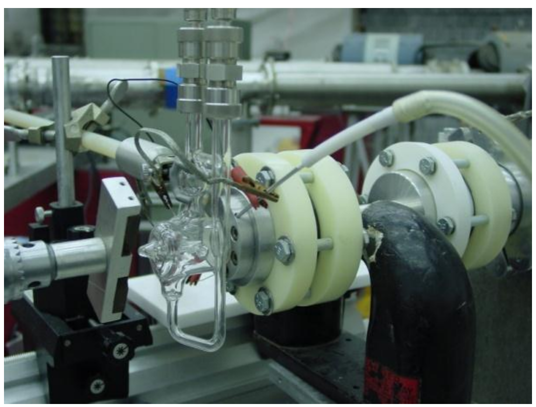
$$H_2O \wedge\wedge\wedge\rightarrow e_{aq}^-,\ H_3O^+,\ OH,\ H,\ H_2$$

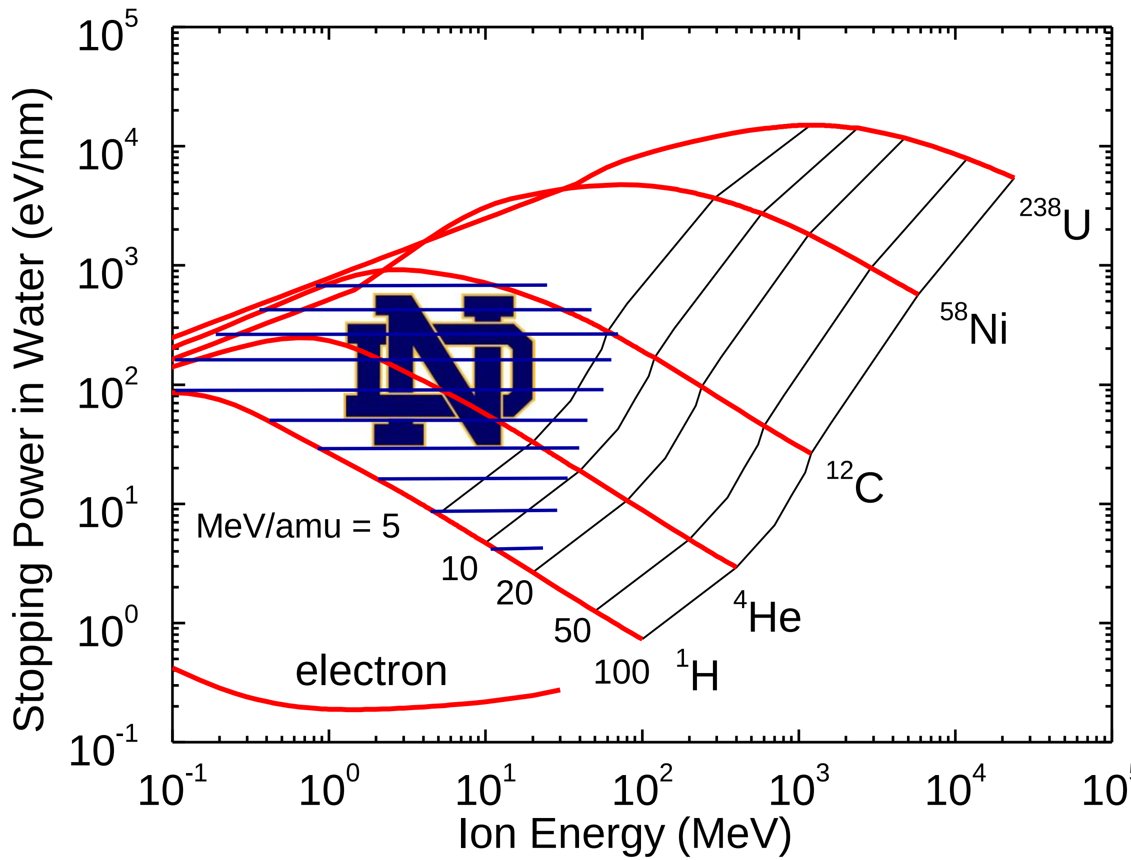
			k ($M^{-1}s^{-1}$)
$\bullet OH + \bullet OH$	$\rightarrow$	H_2O_2	5.5×10^9
$e_{aq} + \bullet OH$	$\rightarrow$	OH^-	3.0×10^{10}
• • •	Track Reactions	• • •	
$\bullet OH + HCOOH$	$\rightarrow$	$H_2O + \bullet COOH$	1.3×10^8
$\bullet H + HCOOH$	$\rightarrow$	$H_2 + \bullet COOH$	4.4×10^5
$\bullet COOH + O_2$	$\rightarrow$	$CO_2 + \bullet HO_2$	

