Joint ICTP-IAEA International School on Nuclear Waste Vitrification

23 - 27 September 2019
Trieste, Italy

Further information:
http://indico.ictp.it/event/8772/
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Metamict
Radiation Damage in ^ Single Crystals

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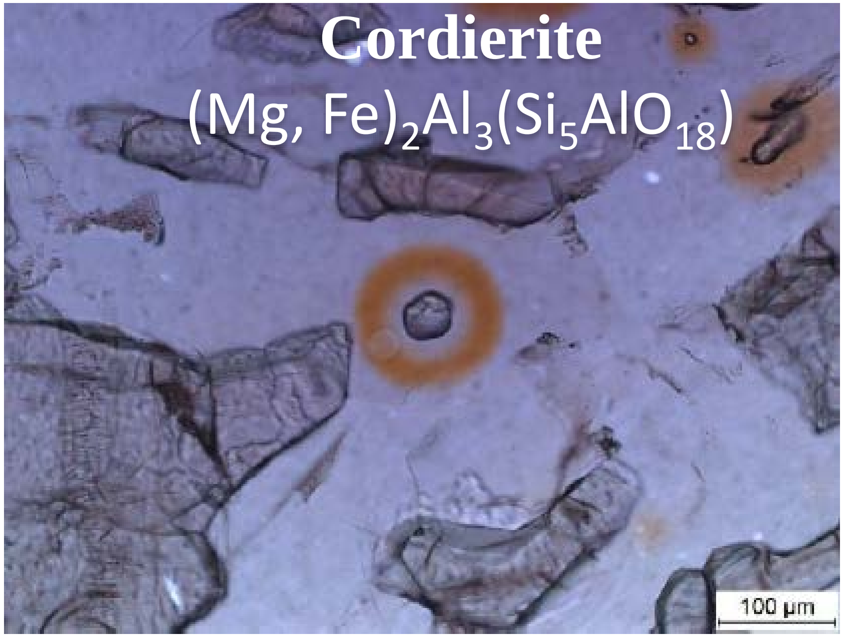
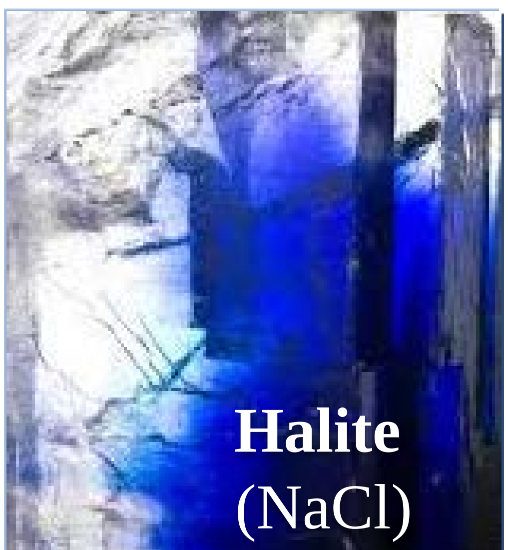
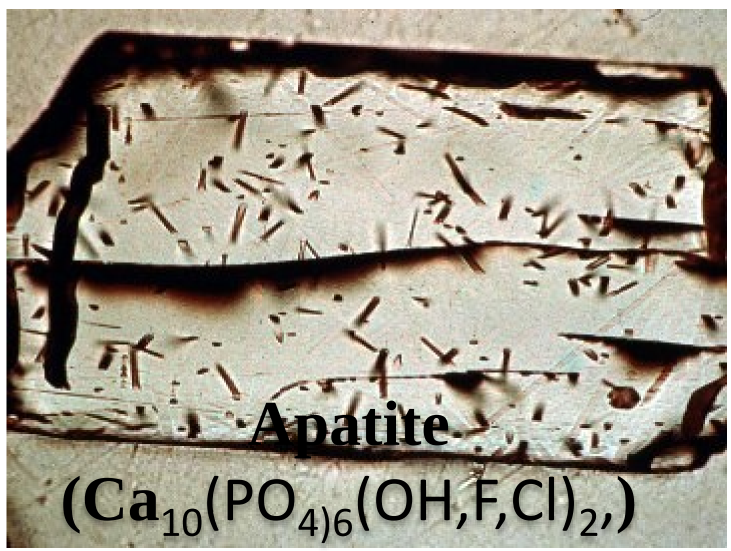
Why such study is required?

- To document collective effects of different radiations (α, β, γ) on different matrices (silicate, aluminosilicate, phosphate) having relevance in waste immobilization over long time scale.
- To understand and predict radiation effects on medium/short range ordering of vitreous wasteform and crystalline components of glass ceramics and ceramic wasteforms.
- To document relative dominance of radiation damage and thermal annealing.
- To establish radiation effects – matrix composition – matrix structure – properties correlations.
- To build-up public confidence on vitrified nuclear waste matrices.

Atlas of METAMICT Natural Single Crystals







Metamictization

is a natural process of CRYSTALLINE to AMORPHOUS phase transformation

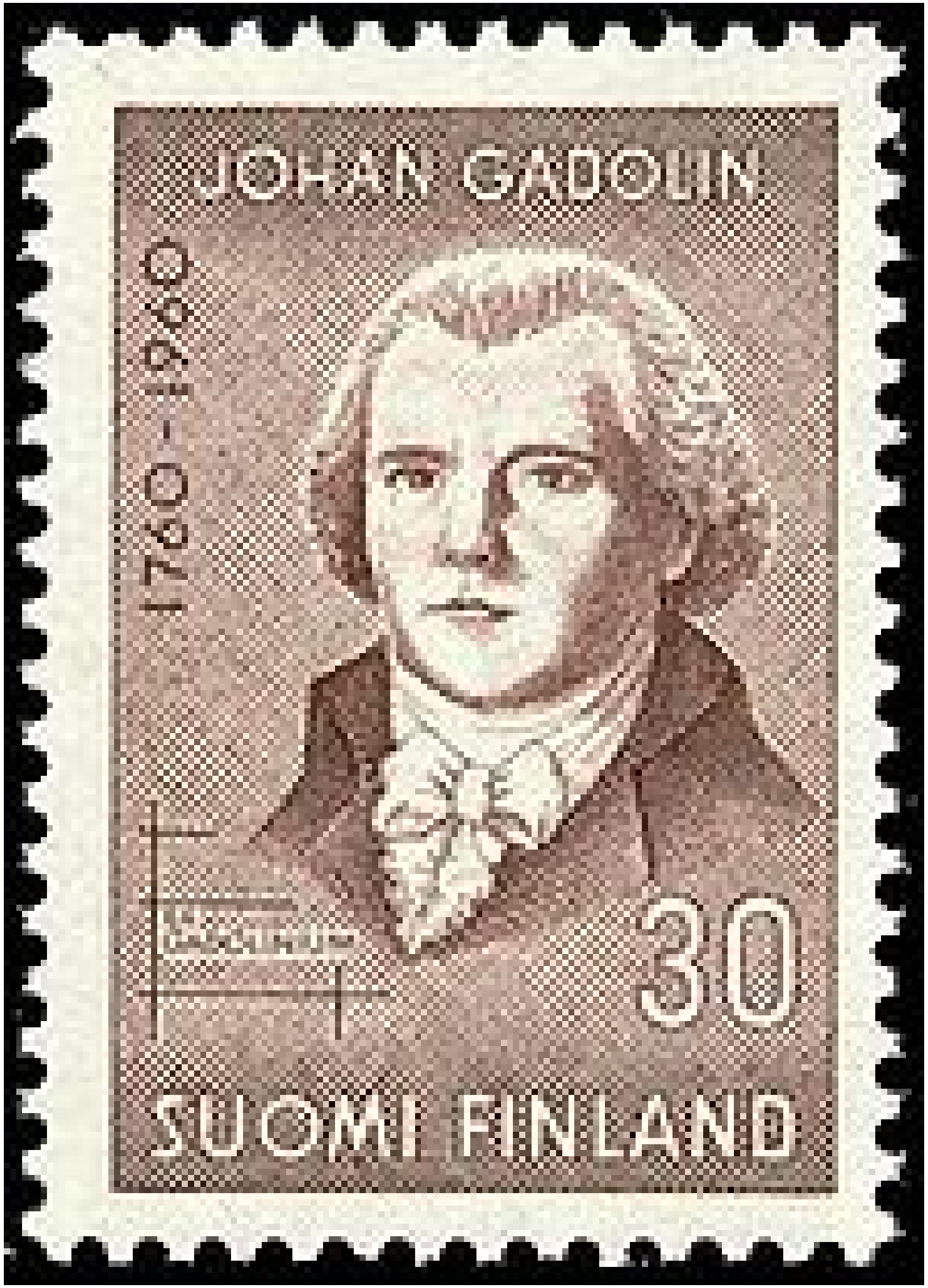
Outcome of two counteracting processes: **radiation damage accumulation** & **thermal annealing**.

Some mineral species (**zircon, thorite, pyrochlore, fergusonite**) commonly become **metamict**. Others (**huttonite, monazite, uraninite, apatite**) are mostly observed in **crystalline state**, even though often being experienced similar radiation doses.

Johan Gadolin

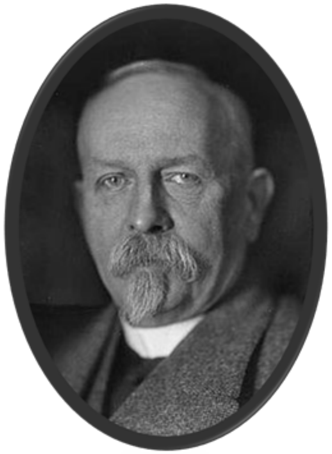
(5 June 1760 – 15 August 1852) was a Swedish later Finnish chemist, physicist and mineralogist. Gadolin discovered a "new earth" containing the first rare-earth compound yttrium, which was later determined to be a chemical element. He is also considered the founder of Finnish chemistry research.

He extracted **Y** (1794) from a glass like natural material, which was later named as '**gadolinite**' after him.



