JOHANNES GUTENBERG UNIVERSITÄT MAINZ

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Simulation and experiment for heavy element gas phase chromatography

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INTRODUCTION

Superheavy Elements:

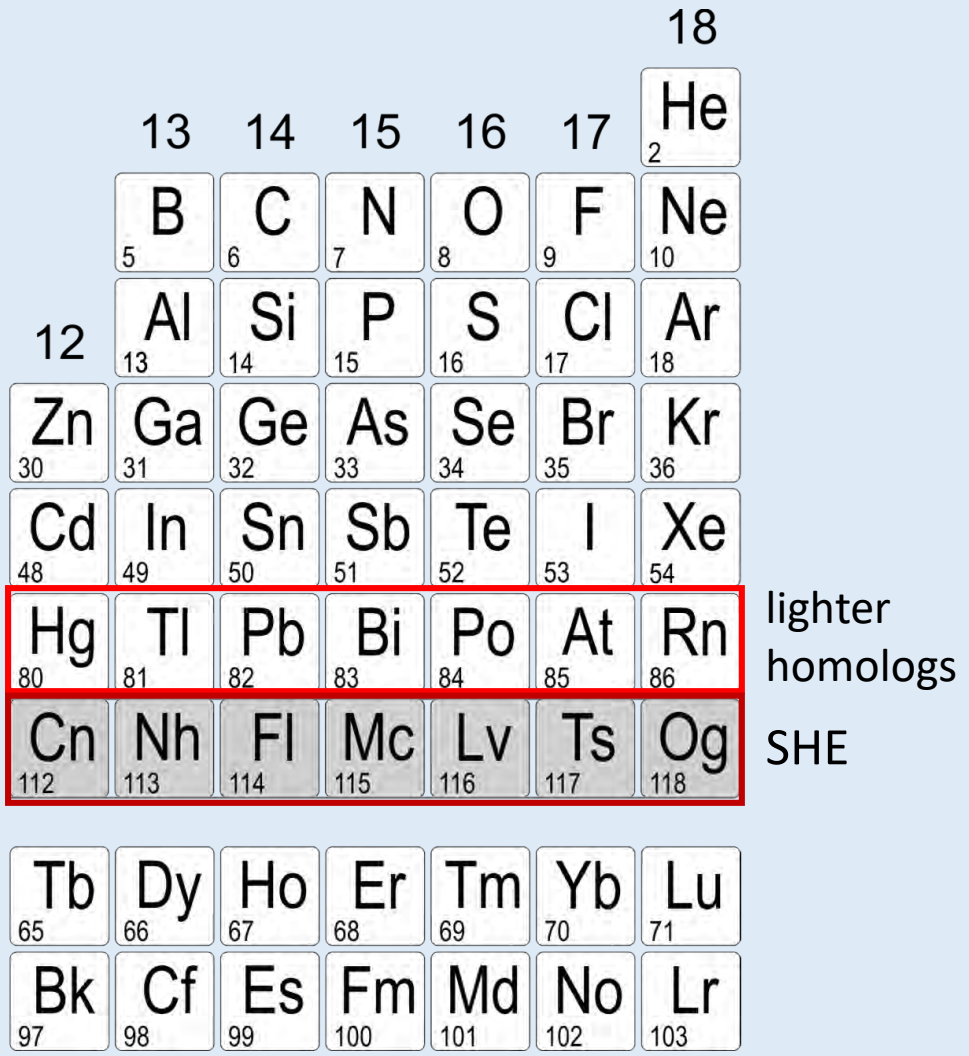
- High nuclear charge
  → effect on chemistry
- short half-lives
- low production rates

→ gas chromatography

Lighter homologs:

