STUC Project :

STudies of **U**ranium **C**ompounds

Impact of UC_2, UC, UBC and UB_2 target compositions on the release of fission products

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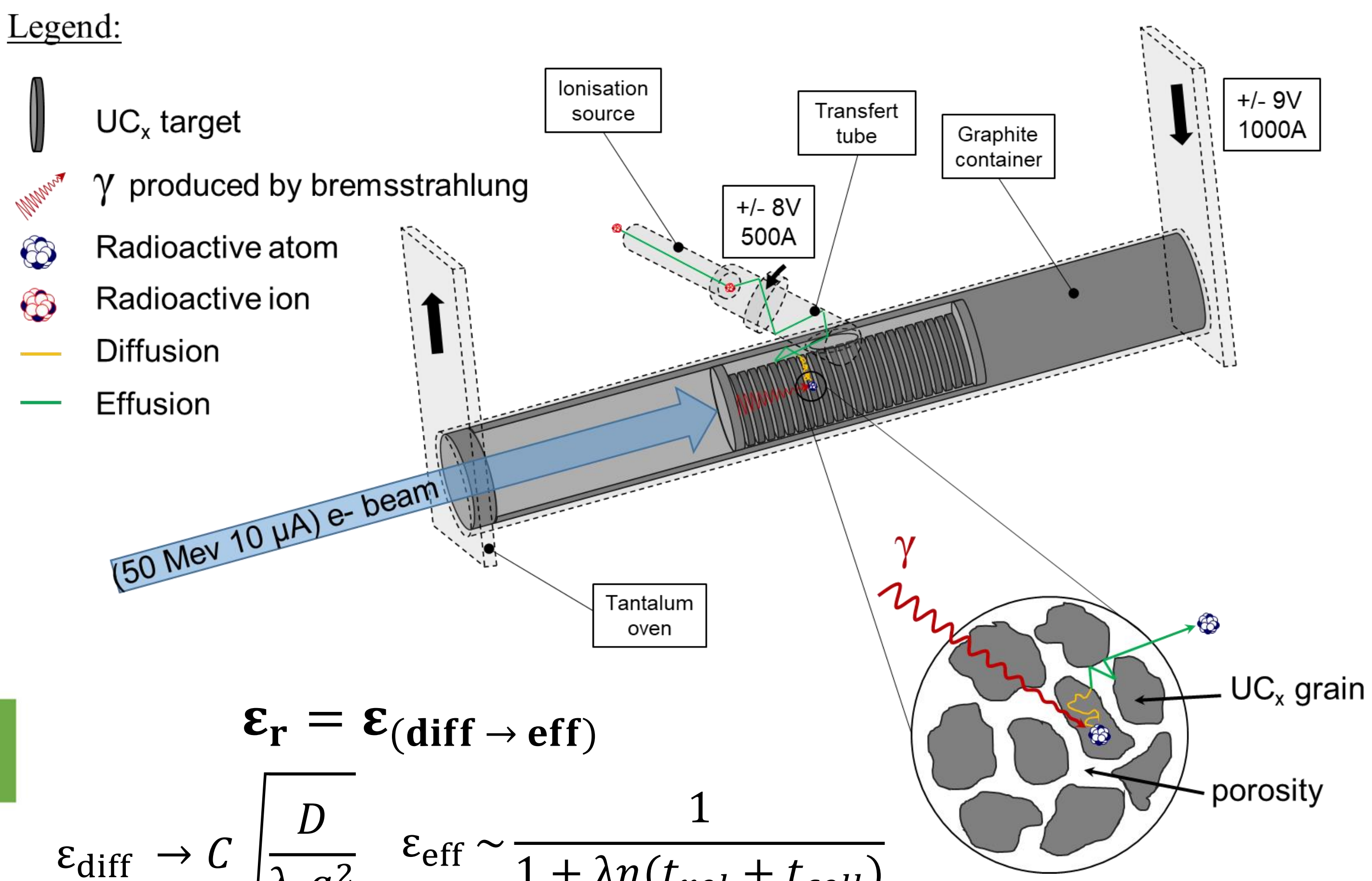
Context

CONTEXT

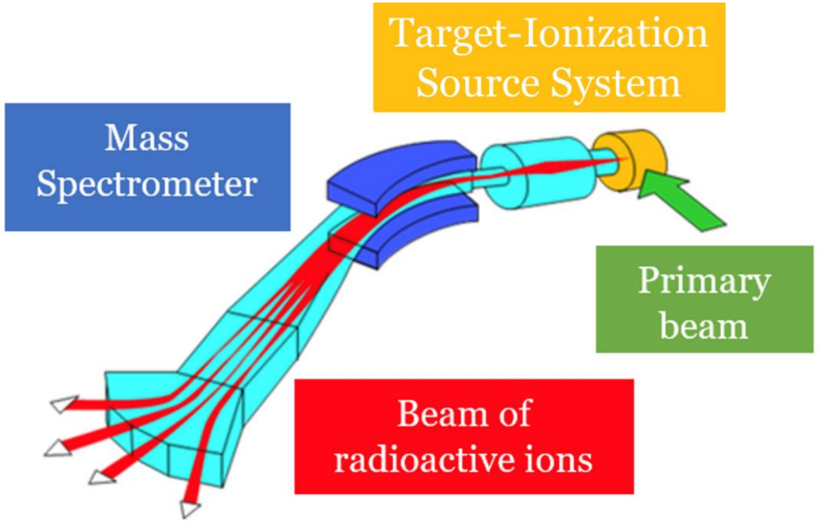
- Strong demand from nuclear physics for exotic beams to study nuclear structure
- Production of radioactive beams at ALTO: ISOL (Isotope Separation On-Line) method

$$\mathbf{I = I_P . \sigma . N . \varepsilon_r . \varepsilon_{ion} . \varepsilon_{tr}}$$



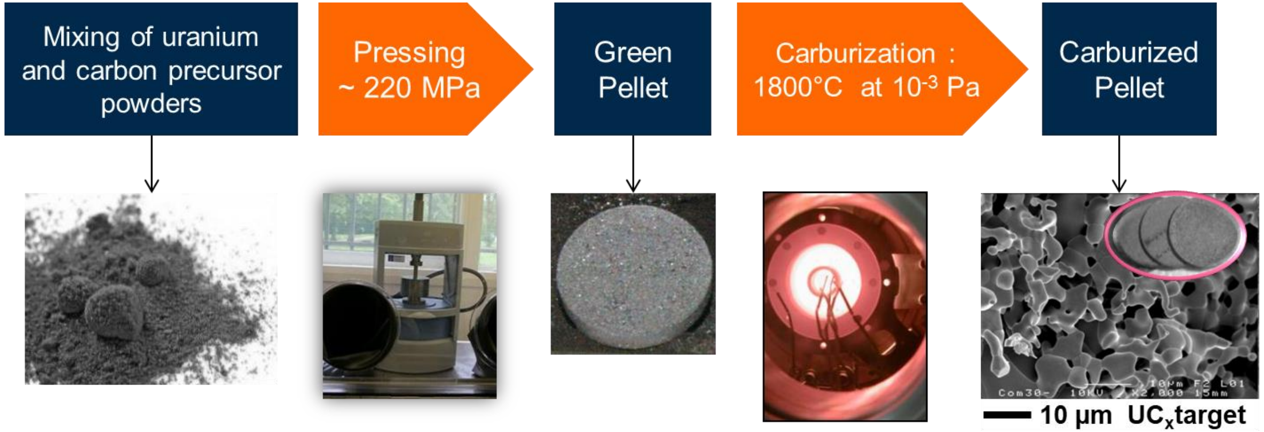
$$\boldsymbol{\varepsilon_r = \varepsilon_{(\mathrm{diff} \rightarrow \mathrm{eff})}}$$

$$\varepsilon_{\mathrm{diff}} \rightarrow C\sqrt{\frac{D}{\lambda . a^2}} \qquad \varepsilon_{\mathrm{eff}} \sim \frac{1}{1+\lambda n(t_{vol}+t_{coll})}$$



How to build a target ? What caracterization?

