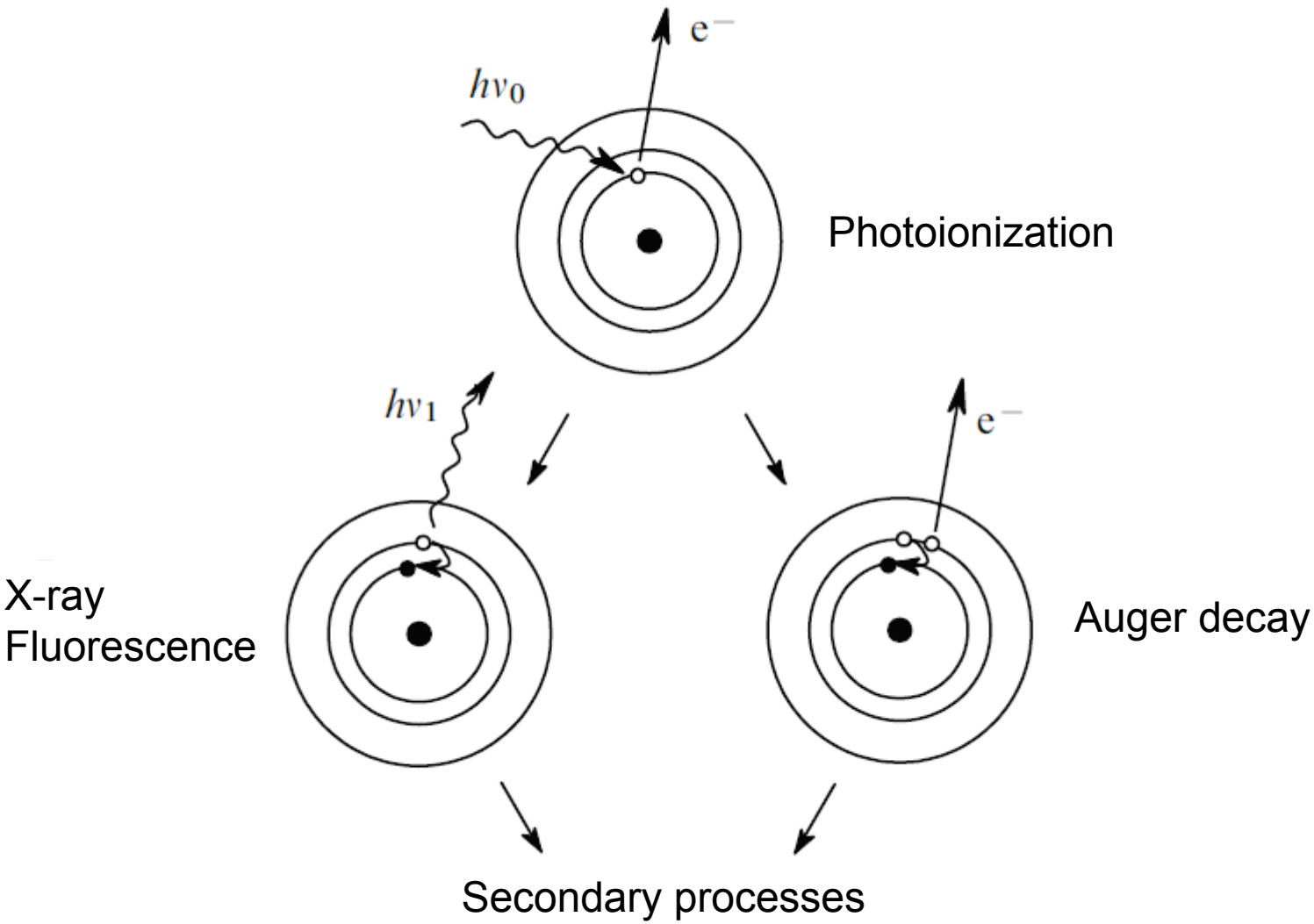
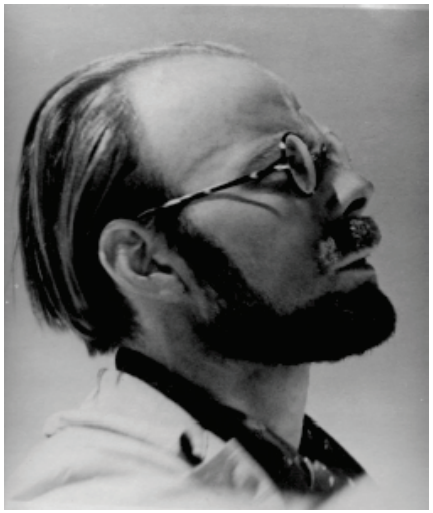
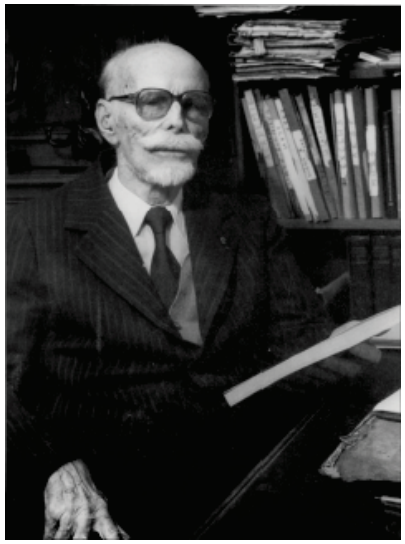
Lecture 7

Notes on
X-ray fluorescence spectroscopy

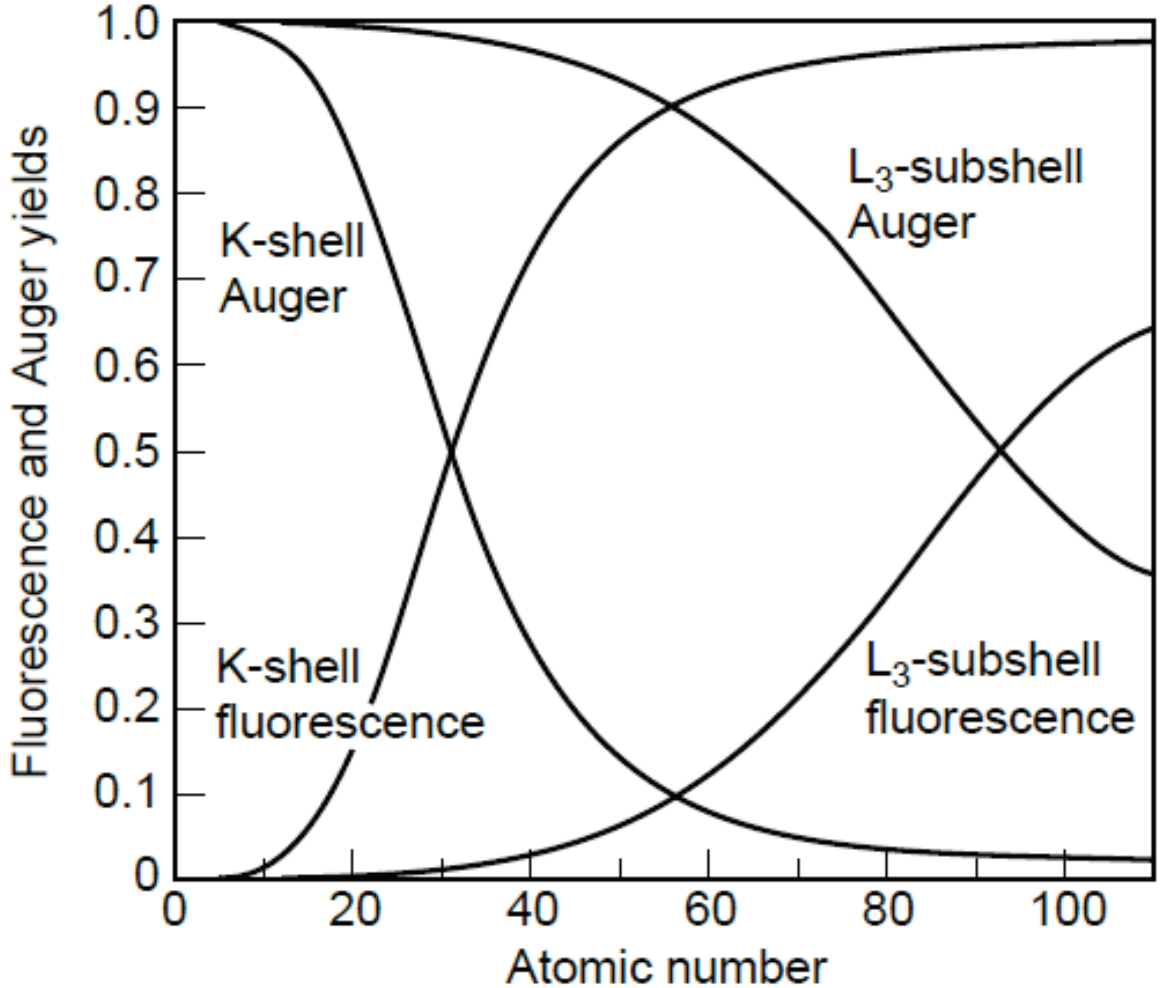

e⁻
$h\nu_0$
Photoionization
$h\nu_1$
e⁻
X-ray
Fluorescence
Auger decay
Secondary processes

Relative contribution of fluorescence and Auger emission in the decay of a vacancy





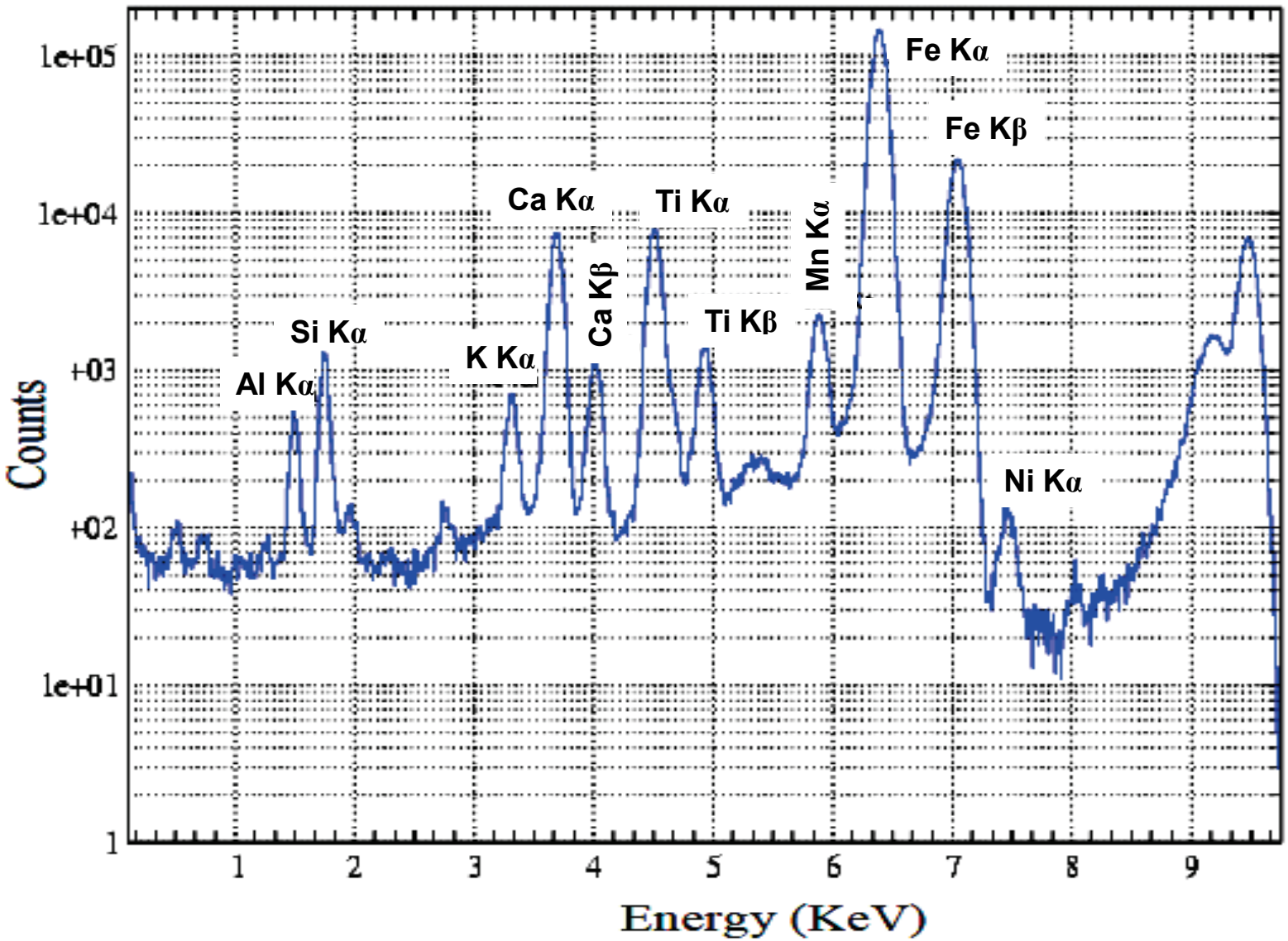
Pierre Victor Auger
1899-1993



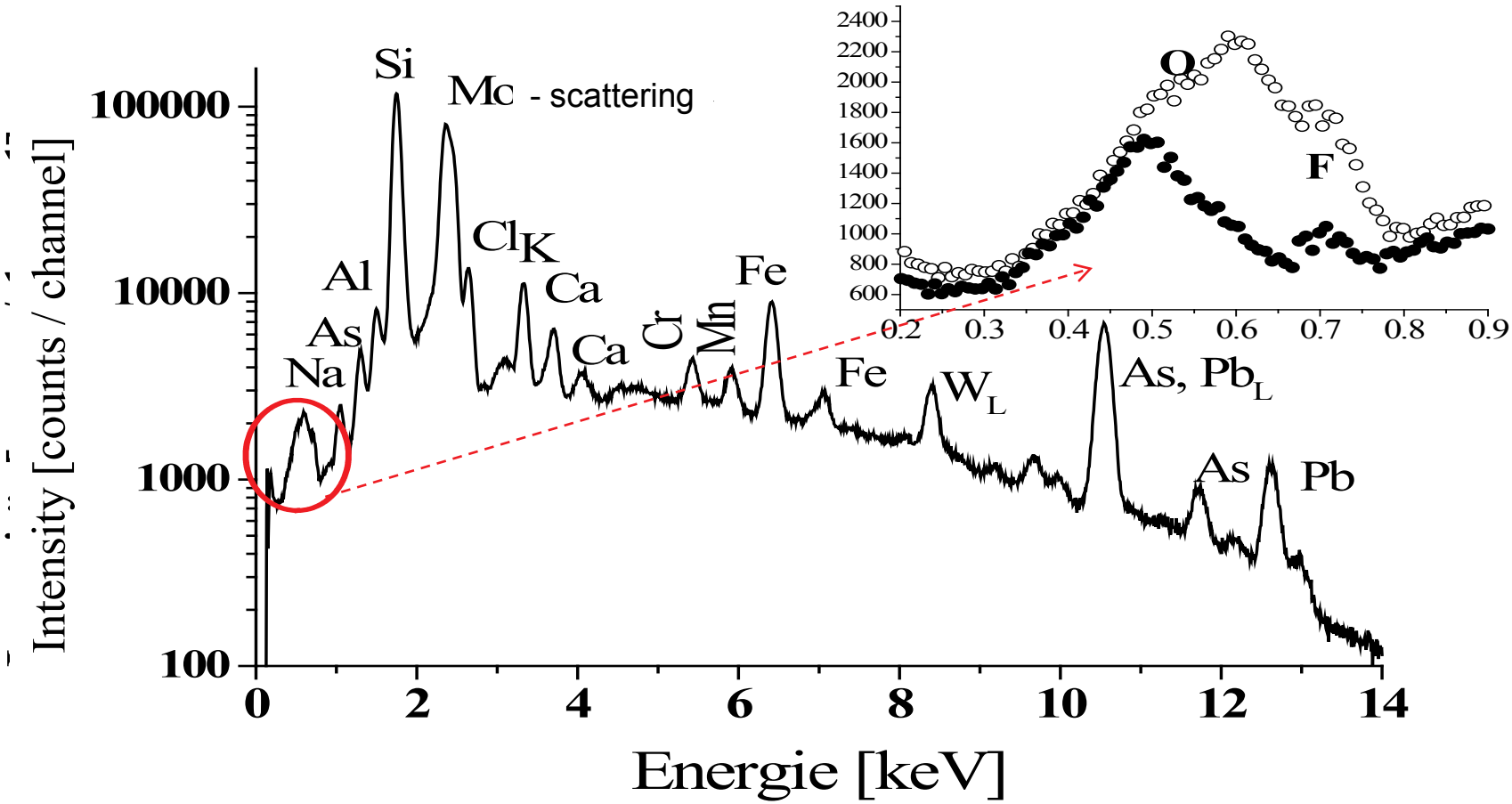
(Courtesy of M. Krause, Oak Ridge)

Fluorecsence spectrum of basalt

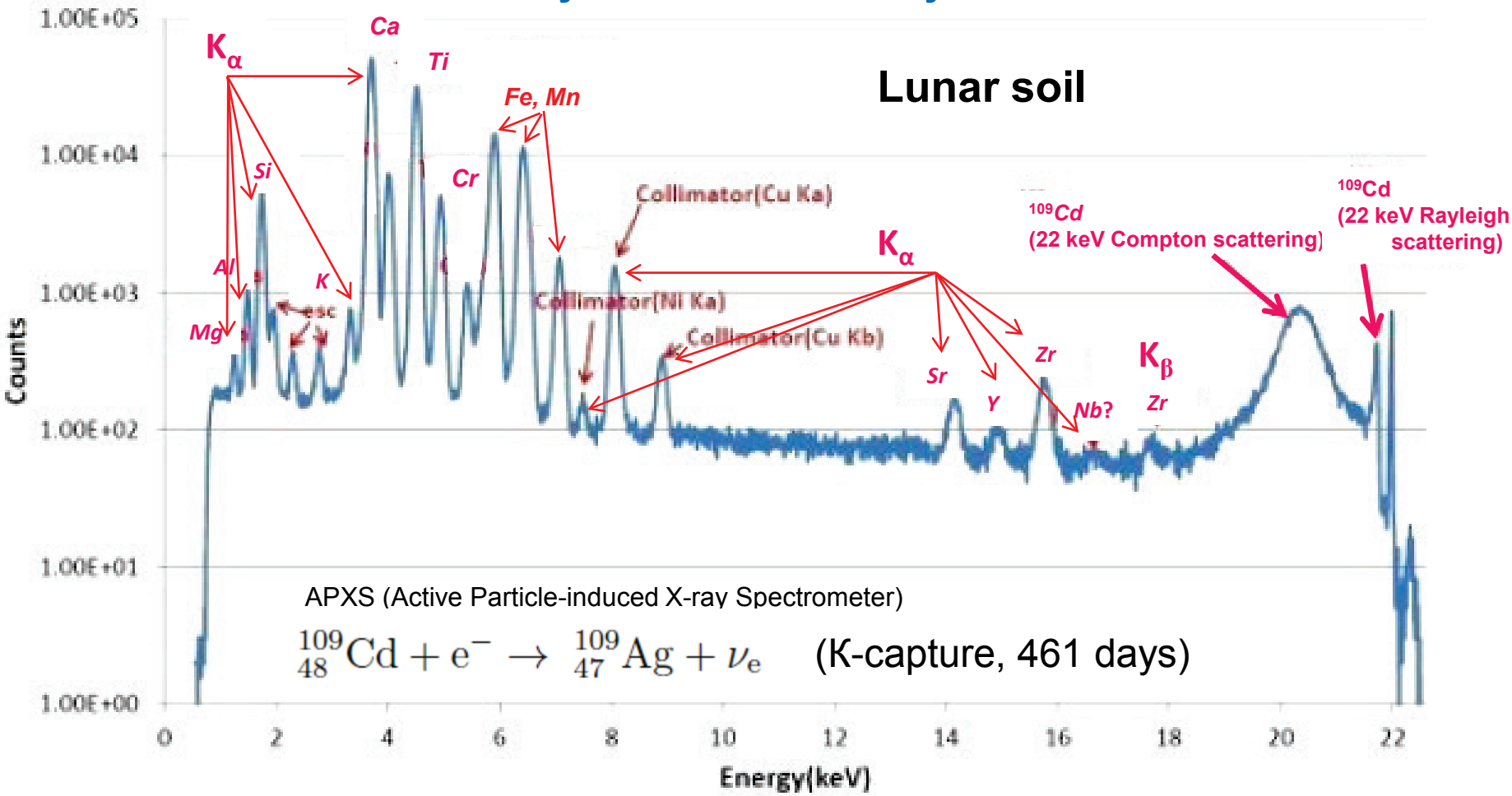
Incident photon energy 9.5 кэВ



Fluorecence spectrum of an enamel

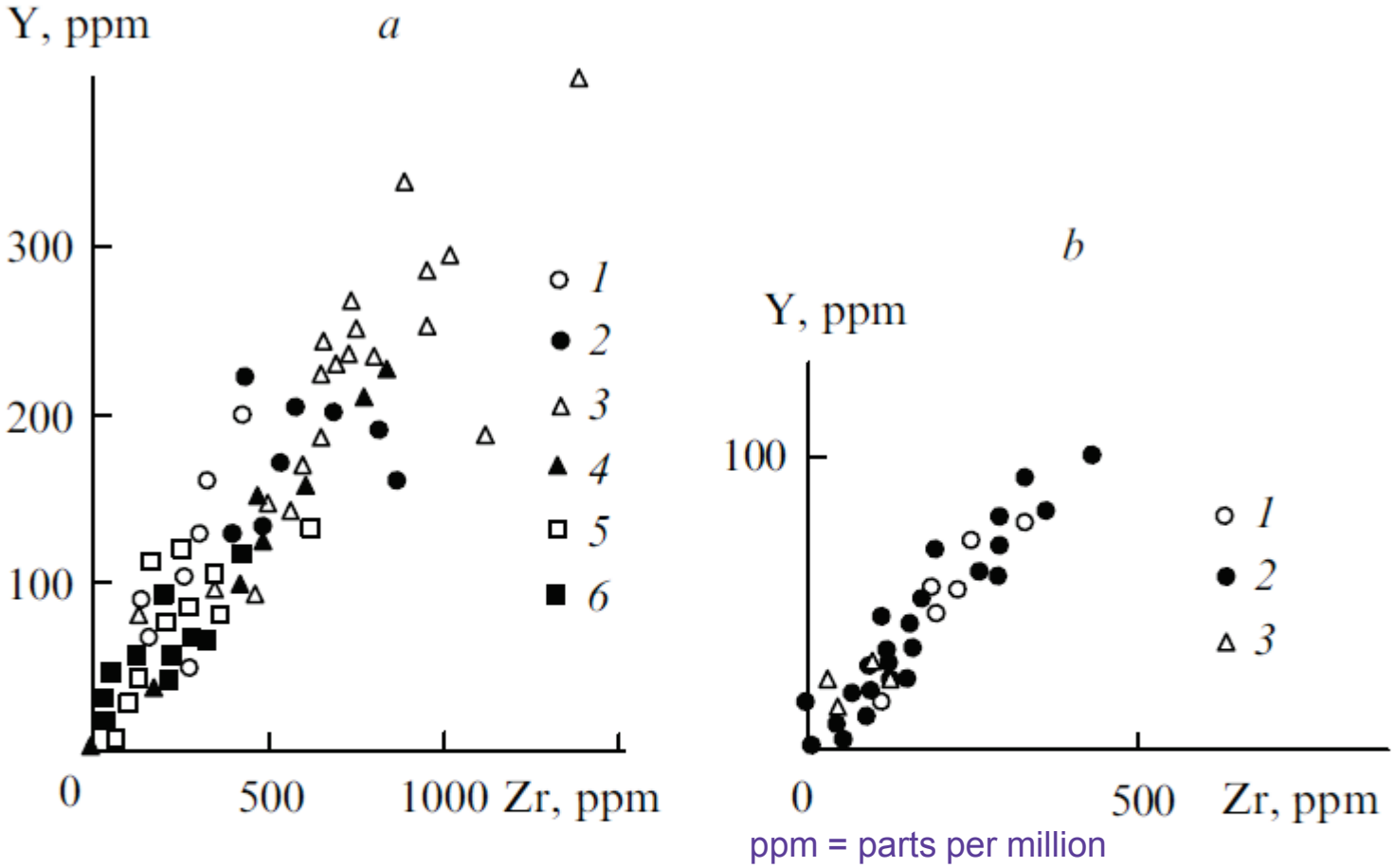


X-ray fluorescence analysis



X-ray fluorescence spectrum of lunar regolith, taken by the APXS device mounted on Chinese moon rover (first spectrum on December 25, 2013).
Eight main elements: Mg, Al, Si, K, Ca, Ti, Cr, Fe with Mg, Al, Si, K, Ca, Ti, Cr, Fe.
Besides, some traces of Sr, Y, Zr.

