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# Radiation Chemistry of Gases in contact with Ceramic Oxides

DISTINCTIVE Theme 2 Meeting
University of Lancaster 12th Nov. 2015


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# Talk Outline

- Research Objectives
- $H_2 - O_2$ Radiolysis Results
- Preliminary Accelerator Experiments
- Further Work

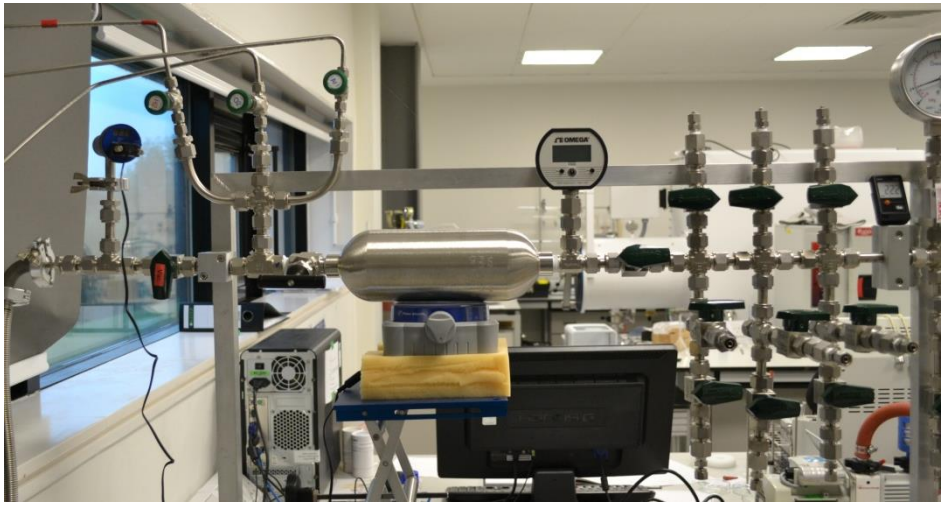
# Research Objectives

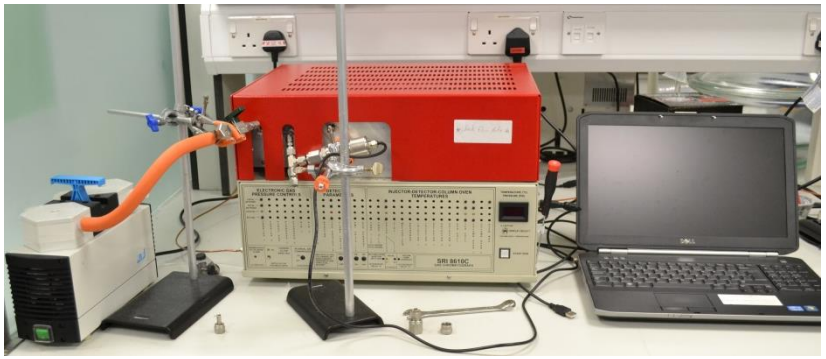
- Investigate irradiation of two gaseous systems
  - $H_2$-$O_2$-Ar
  - Moist Air (not discussed)

- $PuO_2$ surrogates

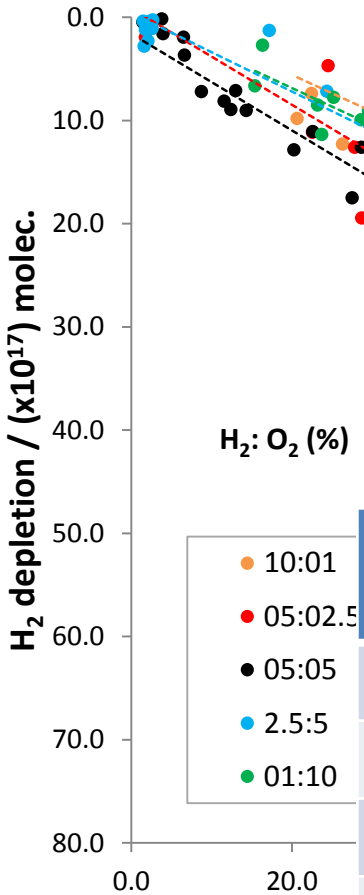
- Two sources of external radiation
  - $^{60}Co$ γ-rays
  - 5.5MeV $He^{2+}$ accelerated ions