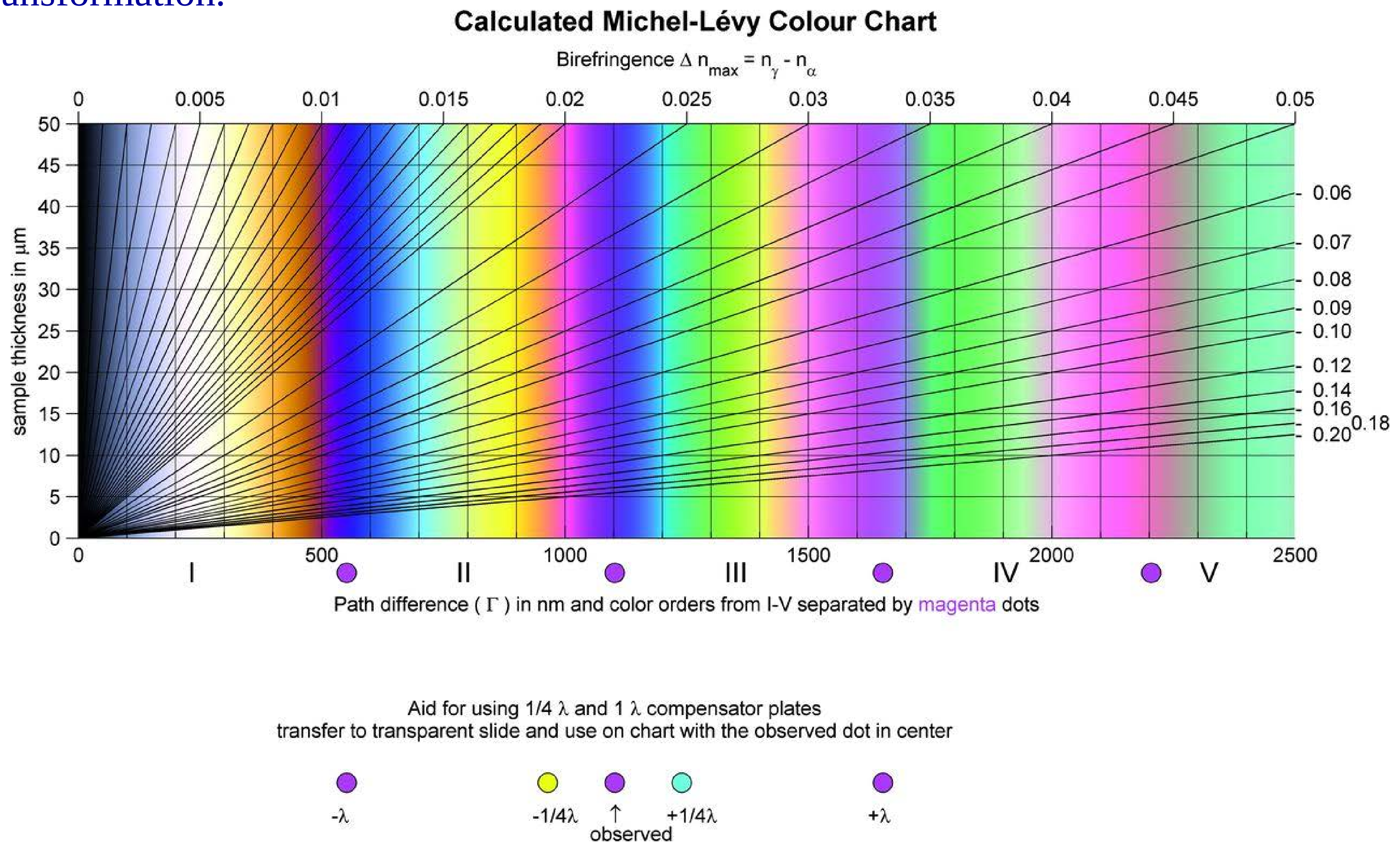
Jacob Berzelius (Swedish; 20 Aug 1779 – 7 Aug 1848), isolated several new elements including cerium and thorium.

J Berzelius extensively studied natural minerals including gadolinite and reported about its '**pyrognomic behaviour**', which **upon heating exhibited sudden glowing followed by shattering into pieces**.

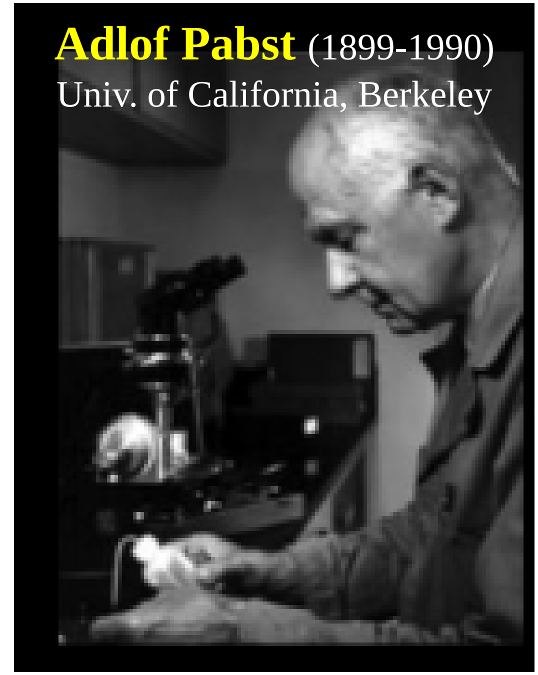


Waldemar Christofer Brøgger (10 Nov. 1851 – 17 Feb. 1940, Norway) first used the term '**metamikte**', in the year **1893**, as a **class of naturally occurring amorphous materials**. Brϕgger speculated that metamictization was due to "**outside influences**" and that complicated structures might be more susceptible to this effect. **Spencer (1904)** considered **hydration as a possible cause**, as the molecular water content of these phases could be exceedingly high (10 – 15wt%).

Other workers during the second half of the 19th century (~1860s) established that these phases were **initially isotropic but become birefringent and increase in specific gravity on heating**. As this work predated the discovery of radioactivity in 1896 by Becquerel, metamictization was not recognized as radiation induced transformation.



Tabulated the changes in properties (e.g. release of stored energy and decreased resistance to leaching) which resulted from the radiation damage.



Pabst specifically noted that some structures are 'resistant' to damage accumulation (e.g. Monoclinic $ThSiO_4$) while other polymorphs are often found in the metamict state (e.g. Tetragonal $ThSiO_4$).