X-ray fluorescence analysis

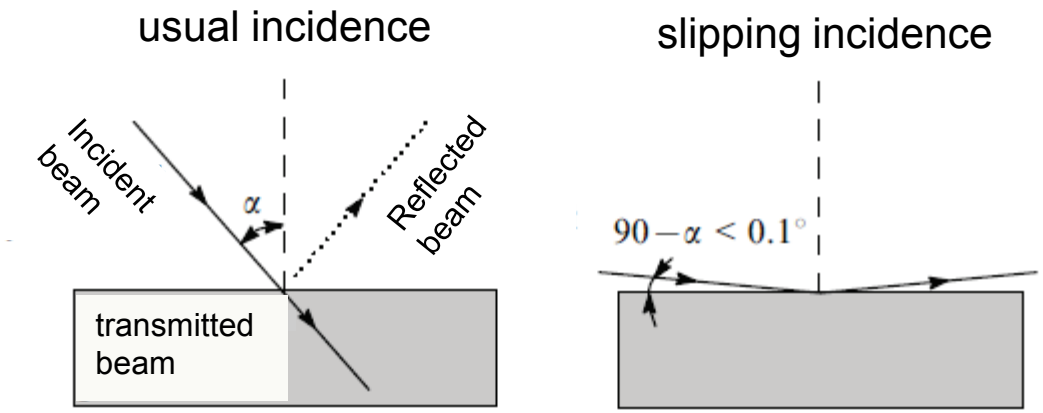


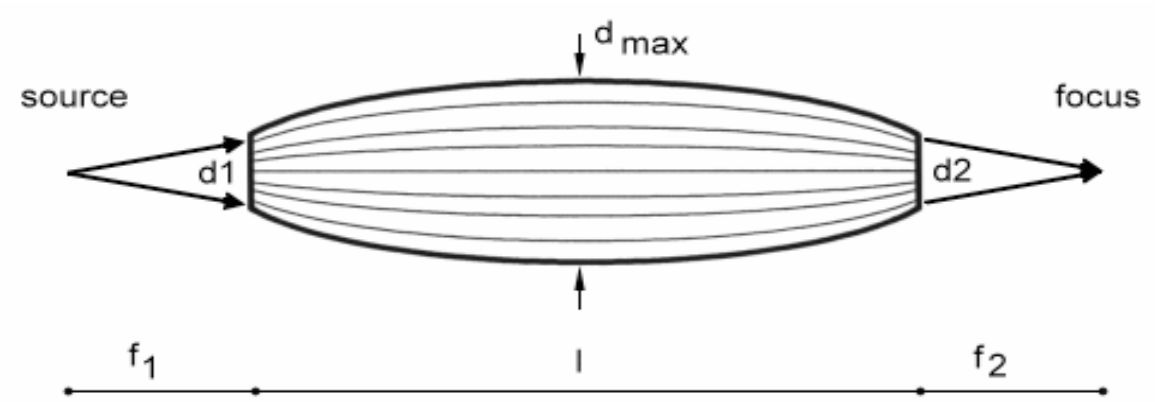
ppm = parts per million

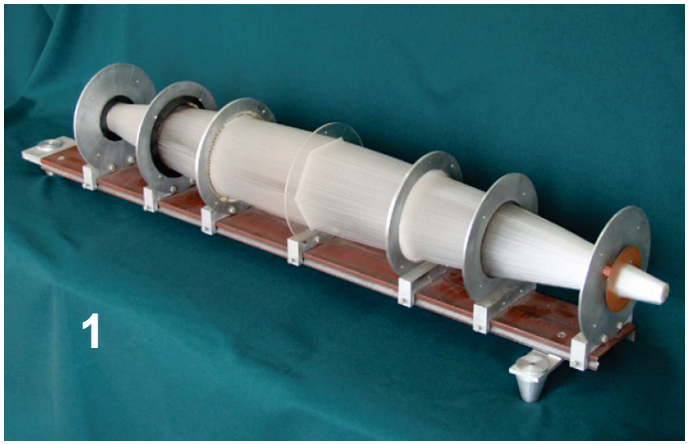
Correlation between contents of Y and Zr in the lunar soil,obtained in “Apollo” and “Luna” missions by X-ray fluorescence analysis:
(a) 1 - Apollo-11, 2 – Apollo-12, 3 – Apollo-14, 4 - Apollo-15, 5 – Apollo-16, 6 – Apollo-17;
(b) 1 – Luna-16, 2 – Luna-20, 3 – Luna-24.

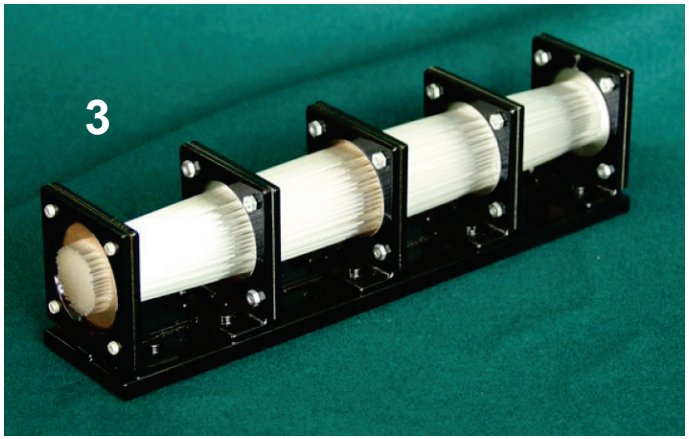
L.N.Tarasov et al Nucl. Instrum. Methods Phys. Res. A, **405**, 590 (1998)
(Adapted from Ya.V. Zubavichyus, Yu.V. Slovokhotov
Russian Chemical Reviews, **70** ,373 (2001))

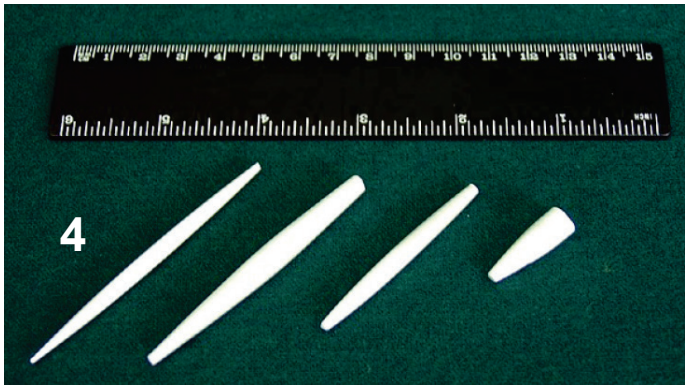
Focusing of X-rays

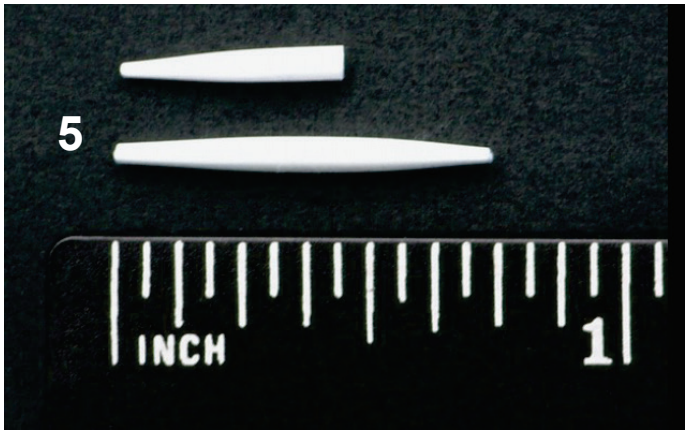












borosilicate glass

SPIE

The International Society for Optical Engineering

2002

Technology Achievement Award

presented to

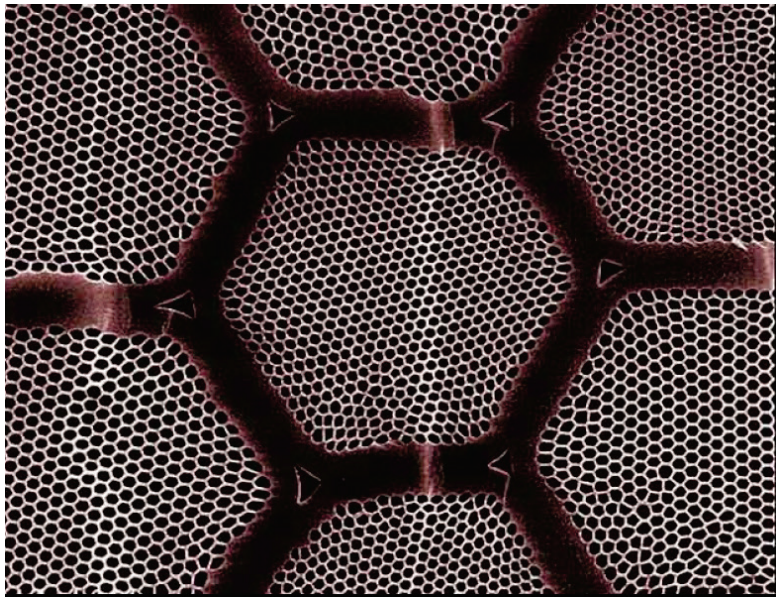
The Institute for Roentgen Optics (IRO)

Muradin Kumakhov, Founder and Director

For outstanding scientific and technological achievements in the development, fabrication, implementation, and reduction to practice of Kumakhov x-ray and neutron capillary and polycapillary optics.

Attested to by James A. Harrington
President of SPIE

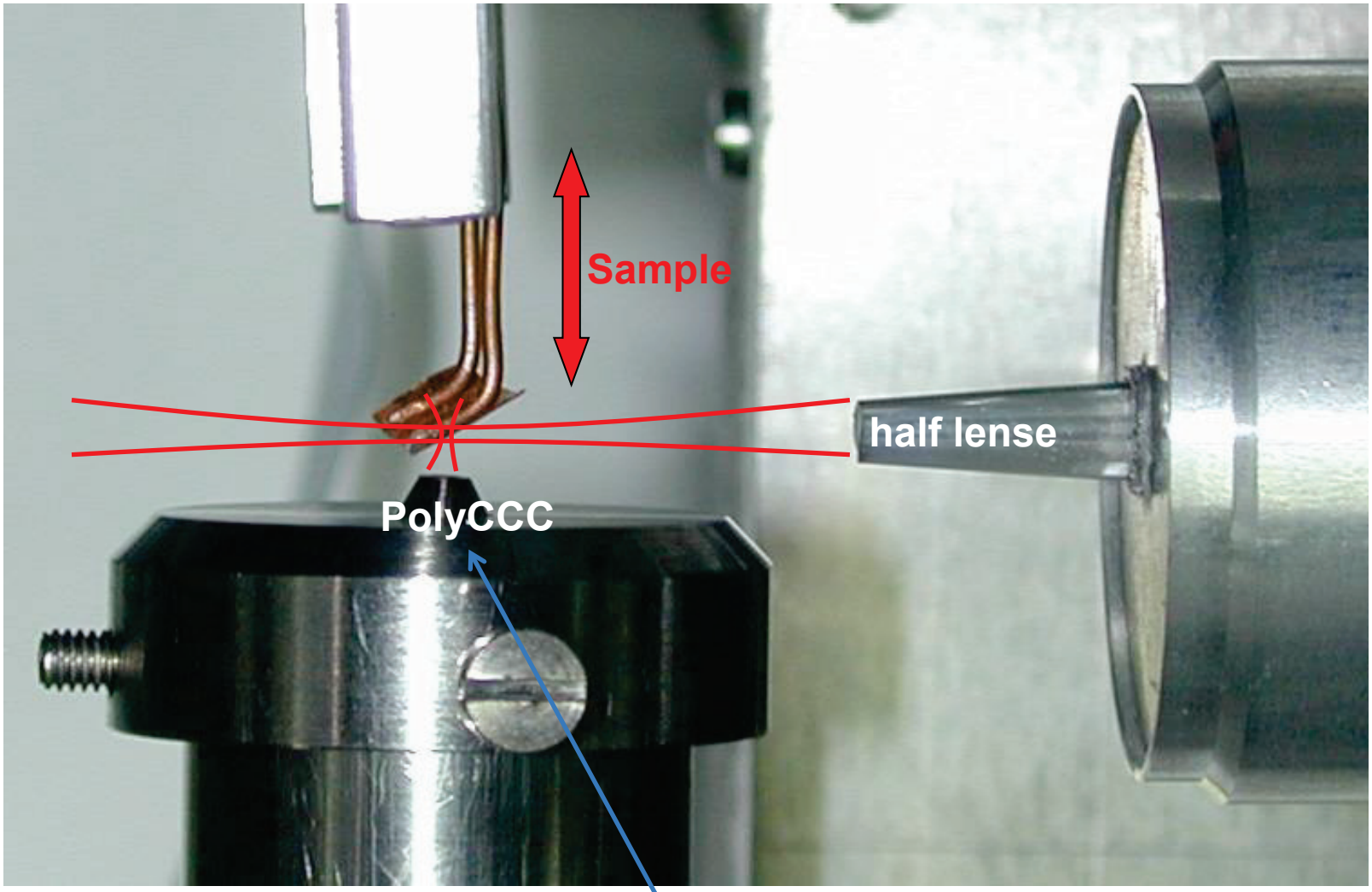
10 July 2002
Seattle, Washington USA



Prof. Muradin Kumakhov (1941-2014)

Institute of X-ray Optics

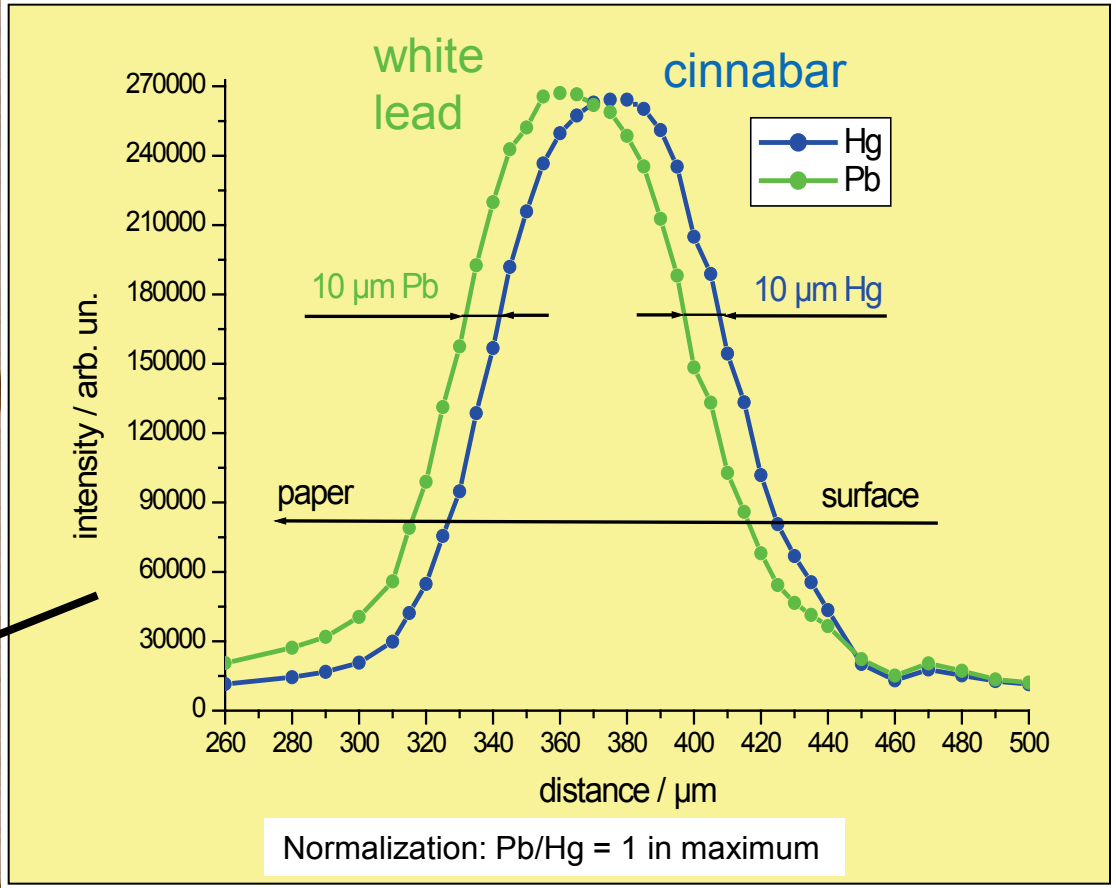
Setup @ BAMline / BESSY



PolyCCC - PolyCapillary Conic Collimator)

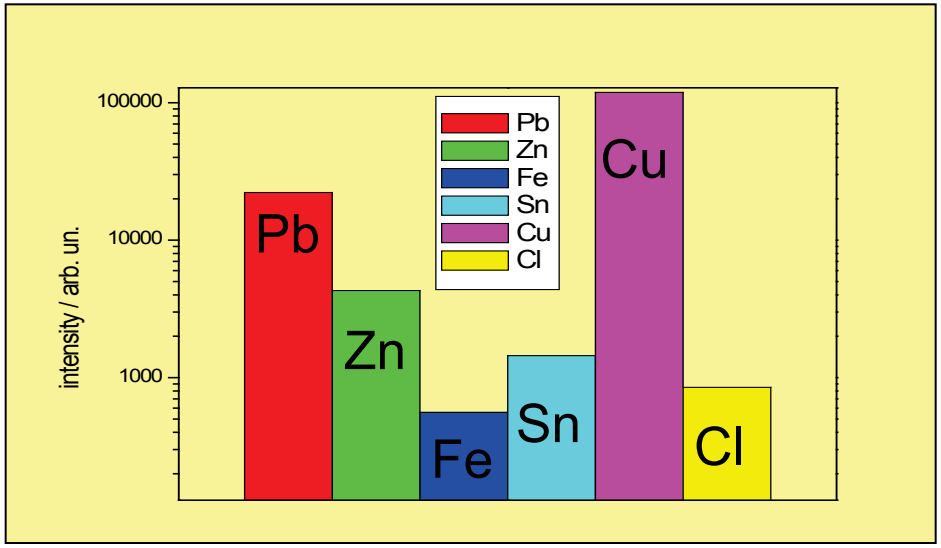
Micro-X-ray fluorescence analysis in 3D

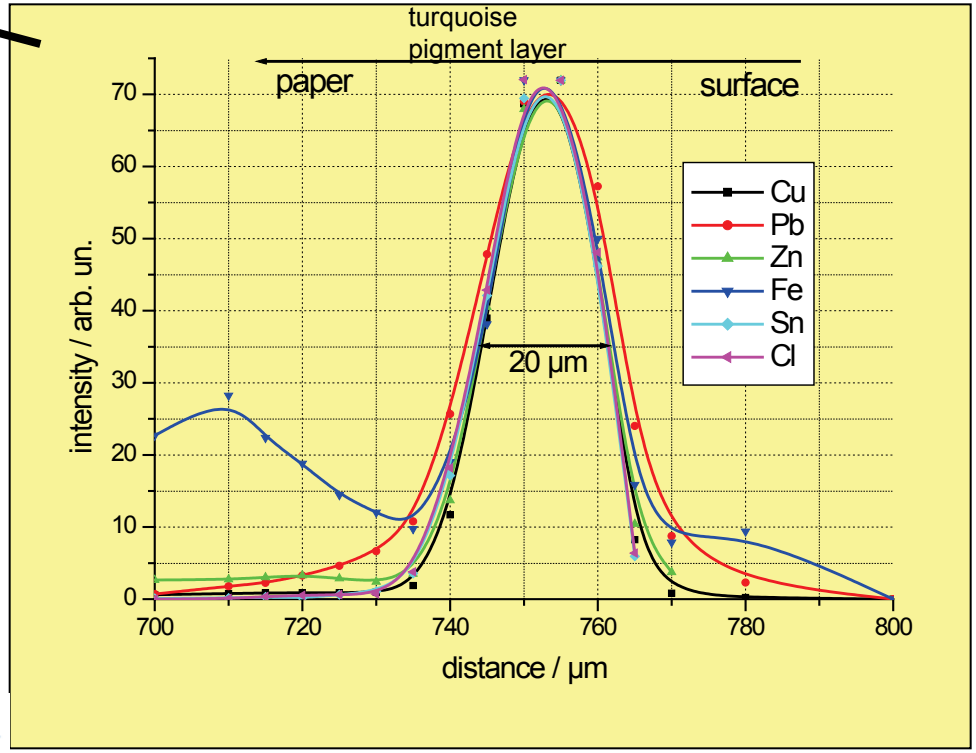
Study of the Mughal miniatures of the 16th – 18th centuries



Micro-XRF depth profiling of a classical Mughal miniature MIK I 5004 (3) dated from the 18th century.

