What is a Reactive-Transport and Water-Rock Interaction Simulator?

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Applications of Reactive-Transport Models

Characterize

Movement of reactive chemicals through sediments and rocks

Interaction among the chemicals, and with the resident material

Carbon Capture and Storage

Nuclear Waste Disposal Site Management

Contaminant Fate and Transport in Groundwater

Mine Tailing Assessment

Uranium Roll-Front Deposits

Reactive Permeability Barriers

Cellular/Biological Models

Petroleum Reservoir Characterization

And so on ...

Water-Rock Interaction: Conservation Equation

Conservation equation, solute species

$$\phi \frac{\partial c_\alpha}{\partial t} = \phi D_\alpha \nabla^2 c_\alpha - \phi \vec{\nabla} \cdot \left(c_\alpha \vec{u} \right) - \sum_{\gamma=1}^{M} \nu_{\alpha\gamma} \rho_\gamma A_\gamma G_\gamma$$

solute evolution — diffusive, advective mass-transfer — kinetic reactions

Evolution of solute concentrations depend on:

mass-transfer (diffusive and advective)
kinetic reaction rate law

ϕ	**porosity**	c	**solute concentration**	K	**equilibrium constant**
D	**diffusion coefficient**	e	**chemical elemental mass**	Ea	**activation energy**
u	**water flow velocity**	G	**mineral reaction rate**	R	**gas constant**
ν	**reaction stoichiometry**	k	**reaction rate constant**	T	**temperature**
A	**mineral surface area**				

Water-Rock Interaction: Conservation Equation

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solute evolution | diffusive advective mass-transfer | kinetic reactions

Diffusive Mass-transfer

$$\frac{dc_\alpha}{dt} = \frac{\phi D_\alpha^*}{\theta} \frac{d^2 c_\alpha}{dx^2}$$

Solute movement through water, from higher to lower concentration region (Fick's law)

Depends on temperature and solute (ionic size, charge)

Tortuosity = ratio of diffusion length of connected pore space to the shortest distance; always > 1

Water-Rock Interaction: Conservation Equation

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solute evolution | diffusive advective mass-transfer | kinetic reactions

Advective Mass-transfer

Solute movement with water

Requires water/fluid saturations and flow velocities to be resolved separately

Phenomenology used to resolve fluid flow (Saturated/unsaturated porous media, multi-phase fluid flow, etc.) does not affect the characteristics of the conservation equation, **BUT** could affect reaction mechanism (rate law)

Water-Rock Interaction: Conservation Equation

$$\phi \frac{\partial c_\alpha}{\partial t} = \phi D_\alpha \nabla^2 c_\alpha - \phi \vec{\nabla} \bullet \left(c_\alpha \vec{u} \right) - \sum_{\gamma=1}^{M} \nu_{\alpha\gamma} \rho_\gamma A_\gamma G_\gamma$$

solute evolution | diffusive | advective mass-transfer | kinetic reactions

Kinetic Reactions

$$G_\gamma = k_{\gamma,diss} \left(\prod_{\substack{\alpha=1, \\ \nu_{\alpha\gamma}<0}}^{N} c_\alpha^{-\nu_{\alpha\gamma}} - \frac{1}{K_\gamma} \prod_{\substack{\alpha=1, \\ \nu_{\alpha\gamma}>0}}^{N} c_\alpha^{\nu_{\alpha\gamma}} \right)$$

$$k_{\gamma,diss} = k_{\gamma,o} \exp\left(-Ea / RT \right)$$

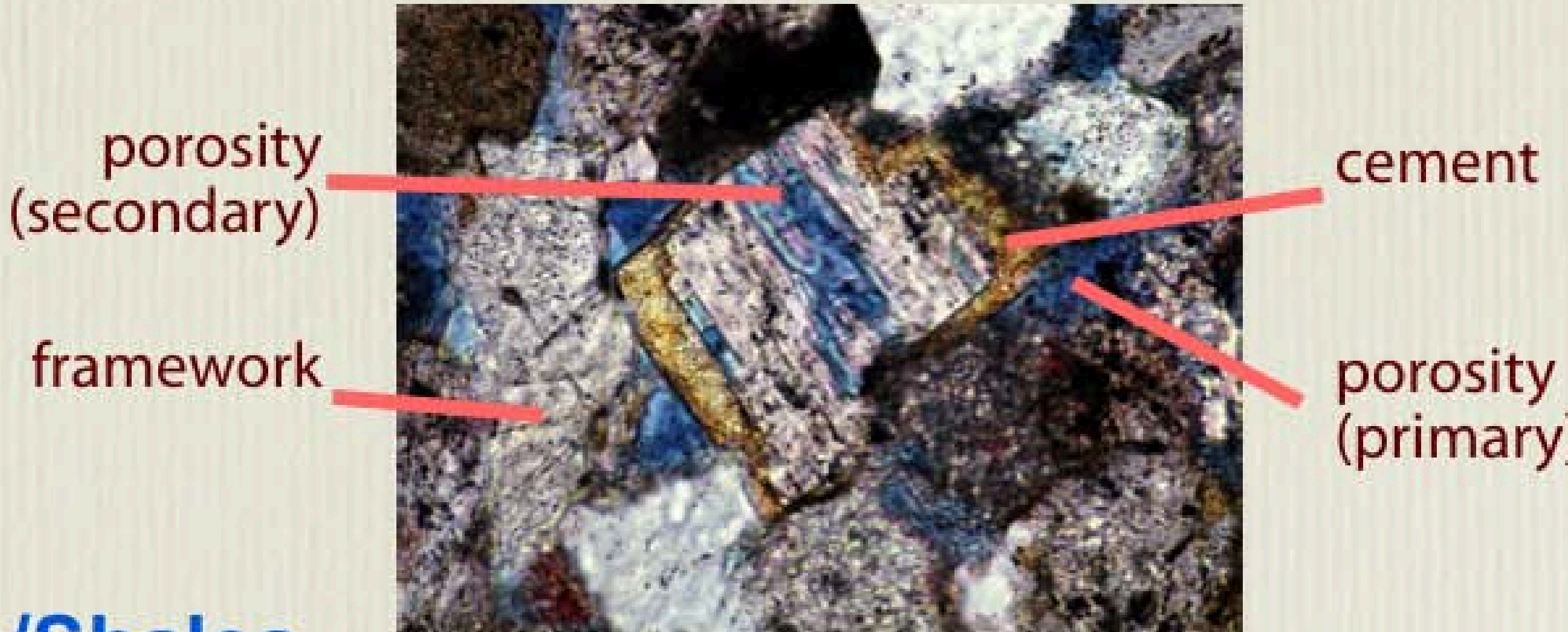
Transformation between solids and solutes

