Material study of Chernobyl “lava” and “hot” particles

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Contents

- Background: fuel inside and outside ruins of 4th Unit
- KRI collection of Chernobyl samples
- Phase and chemical composition
- Mechanical self-destruction of “lava” and hot particles
- Chemical alteration (interaction with natural environment)
- Summary of results and applications

Background (1)

(basic papers)

1. **Chernobyl: The Soviet Report**. Nuclear News, Vol.29, #13, Oct. 1986.

2. Боровой А.А. **Внутри и вне «Саркофага»**. Препринт КЭ ИАЭ, Чернобыль 1990. – *Borovoy A.A.* ***Inside and outside "Sarcophagus"****. Issue of CE IAE, Chernobyl 1990 (in Russian)*.

3. Лебедев И.А., Мясоедов Б.Ф., Павлоцкая Ф.И., Френкель В.Я. **Содержание плутония в почвах европейской части страны после аварии на Чернобыльской АЭС**. Атомная Энергия, т.72, вып.6, июнь 1992, с. 593-598. – *Lebedev I.A., Myasoedov B.F., Pavlotskaya F.I., Frenkel V.Ya.* ***Plutonium contents in the soils of European part of USSR after accident at Chernobyl NPP****. Atomic Energy, Vol.72, #6, June 1992, pp. 593-598 (in Russian).*

4. Киселев А.Н., Ненаглядов А.Ю., Сурин А.И., Чечеров К.П. **Экспериментальные исследования лавообразных топливосодержащих масс (ТСМ) на 4-м блоке ЧАЭС (по результатам исследований 1986-1991 годах)**. Препринт ИАЭ, Москва 1992 – *Kiselev A.N., Nenaglyadov A.Yu., Surin A.I., Checherov K.P.* ***Experimental study of lava-like fuel containing masses (FCM) at 4th Unit of ChNPP (based on results obtained in 1986-1991)****. Issue of IAE, Moscow 1992 (in Russian).*

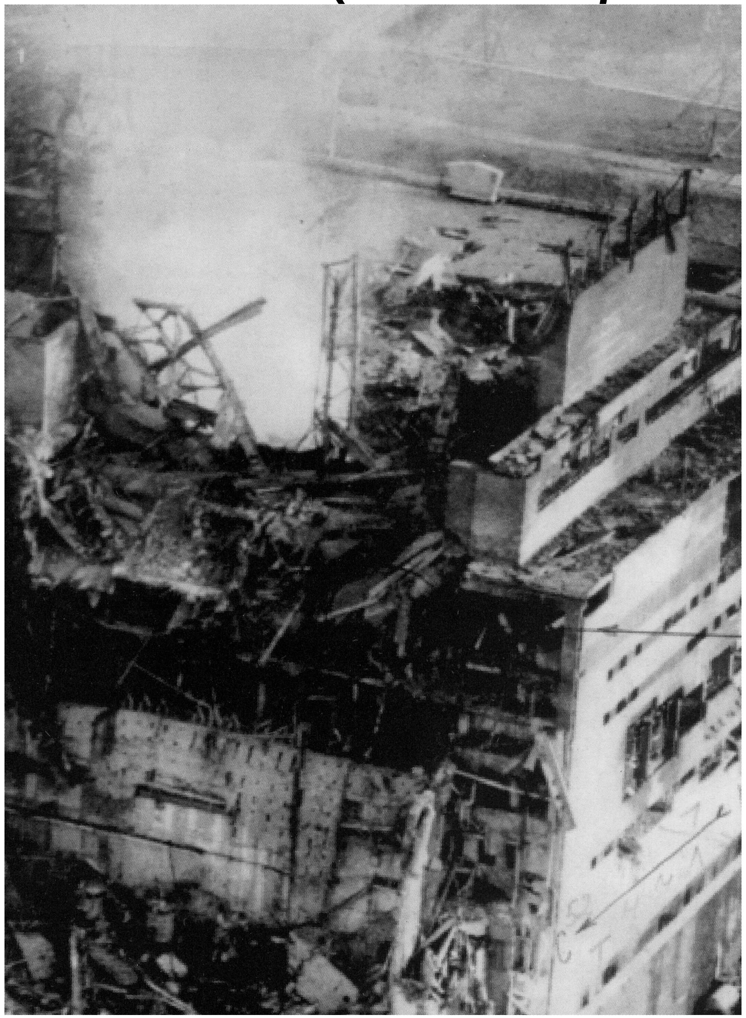
5. Burakov B.E., Anderson E.B., Shabalev S.I., Strykanova E.E., Ushakov S.V., Trotabas M., Blanc J-Y., Winter P., Duco J. **The Behaviour of Nuclear Fuel in First Days of the Chernobyl Accident**. *Mat. Res. Soc. Symp. Proc. Scientific Basis for Nuclear Waste Management XX, Vol.465, 1997,1297-1308.*

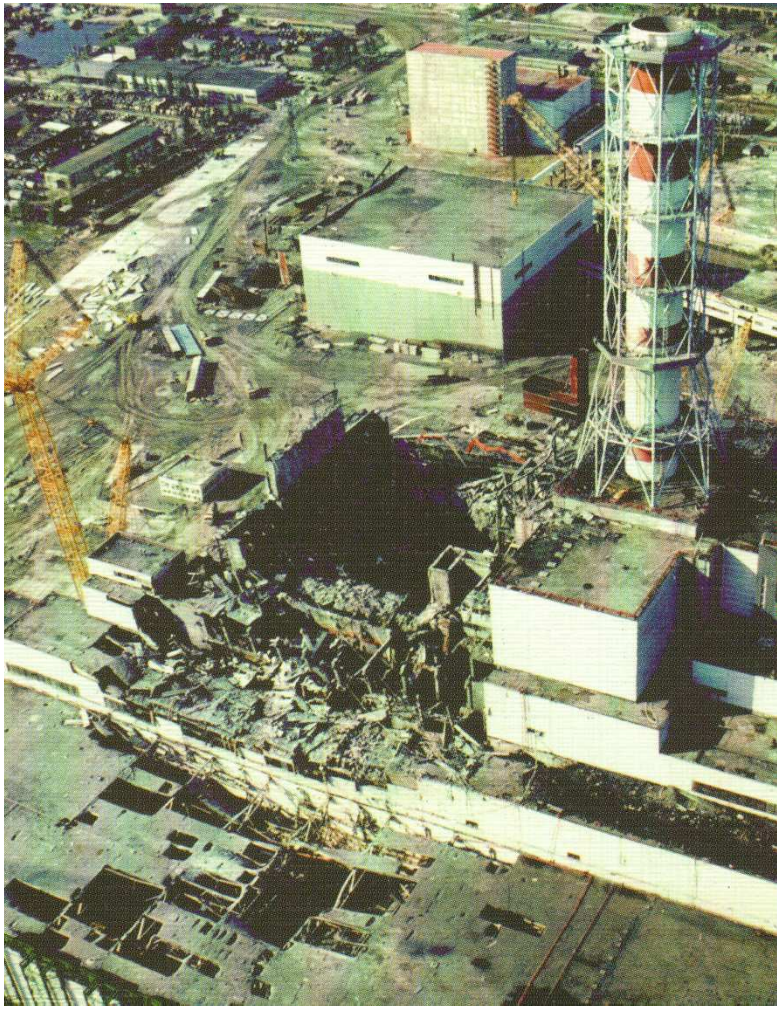
6. Burakov B.E., Anderson E.B., Strykanova E.E. **Secondary Uranium Minerals on the Surface of Chernobyl "Lava"**. *Mat. Res. Soc. Symp. Proceedings Scientific Basis for Nuclear Waste Management XX, Vol.465, 1997, 1309-1311.*

7. Burakov B.E., Shabalev S.I., Anderson E.B. **Principal Features of Chernobyl Hot Particles: Phase, Chemical and Radionuclide Compositions**. In S. Barany, Ed. Role of Interfaces in Environmental Protection, Kluwer Academic Publishers, 145-151, NATO Science Series, Earth and Environmental Sciences, Vol. 24. 2003.

Background (2)

(after explosion – first days)





Background (3)
(general information)

- About 3.5 wt.% spent fuel was ejected from the core [1,2]
- About 50 kg Pu was spread in European part of USSR (it means 6 wt.% of total Pu of 4th Unit) [3]
- More than 90 wt.% fuel is inside "Shelter" ("Sarcophagus") [2]
- At least 11-15 wt.% fuel (inside "Shelter") is related to Chernobyl "lava" [4]

Background (5)

(basic glossary)

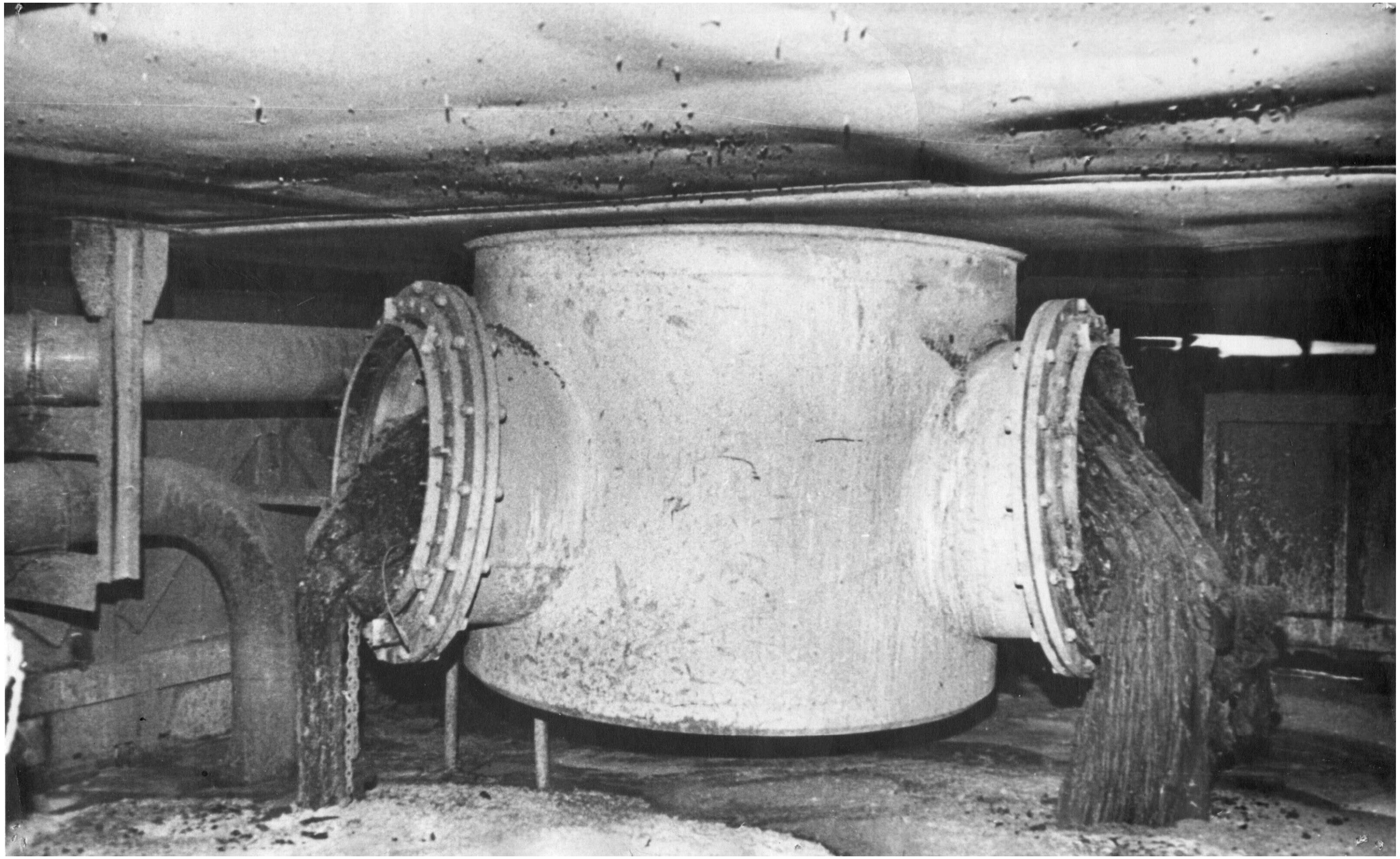
- Chernobyl “lava” or “fuel-containing masses (FCM)” – it is a result of high-temperature interaction between destroyed fuel cladding and silicate materials (concrete, sand, serpentinite)
- Chernobyl “hot” particles – are highly radioactive solid particles from less than 1 µm to hundreds µm in size
- *Note: Chernobyl hot particles usually contain U but not always!*