- **Synthesis of UC_x target:** $UO_2 + 6C \rightarrow (1-x)UC + xUC_2 + (3-x)C + 2CO_{(g)}$



Mixing of uranium and carbon precursor powders

Pressing ~ 220 MPa

Green Pellet

Carburization : 1800°C at 10^{-3} Pa

Carburized Pellet

- **Techniques used for the physico-chemical characterization of UC_x targets :**

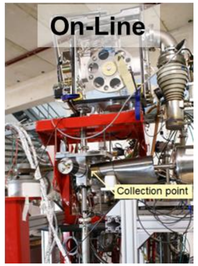
XRD | SEM | BET | He Pycnometry | Hg Porosimetry

XRD: Analysis of phases

SEM, BET: Grain and aggregate size

He Pycnometry, Hg Porosimetry: Proportion and distribution of porosities

- **Equipment for measuring released fractions (off-line) and production (on-line) :**



Study on the influence of the microstructure

N° sample	Sample name					
1	UO_2 ground+CNT PM	🟣	🟢	⚫	🔵	○
2	UO_2 ground+CNT UM	🟣	🟢	🔴	🔵	○
3	UO_2 ground+graphene	🟣	🔵	⚪	🔵	○
4	OXA+graphite PM	⚫	⚫	⚫	🔵	○
5	OXA ground+CNT UM	⚫	🟢	🟠	🔵	○
6	OXA+CNT UM	⚫	🟢	🟠	🔵	○
7	PARRNe BP894	🟣	⚫	⚫	🔵	○
8	PARRNe BP897 PM	🟣	⚫	⚫	🔵	○
9	PARRNe BP897 PM 12d	🟣	⚫	⚫	🔵	🟢
10	UO_2 ground+CNT PM 12d	🟣	🟢	⚫	🔵	🟢
11	UO_2 ground+CNT UM 12d	🟣	🟢	🟠	🔵	🟢
12	UO_2 ground+graphene 12d	🟣	🔵	⚪	🔵	🟢
13	UO_2 ground+CNT-5mol UM	🟣	🟢	🟠	🟣	○
14	UO_2 ground+CNT-7mol UM	🟣	🟢	🟠	🔴	○

Uranium precursor:

- 🟣 Oxyde d'uranium
- ⚫ Oxalate d'uranium

Carbone precursor:

- ⚫ Graphite
- 🔵 Graphene
- 🟢 CNT

Molar ratio C/U

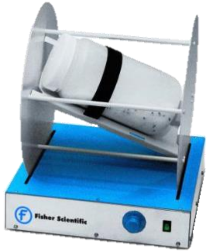
- 🟣 5
- 🔵 6
- 🔴 7

12-day heating after carburation :

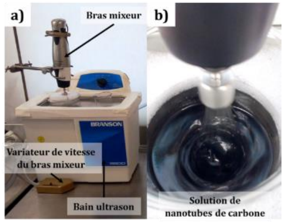
- 🟢 Yes
- ○ No

Precursor powder mixing:

- ⚫ Robin™ Powder Mixer



- 🔴 Ultrasonic liquid mixing



- ⚪ Graphene blender

J. Guillot *et al.* Nuclear Instruments and Methods in Physics Research B 433 (2018) 60-68

Study on the influence of the microstructure

Green pellet

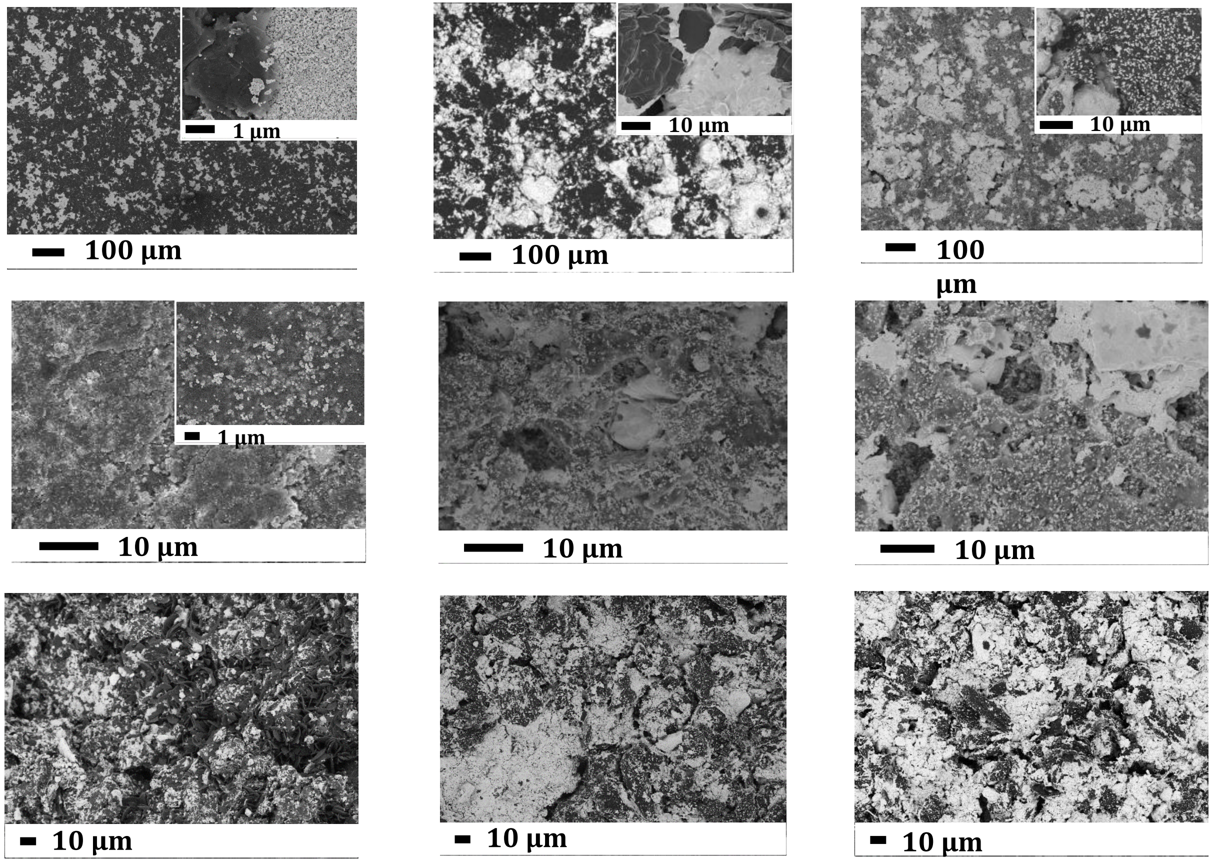
Carburized pellet

Carburized pellet
+ 12-day heating

Powder Mixer

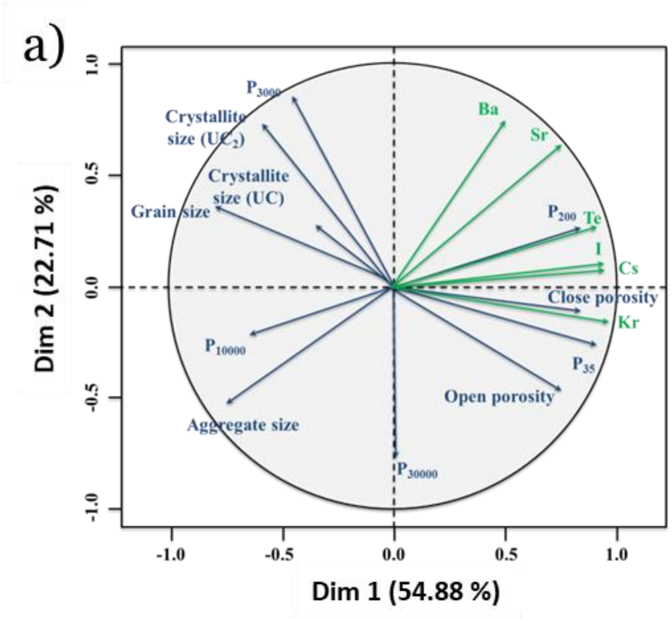
Ultrasonic
liquid mixing

Graphene blender

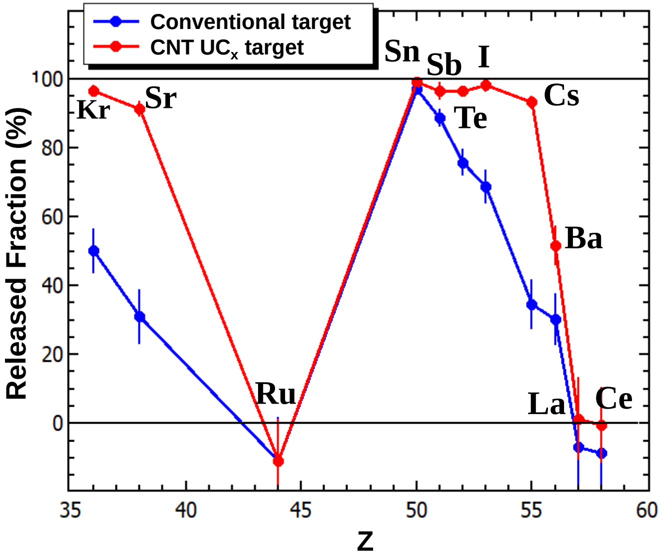


J. Guillot *et al.* Nuclear Instruments and Methods in Physics Research B 433 (2018) 60-68

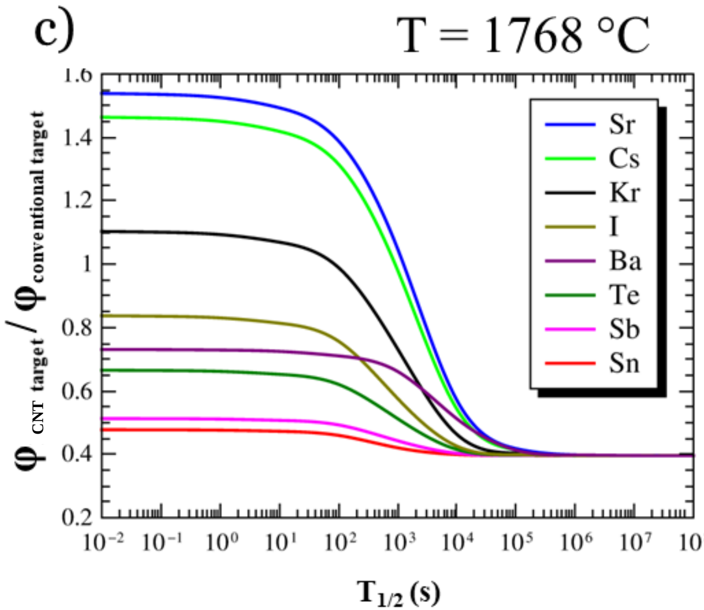
Study on the influence of the microstructure



a) Correlations between release fractions (in green) and target properties (in blue)



b) Released fraction comparison between conventional target (mostly UC_2) and an R&D target made with CNT