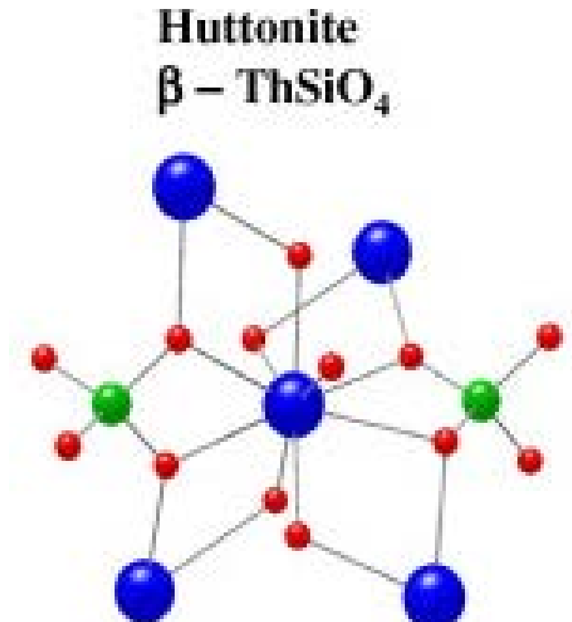
ThO_8 Coordination Polyhedra

Tetragonal, $I4_1/amd$

Isostructural Zircon

Partially/completely Metamict

$a = b = \sim 7.1328$ Å, $c = 6.3188$Å, $\beta = 104.92^0$



ThO_9 Coordination Polyhedra

Monoclinic, $P2_1/n$

Isostructural Monazite

NEVER Metamict

$a = \sim 6.784$Å, $b = \sim 6.974$Å, $c = \sim 6.500$Å, $\beta = 104.92^0$

Acta Cryst. (1978). B**34**, 1074–1079

MARK TAYLOR AND R. C. EWING

The Crystal Structures of the $ThSiO_4$ Polymorphs: Huttonite and Thorite

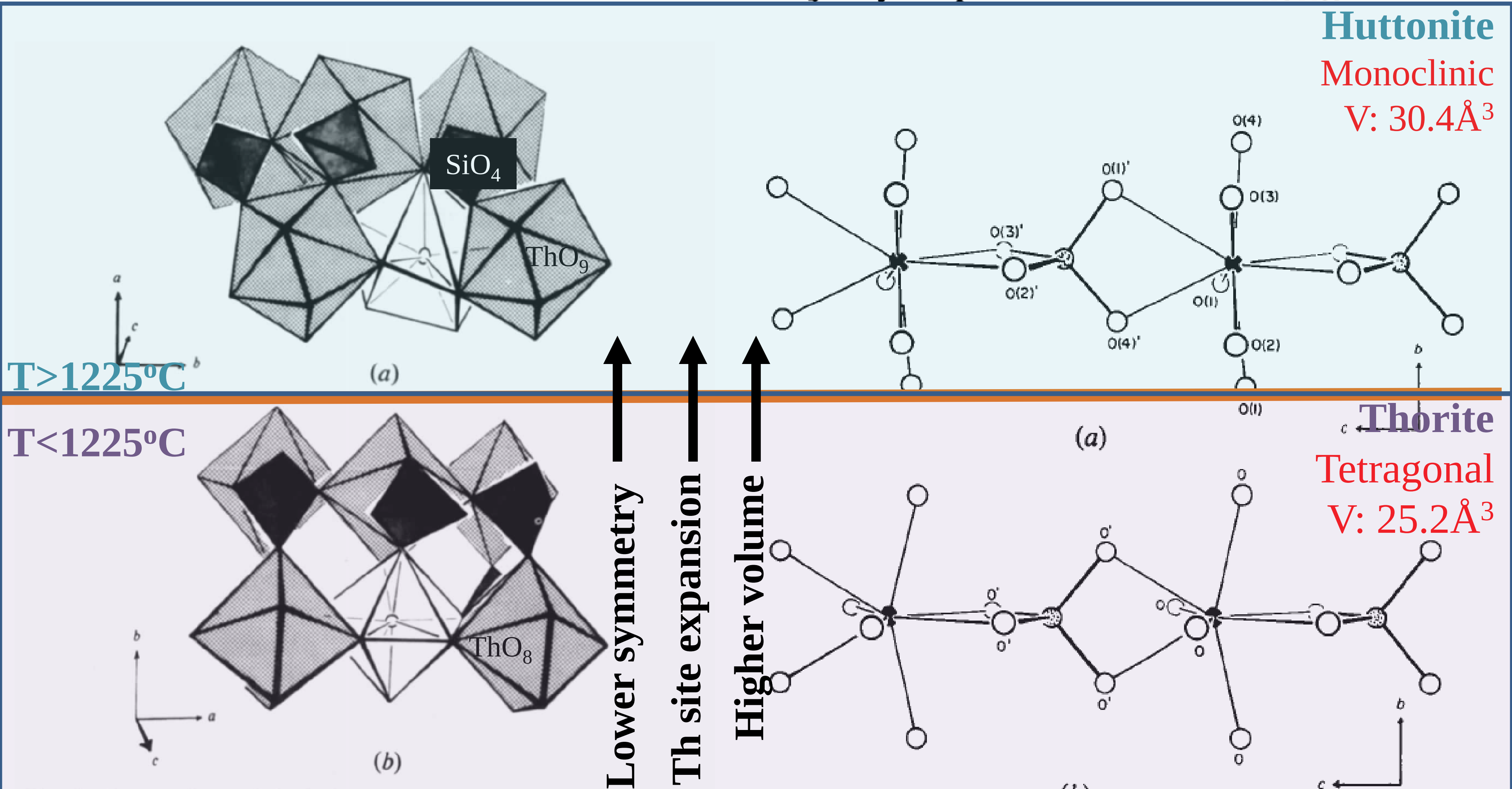


Fig. 1. Perspective polyhedral representation of the (*a*) huttonite, and (*b*) thorite structures. Darker tetrahedra are SiO_4 groups and lighter polyhedra are (*a*) ThO_9 and (*b*) ThO_8 groups.

Fig. 3. The *c*-axis chains in (*a*) huttonite and (*b*) thorite.

Both phases occur naturally, but show markedly different behavior toward metamictization

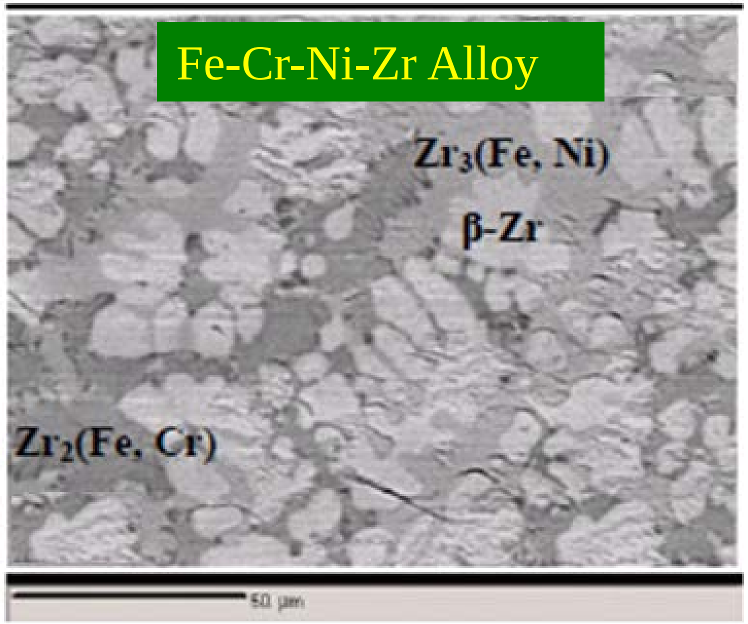
Thorite vs. Huttonite: $ThSiO_4$

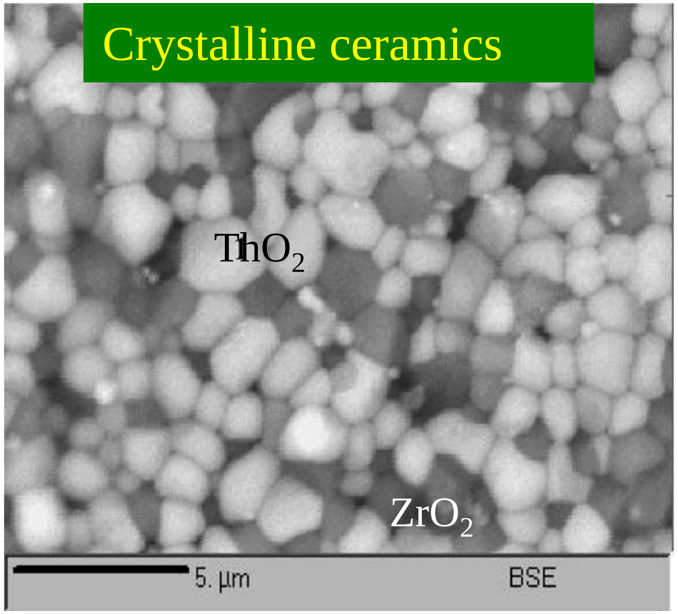
Stability criteria based on radius ratio and charge balance are inconclusive; the Th/O radius ratio (0.76) suggests that the ninefold coordinated huttonite structure should be preferred, while a calculation of Pauling charge balance indicates that O(1) of huttonite is overbonded (ζ = 2.5). All O atoms in thorite are exactly charge balanced (ζ = 2.0).

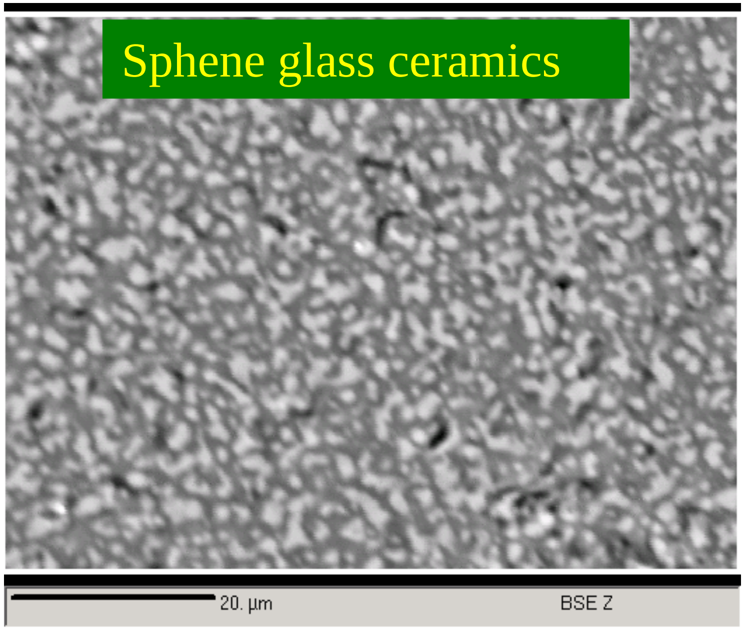
Irradiated powders of monoclinic huttonite and tetragonal thorite, with Ar^+ ions at 3 MeV to investigate structural controls on radiation damage.

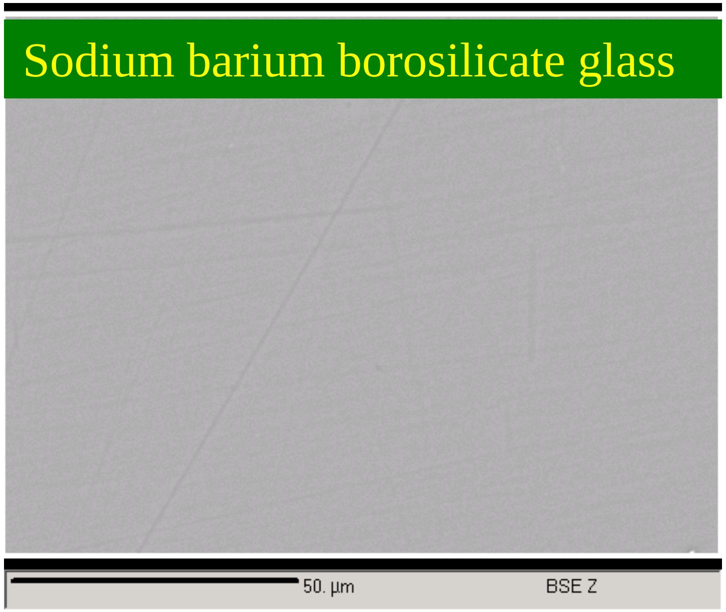
Using XRD analysis, it was demonstrated that both thorite and huttonite can become metamict (the damage cross-section for thorite is nearly twice that of huttonite); however, low temperature annealing studies showed that the huttonite recrystallized more easily than thorite. Under ambient conditions over geologic time, huttonite may recrystallize; **therefore, huttonite is not found in the metamict state**.