Assume symmetric and reversible: use only dissolution rate constant

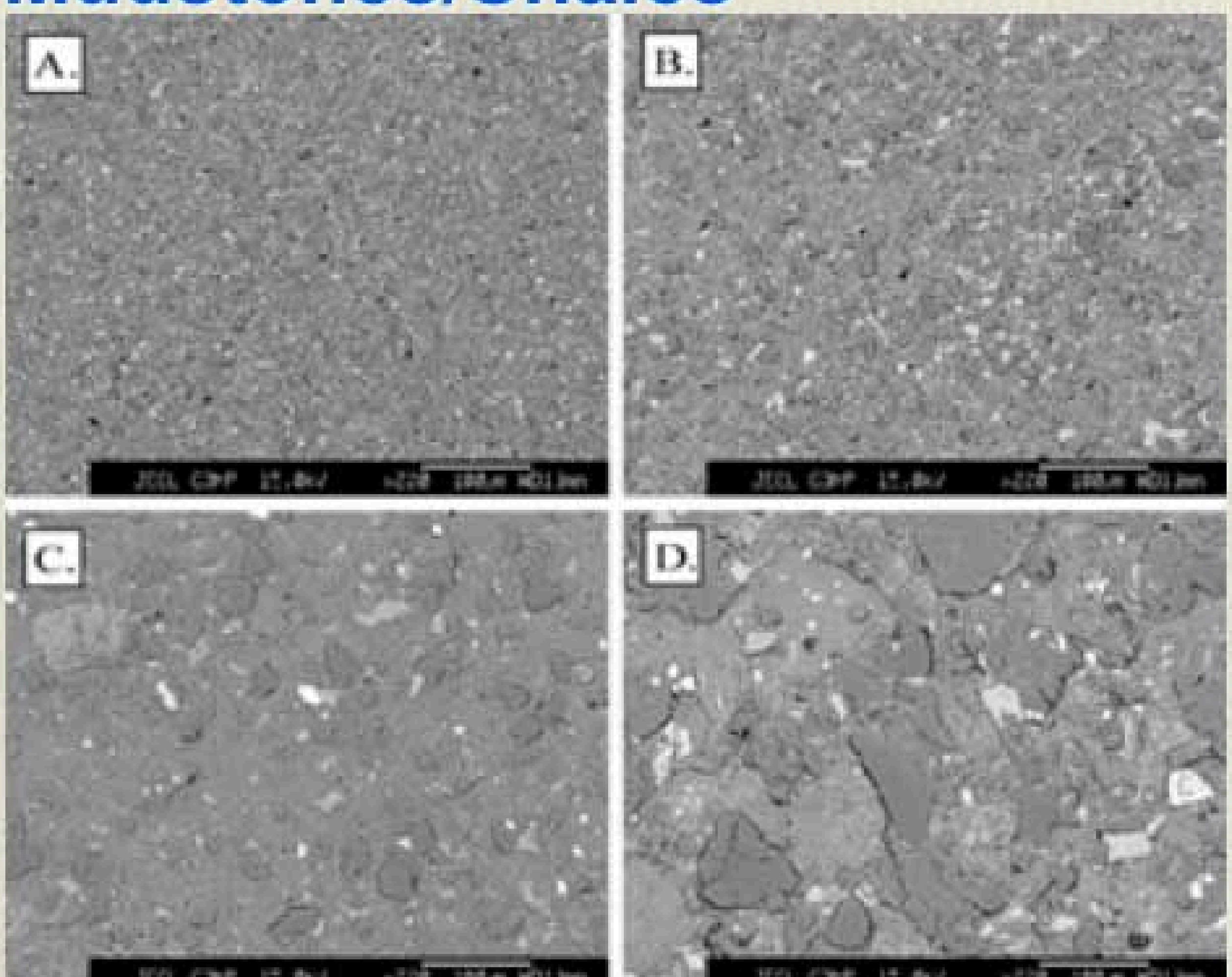
Reaction rate of a mineral depends on water composition, available reactive surface areas of minerals, and temperature