- longer half-lives
- high production rates

→preparation and benchmark data for comparative studies



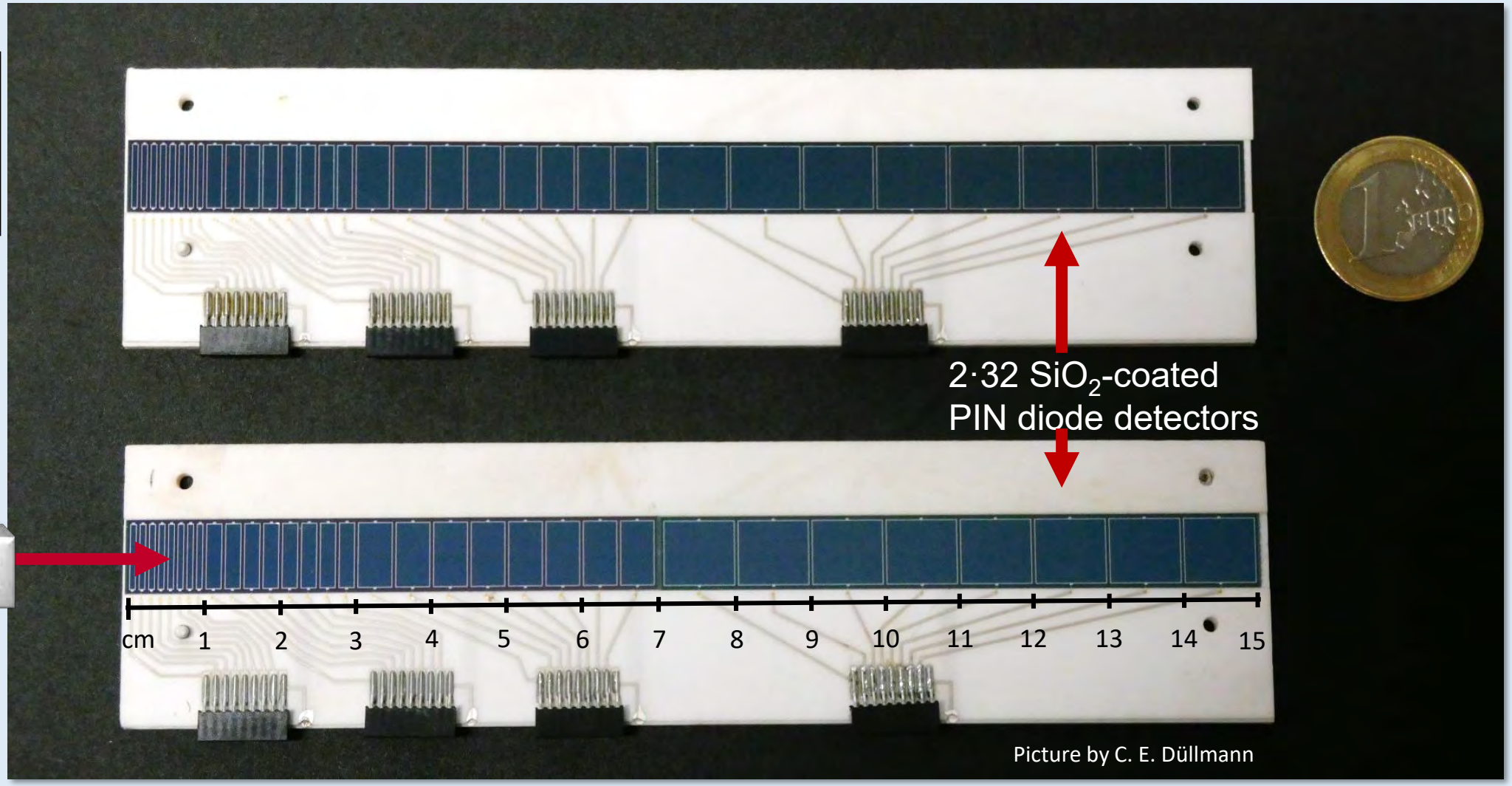
EXPERIMENT: miniCOMPACT

Bi 211
2.14 m
α

Pb 211
36.1 m
β^-

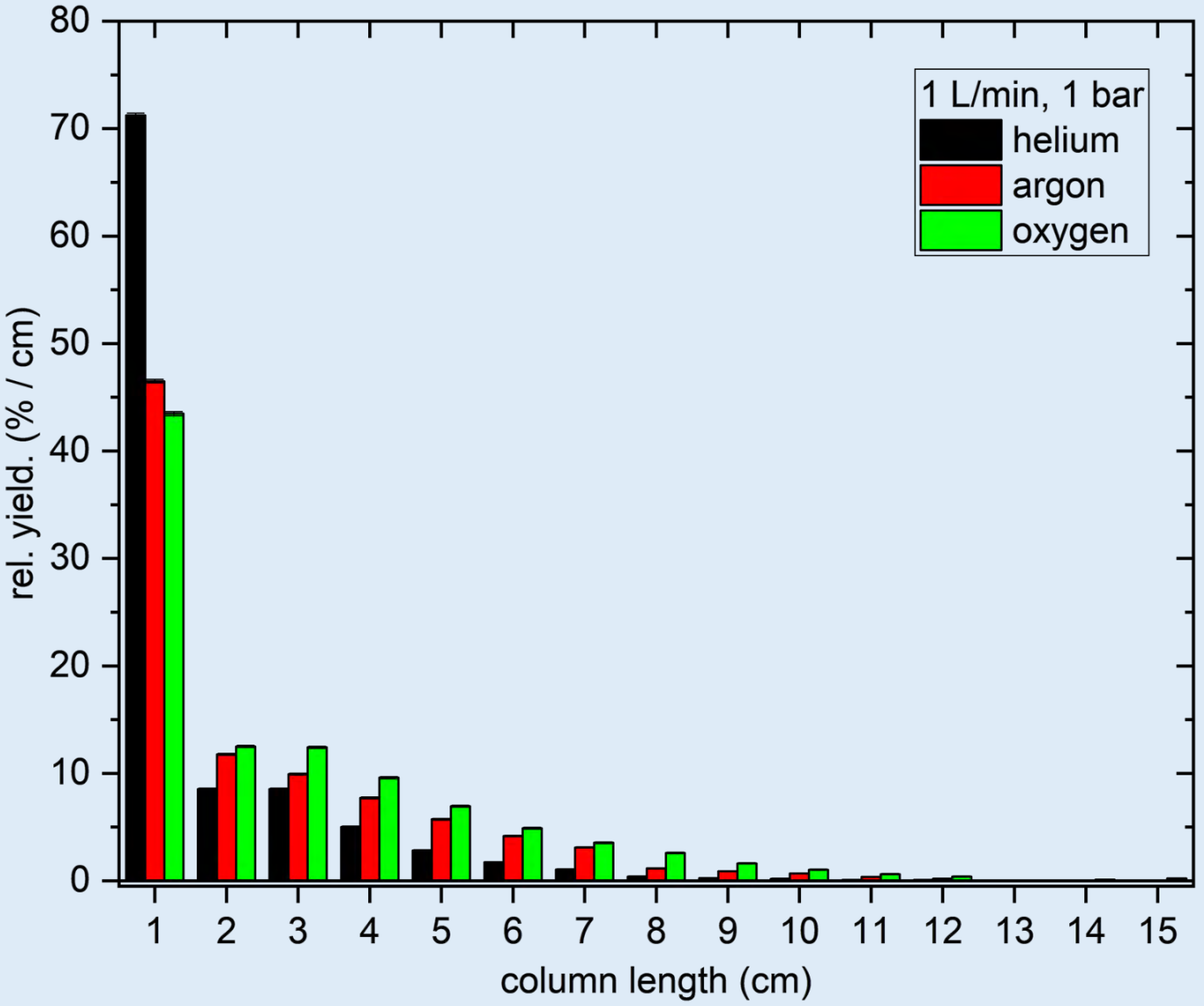
carrier gas
+ analyte
He, Ar, O_2

RTC



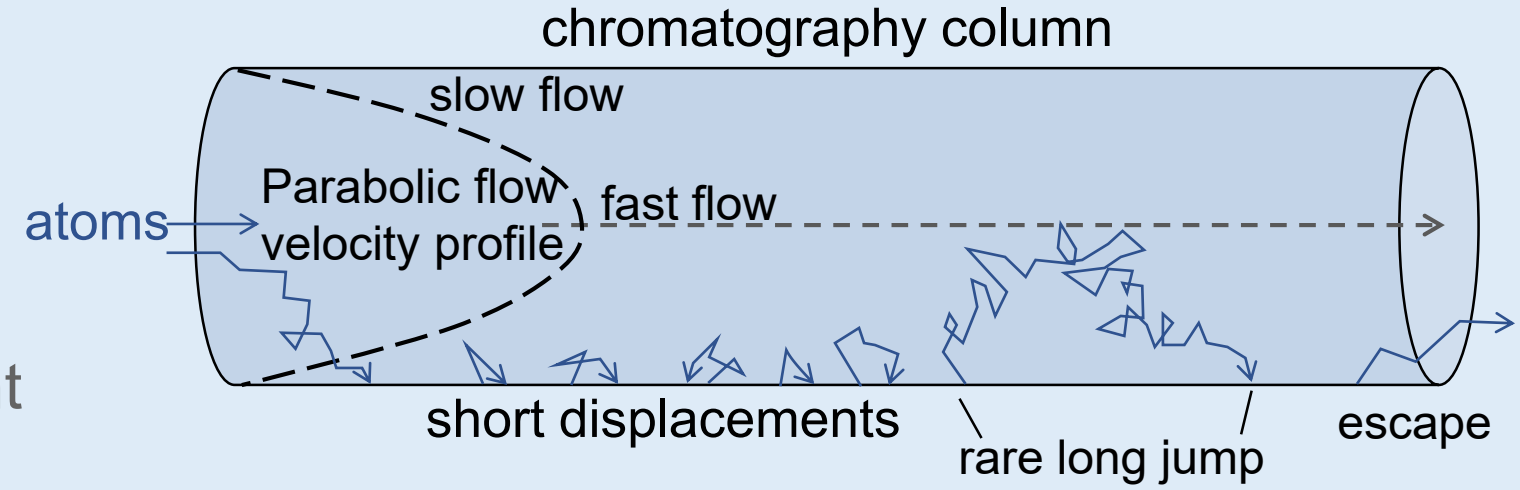
DISTRIBUTION OF ^{211}Bi ACTIVITY IN miniCOMPACT

- Strong interaction with SiO_2 surface
- Diffusion controlled deposition



MONTE CARLO SIMULATION

- Simulation of random pathways of atoms through the column
- Decay marks final position
- Comparison with experiment
  → Estimation of $-\Delta H_{ads}$



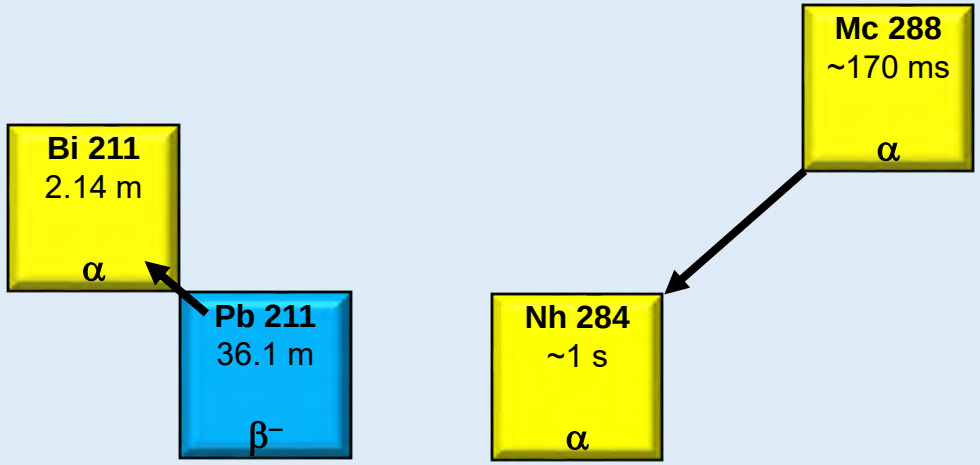
I. Zvara, Radiochimica Acta **38** (1985)
I. Zvara, The Inorganic Radiochemistry of Heavy Elements, *Springer Netherlands* (2008)