formic acid



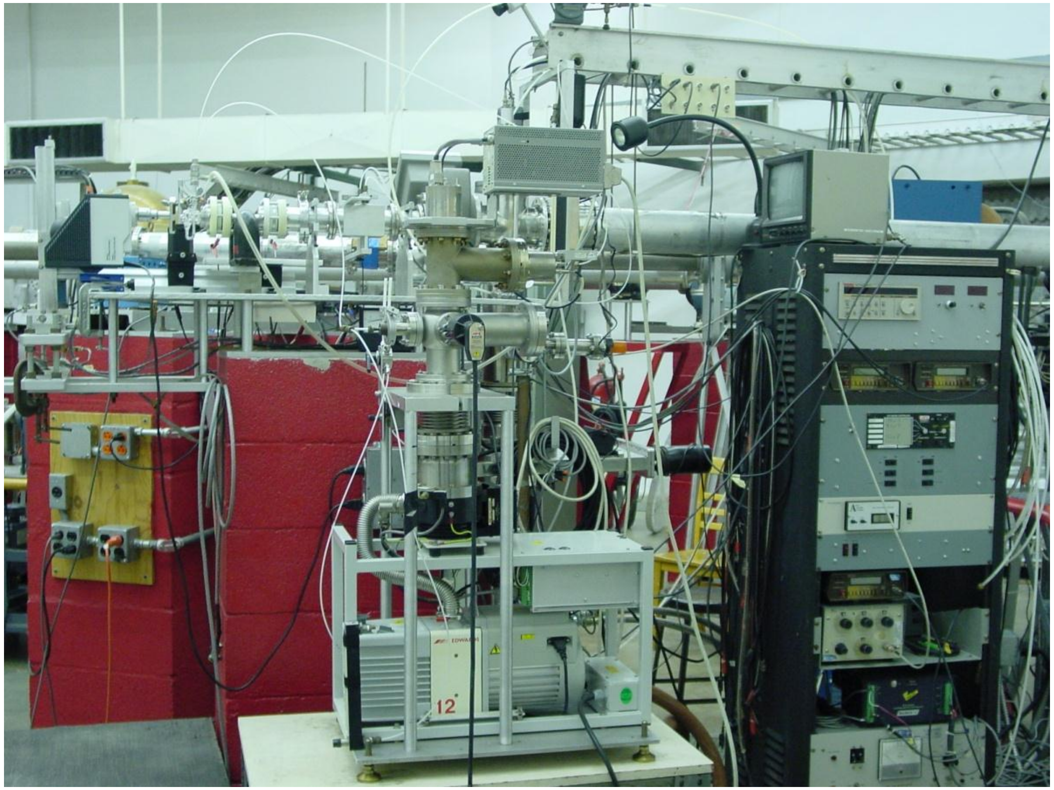
Ion Characteristics

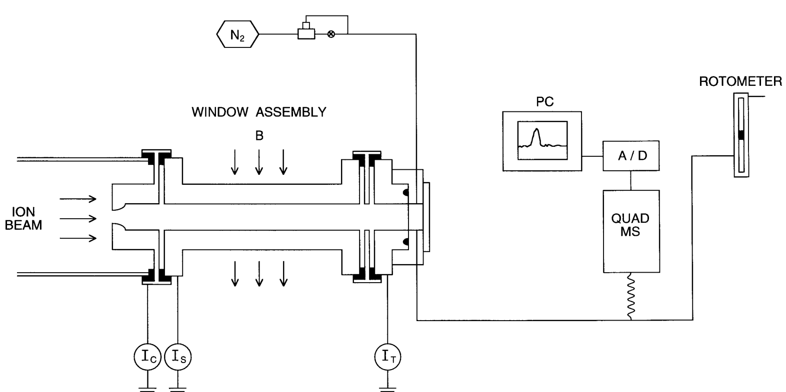