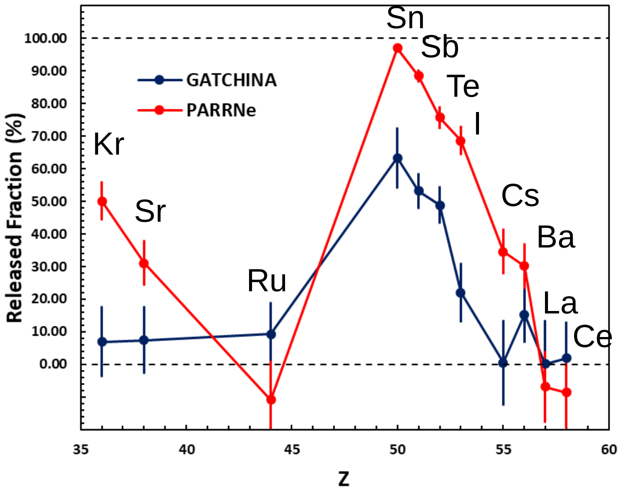


c) Comparison of fission products released between R&D target and conventional target

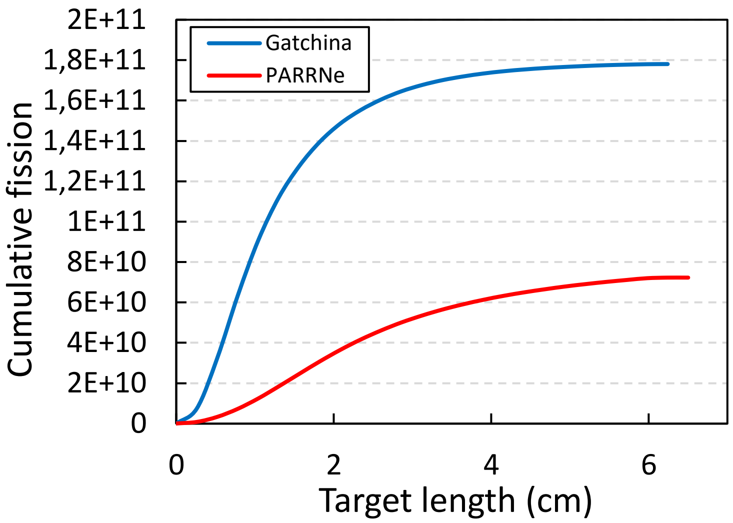
Loss of production is compensated by improved release (Sr, Cs and Kr)

J. Guillot *et al.* Nuclear Instruments and Methods in Physics Research B 440 (2019) 1-10
J. Guillot *et al.* Nuclear Instruments and Methods in Physics Research B 468 (2020) 1-7

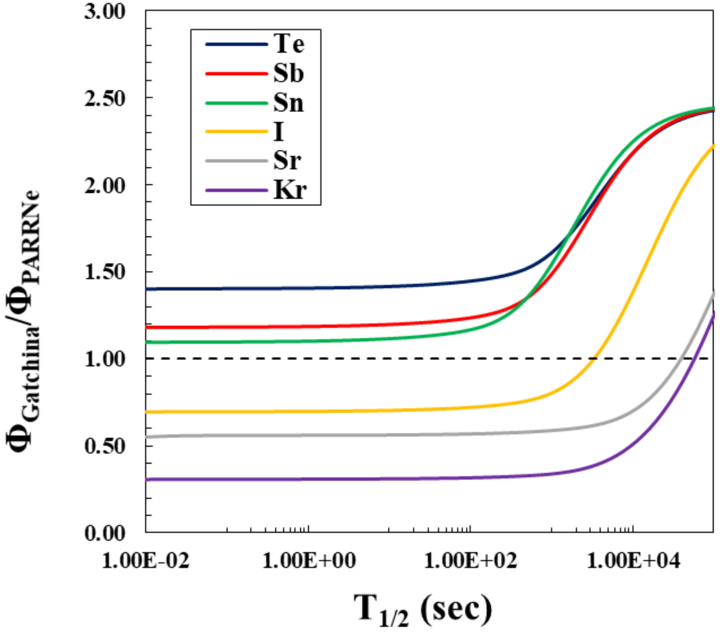
Study on the influence of the microstructure



Released Fractions from:
PARRNe pellet (Ø=13 mm, th=1.7 mm) heated to 1768°C
Gatchina pellet (Ø=13.2 mm, th=1 mm) heated to 1700°C.



Number of fissions per second cumulated along the PARRNe and Gatchina targets and normalized for a 10 µA electron beam



Estimation of the production ratio between a Gatchina target and a PARRNe target

Physico-chemical characteristics obtained by XRD and Helium pycnometry

		Gatchina	PARRNe
Quantity of phases (%)	UO_2	4.5	-
	UC	86.9	5
	UC_2	8.6	87
	C	-	8
Apparent density (g/cm^3)		12.4	3.82
Porosity (%)	Open	5	51
	Close	2	5

The loss in releases is compensated by improved production (Sn, Te and Sb)

S. Tusseau-Nenez *et al.* Nuclear Instruments and Methods in Physics Research B 370 (2016) 19–31

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Elements	Release process	Target caracteristics
Sr	-	Low density Small grain Open pores
Cs	Diffusion[1]	
Kr	Diffusion[2]	
I	Diffusion/Effusion[2]	
Te	-	High density Open pore (?)
Sb	-	
Sn	Effusion[2]	

1: F. Hosni *et al.* NIM B 247 (2006) 205–209
2: B. Roussière *et al.* NIM B 246 (2006) 288–296

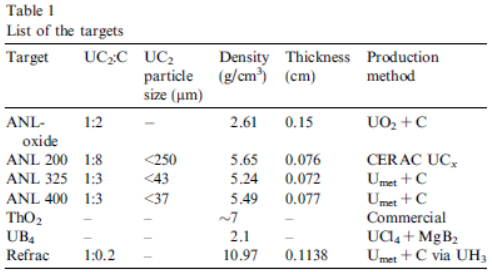
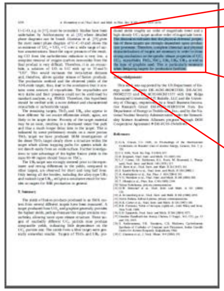
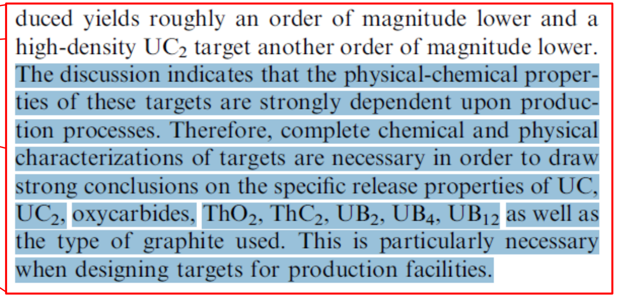


Table 1
List of the targets

Target	UC$_2$:C	UC$_2$ particle size (μm)	Density (g/cm^3)	Thickness (cm)	Production method
ANL-oxide	1:2	–	2.61	0.15	$UO_2 + C$
ANL 200	1:8	<250	5.65	0.076	CERAC UC_x
ANL 325	1:3	<43	5.24	0.072	$U_{met} + C$
ANL 400	1:3	<37	5.49	0.077	$U_{met} + C$
ThO_2	–	–	~7	–	Commercial
UB_4	–	–	2.1	–	$UCl_4 + MgB_2$
Refrac	1:0.2	–	10.97	0.1138	U_{met} + C via UH_3





duced yields roughly an order of magnitude lower and a high-density UC_2 target another order of magnitude lower. The discussion indicates that the physical-chemical properties of these targets are strongly dependent upon production processes. Therefore, complete chemical and physical characterizations of targets are necessary in order to draw strong conclusions on the specific release properties of UC, UC_2, oxycarbides, ThO_2, ThC_2, UB_2, UB_4, UB_{12} as well as the type of graphite used. This is particularly necessary when designing targets for production facilities.

A. Kronenberg *et al.* Nucl. Instr. and Meth. in Phys. Res. B 266 (2008) 4267–4270

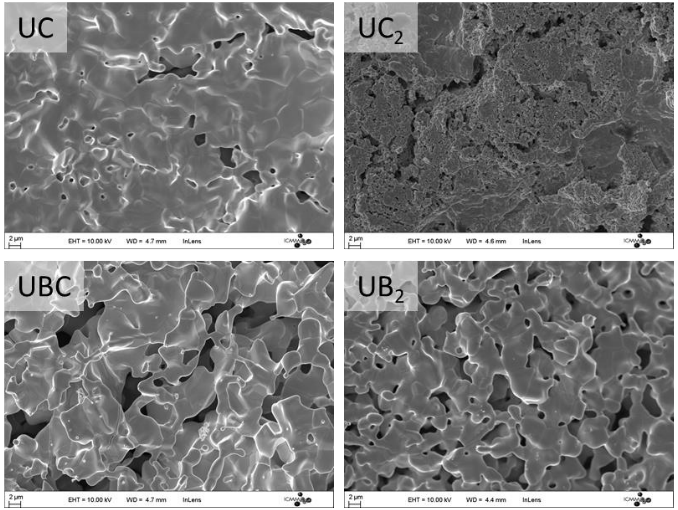
Synthesis of various uranium compounds (UC, UBC, UB_2 and UC_2) :
(**Aim:** To study the influence of uranium alloy density on the release of fission products.)