# Experimental (γ-source)

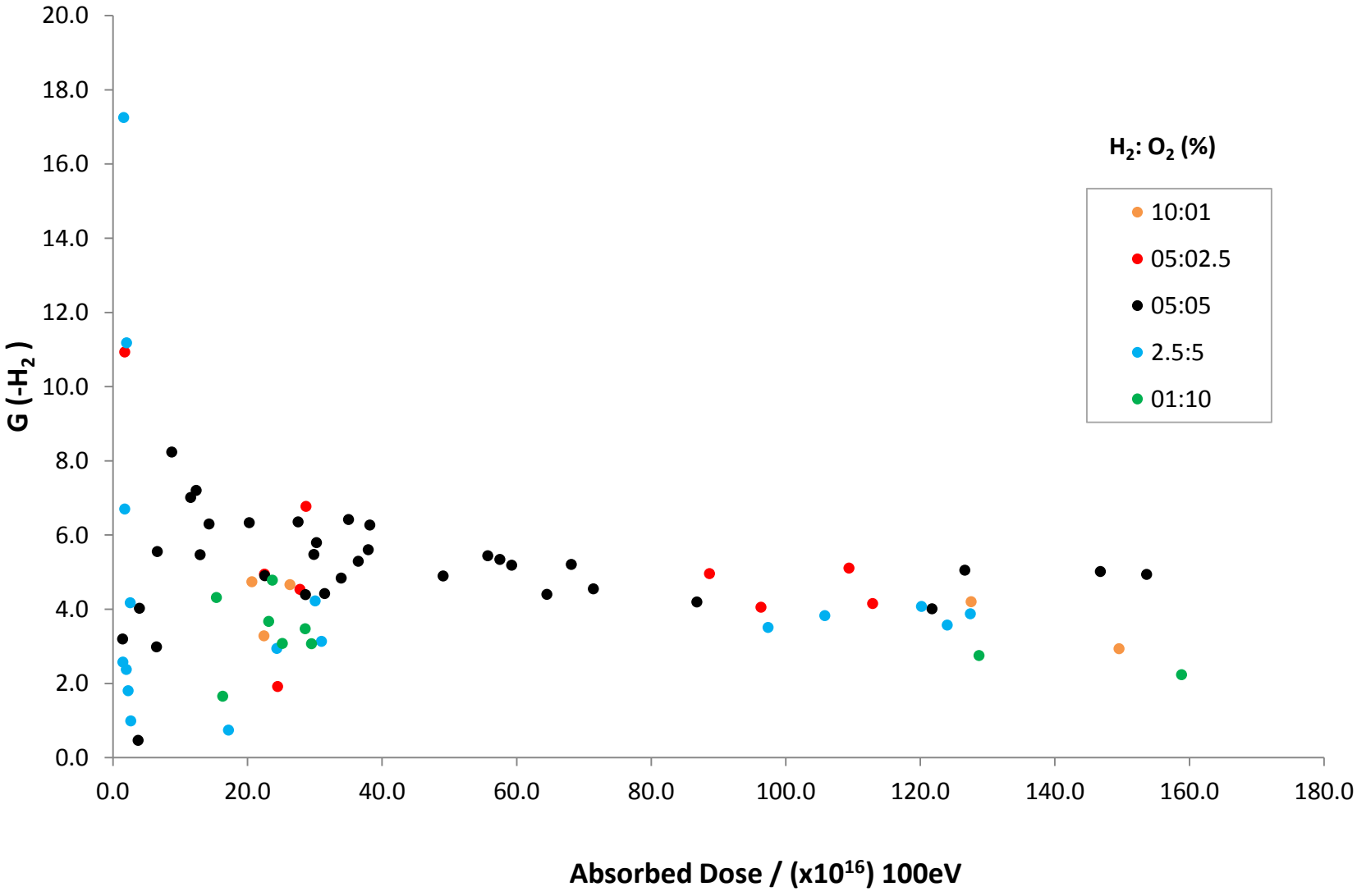




# Gas Phase Results




| $H_2 - O_2 - Ar$ / (by volume) | G(-$H_2$) | Error ($\sigma_{slope}$) |
|---|---|---|
| 10: 1 : 89 | 0.36 | ±0.07 |
| 5 : 2.5 : 92.5 | 0.47 | ±0.04 |
| 5 : 5 : 90 | 0.47 | ±0.01 |
| 2.5 : 5 : 92.5 | 0.38 | ±0.01 |
| 1 : 10 : 89 | 0.36 | ±0.16 |


20.0
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
G (-H2 )
0.0
20.0
40.0
60.0
80.0
100.0
120.0
140.0
160.0
180.0
Absorbed Dose / (x10^16) 100eV
H2: O2 (%)
10:01
05:02.5
05:05
2.5:5
01:10

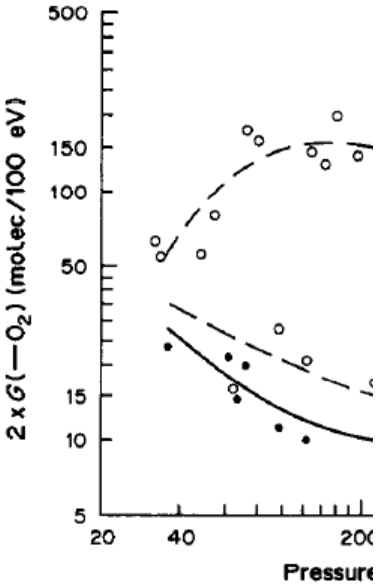



Fig. 2. $2XG(-O_2)$ vs pressure, $H_2$-rich mixtures $H_2$:$O_2$ (9:1) a 210°C.

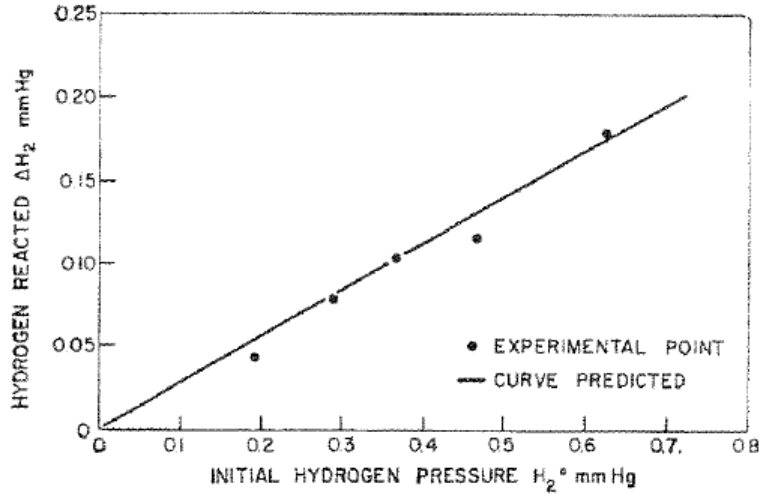
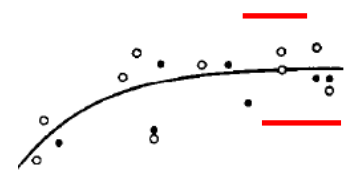



Fig. 4 - Effect of initial hydrogen concentration. Mean initial partial pressure of oxygen, $p^i_{O_2} = 0.778$ mm Hg; water density, 0.7 mgm/ml; temperature, 224 °F; 10 Cs-137 pencils; irradiation time, 15 hours.



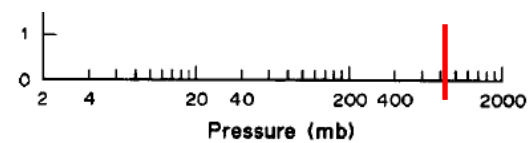



Fig. 4. $G(-H_2)$ vs pressure, outgassed ampoules; 35°C; ○: $H_2 + 9\,O_2$; ●: $H_2 + 17\,O_2$.


[1] D. Dautzenberg; *Radiat. Phys. Chem.*, 1989, **Vol. 33**, 1, pp 61-67
[2] BM Benjamin and HS Isbin; *Energie Nucleare*, 1966, **Vol. 13**, 4, 165-

# Mechanism

Initial excitation

$Ar \rightsquigarrow Ar^+ + e^-$

$H_2 \rightsquigarrow H_2^+ + e^- \rightarrow H_2^* \rightarrow 2H$

$O_2 \rightsquigarrow O_2^+ + e^- \rightarrow O_2^* \rightarrow O(D^1) + O(P^3)$

Charge Transfer

$Ar^+ + H_2 \rightarrow Ar + H_2^+$

$Ar^+ + O_2 \rightarrow Ar + O_2^+$

$H_2^+ + O_2 \rightarrow H_2 + O_2^+$

$O(^1D) + H_2 \rightarrow OH + H$ k= $2.87 \times 10^{-10}$ $cm^3$ $molecule^{-1}$ $sec^{-1}$

$O(^3P) + H_2 \rightarrow OH + H$ k= $9.08 \times 10^{-18}$ $cm^3$ $molecule^{-1}$ $sec^{-1}$

