Comparison of bulk and interfacial diffusion of $^{8}Li^{+}$ in solid-state battery materials with β-NMR spectroscopy

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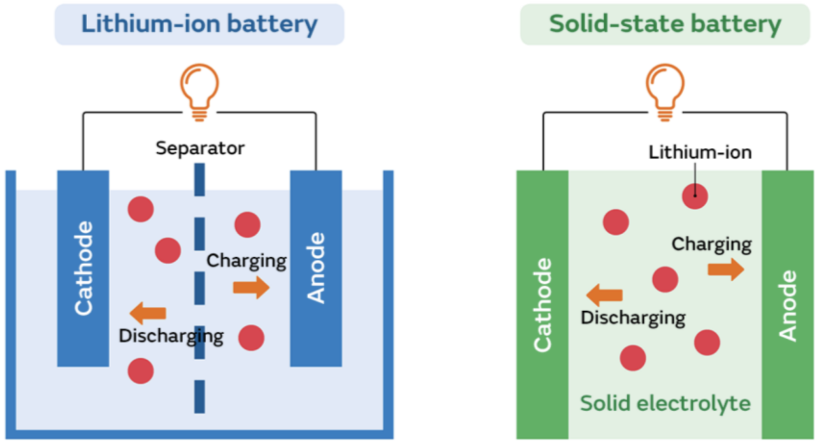
Motivation



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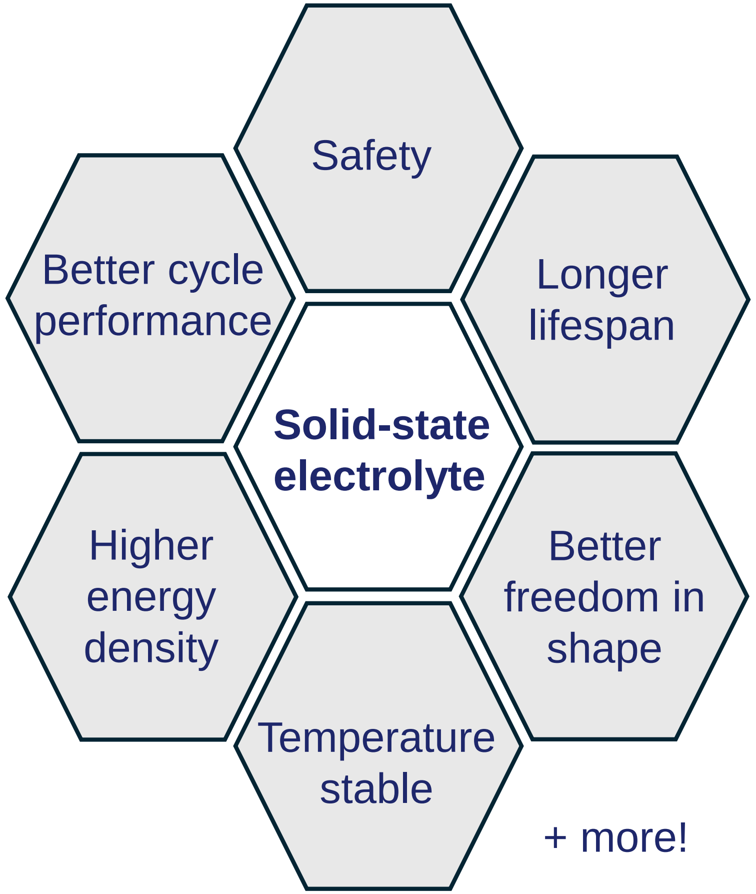
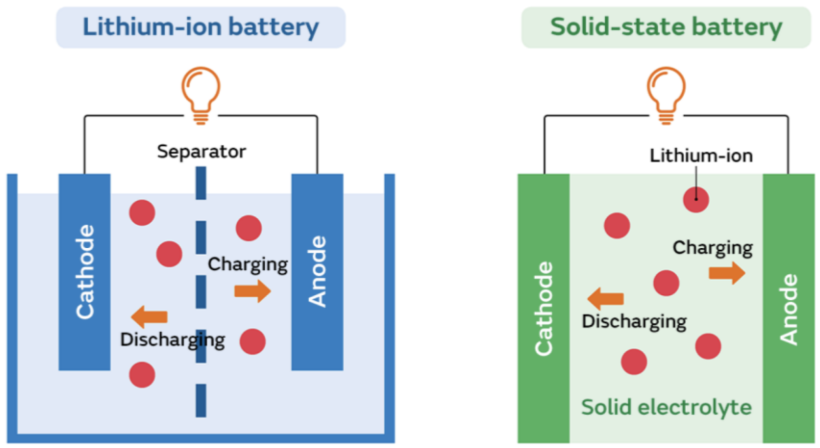