B. Kanngießer et al, Nucl. Instr. Meth. B **211**, 259 (2003)

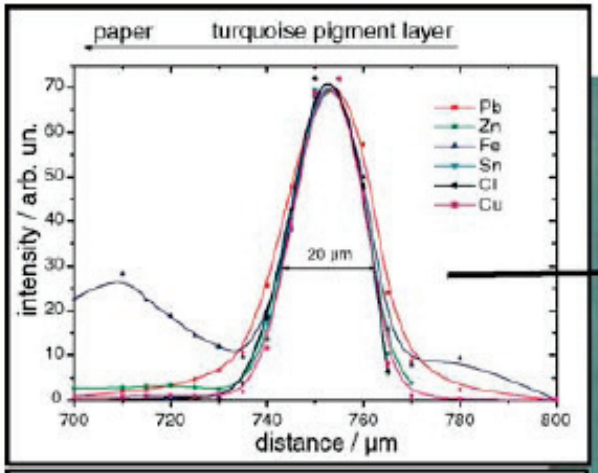


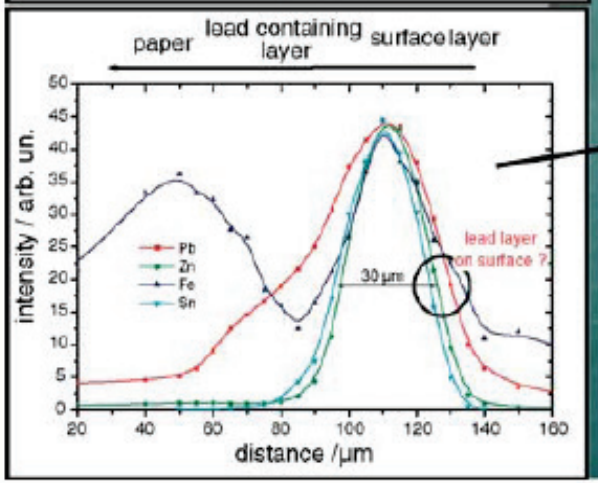


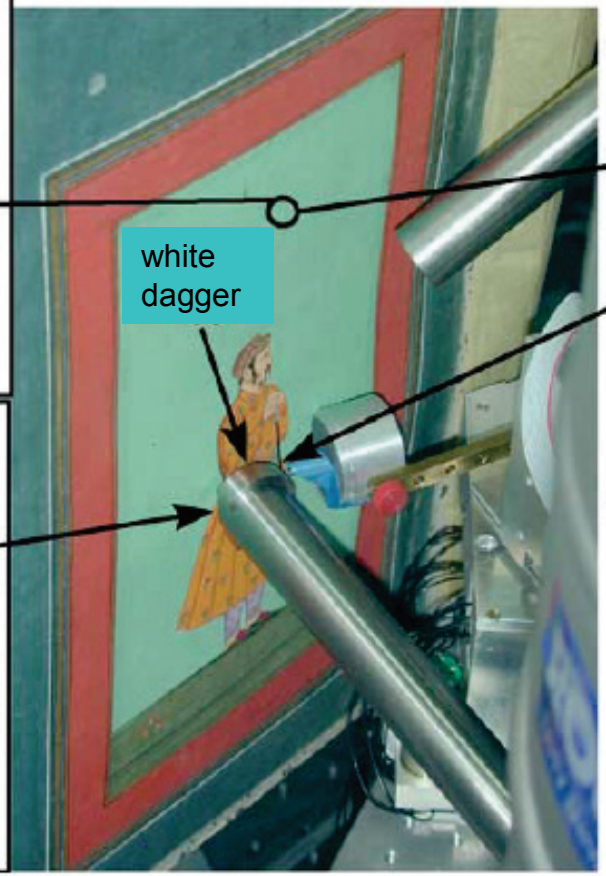
Micro-XRF depth profiling of a Mughal miniature MIK I 5004 (10) "Abdallah Zakhmi" of doubtful origin (stylistically dated to the 17th century).

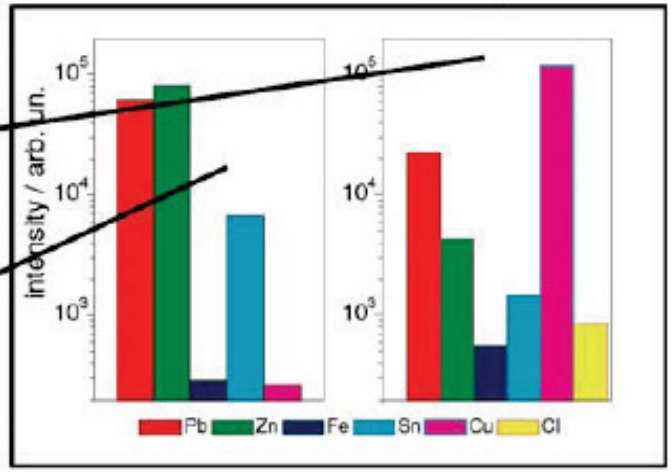
B. Kanngießer et al, Nucl. Instr. Meth. B **211**, 259 (2003)

Micro-X-ray fluorescence analysis in 3D





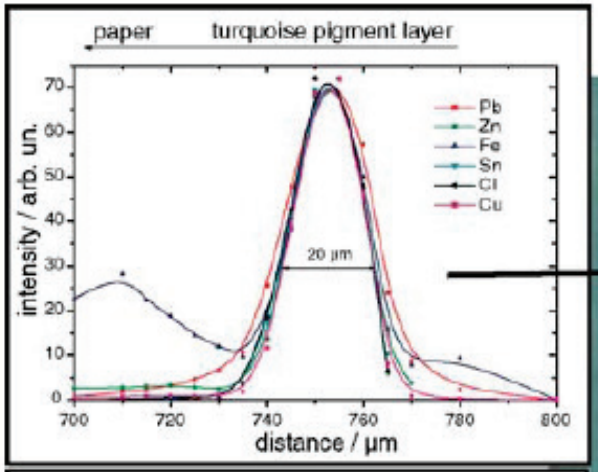


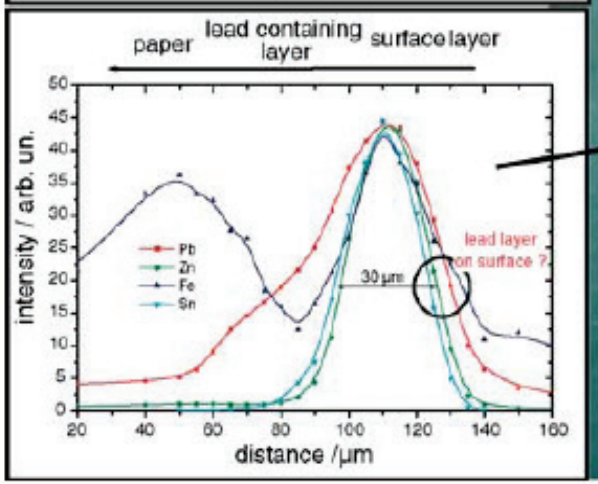


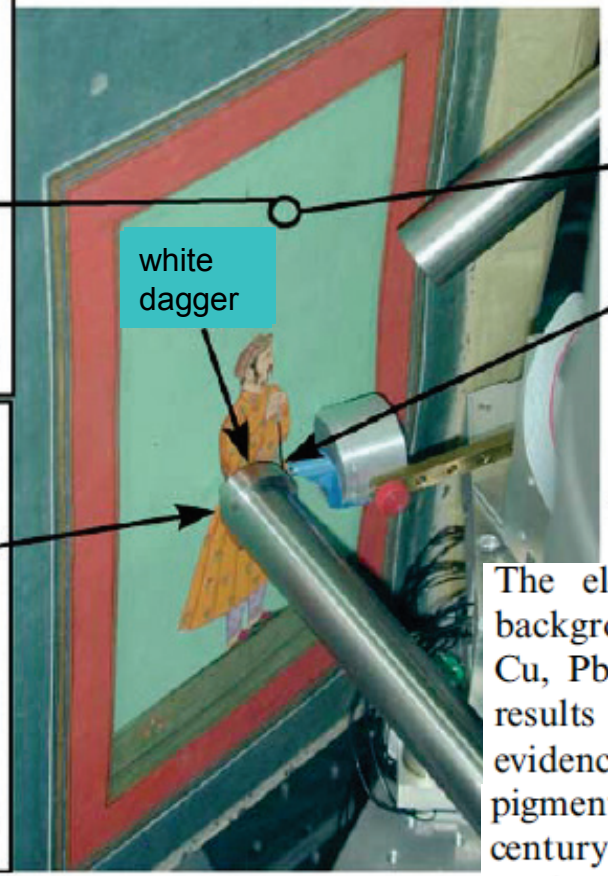
MIK 5004 (10)
"Abdallah Zakhmi"
dated to the end of the 17th c.

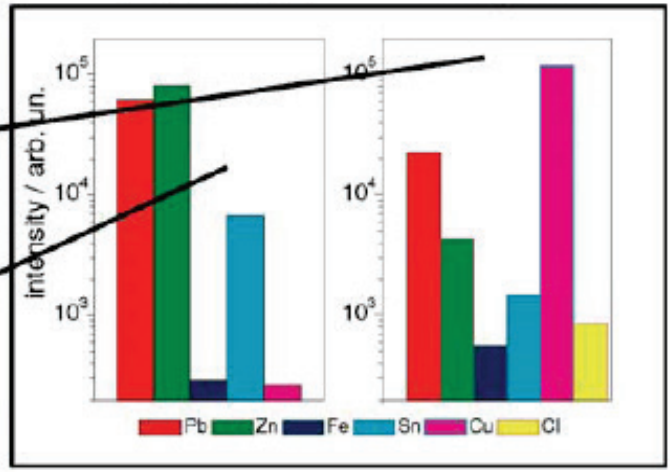
B. Kanngießer et al, Nucl. Instr. Meth. B **211**, 259 (2003)

Micro-X-ray fluorescence analysis in 3D







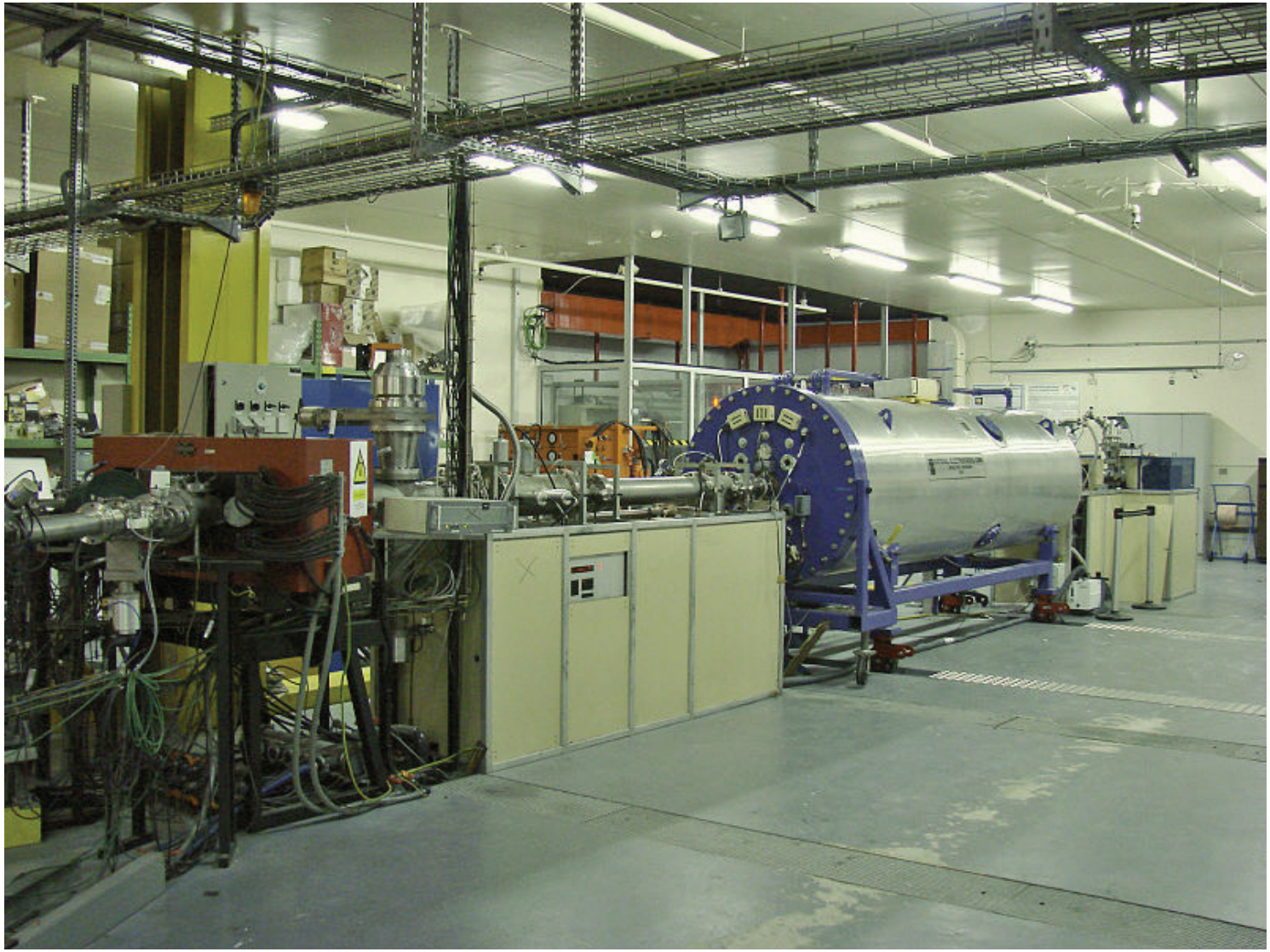


Thus, this painting represents either the first scientifically proved sample of an early use of zinc white in India or it is simply a copy manufactured in the 19th century. The analysis and comparison of ancient zinc white pigments from India will contribute to finally solve this problem.

The element depth profiles for the turquoise background clearly show a single paint layer with Cu, Pb and Zn as the main components. These results are surprising as, up to now, there is no evidence of the use of Zn and Sn containing white pigments in art before the beginning of the 19th century, at least in Europe. In addition, the investigation of the white poniard showed a three layered structure which is in its succession inverted to the expected one. The first layer on the paper contains only lead. The second layer is again a mixture of mainly Pb, Zn and Sn. In addition, there seems to be a very thin third layer containing mainly Pb on the top.

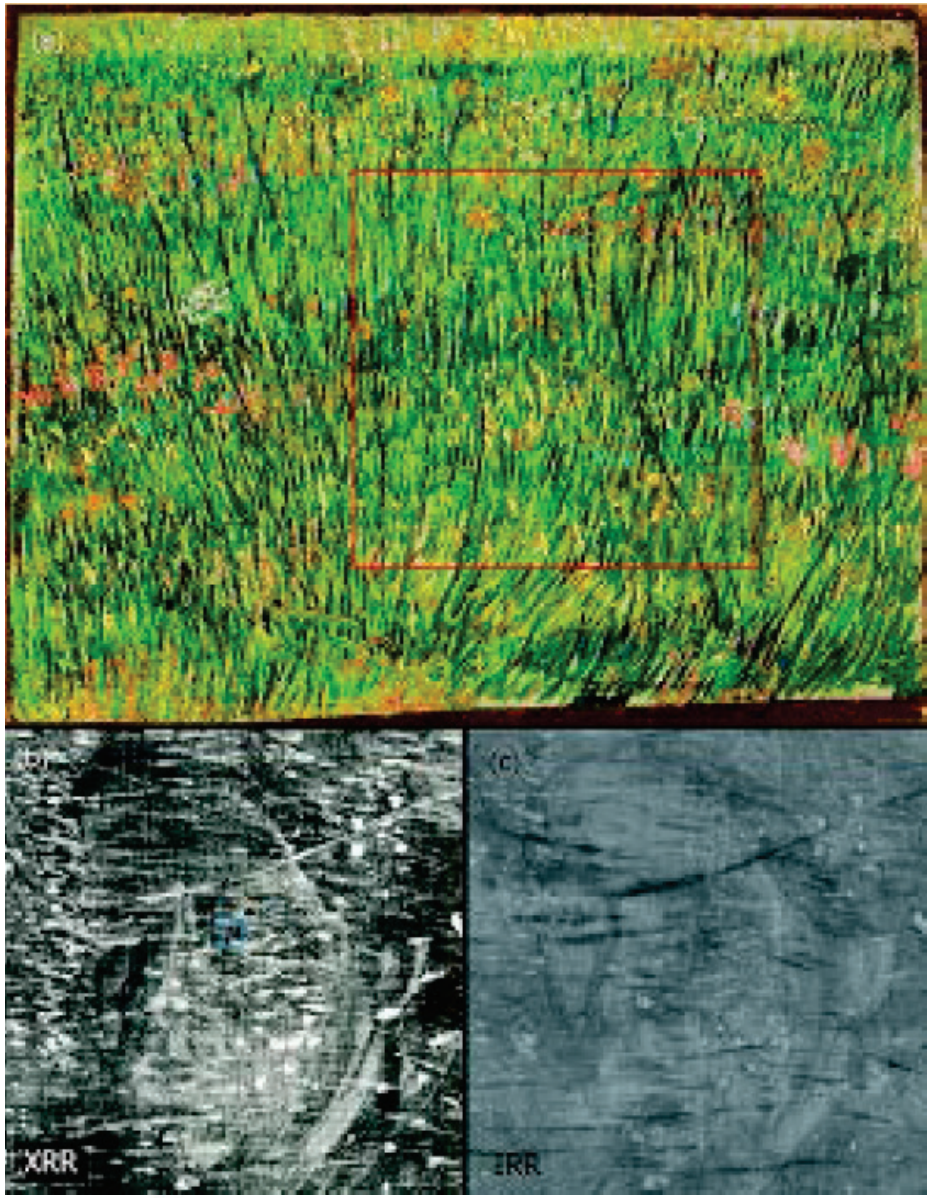
B. Kanngießer et al, Nucl. Instr. Meth. B **211**, 259 (2003)

AGLAE (Accélérateur Grand Louvre d'analyse élémentaire), 1989 -....
(analysis with the ion beam)

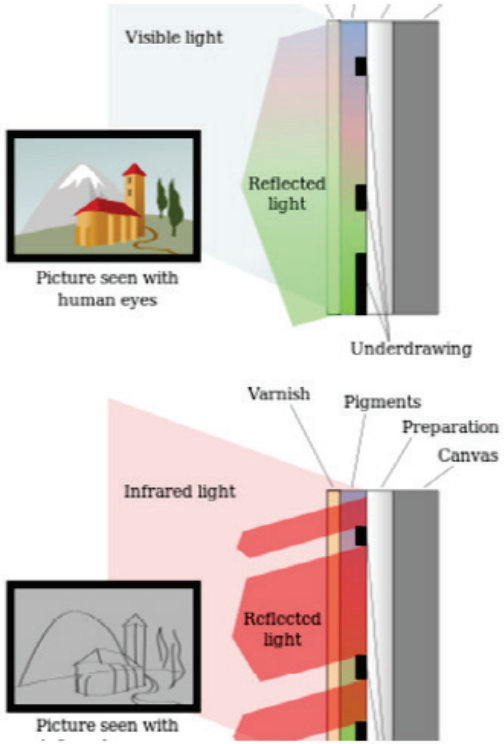


Vincent Van Gogh, Patch of Grass, Paris, 1887

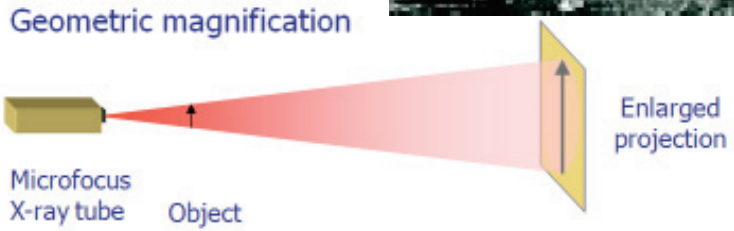
Different techniques of revealing hidden images