Various waste forms









Wasteform Selection Criteria

Homogeneous Microstructure

Solubility limit, waste loading, uncontrolled crystallization

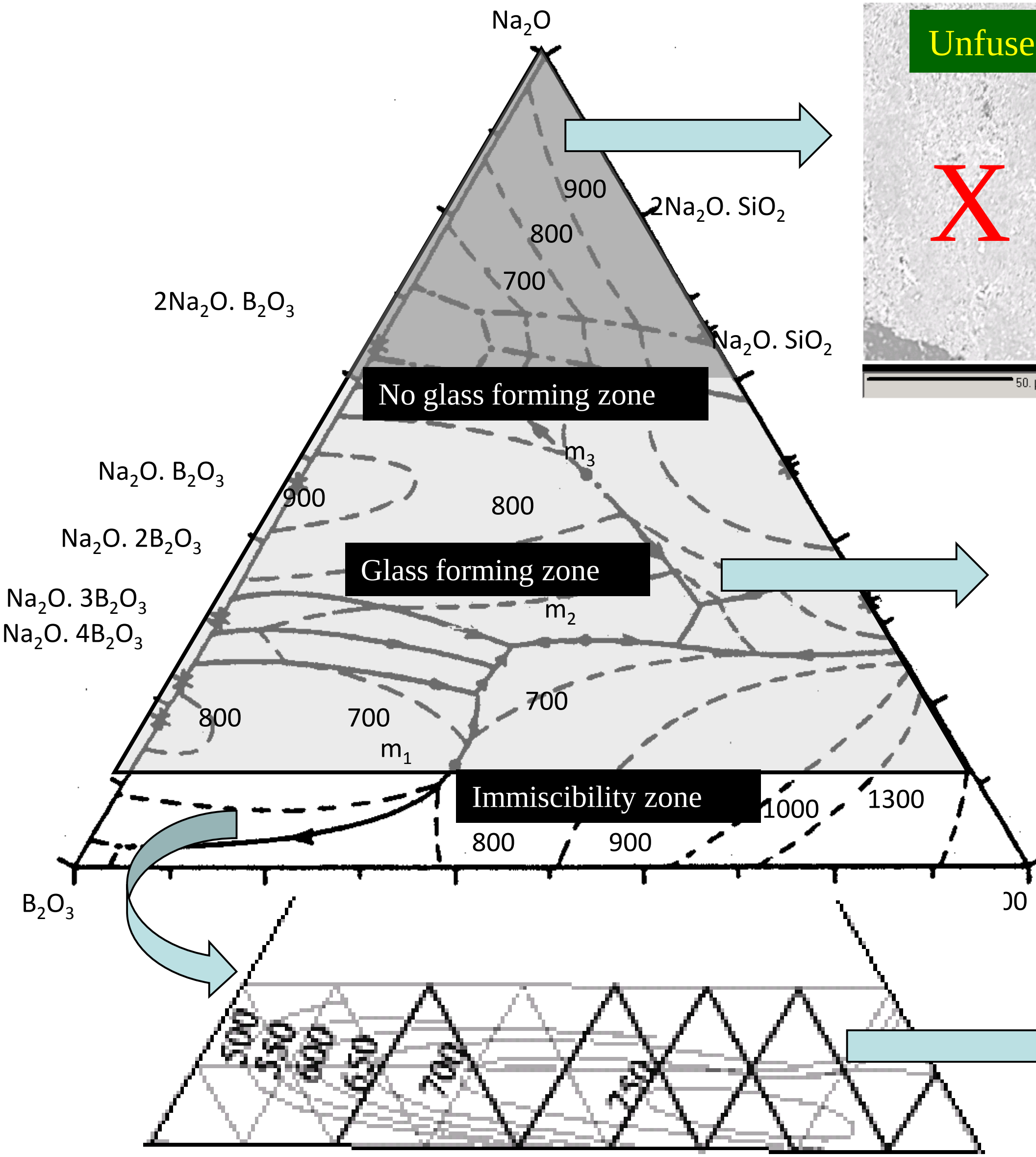
Chemical durability

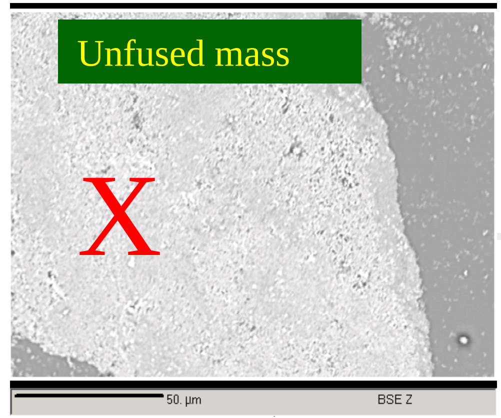
Leaching

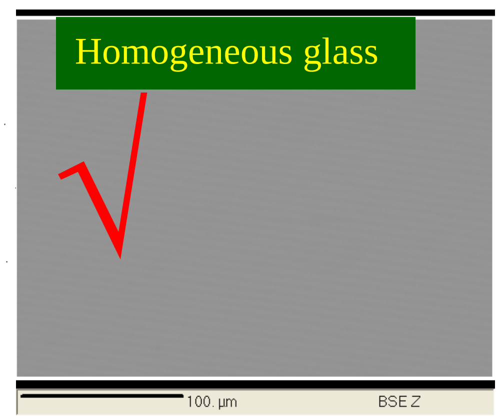
Available Technology

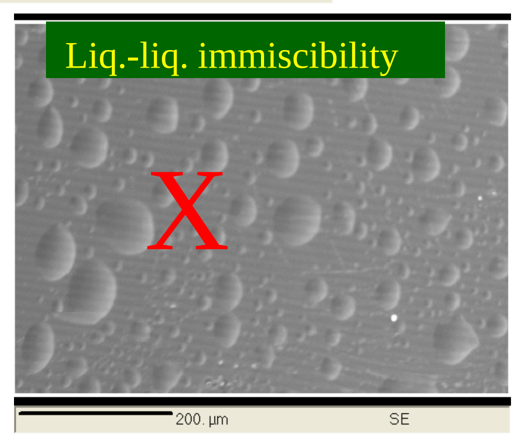
Processing temperature