Motivation

- **Interfaces** in SSBs are often the expected **bottlenecks for ion diffusion**
- How to obtain **good rate capability?** → **a major challenge in SSB development**



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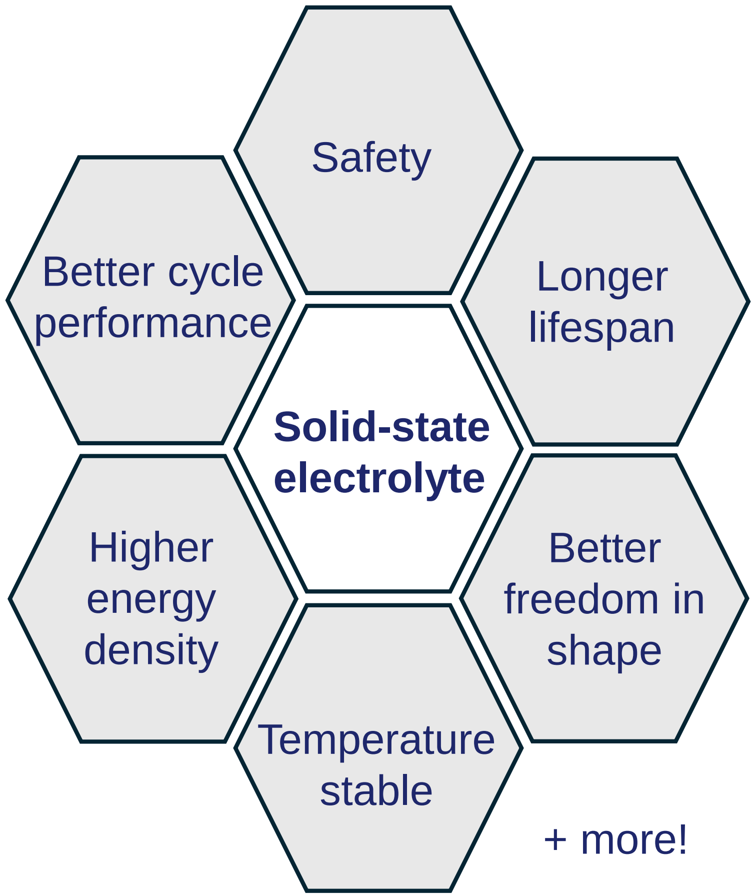

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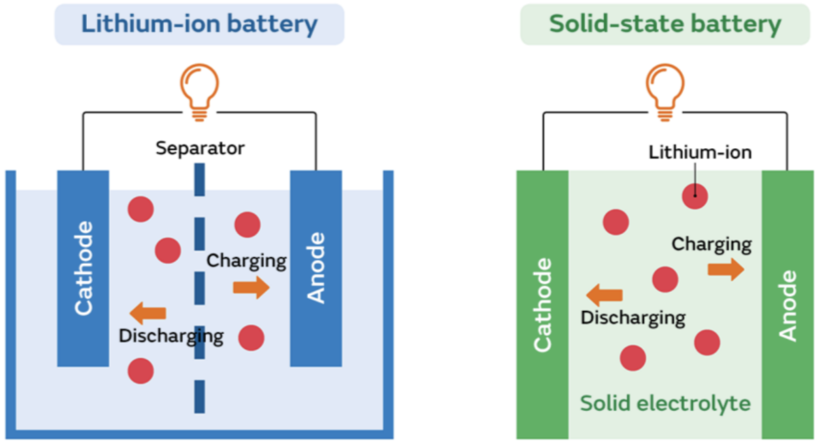

