The nature of U behaviour in the processes of transformation of volcanic glasses of different composition

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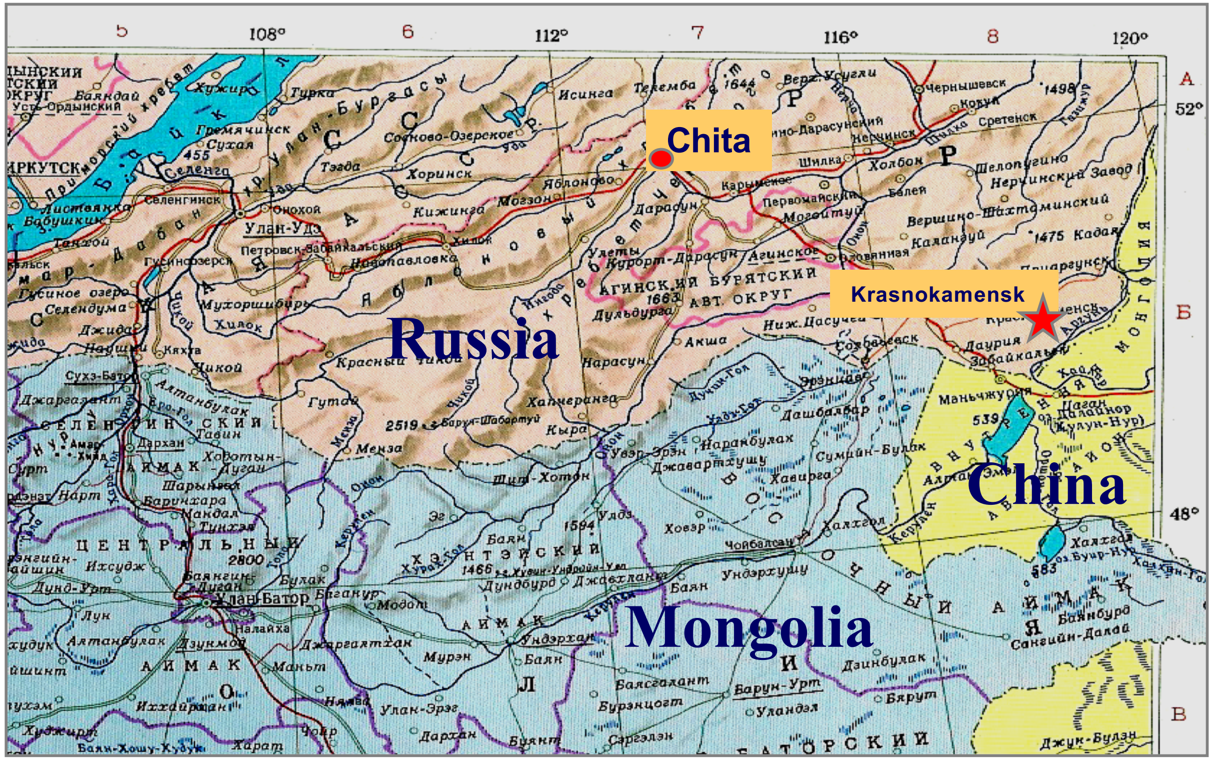
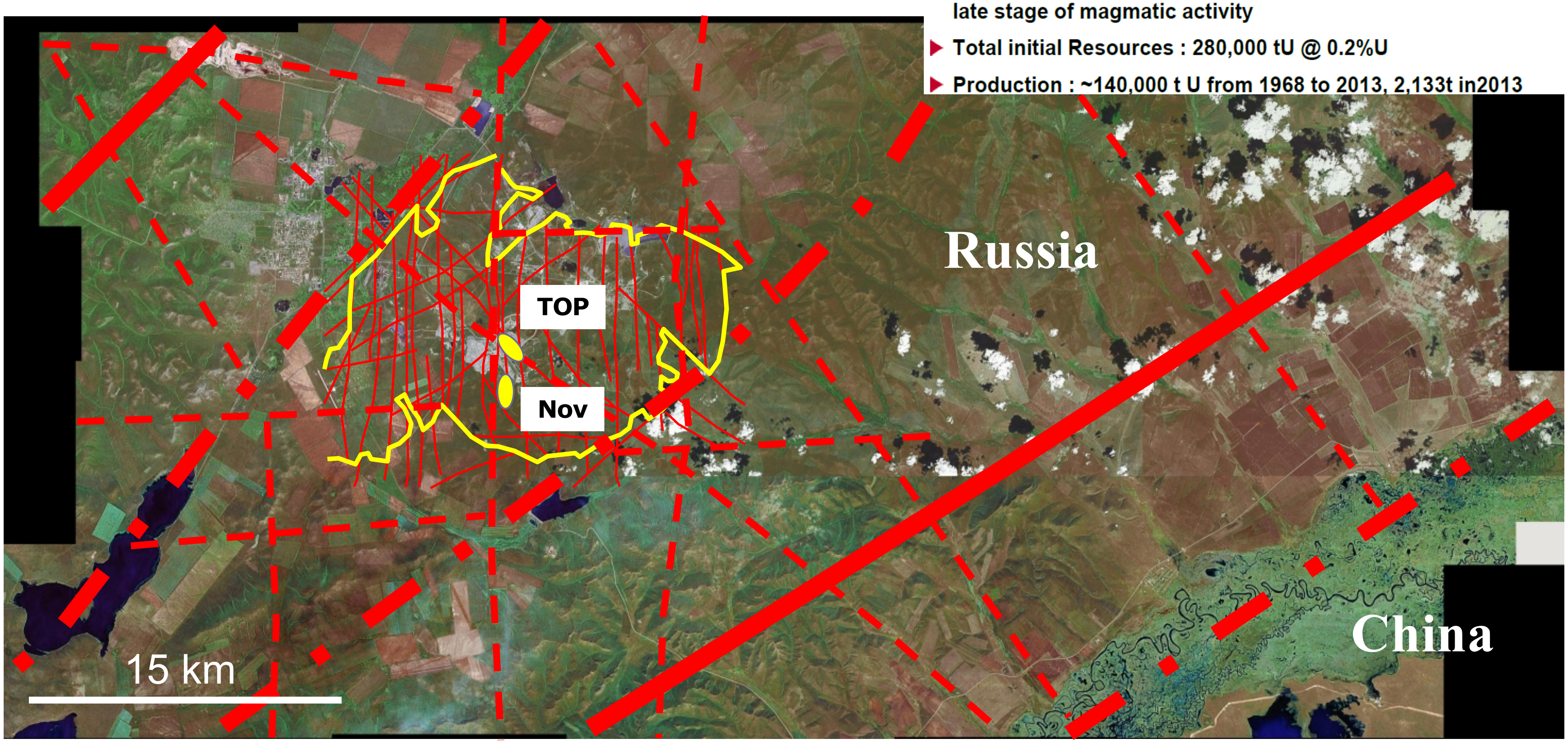
Location and traits of the Transbaikal Region

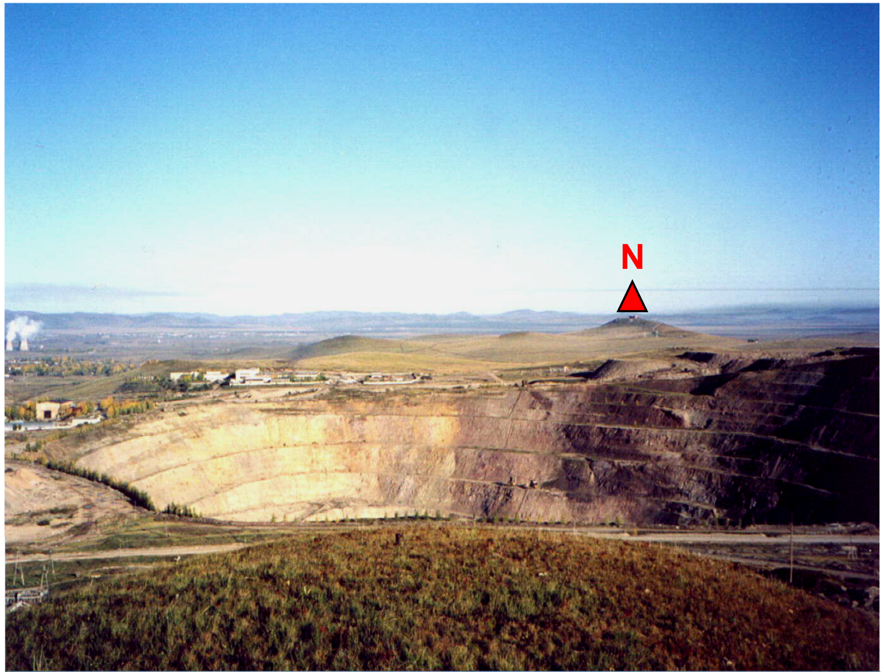


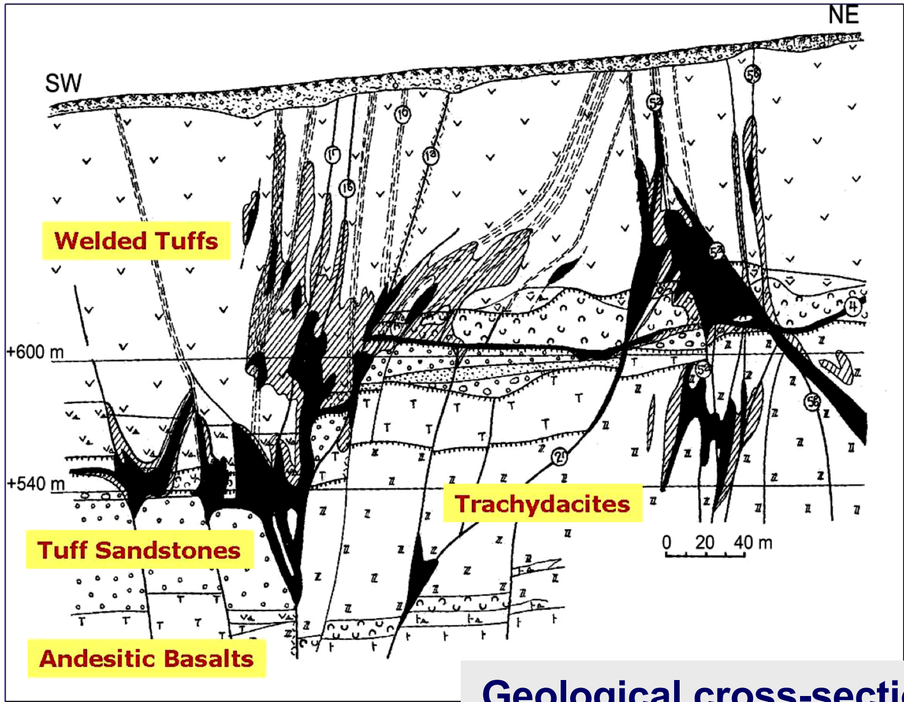
Satellite view of the area with the main faults and caldera edge

- Volcanic Caldera of 20 km in diameter (180 km2) comprises 19 ore bodies
- Host rocks: up to 1.4 km of volcano-sedimentary accumulation within the caldera lying on a granitic Proterozoic basement
- Host structures: Vertical and sub horizontal faults
- Age : Cretaceous (145-140 Ma)
- Ore lies within veins, sub-vertical stockworks and along stratiform layers in the sandstone units.
- Ore: pitchblende, coffinite, and branerite,
- Genetic Model: Hydrothermal remobilisations synchronous of late stage of magmatic activity
- Total initial Resources : 280,000 tU @ 0.2%U
- Production : ~140,000 t U from 1968 to 2013, 2,133t in2013