Waste glass system: Sodium borosilicate glass



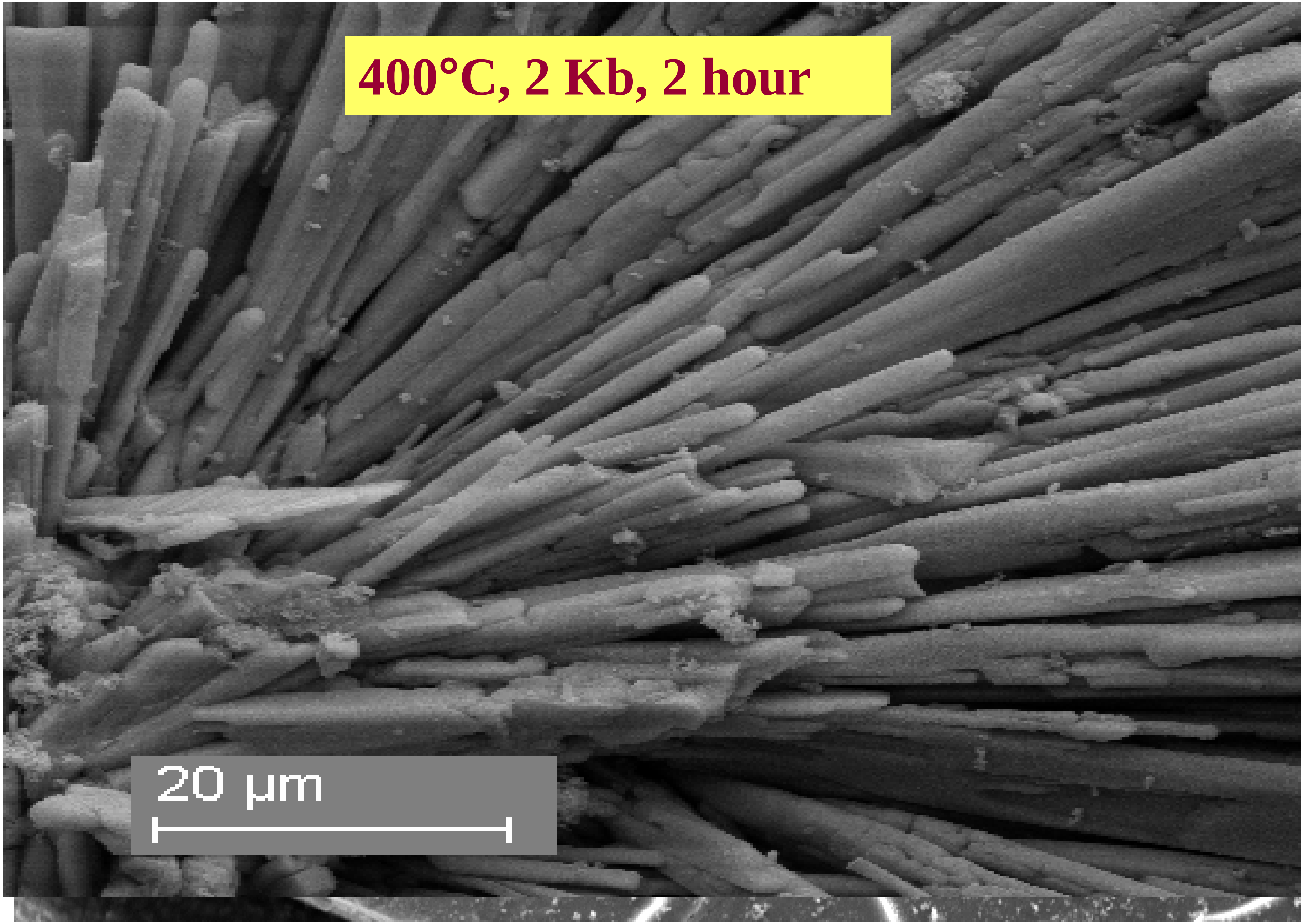


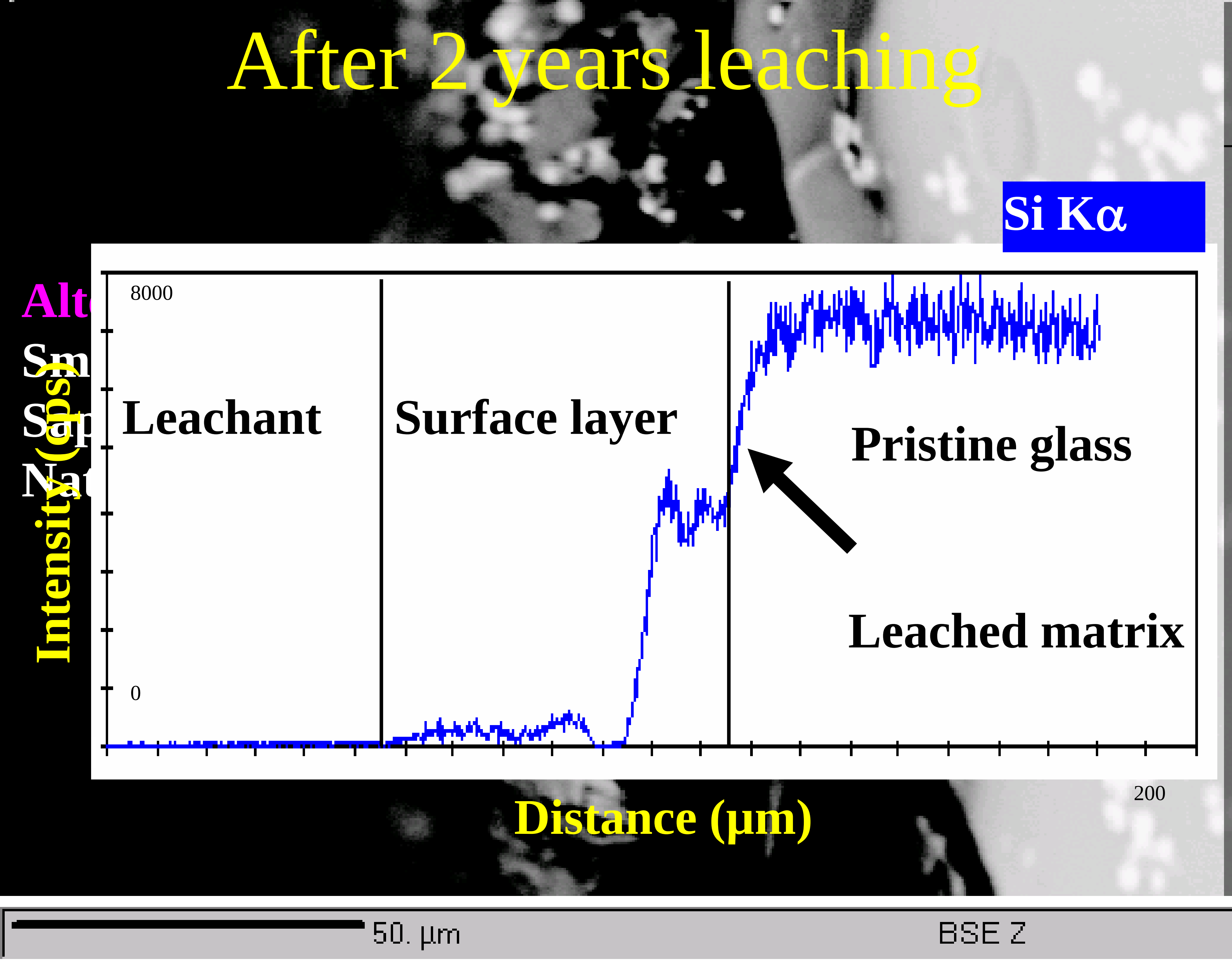




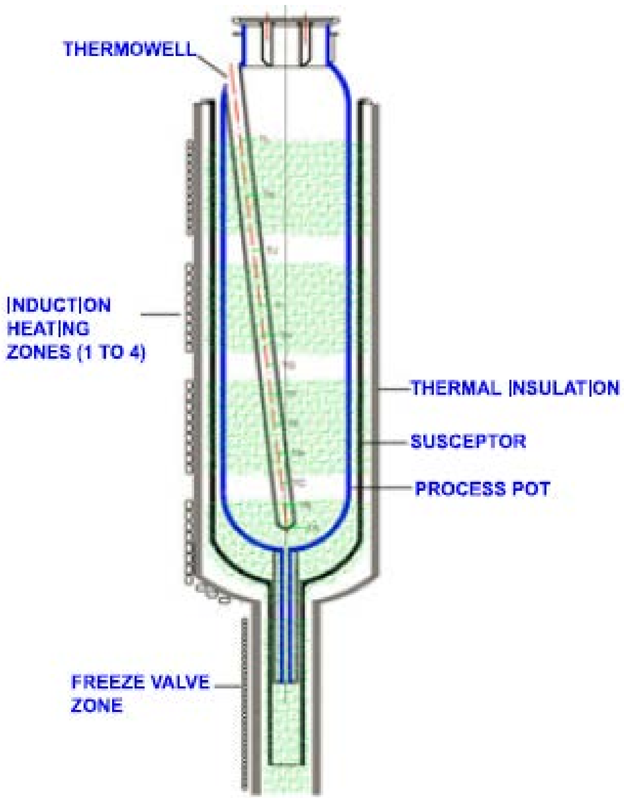
Sodium Borosilicate glass

Chemical durability assessments: P - T dependence




After 2 years leaching
Si Kα
8000
0
200
Intensity (cps)
Distance (µm)
Leachant
Surface layer
Pristine glass
Leached matrix
50. µm
BSE Z