Water-Rock Interaction: Geologic Material

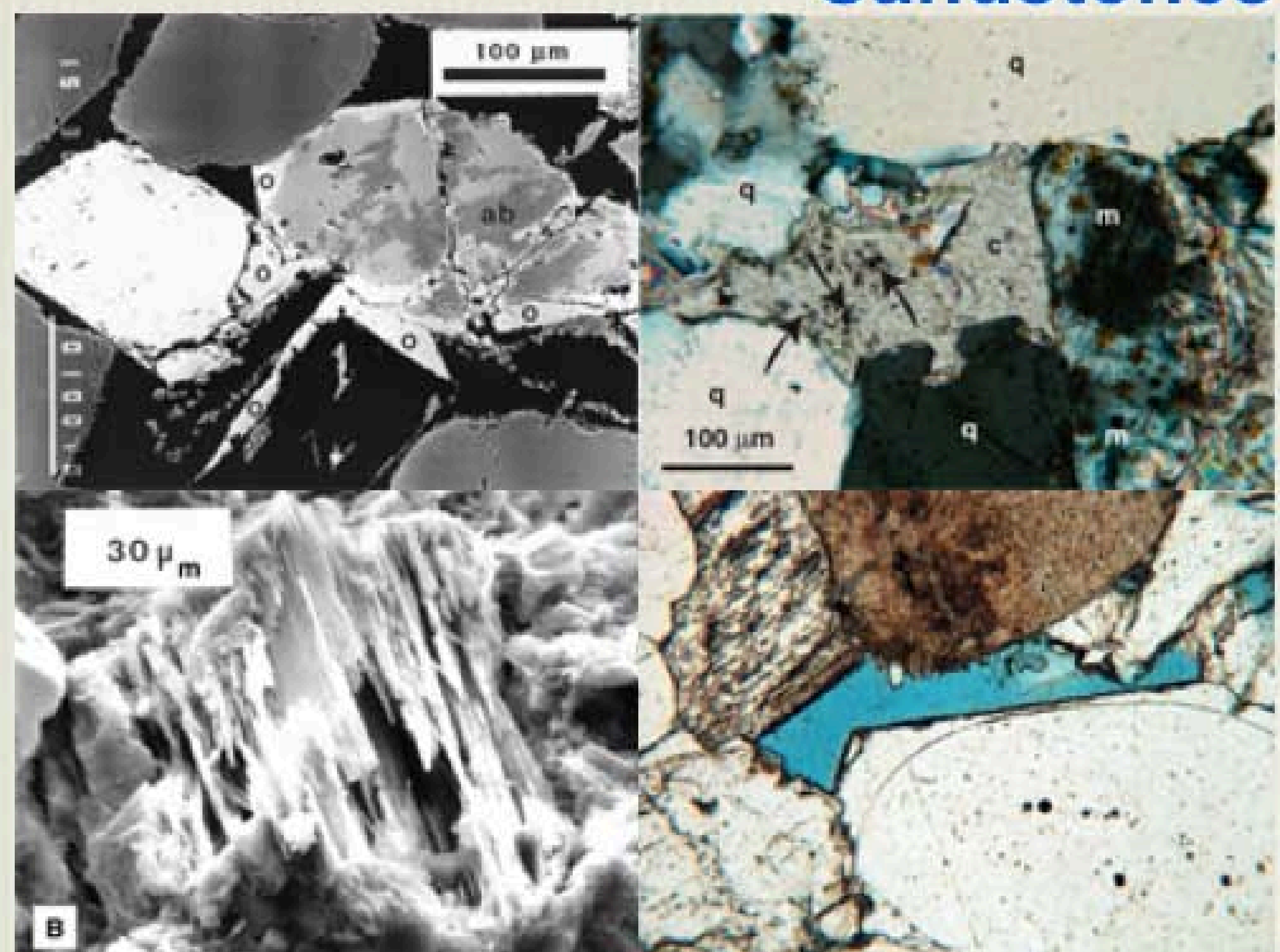
Water-Rock Interaction: Geologic Material