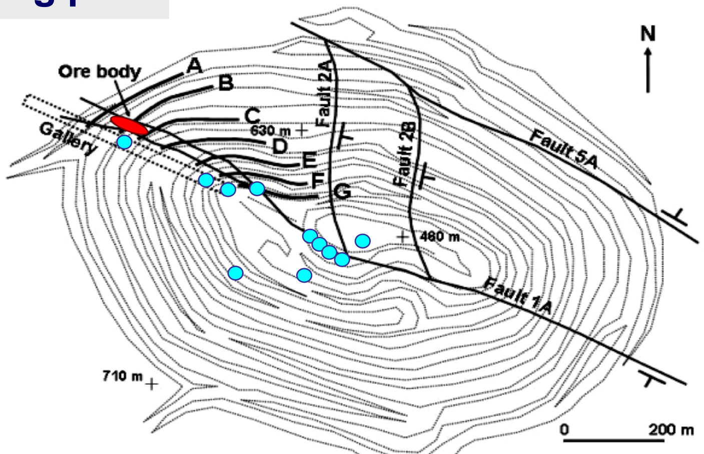
The Tulukuevskoe Open Pit (TOP): 50,000 tU@0.2%U





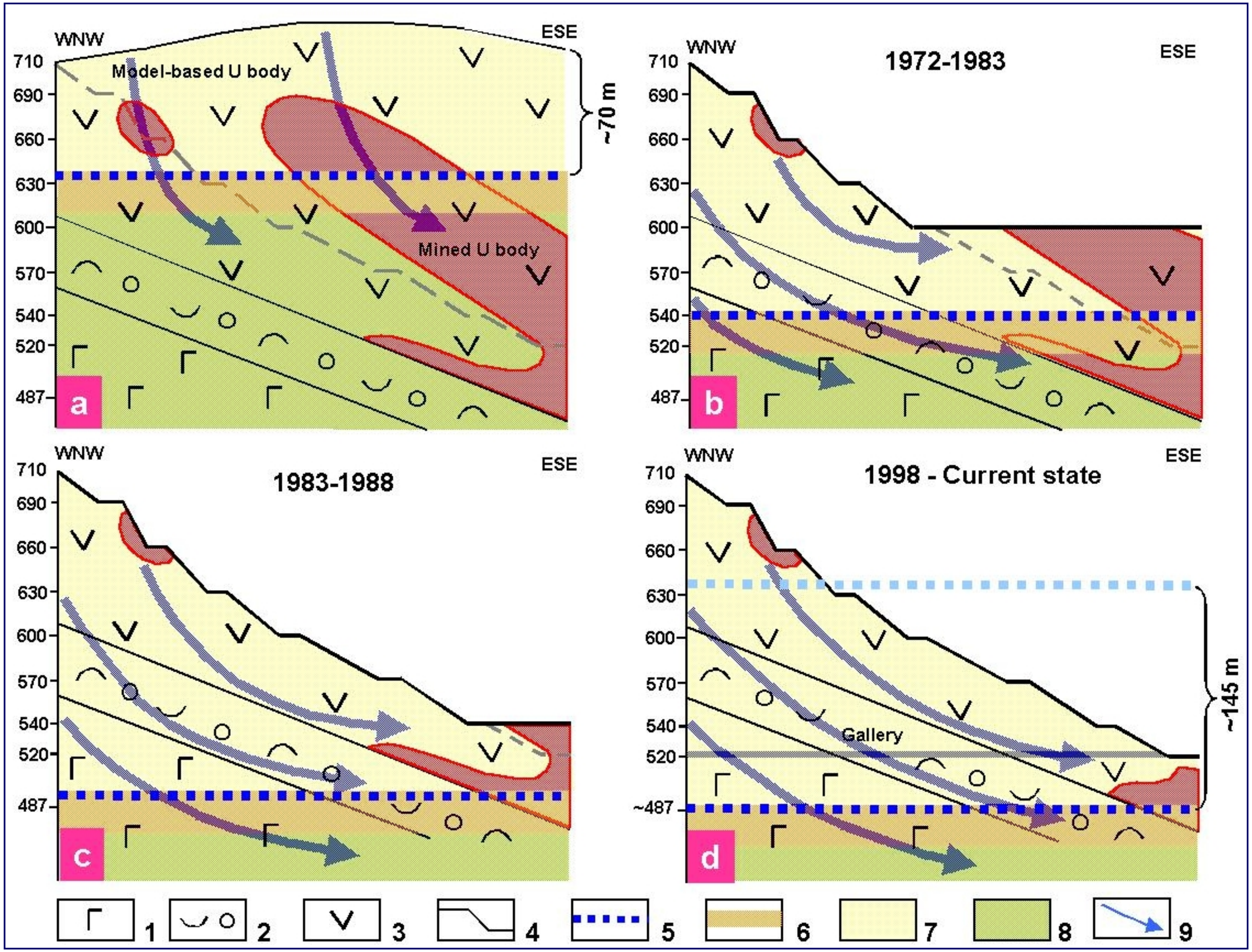
Geological cross-section

Surveying plan

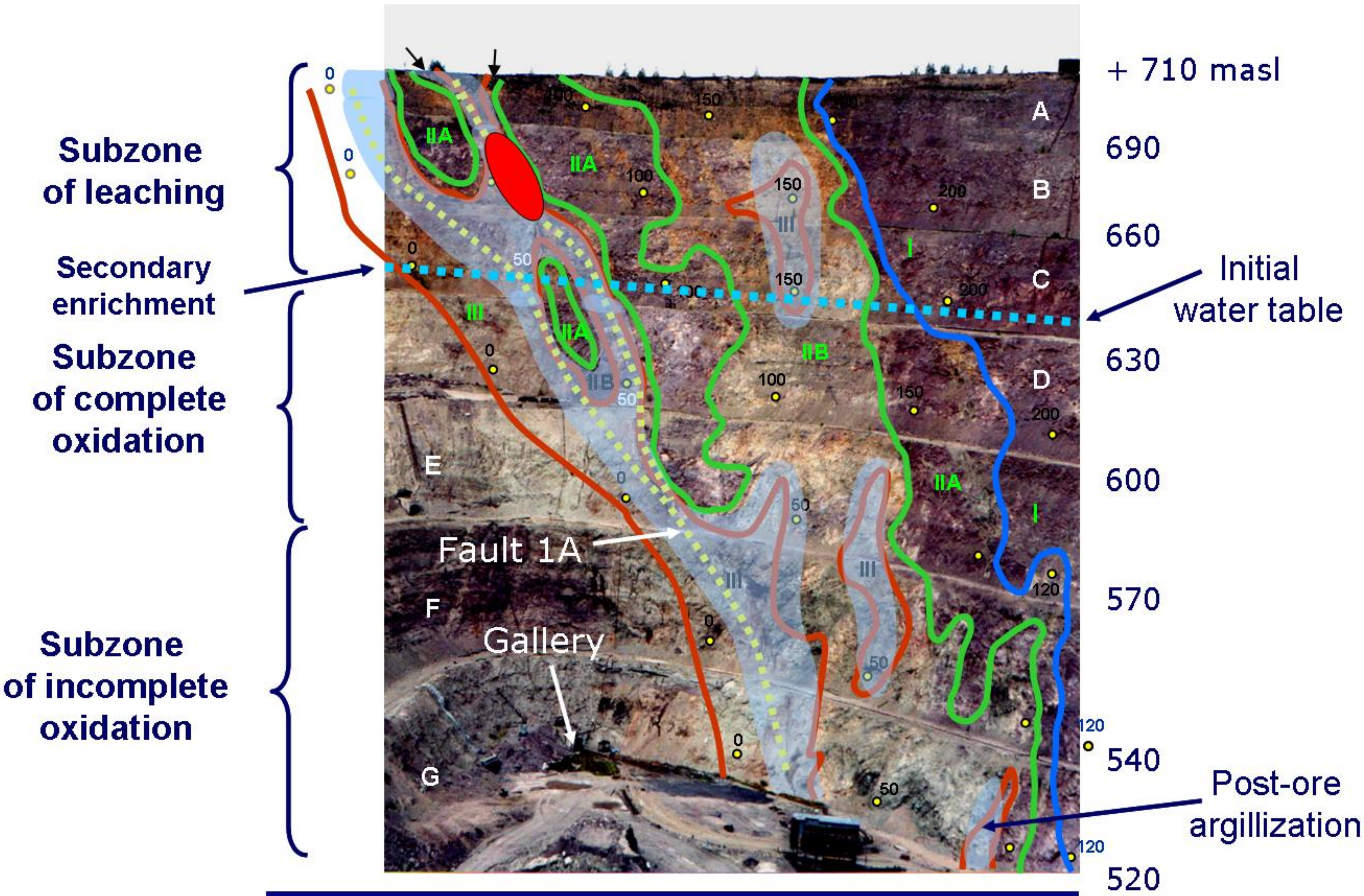


Vein-fracture water source

Dynamics of water table recession and changing of oxidizing/reducing conditions during the TOP mining



General view of the NW block of the TOP with mineral zoning of hydrothermal and hypergene transformations of rocks



I - external (relic: KFs, Olg, Q, Bt, Hem / neogenic: Ilt-Sm, Car)
II - intermediate (Q, KFs, Alb / Ilt-Sm, Car, Q, LA)
III - internal (Q, KFs / Q, Ilt-Sm, Car, Hem, LA, Ber, Kaol)

Pitchblende (a) and pitchblende-molibdenite (b) ores and consecution of U mineralization

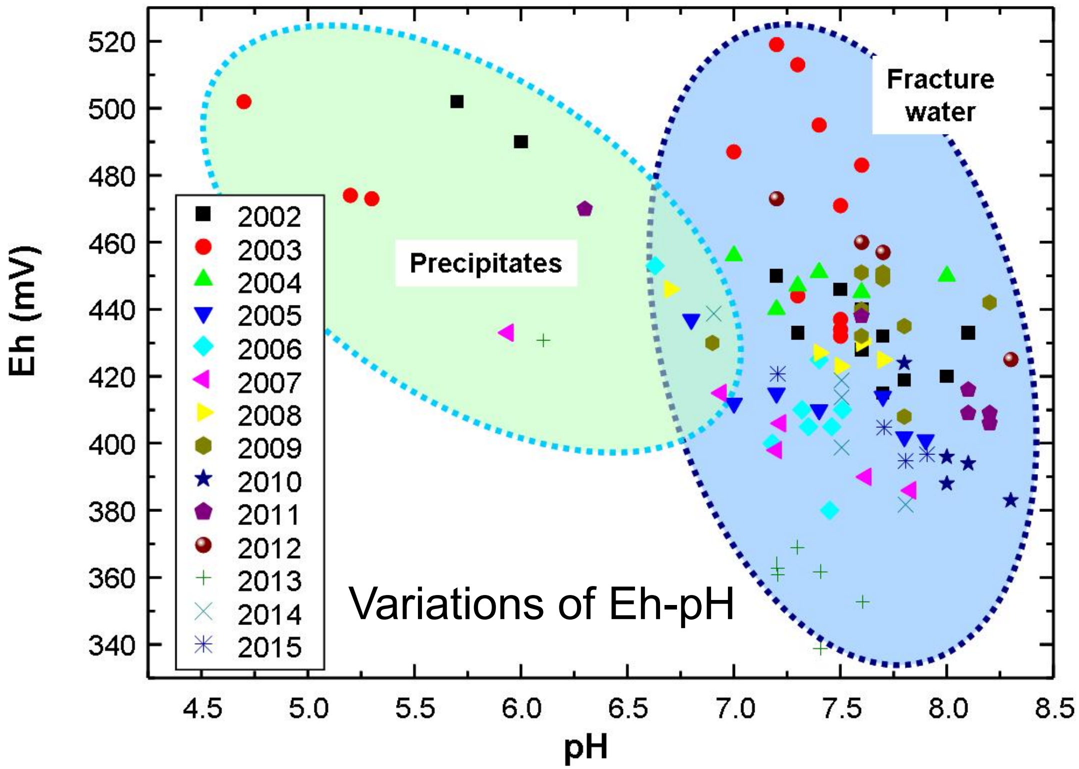
Time consecution of U mineralization:

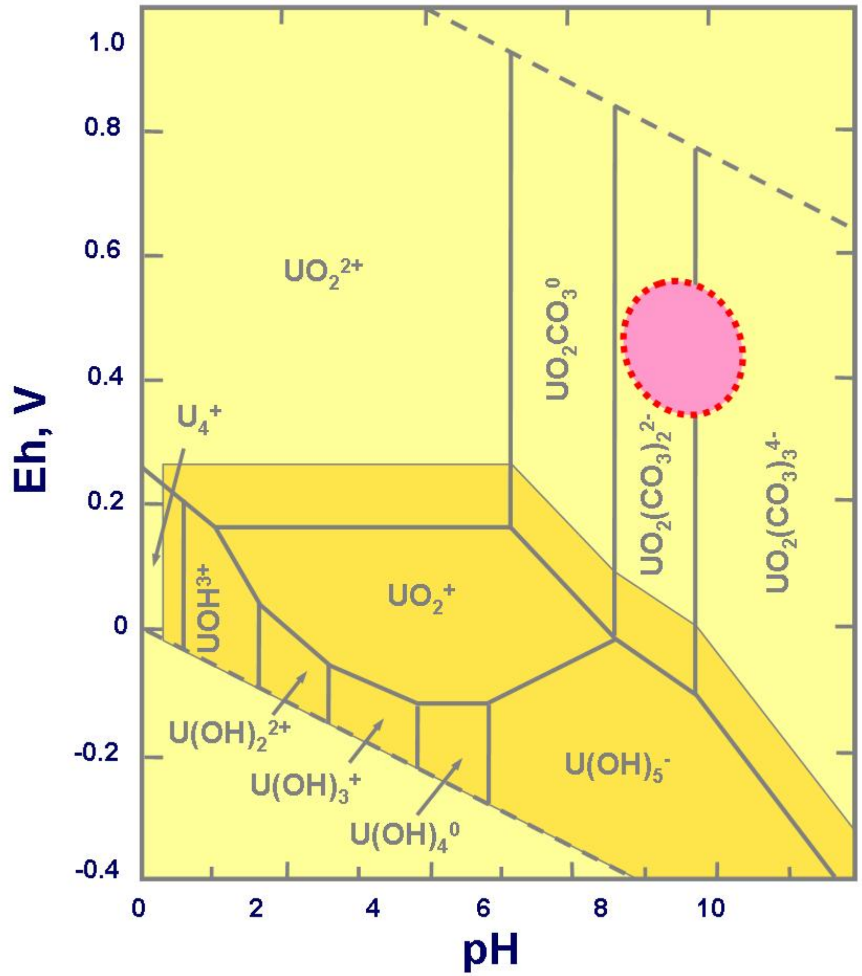
Hypogene (pitchblende and tucholite)

U minerals of the ancient oxidation zone (beginning: blacks and urhyte, completion: uranophane)

Secondary (uranophane, heyviite, calcurmolite, liebigite etc.)

Hydrochemistry of fracture-vein waters and atmospheric precipitates of the TOP (2002-2015)

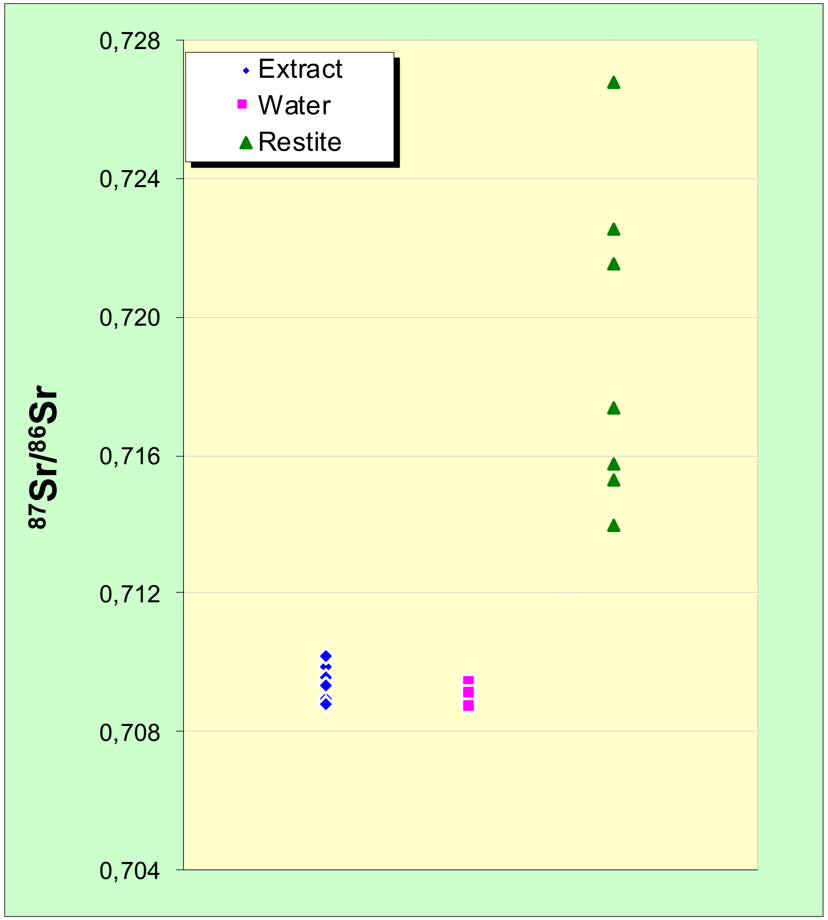




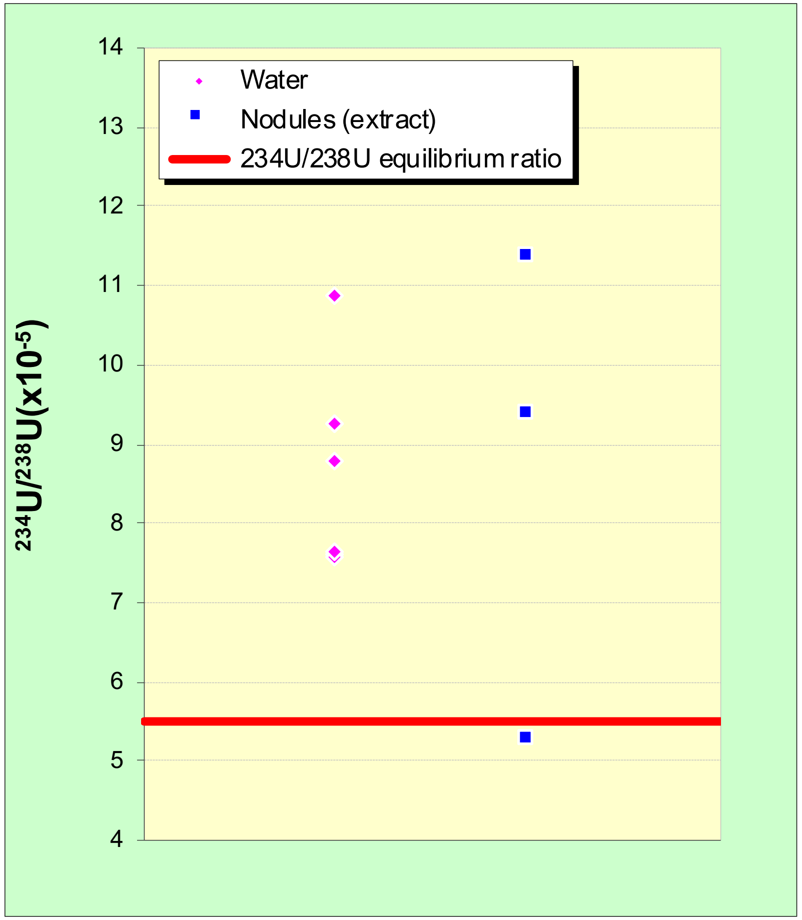
Eh-pH diagram of U-O_2-H_2O-CO^2 system, T=25^{o}C, P=1 atm for U=10^{-6} mol, P_{CO2}=10^{-2} atm (*after Langmuir, 1978*).

U speciation dominated by carbonate complexes

Isotopic data for high-siliceous glasses and fracture waters from the TOP

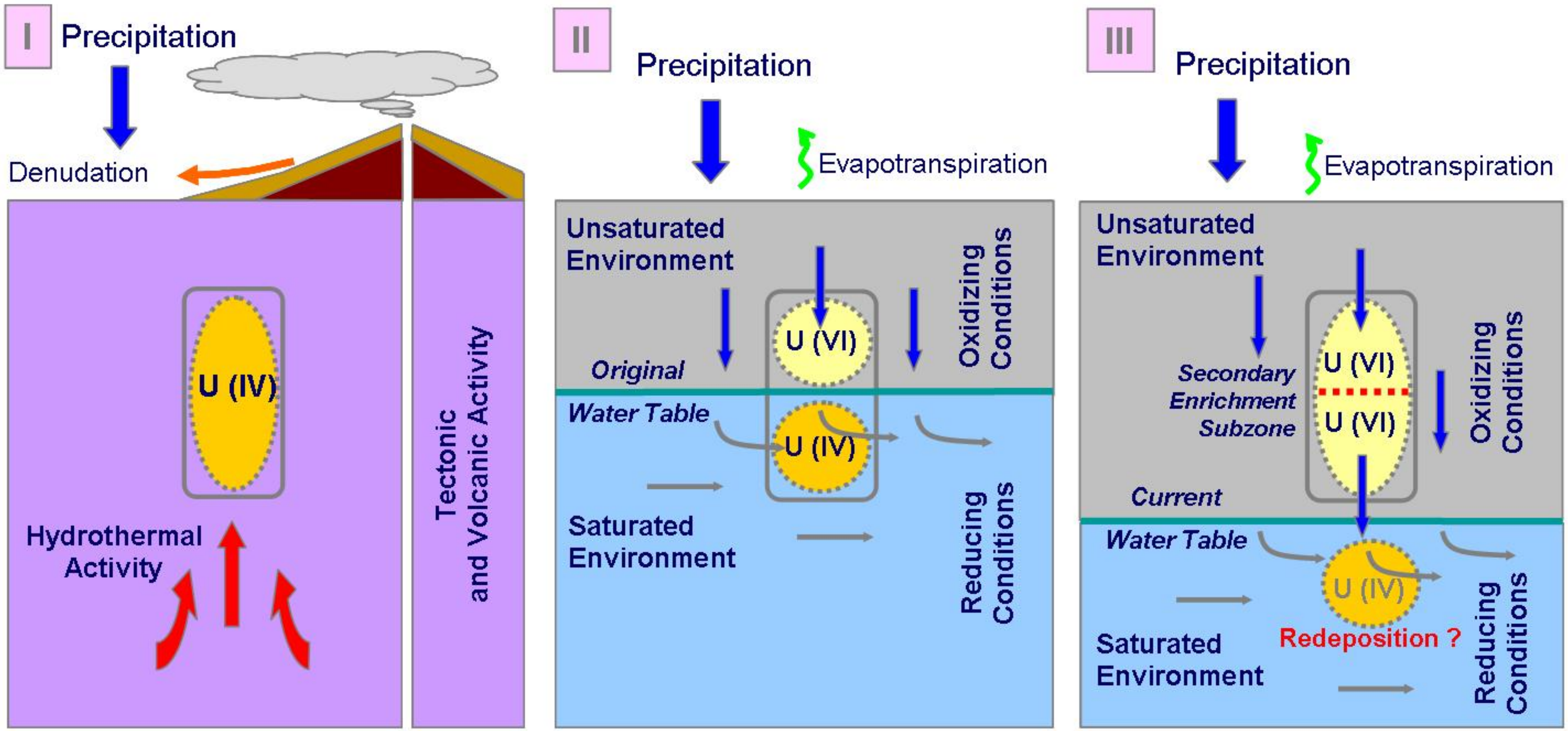


Isotopic composition of Sr extract and restite of high-siliceous glass in relation to isotopic composition of Sr for fracture water