Indigenous development of vitrification technology



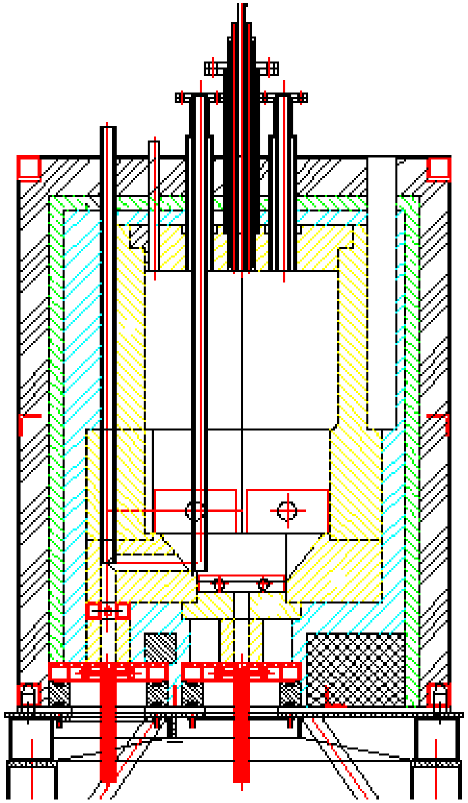
Metallic melter pot

Proven technology

Induction heating

~1000°C

Borosilicate glass



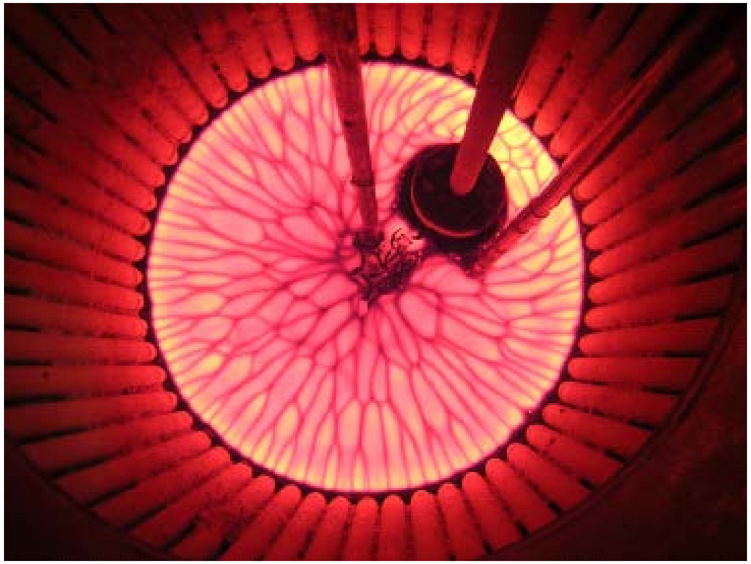
Ceramic melter pot

Proven technology

Joule heating

~1150°C

Borosilicate glass



Cold crucible

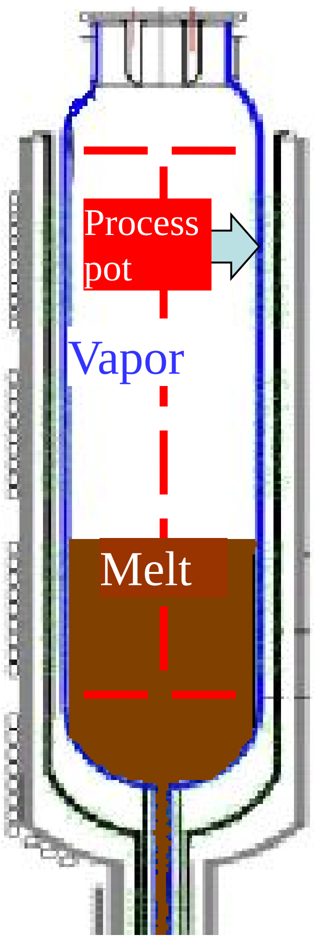
Demonstration stage

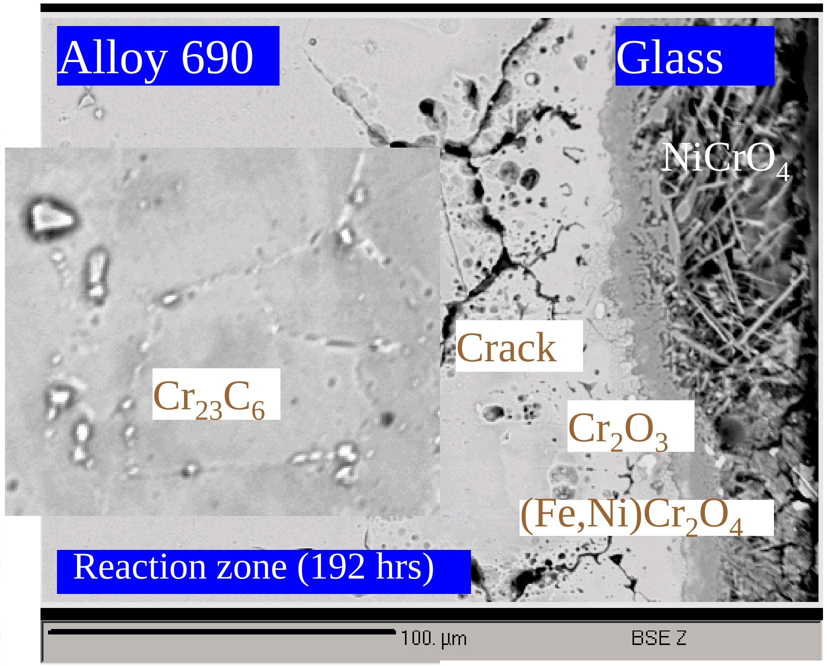
Induction heating

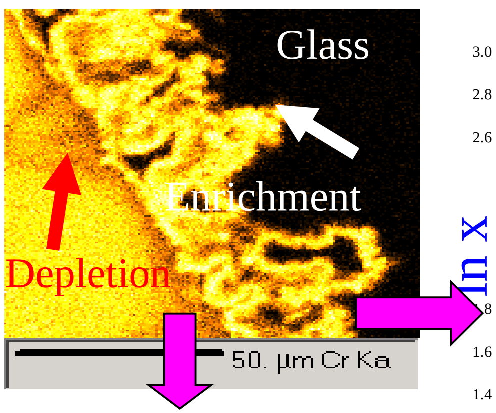
~1500°C

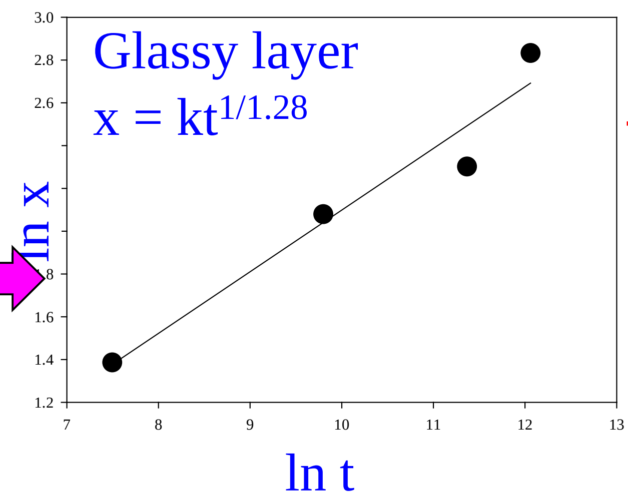
Aluminosilicate glass

Pre-mature degradation of furnace may also influence matrix selection!









Cr depleted zone

$x = 10.9 \times 10^{-6} + 1 \times 10^{-8} t^{1/2} m$

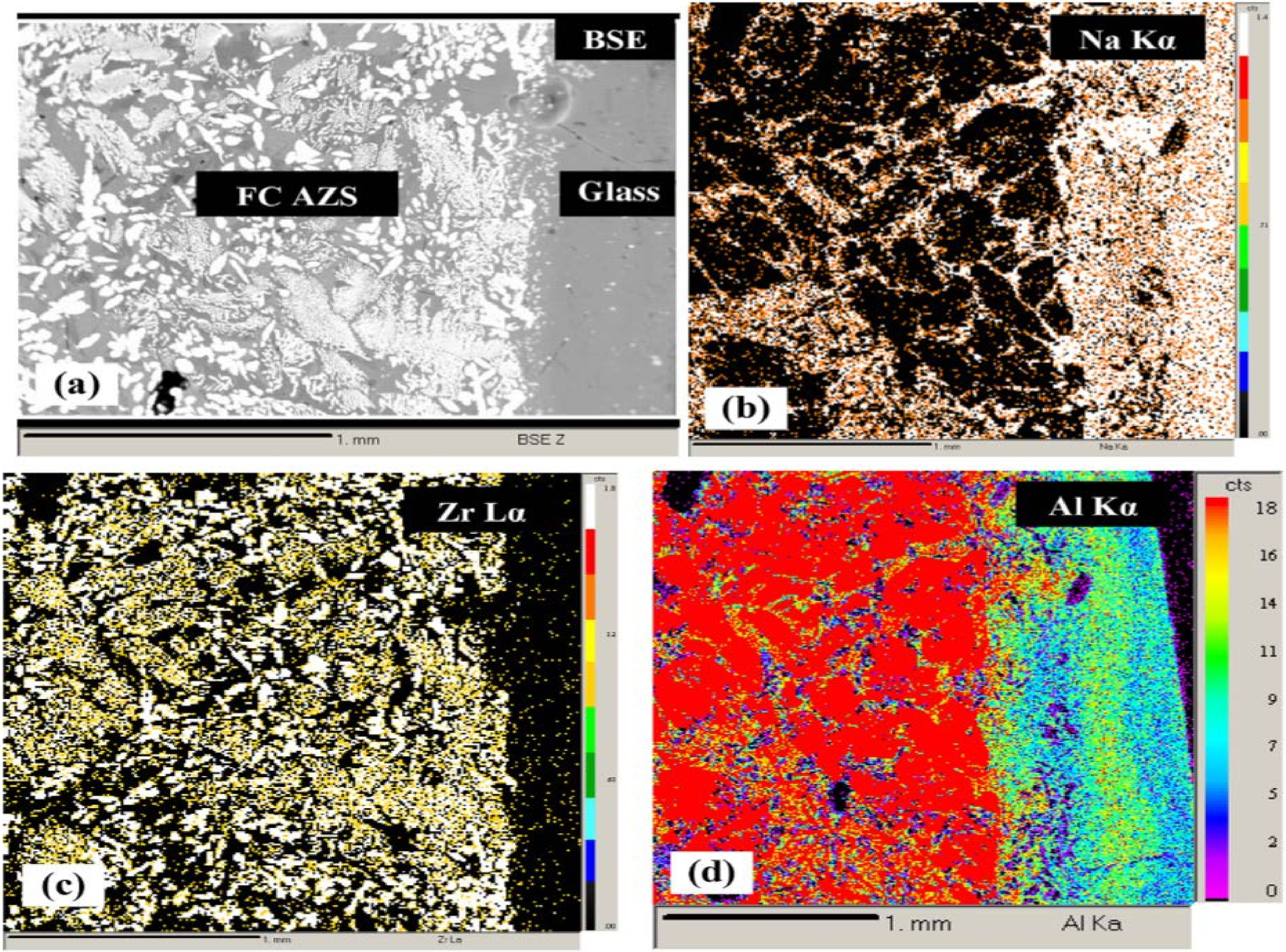

BSE
FC AZS
Glass
(a)
1. mm
BSE Z
Na Kα
(b)
Zr Lα
(c)
Al Kα
(d)
cts
18
16
14
11
9
7
5
2
0
1. mm
Al Ka

Table 1. Glass matrix compositions (Wt%) used at WIPs Tarapur and Trombay

Composition	Modified Sodium Borosilicate (IR111 Tarapur)	Lead based borosilicate (WTR-62 Trombay)	Barium based borosilicate (SB-44 Trombay)
Glass formers (SiO_2+B_2O_3)	46	50	50.5
Glass network intermediate (TiO_2)	7	--	--
Glass modifiers (Na_2O+ MnO_2+ PbO+BaO)	16	30	28.5
Waste Oxide	31	20	21

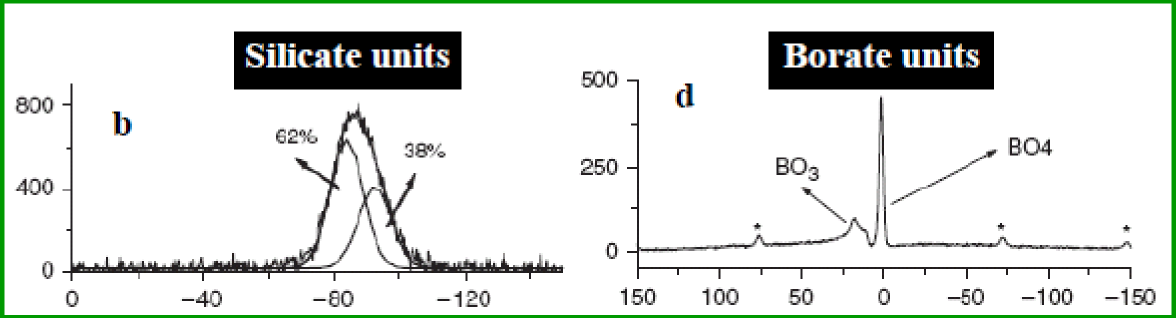
Table 2. Salient features of VWP

Properties	Sodium Borosilicate Glass (IR-111)	Lead Borosilicate Glass (WTR-62)	Barium Borosilicate Glass (SB-44)
Mechanical Properties :			
Density (g/cc)	2.99	3.5	3.0
Impact strength (RIAJ)#	1.06	1.12	0.85
Thermal Properties:			
Thermal conductivity,373K ($Wm^{-1}K^{-1}$)	1.045	1.15	0.95
Co-eff. of thermal expansion (/K)	102×10^{-7}	83×10^{-7}	101×10^{-7}
Viscosity, 1173K (dPa.s)	40	135	70
Pouring temperature (K)	1273	1223	1198
Softening temperature (K)	813	763	809
Chemical Properties:			
Average stabilized leach rate using ASTM C1885-02 procedure ($g.m^{-2}.d^{-1}$)	9.2×10^{-2}	1.8×10^{-1}	4.2×10^{-2}
Waste Oxides (%)	31	20	21
Phase homogeneity	Homogeneous	Non-homogeneous	Homogeneous

#Relative Increase in Area per Joule (RIAJ)