Background (6)

(lava-stream "Elephant foot", 1990 [2])

Background (7)

(lava in steam discharge corridor, 1990 [2])



Background (8)

(general information)

- Initial mechanical durability of Chernobyl “lava” was very high. Machine-gun AK-47 was used to collect first samples of “Elephant foot” in 1987 [2]
- Dramatic decrease and even self-destruction of lava matrices was observed in 1990 [2]
- Chemical alteration of “lava” matrices was observed in 1990 – formation of secondary uranium minerals (uranyl-phases) [6]

Background (9)

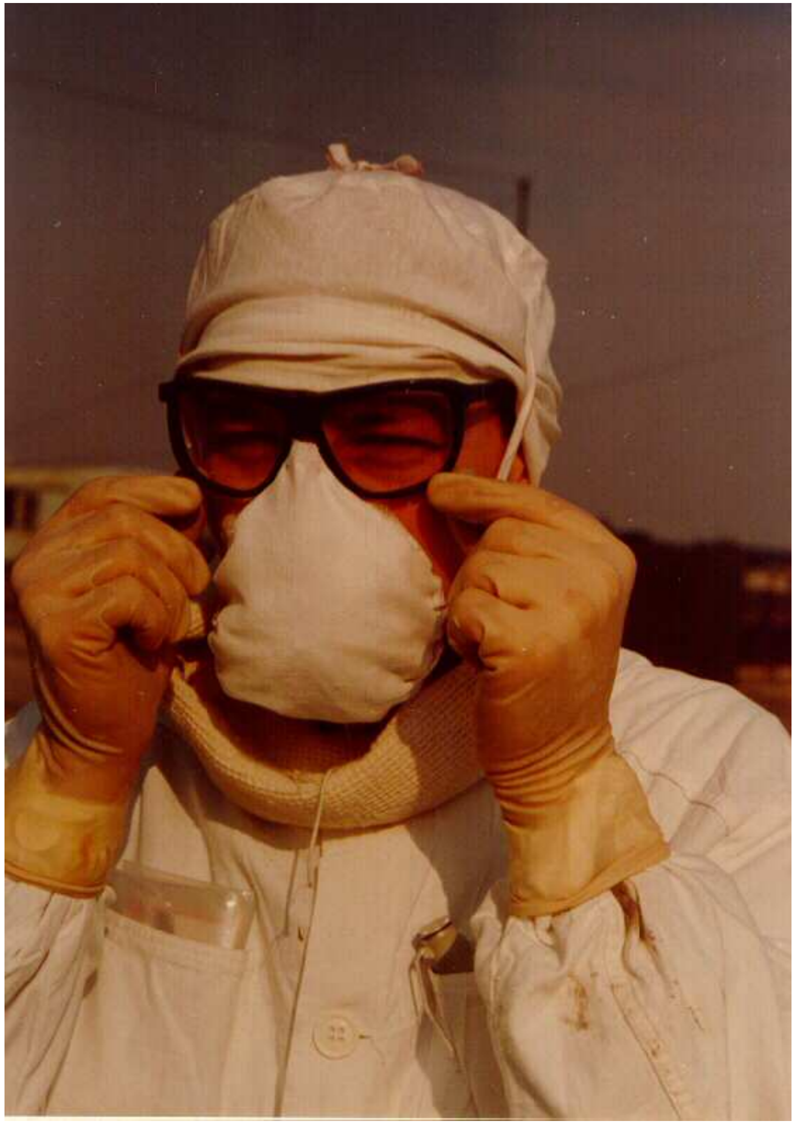
(New-formed yellow minerals at the surface of Chernobyl "lava", 1991)

Samples of Chernobyl “lava”

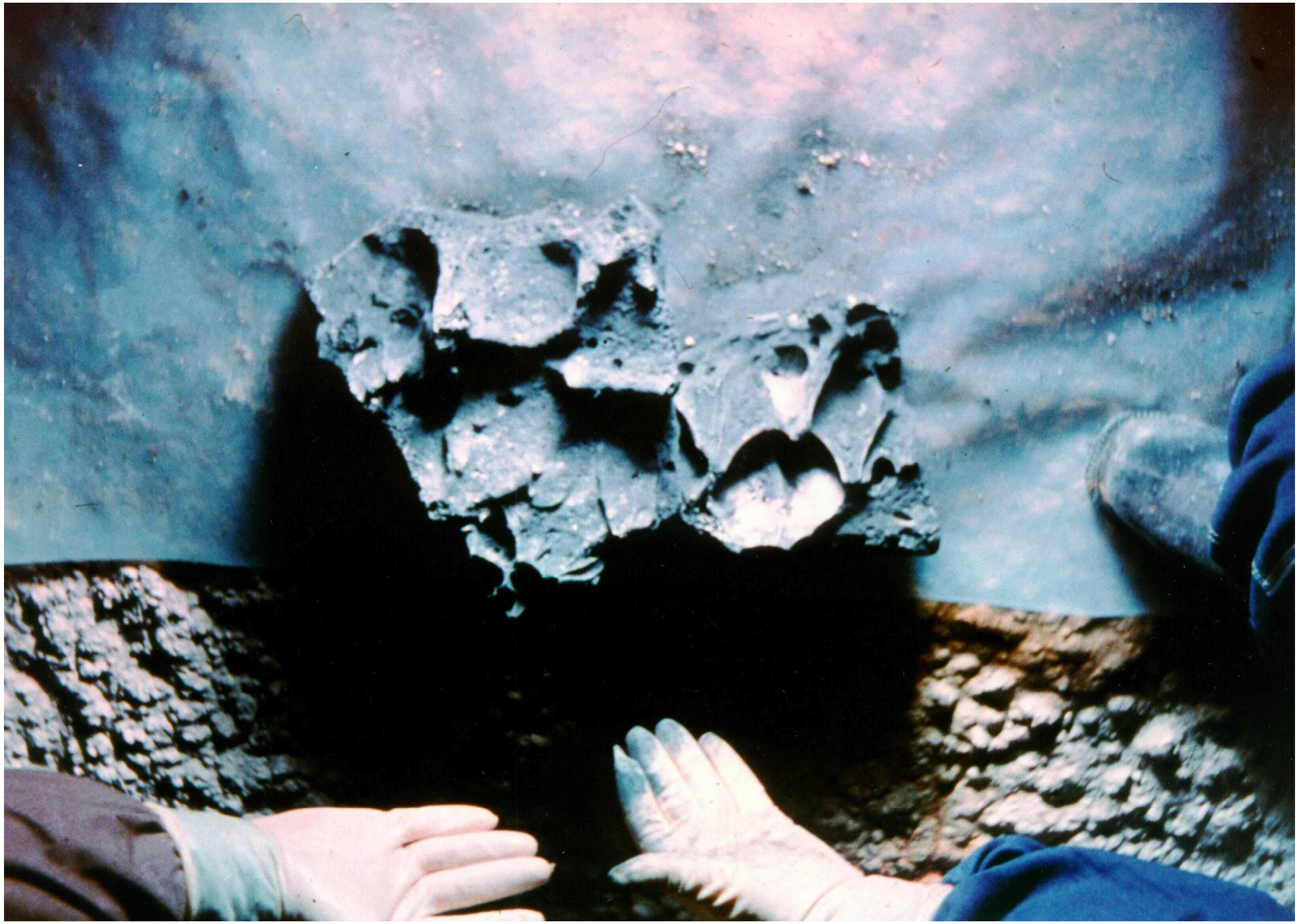
collection of V.G. Khlopin Radium Institute

- Most samples of “lava” were collected at different locations in 1990 (*using hands and hammer only*)
- Some pieces of “lava” (dozens cubic cm each) were partially dissolved in HF in order to extract inclusions of different uranium-bearing phases