U isotopic composition from the extract of high-siliceous glass and fracture water in relation to equilibrium $^{234}U/^{238}U$ ratio

U ore formation, modification and redeposition in the context of spatial-temporal changes of oxidizing/reducing conditions at the TOP

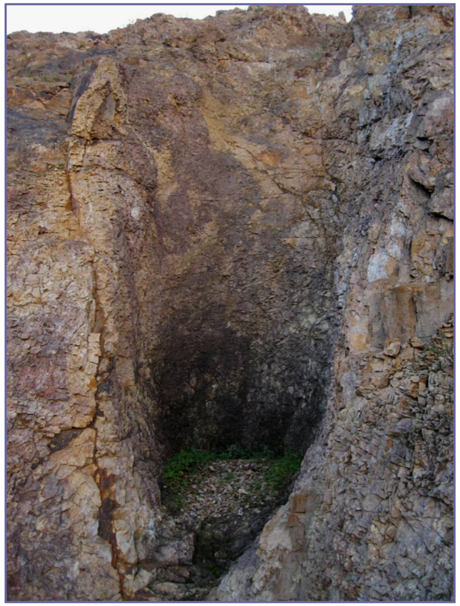


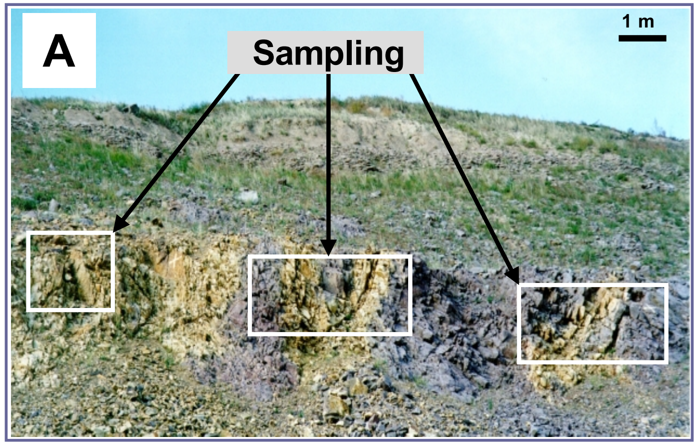
Stage of hydrothermal ore formation

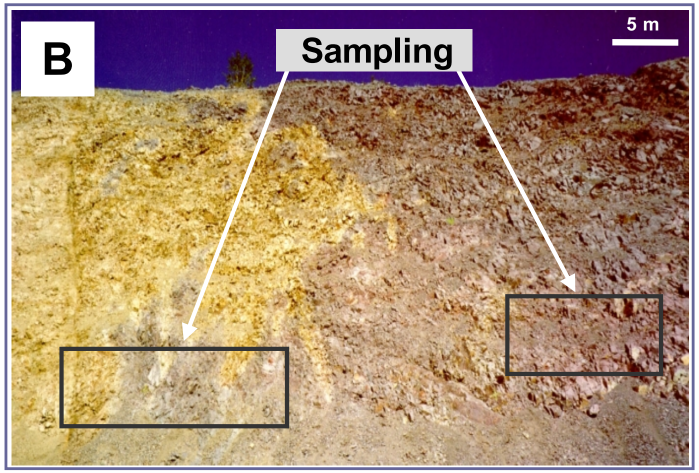
Stage of the original state of the geological environment before the deposit opening

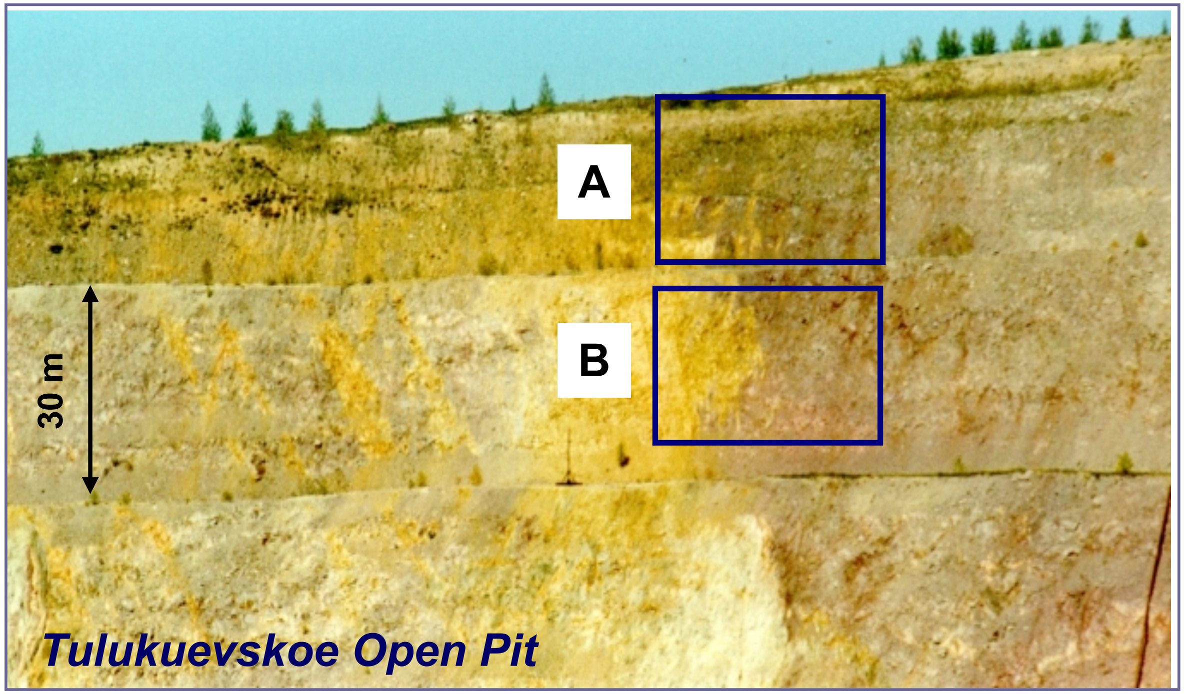
Stage of the deposit opening by an open pit, recession of water table, U transport and redeposition

Location for glass samples







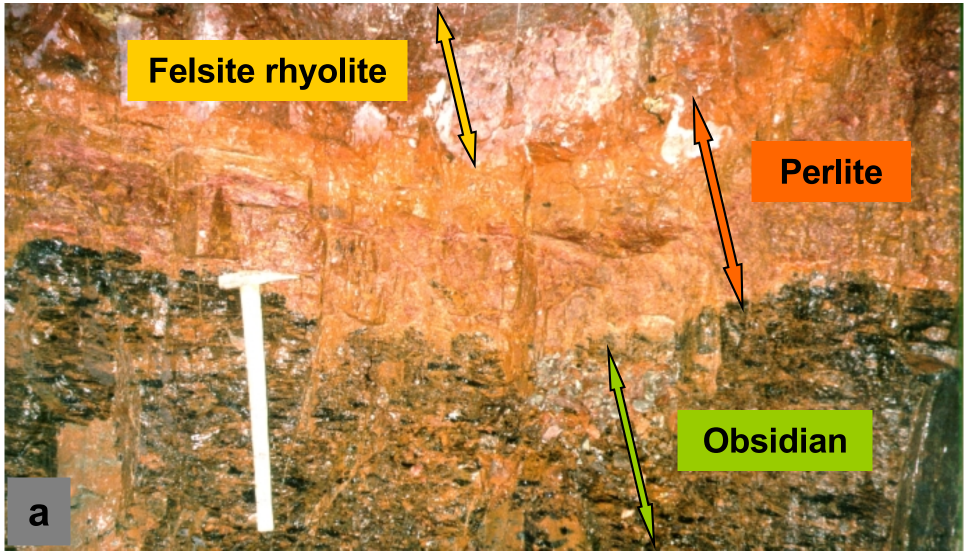


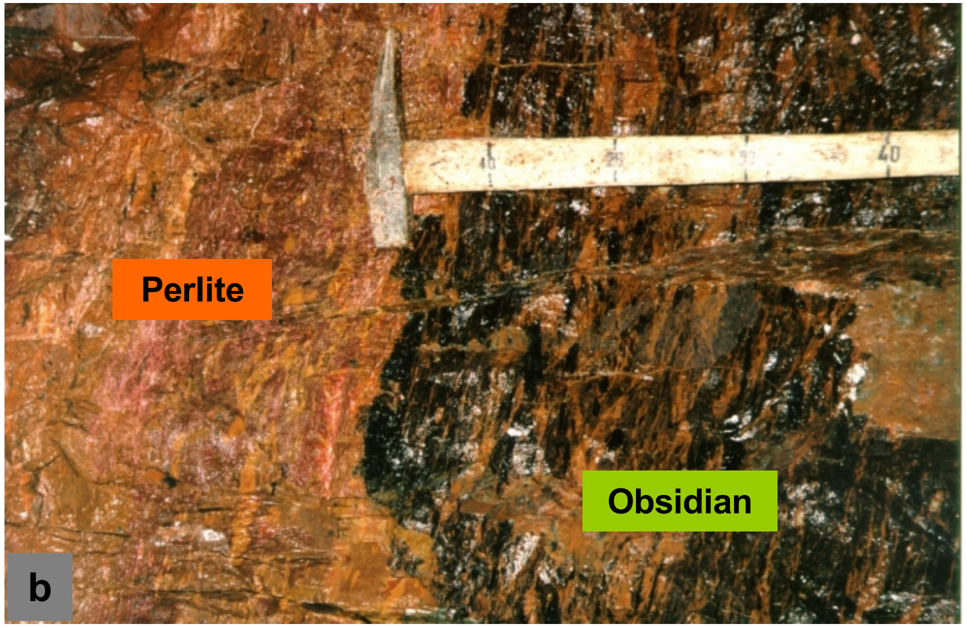
1. **Highly siliceous massive volcanic glass and apoglassy rock**

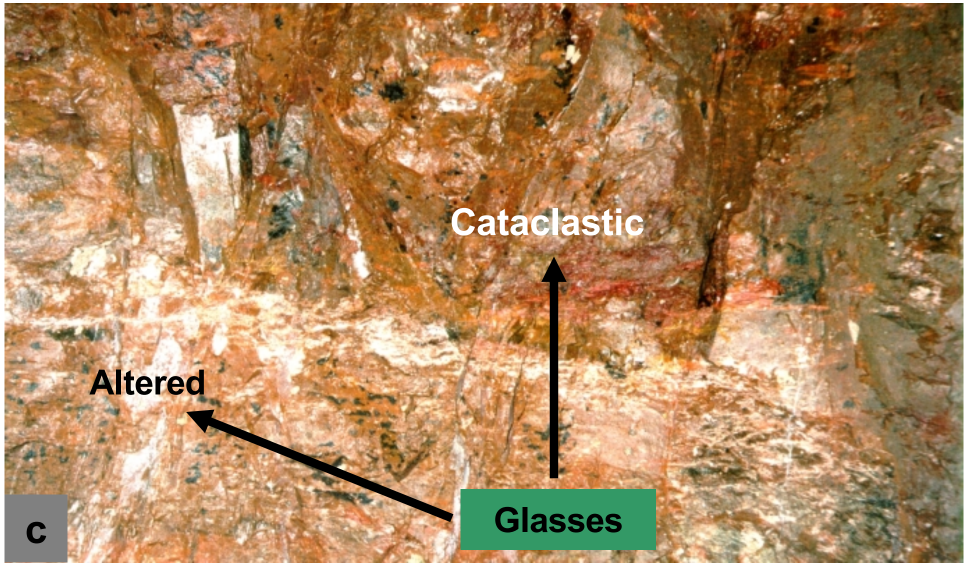
2. **Glass in form of fiamme and matrix in ignimbrites**