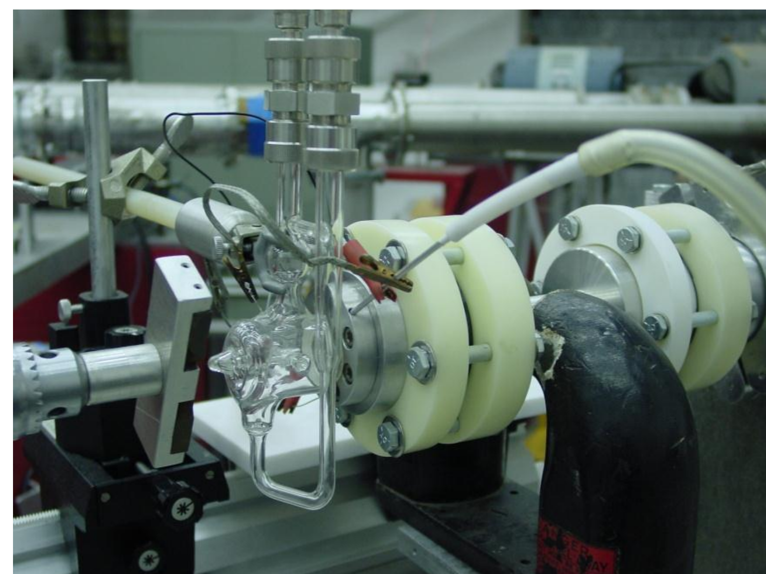


Notre Dame has a core set of ion accelerators.
Each ion has a different track structure, physics and chemistry.