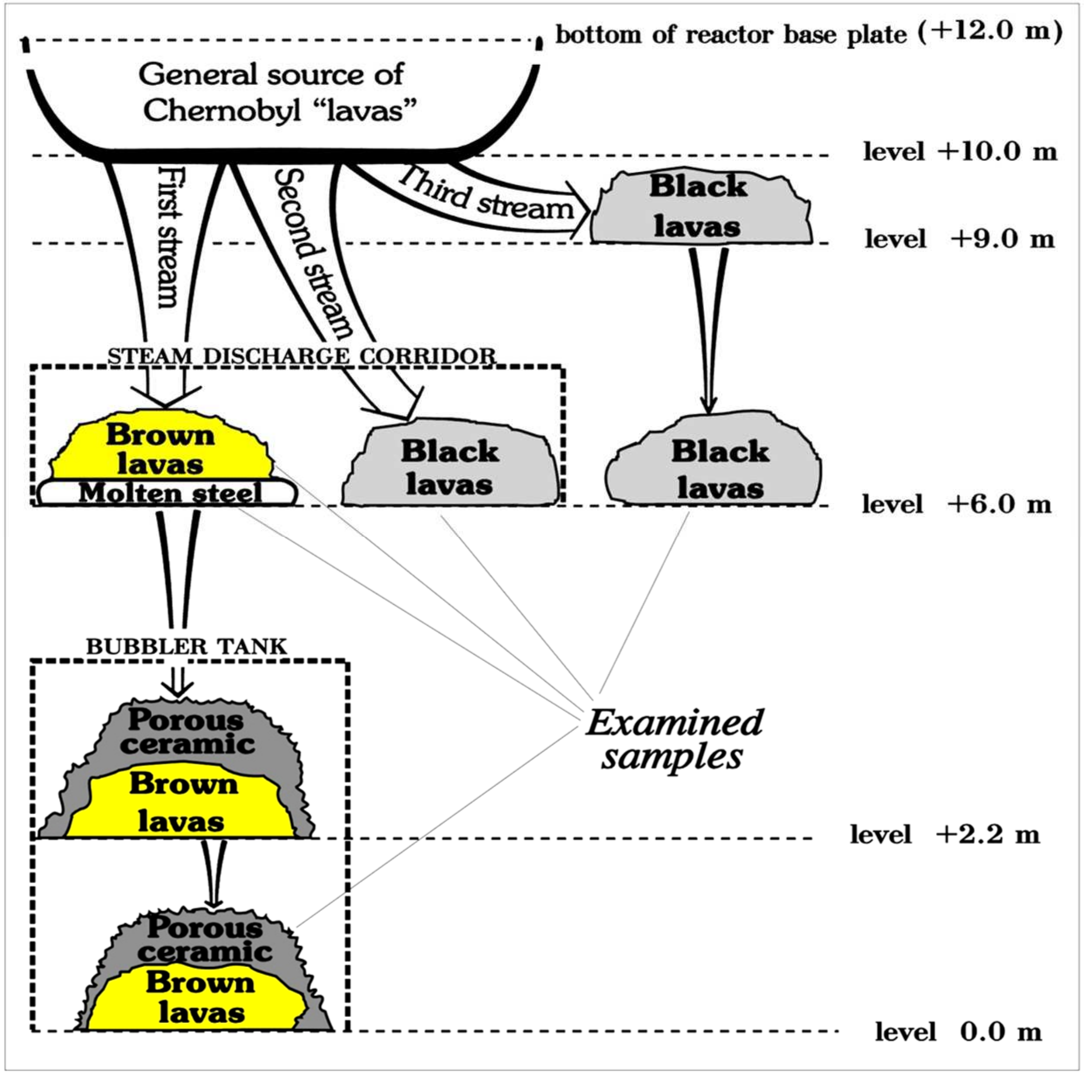
Before going inside “Sarcophagus”, 1990



Inside “Sarcophagus” – packing “lava” sample for shipment to Leningrad, 1990



Map of KRI sampling [5]

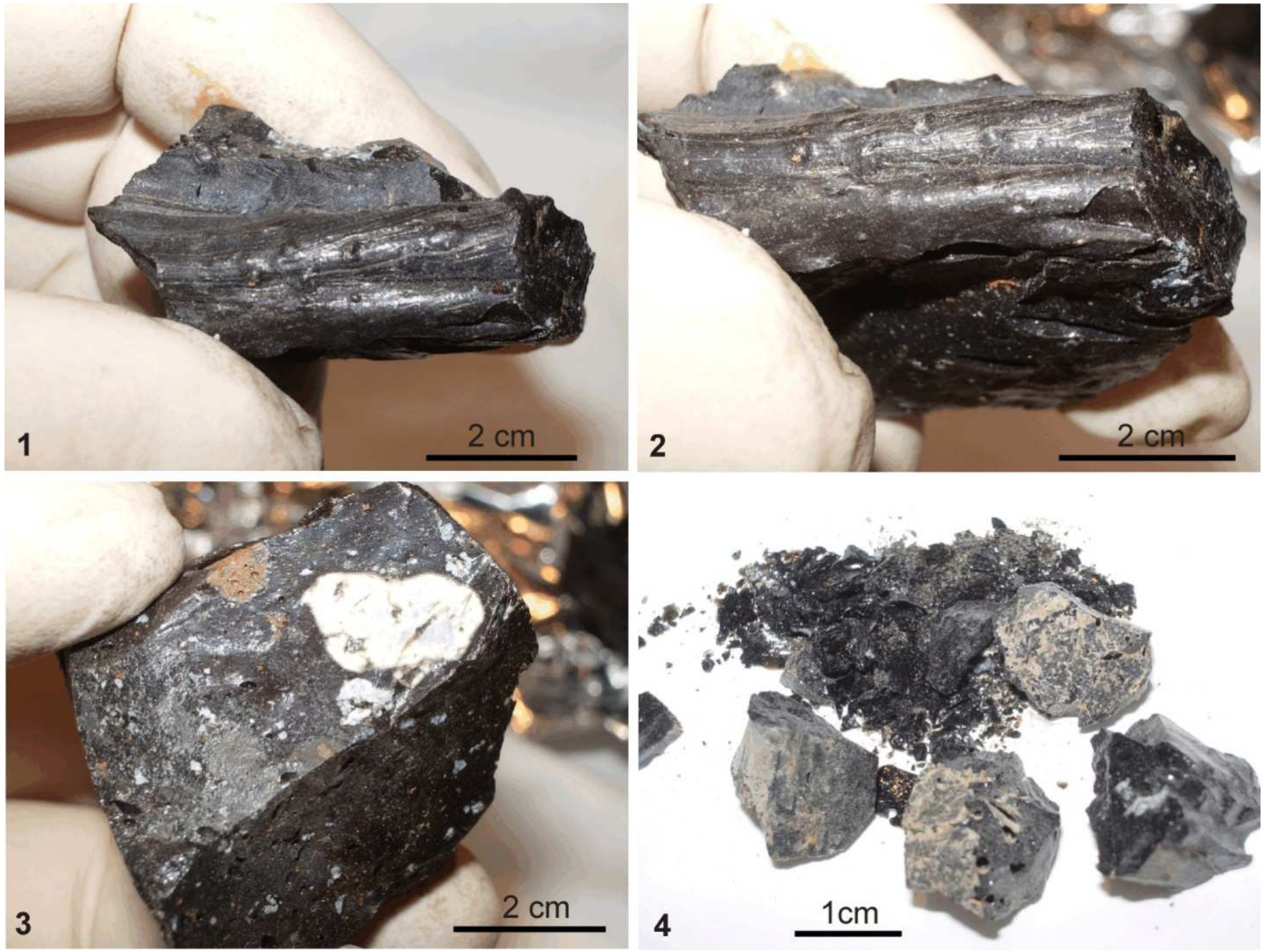


Samples of black “lava” – “Elephant foot”

collection of V.G. Khlopin Radium Institute

samples were collected in 1990 and stored at KRI under laboratory conditions

partial self-destruction was observed for some pieces in 2011 (picture 4)



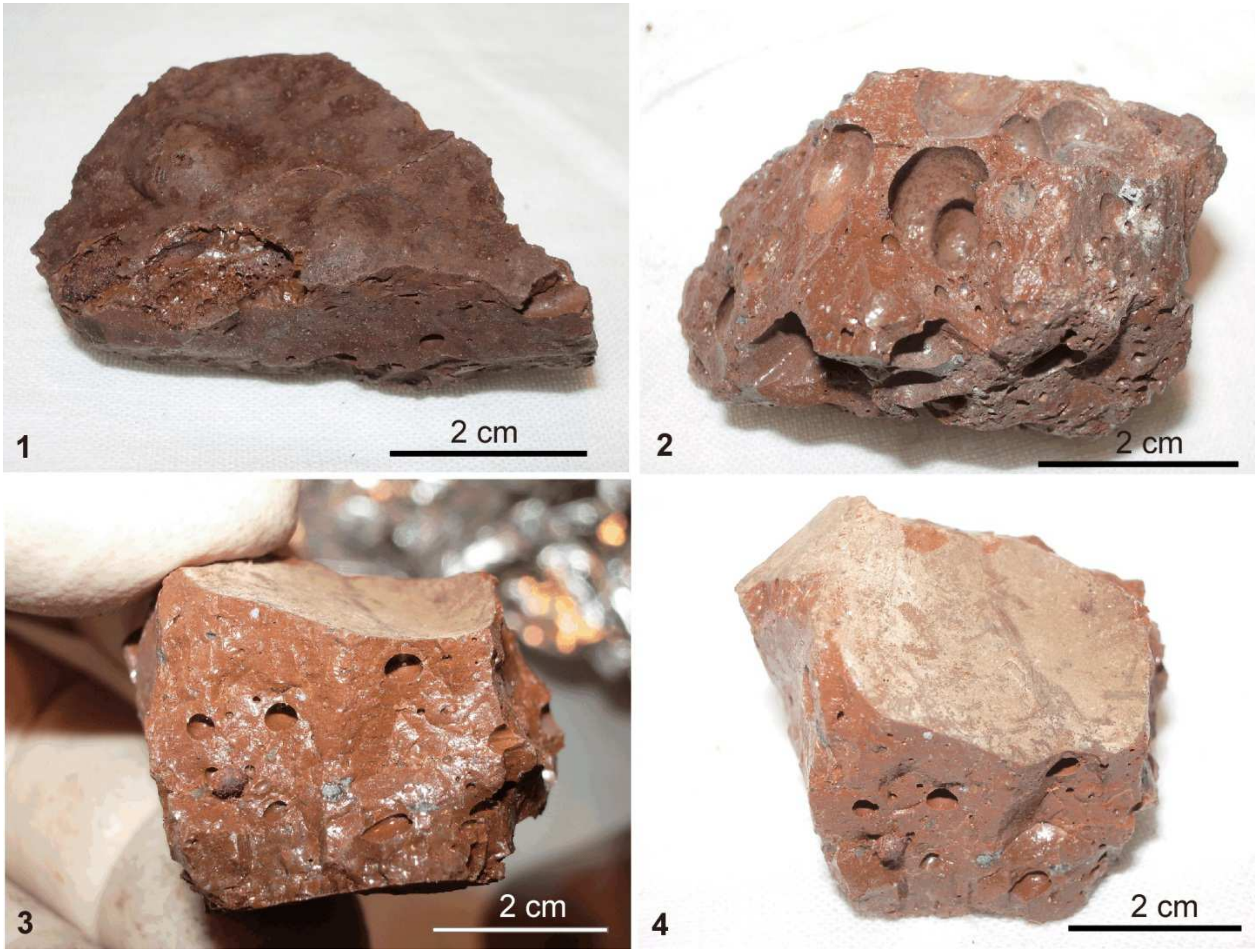
Burakov B.E. Material study of Chernobyl “lava” and “hot” particles
International Experts’ Meeting on Decommissioning and Remediation after a Nuclear Accident
Vienna, Austria, 28 January – 1 February 2013