3. **Massive and fluidal rhyolite-rhyodacite volcanic glass**

Volcanic glass in felsite rhyolite of the Novogodnee deposit (mine horizon at depth of 300 m)







Near-contact parts of a volcanic glass bed-like body in felsite rhyolite:

(a) the top of the fresh obsidian-perlite volcanic glasses bed

(b) well-preserved obsidian-perlite glasses

(c) bottom of the cataclastic and altered glasses bed

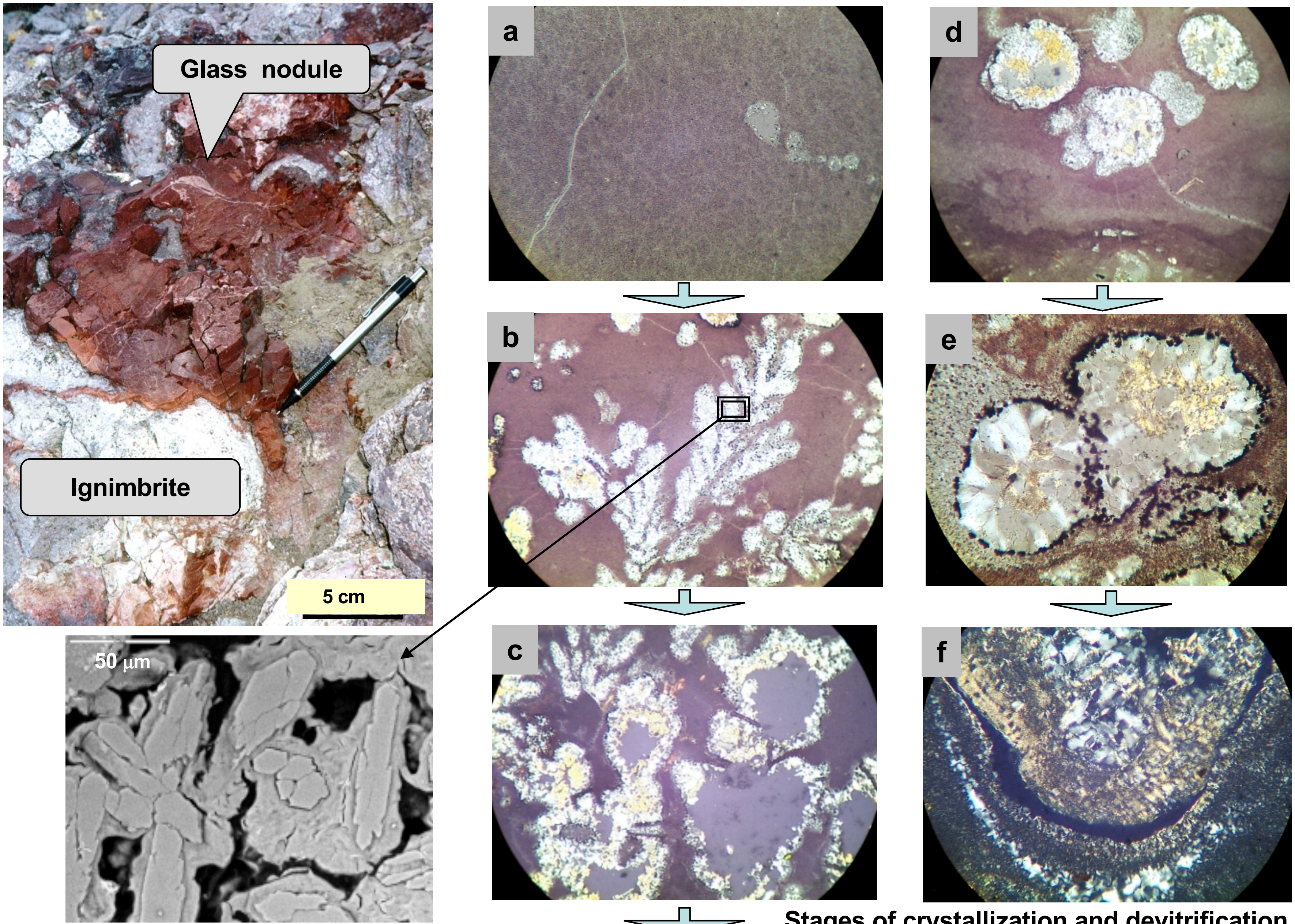
Table B6-1
Chemical composition (w. %) of volcanic glasses with different intensity of devitrification and epigenetic transformations

NN	SiO_2	TiO_2	Al_2O_3	ΣFe	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	S	LOI
F2-a	83.09	0.09	6.99	4.05	0.06	0.68	0.50	0.50	1.79	0.015	0.030	2.21
F2-c	67.90	0.57	15.22	4.45	0.06	1.02	0.61	4.42	3.39	0.091	0.041	2.23
F5	88.19	0.09	2.30	1.89	0.05	1.27	2.40	0.21	0.55	0.012	0.040	3.00
F6	83.53	0.13	4.33	5.13	0.11	0.54	1.46	0.47	1.17	0.272	0.039	2.79
F7-0	50.25	0.12	3.99	33.03	0.15	0.96	3.11	0.18	1.14	0.087	0.019	7.00
F7	80.95	0.12	3.97	9.16	0.05	0.45	0.71	0.27	1.11	0.035	0.039	3.12
F8	73.06	0.11	4.69	15.96	0.10	0.38	0.45	0.30	1.54	0.064	0.019	3.31
F9	64.23	0.22	9.69	10.21	0.46	1.15	3.11	1.32	2.92	0.035	0.019	6.62
F10	72.02	0.18	10.53	2.60	0.06	1.10	1.42	3.14	1.95	0.027	0.090	6.88

Note: *chemical composition is determined with the use of the XRF, IGEM RAS laboratory. Oxides sum is reduced to 100%.*

F2a-F10 *- volcanic glasses transformed to a various degree:* ***F10 -****relatively fresh glass;* ***F9, F8, F7-0*** *- slightly devitrificated and altered glasses;* ***F7, F2-a, F6, F5 -*** *intensly altered and devitrificated glasses (highly siliceous apoglass rock);* ***F2-c*** *- ignimbrite of rhyodacite composition, formed by glassy and partly recrystallized welded tuff and the basic mass, the sample was picked out from the area immediately adjacent to volcanic glass*

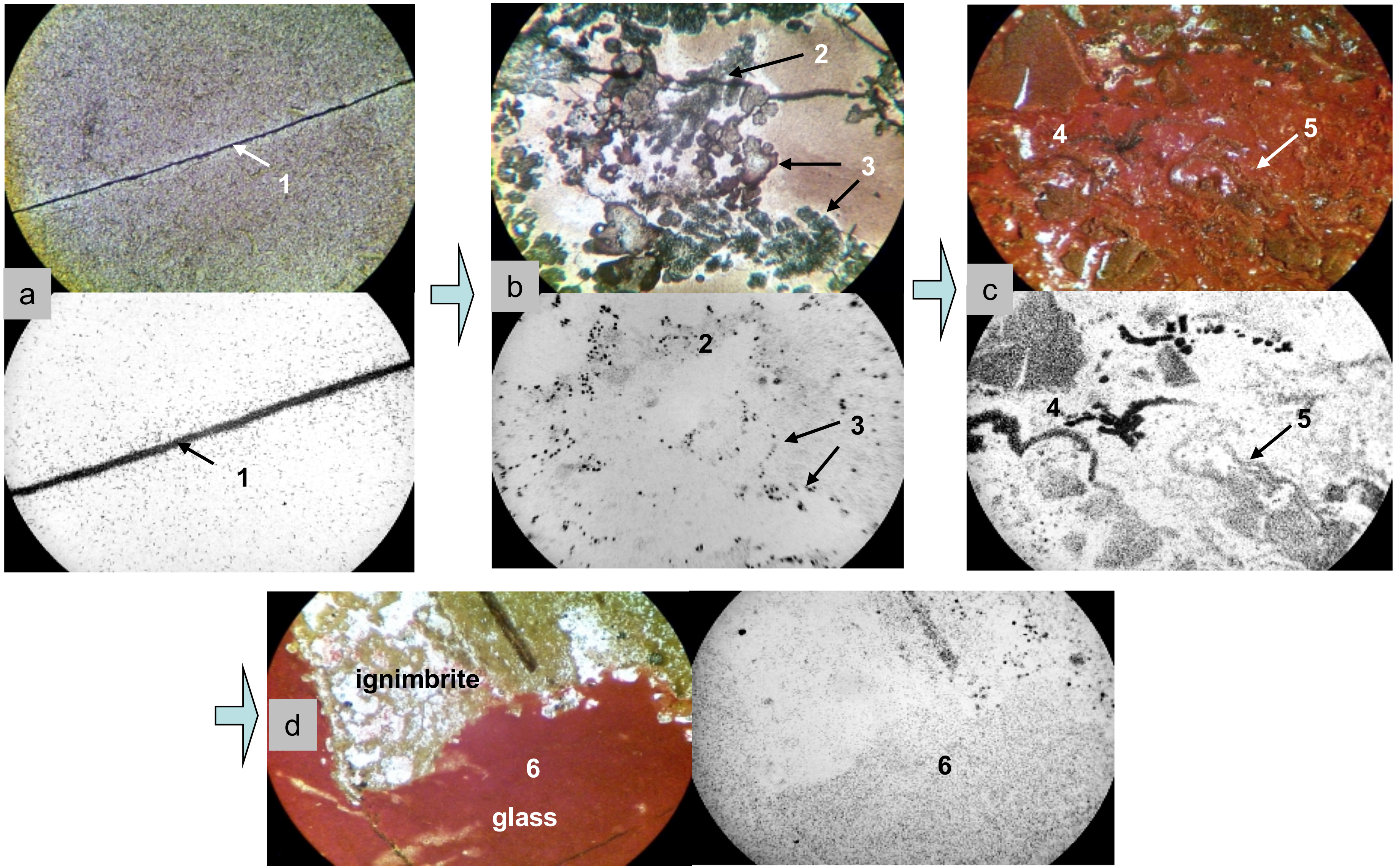
Highly siliceous massive volcanic glasses and apoglassy rocks of the TOP



SEM image in backscattered electrons of the crystallites of scopulite type

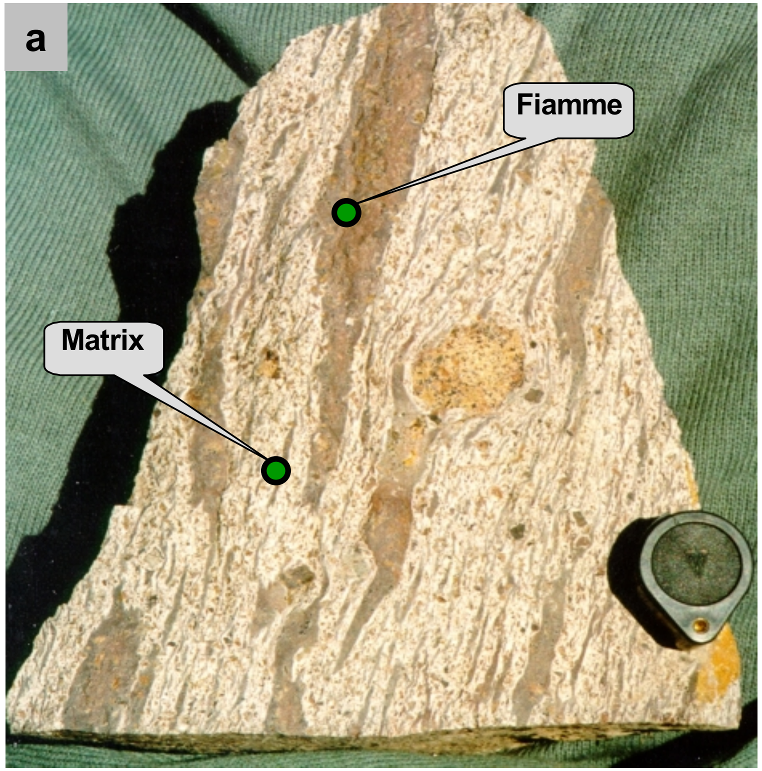
Stages of crystallization and devitrification of volcanic glasses at formation of crystallites and spherulites of quartz-micaceous-feldspathic composition (a⇒b⇒c⇒d⇒e⇒f).