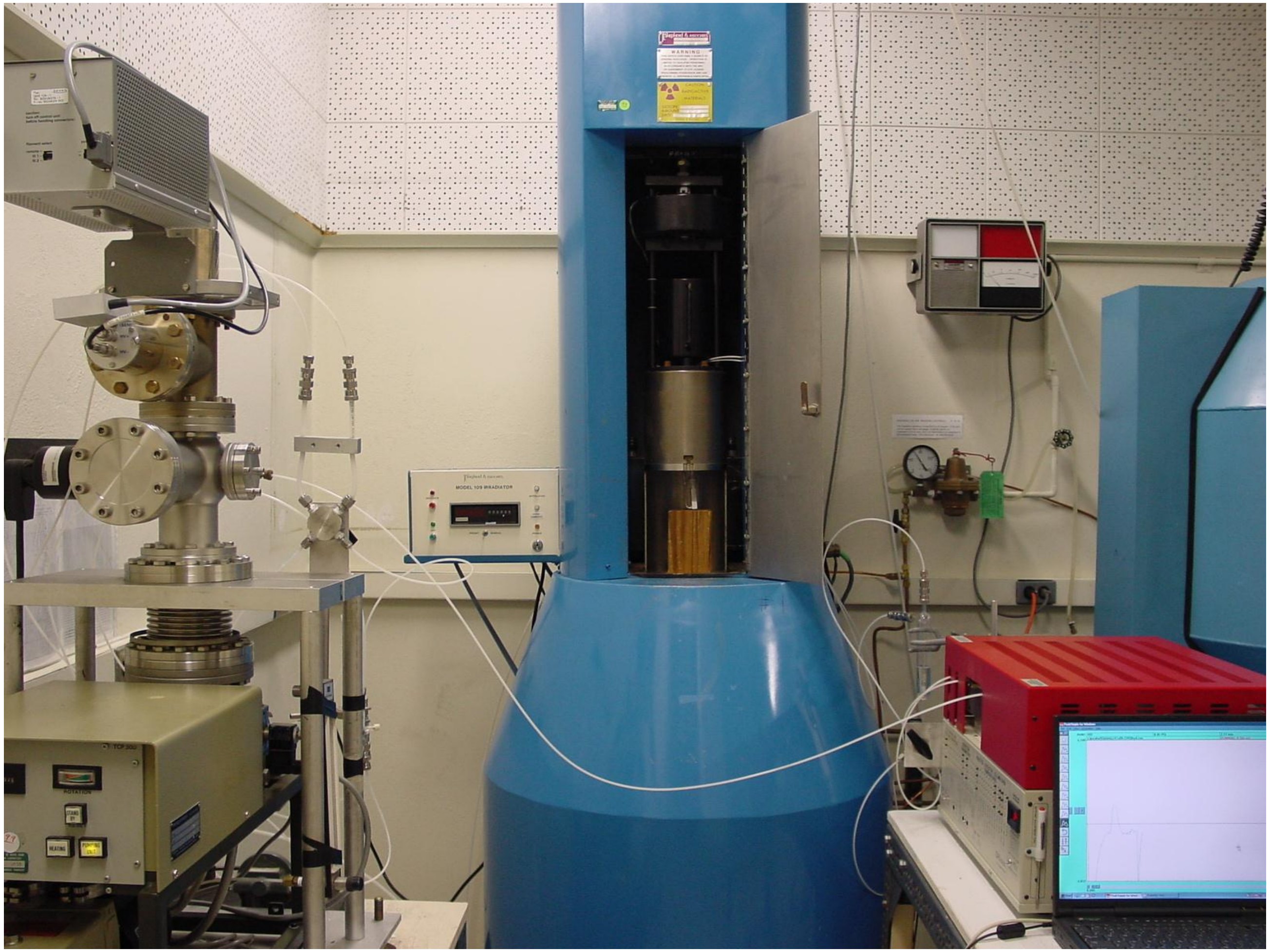
Heavy Ion Beamline





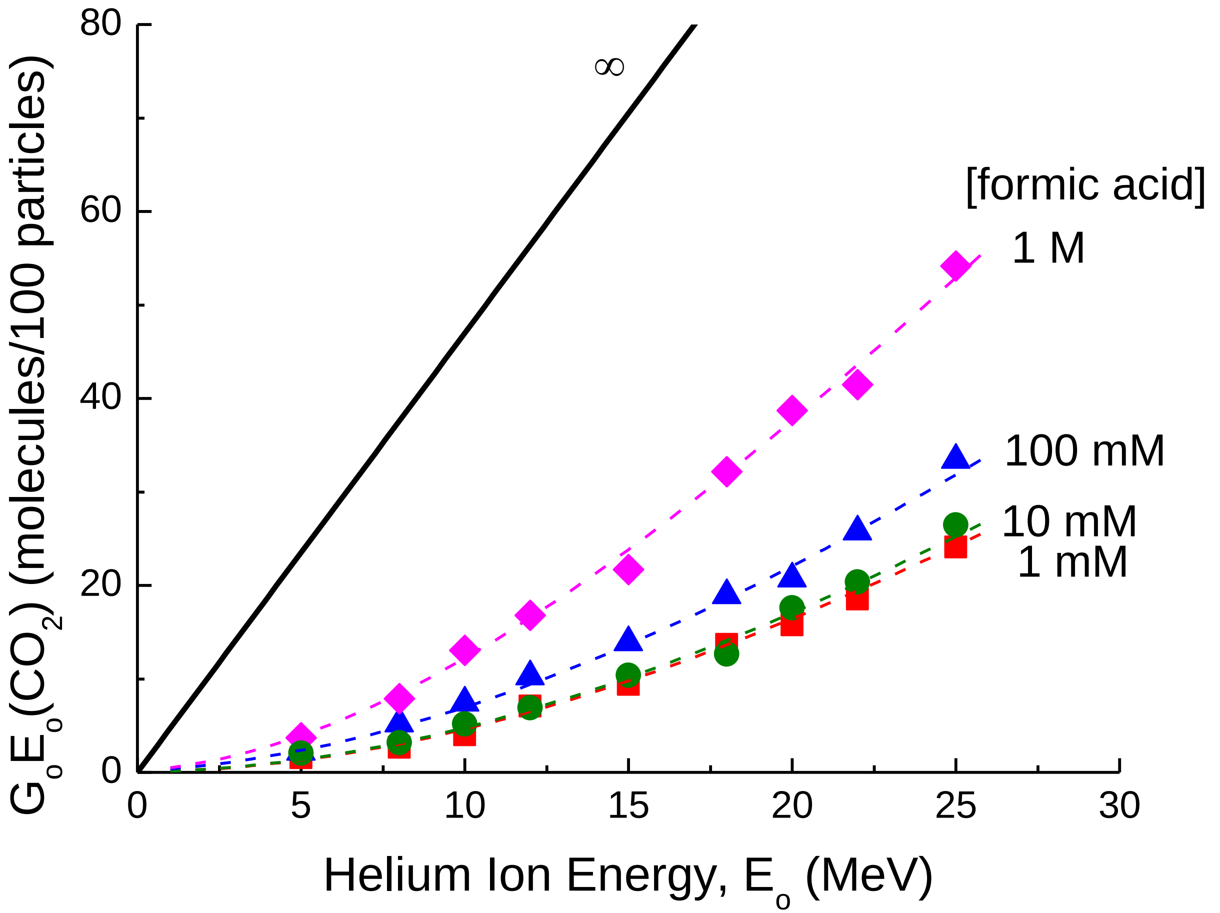