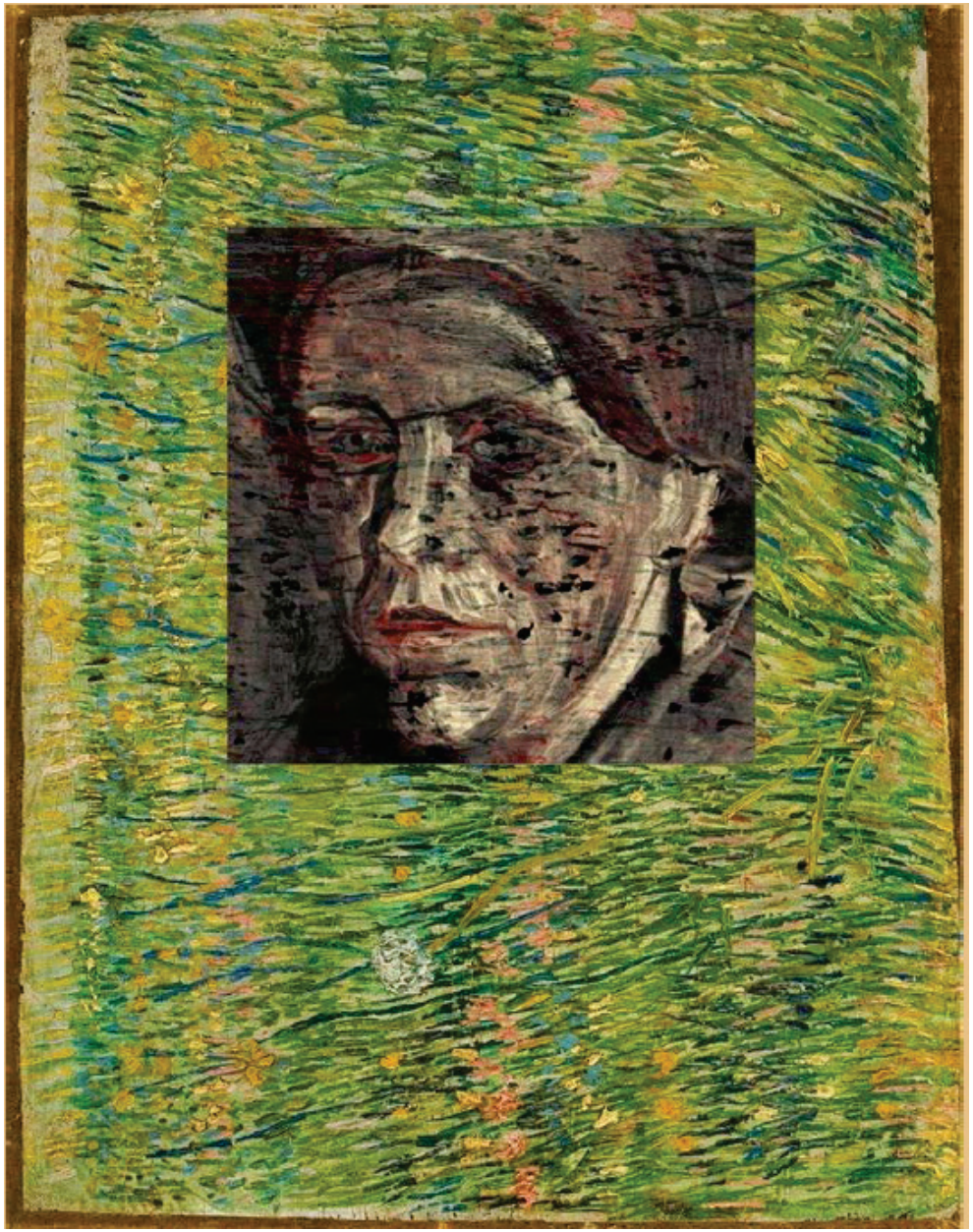
Infrared reflectography



X-ray radiation transmission radiography



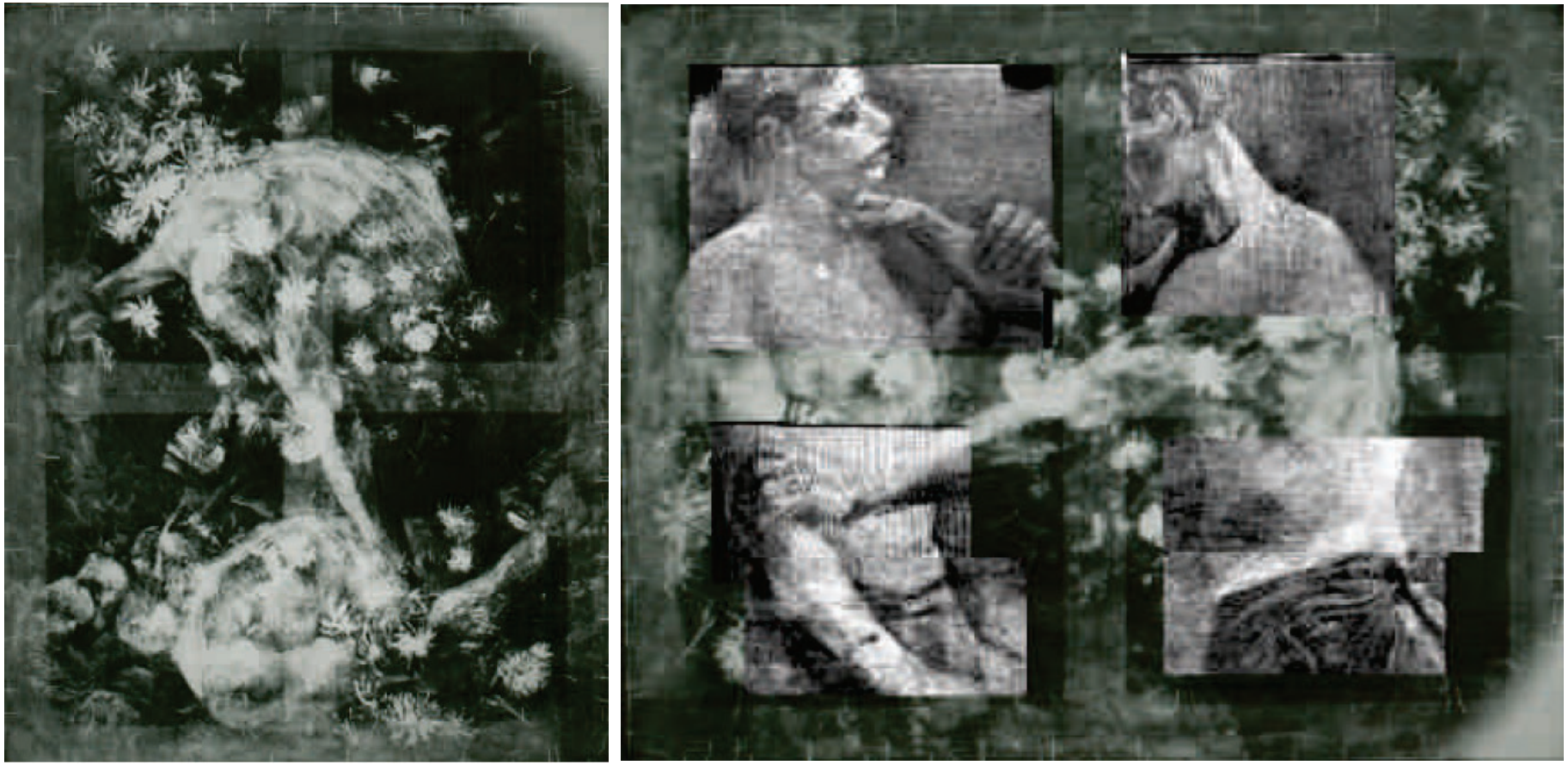
Patch of grass
radiography
SR-XRF
mapping
Similar painting by VGogh



Vincent van Gogh, «Still life with meadow flowers and roses»

Vincent van Gogh, *Still life with meadow flowers and roses*, 1886-87, oil on canvas, 99 x 79 cm. Kröller-Müller Museum, Otterlo; F 278 JH 1103

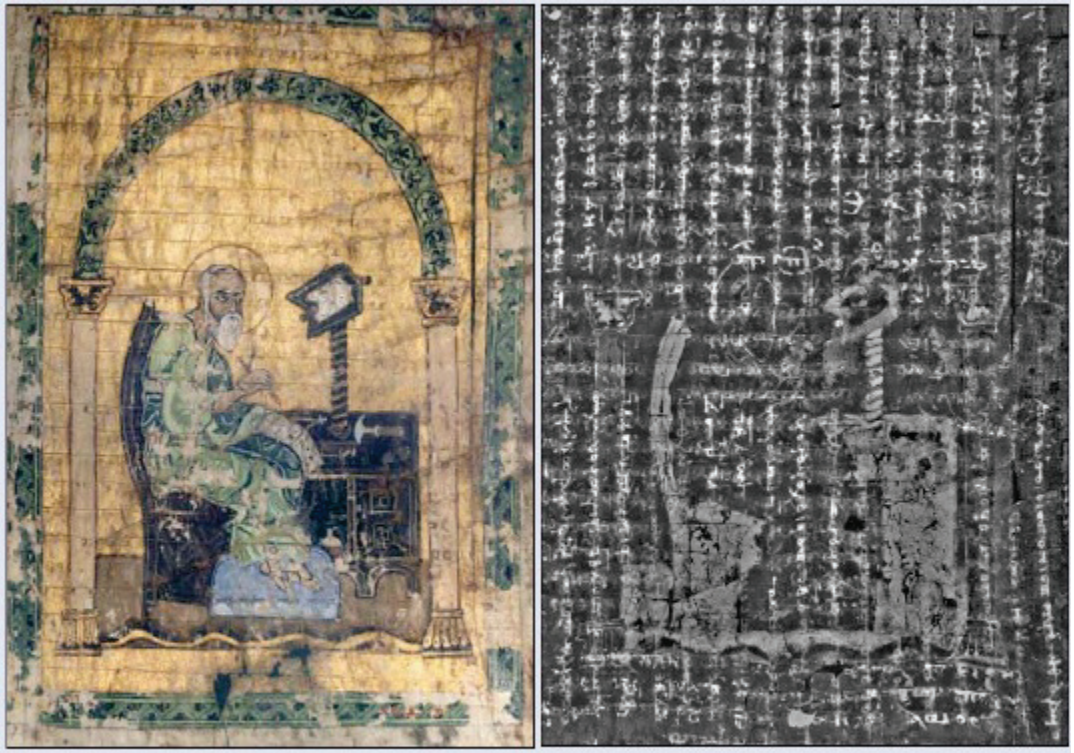
X-ray of illustration 1



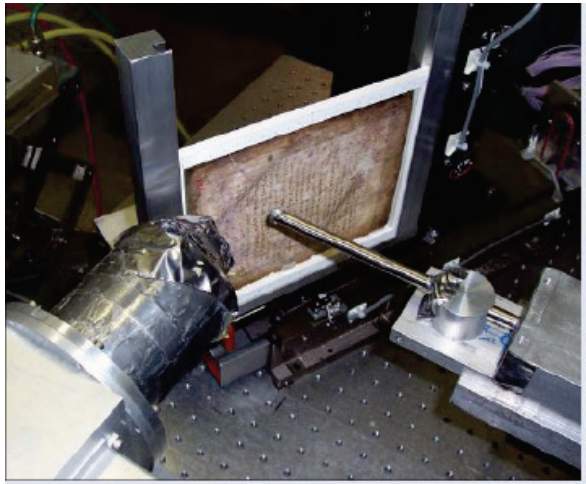
Four images showing the distribution of zinc white (ZnO), captured using MA-XRF from the verso at DESY (Hamburg) and the coarser scans at the Kröller-Müller Museum; overlaid with the X-ray image. In interpreting this zinc file, it must be taken into account that lead white impedes zinc radiation.

X-ray fluorescence analysis

2007 г. Uwe Bergmann, SLAC
Deciphering the text of the manuscript writings of Archimedes X century ("On floating bodies" and others.) Later, the text has been overwritten. The pigments of the ink contained iron - it is iron, which was recorded by X-ray fluorescence. Scanning speed ~ 12 hours per pageBergmann U.
(2007) Archimedes brought to light. Phys. World 20:39-42.



A leaf (folio 57r) of the Palimpsest, covered with a forged painting from the 20th century, viewed in normal light (left). The other image of the same page, which was created by measuring the X-ray fluorescence from iron in the ink, reveals the Archimedes text (vertical) beneath the forgery.



A leaf of the Archimedes Palimpsest exposed to X-rays from the Stanford Synchrotron Radiation Facility in the US. The leaf moves on a stage so that the beam scans across the text, line by line. The detector, which is covered in lead and placed at 90 degrees to the incoming beam, measures the X-ray fluorescent photons emitted by atoms in the paper.

26.03.2018 14:05

Рукопись античного врача Галена прочли спустя тысячу лет

Текст: Николай Грищенко **Фото: Farrin Abbott/ SLAC**

Сотрудники Национальной ускорительной лаборатории SLAC (Stanford), обнаружили ранее неизвестный медицинский трактат античного врача Галена. Записки выдающегося медика времен древнего Рима удалось обнаружить на палимпсесте с помощью рентгеновской томографии.

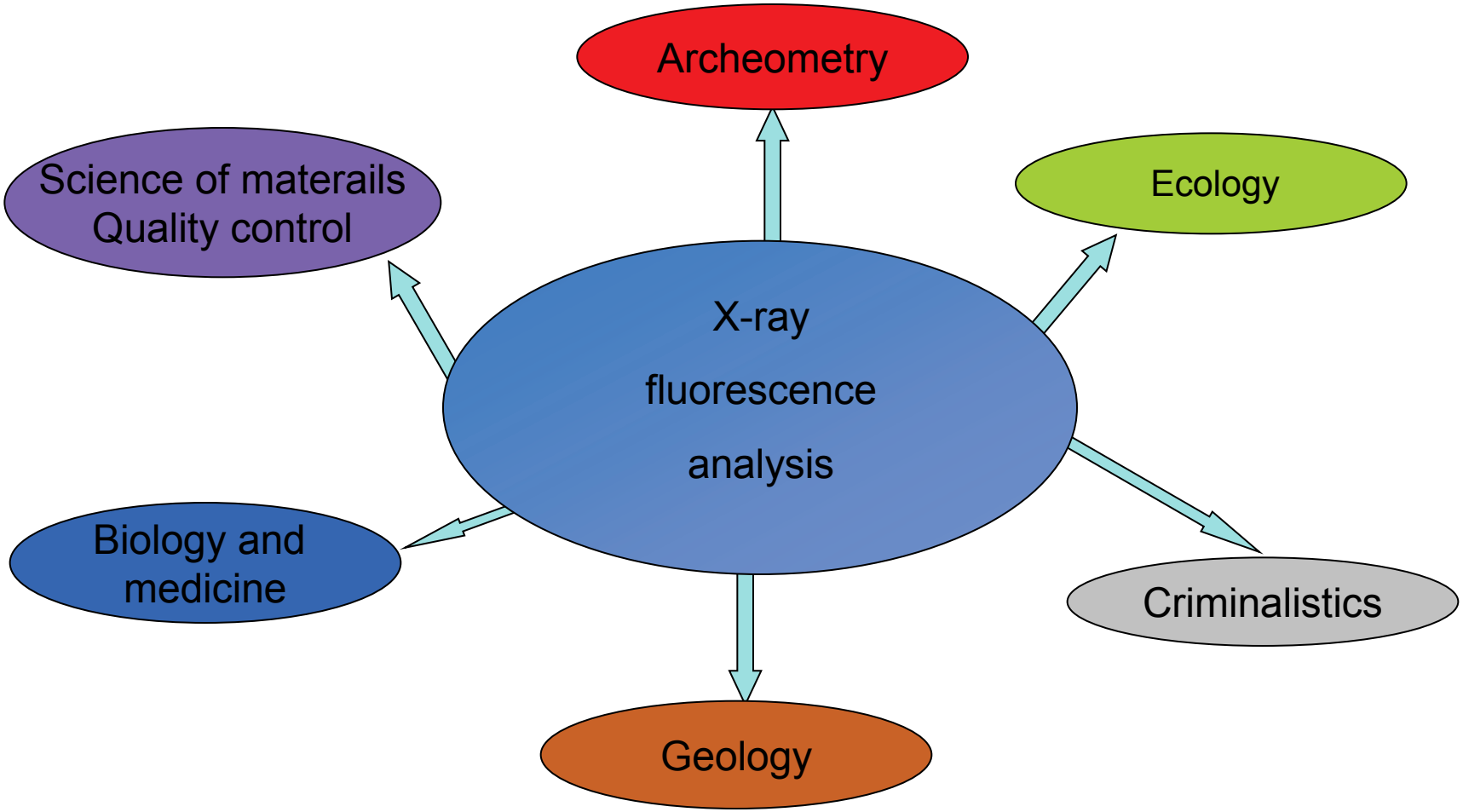
Первоначально манускрипт хранился в монастыре святой Екатерины на Синае. Его текст содержал псалмы на сирийском языке и был записан в XI веке. Скрытый текст - медицинское сочинение Галена "О смесях и силе простых лекарств" - был записан значительно раньше, в VI веке. Из-за экономии места средневековые монахи стерли медицинский трактат и записали тексты богослужения.

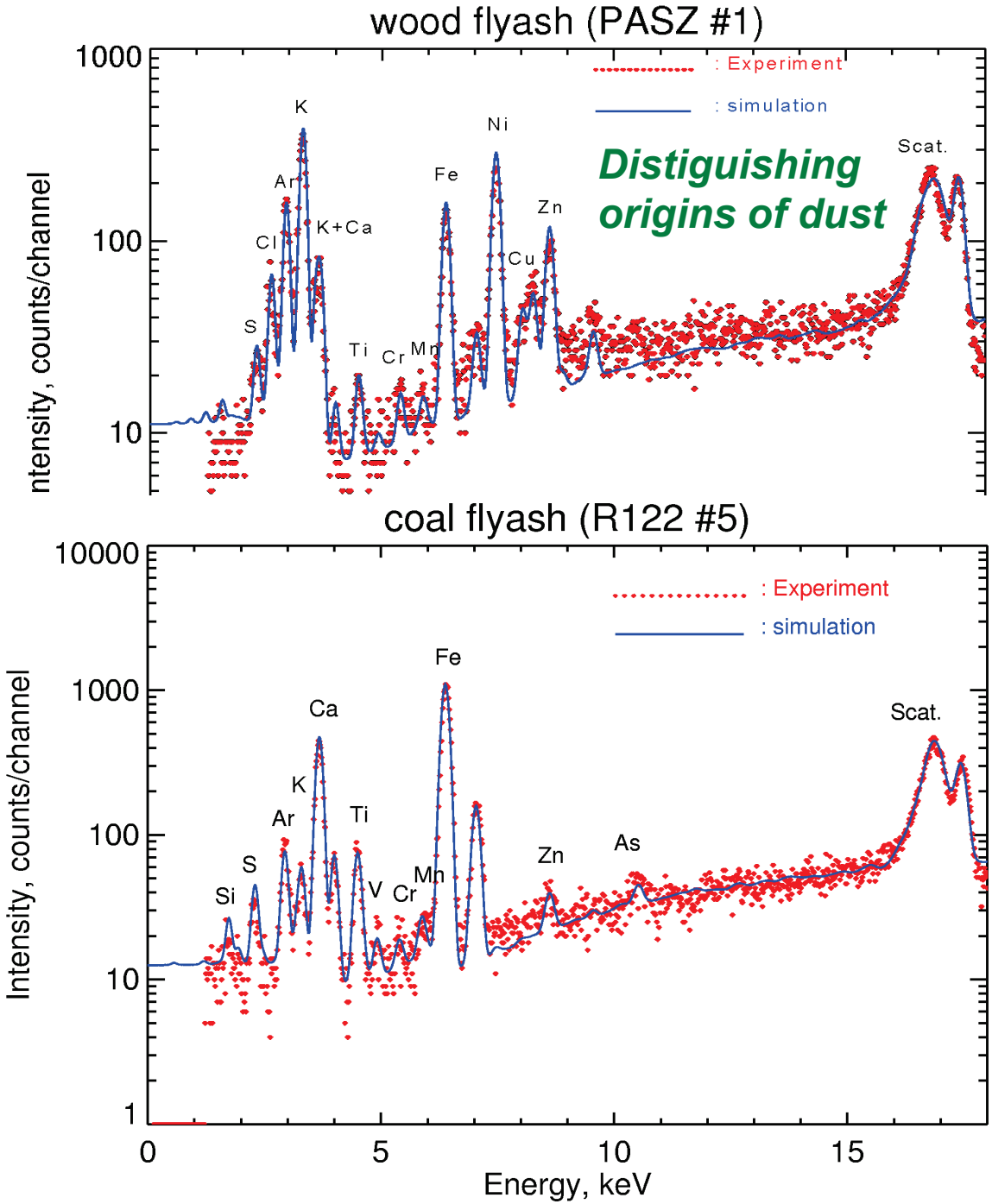
Выявить уникальный текст удалось благодаря рентгеновским лучам, которые были сгенерированы на ускорителе частиц в SLAC. Это позволило выявить крошечные частицы более древних чернил на бумаге. С помощью обычного ультрафиолетового и инфракрасного излучения их обнаружить не удалось. На проявление "невидимых чернил" одной страницы ученым потребовалось около десяти часов. К настоящему времени расшифровано 26 страниц из 200. В нем Гален в алфавитном порядке перечисляет 473 вещества растительного, животного и минерального происхождения и рассказывает об их медицинском применении.

Рукописи с сирийскими переводами отдельных частей этого труда известны ученым давно, но нынешний манускрипт является самым древним известным памятником с фрагментами ее текста. После завершения работы ученые планируют опубликовать онлайн все страницы, на которых найден галеновский текст, чтобы сделать их доступными для коллег.