$O + O_2 + M \rightarrow O_3 + M$ k= $5.8 \times 10^{-34}$ $cm^6$ $molecule^{-2}$ $sec^{-1}$ k= $1.26 \times 10^{-19}$ $cm^3$ $molecule^{-1}$ $sec^{-1}$

$H + O_2 \rightarrow O + OH$ k= $4.25 \times 10^{-13}$ $cm^3$ $molecule^{-1}$ $sec^{-1}$

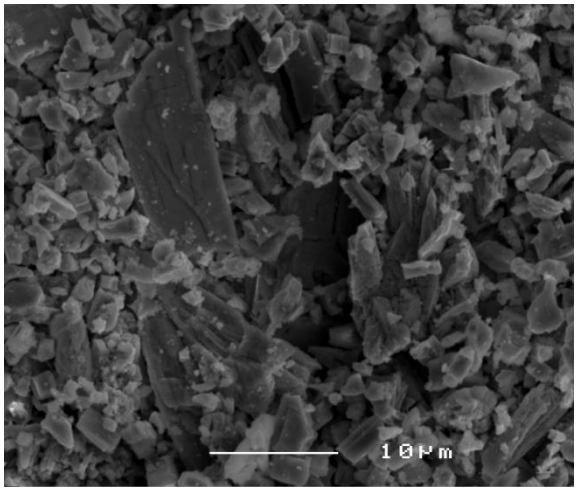
$OH + H_2 \rightarrow H_2O + H$ k= $6.96 \times 10^{-15}$ $cm^3$ $molecule^{-1}$ $sec^{-1}$

$OH + O(^3P) \rightarrow O_2 + H$ k= $2.92 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $sec^{-1}$

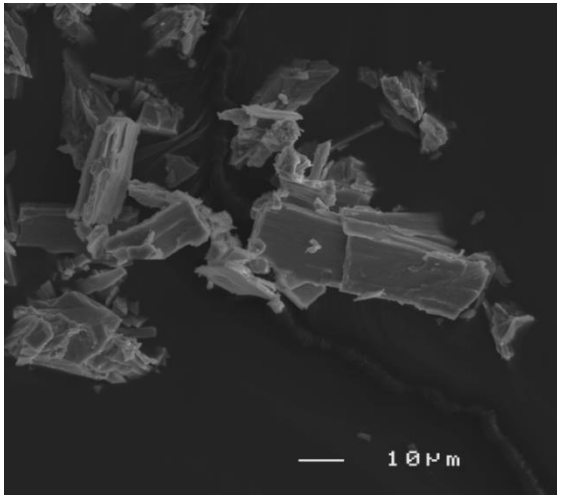
$H + O_2 + M \rightarrow HO_2 + M$ k= $6.72 \times 10^{-21}$ $cm^6$ $molecule^{-2}$ $sec^{-1}$ k= $1.46 \times 10^{-6}$ $cm^3$ $molecule^{-1}$ $sec^{-1}$