Samples of brown "lava" – from steam discharge corridor

collection of V.G. Khlopin Radium Institute

samples were collected in 1990 and stored at KRI under laboratory conditions

pictures were taken in 2011



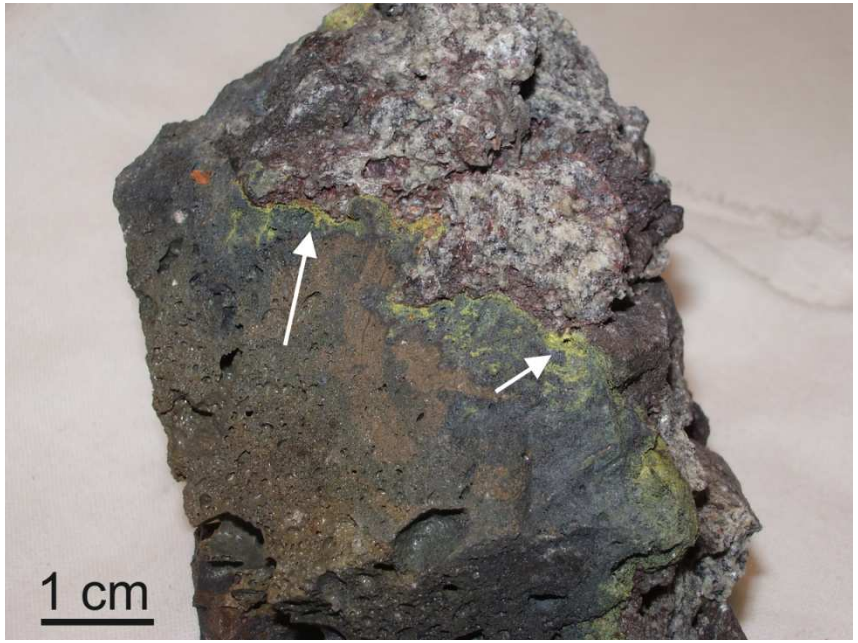
Samples of brown “lava” – from room #305

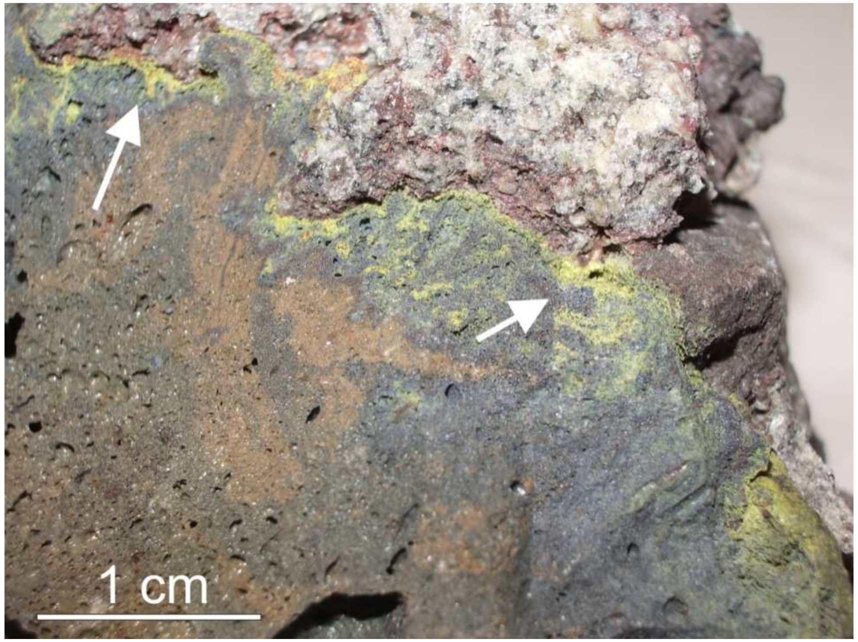
collection of V.G. Khlopin Radium Institute

sample was collected in 1990 and stored at KRI under laboratory conditions

pictures were taken in 2011

formation of secondary uranium minerals under laboratory conditions ?





Samples of Chernobyl hot particles

collection of V.G. Khlopin Radium Institute

- Some particles were separated from soil samples collected near 4th Unit in 1986
- Most particles were separated from soil samples collected at Western Plume (0.5-12 km from 4th Unit) in 1990-1991
- Some fuel fragments and particles were collected inside "Sarcophagus" in 1990

Collecting hot particles, 1990

Separation of hot particles from soil sample [7]

at V.G. Khlopin Radium Institute – using collimated beta-gamma-detector

Methods of analyses

at V.G. Khlopin Radium Institute

- Optical microscopy
- SEM (BSE imaging)
- Quantitative and qualitative EMPA
- Bulk powder XRD (secondary uranium minerals, mineral inclusions separated from “lava” matrices)
- Precise XRD of single hot particles and mineral inclusions separated from “lava” matrices
- Gamma-spectrometry of bulk samples and single hot particles (not considered in this presentation)

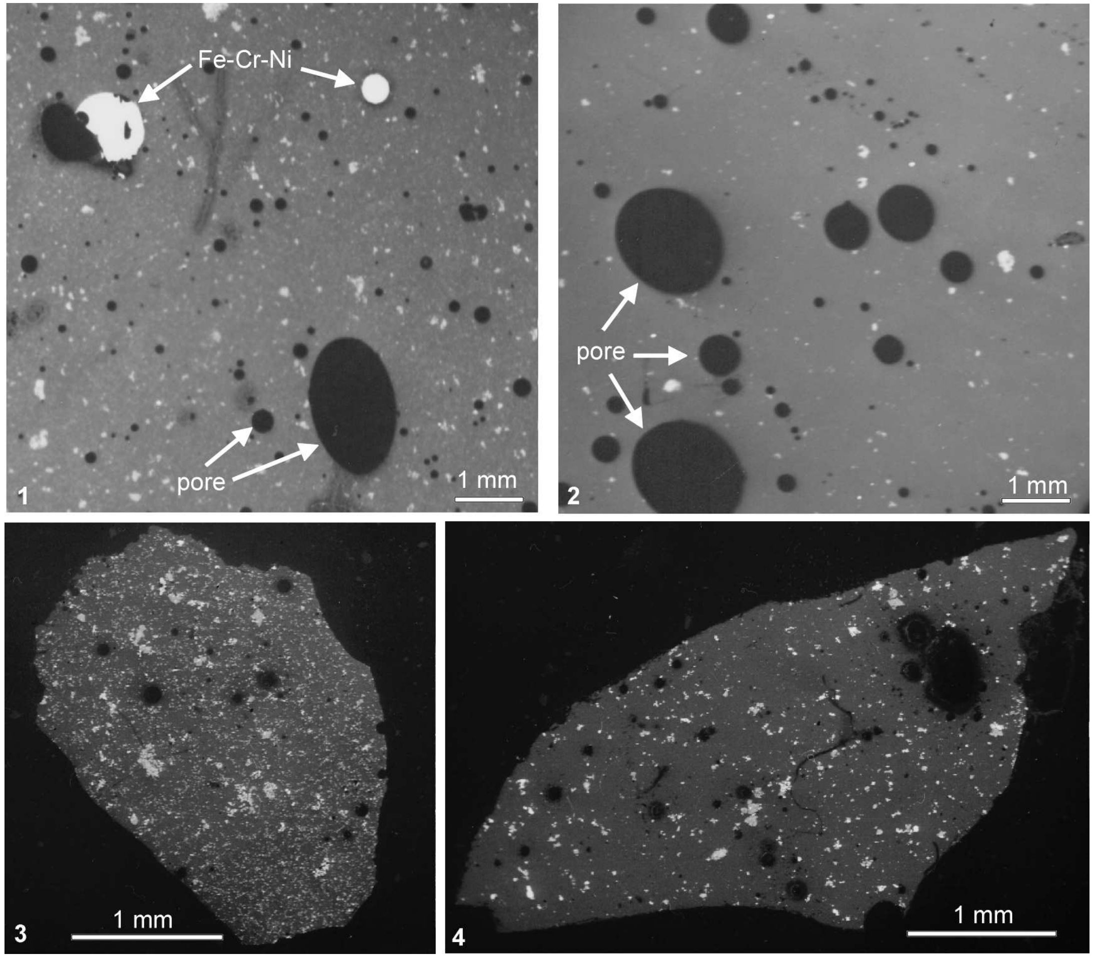
Chernobyl “lava”

brief summary or the results obtained at V.G. Khlopin Radium Institute

Images of polished “lava” samples

1,2 – in reflected light in optical microscope; 3,4 – SEM-BSE

1,3 – brown “lava” from steam discharge corridor; 2 – black “lava” from “Elephant foot; 4 – black “lava” from steam discharge corridor



Chernobyl “lava” consists of silicate glass matrix + inclusions

Chemical composition of "lava" glass avoiding inclusions (in wt.% from EMPA [5])

Type of "lava"	Fe	Na	Si	Al	Mg	K	Ca	Zr	U
porous	0.2	0.5	35.2	3.8	4.5	2.3	7.5	4.0	2.9
brown	0.2	0.6	36.6	4.0	4.4	2.3	7.2	2.9	2.0
black	0.3 to 6.7	0.4	37.2	3.8	1.3 to 3.2	2.7	8.2	3.7	3.2

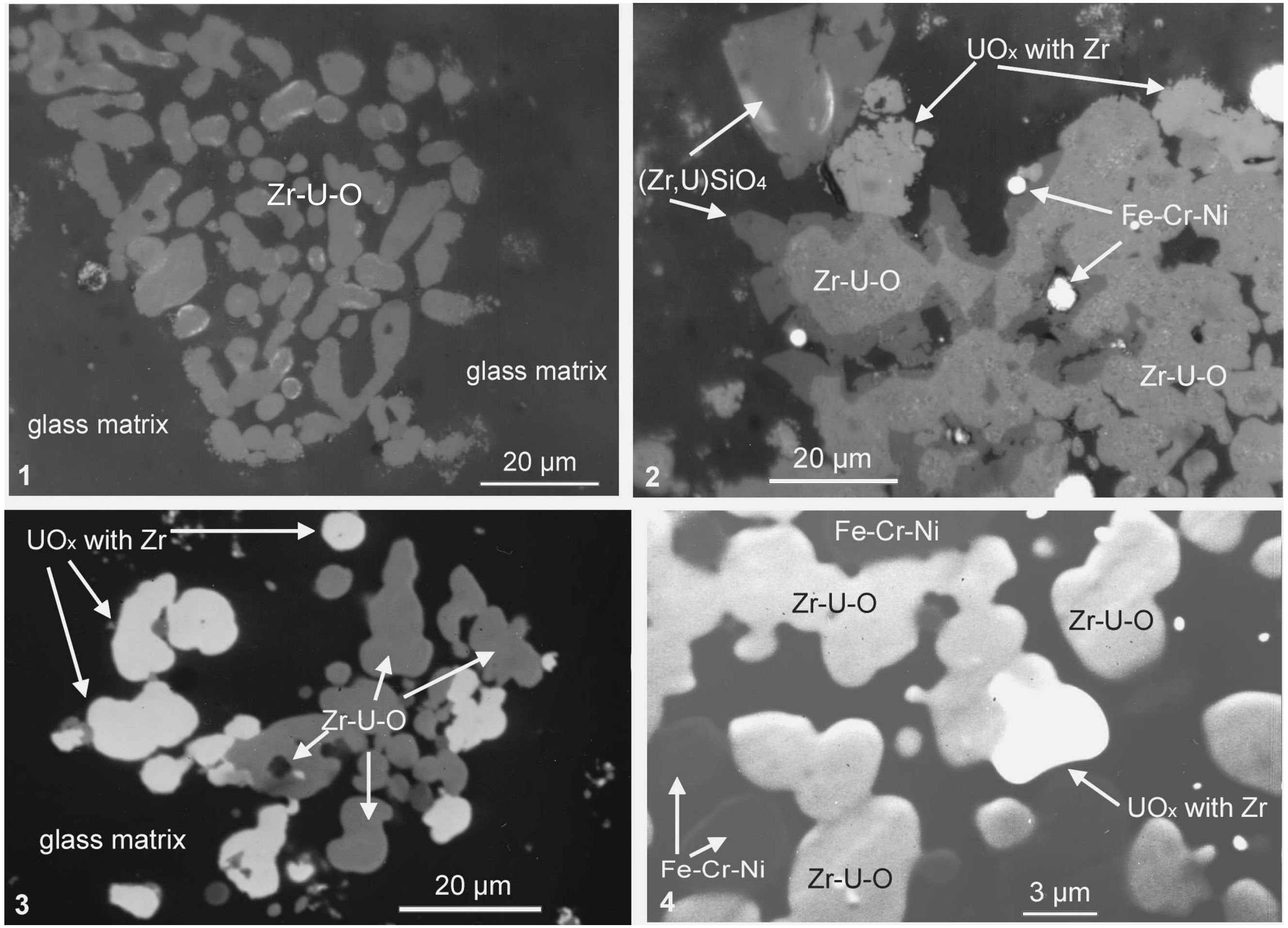
Inclusions in matrices of Chernobyl “lava”

very different phase and chemical compositions!