Gamma Radiolysis

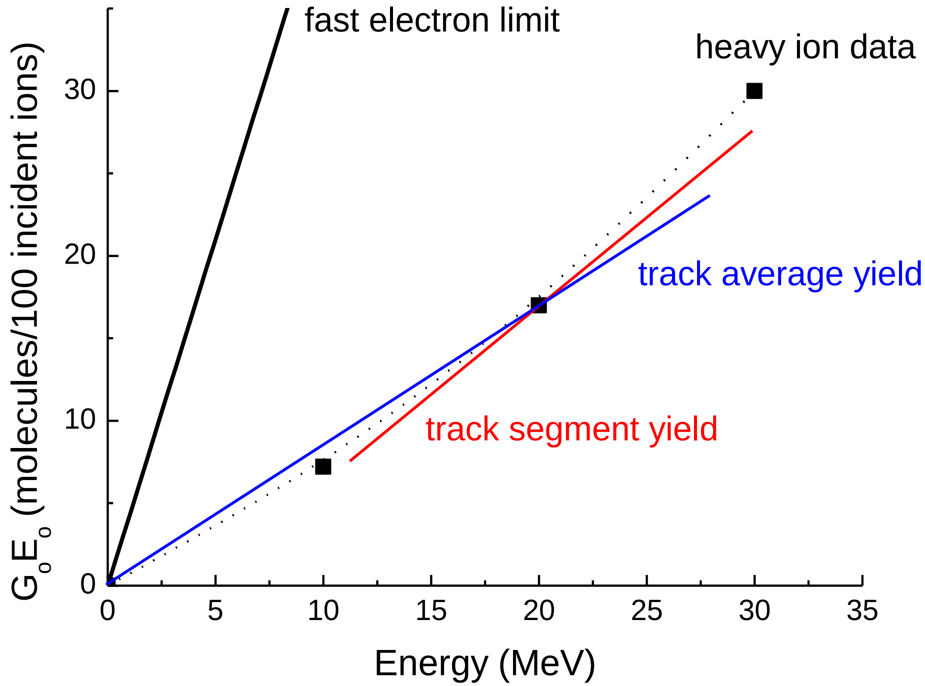


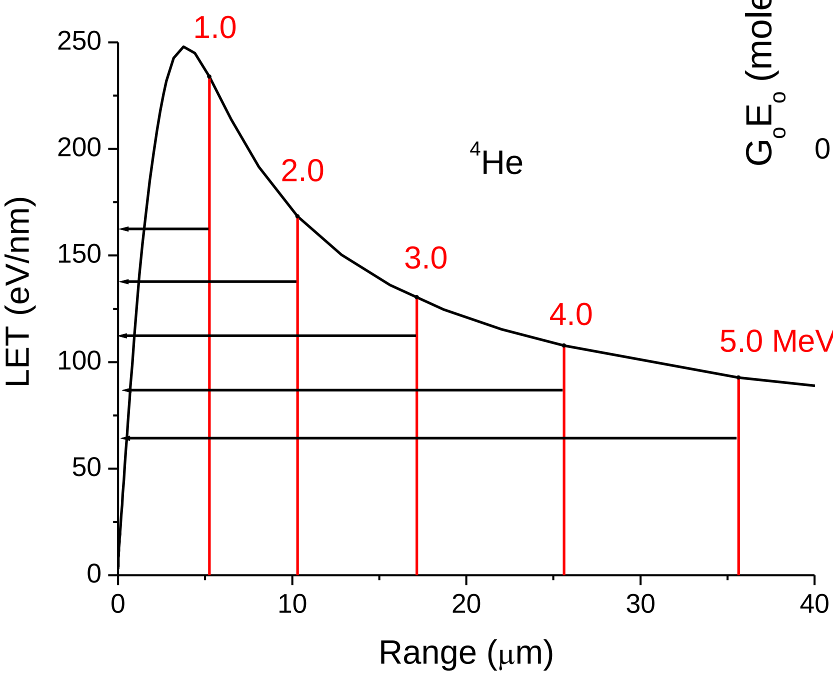