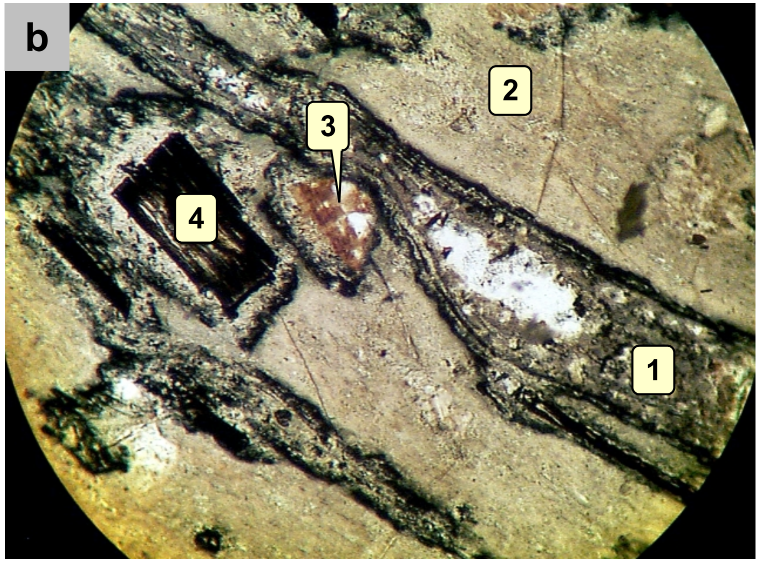
TOP: U distribution in massive highly-siliceous glasses from center to periphery (*from* a *to* d) of zonal nodules (FTR data)



High density of tracks is connected with mineralized fracture (1). The most density area of tracks in spherulites is associated with near-contact rim (2), especially with Fe and Ti oxides (3). Extremely irregular distribution of tracks is associated with cataclastic areas (4) and banded textures (5). High density and uniform distribution of tracks in brown-red siliceous glass (6) near the contact with ignimbrite.

Glass in form of matrix and fiamme in ignimbrites of the TOP

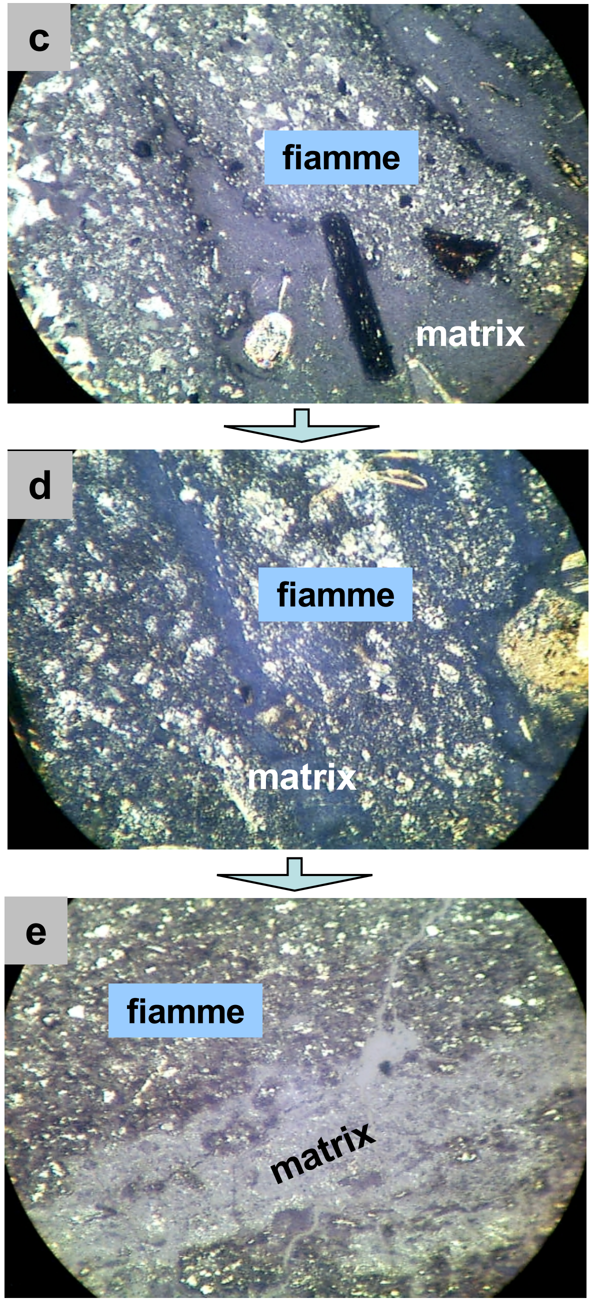




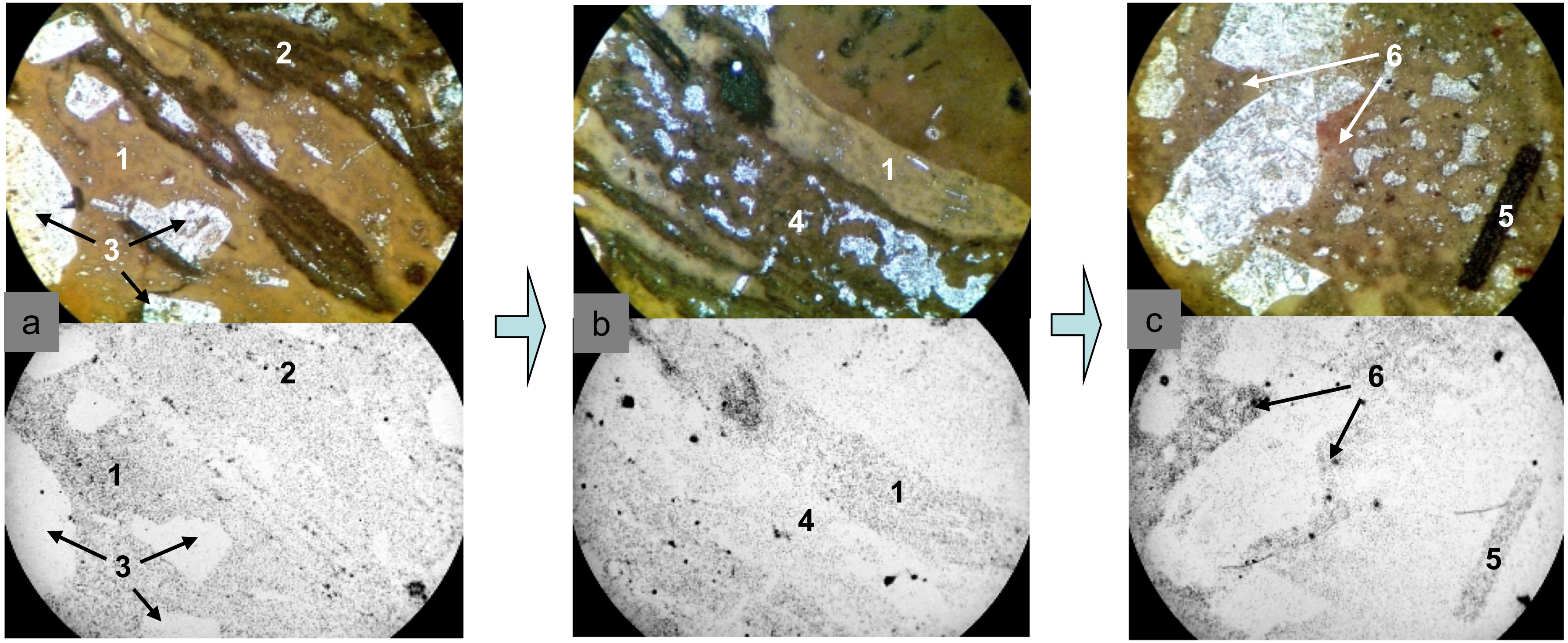
(a) glass flattened lenses (fiamme) and glassy matrix in ignimbrite of trachydacites

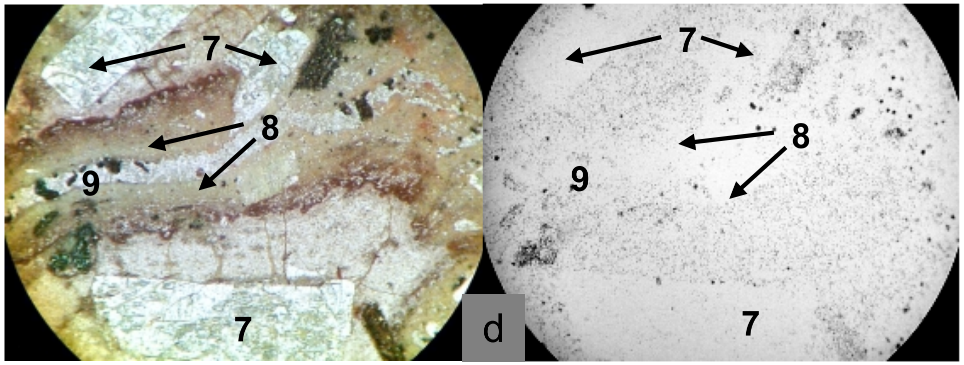
(b) Microstructure of ignimbrite: partly crystallized zonal fiamme (1) in glassy matrix (2). Porphyric segregations of polysynthetically twinned plagioclase (3) and opacitized and hematitized biotite (4) are fixed distinctly

(c – e) samples of the weakly and intensively alterated glassy fiamme and matrix of the ignimbrite



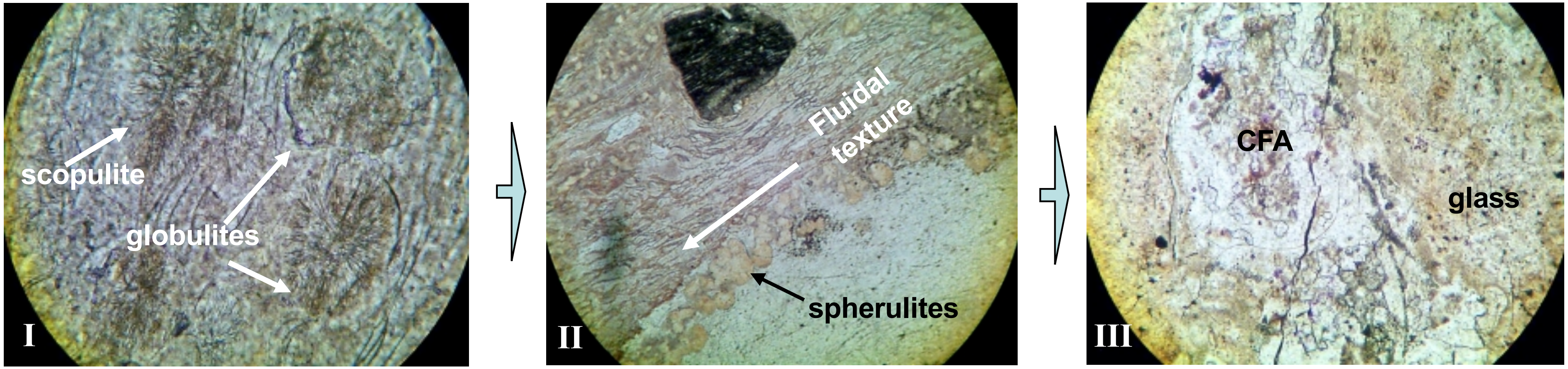
TOP: U distribution in fresh (a) and altered (b ⇒ c ⇒ d) vitrous matrix, fiamme and phenocrysts of ignimbrites