Mudstones/Shales

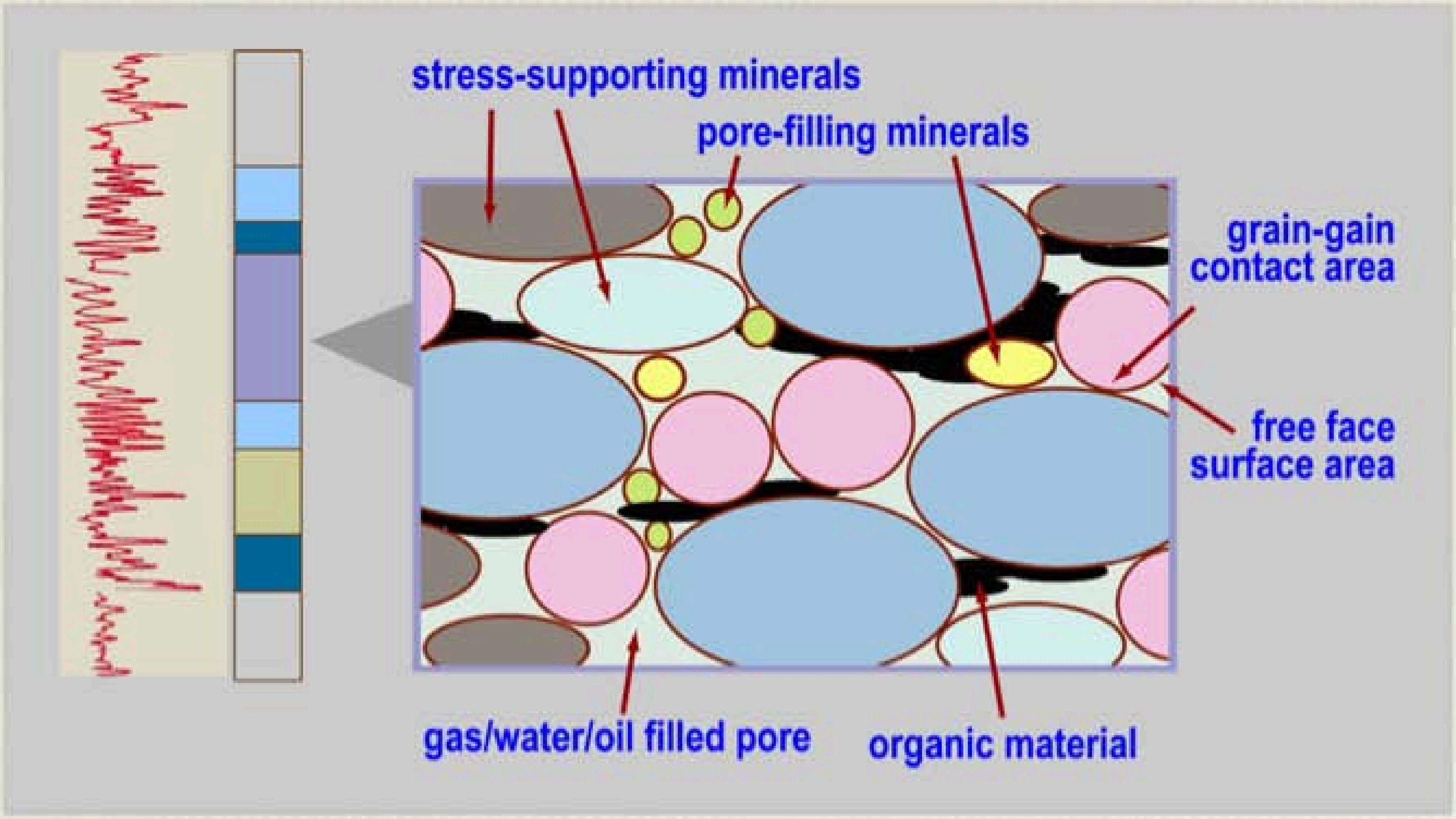


Sandstones



photomicrographs courtesy of K. Milliken, BEG

Water-Rock Interaction: Geologic Material



Sediments and rocks as porous composite media

Made up of a number of mineral types, each with variable shape, size, and population distribution. Each mineral has unique material properties.

GROSS GENERALIZATION, BUT A NECESSARY PROCESS

Reactive-Transport Model: Review of Parameters

Rock mechanics or rheology
stress distribution, viscosity, moduli

Heat transfer (temperature)
enthalpy: heat capacity, conductivity

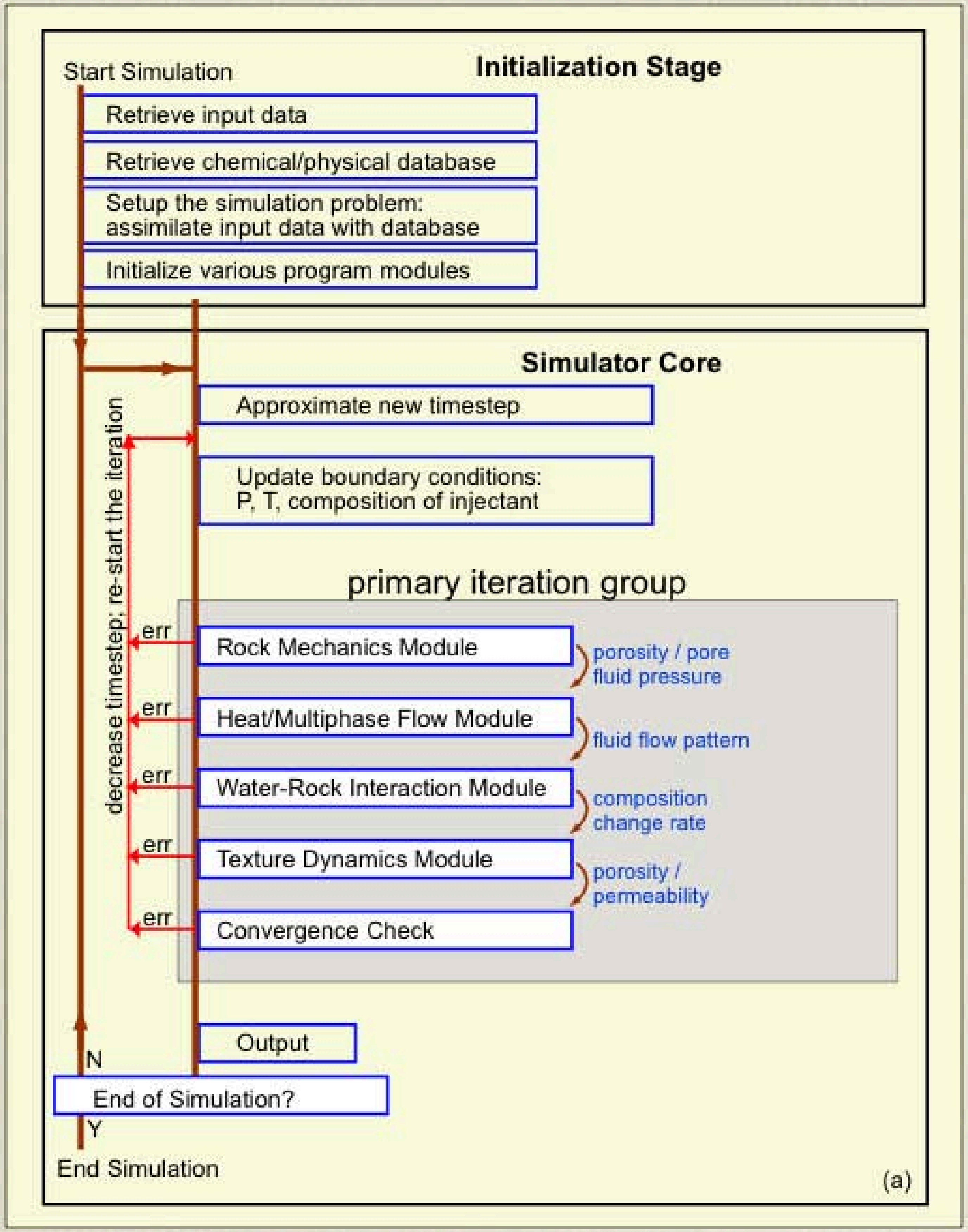
Fluid pressure (fluid flow)
pressure/saturation: temperature, saturations, relative perms

Reactions (kinetic and/or equilibrium)
reaction rate laws and/or reactions: temperature, fluid composition, solute/solvent properties

Composite media and material properties
composition, density, textural descriptions, porosity, permeability, tortuosity, etc.