Inclusions in brown “lava” matrix

(from steam discharge corridor)

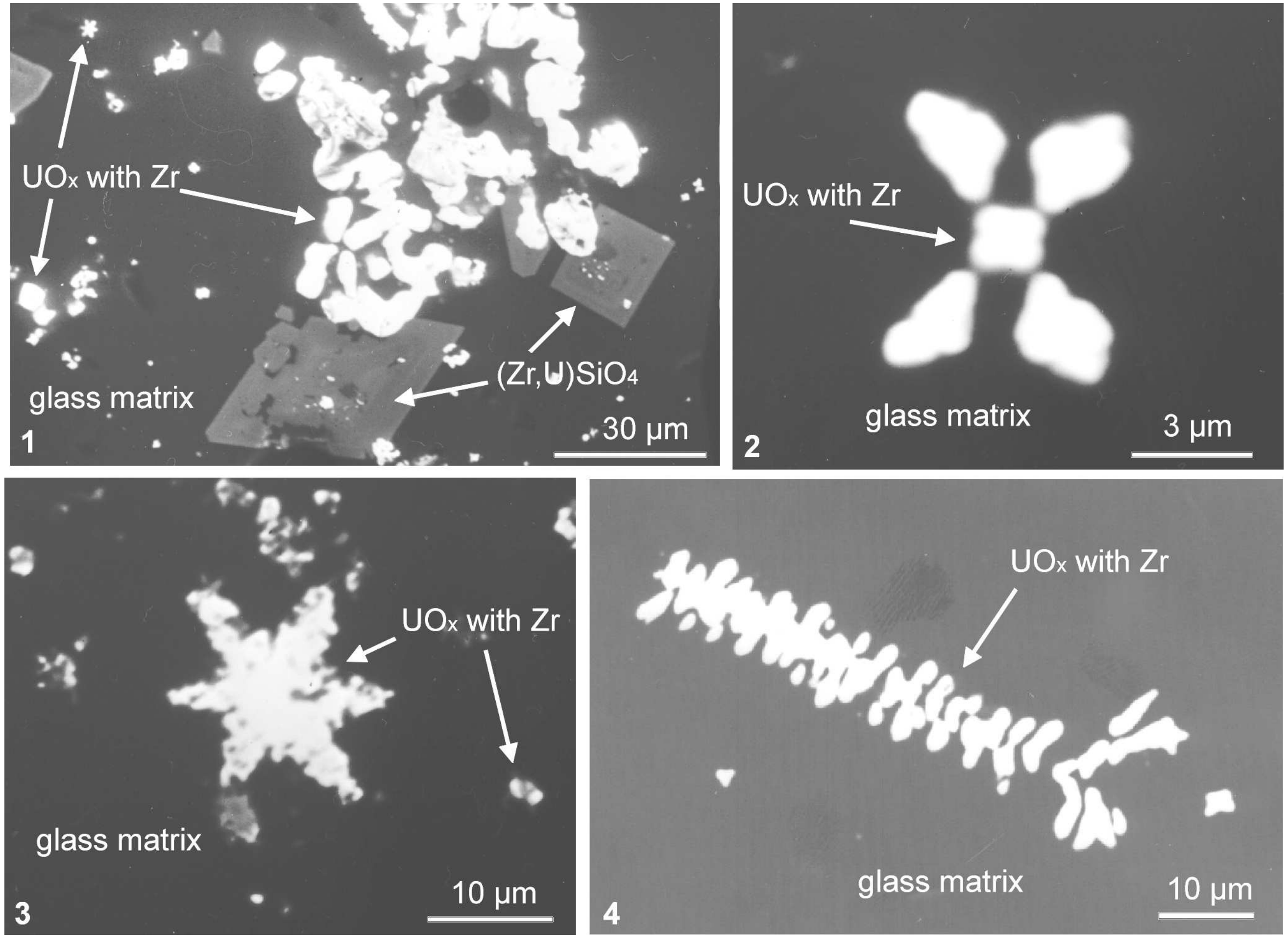
1,2 – in reflected light in optical microscope; 3,4 – SEM-BSE



Inclusions in black and brown “lava” matrices

SEM-BSE

1,2 – black “lava” from steam discharge corridor; 3 – brown “lava” from steam discharge corridor;
4 – black “lava” from “Elephant foot

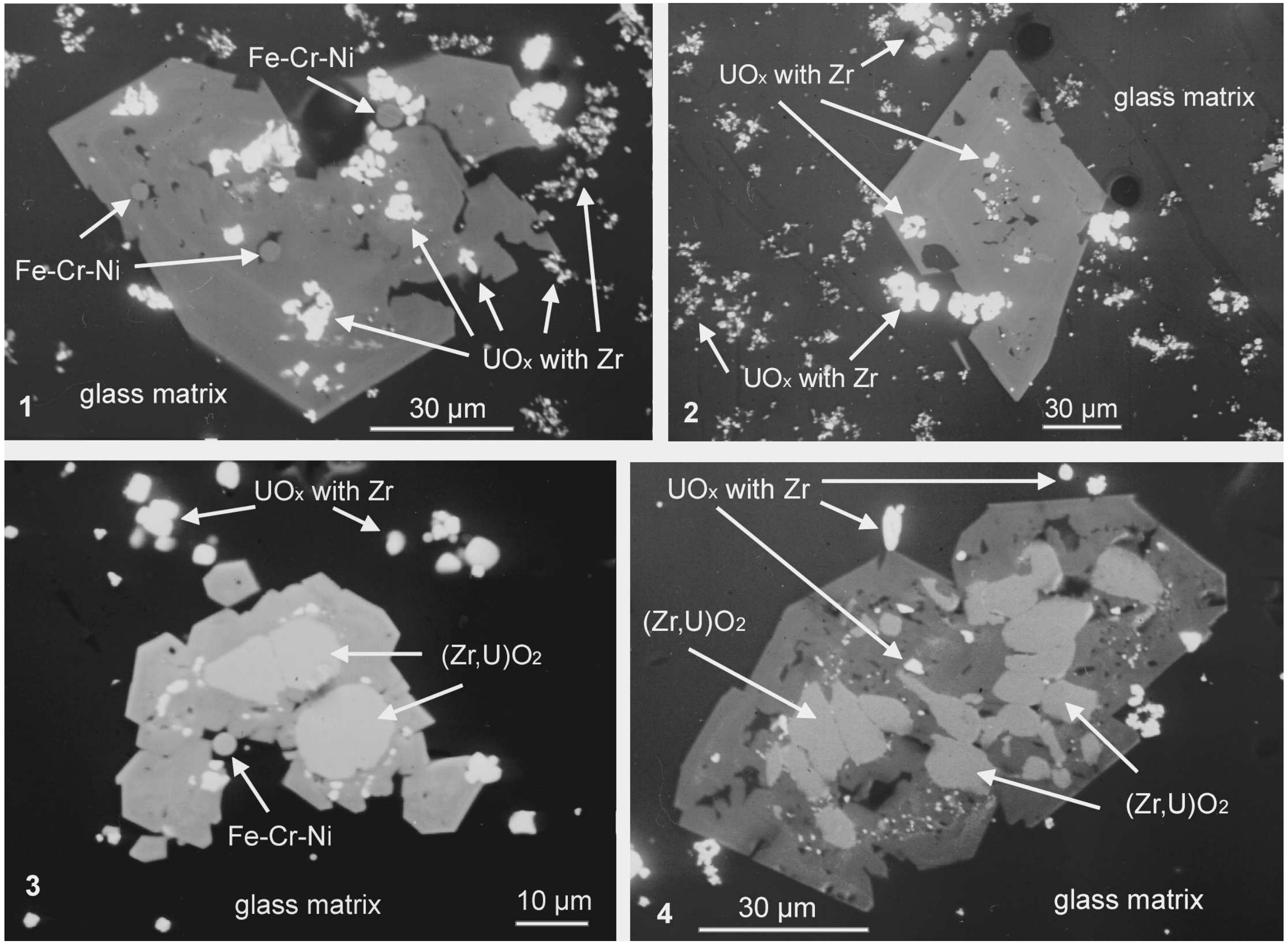


Inclusions in black and brown “lava” matrices

(from steam discharge corridor)

SEM-BSE

1,2 – brown “lava”; 3,4 – black “lava”