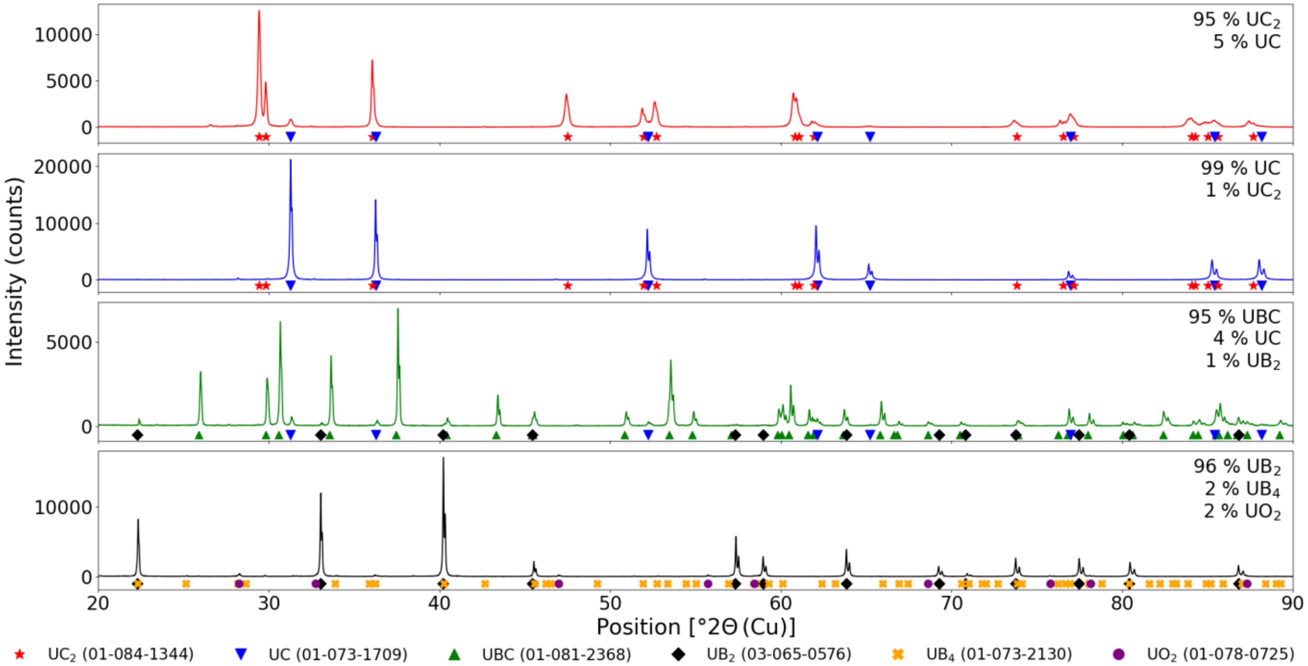
- If we add porosity to a very dense target, does this improve release ?
- Is there a difference in release if we use uranium compounds with theoretical densities for UC, UBC, UB_2 and UC_2?
- Is there any influence of the chemical environment ?

STUC PROJET: STudy of Uranium Compounds

- $UO_{2\,(s)} + 4C_{(s)} \longrightarrow UC_{2\,(s)} + 2CO_{(g)}$
- $UO_{2\,(s)} + 3C_{(s)} \longrightarrow UC_{(s)} + 2CO_{(g)}$
- $UO_{2\,(s)} + 3C_{(s)} \longrightarrow UC_{(s)} + 2CO_{(g)}$
  $UC_{(s)} + BN_{(s)} \longrightarrow UBC_{(s)} + N_{(g)}$
- $2UO_{2\,(s)} + 3C + B_4C_{(s)} \longrightarrow 2UB_{2\,(s)} + 4CO_{(g)}$

Target	Mass (g)	Diameter (mm)	Thickness (mm)	Apparent density (g/cm^3)	Porosity (%)		SSA (m^2/g)	Open pore size distribution (%)	
					Open	Close		0.1 - 10 µm	100 - 150 µm
UC_2	0.77	11.30	1.35	5.86	46	3	0.3965	88	12
UC	0.77	10.20	1.15	8.16	39	1	0.0763	94	6
UBC	0.92	12.76	1.02	6.93	42	1	0.0496	100	0
UB_2	0.75	10.98	1.42	5.78	53	2	0.1032	80	20





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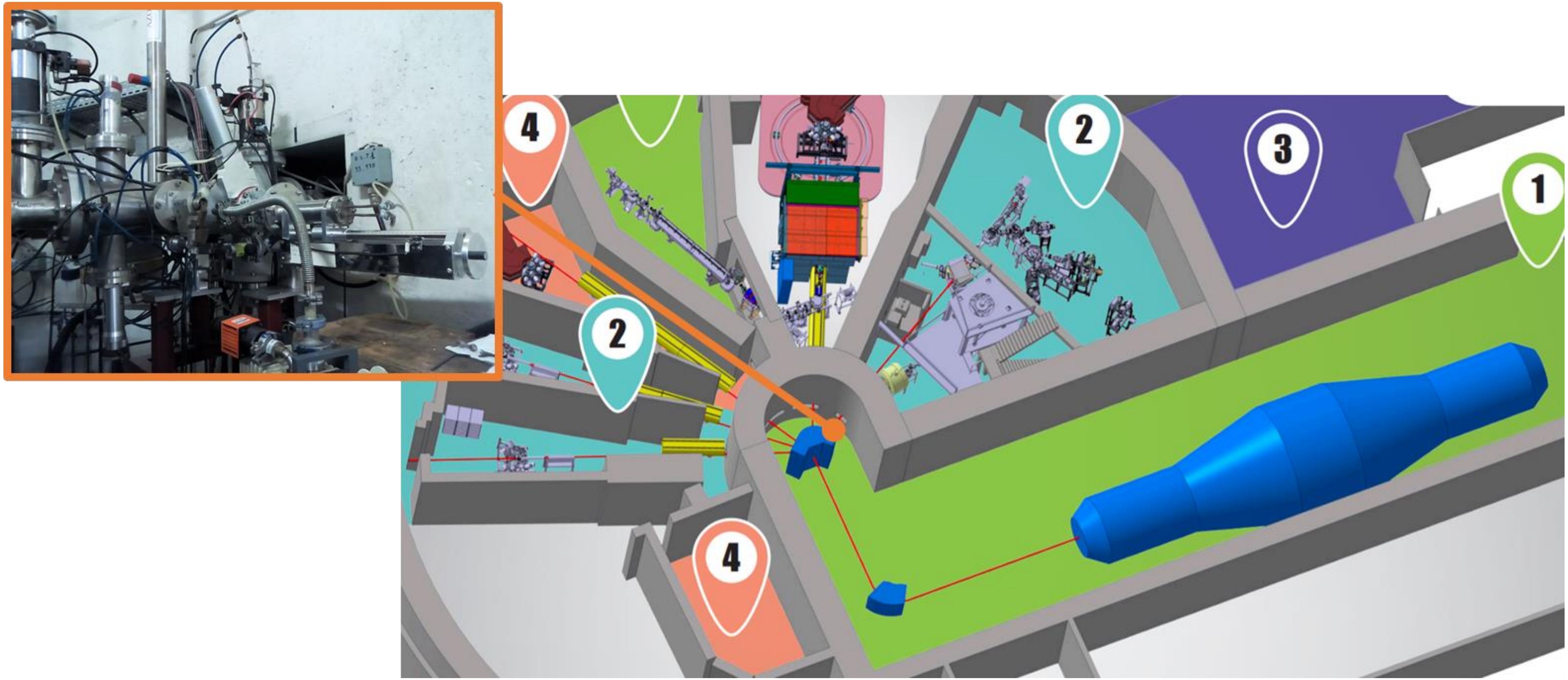

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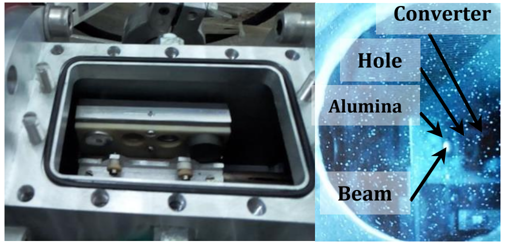
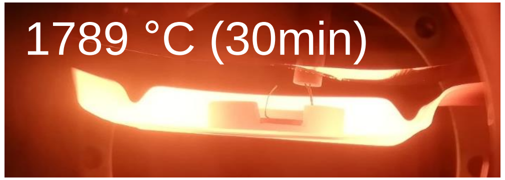
Irradiation:



1st measurement :

Heating:

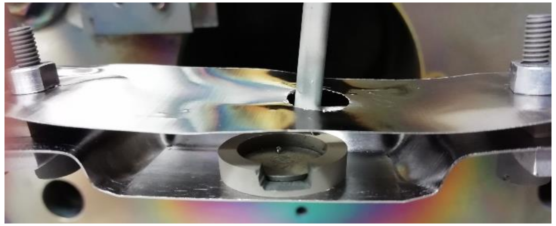


2nd measurement :