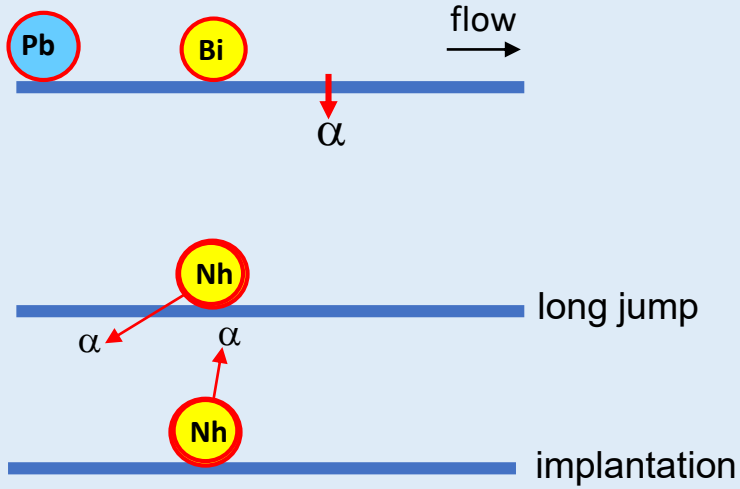
1. PRECURSOR EFFECT

- Off-line chromatography experiments with ^{211}Bi
- Detection of ^{211}Bi as the daughter of ^{211}Pb
- 99.98% of the atoms enter the column as ^{211}Pb

- Bismuth emerges from lead distribution
  → daughter atoms can travel further
  → potential broadening of distribution

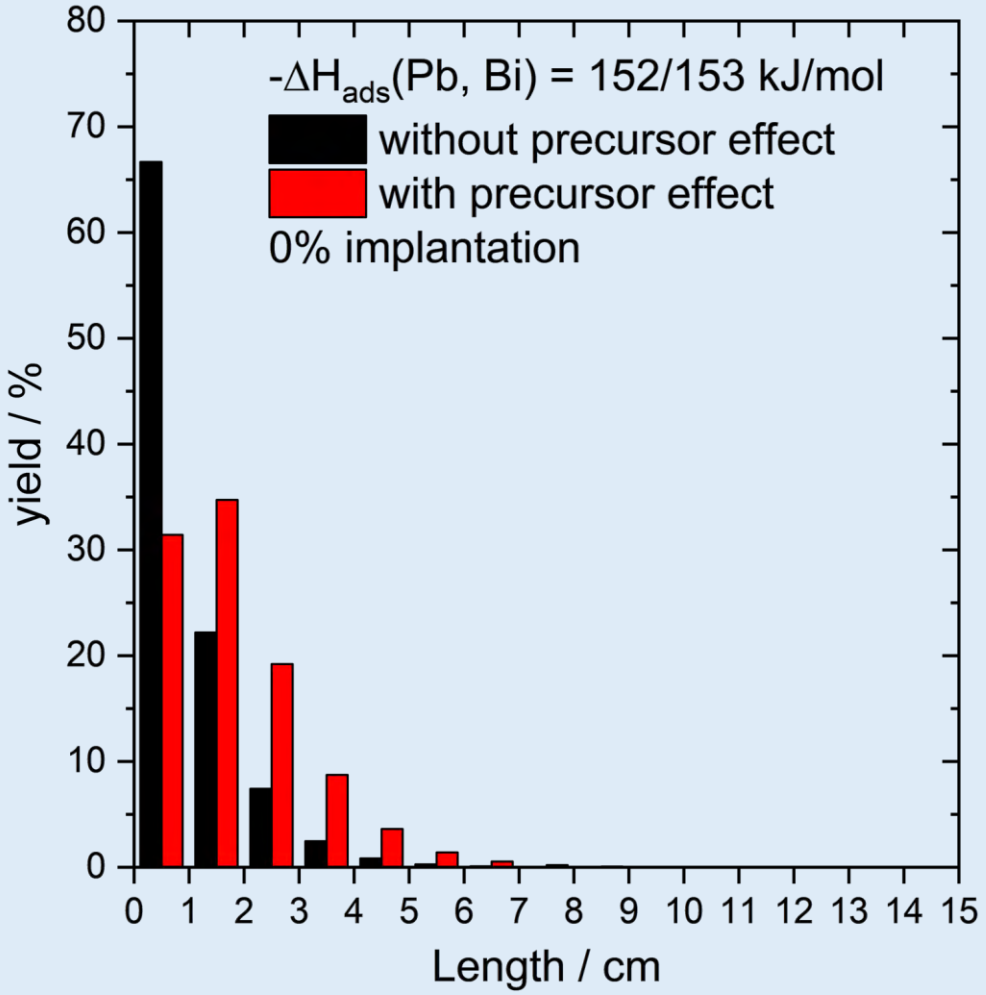
- Important for Mc-Nh-chain
  - Long jumps and implantation into the surface can be possible after alpha-decay