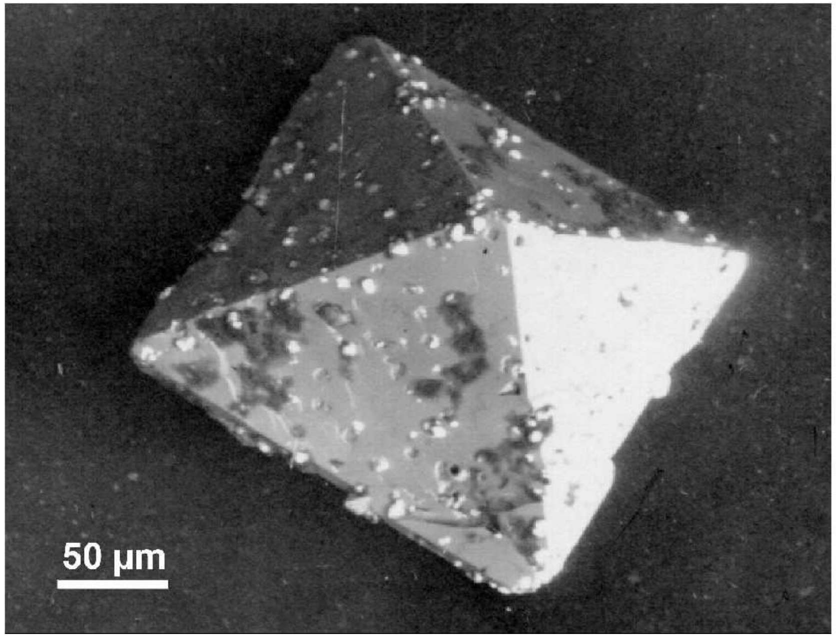


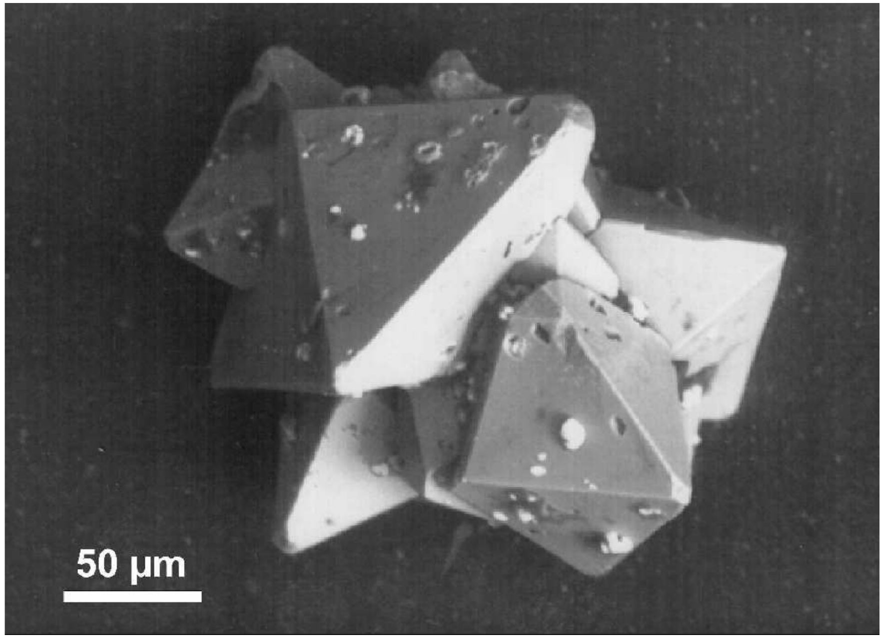
Crystals of unusual high-uranium zircon, $(Zr,U)SiO_4$, are typical for all types of Chernobyl “lava”

Up to 10 wt. % uranium was incorporated into the crystalline structure of zircon in the form of solid solution !

High-uranium zircon, $(Zr,U)SiO_4$, from Chernobyl “lava”

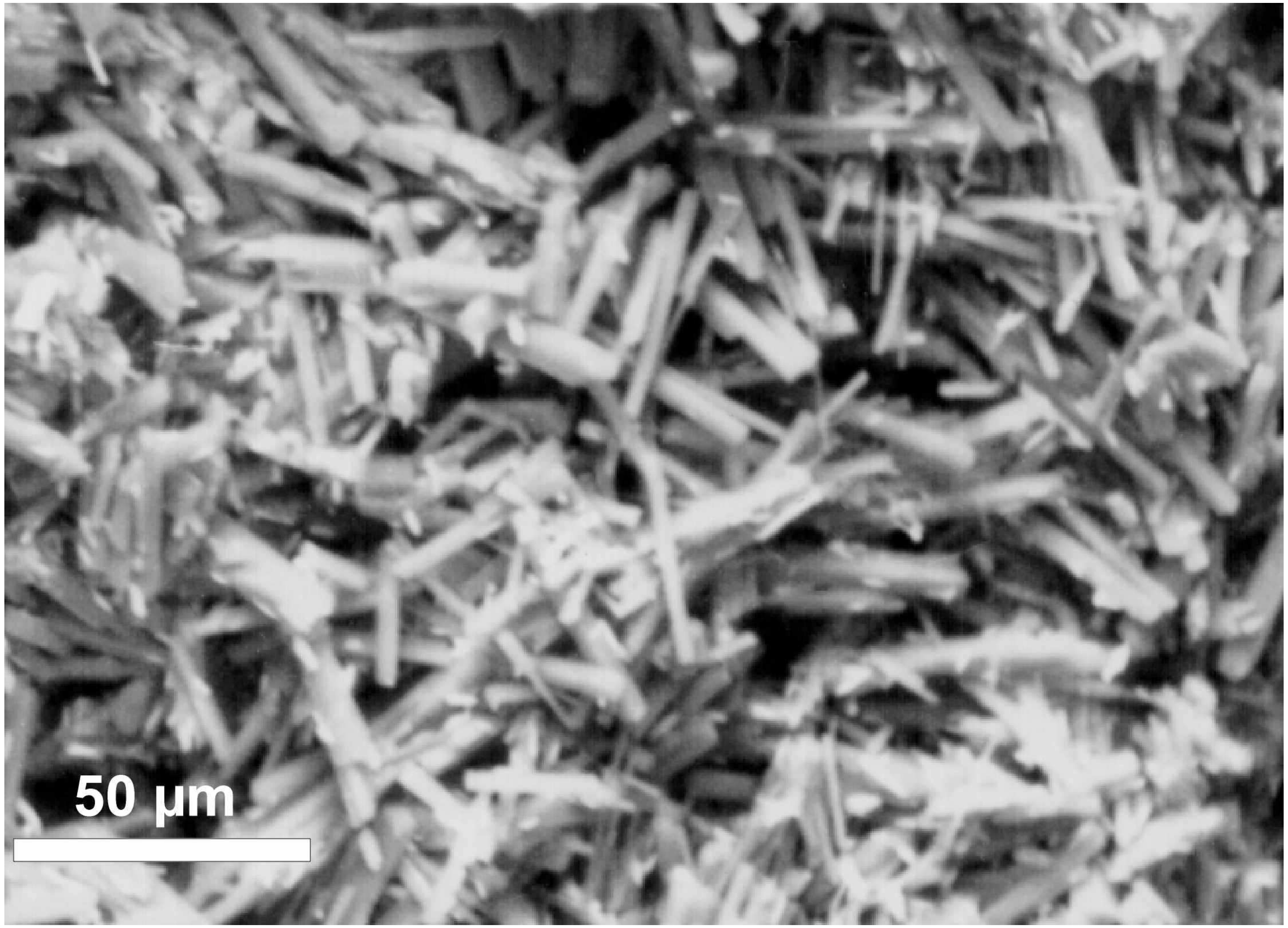
crystals were extracted after partial dissolution of “lava” matrix in HF





New-formed yellow minerals at the surface of Chernobyl "lava", 1991

SEM-BSE image of new-formed minerals at the surface of Chernobyl "lava" [6]



Phase composition of new-formed minerals at the surface of Chernobyl “lava” (from powder XRD analysis [6])

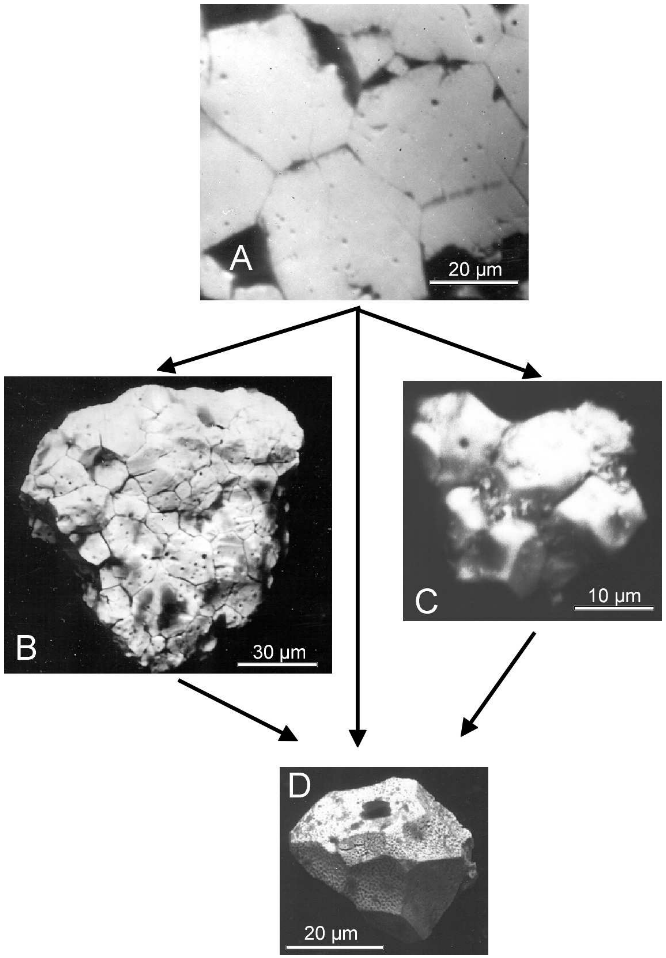
- $Na_3H(CO_3)_2 \times 2H_2O$
- $UO_3 \times 2H_2O$
- $Na_4(UO_2)(CO_3)_3$
- $Na_2CO_3 \times 2H_2O$
- $UO_4 \times 4H_2O$
- UO_2CO_3

Chernobyl “hot” particles

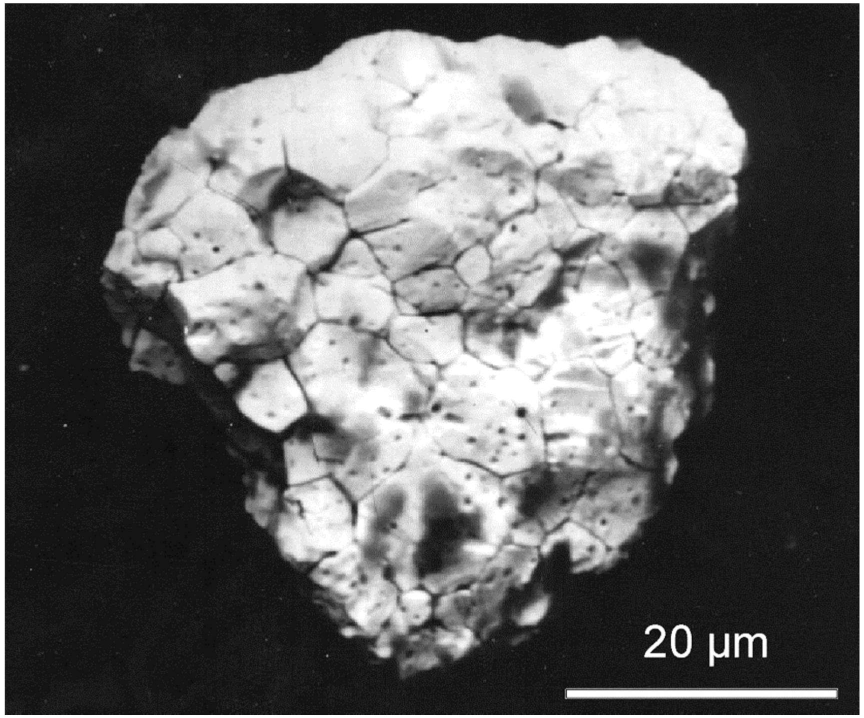
brief summary or the results obtained
at V.G. Khlopin Radium Institute

SEM-BSE images of fuel fragment (A) and hot particles (B,C,D) of fuel composition (UO_x) [7]