# Oxide Properties

$CeO_2$

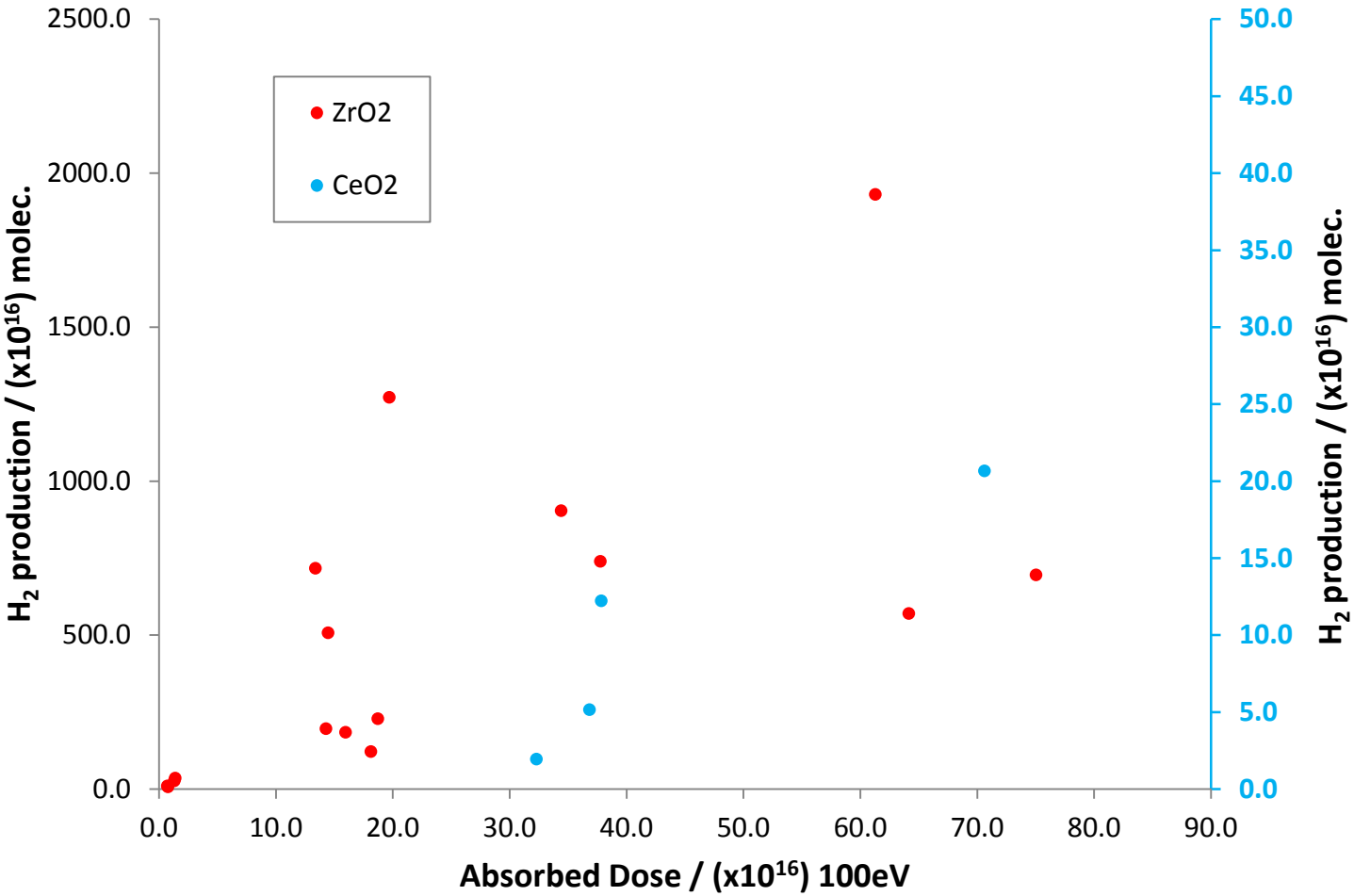



$ZrO_2$

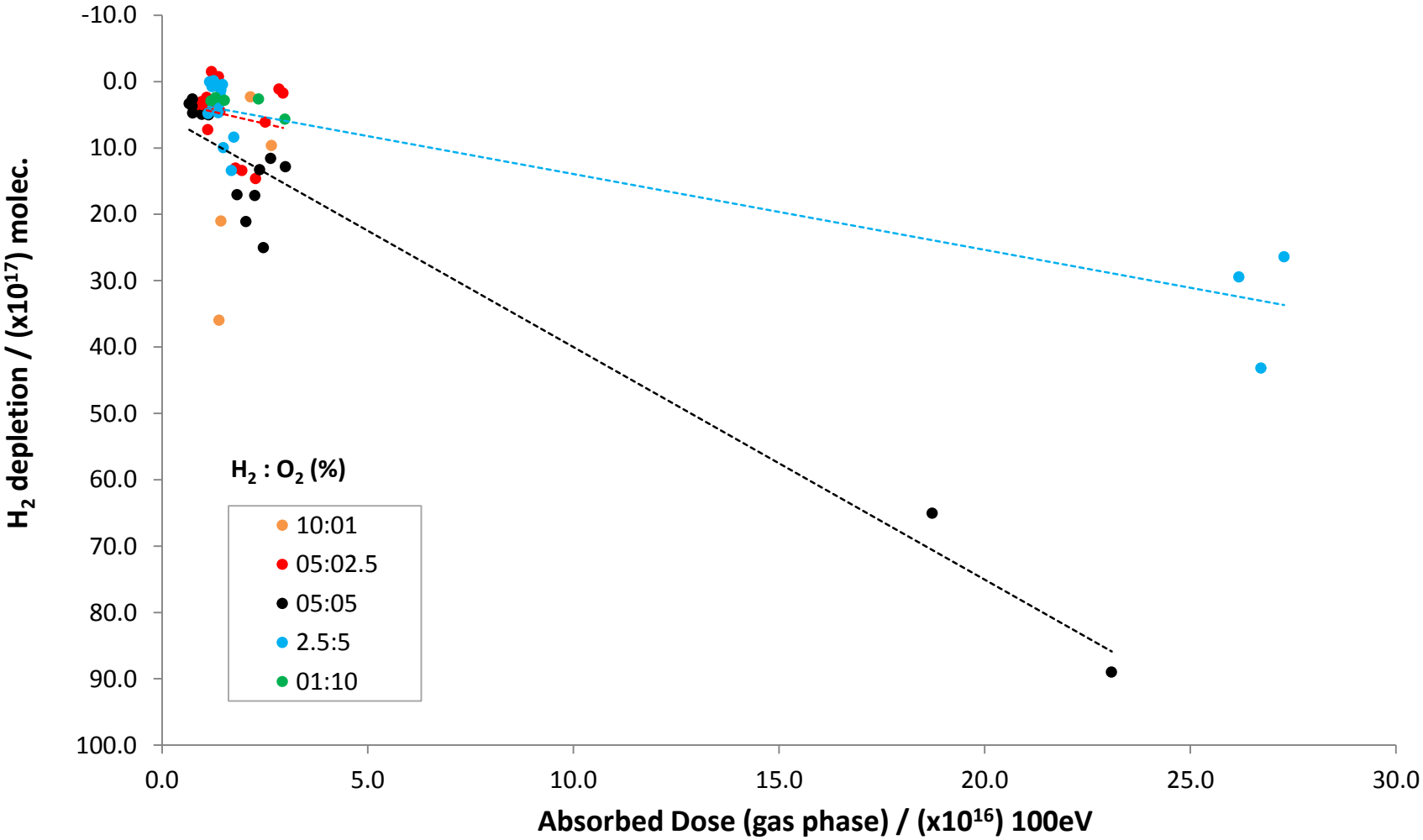



| | | |
|---|---|---|
| **SSA / $m^2\ g^{-1}$** | 7.42 | 2.24 |
| **Bulk Density / $g\ cm^{-3}$** | 1.42 | 2.06 |
| **Crystal Density / $g\ cm^{-3}$** | 7.21 | 5.68 |