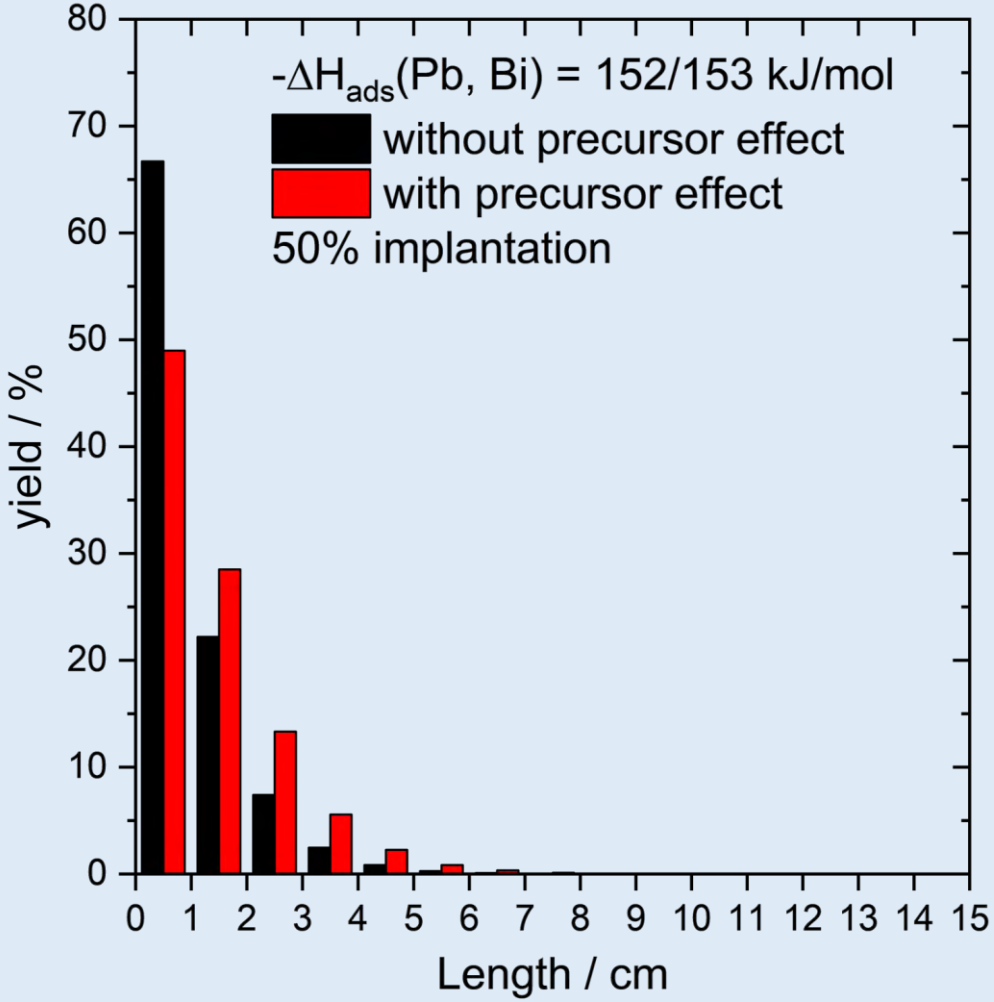


IMPACT OF THE PRECURSOR EFFECT

Simulations with similar parameters and strongly adsorbing species



in case of weak recoil

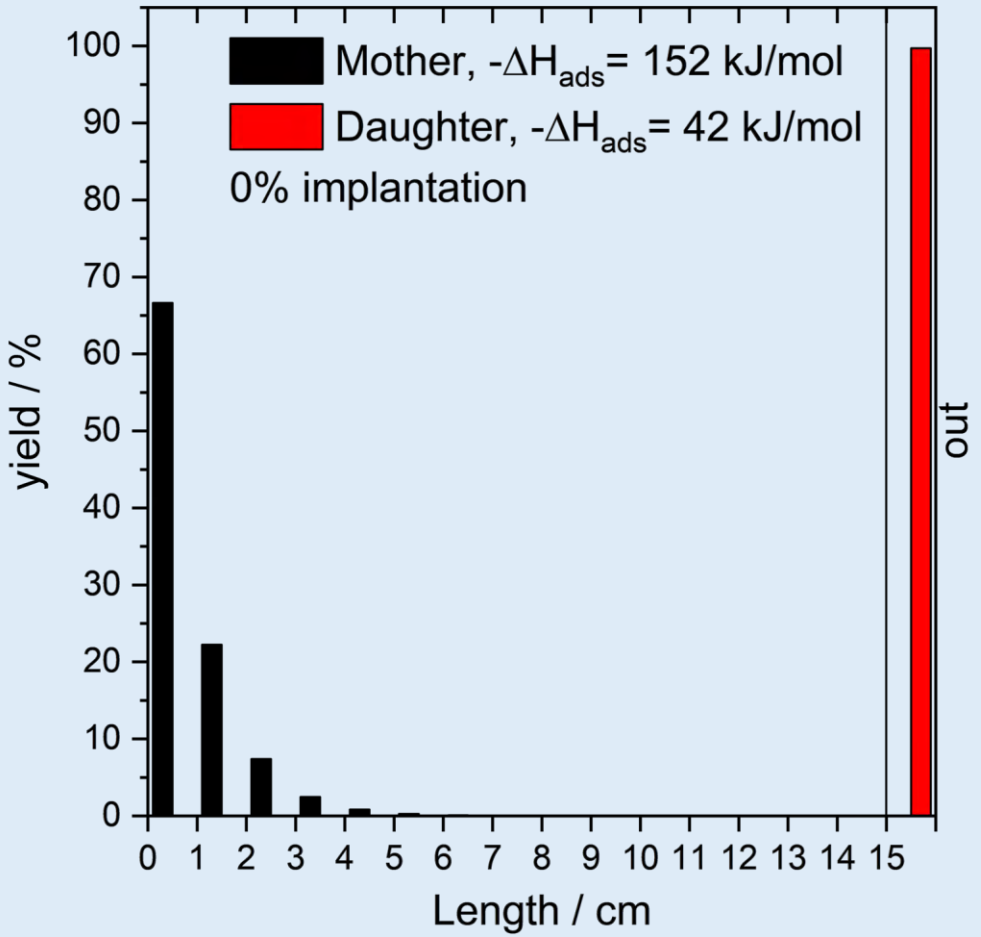


in case of strong recoil

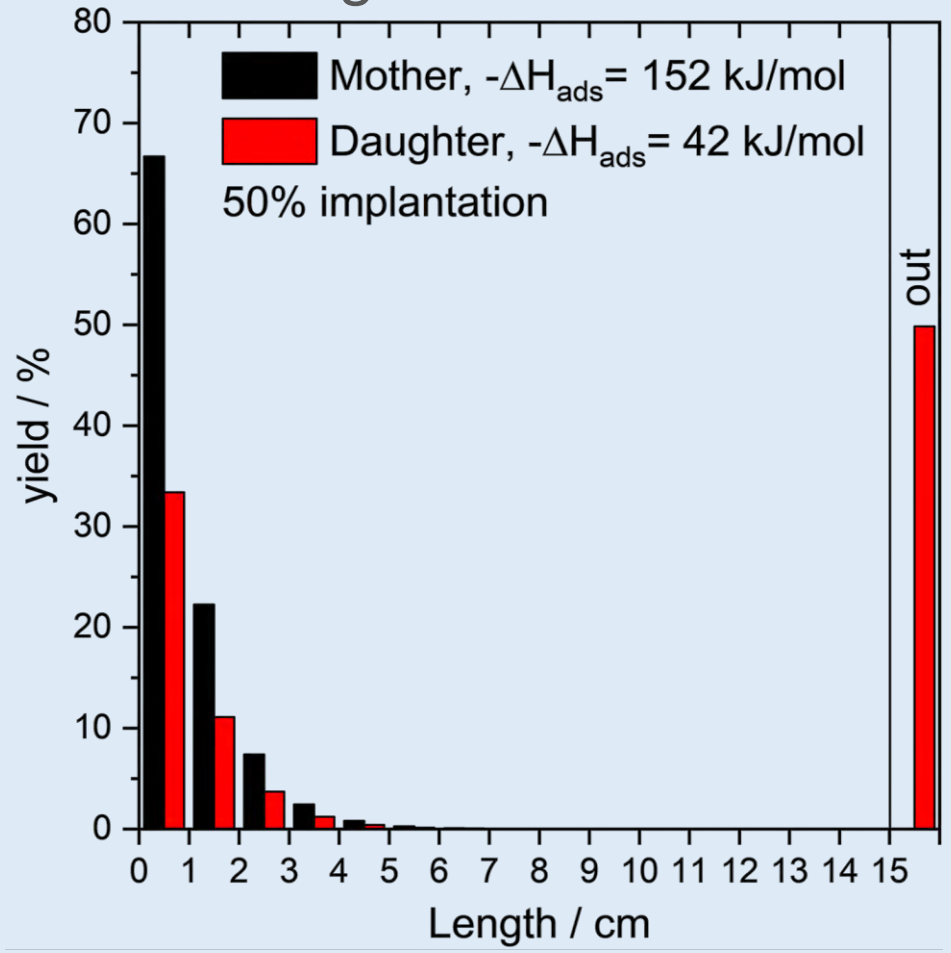
Pershina et. al., Inorg. Chem. **60** (2021)

IMPACT OF THE PRECURSOR EFFECT

Simulations with similar parameters:
Strongly adsorbing mother, volatile daughter