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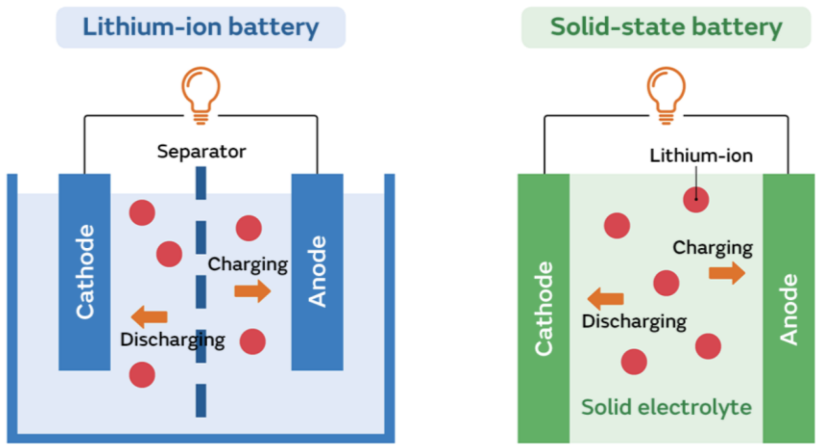

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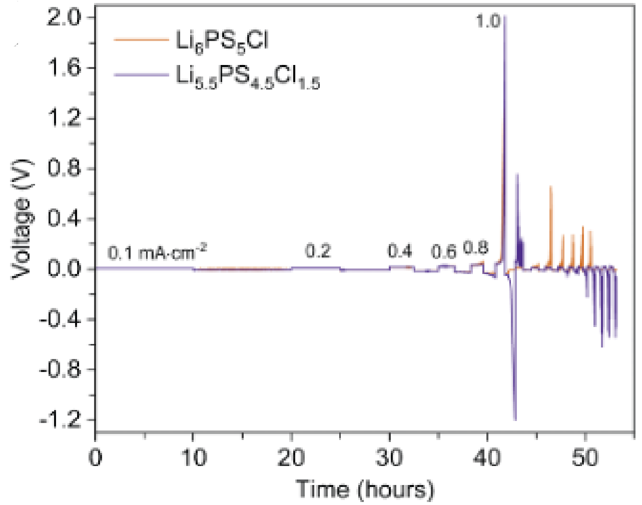

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<u>Commercially relevant electrolytes:</u>

Li_7PS_6 (bulk conductivity ~0.1 mS cm^{-1})

Li_6PS_5Cl (bulk conductivity 1-3 mS cm^{-1})

$Li_{5.5}PS_{4.5}Cl_{1.5}$ (bulk conductivity 6-9 mS cm^{-1})

Decreasing S content

**Liquid-state electrolytes (1-10 mS cm^{-1})*

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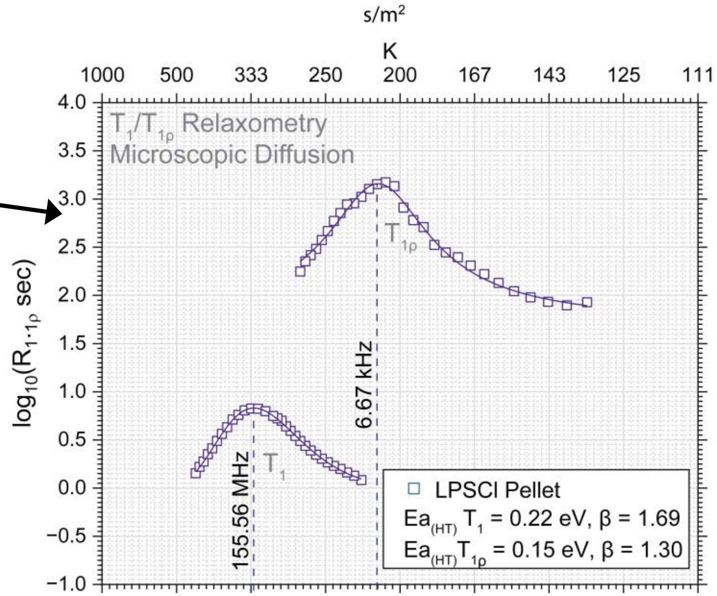
Relaxometry and β-NMR

- Our measurements will be based on established conventional methods – **but with spatial resolution!**
- **Conventional → NMR relaxometry:** Nuclear spin parameter $\boldsymbol{T_1}$ is related to jump rate τ^{-1} and activation energy E_a between lattice sites → **way to correlate ion diffusion**
- Extracted by fit of $\boldsymbol{T_1}$ as a function of **temperature**
- Bloembergen, Purcell, and Pound (BPP) model