Справка: *Клавдий Гален из Пергама - известный врач греко-римской античности жил во II веке нашей эры. Он лечил римского императора Марка Аврелия. Гален считается автором более сотни медицинских и философских работ. Наиболее полное издание сочинений Галена, выпущенное в 1821-1833 годах историком медицины Карлом Кюном, состоит из 22 томов и включает 122 отдельных произведения.*

X-ray fluorescent analysis:
non-destructive quantitative elemental analysis





wood

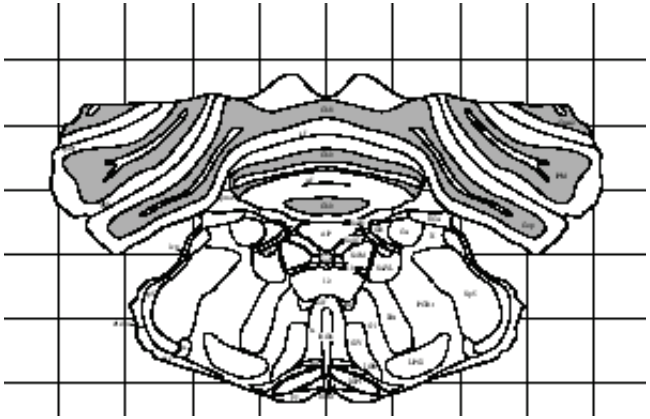
Elements	Intial conc. (%)
O*	15
S	7
Cl	9
K	14
Ca	1.2
Ti	0.2
Cr	0.05
Mn	0.03
Fe	0.8
Ni	1.3
Cu	0.1
Zn	0.4

coal

Elements	Intial conc. (%)
O*	48
Si	27
S	7.0
K	1.5
Ca	9.8
Ti	0.7
Cr	0.05
Mn	0.08
Fe	6.3
Zn	0.07
As	0.01

Life Science

Distiguishing infected and not infected tissues

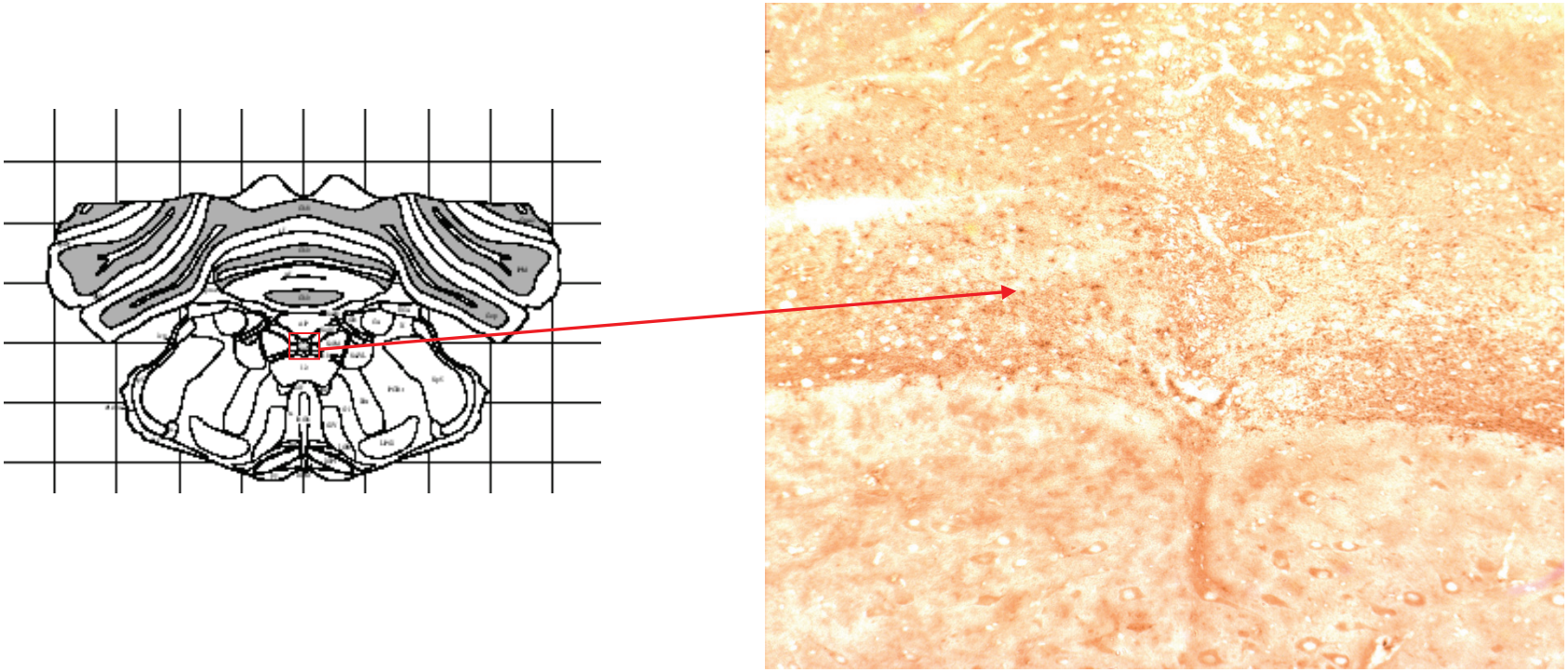


© M. Kühbacher[1], G. Weseloh[1], A. Thomzig[2], J. Kneipp[2], M. Beekes[2], G. Falckenberg[3], A. Kyriakopoulos[1], D. Behne[1]

[1] Hahn-Meitner-Institut Berlin, Department Molecular Trace Element Research in the Life Sciences, 14109 Berlin, Germany
[2] Robert Koch-Institut, Nordufer 20, 13353 Berlin, Germany
[3]Hamburger Synchrotronstrahlungslabor HASYLAB at Deutsches Elektronen-Synchrotron DESY, Notkestr. 85, 22607 Hamburg, Germany

Life Science

Distiguishing infected and not infected tissues



© M. Kühbacher[1], G. Weseloh[1], A. Thomzig[2], J. Kneipp[2], M. Beekes[2], G. Falckenberg[3], A. Kyriakopoulos[1], D. Behne[1]

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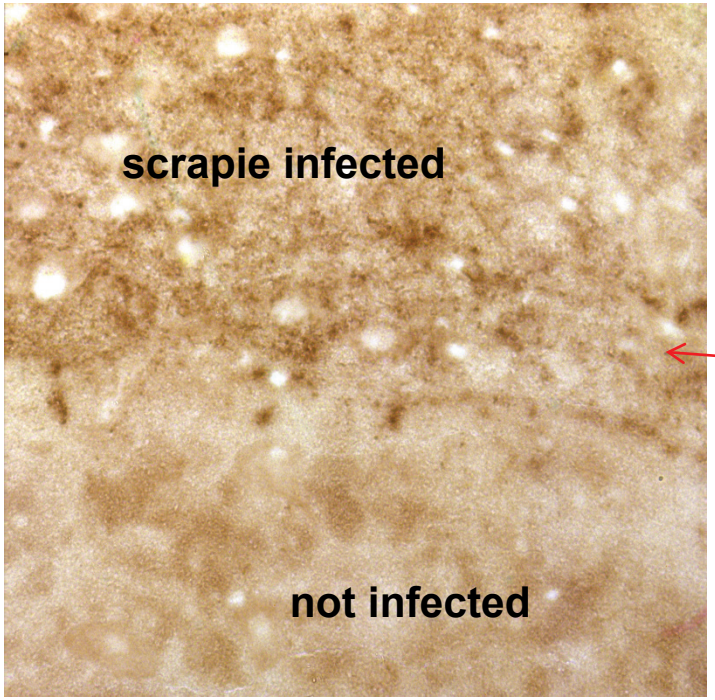

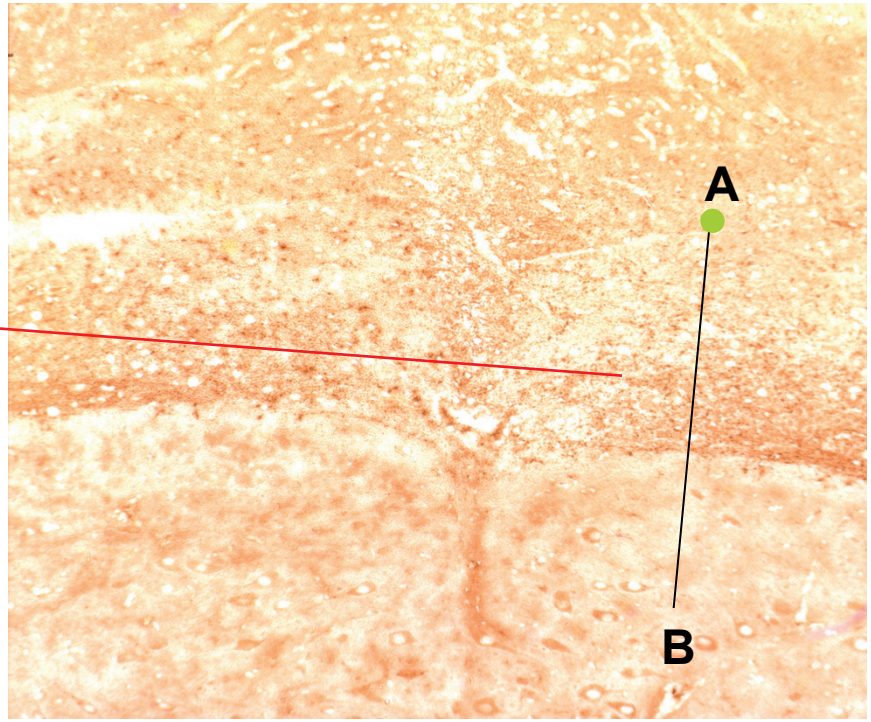

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Life Science

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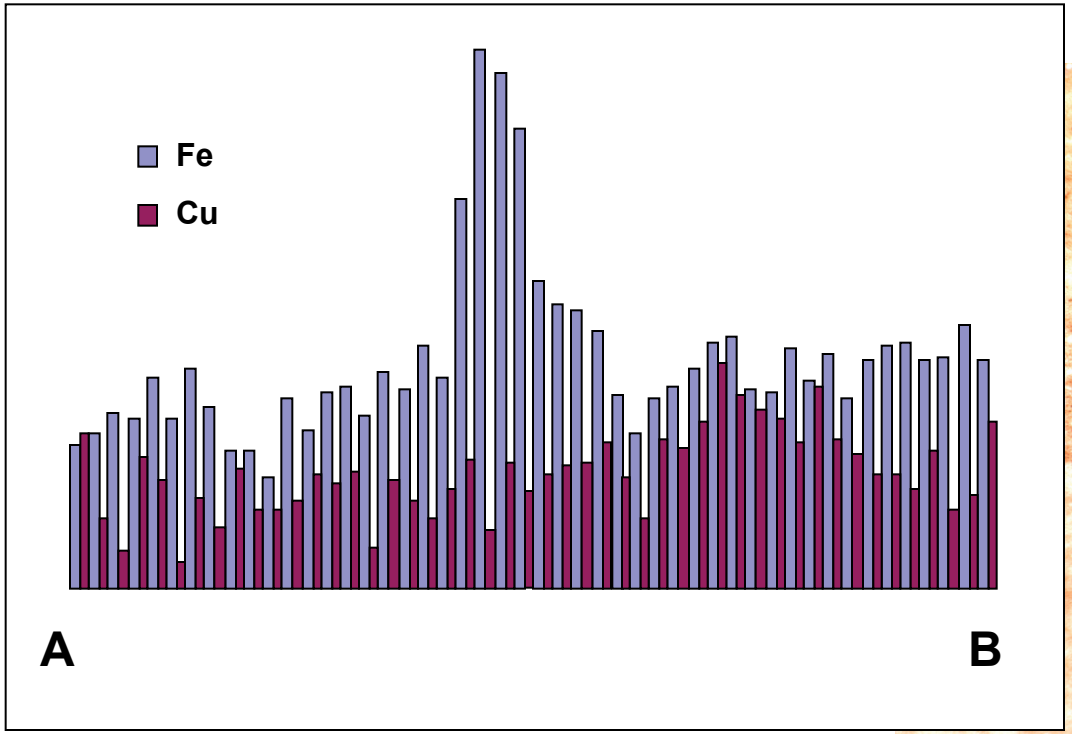

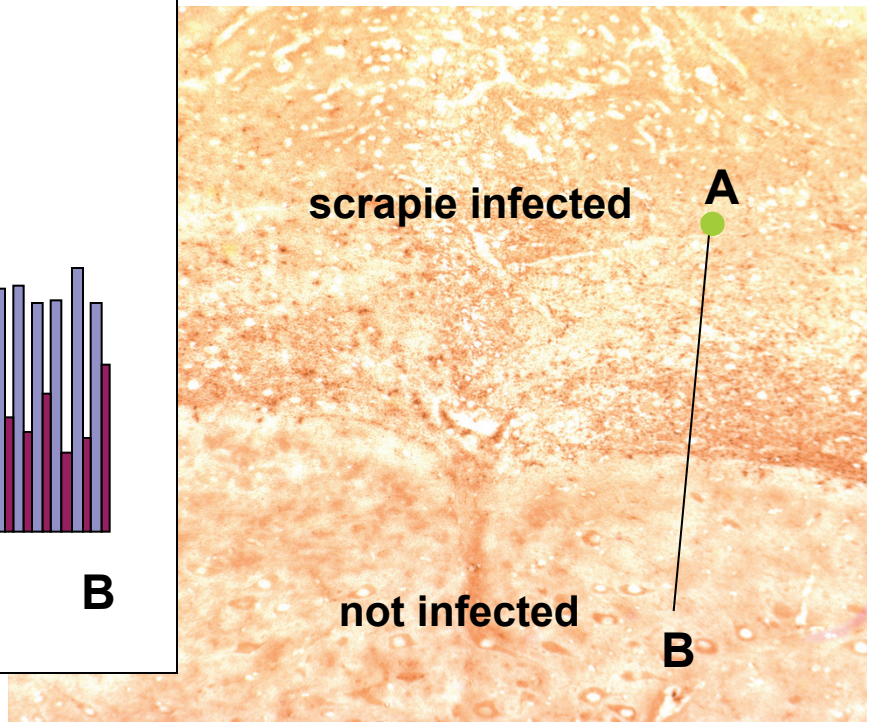

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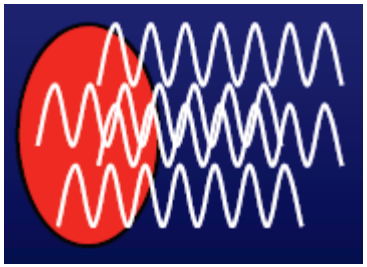
Free electron lasers

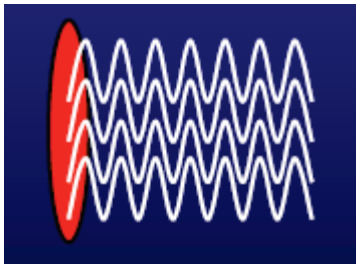
X-ray
Free
Electron
Laser

(ЛСЭ, лазер)

Light
amplification by
stimulated
emission of
radiation



Non-coherent radiation from electron bunch

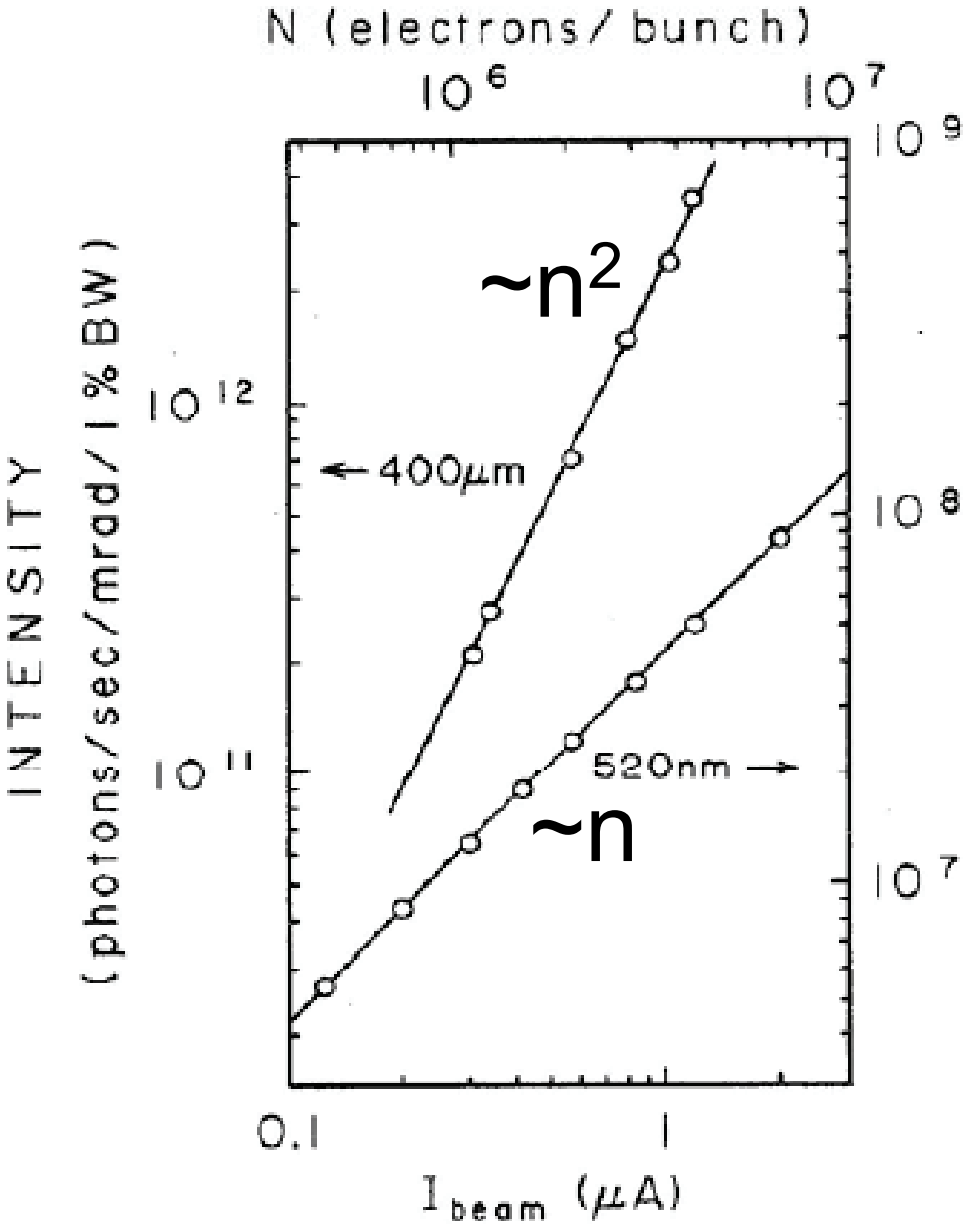


Coherent radiation from electron bunch

Intensity ~ n

Intensity ~ n^2

Coherent radiation of electrons. Is it possible?

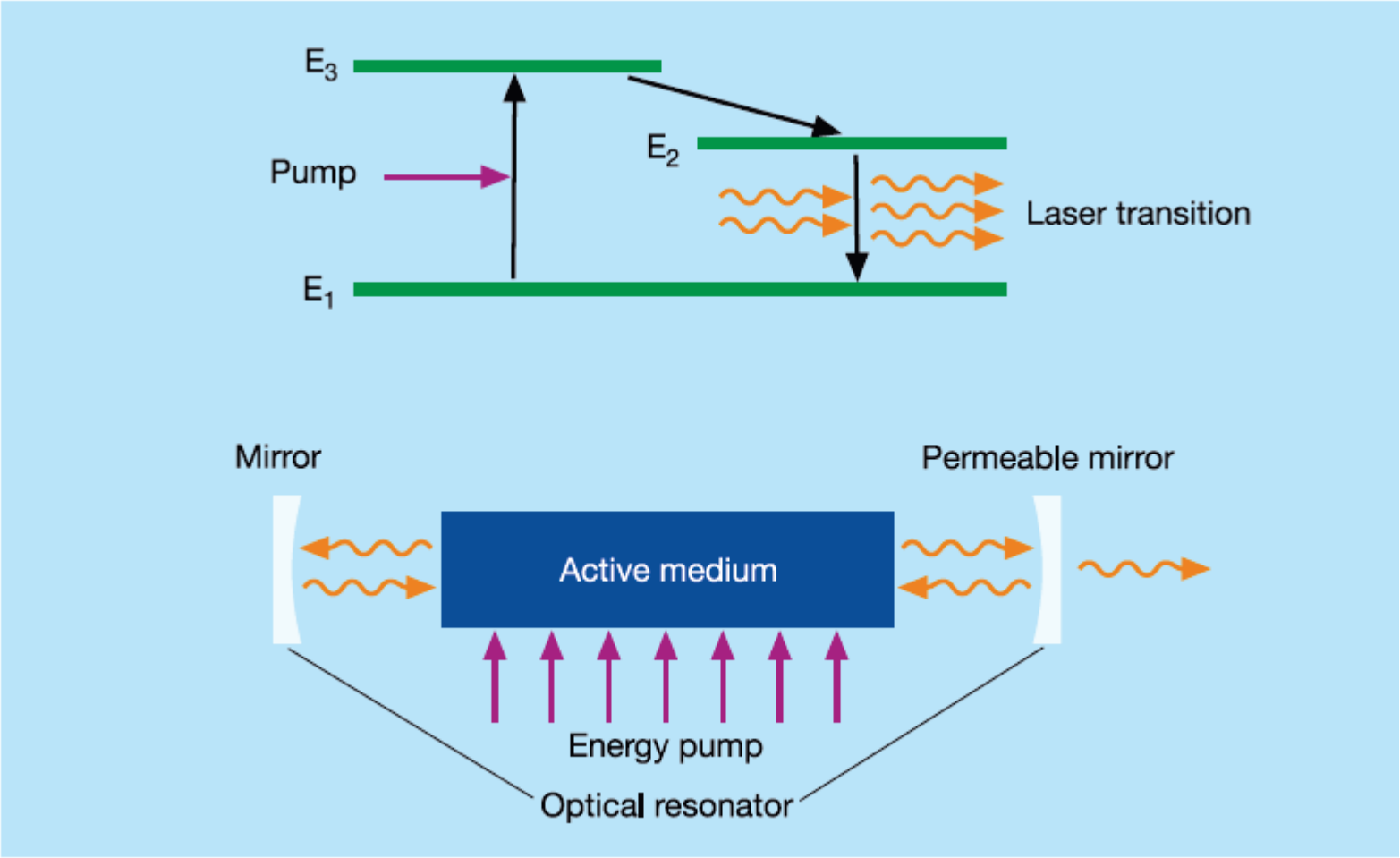


T. Nakazato et al,
Tohoku Univ., Japan

180 MeV electrons

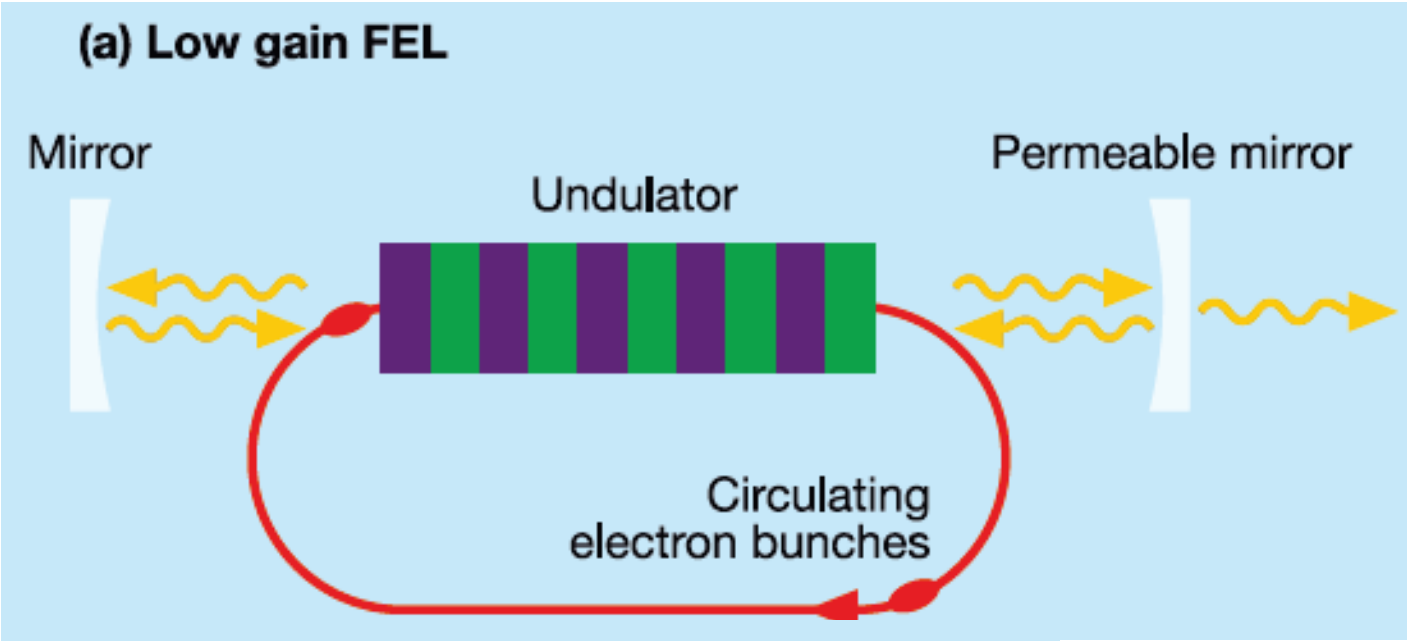
High-quality electron beam: size of the bunch must be comparable with the wavelength of the radiation.