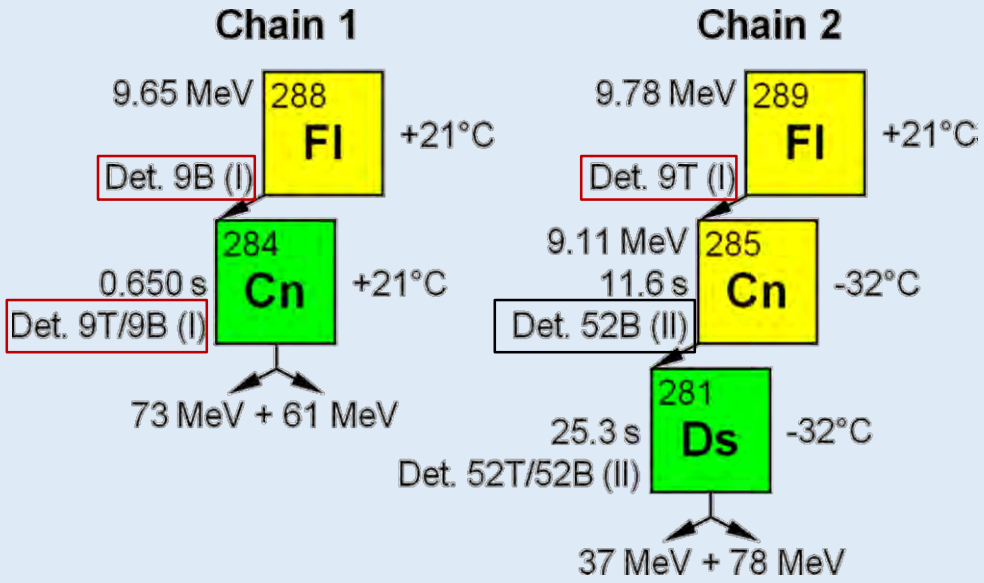
in case of weak recoil



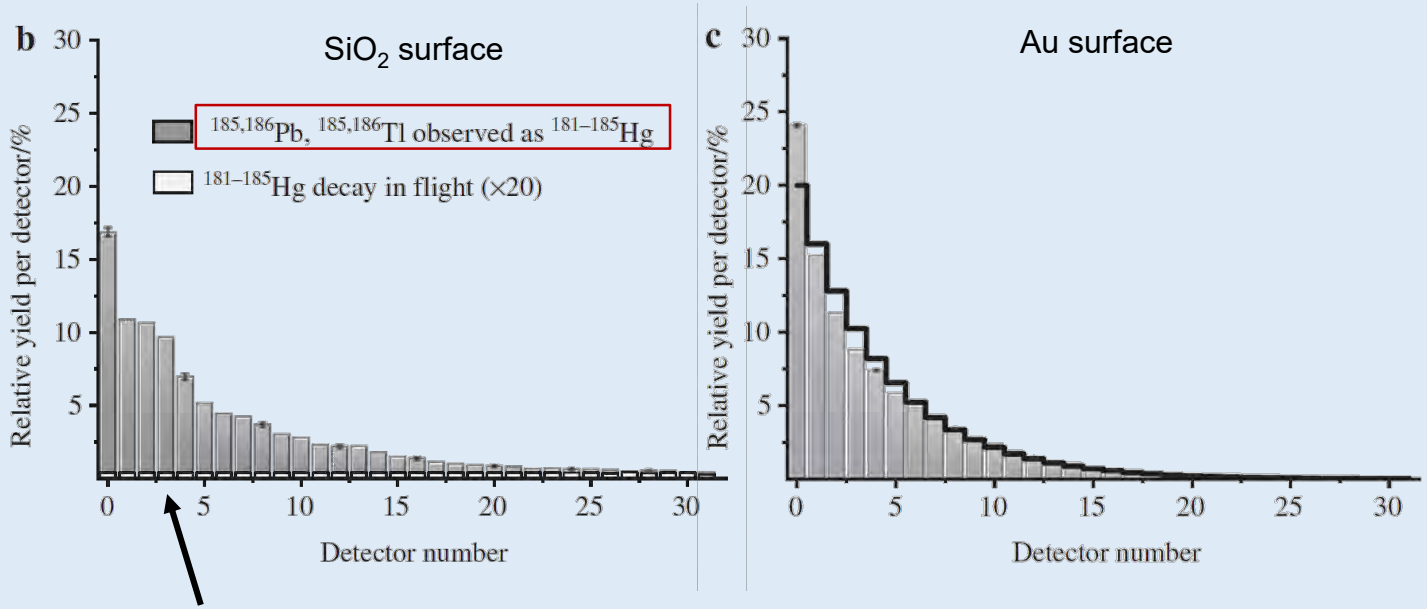
in case of strong recoil

Pershina et. al., Inorg. Chem. **60** (2021)
L. Lens et al., Radiochim. Acta **106** (2018)

EXAMPLES



Tl → Hg (β^+)



Implantation of Hg

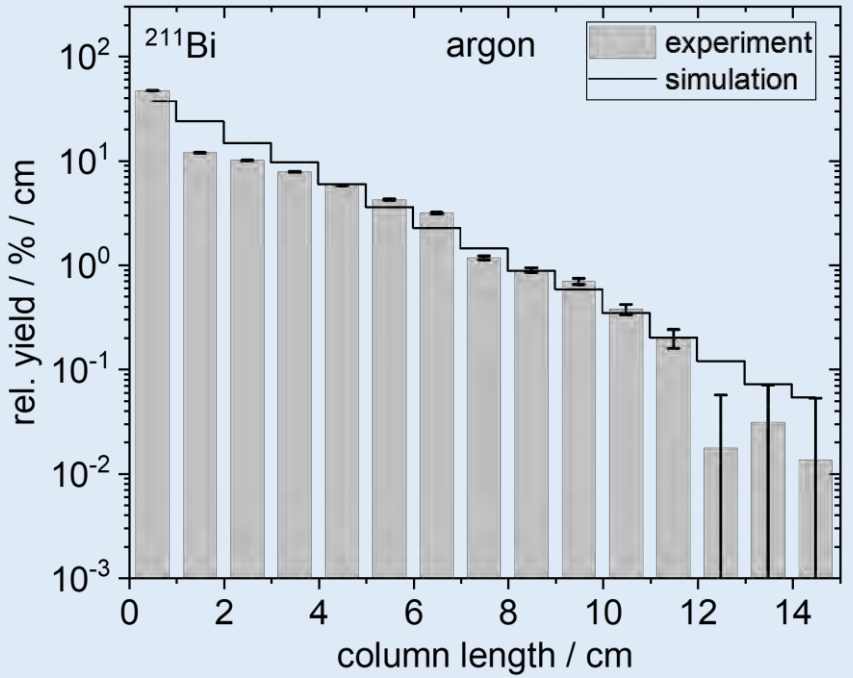
A. Yakushev et al., Inorg. Chem. **53** (2014)
L. Lens et al., Radiochim. Acta **106** (2018)

RESULTS

- Comparison with Monte Carlo-simulation → Limit for $-\Delta H_{ads}$
- lower limit for pure diffusion controlled adsorption
- With best fit: average limit for $-\Delta H_{ads.}$(Bi) ≈ 76 kJ/mol

Limits of the adsorption enthalpies for different gases and gas flow rates estimated with Monte Carlo-simulations.