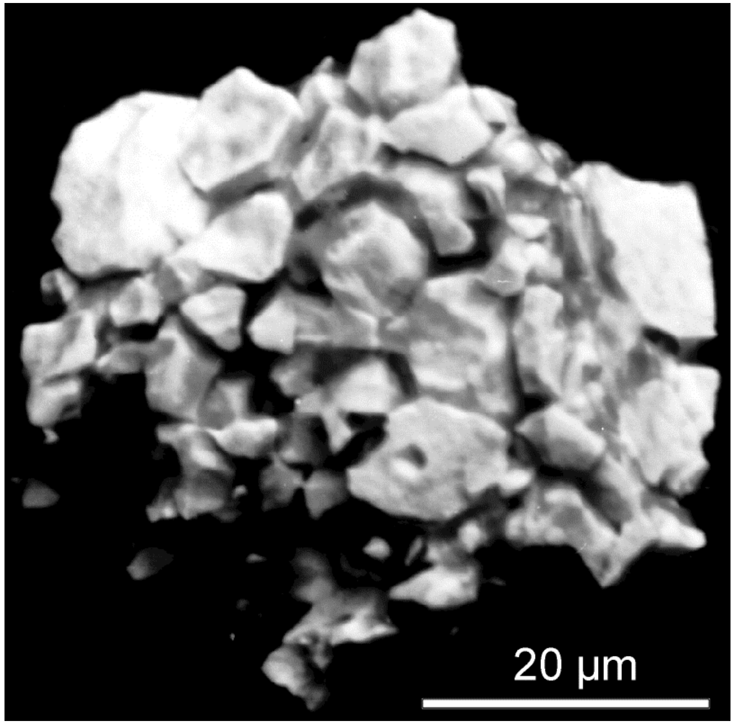
possible mechanical self-destruction along grain boundaries



Multi-grain fuel (UO_x) hot particles (collected in 1990)



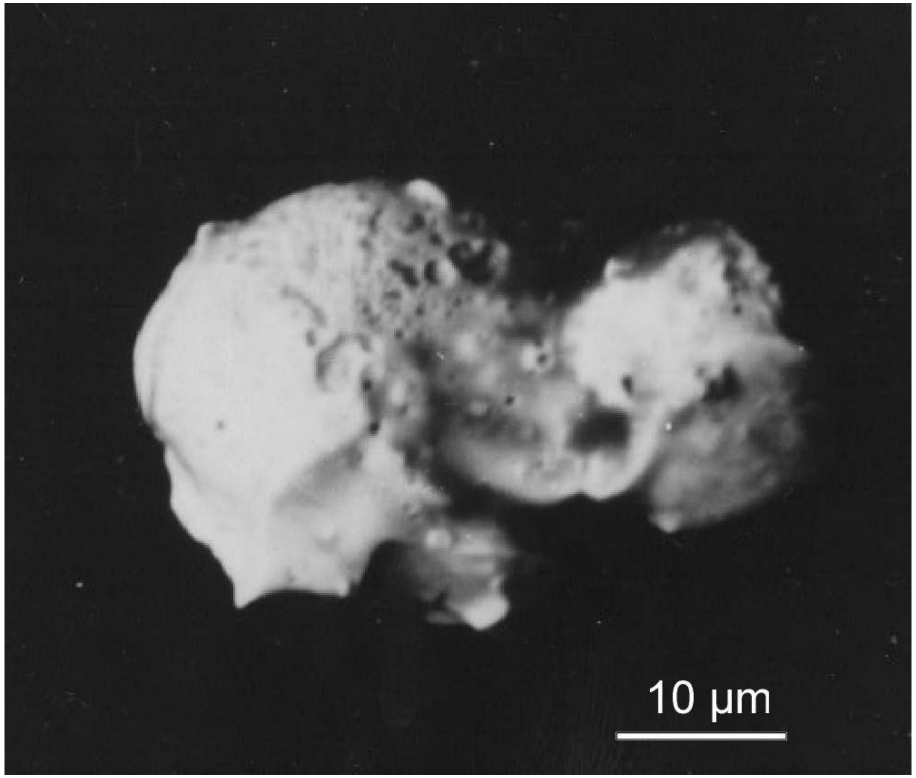
non-altered

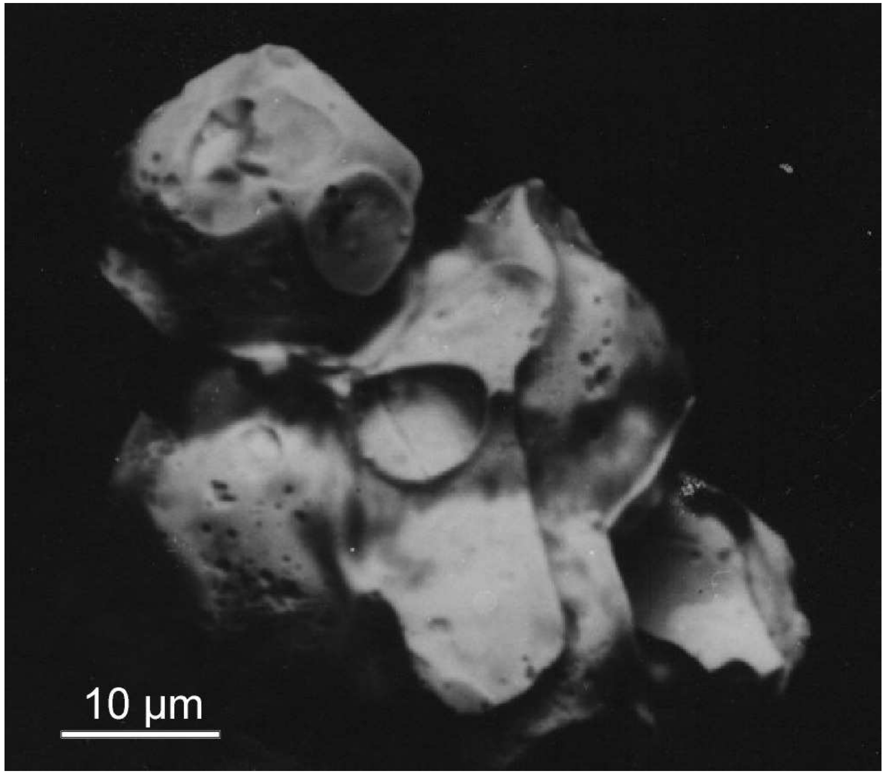


altered ???

dissolution along grain boundaries ?

Fuel hot particles (UO_x) with molten morphology (?)



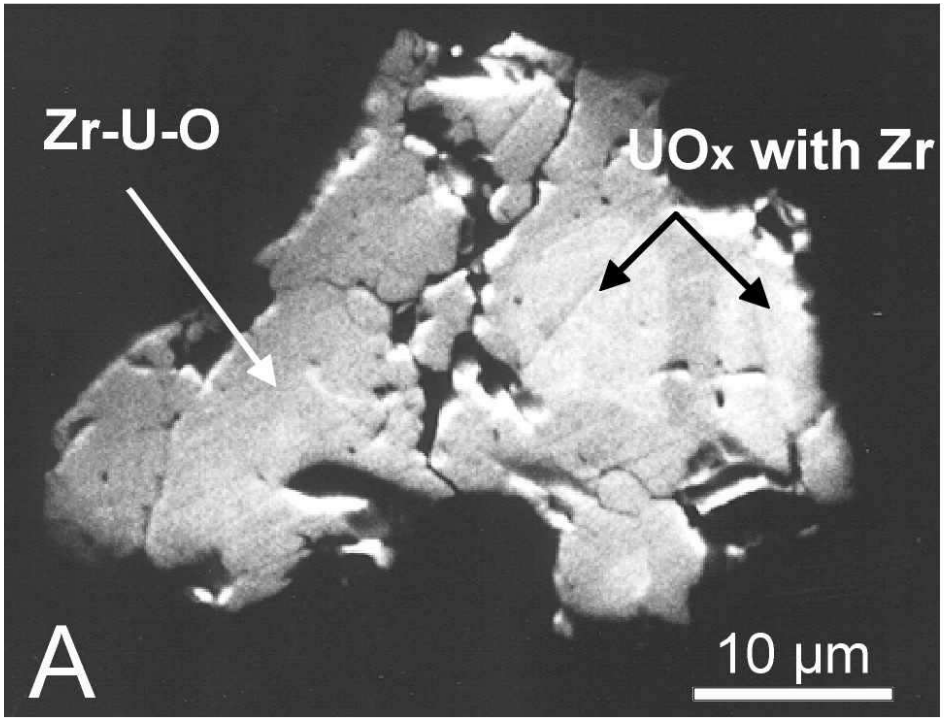


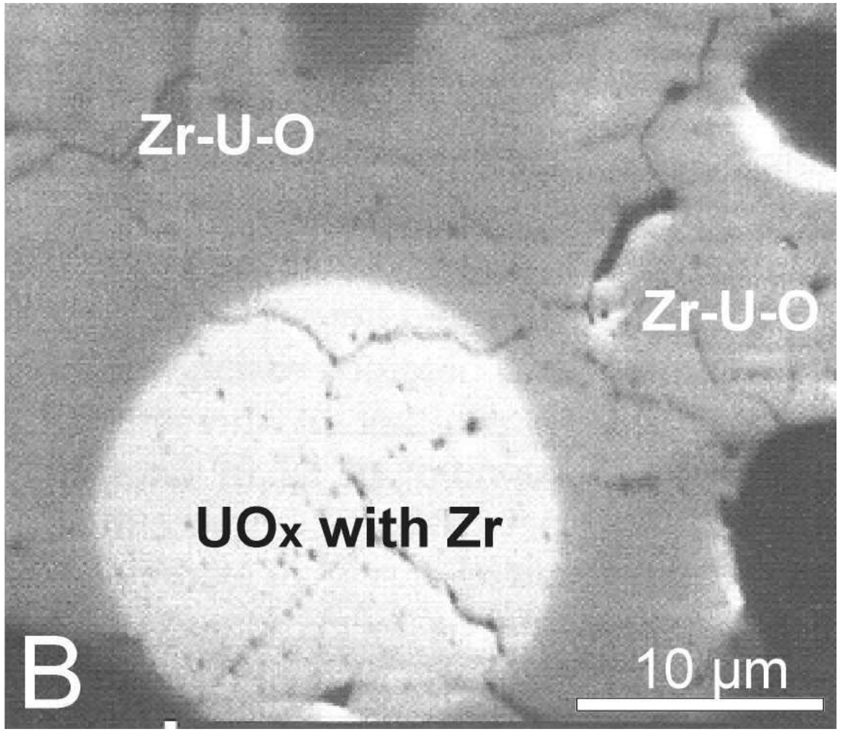
We also found Zr-bearing hot particles with phases:
Zr-U-O and UO_x with Zr etc.

up to 40 % of all particles in some places of Western Plume !