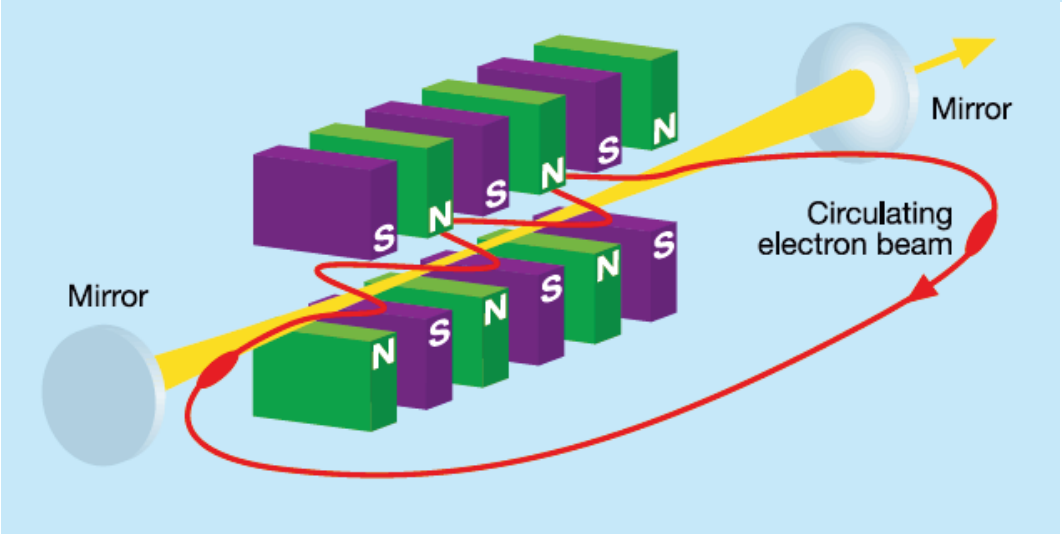
First demonstrations of coherence of the undulator radiation (1989-1990)



Traditional laser on the “bound electrons”

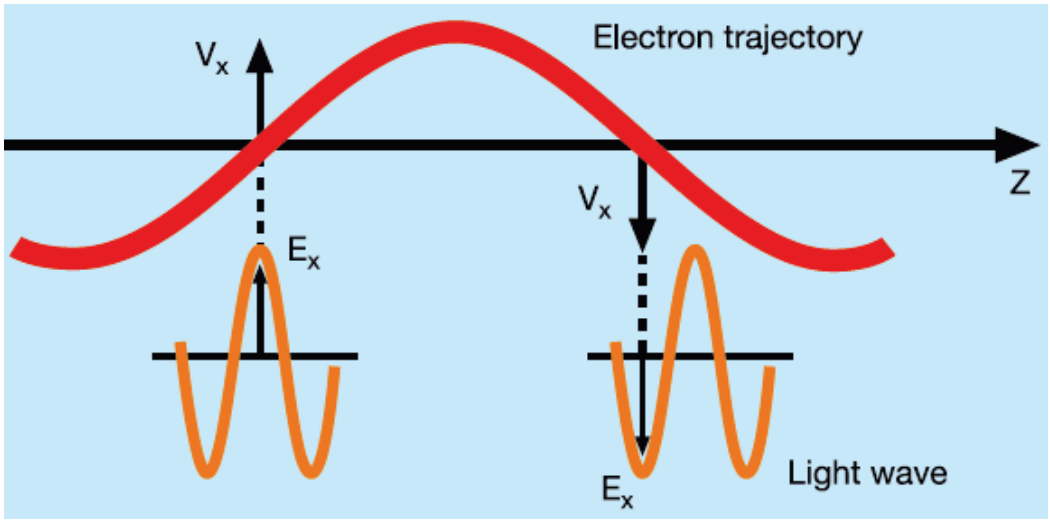
Free electron laser with small gain (IR and visible): a few percent gain during one passage through the undulator





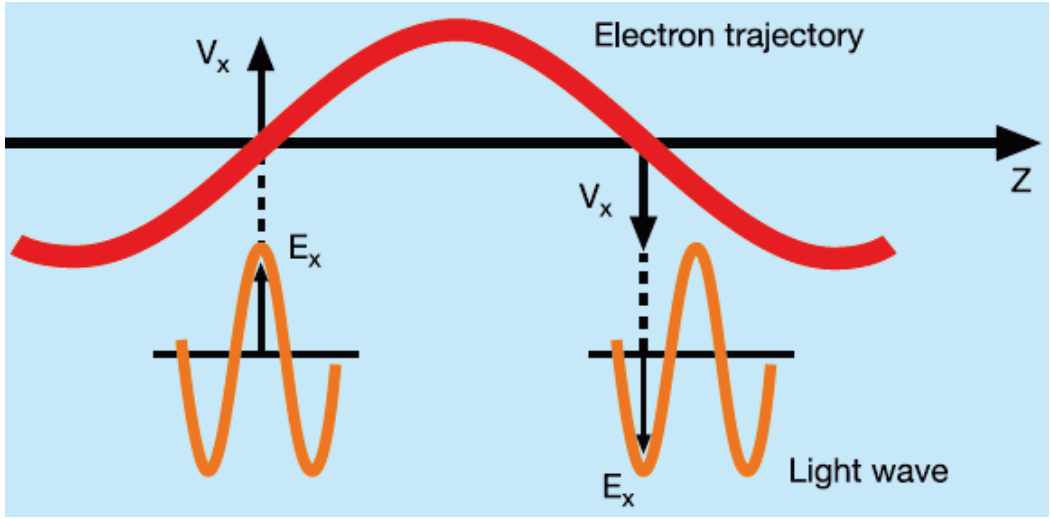
First free electron laser was realized in 1976 (Stanford, USA)

Condition of the energy transfer from electron to the field: the wave of light must shift by λ/2 during the half period of the electron trajectory.



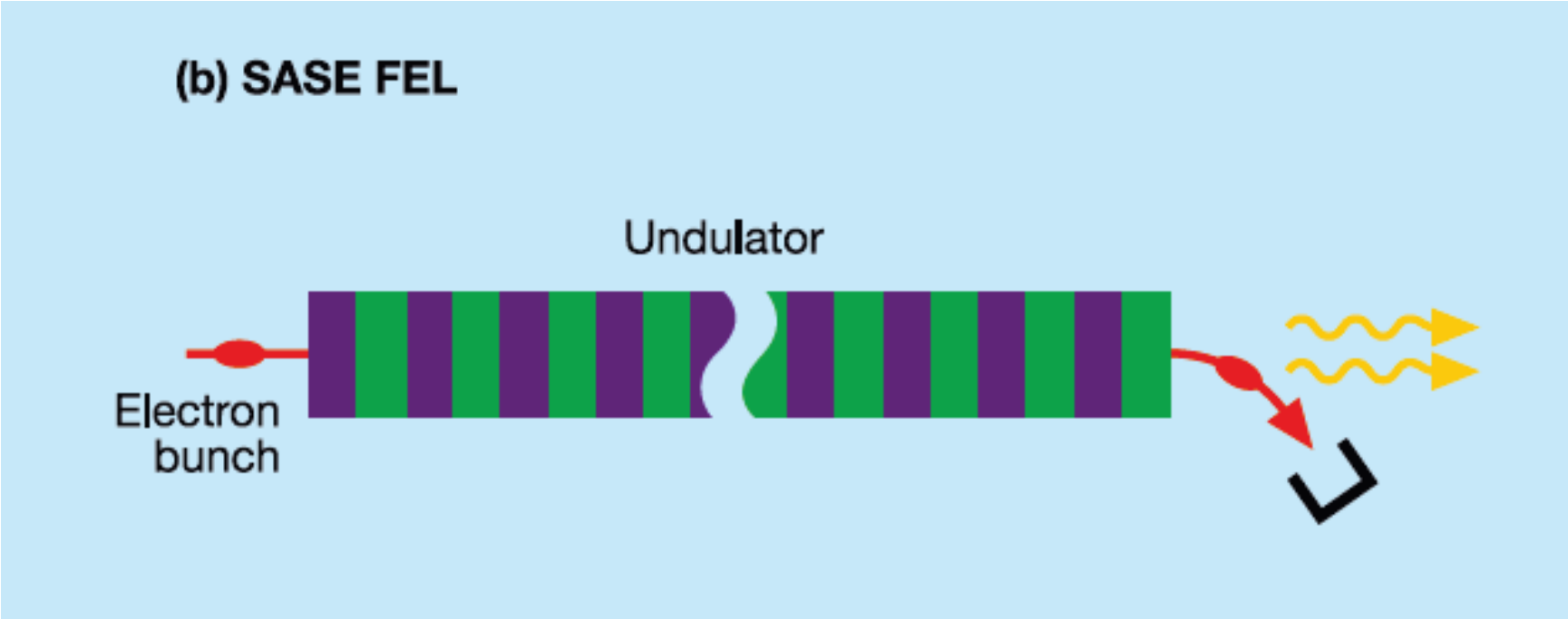
$$\lambda_\ell = \frac{\lambda_u}{2\gamma^2}\left(1 + \frac{K^2}{2}\right)$$

The wavelength of the amplified light coincides with the wavelength of the undulator radiation forward.



The active medium and pumping are carried out by a relativistic electron beam.
Stimulated radiation generates during the transition from a state with a higher kinetic energy to a state with a lower kinetic energy under the action of an already existing wave.

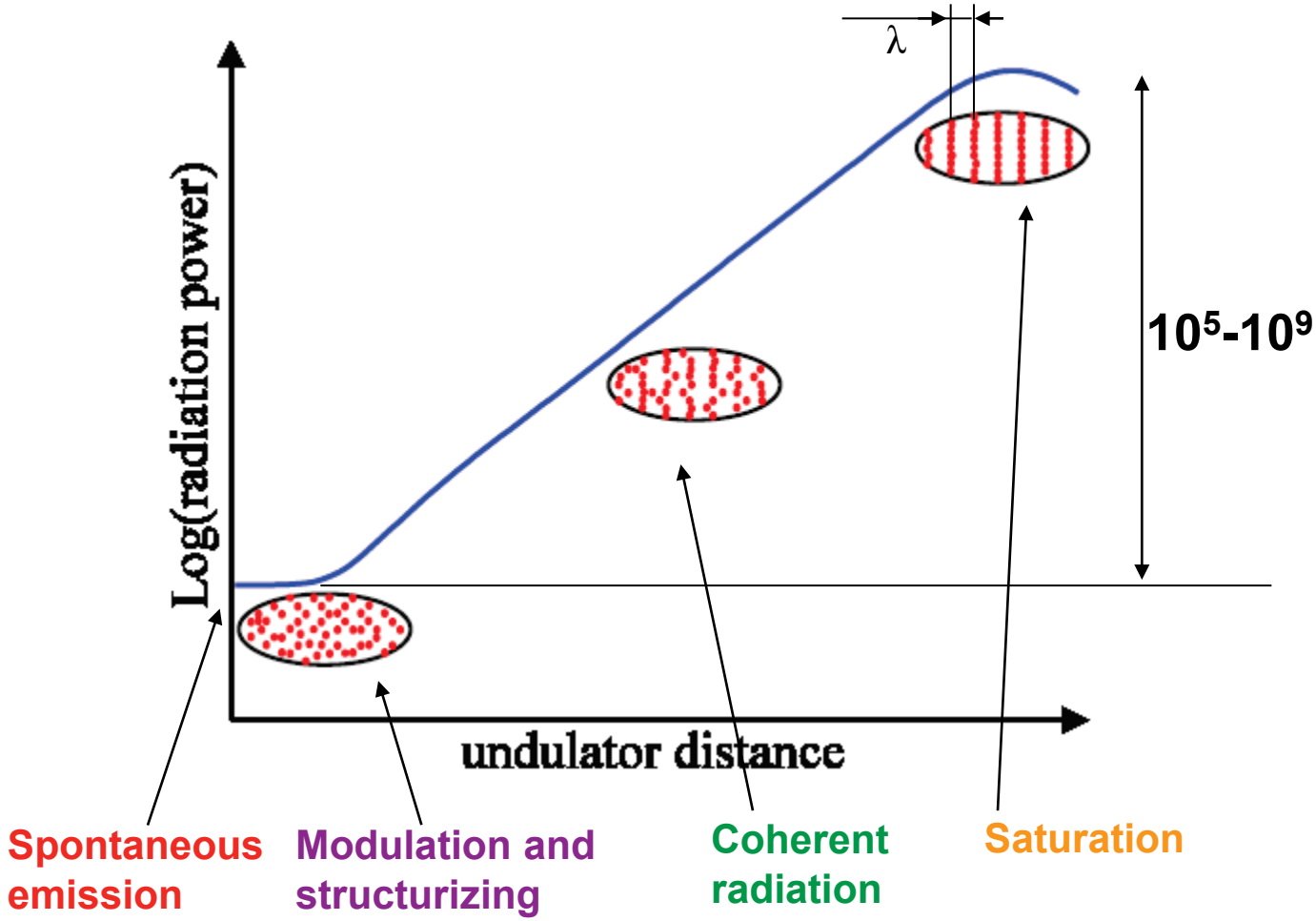
This is a classical, not quantum system!



Self-Amplified Spontaneous Emission - SASE

No appropriate mirrors in VUV and X-ray. The amplification should be done within one passage of the undulator.

Self Amplification of Spontaneous Emission (SASE) regime
(Amplification without optical cavity)

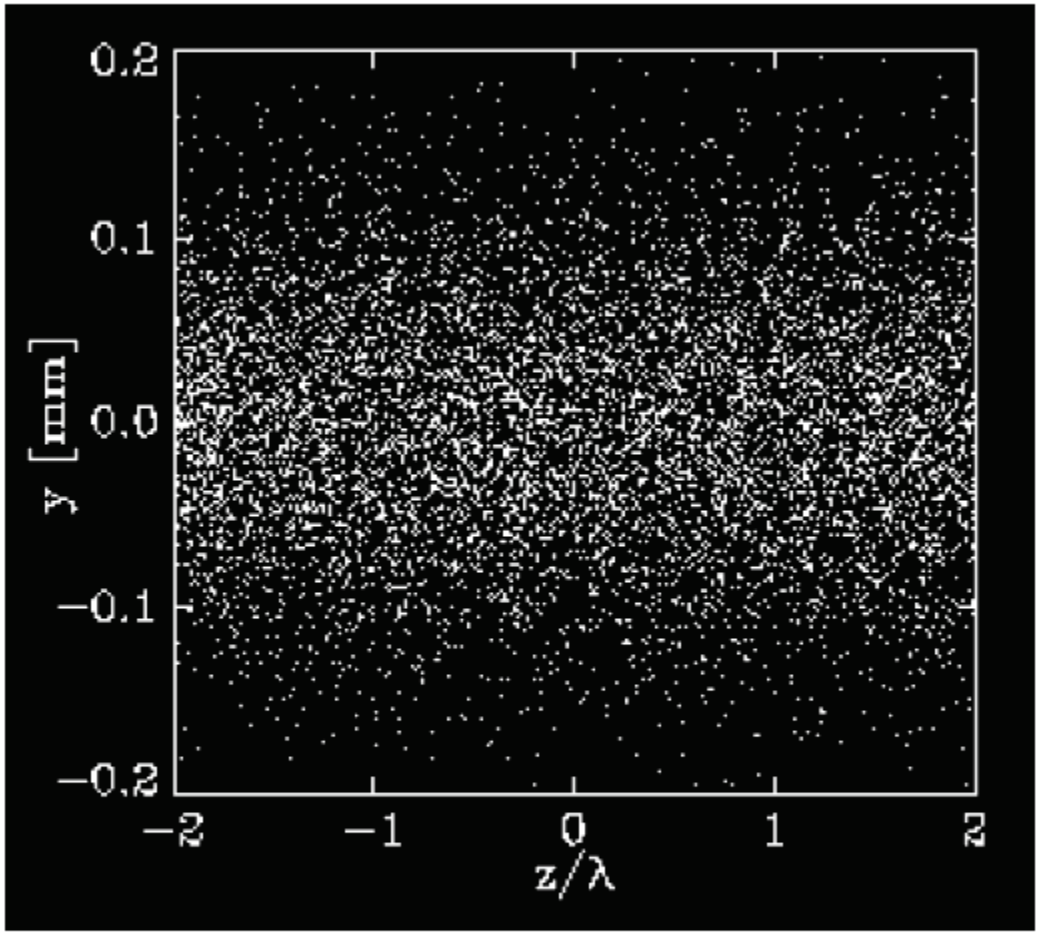


First theoretical predictions:

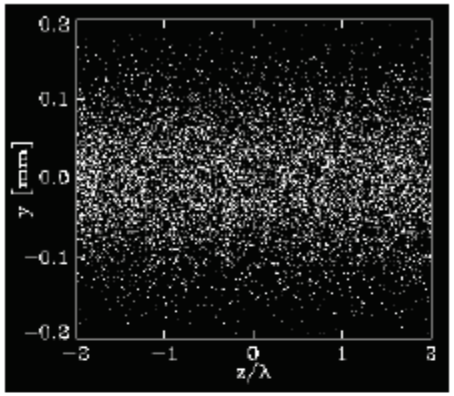
A. Kondratenko and E. Saldin, Part. Accel. 10, 207 (1980).

Y. Derbenev, A. Kondratenko, and E. Saldin, Nucl. Instrum. Methods Phys. Res., Sect. A 193, 415 (1982).

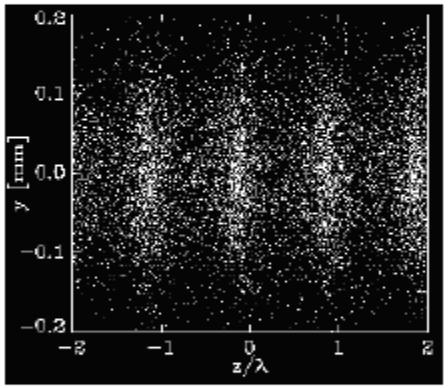
Microbunching through SASE Process



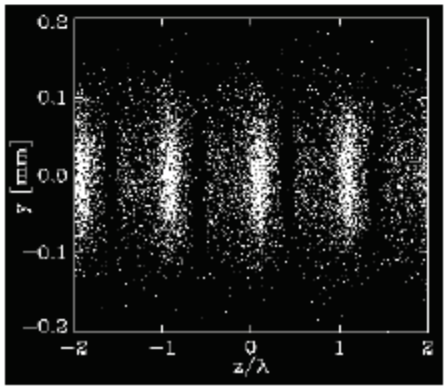
undulator entrance



half-way saturation



full saturation

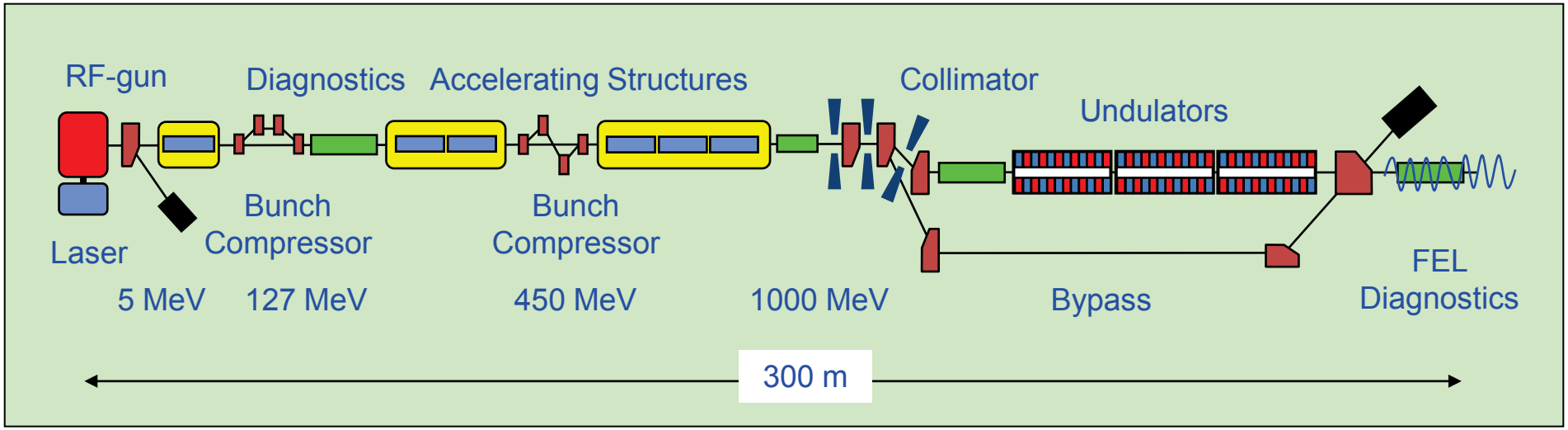


GENESIS **- simulation for TTF parameters**

Courtesy - Sven Reiche (PSI)

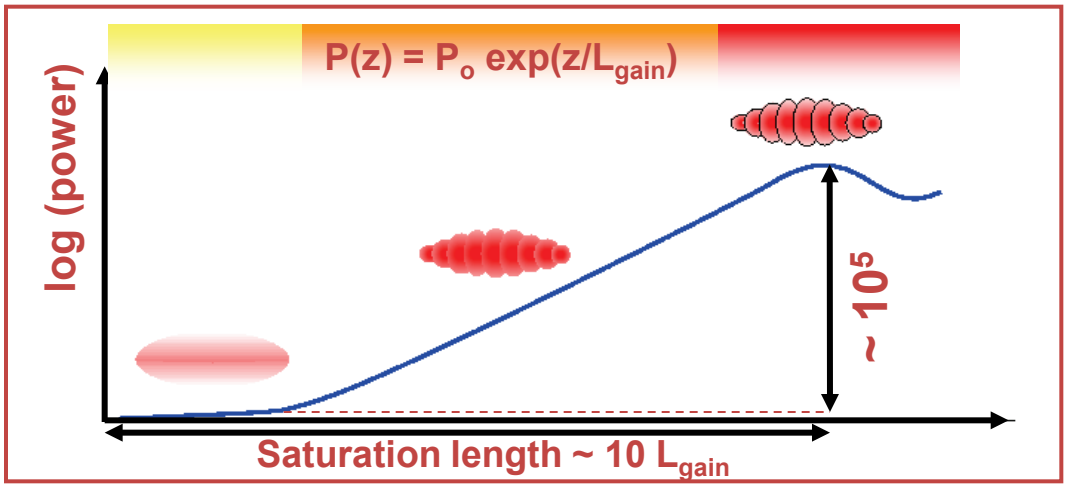
Free Electron LASers in Hamburg

Ackermann et al, Nature Photonics, 1, 336 (2007)