INTERDEPENDENCE OF ALL OF ABOVE PROCESSES: POTENTIAL FOR DYNAMIC NONLINEAR FEEDBACK

Reactive-Transport and Mechanical (RTM) Simulator



- Layered iterative forward-timestepping approach
- Construct and implement each process as a module
- Capture nonlinear behavior of the system by reserving the feedback among the processes
- Sequence of computation is important
- Time step determined by the fastest changing parameter

Water-Rock Interaction: Conservation Equation

Conservation equation, solute species

$$\phi \frac{\partial c_\alpha}{\partial t} = \phi D_\alpha \nabla^2 c_\alpha - \phi \vec{\nabla} \bullet \left(c_\alpha \vec{u} \right) - \sum_{\gamma=1}^{M} \nu_{\alpha\gamma} \rho_\gamma A_\gamma G_\gamma$$

solute evolution | diffusive | advective mass-transfer | kinetic reactions

Conservation equation, theoretically accurate formulation

$$\phi \frac{\partial c_\alpha}{\partial t} = \phi D_\alpha \nabla^2 c_\alpha - \phi \vec{\nabla} \bullet \left(c_\alpha \vec{u} \right) - \sum_{\eta=1}^{Ne} \nu_{\alpha\eta} F_\eta - \sum_{\gamma=1}^{M} \nu_{\alpha\gamma} \rho_\gamma A_\gamma G_\gamma$$

solute evolution | diffusive | advective mass-transfer | reactions among solutes | kinetic reactions

Difficult to implement in a simulator:
timestep is controlled by the fastest solute reaction rate

Water-Rock Interaction: Conservation Equation

Conservation equation, solute species

$$\phi \frac{\partial c_\alpha}{\partial t} = \phi D_\alpha \nabla^2 c_\alpha - \phi \vec{\nabla} \cdot \left(c_\alpha \vec{u} \right) - \sum_{\eta=1}^{Ne} \nu_{\alpha\eta} F_\eta - \sum_{\gamma=1}^{M} \nu_{\alpha\gamma} \rho_\gamma A_\gamma G_\gamma$$

solute evolution | diffusive / advective mass-transfer | reactions among solutes | kinetic reactions

combined with

unpublished equation, removed for record

Conservation equation, chemical elements

unpublished equation, removed for record

element evolution | diffusive / advective mass-transfer | kinetic reactions

Water-Rock Interaction: System of Equation

Example: Calcite dissolution in water

$$\text{Calcite}_{(s)} = \text{Ca}^{2+}_{(aq)} + \text{CO}^{2-}_{3(aq)}$$

calcite dissolution / precipitation reaction

$$H_2O_{(l)} = H^+_{(aq)} + OH^-_{(aq)}$$

hydrolysis

$$\text{CO}_{2(g)} = \text{H}_2\text{O}_{(l)} + \text{H}_2\text{CO}_{3(aq)}$$
$$\text{H}_2\text{CO}_{3(aq)} = \text{H}^+_{(aq)} + \text{HCO}^-_{3(aq)}$$
$$\text{HCO}_{3(aq)} = \text{H}^+_{(aq)} + \text{CO}^{--}_{3(aq}$$

bicarbonate speciation (equilibrium) reactions

$$C_{total} = \phi\left([H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] + fCO_3^{2-} \right) - \rho AG_{Calcite}$$

mass-balance expression (example, for Carbon)

$$\text{Ca}^{2+}_{(aq)},\ \text{CO}^{2-}_{3(aq)},\ \text{HCO}^{2-}_{3(aq)},\ \text{H}_2\text{CO}^{2-}_{3(aq)},\ \text{CO}_{2(g)},\ \text{H}^+_{(aq)},\ \text{OH}^-_{(aq)},\ \text{H}_2\text{O}$$

unknown variables (solute species)

Ca, C, H, O

chemical elements associated with the reactions

	solute mass-conservation	element mass-conservation
unknown variables (solute species)	8	8
equilibrium reactions (solute speciation)	4	4
	bicarbonate speciation reactions, and the hydrolysis reaction	
mass-conservation equations	variable, 2 - 6 minimum required: Ca and a bicarbonate additional options: other bicarbonates, H, and O	4 one for each chemical element
mass-balance expressions	variable, 1 - 4 minimum required: C additional options: O, H, Ca	0

A typical geochemical system consists of: 10+ minerals, 20+ solute species, of 10+ chemical elements

Water-Rock Interaction: Numerical Approach

P, T, σ, are solved globally in their respective modules.

For water-rock interaction, *Ne* number of equations are solved for each numerical grid individually.

This is achieved by iterating between discretization of mass-transfer coefficients, and solving discretized form of elemental conservation equations and equilibrium reaction expressions