Multi-phase hot particles [7]

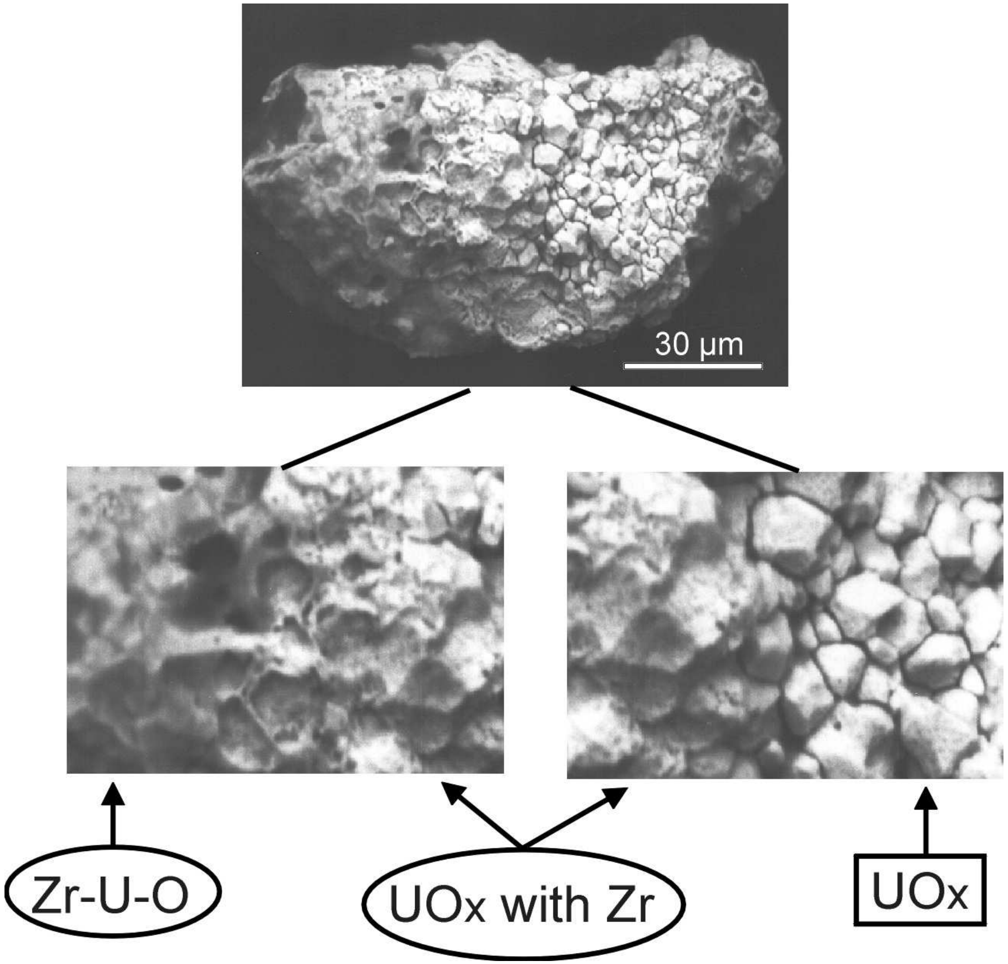
polished cross-sections, SEM-BSE





Multi-phase hot particle [7]

SEM-BSE image



No interaction between fuel (UO_x) and zircaloy (almost pure metallic Zr) is possible in air. Fast oxidation of metallic Zr blocks this process

No conditions for Zr-U-O melt formation after explosion of reactor core !

Crystalline U-bearing phases identified in Chernobyl "lava" and hot particles

- Cubic UO_x – similar to stoichiometric UO_2 (***a* = 5.462-5.473 Å**)

- Cubic UO_x with Zr (0,5 to 20 wt.% Zr) (***a*** decreases from **5.468 to 5.318 Å**). Chemical composition – $(U_{0,985}Zr_{0,015})O_2$-$(U_{0,895}Zr_{0,105})O_2$. In some hot particles Zr content is higher – up to $(U_{0,56}Zr_{0,44})O_2$

- Tetragonal phase Zr-U-O with varied chemical composition from $(Zr_{0,86}U_{0,14})O_2$ to $(Zr_{0,89}U_{0,11})O_2$

- Monoclinic zirconia with U (up to 6 wt.% U) with varied chemical composition from $(Zr_{0,995}U_{0,005})O_2$ to $(Zr_{0,967}U_{0,.033})O_2$

- Solid solutions with non-identified structures: $(Zr_{0,56}U_{0,44})O_2$; $(Zr_{0,68-0,71}U_{0,32-0,29})O_2$; $(Zr_{0,75-0,77}U_{0,25-0,23})O_2$ – only in hot particles

- High-uranium zircon, $(Zr_{0,95}U_{0,05})SiO_4$-$(Zr_{0,90}U_{0,10})SiO_4$
  (for bulk concentrate: ***a* = 6.617; *c* = 5.990 Å**).

Conclusions

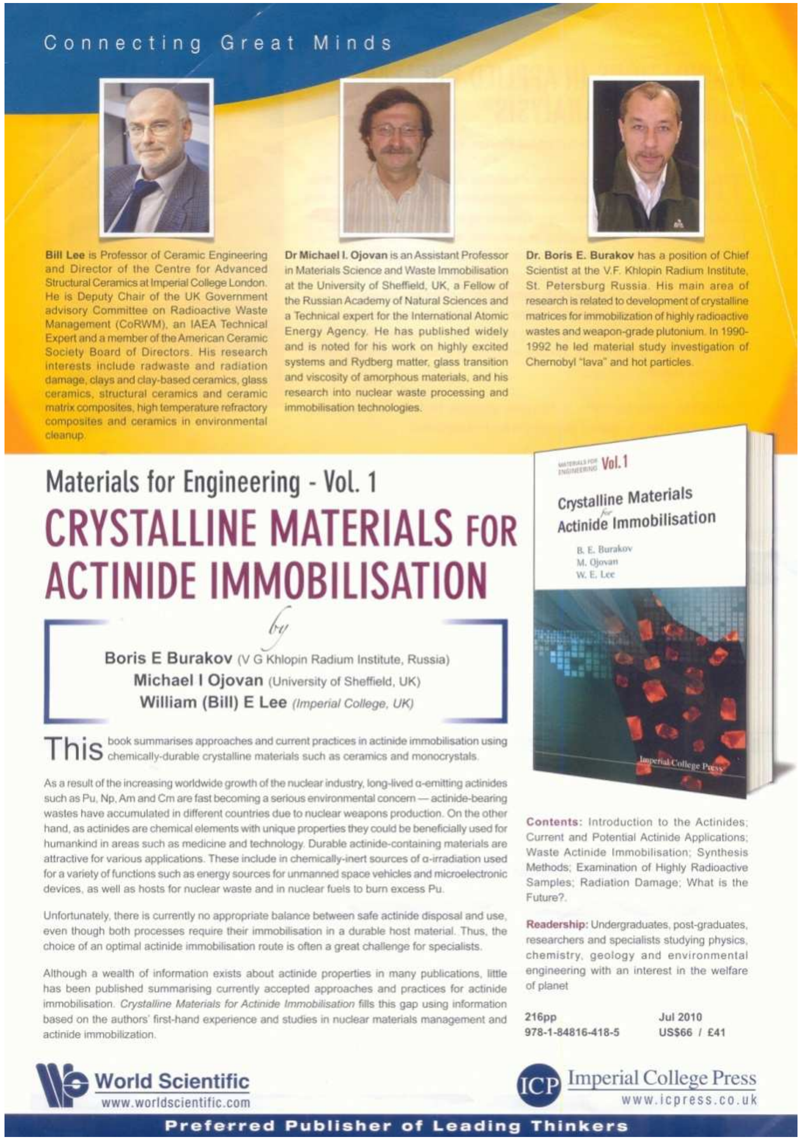
- High-temperature (at least 2600°C) interaction between nuclear fuel and zircaloy cladding took place in local part of Chernobyl reactor core before the explosion

- Solid highly radioactive materials were formed and partially dispersed as a result of Chernobyl accident. **They have different phase and chemical composition.** It means their different behavior in environment

- Active chemical alteration of Chernobyl "lava" is going on

- Results of Chernobyl material study can be used for modeling severe nuclear accident at different types of nuclear reactors (not only RBMK)

- *Results of Chernobyl material study can be used for development of ceramic waste forms and other durable advanced materials (more information – in a book attached)*



Connecting Great Minds

Bill Lee is Professor of Ceramic Engineering and Director of the Centre for Advanced Structural Ceramics at Imperial College London. He is Deputy Chair of the UK Government advisory Committee on Radioactive Waste Management (CoRWM), an IAEA Technical Expert and a member of the American Ceramic Society Board of Directors. His research interests include radwaste and radiation damage, clays and clay-based ceramics, glass ceramics, structural ceramics and ceramic matrix composites, high temperature refractory composites and ceramics in environmental cleanup.

Dr Michael I. Ojovan is an Assistant Professor in Materials Science and Waste Immobilisation at the University of Sheffield, UK, a Fellow of the Russian Academy of Natural Sciences and a Technical expert for the International Atomic Energy Agency. He has published widely and is noted for his work on highly excited systems and Rydberg matter, glass transition and viscosity of amorphous materials, and his research into nuclear waste processing and immobilisation technologies.

Dr. Boris E. Burakov has a position of Chief Scientist at the V.F. Khlopin Radium Institute, St. Petersburg Russia. His main area of research is related to development of crystalline matrices for immobilization of highly radioactive wastes and weapon-grade plutonium. In 1990-1992 he led material study investigation of Chernobyl "lava" and hot particles.

Materials for Engineering - Vol. 1

CRYSTALLINE MATERIALS FOR ACTINIDE IMMOBILISATION

by

Boris E Burakov (V G Khlopin Radium Institute, Russia)
Michael I Ojovan (University of Sheffield, UK)
William (Bill) E Lee *(Imperial College, UK)*

This book summarises approaches and current practices in actinide immobilisation using chemically-durable crystalline materials such as ceramics and monocrystals.

As a result of the increasing worldwide growth of the nuclear industry, long-lived α-emitting actinides such as Pu, Np, Am and Cm are fast becoming a serious environmental concern — actinide-bearing wastes have accumulated in different countries due to nuclear weapons production. On the other hand, as actinides are chemical elements with unique properties they could be beneficially used for humankind in areas such as medicine and technology. Durable actinide-containing materials are attractive for various applications. These include in chemically-inert sources of α-irradiation used for a variety of functions such as energy sources for unmanned space vehicles and microelectronic devices, as well as hosts for nuclear waste and in nuclear fuels to burn excess Pu.

Unfortunately, there is currently no appropriate balance between safe actinide disposal and use, even though both processes require their immobilisation in a durable host material. Thus, the choice of an optimal actinide immobilisation route is often a great challenge for specialists.

Although a wealth of information exists about actinide properties in many publications, little has been published summarising currently accepted approaches and practices for actinide immobilisation. *Crystalline Materials for Actinide Immobilisation* fills this gap using information based on the authors' first-hand experience and studies in nuclear materials management and actinide immobilization.

Materials for Engineering Vol. 1
Crystalline Materials for Actinide Immobilisation
B. E. Burakov
M. Ojovan
W. E. Lee
Imperial College Press

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