Formation of OH Radicals with He Ions

J.A. LaVerne Radiat. Res. 1989



Track Segment and Track Average Yields

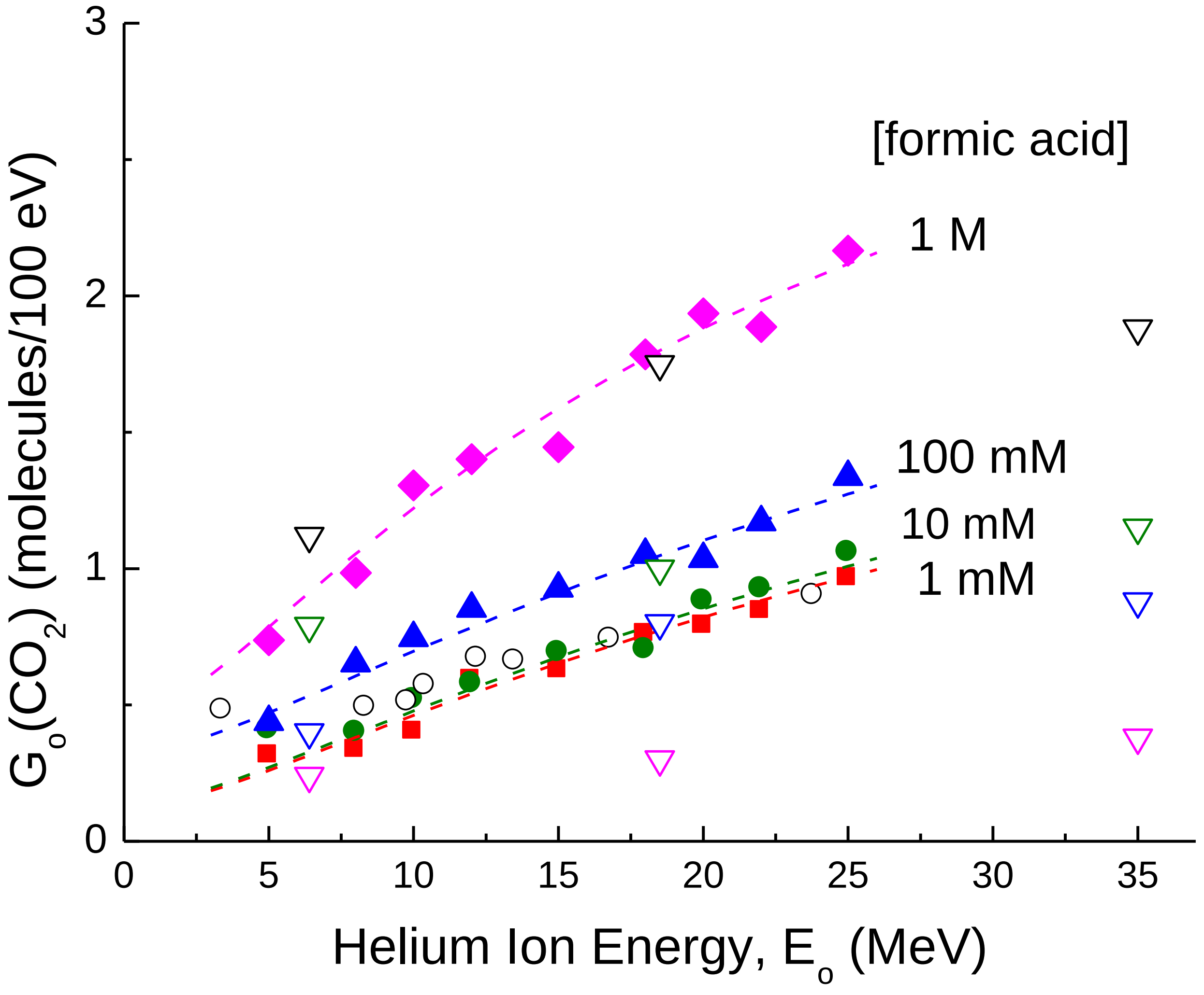




Track segment and track average yields are not the same, but related.