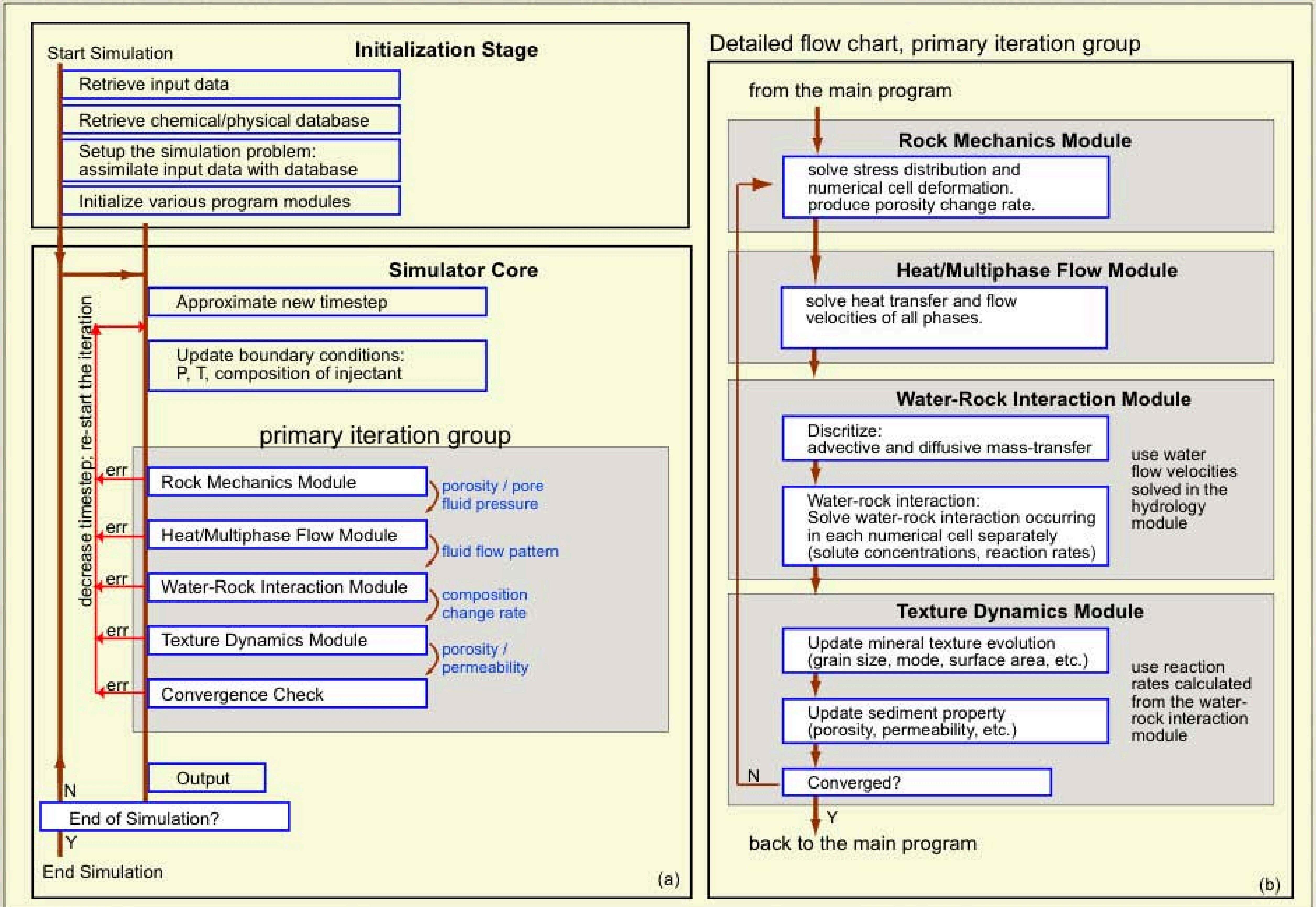
ex., discretized form finite difference (1D)
of elemental conservation equation,

unpublished equation, removed for record

mass-transfer coefficient matrices A and B are derived from
fluid flow velocities and solute concentrations
from the previous numerical iteration

unpublished equation, removed for record

Reactive-Transport and Mechanical (RTM) Simulator



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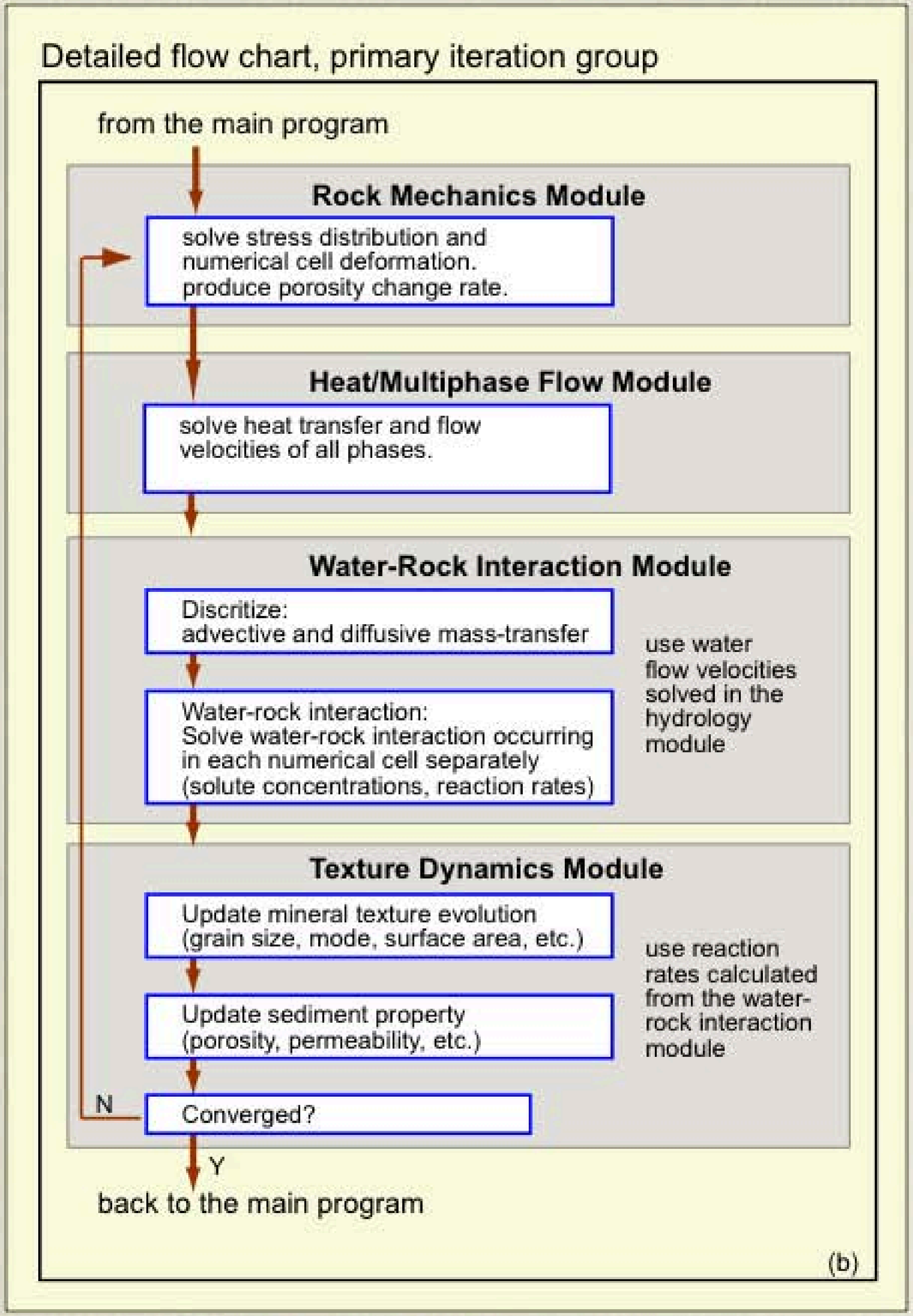