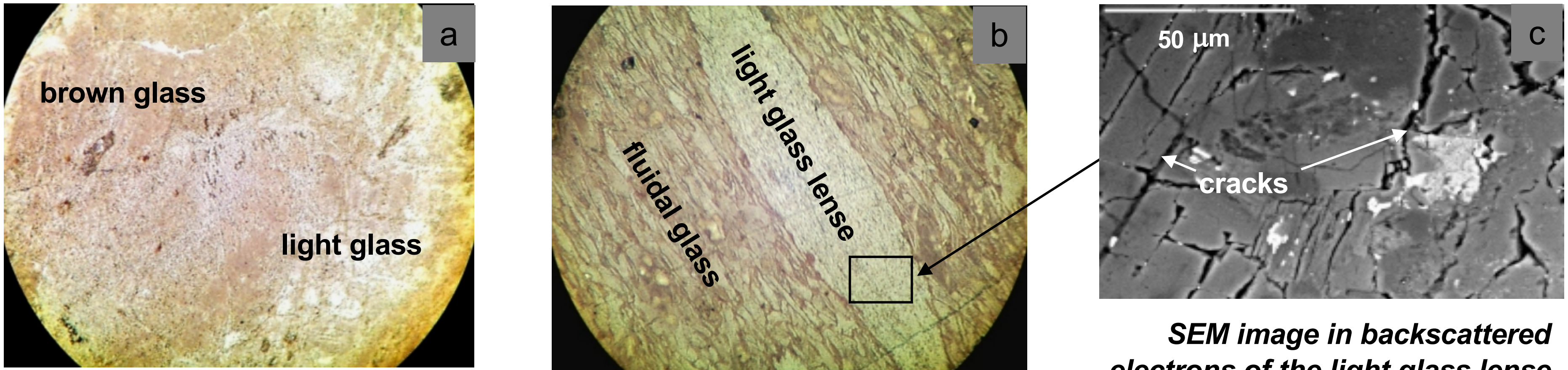


Dense and uniform tracks distribution in matrix (1) and fiamme (2) of ignimbrites. Quartz and feldspars (3) contain no uranium. Tracks rarefaction is connected with devitrification of fiamme and formation of spotted textures (4). The highest tracks density is marked in leucoxenized biotite (5) and near accumulations of mineral phenocrysts and rock fragments (6). Carbonate-hydromica aggregate, replacing plagioclase, does not contain tracks (7). Tracks connected with hematite dissolution (8) are observed into the near-contact part of carbonate veinlet (9).

Massive and fluidal rhyolite-rhyodacite volcanic glasses of the Tulukuevskoe and Novogodnee deposits



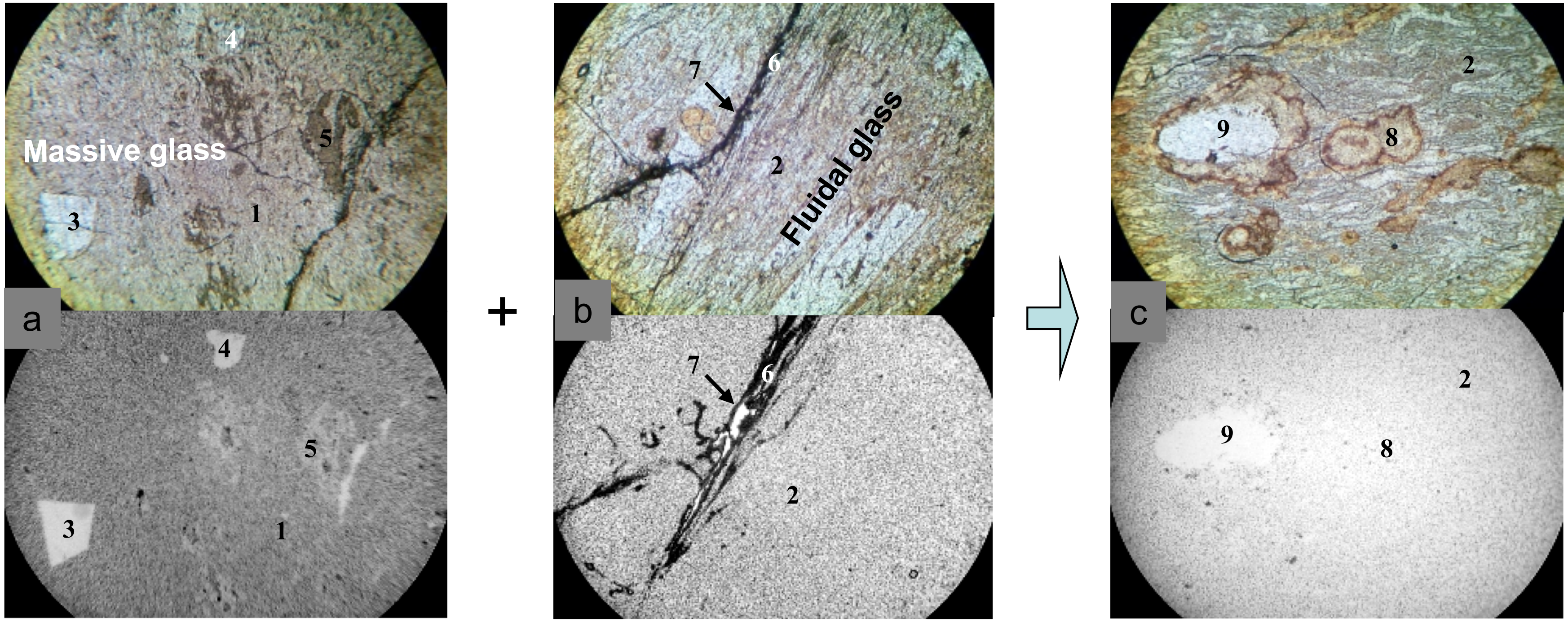
Stages of glass devitrification: (I) formation of crystallites (hair-like crystallites - trichites, globulites and scopulites), (II) spherulites and (III) microcrystalline crystallization. Crystallites are changed by spherulites and mineral phases crystallization (quartz-feldspathic aqqregate, carbonate and fluorite - CFA).

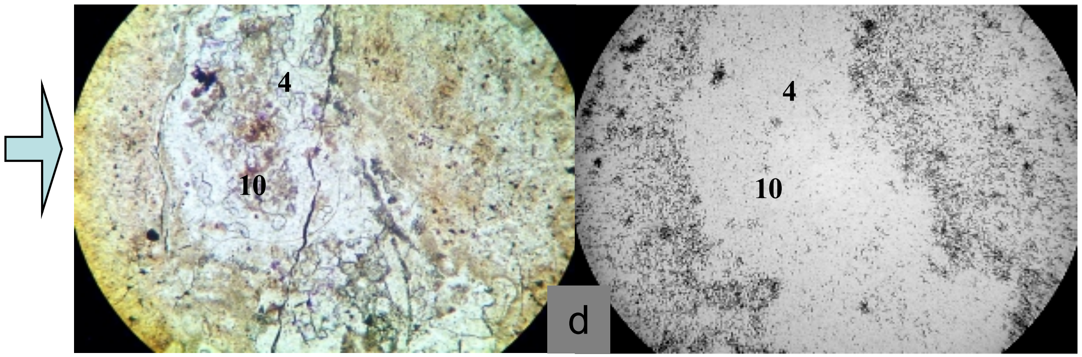


SEM image in backscattered electrons of the light glass lense

Fresh massive (a) and fluidal (b) glasses with nonmineralized and serpentin filled cracks (c).

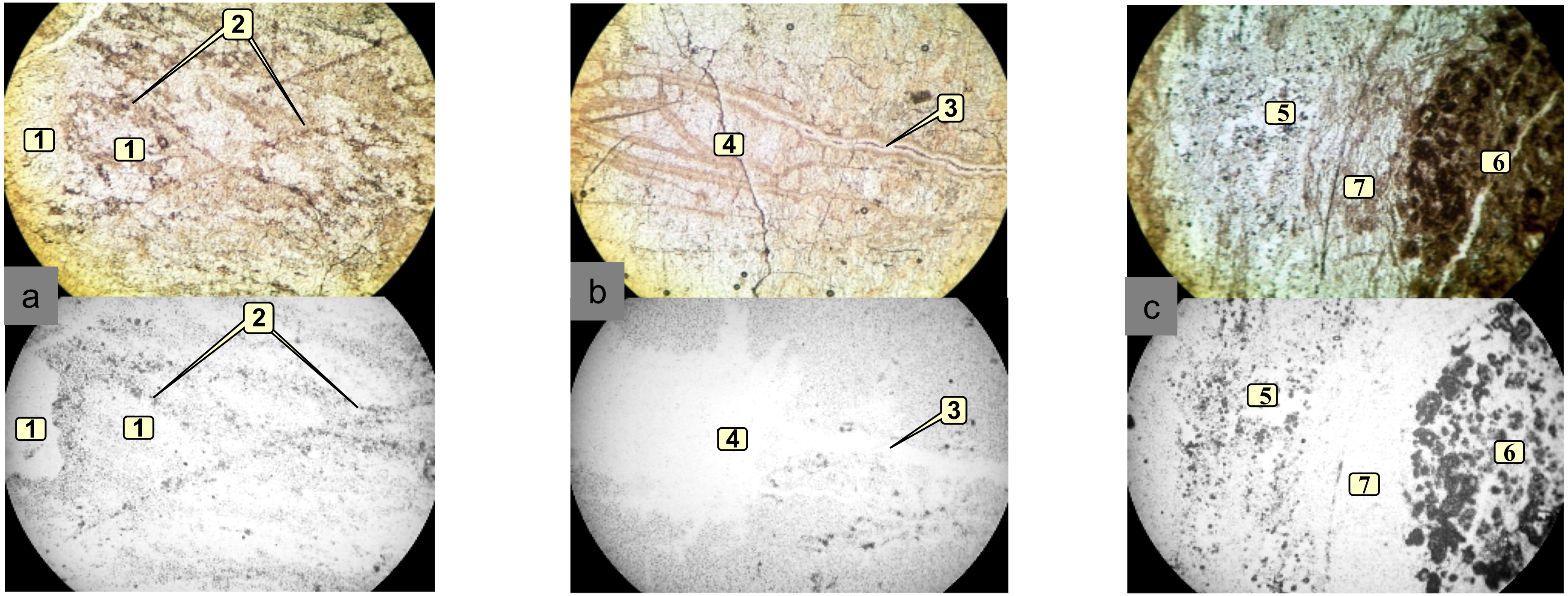
Tulukuevskoe and Novogodnee deposits: U distribution in massive and fluidal rhyolite-rhyodacite volcanic glasses as function of devitrification (FTR data)

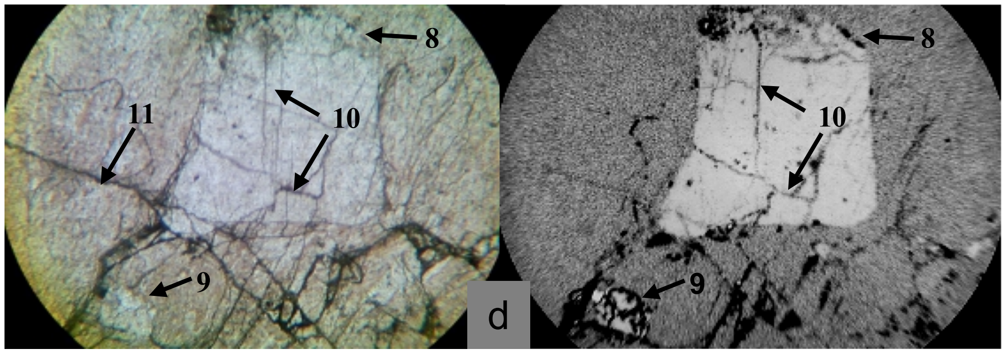




Uniform and dense tracks distribution in massive (1) and fluidal (2) volcanic glasses. “Fresh” grains of quartz (3), plagioclase (4) and orthoclase (5) do not contain tracks. The most dense track accumulations (6) and areas with the through out holes (7) are associated with fractures filled by Fe and Ti oxides and hydroxides. Stages of successive devitrification [(a, b)⇒c⇒d] of glasses with various degree of crystallization, accompanied by distinct uranium extraction: (c) - crystallites and spherulites formation (8) with crystallization center (9); (d) formation of local sites of quartz-feldspar-fluorite composition crystallization (10).