Track Average OH Radical Yields with He Ions

J.A. LaVerne Radiat. Res. 1989



OH Radical Scavenging Capacity

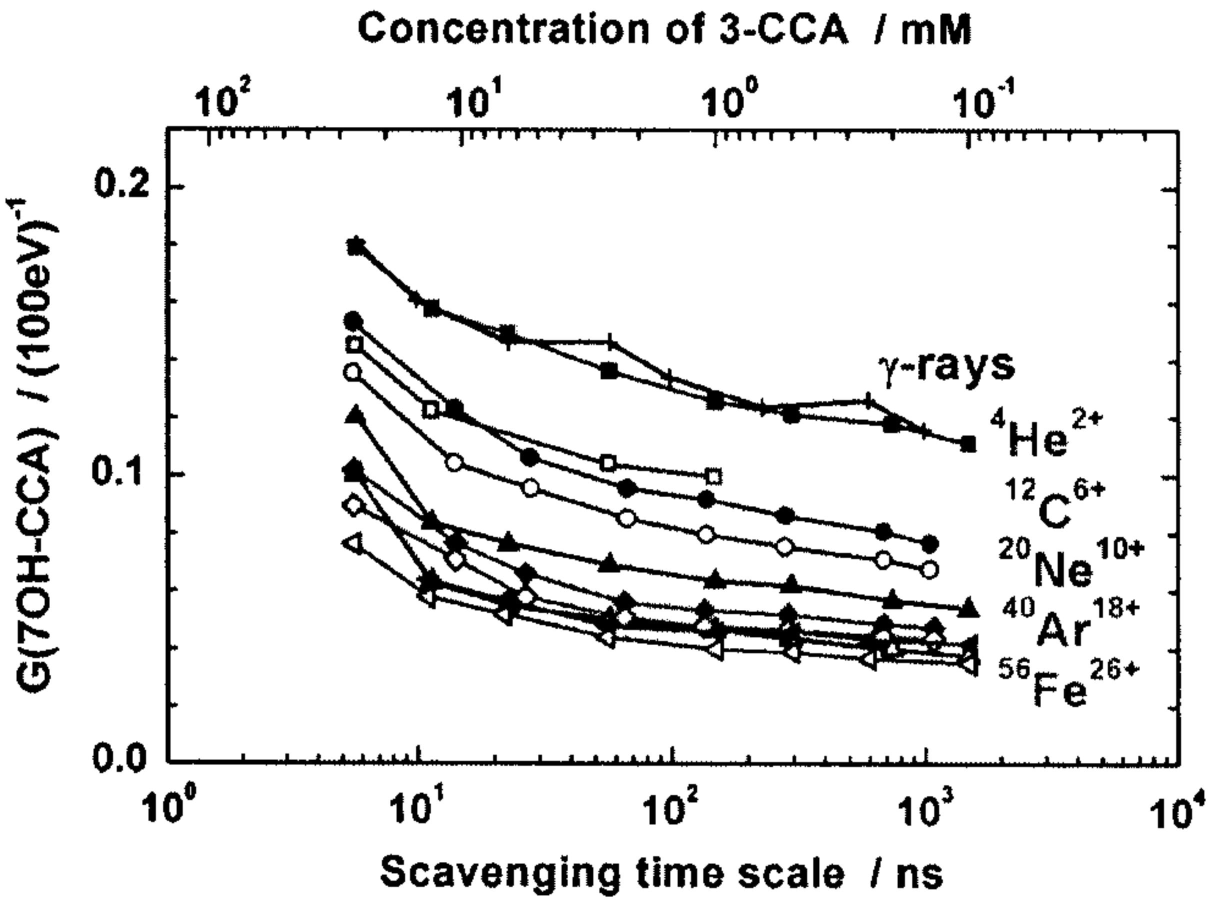
H_2O ^^^→ e_{aq}^-, H_3O^+, OH, H, H_2

			k ($M^{-1}s^{-1}$)
•OH + •OH	→	H_2O_2	5.5×10^9
e_{aq} + •OH	→	OH^-	3.0×10^{10}
• • •	Track Reactions	• • •	
•OH + HCOOH	→	H_2O + •COOH	1.3×10^8
•H + HCOOH	→	H_2 + •COOH	4.4×10^5
•COOH + O_2	→	CO_2 + •HO_2	

Scavenging Capacity = [HCOOH] x 1.3 x 10^8 (s^{-1})

Track Segment LET Dependence of OH Radicals

T. Maeyama, S. Yamashita, G. Baldacchino, M. Taguchi, A. Kimura, T. Murakami, Y. Katsumura, Radiat. Phys. Chem. 2011



He: 2.3, 6.7 eV/nm
C: 11, 22 eV/nm
Ne: 48, 103 eV/nm
Ar: 98, 148 eV/nm
Fe: 205, 441 eV/nm

Conclusions

Heavy ion studies began in the Curie laboratory.

Heavy ion studies are still important for many applications.

OH radical yields are important for medical applications.

OH radical yields are being determined for a wide variety of radiation type and LET.

Determining temporal dependence of OH radical yields.

Model techniques are still being developed and compared with experiment.

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Jaime Milligan – DNA experiments

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