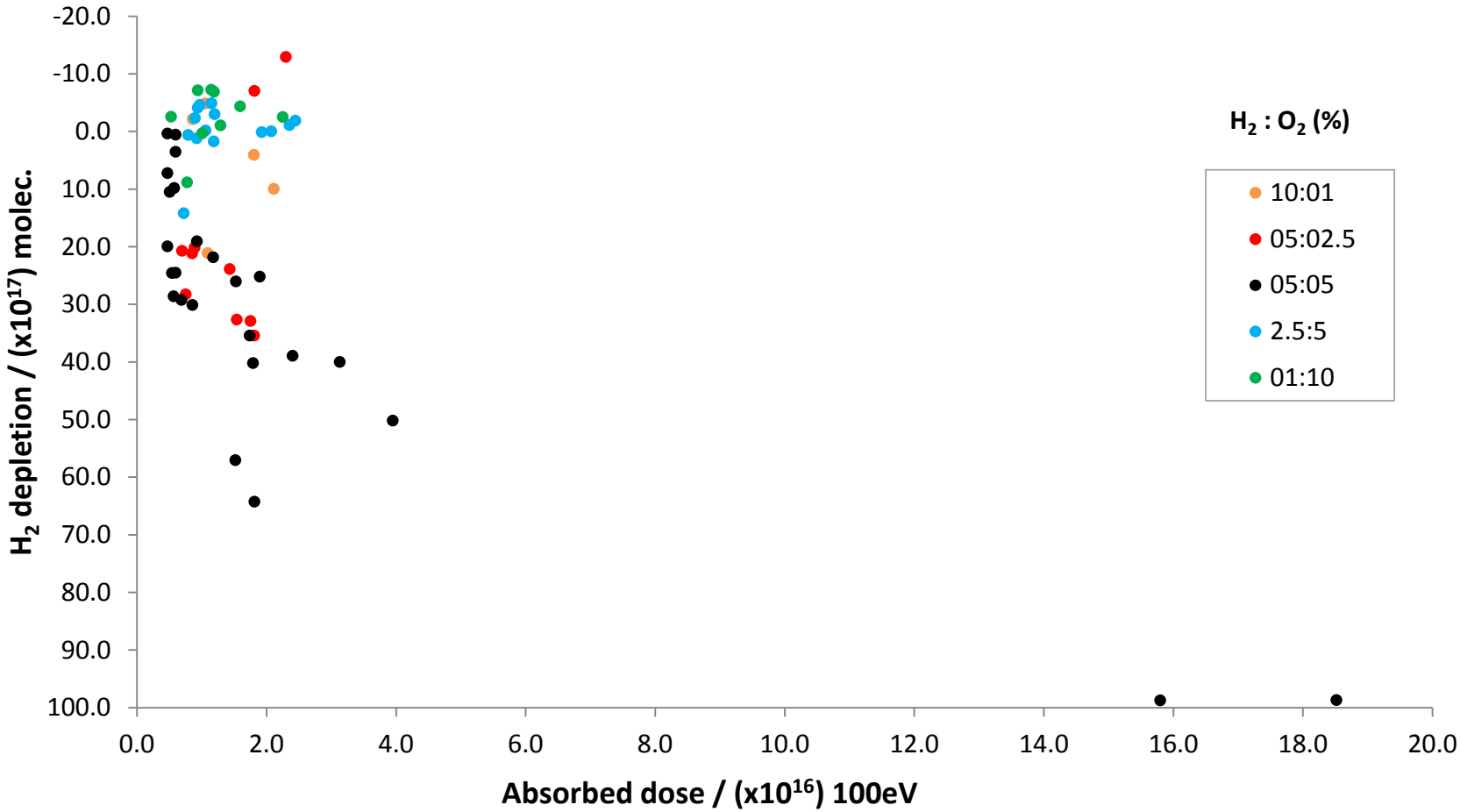
# $H_2$ production from adsorbed $H_2O$



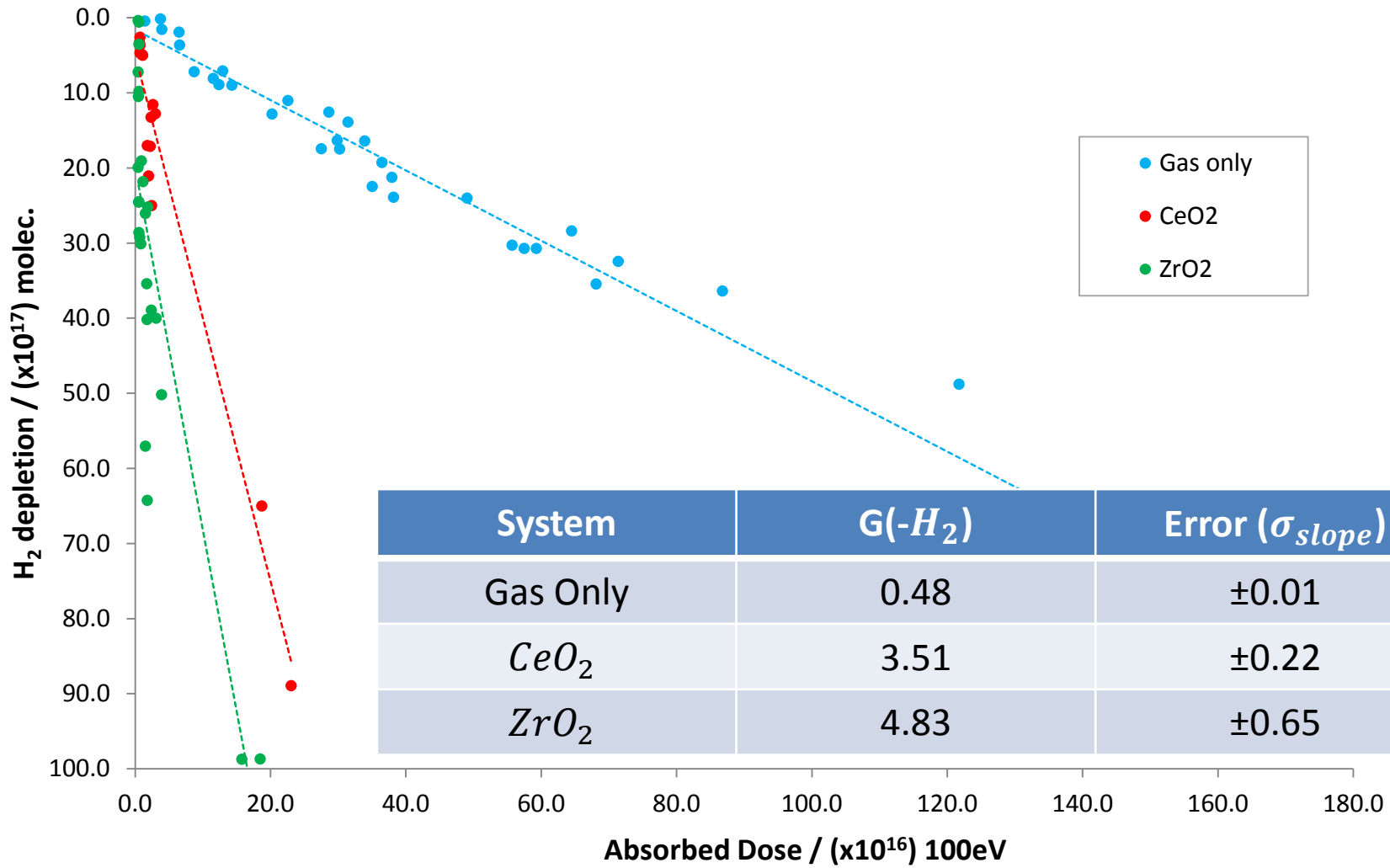
# $H_2 - O_2$ Radiolysis over $CeO_2$



# $H_2 - O_2$ Radiolysis over $ZrO_2$

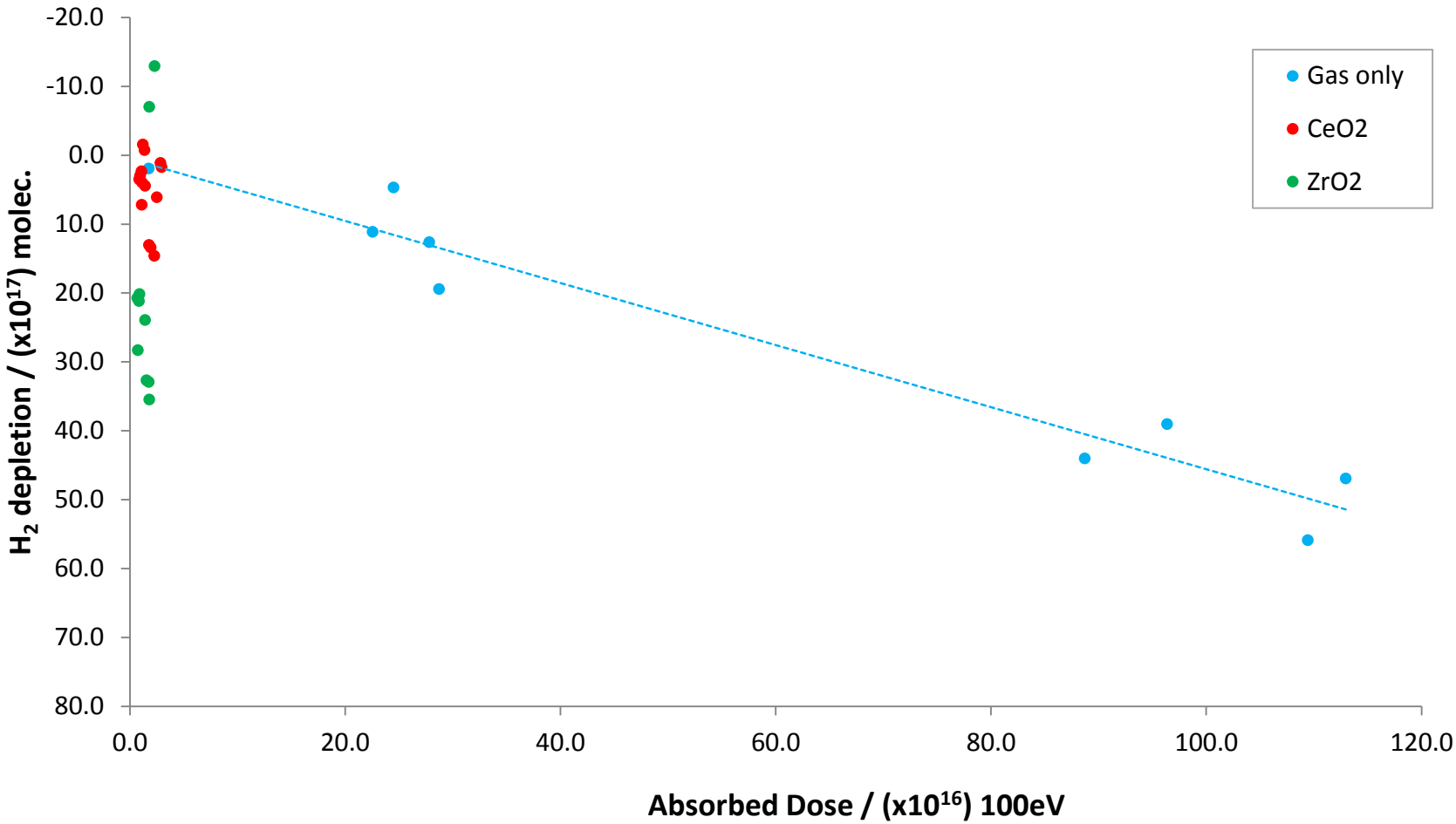