The Problem: Structural analysis by ^{29}Si & ^{11}B NMR

Borosilicate glass

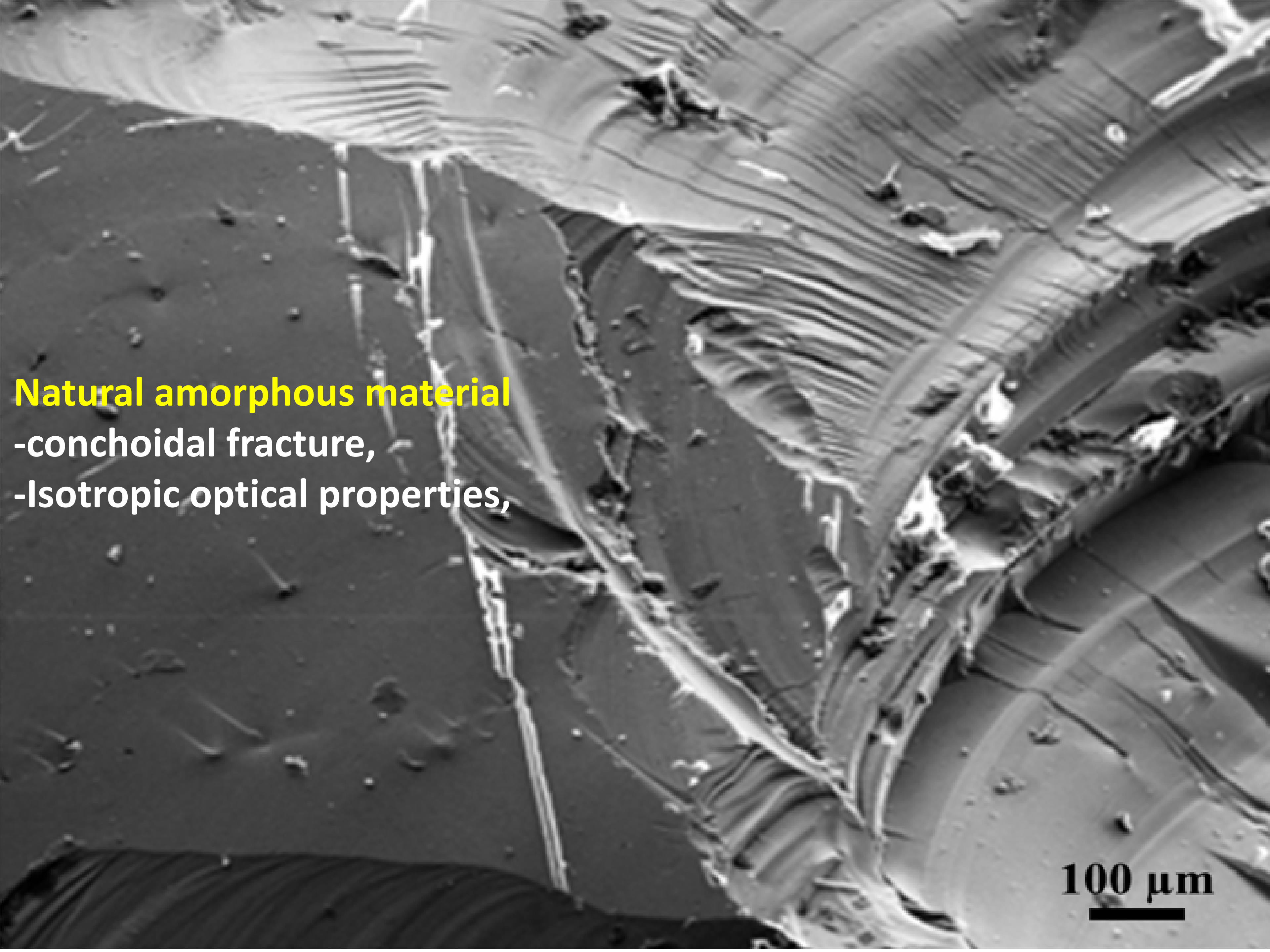


(Q^3: 38%, Q^2: 62%; BO_4: 39%, BO_3: 61%)

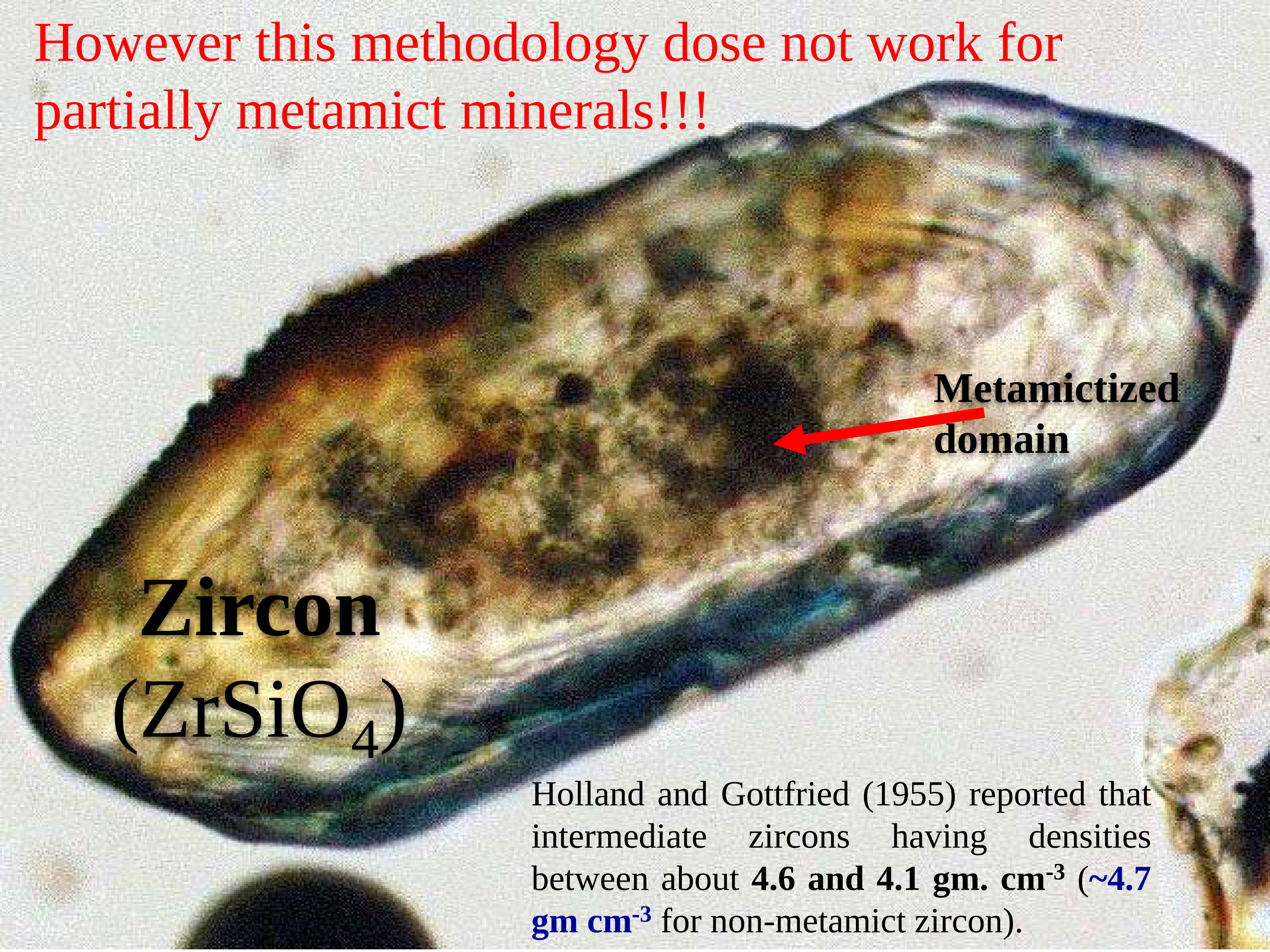
Radiation damage in Single Natural Crystals

Gadolinite

($Y_2FeBe_2Si_2O_{10}$)


Natural amorphous material
-conchoidal fracture,
-Isotropic optical properties,
100 μm

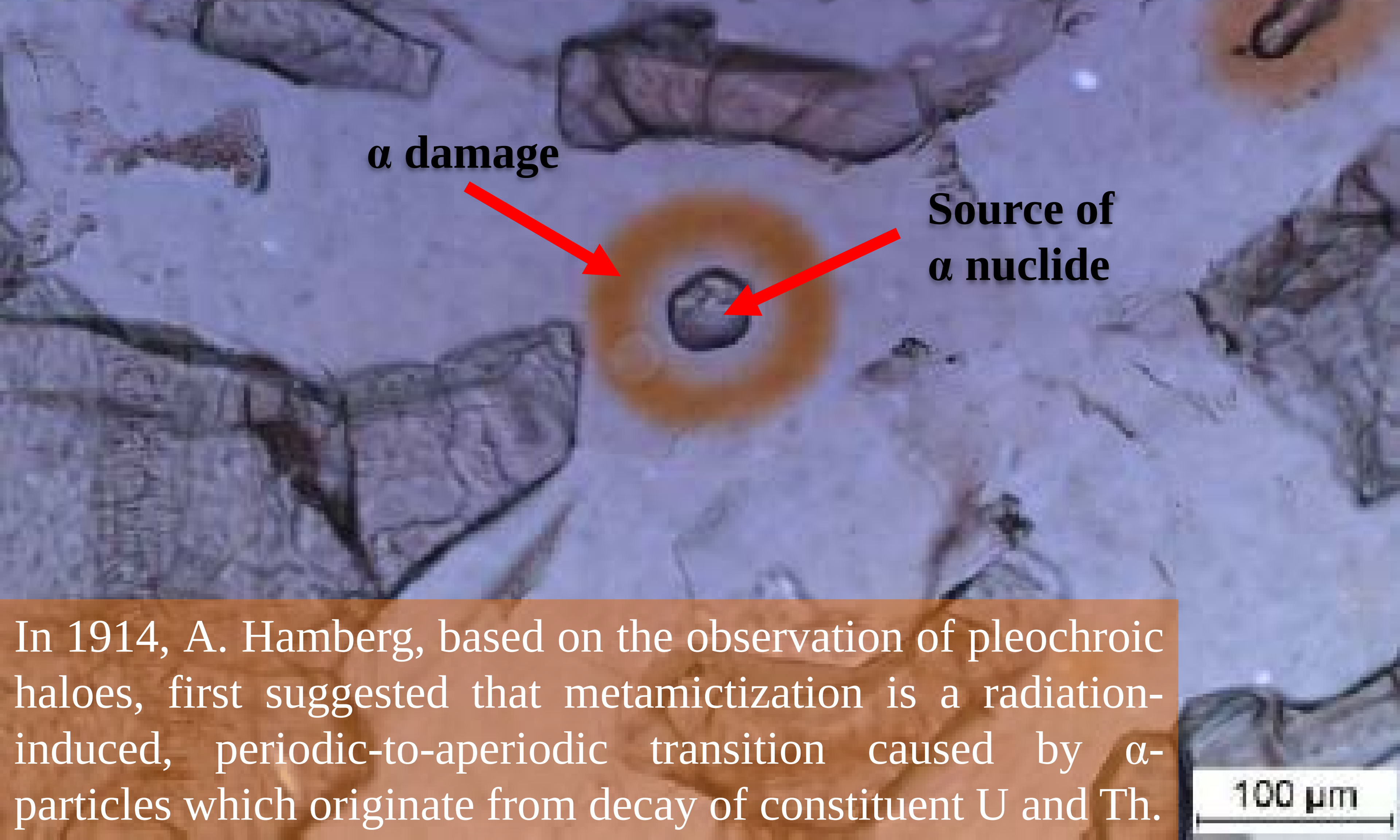
However this methodology dose not work for partially metamict minerals!!!



