

Powder diffraction data analysis: an overview

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Powder Diffractometers

high-resolution
engineering
high-pressure
high-intensity

MLZ:	SPODI , STRESS-SPEC , POWTEX, SAPHIR , ERWIN, FIREPOD
ILL:	D1B, D2B , D4, D16, D20, SALSA , XTREME-D
ANSTO:	Echidna , Wombat, KOWARI
PSI:	HRPT , DMC, POLDI
ISIS:	GEM, HRPD , NIMROD, POLARIS, WISH, PEARL , ENGIN-X
ORNL:	WAND ² , POWDER , POWGEN , NOMAD, DEMAND, SNAP , VULCAN , HIDRA
J-PARC:	<u>SuperHRPD</u> , SPICA, PLANET , NOVA, <u>iMATERIA</u> , TAKUMI
ESS:	DREAM , BEER , HEIMDAL

Courtesy: Dr. M. Hölzel (FRM II)

Powder diffraction: a short history

1912: Max von Laue, Walther Friedrich, and Paul Knipping discovered X-ray diffraction using single crystals in Munich

1912: Complex mathematical model of Max von Laue did not fully explain all observed interference spots. Lawrence Bragg – (22 years old student at Cambridge University) simplified the problem by modeling the crystal as a set of parallel, reflective atomic planes and presented the simple condition for constructive interference at Cambridge Philosophical Society.

1916-1917: Peter Debye and Paul Scherrer in Göttingen (Germany), along with Albert W. Hull independently in Schenectady (USA), invented the powder technique during World War I

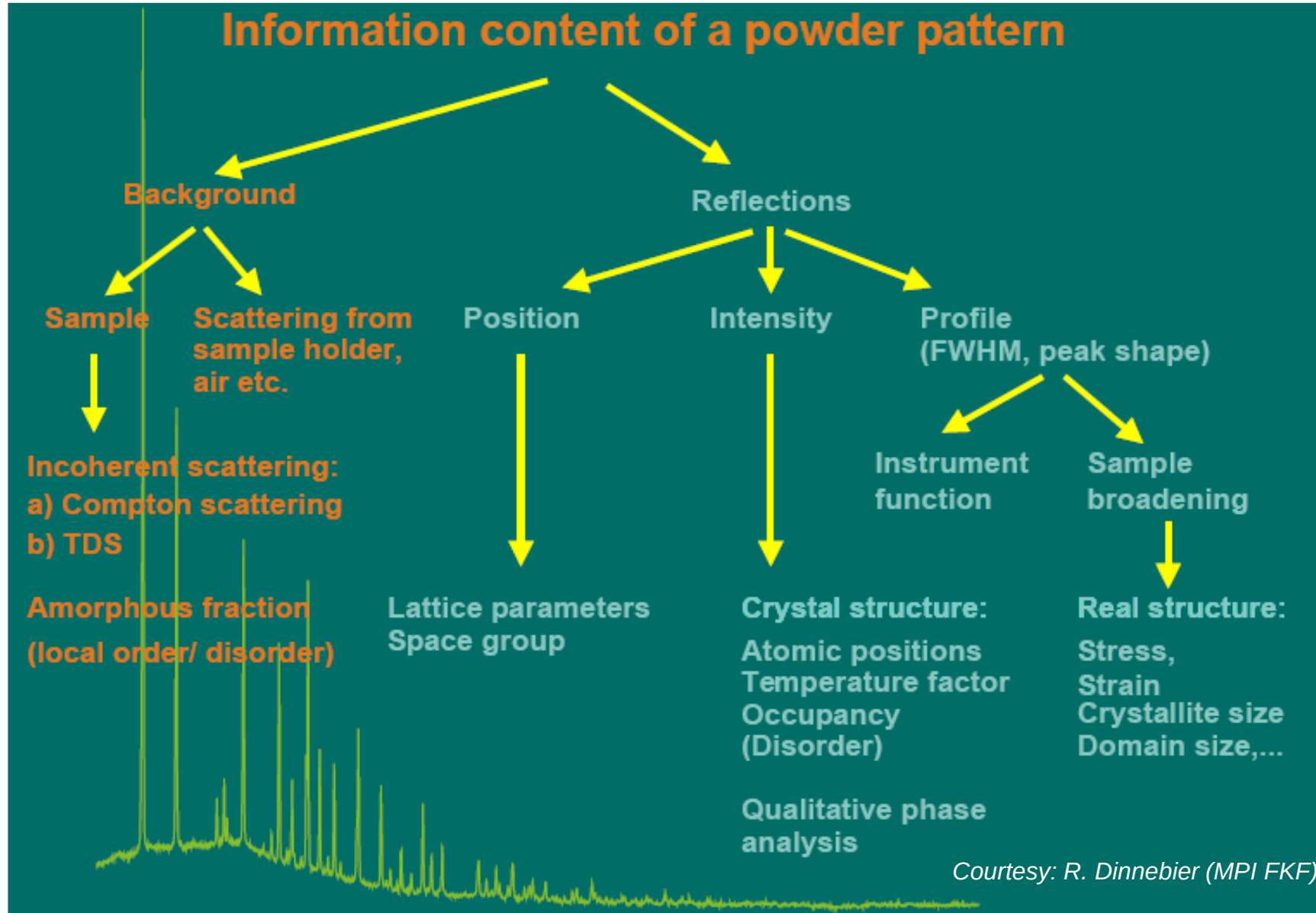
1919: Albert W. Hull proposed X-ray powder patterns as unique "fingerprints" for material identification