Irradiation conditions :

- Beam ^{2}H
- Energy 26 MeV
- Intensity 20 nA
- Time of irradiation 20 min

$$R = \frac{I_{P1}}{I_{P2}}$$



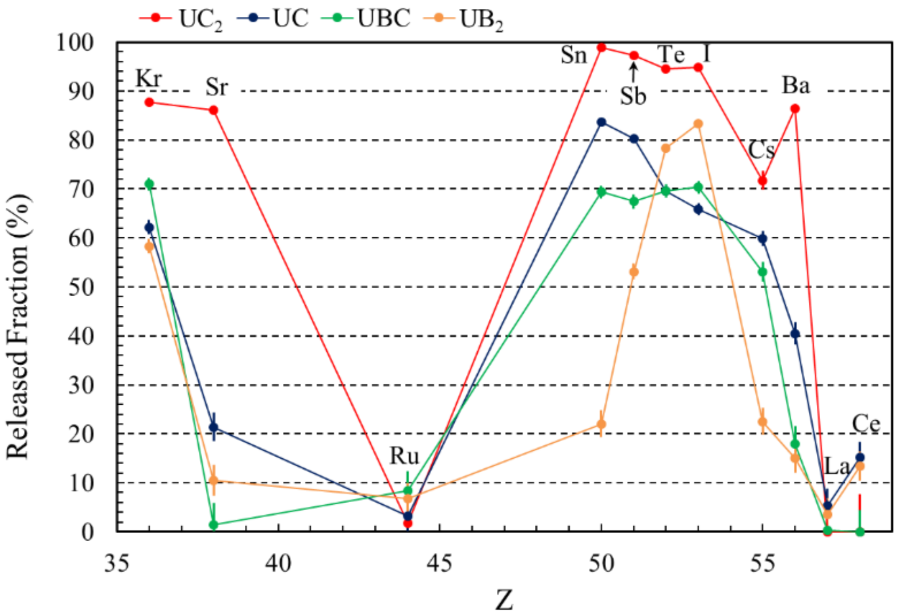
Temperature controlled by thermocouple

$$RF = 100\left(1 - \frac{I_{heated}}{I_{unheated}}\right) \quad \begin{array}{l} with \quad I_{unheated} = I'_{P2} \times R \\ and \quad \quad I_{heated} = I'_{P1} \end{array}$$

Hy *et al.* Nuclear Instruments and Methods in Physics Research B 288 (2012) 34-41

STUC PROJET: STudy of Uranium Compounds

Experiment performed in July 2023

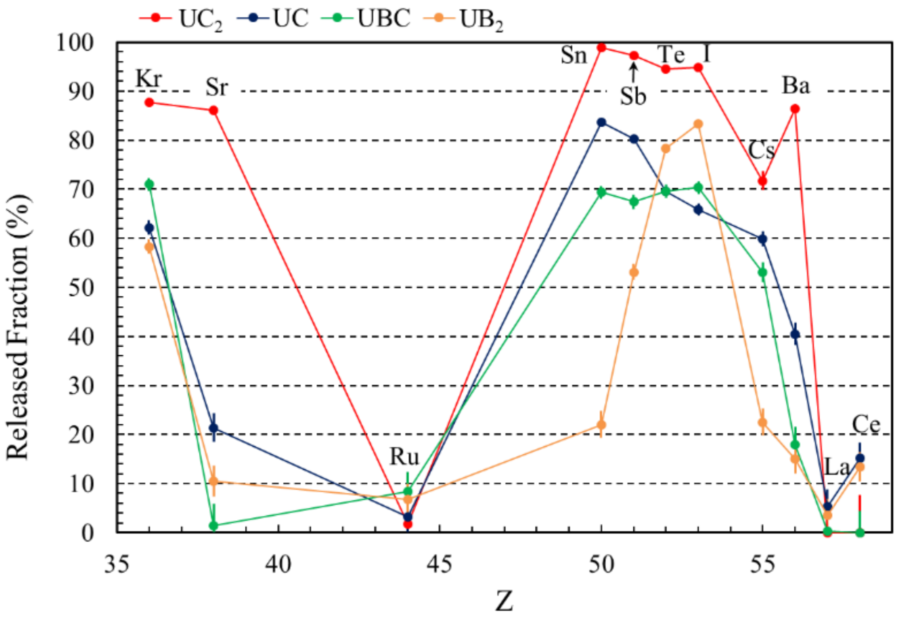


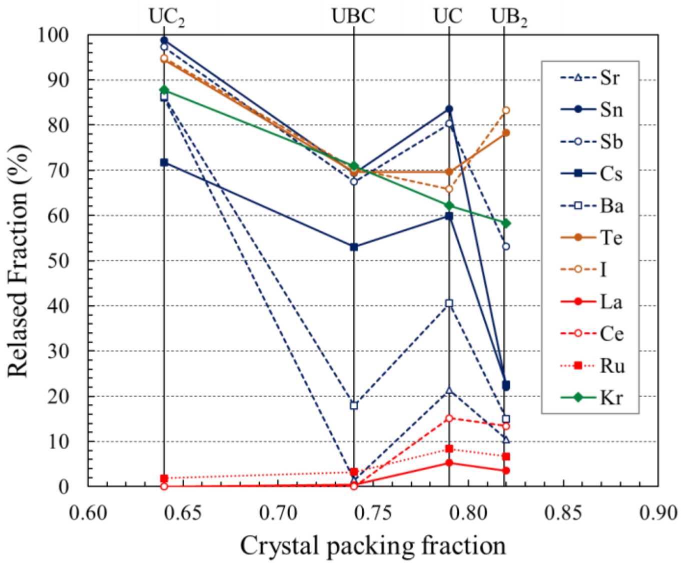
- crystal packing fraction
- the atomic radius

STUC PROJET: STudy of Uranium Compounds

Experiment performed in July 2023

- crystal packing fraction
- the atomic radius





The figure demonstrates that Kr release increases linearly with decreasing packing fraction, while other elements show varying behaviours, suggesting that factors other than packing fraction influence their release.

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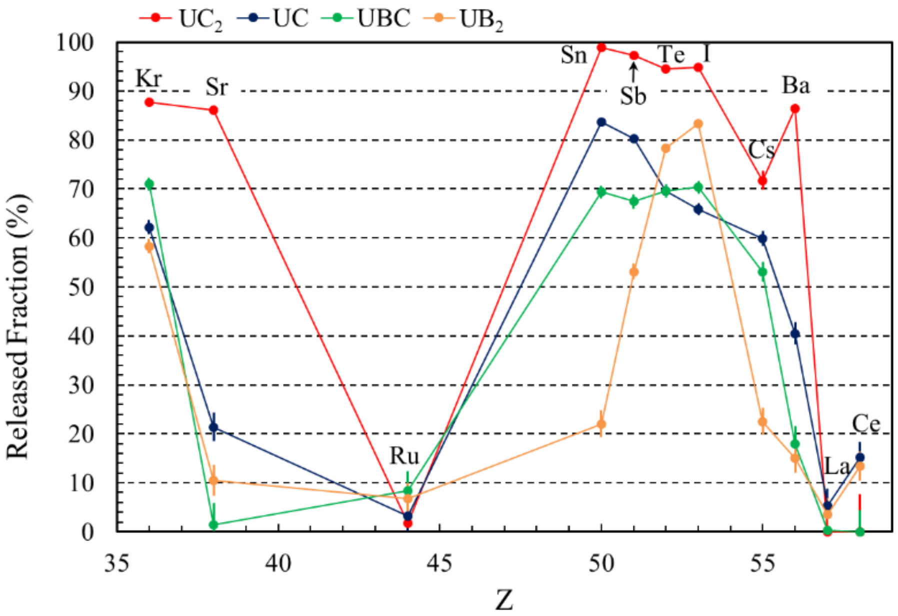
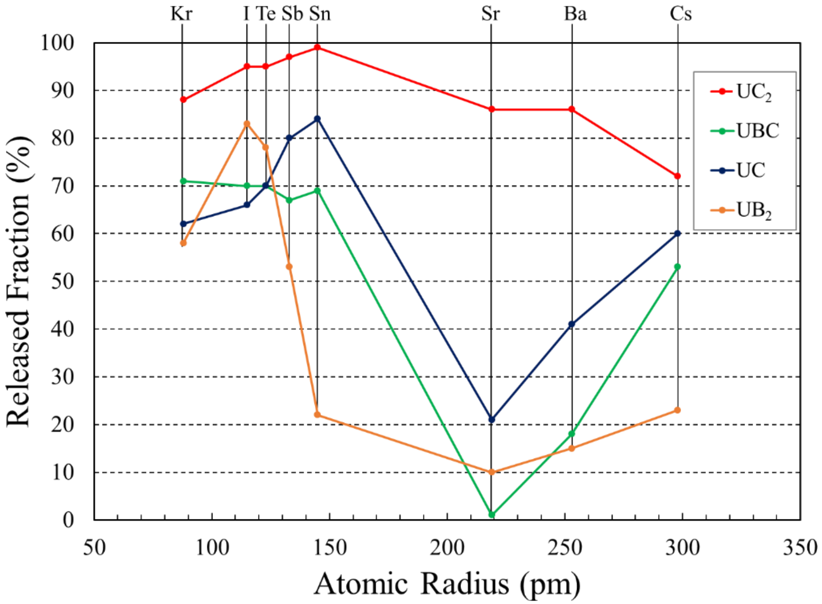
Experiment performed in July 2023