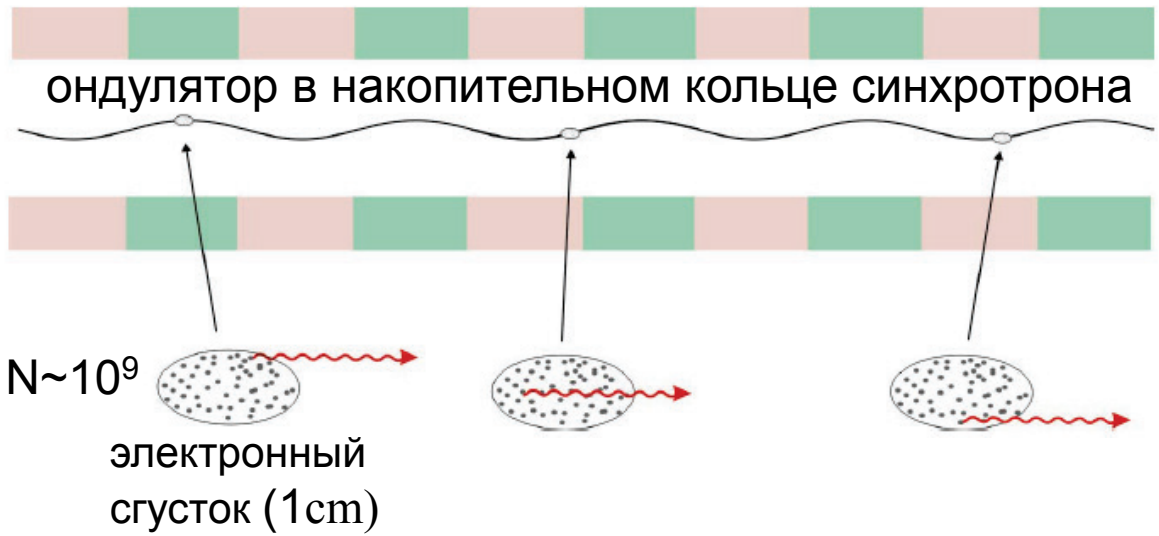


LINAC : 1 GeV
30 м undulator
macrobunches10 Hz
30 bunches with the interval 10^{-6} s

Self Amplification of Spontaneous Emission (SASE) regime

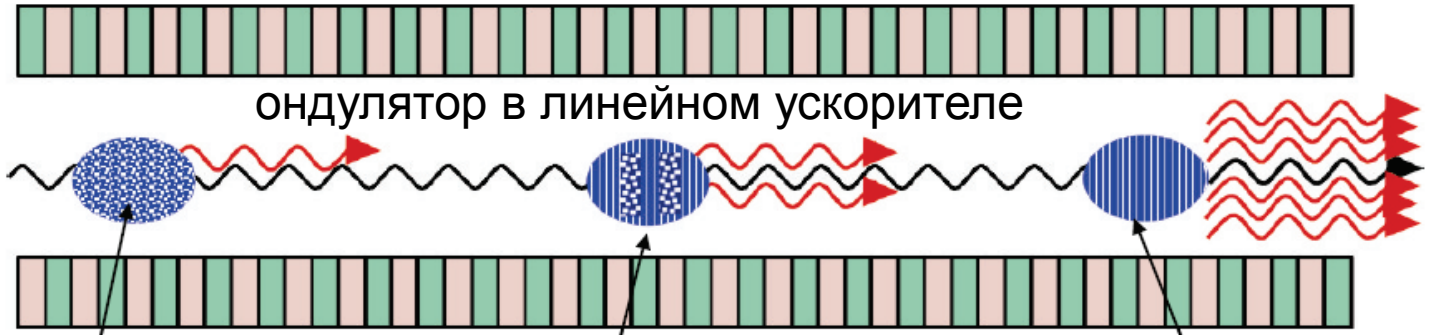


Почему источники 4-го поколения настолько интенсивнее?



Интенсивность ~ N

электроны излучают спонтанно и излучение не когерентно



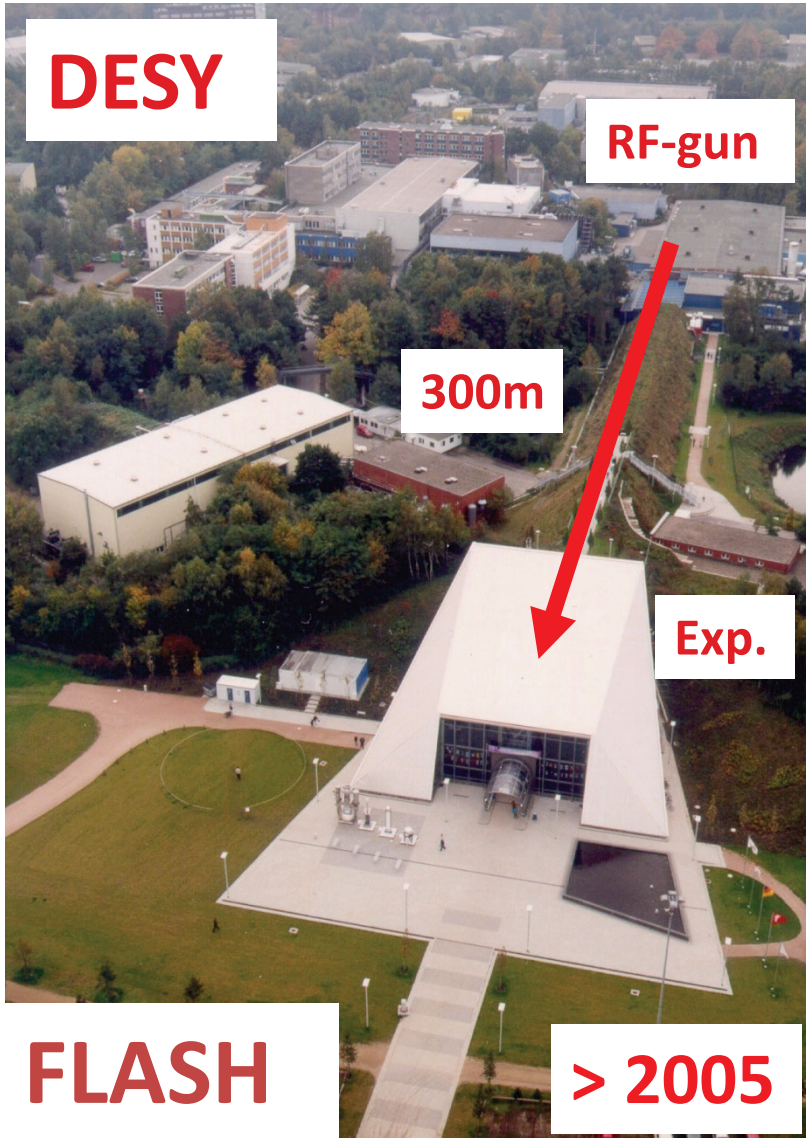
Интенсивность ~ N^2

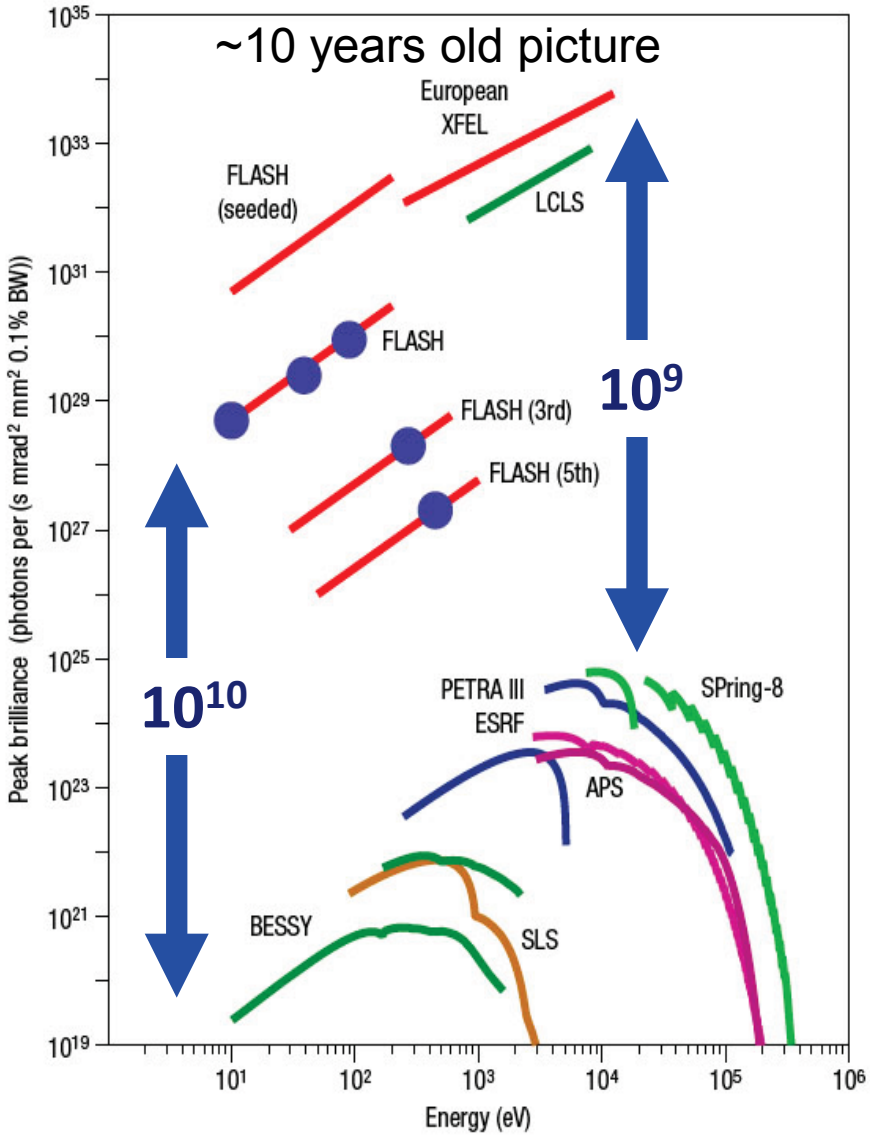
короткий электронный сгусток (1μm)

взаимодействие излучения задней части сгустка с остальным сгустком порождает порядок

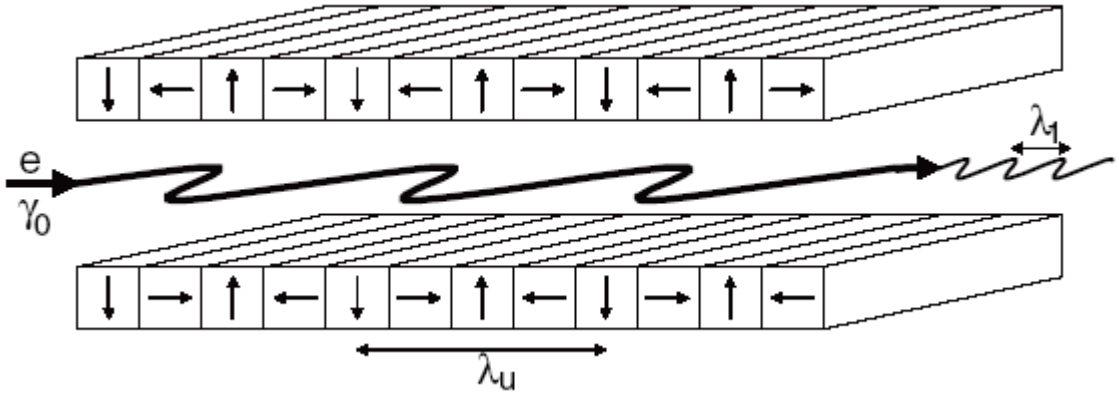
упорядоченные электроны излучают когерентно (в фазе)

Free Electron LASers in Hamburg





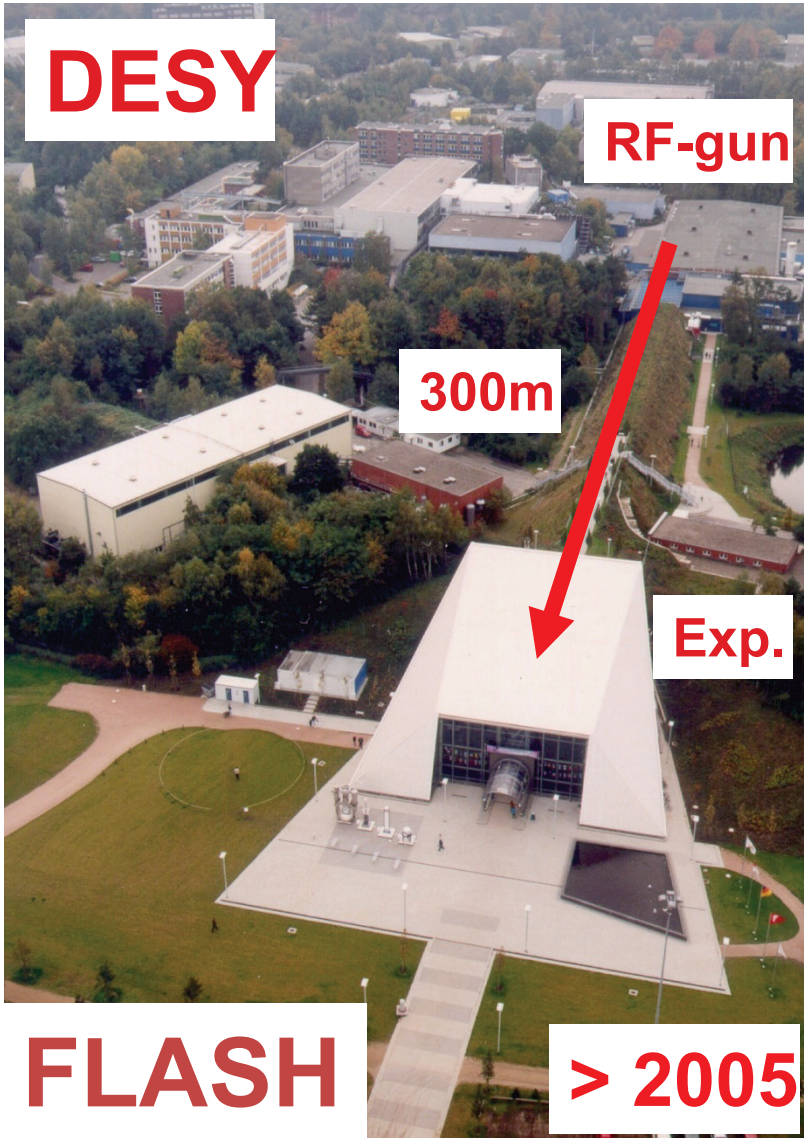
The undulator section in the FLASH tunnel

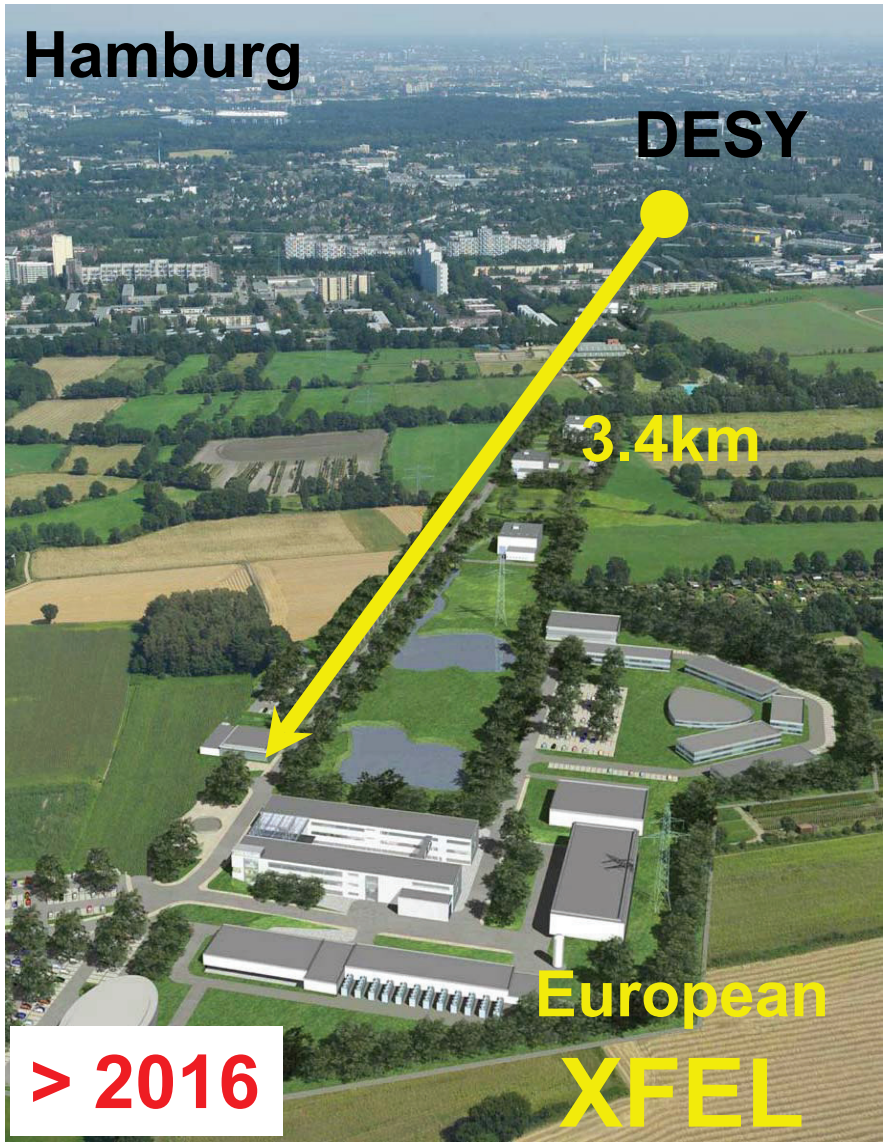


The

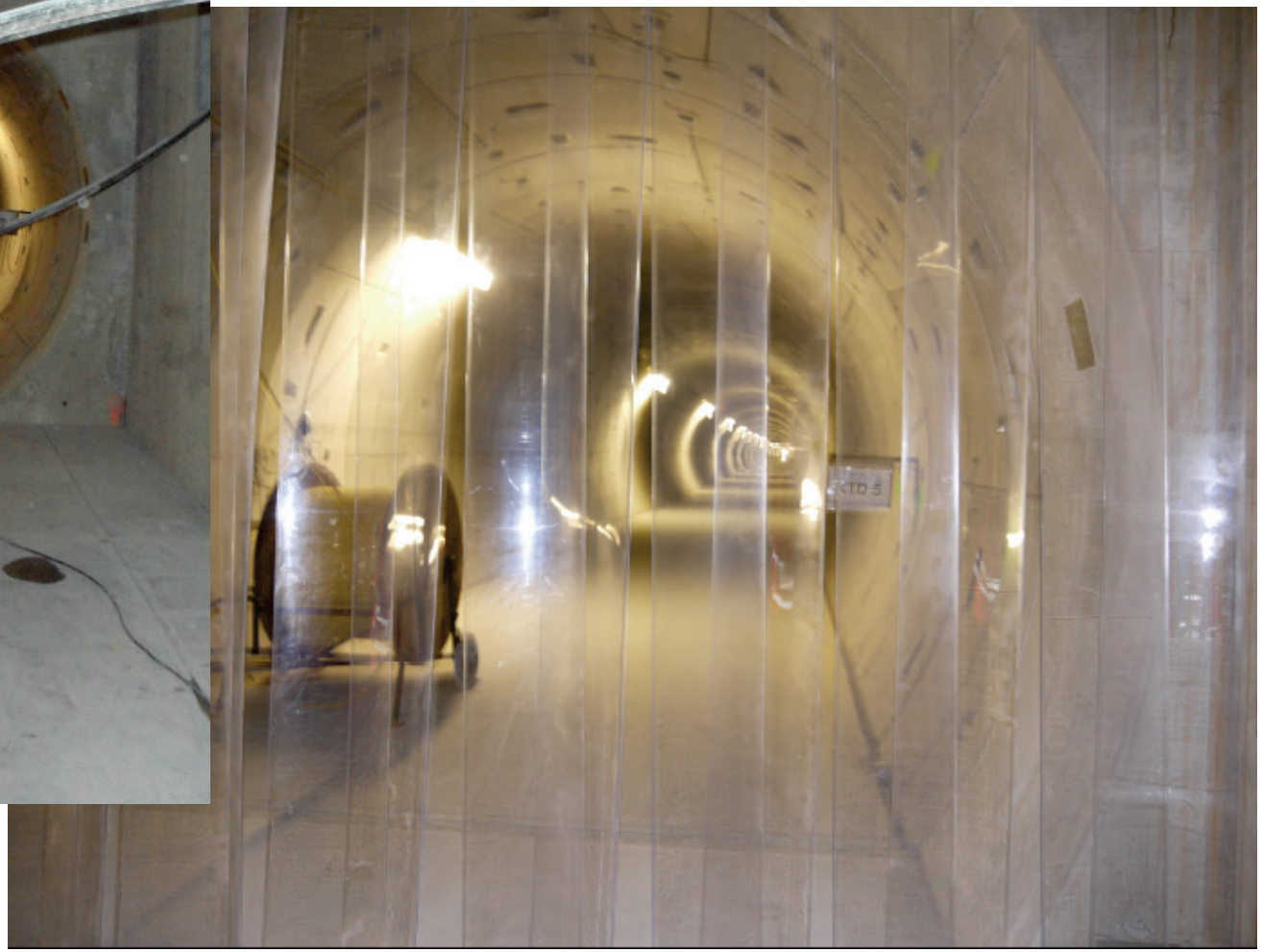
Photo of a FLASH undulator magnet. The gap height is 12 mm, the period is λ_u = 27 mm and the peak magnetic field is B_0 = 0.47 T.