# $5:5:90\ \ H_2 - O_2 - Ar$

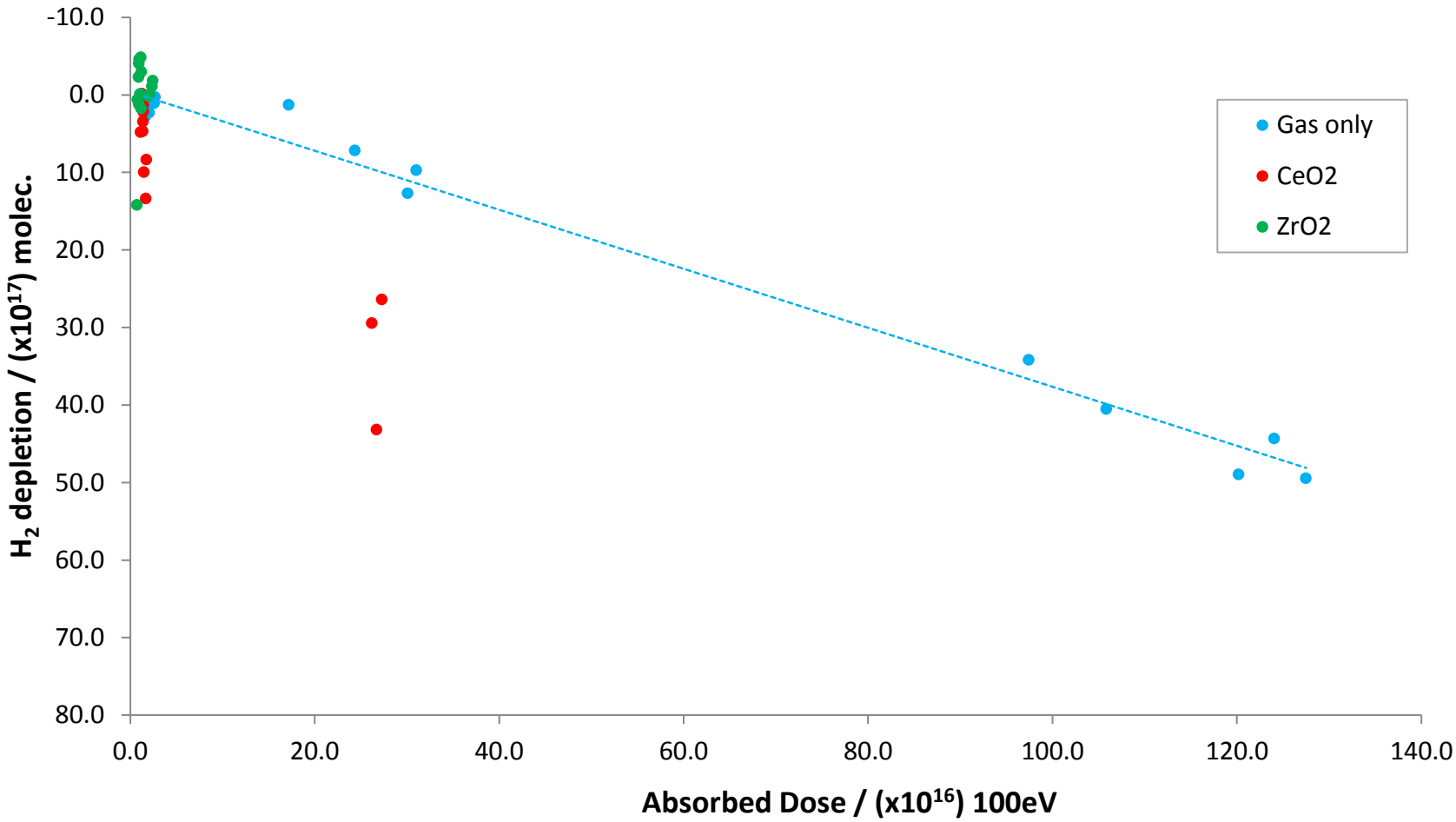



| System | G(-$H_2$) | Error ($\sigma_{slope}$) |
|---|---|---|
| Gas Only | 0.48 | ±0.01 |
| $CeO_2$ | 3.51 | ±0.22 |
| $ZrO_2$ | 4.83 | ±0.65 |