Bulk measurement → interfacial layer consists ~0.025% of the NMR signal



G. Rees, B. Payne, University of Oxford

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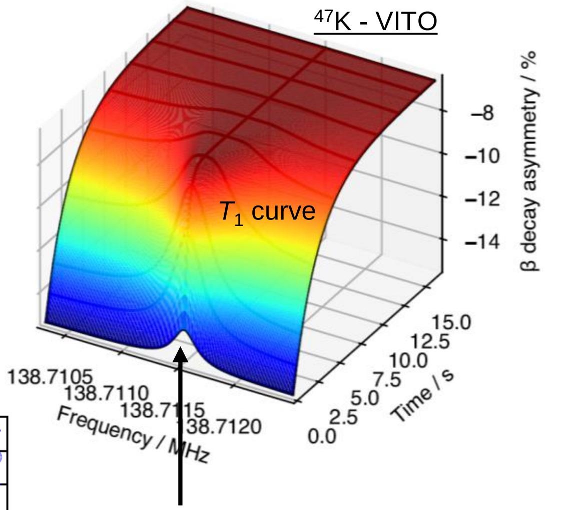
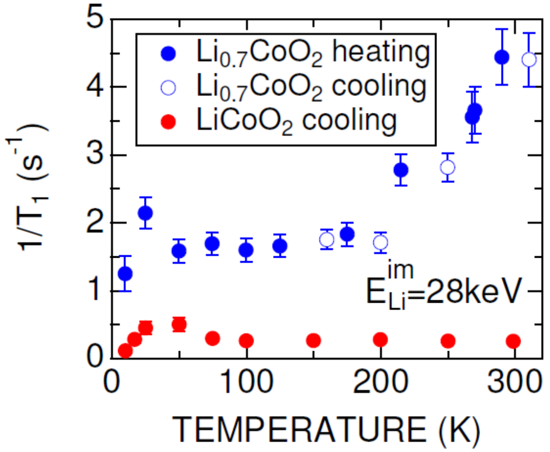
- **<u>Our proposal → β-NMR relaxometry</u>:** $\boldsymbol{T_1}$ through measurement of the changes in **β-particle asymmetry over time** of implanted ion → **depth selectivity!**
- <u>^{8}Li is a good candidate for β-NMR and already carried out in similar materials:</u>
  (1) Produced with good yields at ISOLDE
  (2) Sufficiently long $t_{1/2}$ = 840 ms and measurable T_1 values ~ 100-200 ms
  (3) Can be polarised with VITO dye laser (^{8}Li previously polarised at COLLAPS)
  (4) 100% β-decay to ^{8}Be, with good β-asymmetry, 5-10%
  (5) Minimal quadrupolar effects in these materials
  (6) Larmor frequency of ^{8}Li is well-known



M. Jankowski et al, arXiv:2410.00186, *(2024)*



J Sugiyama et al, J Phys.: Conf. Series 551, 012009 (2014) ^{8}Li β-NMR at TRIUMF