1937: invention of Guinier camera (*André Guinier*)

1944: first neutron diffraction patterns of calcite single crystals were recorded at Clinton pile and Chicago pile in Oak Ridge (USA)

1949: patent of the first X-ray diffractometer (*William Parrish*) with an appropriate electronic detector

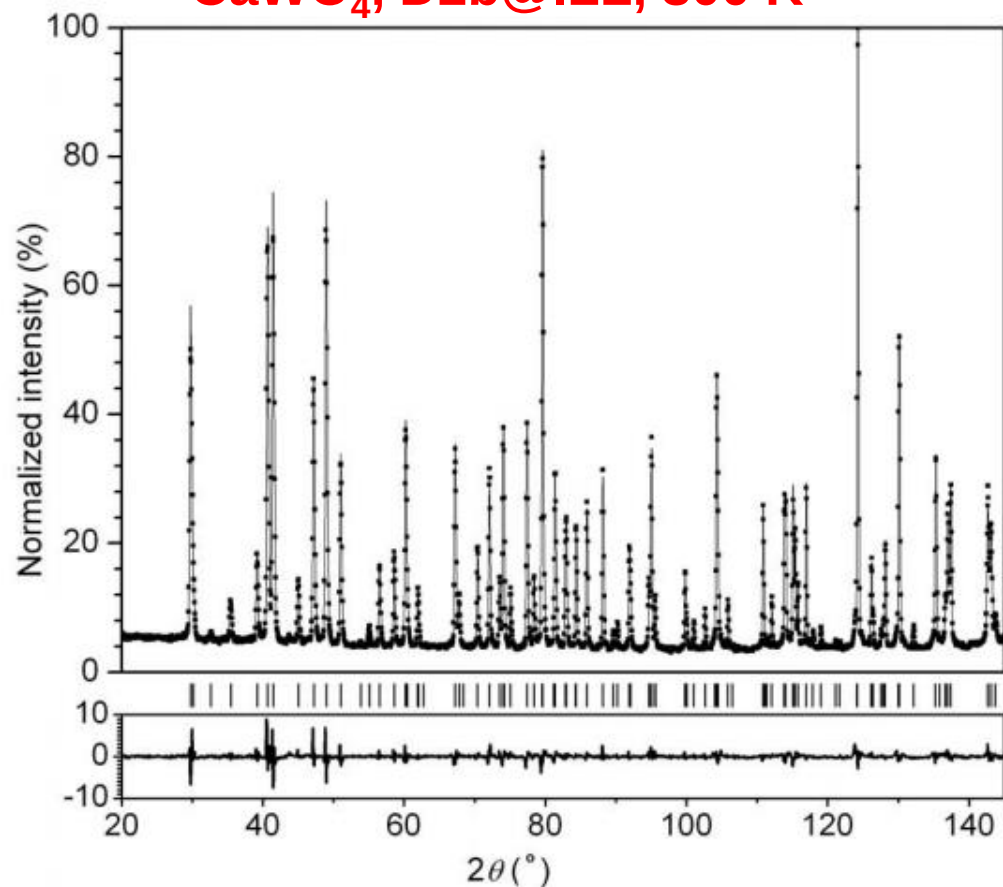
Etter, M. and Dinnebier, R.E. (2014), A Century of Powder Diffraction: a Brief History. Z. anorg. allg. Chem., 640: 3015-3028.