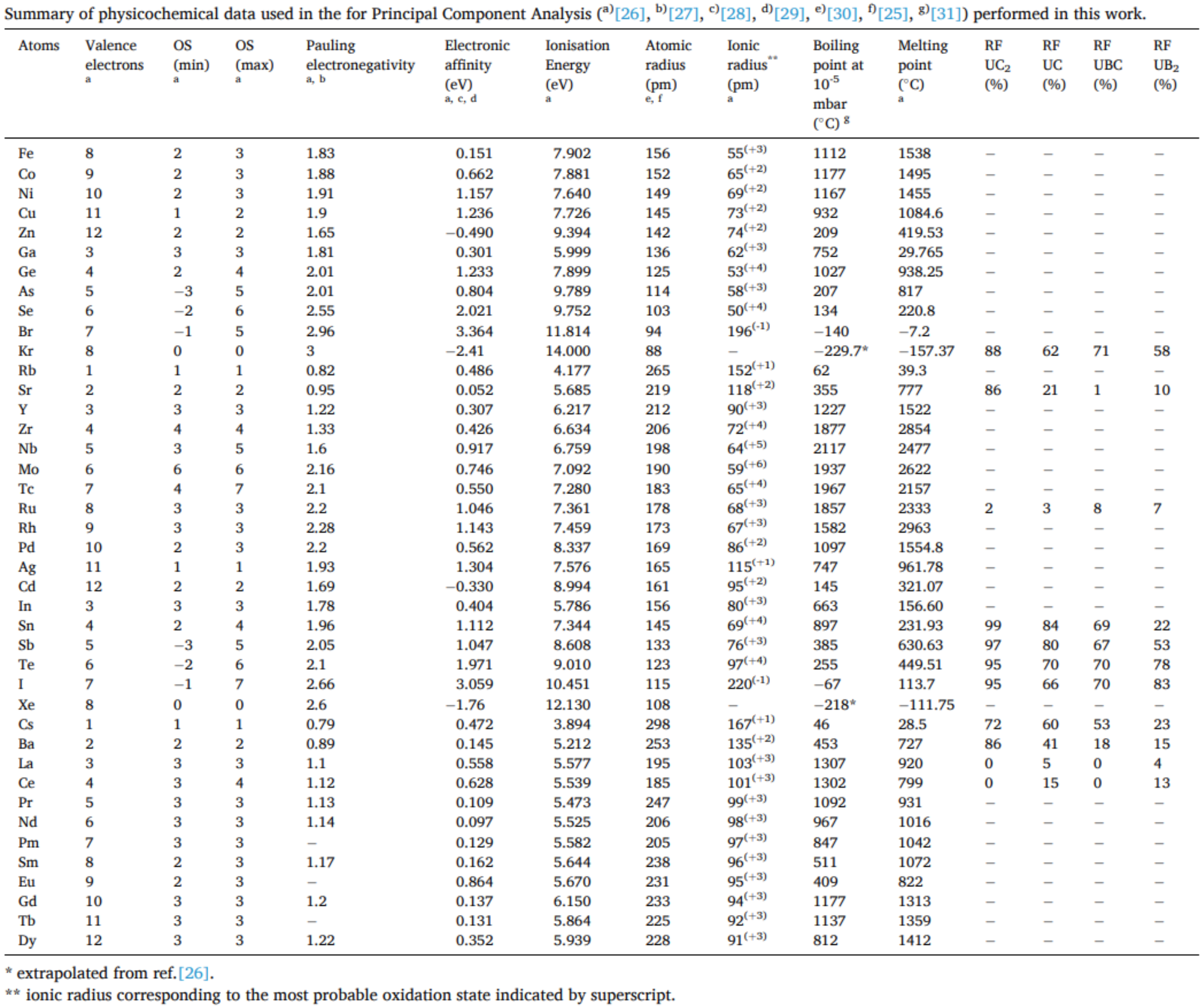


- crystal packing fraction
- the atomic radius



The graph helps analyse the influence of atomic size on the release efficiency, indicating how larger atomic radii may affect the mobility of elements within different crystal structures

STUC PROJET: STudy of Uranium Compounds



Summary of physicochemical data used in the for Principal Component Analysis ([a] [26], [b] [27], [c] [28], [d] [29], [e] [30], [f] [25], [g] [31]) performed in this work.

Atoms	Valence electrons [a]	OS (min) [a]	OS (max) [a]	Pauling electronegativity [a, b]	Electronic affinity (eV) [a, c, d]	Ionisation Energy (eV) [a]	Atomic radius (pm) [e, f]	Ionic radius** (pm) [a]	Boiling point at 10^{-5} mbar (°C) [g]	Melting point (°C) [a]	RF UC_2 (%)	RF UC (%)	RF UBC (%)	RF UB_2 (%)
Fe	8	2	3	1.83	0.151	7.902	156	$55^{(+3)}$	1112	1538	–	–	–	–
Co	9	2	3	1.88	0.662	7.881	152	$65^{(+2)}$	1177	1495	–	–	–	–
Ni	10	2	3	1.91	1.157	7.640	149	$69^{(+2)}$	1167	1455	–	–	–	–
Cu	11	1	2	1.9	1.236	7.726	145	$73^{(+2)}$	932	1084.6	–	–	–	–
Zn	12	2	2	1.65	−0.490	9.394	142	$74^{(+2)}$	209	419.53	–	–	–	–
Ga	3	3	3	1.81	0.301	5.999	136	$62^{(+3)}$	752	29.765	–	–	–	–
Ge	4	2	4	2.01	1.233	7.899	125	$53^{(+4)}$	1027	938.25	–	–	–	–
As	5	−3	5	2.01	0.804	9.789	114	$58^{(+3)}$	207	817	–	–	–	–
Se	6	−2	6	2.55	2.021	9.752	103	$50^{(+4)}$	134	220.8	–	–	–	–
Br	7	−1	5	2.96	3.364	11.814	94	$196^{(-1)}$	−140	−7.2	–	–	–	–
Kr	8	0	0	3	−2.41	14.000	88	–	−229.7*	−157.37	88	62	71	58
Rb	1	1	1	0.82	0.486	4.177	265	$152^{(+1)}$	62	39.3	–	–	–	–
Sr	2	2	2	0.95	0.052	5.685	219	$118^{(+2)}$	355	777	86	21	1	10
Y	3	3	3	1.22	0.307	6.217	212	$90^{(+3)}$	1227	1522	–	–	–	–
Zr	4	4	4	1.33	0.426	6.634	206	$72^{(+4)}$	1877	2854	–	–	–	–
Nb	5	3	5	1.6	0.917	6.759	198	$64^{(+5)}$	2117	2477	–	–	–	–
Mo	6	6	6	2.16	0.746	7.092	190	$59^{(+6)}$	1937	2622	–	–	–	–
Tc	7	4	7	2.1	0.550	7.280	183	$65^{(+4)}$	1967	2157	–	–	–	–
Ru	8	3	3	2.2	1.046	7.361	178	$68^{(+3)}$	1857	2333	2	3	8	7
Rh	9	3	3	2.28	1.143	7.459	173	$67^{(+3)}$	1582	2963	–	–	–	–
Pd	10	2	3	2.2	0.562	8.337	169	$86^{(+2)}$	1097	1554.8	–	–	–	–
Ag	11	1	1	1.93	1.304	7.576	165	$115^{(+1)}$	747	961.78	–	–	–	–
Cd	12	2	2	1.69	−0.330	8.994	161	$95^{(+2)}$	145	321.07	–	–	–	–
In	3	3	3	1.78	0.404	5.786	156	$80^{(+3)}$	663	156.60	–	–	–	–
Sn	4	2	4	1.96	1.112	7.344	145	$69^{(+4)}$	897	231.93	99	84	69	22
Sb	5	−3	5	2.05	1.047	8.608	133	$76^{(+3)}$	385	630.63	97	80	67	53
Te	6	−2	6	2.1	1.971	9.010	123	$97^{(+4)}$	255	449.51	95	70	70	78
I	7	−1	7	2.66	3.059	10.451	115	$220^{(-1)}$	−67	113.7	95	66	70	83
Xe	8	0	0	2.6	−1.76	12.130	108	–	−218*	−111.75	–	–	–	–
Cs	1	1	1	0.79	0.472	3.894	298	$167^{(+1)}$	46	28.5	72	60	53	23
Ba	2	2	2	0.89	0.145	5.212	253	$135^{(+2)}$	453	727	86	41	18	15
La	3	3	3	1.1	0.558	5.577	195	$103^{(+3)}$	1307	920	0	5	0	4
Ce	4	3	4	1.12	0.628	5.539	185	$101^{(+3)}$	1302	799	0	15	0	13
Pr	5	3	3	1.13	0.109	5.473	247	$99^{(+3)}$	1092	931	–	–	–	–
Nd	6	3	3	1.14	0.097	5.525	206	$98^{(+3)}$	967	1016	–	–	–	–
Pm	7	3	3	–	0.129	5.582	205	$97^{(+3)}$	847	1042	–	–	–	–
Sm	8	2	3	1.17	0.162	5.644	238	$96^{(+3)}$	511	1072	–	–	–	–
Eu	9	2	3	–	0.864	5.670	231	$95^{(+3)}$	409	822	–	–	–	–
Gd	10	3	3	1.2	0.137	6.150	233	$94^{(+3)}$	1177	1313	–	–	–	–
Tb	11	3	3	–	0.131	5.864	225	$92^{(+3)}$	1137	1359	–	–	–	–
Dy	12	3	3	1.22	0.352	5.939	228	$91^{(+3)}$	812	1412	–	–	–	–

* extrapolated from ref.[26].