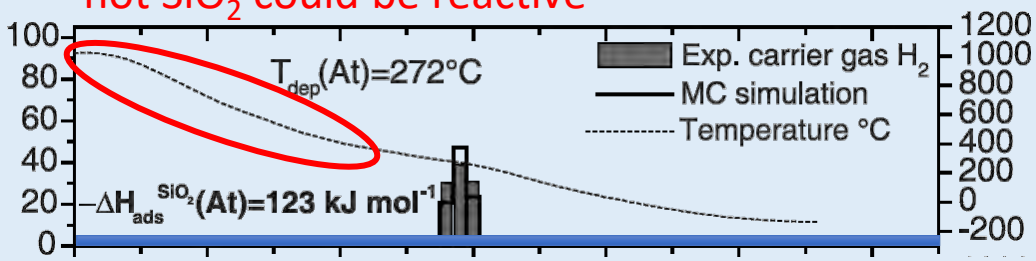
Gas, gas flow rate	$-\Delta H_{ads}$ (limit)
He, 1 L/min	75 kJ/mol
He, 2 L/min	76 kJ/mol
He, 3 L/min	77 kJ/mol
Ar, 1 L/min	76 kJ/mol
O_2, 1 L/min	74 kJ/mol

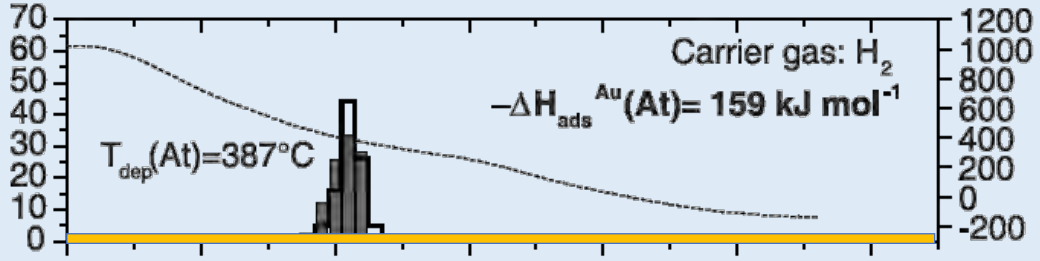


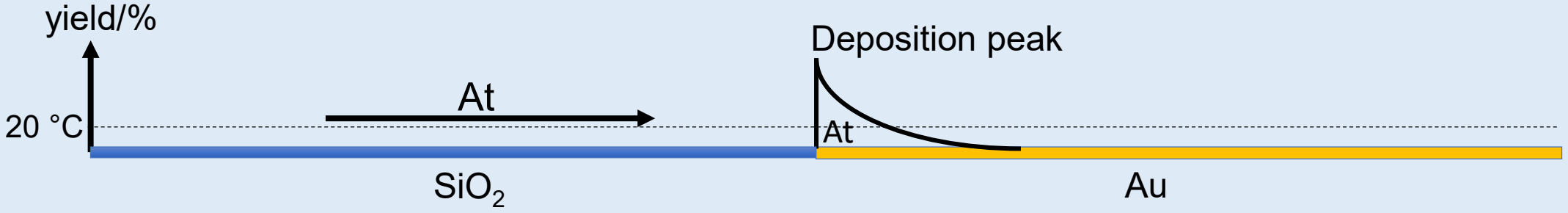
2. ACTIVATED ADSORPTION

Ongoing discussion about experiments with superheavy elements and homologs:
Which species is measured? What method is the most suitable? What happened in the experiments?
Example: Astatine experiments in the past

hot SiO_2 could be reactive







With high temperatures at the beginning: Probably not deposition of pure metals, but rather product of chemical reaction with the surface! Two different things happen in the experiments.

Description of pure adsorption-desorption process does not take possible chemical interactions with the surface into account!

A. Serov *et al.*, Radiochim. Acta **99** (2011)

ADVANCED SIMULATIONS OF SURFACE PROCESSES

Simple mobile adsorption model with ONE value for $\Delta H_{ads.}$

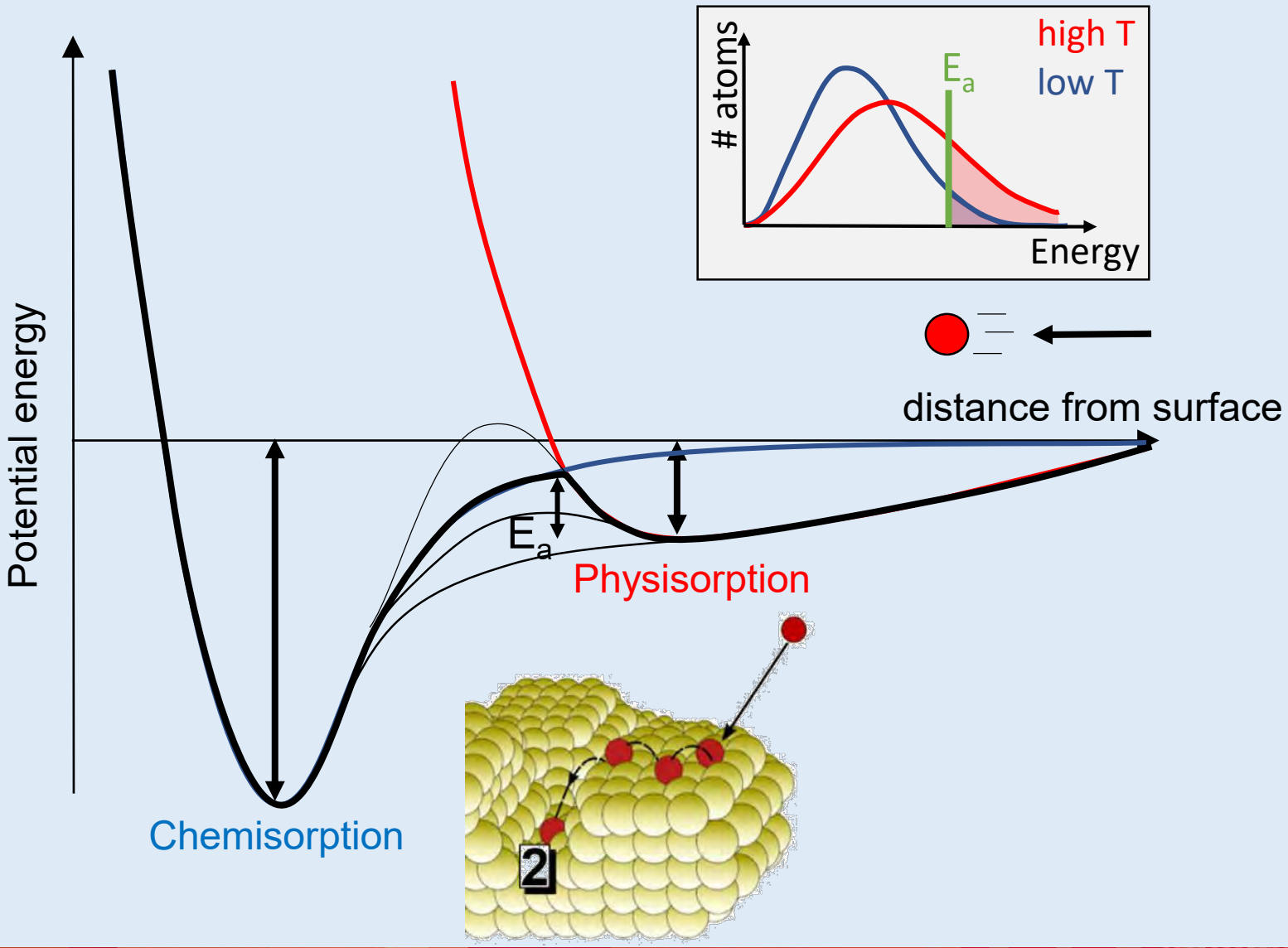
- no distinction between binding sites of different strength
- no surface diffusion
- no chemical reaction, only physisorption

→Lack of accuracy

New: more complex and detailed adsorption model

- simulation includes activation energy barrier for chemical reaction
- chemical reaction can cause a change of interaction strength