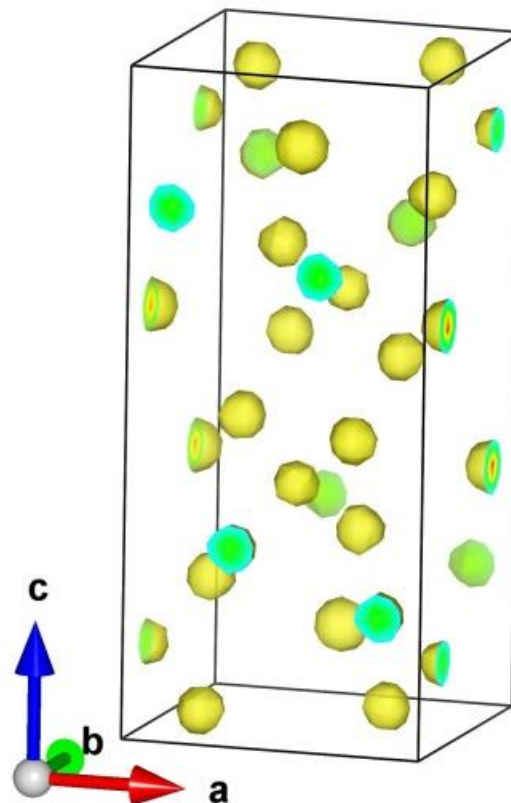
Courtesy: R. Dinnebier (MPI FKF)

Example of full-profile Rietveld method

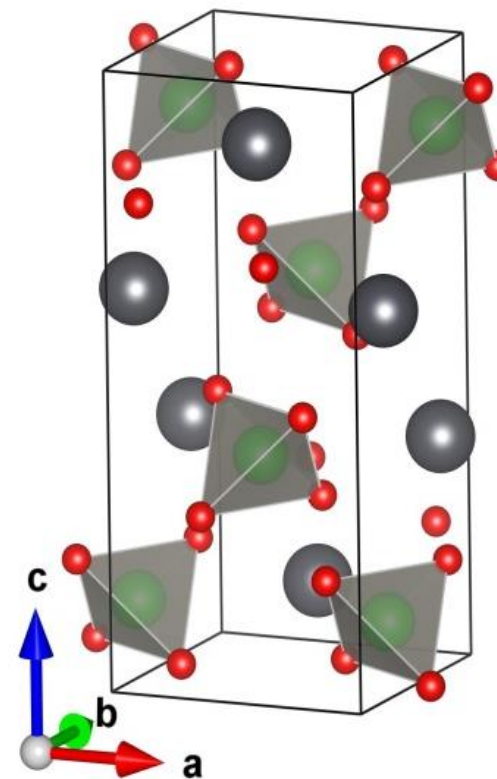
CaWO₄, D2b@ILL, 300 K



**Nuclear scattering
density (isoline = 10 fm)**



Model



Hugo Rietveld

- Dutch crystallographer
- In the late 1960's he wrote computer code to **fit the entire profile** of neutron powder diffraction patterns
- This later became known as the Rietveld method



Rietveld, H. M. "A profile refinement method for nuclear and magnetic structures". *Journal of Applied Crystallography*. International Union of Crystallography (IUCr). **2** (2): 65–71 (1969).

Most popular Rietveld codes

GSAS / EXPGUI: Larson & Von Dreele, Los Alamos. X-ray, neutron and TOF data. Long the standard. **GSAS-II:** The Python successor to GSAS, with a modern GUI, single-crystal support, and PDF and SAXS tools.

FullProf Suite: *Rodríguez-Carvajal. Strong for magnetic structures, with WinPLOTR as the GUI.*

JANA2006/JANA2020: *Petříček et al. Handles modulated and incommensurate structures and composites.*

TOPAS / TOPAS-Academic (Bruker): *Coelho. Uses a flexible macro and scripting language, with fundamental parameters, rigid bodies, and simulated annealing.*

MAUD: Lutterotti. Combines Rietveld with texture, stress and microstructure analysis, and also handles thin films.