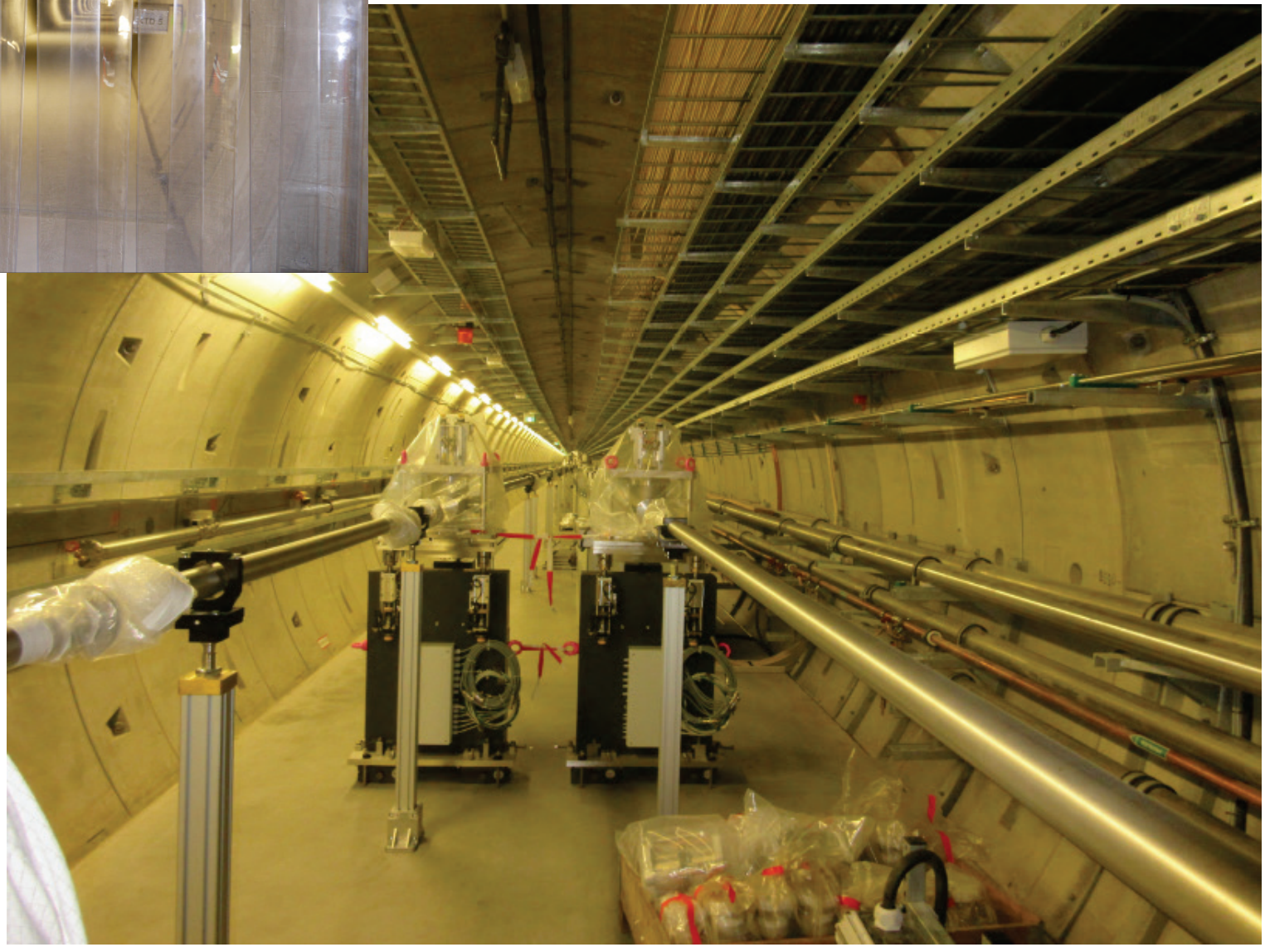
Free Electron LASers in Hamburg

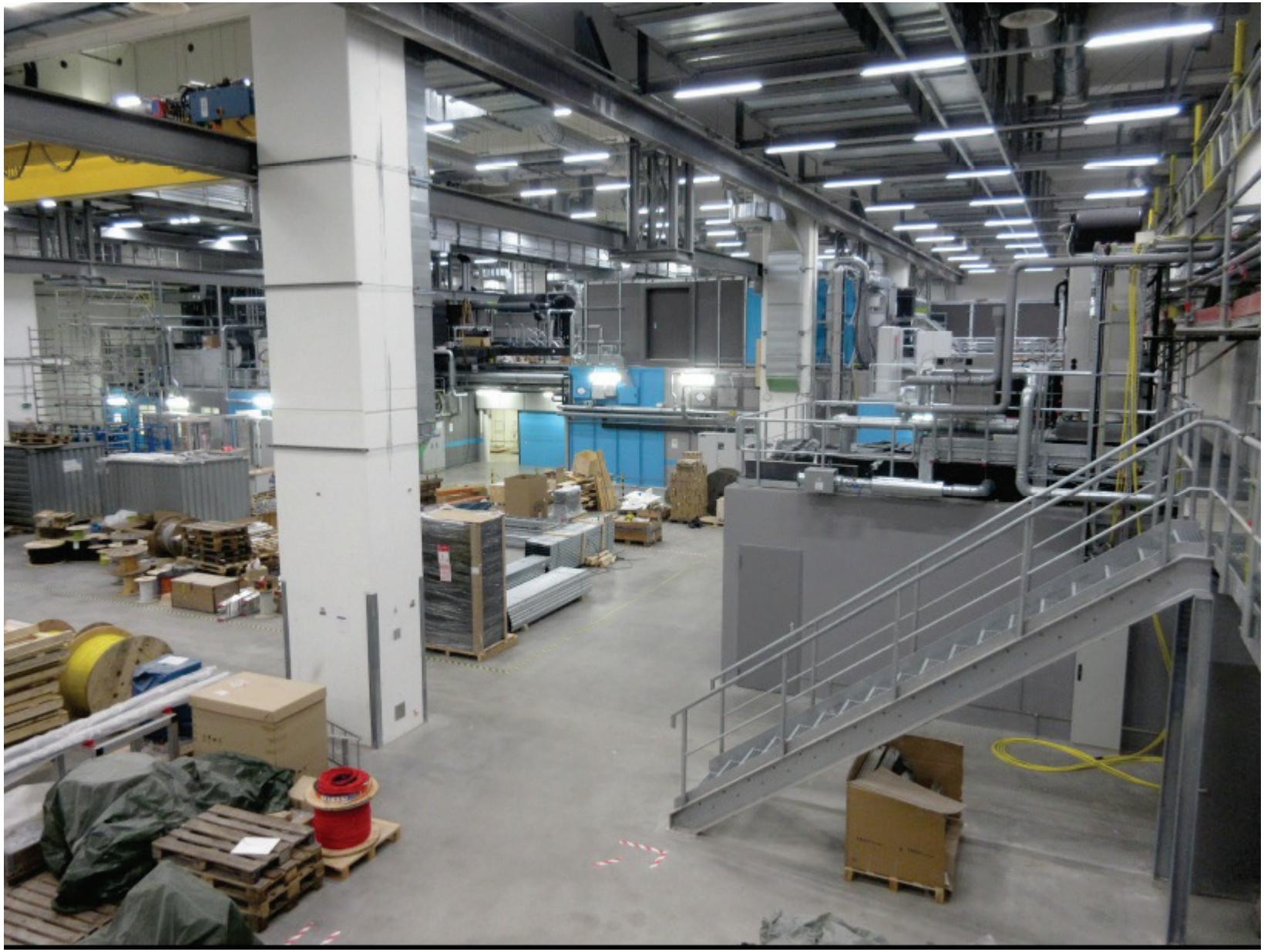




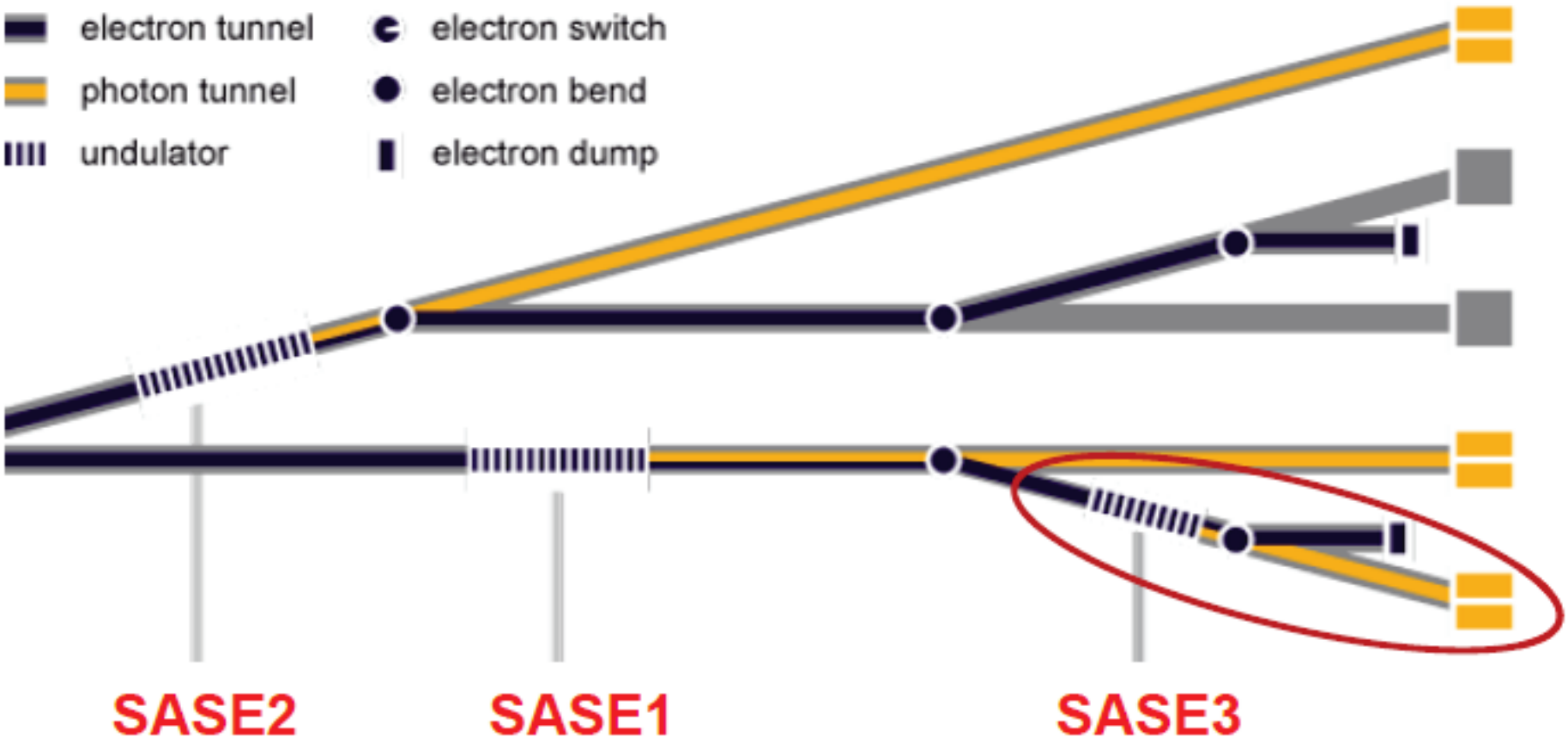
Finishing the tunnels, 6 June 2012

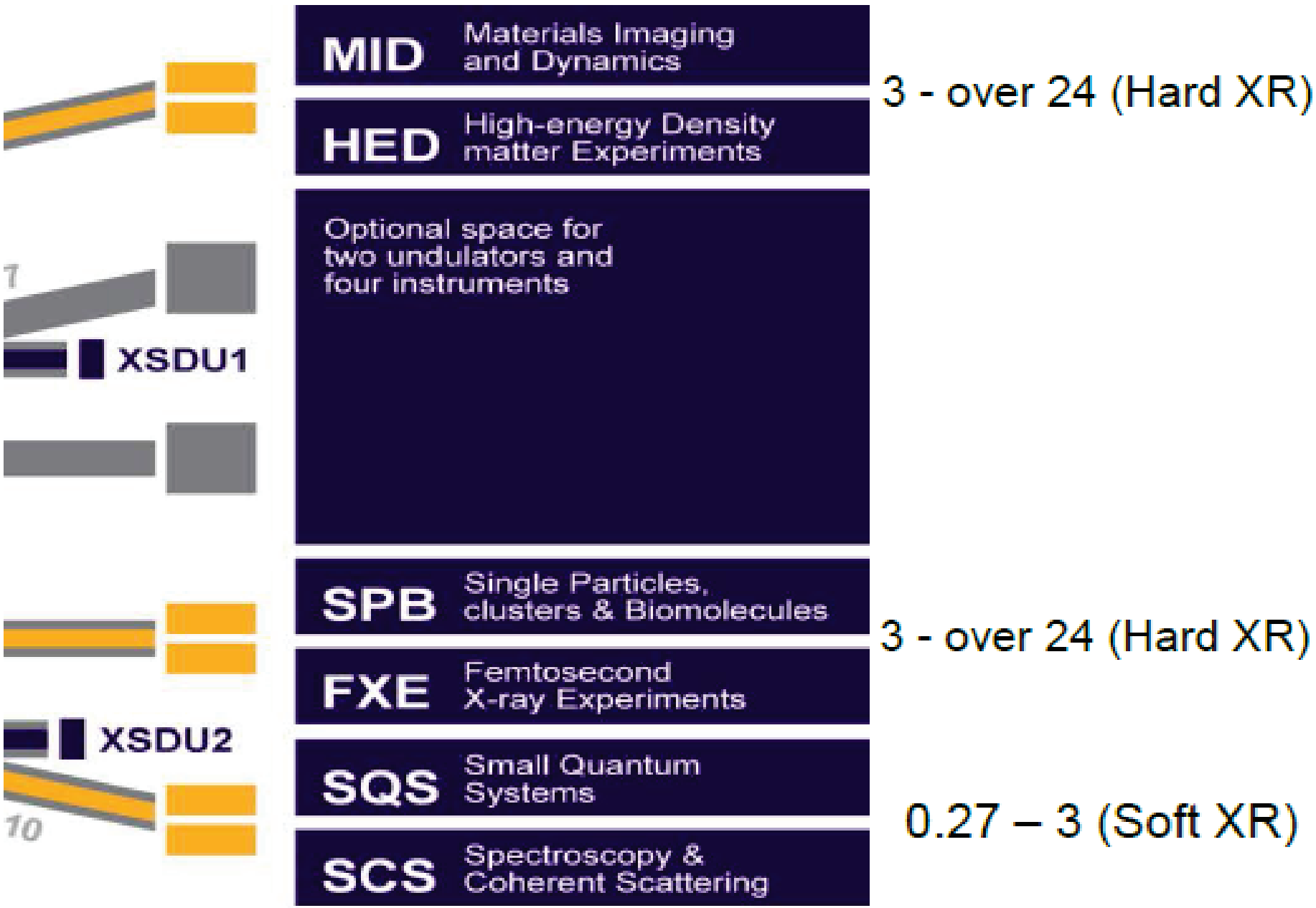

KTD 5



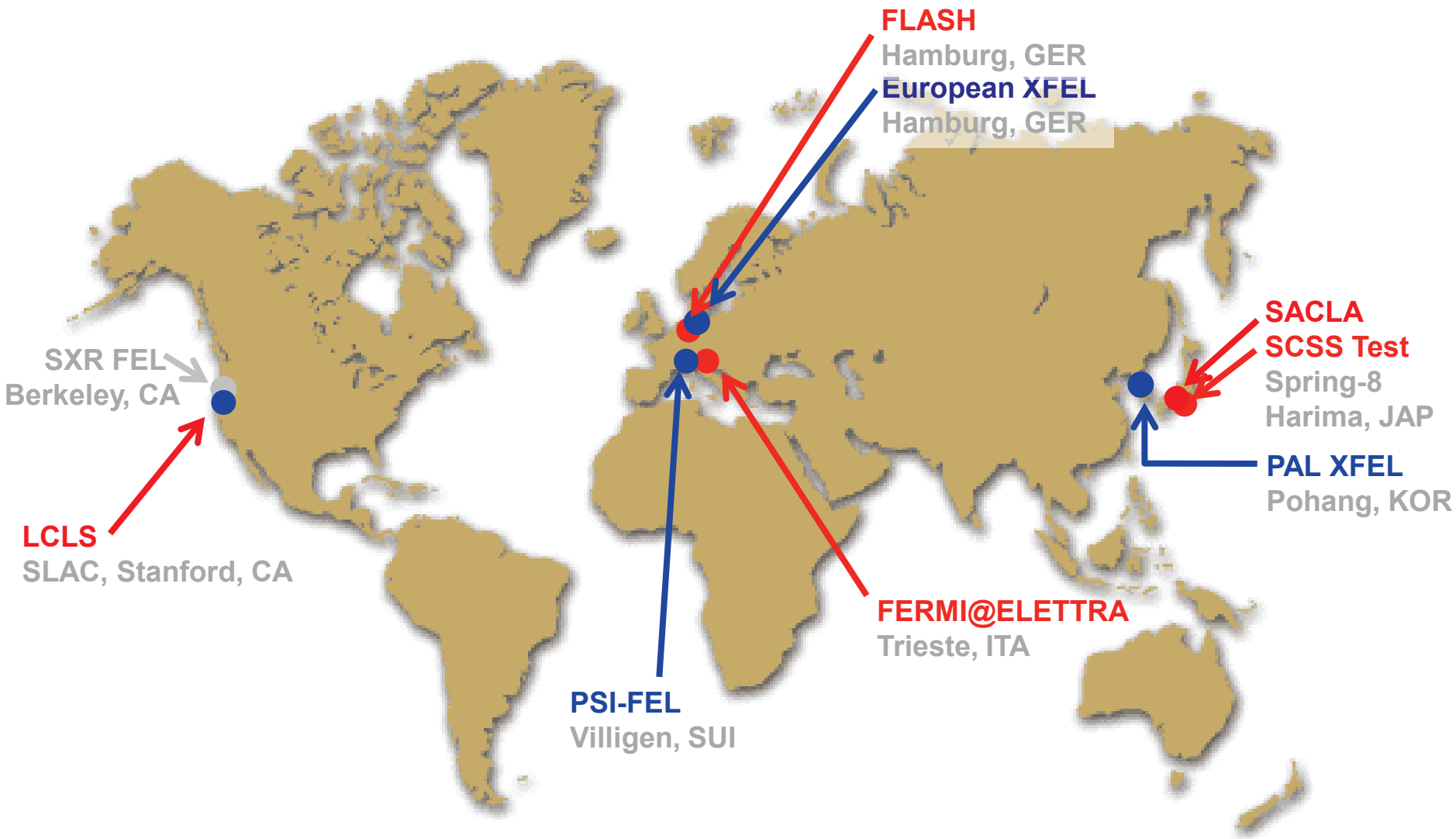


Serguei Molodtsov, February 12, 2018

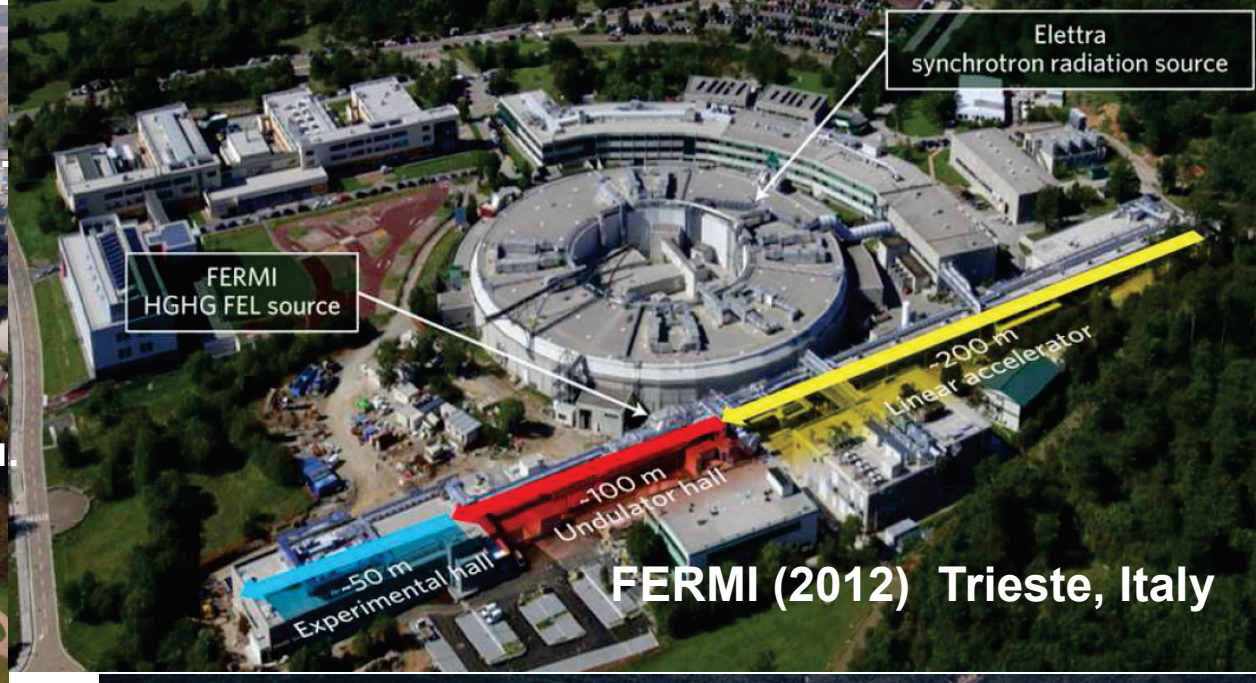



MID
Materials Imaging and Dynamics
HED
High-energy Density matter Experiments
3 - over 24 (Hard XR)
Optional space for two undulators and four instruments
1
XSDU1
SPB
Single Particles, clusters & Biomolecules
FXE
Femtosecond X-ray Experiments
3 - over 24 (Hard XR)
XSDU2
SQS
Small Quantum Systems
10
SCS
Spectroscopy & Coherent Scattering
0.27 – 3 (Soft XR)

XFELs in the world



FLASH (2006),
Hamburg
Источ.
Эксп.


Elettra
synchrotron radiation source
FERMI
HGHG FEL source
200 m
Linear accelerator
~100 m
Undulator hall
~50 m
Experimental hall
FERMI (2012) Trieste, Italy

LCLS (2009) Stanford

SPring-8
SACLA
SACLA(2011), Japan

End of lecture 7