ACTIVATED ADSORPTION



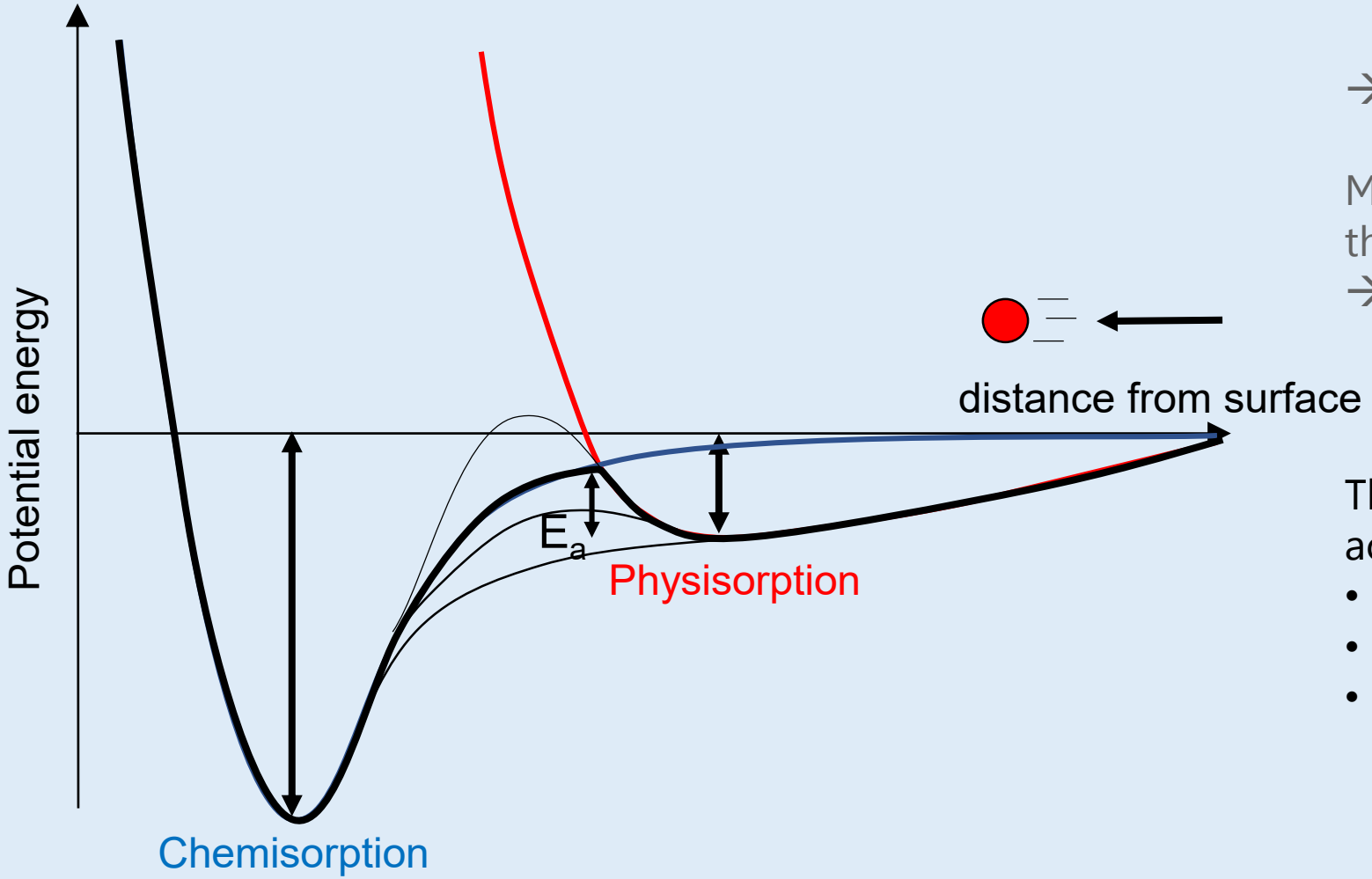
- Physisorption: <50 kJ/mol based on VdW-forces
- Chemisorption: ~50-300 kJ/mol orbital interaction or diffusion to a strongly bound site
- Activation energy E_A: ≥ 0 kJ/mol

- Probability to overcome energy barrier becomes larger in higher temperatures
  $\#Atoms(>E_a) \propto \exp(-E_A/RT)$

- Chemisorption or reaction with surface favorably in **high T**, it **increases** with an increase in temperature

J. E. Lennard-Jones, *Trans. Faraday Soc.* **28** (1932)
A. Yakushev et al., *Front. Chem* (2022)

ACTIVATED ADSORPTION



- If the barrier was passed, the atom could desorb from the surface as a new species

→ more volatile or less volatile

Misinterpretation if all atoms have reacted at the beginning of the column

→only measurement of Species 2 possible!

The more complex system of processes accounts for:

- physisorption
- activation energy barrier
- desorption as a different species!

J. E. Lennard-Jones, *Trans. Faraday Soc.* 28, 333 (1932)
A. Yakushev et al., *Front. Chem* (2022)

IMPACT OF THE ACTIVATED ADSORPTION

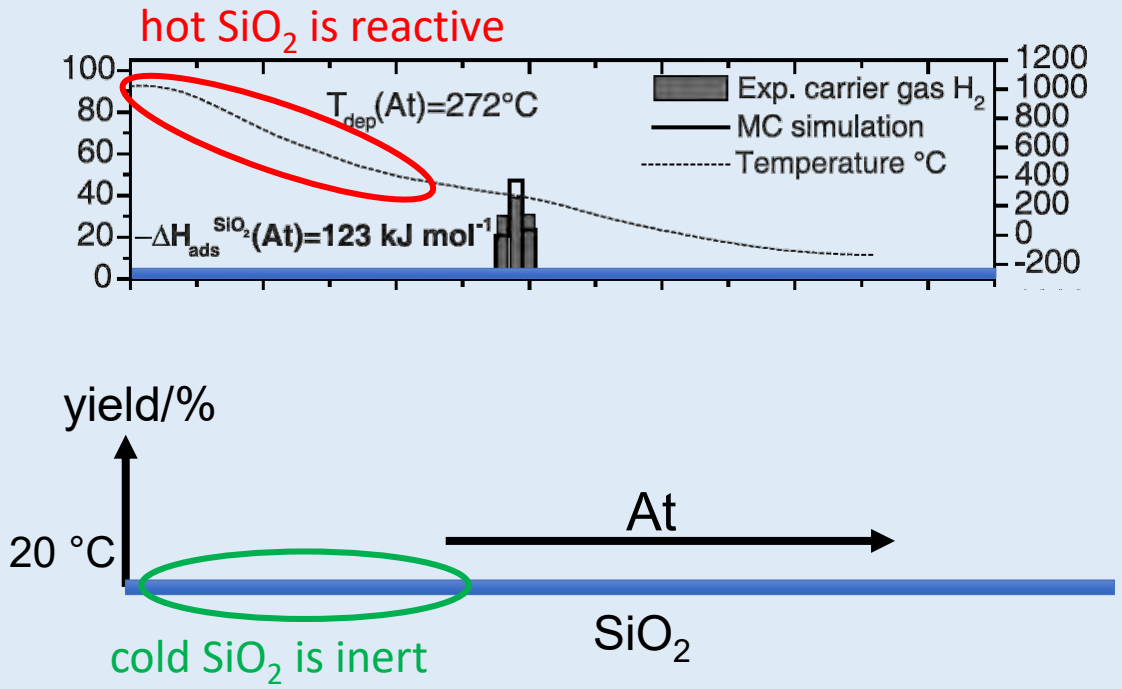
Astatine experiments summary:

- „non-volatile“ species in thermochromatography (high T)
- „volatile species in isothermal chromatography (low T)