RIETAN-2000 / RIETAN-FP / VESTA: *Izumi. Popular in Japan and widely used for neutron and synchrotron data.*

BGMN / Profex: *Bergmann, with the open-source Profex GUI by Doebelin. Fundamental-parameters approach, good for quantitative phase analysis.*

Mag2Pol: *Qureshi. Free, optimised for magnetism and polarised data, GUI*

WinCSD: *Akselrud/Grin Free, chemical crystallography and modulated structures*

Rietica (LHPM): *Hunter. Free, with a Windows GUI.*

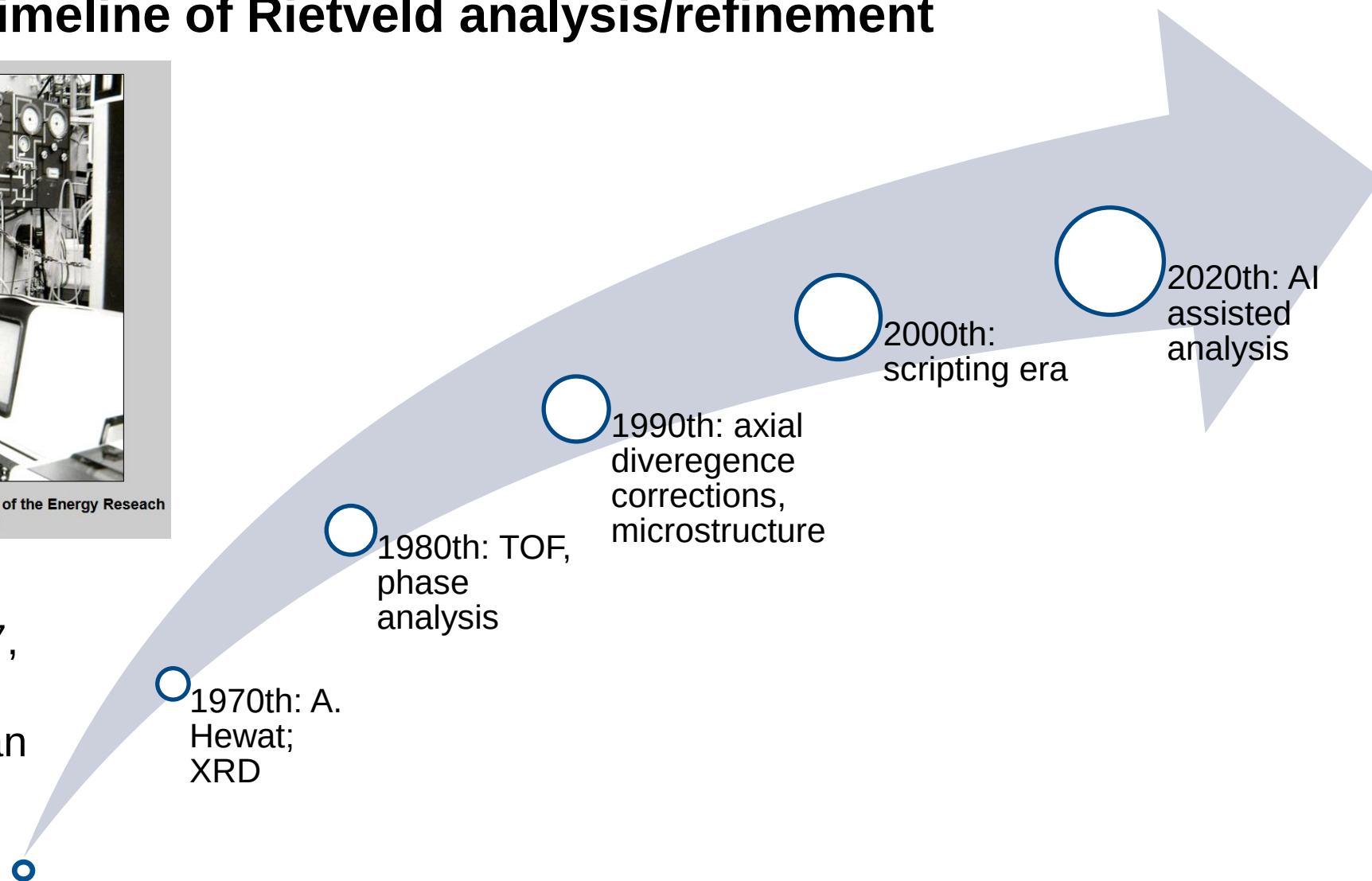
DBWS / DBWSTOOL: *Young, Wiles & Sakthivel. A classic Fortran code.*