Porosity and permeability: two most important feedback controlling parameters

Order of computation follows the order of magnitude of effects on sediment porosity and permeability

Sediment properties, including densities, porosity, permeability, heat capacity, conductivity, etc., depend on composite media model and extent of alteration imposed by water-rock interaction

Pattern Formation and Self-Organization

Regular or periodic array of mineralization

Result of nonlinear geochemical and/or mechanical feedback between various natural processes
(reactions, fluid flow, mechanical stress/strain, etc)

Patterns do not follow inherent or imposed templates, e.g., autonomously self-generated
(sedimentary features, episodic fluid flow / deformation, etc.)

Examples discussed today: Iron-oxide (hematite)

Liesegang Bands (1D), Concretions or Nodules (2D/3D)
Jurassic Navajo sandstone, Utah, and Mars sediments

Snow Canyon, Near St. George, Utah

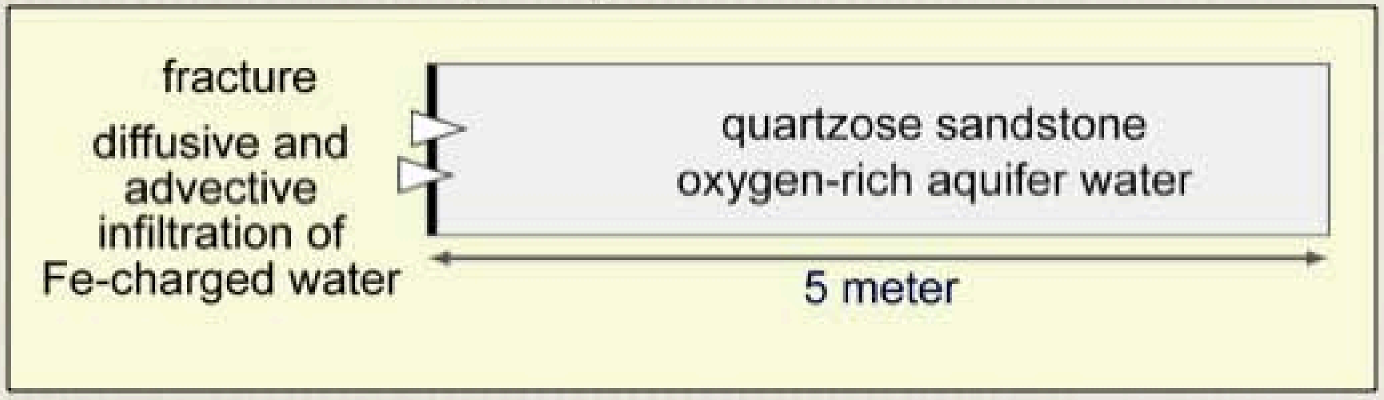
Iron-Oxide Precipitates in Sandstones: Simulation

Table 2. Chemical and physical properties, patterned hematite precipitation simulation.

mineral	reaction stoichometry	log K [1]	Ea [2]	k_d [3]	volume	grain radii
Hematite	$Fe_2O_{3(s)} + 2H_2O_{(l)} = 2Fe^{++}_{(aq)} + 0.5O_{2(g)} + 4OH^-_{(aq)}$	-8.59	66.2	2.5×10^{-15}	0	0
Quartz	$SiO_{2(s)} + 2H_2O_{(l)} = SiO_{2(aq)}$	non-reactive			65%	0.04 cm

log K: $\log_{10}$ of equilibrium constant; Ea: activation energy, Kjoules; k_d: dissolution rate constant, mol/cm^2-sec; volume: starting volume fraction of mineral, clean quartzose sandstone; grain radii: starting mineral grain radii, cm; [1] from EQ3/6 database, Wolery et al. (1990); [2,3] from Palandri and Kharaka (2004)

	Formation Water	Water in Fracture	Solute Diffusivity [4]
H^+	2.1×10^{-7}	1.0×10^{-5}	4.1×10^{-5}
Fe^{++}	4.0×10^{-18}	6.6×10^{-14}	3.4×10^{-6}
$O_{2(g)}$	1.0×10^{-8}	5.0×10^{-14}	5.5×10^{-6}

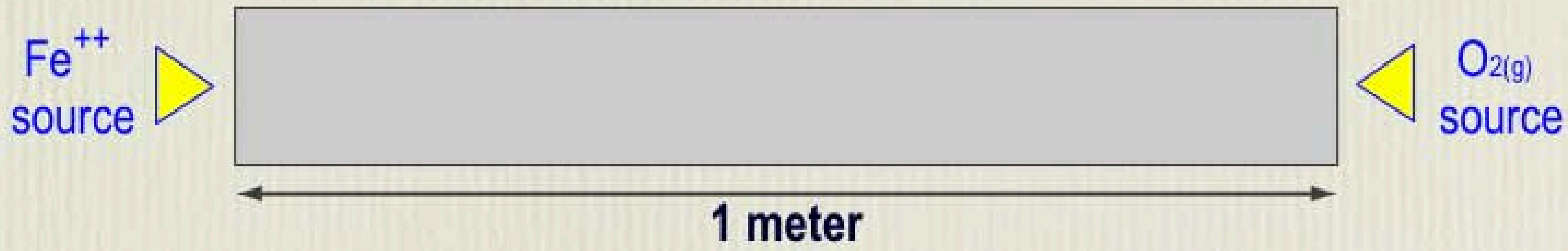


Numerical resolution: 500 finite difference grids; Temperature fixed, 64 °C; Water flux 0, 10, 50, 100 cm/year
[4] from Boudreau (1996), cm-cm/sec