** ionic radius corresponding to the most probable oxidation state indicated by superscript.

PCA ⟶ examine the correlations between the physico-chemical properties of the elements (Fe to Dy) as active variables and their release behaviours (RF) as additional variables.

- Thermal properties (melting/boiling points) influence volatility.
- Electronic properties (ionisation energy, electronegativity) affect chemical interactions.
- Geometric properties (atomic/ionic radii) determine diffusion.

J. Guillot *et al.* Nuclear Instruments and Methods in Physics Research B 559 (2025) 165600

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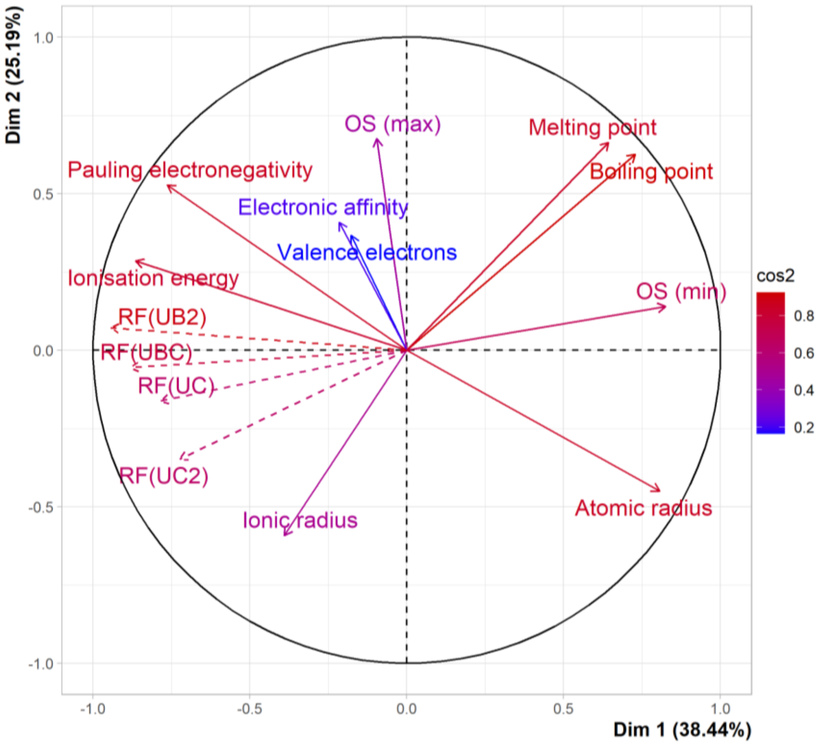

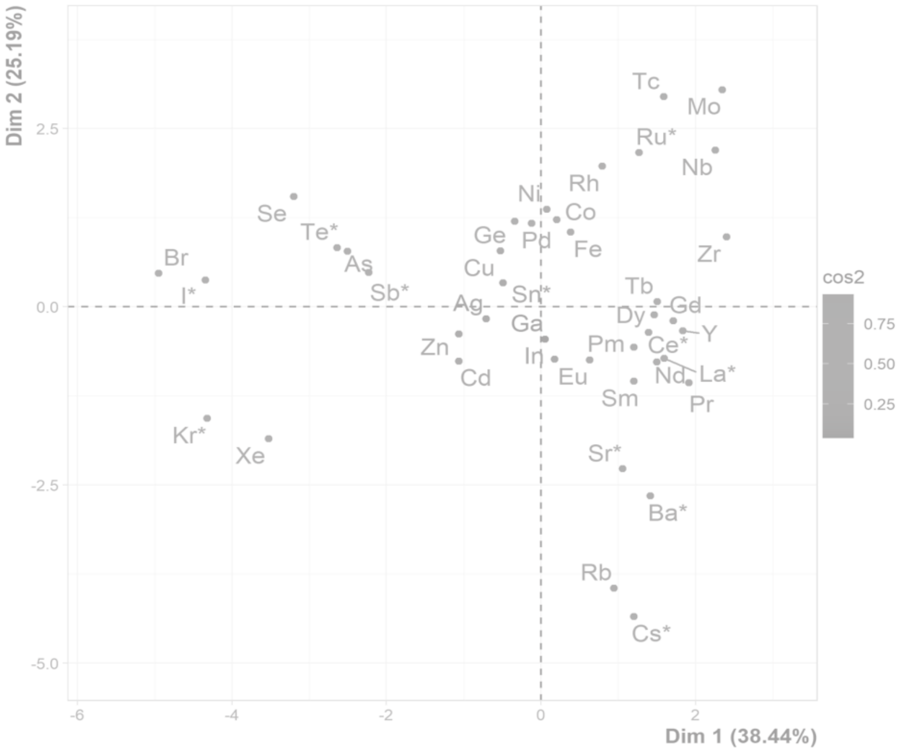

The **Released Fraction (RF) variables** are defined along **dimension 1**. The **RF variables** demonstrate a **positive correlation** with electronic properties, such as **“ionisation energy”** and **“electronegativity”**, and an **inverse correlation** with properties, such as **“atomic radius”**, **“OS (min)”**, and characteristic **temperatures** (melting/boiling).

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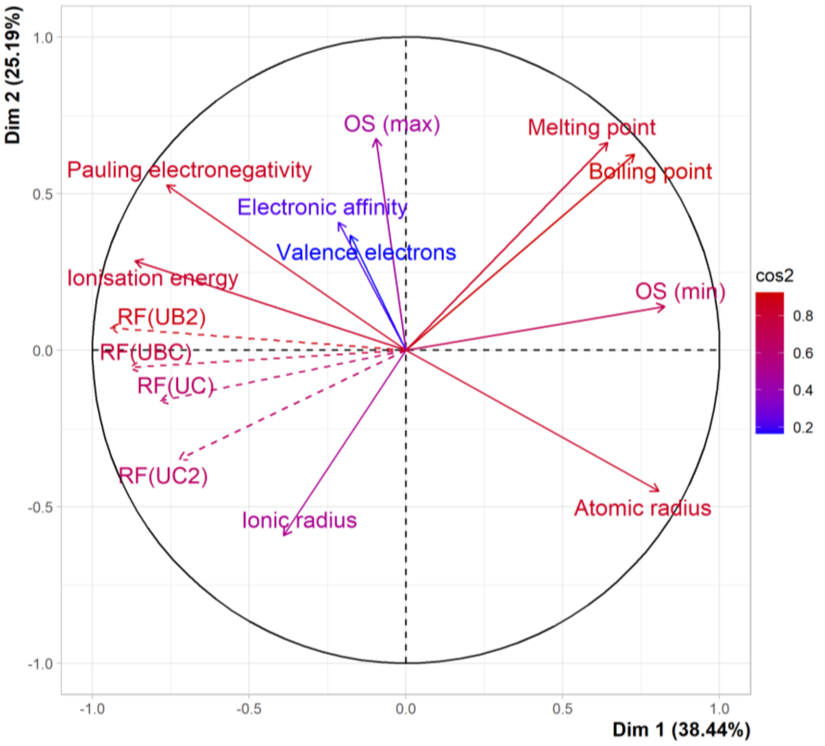

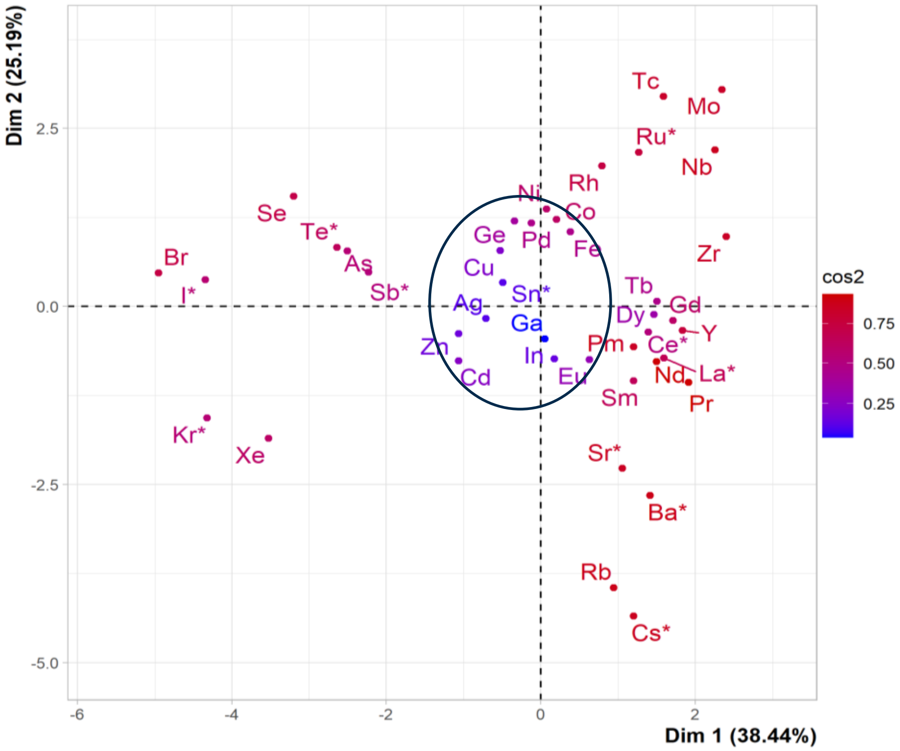

The physico-chemical properties employed in the PCA analysis are inadequate in providing a comprehensive description of the release behaviour of Sn ($\cos^2 < 0.5$).
It is imperative to identify and consider further factors that may contribute to its observed behaviour.