Timeline of Rietveld analysis/refinement

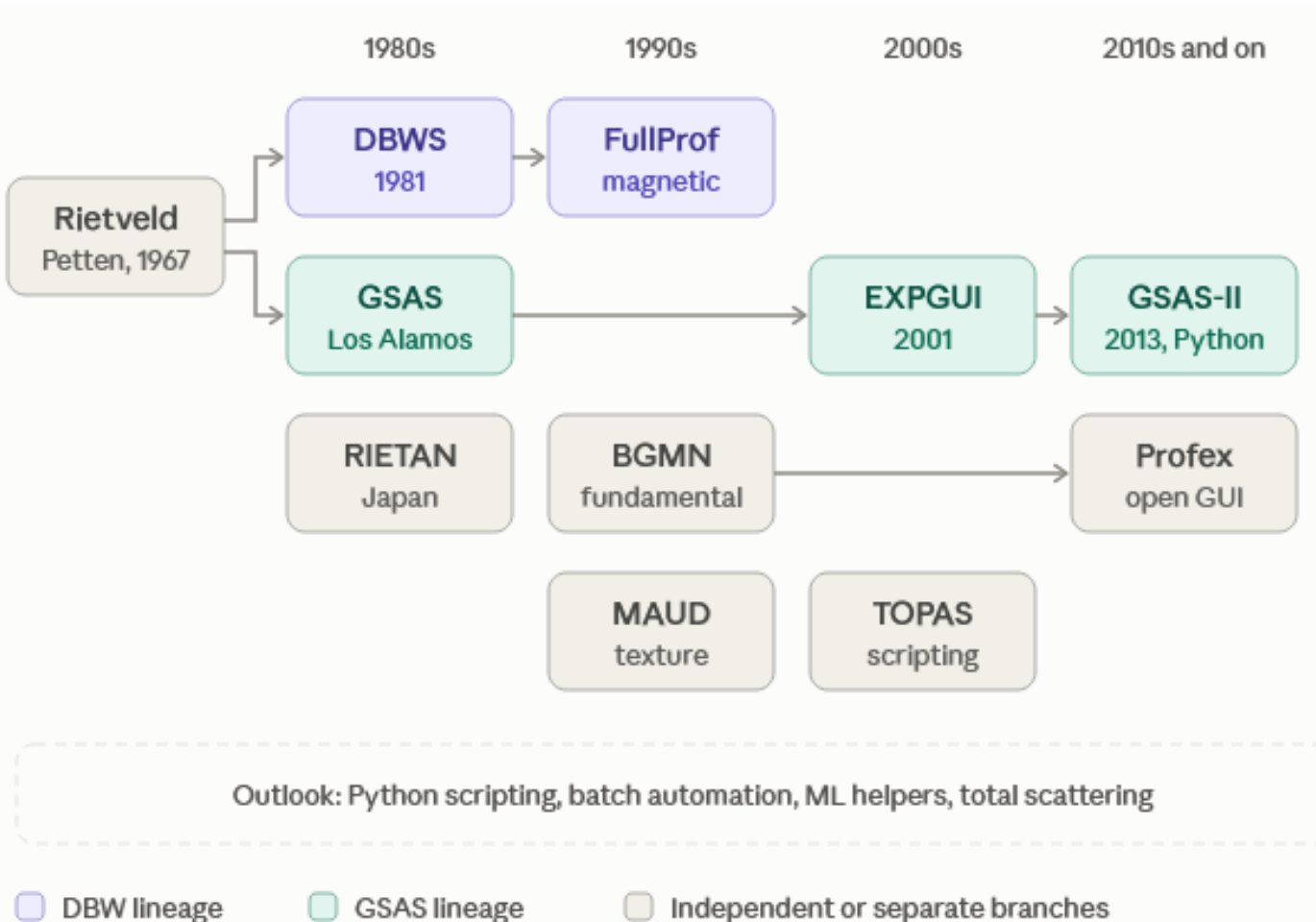


Dr. Rietveld at the neutron powder diffractometer at the High Flux Reactor of the Energy Research Foundation ECN in Petten, The Netherlands. (1987)

Created the first computer program between 1964-1967, released a complete ALGOL version in 1969, and a Fortran version in 1972.



Versatility of Rietveld software



Each Rietveld package is an eco system by its own

- Combination of techniques
- Real samples
- Magnetic structures
- Incomensurate structures
- Structure Solution
- Anharmonic refinements
- Maximum entropy filtering

Summary

Mature method, stable core

**A few lineages
dominate**

**Profile modelling is the main
technical legacy**

Two main use communities

**Spread of data
types**

**Free vs. commercial
split**

Outlook

Python and scripting

Automation and high throughput

Machine learning assistance

Integration with other techniques

Better reproducibility

Beyond ideal crystals

Pressure on user-friendliness

Thank you
for listening