→not explicable with standard mobile adsorption model

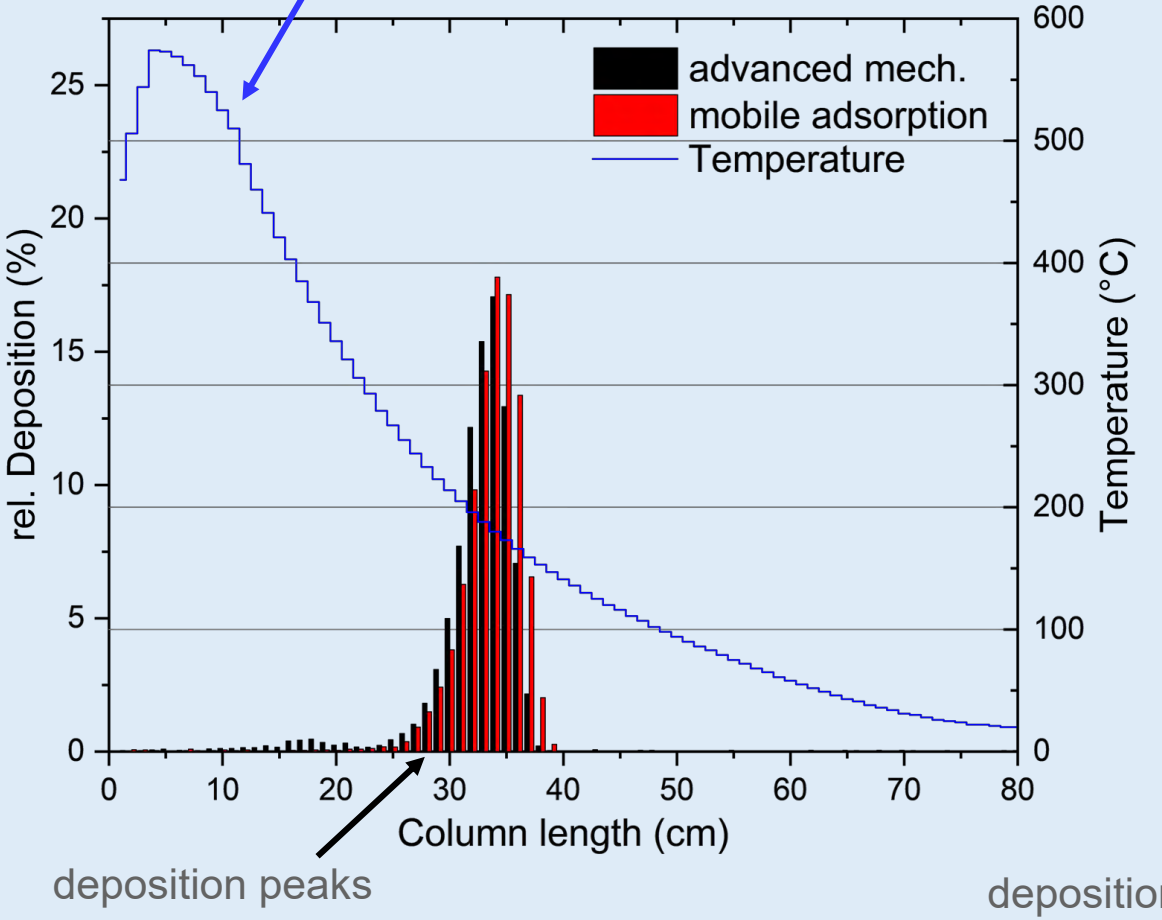
Explanation with advanced adsorption process:

- REACTIVE only at high temperatures (E > E_a)
- NON-REACTIVE at low temperatures



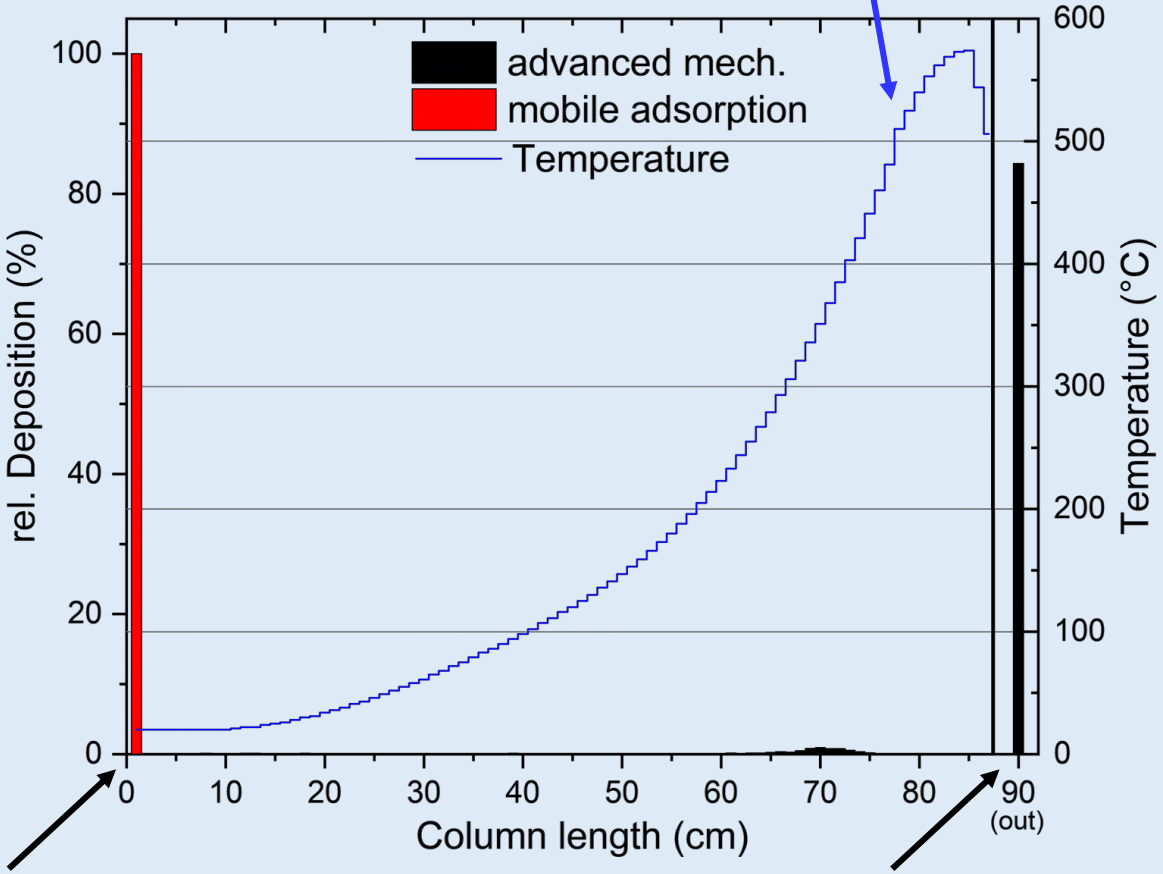
IMPACT OF THE ACTIVATED ADSORPTION

negative temperature gradient



deposition peaks

positive temperature gradient



deposition peak

breakthrough

CONCLUSION

1. new experiments and results demand for adapted and improved MCS
2. precursor effect was implemented for $^{211}Pb/^{211}Bi$ system
   - The observed adsorption enthalpy of Bi on SiO_2 is $\mathbf{-\Delta H_{ads} > 76\ kJ / mol}$
3. mobile adsorption was substituted by more complex mechanism
   - physisorption, chemisorption, different binding sites, activation energy barrier, second species…
4. Discrepancies can be explained
5. Combination of multiple experiments (TC, Reverse TC, IC) necessary or advantageous
6. Outlook: Both physisorption and chemisorption have to be considered in studies.
   - Candidates: Hg, Cn, Tl, Nh, Fl, Po, At

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THANK YOU FOR YOUR KIND ATTENTION!

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