Tulukuevskoe and Novogodnee deposits: U distribution in cataclasites, microbrecciation and near-contact minerals (Ti-bearing accessory, phenocryst) in massive and fluidal rhyolite-rhyodacite volcanic glasses (FTR data)





(a) Formation of lenticular-banded, partly crystallized (quartz, feldspar) glasses (1) with the textures specific for cataclase and microbrecciation (2).
(b) U extraction from the glasses near micro-veinlets of quartz-feldspatic composition (3) and from the sites (4) with the intensive veinlet formation.
(c) U redistribution (5) in near-contact zone of Ti-bearing accessory minerals with U accumulation in leucoxene (6) and U extraction (7) of neighboring glasses sites.
(d) Tracks of high density are associated with near-contact parts of orthoclase grains (8), quartz (9), and intersecting fractures (10) as well as fractures in the glass (11).

U distribution in different intesity of alteretions and devitrification rhyolite-rhyodacite glasses (massive and fluidal) at the Tulukuevskoe (A) and Novogodnee (B) deposits

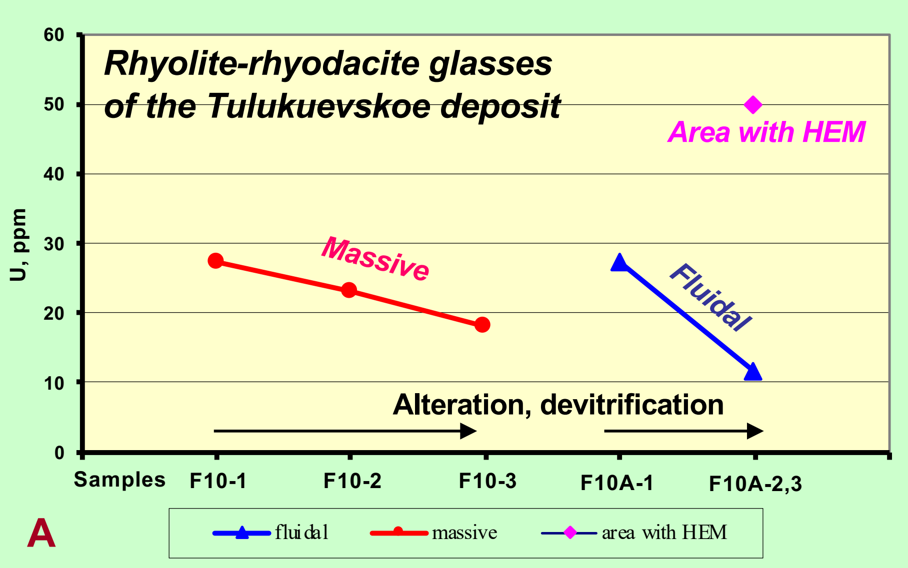
A

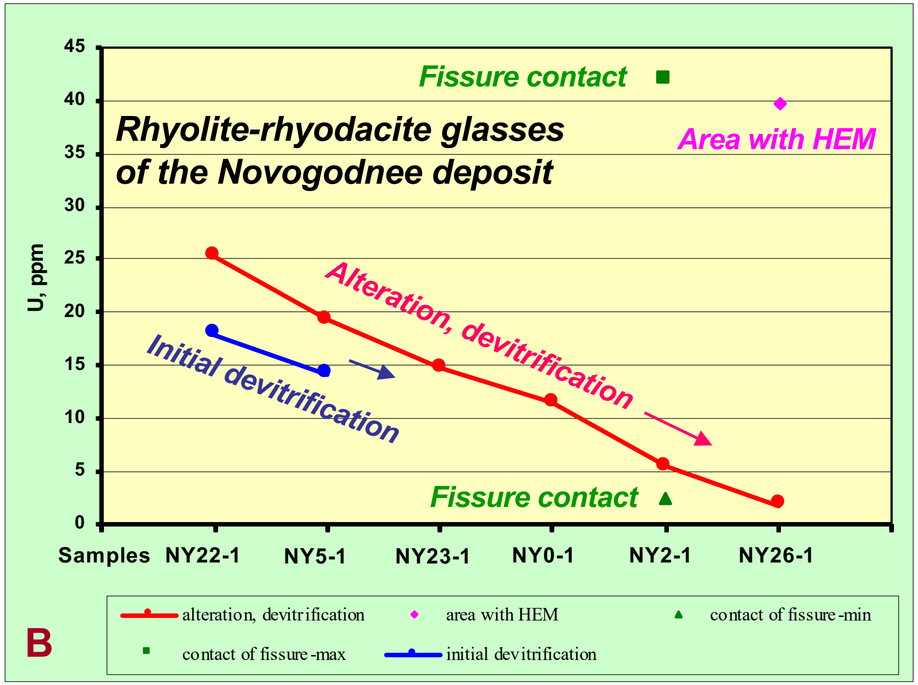
Samples, section	The number of sites[1]	U content, ppm		Coefficient of variation
		Average[2]	Range	
Massive glass				
Fresh glass (F10-1)	6	27.35	22.75-28.98	8.45
Altered[3] I glass (F10-2)	6	23.16	20.08-28.35	14.16
Altered II glass (F10-3)	3	18.07	17.34-18.42	3.04
Fluidal glass				
Fresh glass (F10A-1)	5	27.26	23.54-33.24	14.35
Altered I glass (F10A-2)	4	11.55	9.81-17.04	27.53
Area with HEM (F10A-3)	4	49.79	30.74-59.21	26.61

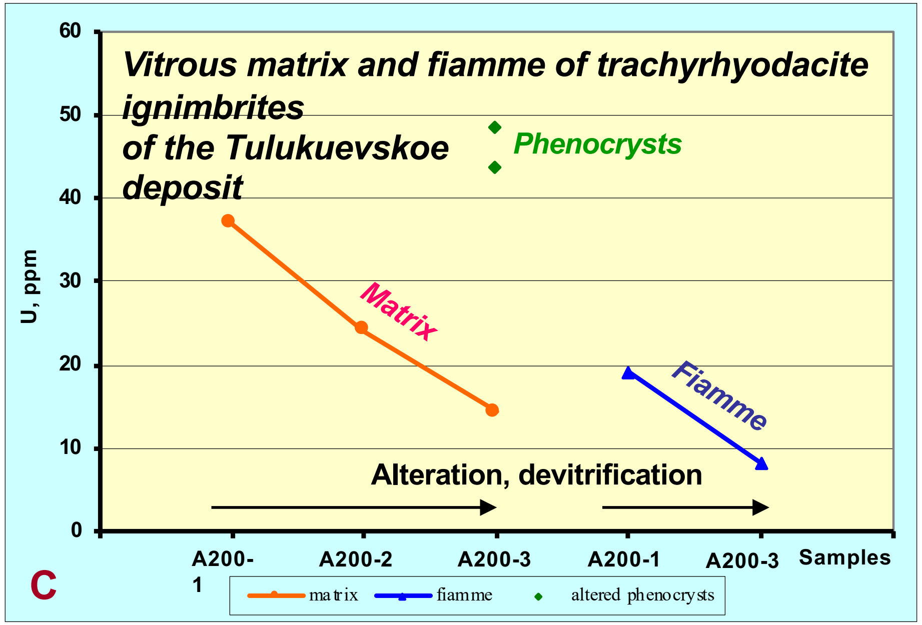
B

Samples, section	The number of sites[1]	U content, ppm		Coefficient of variation
		Average[2]	Range	
Relatively unaltered massive and fluidal glasses				
Fresh glass (NY22_1)	8	25.26	23-97-27-47	5.31
Fresh glass (NY5_1)	9	19.30	18.17-21.03	4.97
Initial devitrification[3] I (NY22_1)	9	17.85	17.30-19-11	3.59
Initial devitrification II (NY5_1)	9	14.12	12.54-15-18	6.94
Alteration and devitrification of glasses				
Altered[4] I glass (NY23_1)	9	14.75	13.12-17.75	10.78
Altered II glass (NY0_1)	9	11.42	9.49-12.19	8.06
Altered III glass (NY2_1)	9	5.34	5.06-6.62	10.86
Altered IV glass (NY26_1)	9	1.72	1.60-2.69	26.16
Area with HEM (NY26_1)	5	39.55	32-12-55.33	22.66
Deformated glasses (fissure (contact)				
Contact of fissure[5] /min/ (NY2_1)	5	2.20	1.44-3.24	29.55
Contact of fissure /max/ (NY2_1)	5	41.96	20.51-53-32	30.67

Tulukuevskoe and Novogodnee deposits: U distribution in fresh and altered massive and fluidal glasses (A, B) and in vitrous matrix and fiamme of trachyrhyodacite ignimbrites (C) (FTR data)







Simplified matrix showing interrelation of U transport processes into the TOP vadose zone

→ Processes contributed to U retardation

↓ Processes contributed to U release

Precipi-tation, Humidity, Moisture	Water/rock interactions	Redox potential (reduction)	Pore/frac-ture sealing	Accretion of mineral-concentra-tors	Durability
Changed flow conditions	**Hydrolo-gic properties**	Reductive conditions	Pore/fractu-re closing, Diffusion	Positive wa-ter/mineral interaction (clay swelling)	Biomass sealing
Redox potential (oxidation), Vapor par-tial pressure	Oxidizing conditions	**Water chemistry**	Positive pore-water chemistry changes	Precipita-tion, Sorption, Altered minerals	Biomass generation, Nutrient supply, Metabolic processes
Pore/frac-ture ablution	Pore/fract. opening, Weakening, Coales-cence flow path	Negative pore- water chemistry changes	**Pore/frac-ture space changes**	Positive volumetric effect, Growth of specific surface area	Positive volume changes
Leaching	Colloid transport	Mineral/ water inter-action, Solubility, Desorption	New surfaces	**Changes of mineral material**	Biomass accumula-tion, Forma-tion of metal-loorganic compounds
Biomass water consumption /releaze	Biomass dilution	Biomass microche mistry, Nutrient dilution	Biomass microfrac-turing, Negative volume changes	Biomass dissolution/ minerali-zation	**Microbiotic conditions**

Summing up the obtained field and lab test data we could say that the overriding characteristic of the interactions in the vadose zone of the Tulukuevskoe Open Pit results from coupled processes.
The dominant processes can be grouped into two categories: those contributing to U release and those contributing to U retardation.
The significance and magnitude of the coupling varies both spatially and temporally.
To identify priorities, the dominant processes were considered.
The forward and back coupling of processes makes the vadose zone an environment typified by interrelated interactions.
This idea can be shown conceptually by using an interaction matrix of the type proposed by **Hudson** (1989) and developed by **Wilder** (1997).

Recommended reading

Alexander W.R., Reijonen H.M., McKinley I.G. (2015). Natural analogues: studies of geological processes relevant to radioactive waste disposal in deep geological repositories. Swiss Journal of Geosciences. Vol. 108(1). P. 75-100.

Byers C.D., Jercinovic M.J.,Ewing R.C. et al. (1985) Basalt glass: an analogue for evaluation of the long term stability of the nuclear waste form borosilicate glasses. Material Research Society Symposium Proceedings. 44. P. 583

Crovisier J.-L., Advocat T., Dussossoy J.-C. (2003). Nature and role of natural alterations gels formed on the surface of ancient volcanic glasses (natural analogs of waste containment glasses). Journal of Nuclear Materials. 321. P. 91-109.

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