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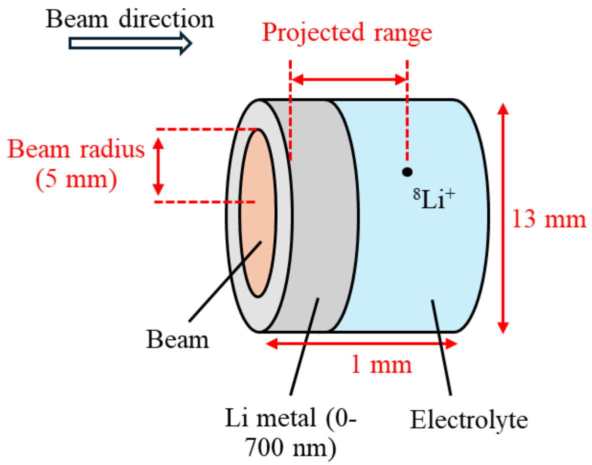
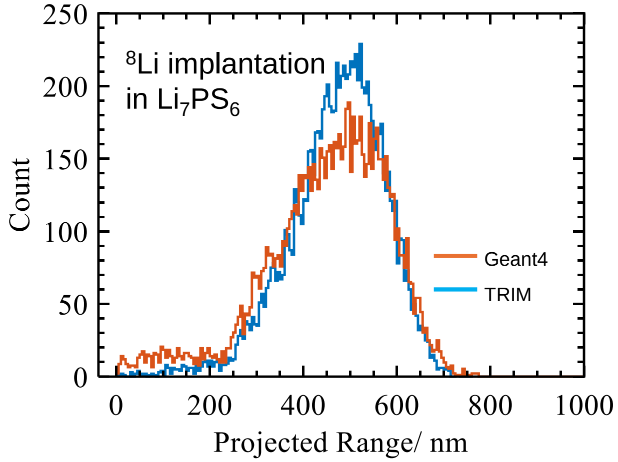
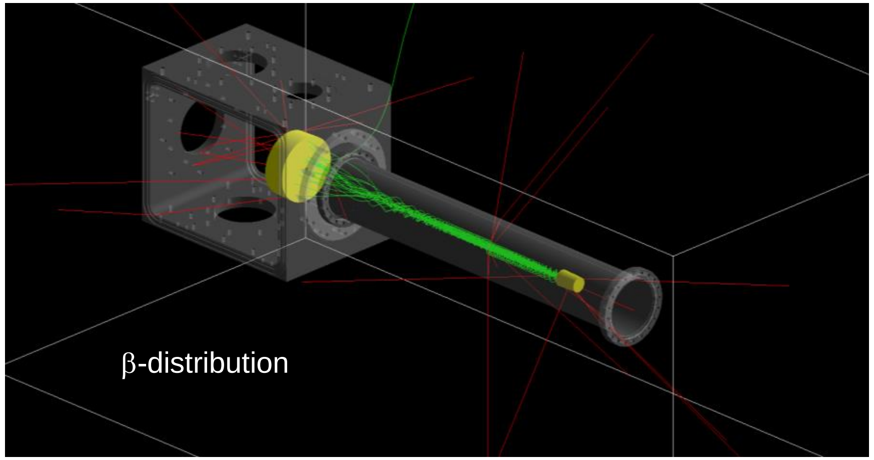
SSB project progress



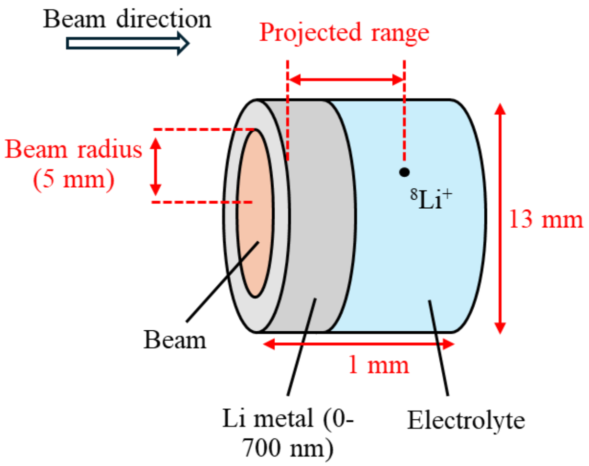
- Temperatures: -10, 50, 100, 150, 200°C (maxima expected ~100°C)
- Two well-separated β-resonances expected (electrolyte and anode)
- We expect to see changes in activation energy for different layers (the extent to which the ion samples the limited diffusion region will vary) + changes in intensity between β-resonances



Electrolyte	Li depth/ nm	Mean projected range/ nm		SEI depth probed/ nm
		Entire sample	Electrolyte	
Li_7PS_6, Li_6PS_5Cl, $Li_{5.5}PS_{4.5}Cl_{1.5}$	0	322±2		322±2
	250	475±2	482±2	232±2
	500	633±1	650±1	150±1
	700	754±2	792±1	92±1