Holland and Gottfried (1955) reported that intermediate zircons having densities between about **4.6 and 4.1 gm. cm^{-3}** (**~4.7 gm cm^{-3}** for non-metamict zircon).

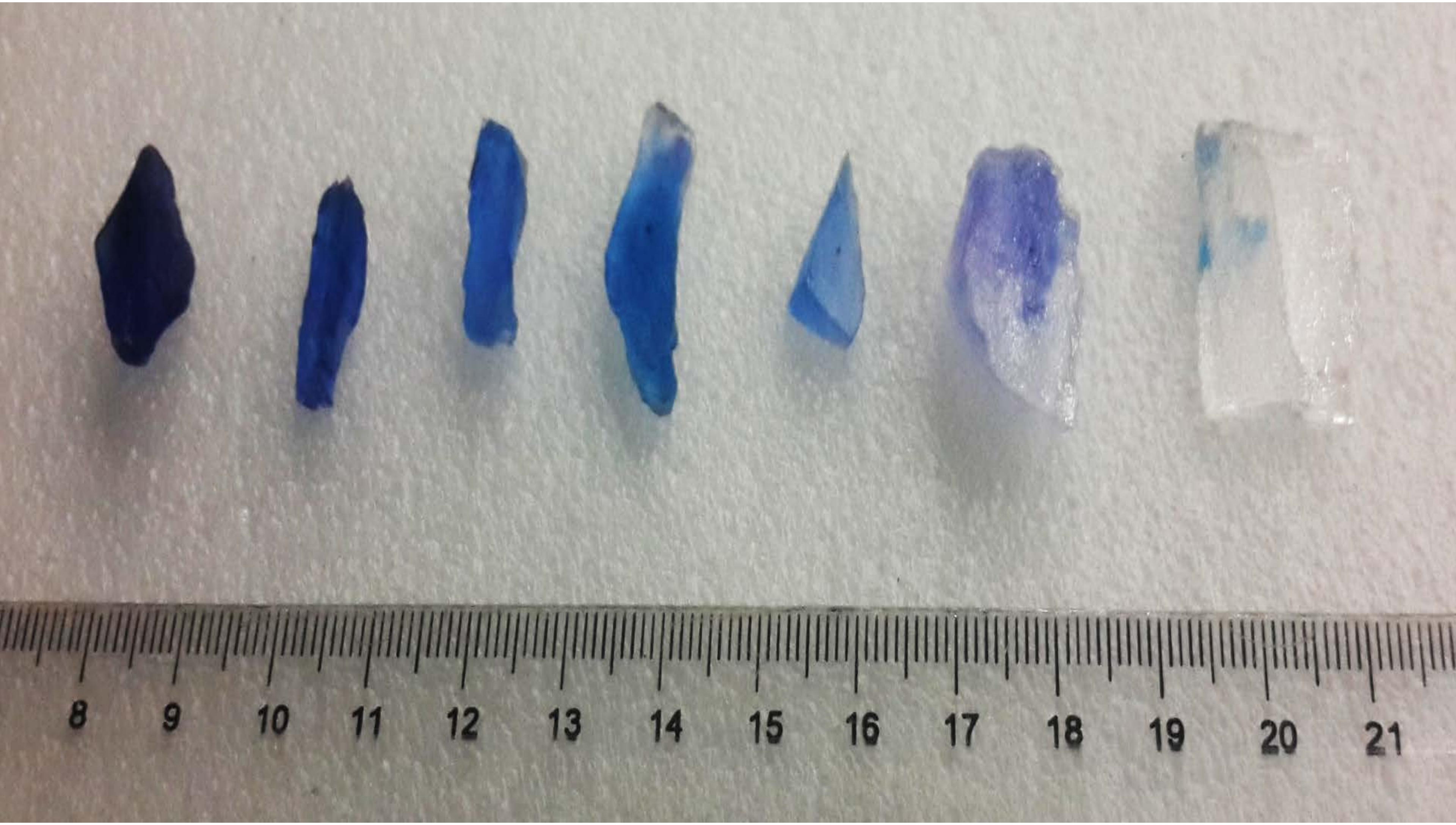
Cordierite

$(Mg, Fe)_2Al_3(Si_5AlO_{18})$

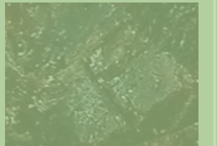


In 1914, A. Hamberg, based on the observation of pleochroic haloes, first suggested that metamictization is a radiation-induced, periodic-to-aperiodic transition caused by α-particles which originate from decay of constituent U and Th.

Halite in nature



Dose coloration always imply RADIATION effects?

Milky white 	Fluid inclusions	Blue 	
Pink / Red 	hematite needles	Violet 	Cl^- removal by ionization radiation
Orange 	Sylvite (KCl) particles 150-180 nm	Purple 	
Yellow 	Sulphur particles 130-150 nm	Dark blue 	
Green 	Chloritic clay particles 110-120 nm	Brownish black 	Organic matter

Non-Radioactive Origin

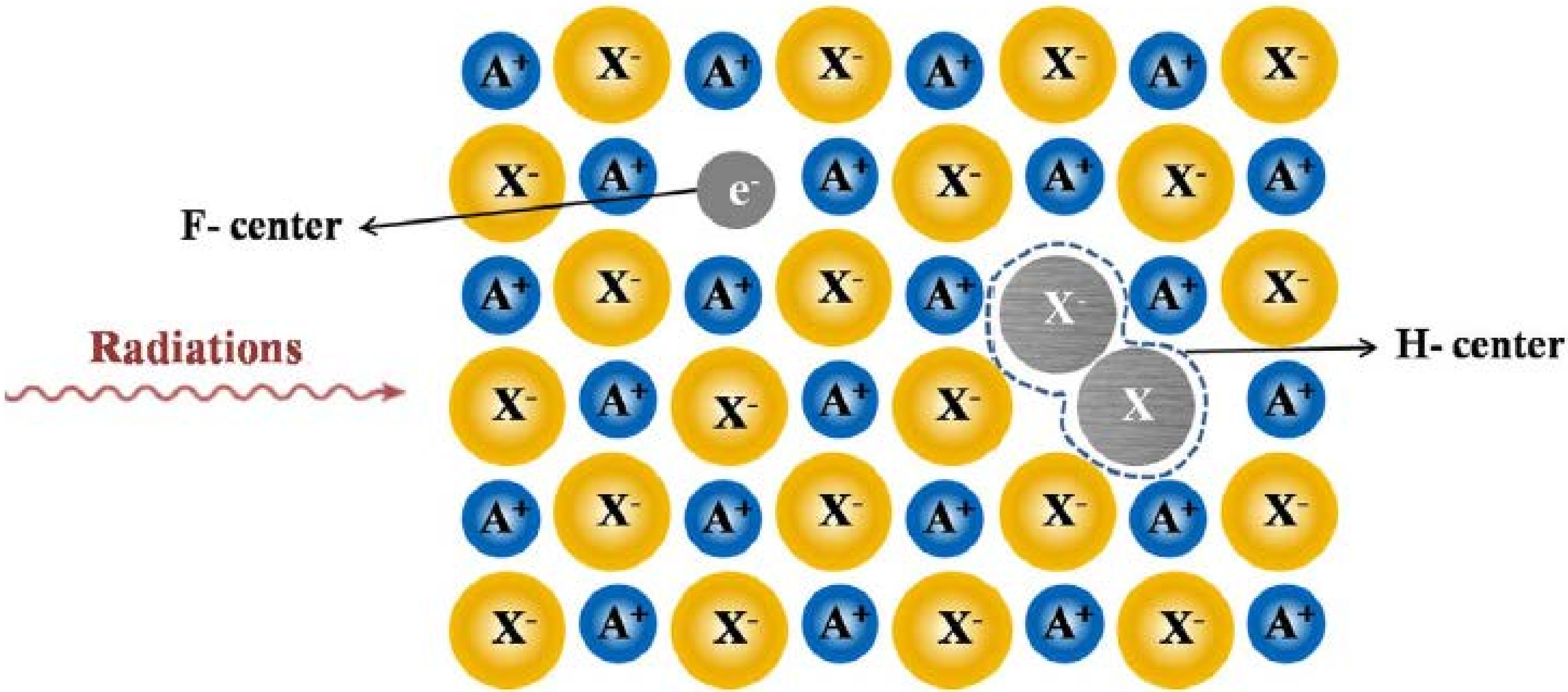
Radioactive Origin

Radiation damage in Halite / Rock salt (NaCl)

•Clusters formed from 2, 3 and 4 F-centers are designated as M, R and N centres respectively.

•Such coagulations of sufficient numbers lead to Na_2Cl colloid formation

•Color caused by different degrees of dispersion & colloid-diameter:
•80-90 nm in size: bluish violet hue; 90-110: blue; 110-120: greenish; 130-150: yellowish; 150-180: orange hue.



Thank You