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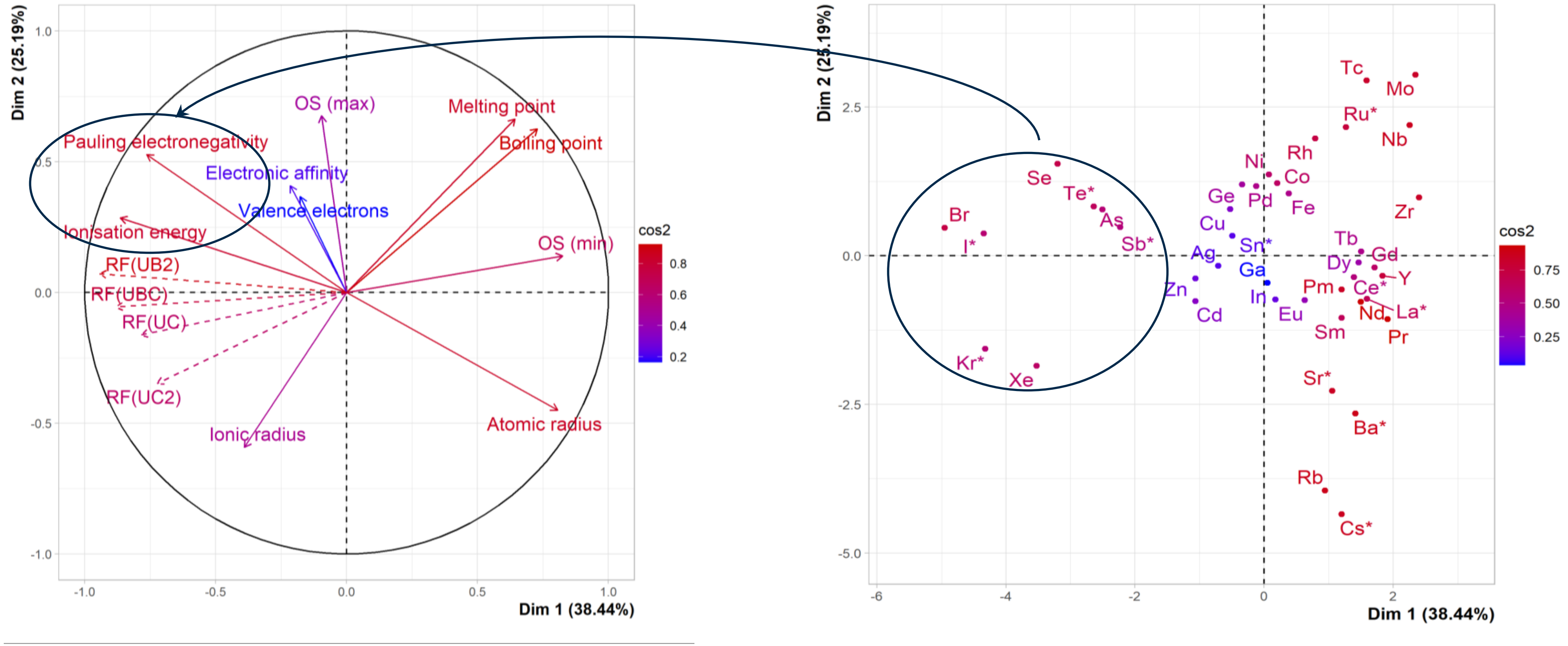

It has been observed that the elements I, Kr, Te, and Sb are readily released from targets (UC2, UC, UBC, UB2). These elements have been shown to be correlated with high electronegativity and ionisation energy values.

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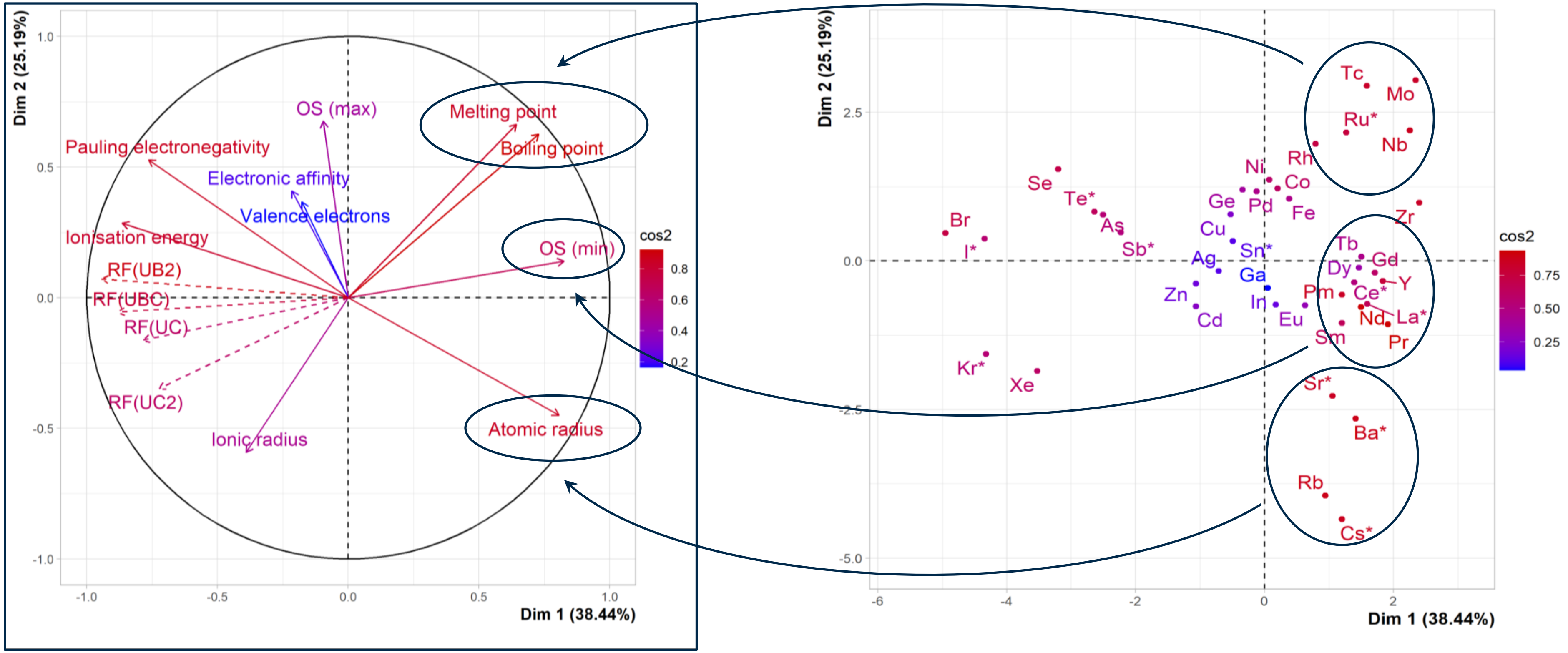

- Ru, Mo, Nb, Tc: These elements are associated with high thermal stability, indicating their refractory nature and low volatility.
- Ln, e.g. La, Ce, Nd...: Their association with positive oxidation states (OS) shows that their release is influenced by their ability to release electrons, making them more likely to bind to the crystalline matrix and thus be trapped.
- Cs, Rb, Ba, Sr: These elements, correlated with the atomic radius, have their mobility in crystals affected by their steric hindrance, which influences their release behaviour.

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Conclusion: There are no universal targets, but one target for each element.

In this study, four uranium compounds (UC_2, UC, UBC and UB_2) were synthesised to investigate the release behaviour of 11 fission-derived elements.

- Analysis of the experimental results showed that crystal packing fraction and atomic size influence the release of the elements.
- Krypton, a noble gas, shows a linear relationship between its release fraction and the crystal packing fraction.

In contrast, the release of the other elements is influenced in a complex way by the chemical environment and the atomic size. PCA revealed that chemical properties control the mobility and reactivity of elements. For example:

- For alkali and alkaline earth metals, atomic size limits their mobility and favours diffusion in matrices with low stacking fractions.
- Lanthanides form chemical bonds more easily than the preceding elements, limiting their escape from crystals.
- Refractory elements such as zirconium, niobium and molybdenum are characterised by very high melting and boiling points, which explains their stability and complex extraction at typical temperatures of 2000°C.

Finally, **this study demonstrates that the behaviour of experimentally inaccessible elements can be inferred from that of observed elements**, allowing extrapolations useful for optimising fission targets in nuclear applications.

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Thank you for your attention

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