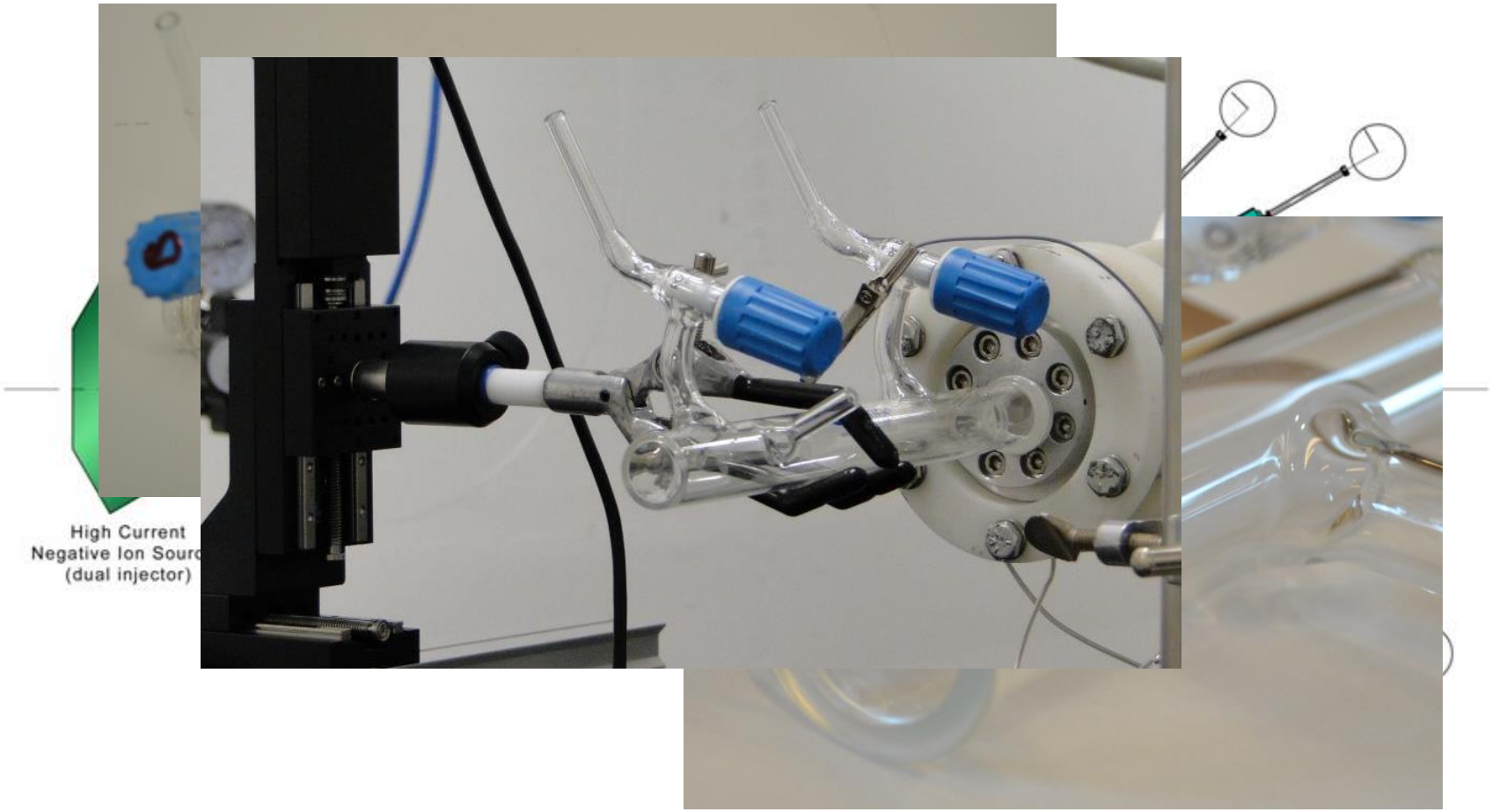
# 5 : 2.5 : 92.5 $H_2 - O_2 - Ar$

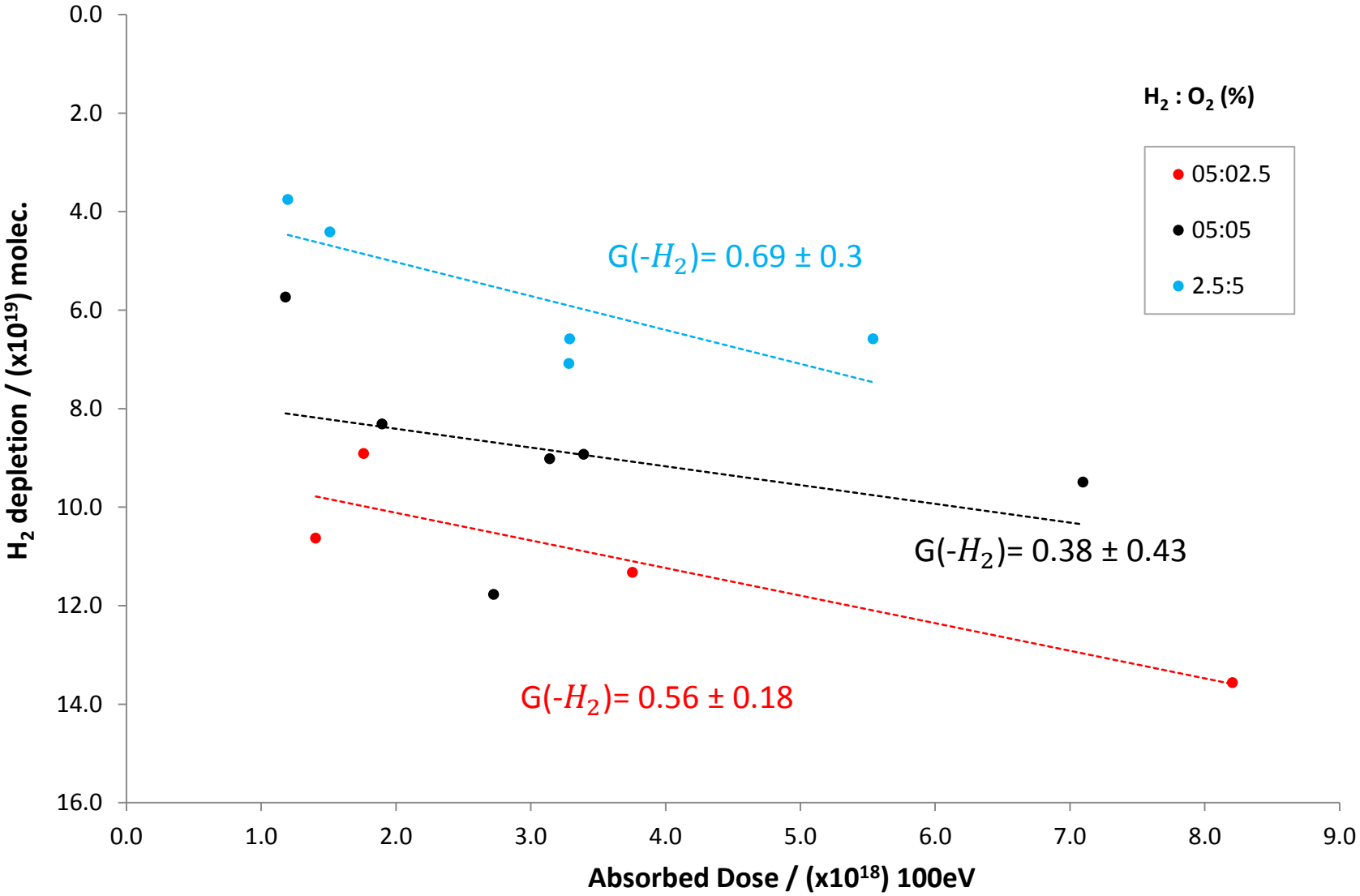


# 2.5 : 5 : 92.5 $H_2 - O_2 - Ar$



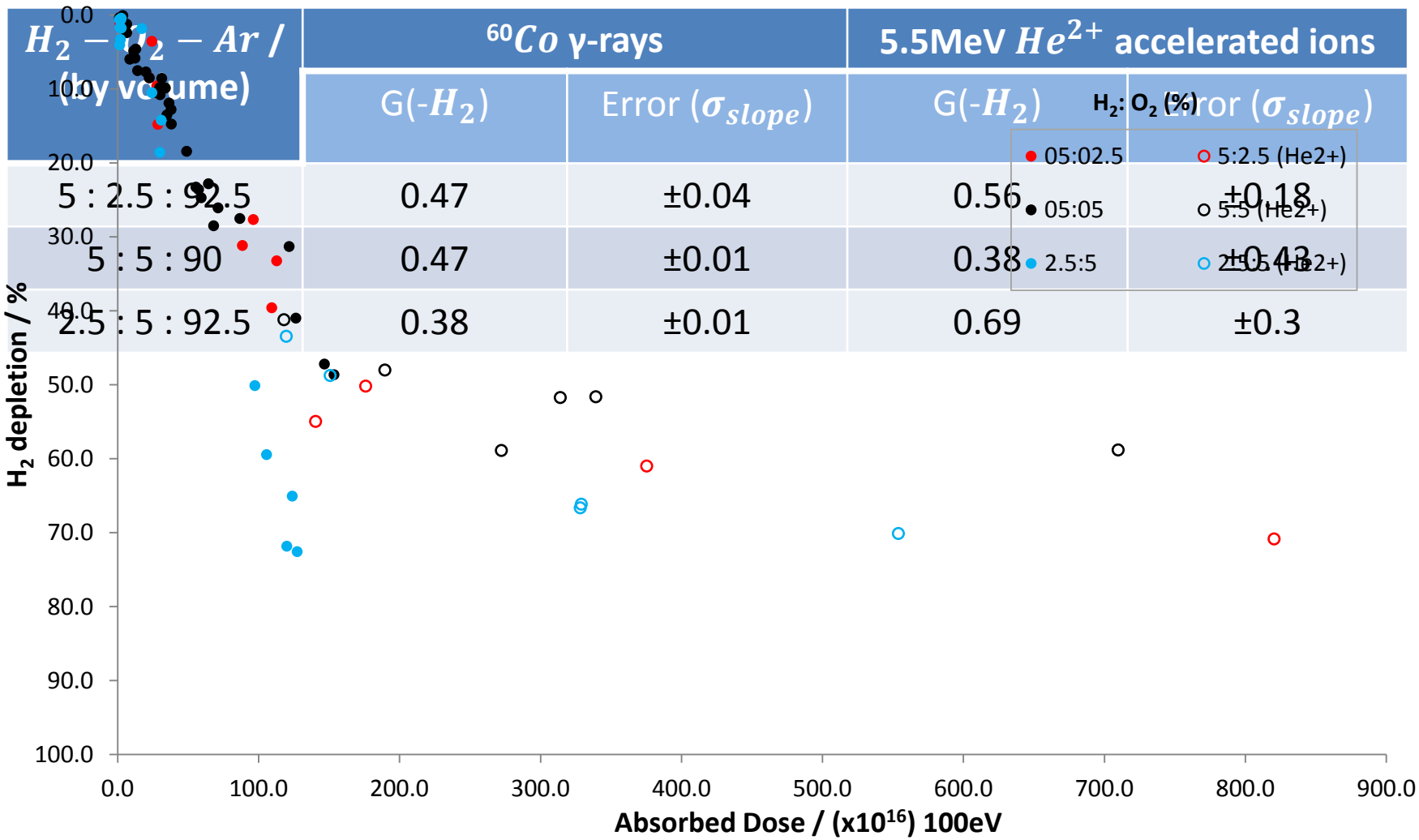
# Accelerated ion Experiments.




0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
H2 depletion / (x10^19) molec.
Absorbed Dose / (x10^18) 100eV
H2 : O2 (%)
05:02.5
05:05
2.5:5
G(-H2)= 0.69 ± 0.3
G(-H2)= 0.38 ± 0.43
G(-H2)= 0.56 ± 0.18

# Radiation type comparison

| $H_2 - O_2 - Ar$ / (by volume) | $^{60}Co$ γ-rays | | 5.5MeV $He^{2+}$ accelerated ions | |
|---|---|---|---|---|
| | G(-$H_2$) | Error ($\sigma_{slope}$) | G(-$H_2$) | Error ($\sigma_{slope}$) |
| 5 : 2.5 : 92.5 | 0.47 | ±0.04 | 0.56 | ±0.18 |
| 5 : 5 : 90 | 0.47 | ±0.01 | 0.38 | ±0.43 |
| 2.5 : 5 : 92.5 | 0.38 | ±0.01 | 0.69 | ±0.3 |



# Conclusions

- Depletion of $H_2$ from homogeneous system is independent of $H_2$ concentration (γ studies)
- Presence of an oxide greatly enhances $H_2$ depletion
- At low doses, $H_2$ is produced from radiolysis of adsorbed water
- High doses are required to reach a steady state between recombination and radiolysis
- Preliminary experiments with accelerated ions are in good agreement with γ data

# Further Work

- Kinetic modelling of homogeneous phase
- SSA studies
- Better surrogates ($UO_2$)
- $PuO_2$ trials
- Further accelerated ion studies (including heterogeneous system)

# Acknowledgements


- Sellafield Sites Ltd. and EPSRC for funding this research
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- Paul Cook and Jeff Hobbs (both SL) for technical advice and context
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