SSB project progress



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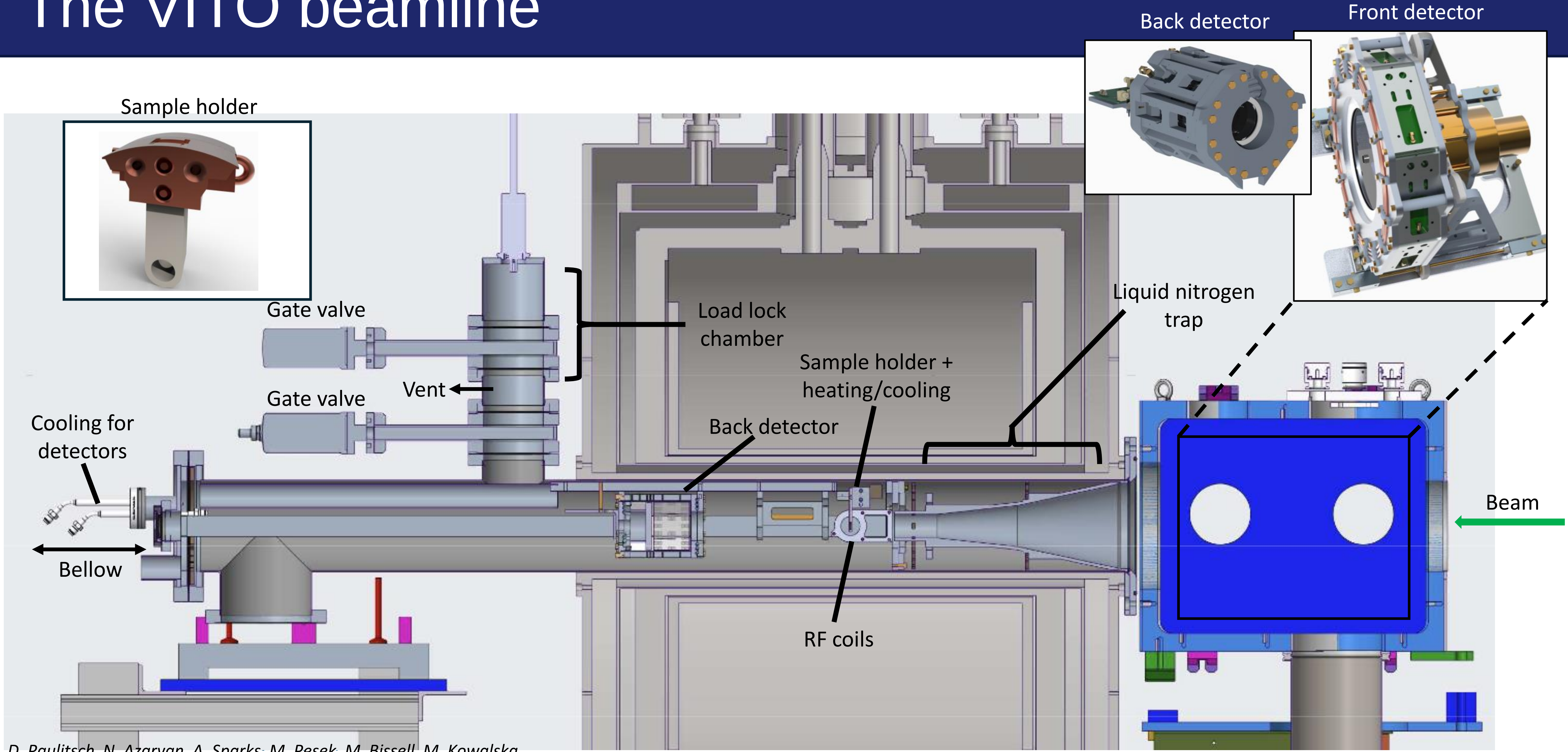
- **The approval of the Nov 2023 LOI played a key role in securing the acceptance of the KT fund**
- **Designs already in place and manufacturing started with support from other departments and simulations**
- **Ready before next INTC call (May 2025)**
- **Experiment time dedicated to two other VITO projects this year, then ready for full SSB measurements in place of LOI**

The VITO beamline



D. Paulitsch, N. Azaryan, A. Sparks, M. Pesek, M. Bissell, M. Kowalska

Summary of shifts

Task	Time required
Establishing and optimising ^{8}Li polarisation	4h, 0.5 shifts
Locating and optimising ^{8}Li signal at the beginning	4h, 0.5 shifts
Sample changes (sample move to load-lock, sample exchange in the loadlock in glove box, loadlock connection back to beamline)	2h x 12 samples, 3 shifts
Temperature stabilisation for each sample	0.5h x 12 samples, ¾ shifts
Measuring β-NMR resonances and T_1 (at stable temperature): 3 samples with 4 different thicknesses of front layers x data at 5 different temperatures	3h x 3 samples x 4 layer depths x 5 temp points = 22.5 shifts

Total: 27.25 online shifts split into 2 runs