Liesegang Diffusion-Reaction Mechanism:

Solutes converging from opposite directions produce patterned precipitate bands
Nucleation thresh-hold: Necessary chemical reaction criteria
Degree of heterogeneity: Along the axis of diffusion (1D)
Natural sediments and rocks: 3D heterogeneity, produce spotty precipitates

Reaction-Diffusion (Liesegang) Process



Simulation Parameters

Temperature	64 degrees C
Hematite reaction rate coefficient	1.8×10^{-13} cm/sec
Equilibrium constant	1.9×10^{-66}
Nucleation threshold	1.5

Solute Diffusivity (cm-cm/sec)

H^+	1.4×10^{-5}
OH^-	9.0×10^{-6}
Fe^{++}	1.2×10^{-6}
$O_{2(g)}$	5.4×10^{-6}

Concentrations (moles/L)

H^+	1.0×10^{-6}
Fe^{++}	4.0×10^{-15}
$O_{2(g)}$	5.0×10^{-14}

System length 1.0 m

Numerical grid resolution 1 grid / cm

Variations in Simulation Conditions:

1. No advective influx of water: Liesegang-type reaction system.
2. Imposed influx of Fe-charged water at a rate of 2.6 cm/yr.
3. Imposed influx of Fe-charged water at a rate of 2.6 cm/yr; pH of water reduced; $[H^+]$ concentration of inlet at 2.0×10^{-6}.

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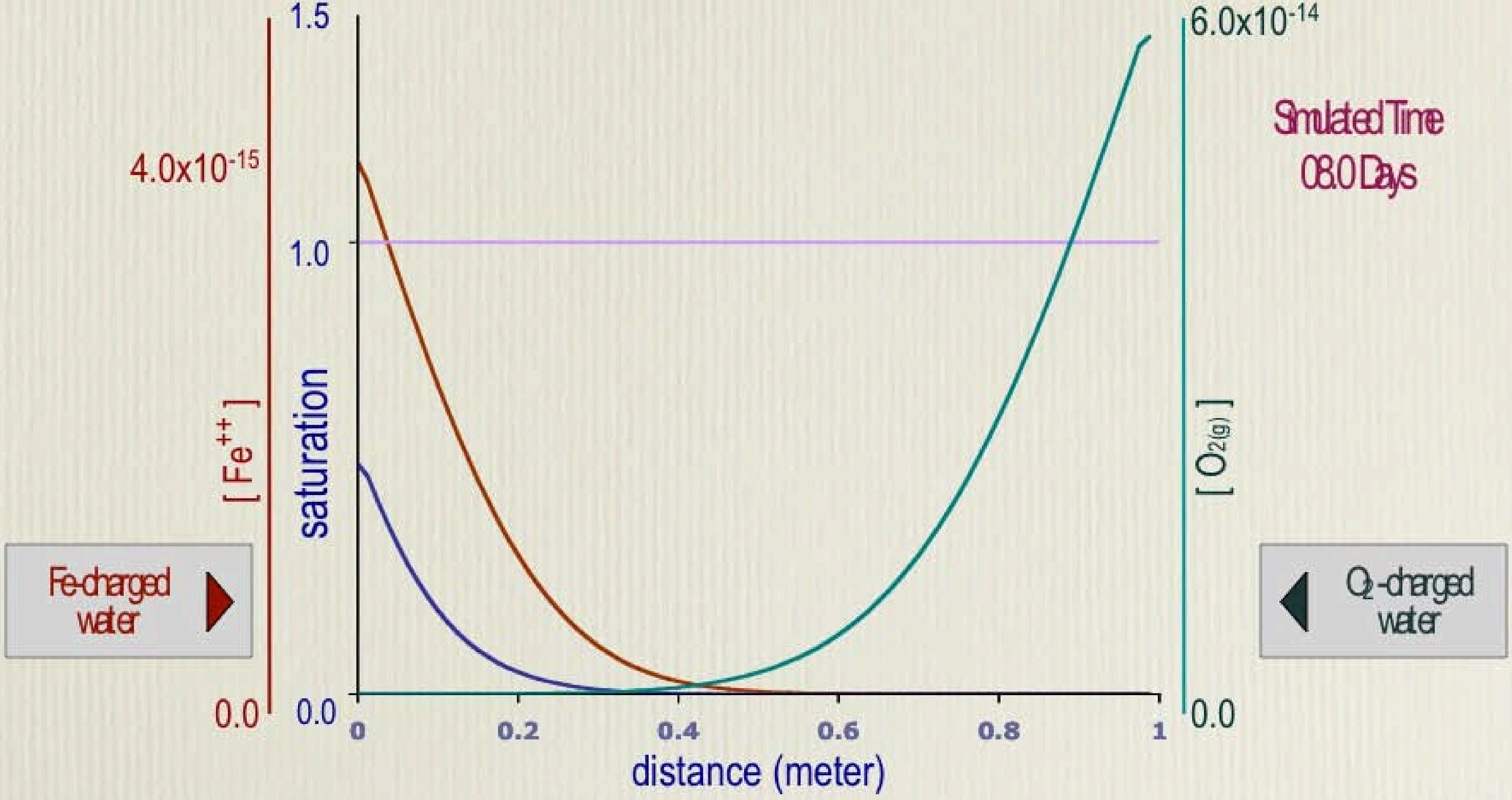

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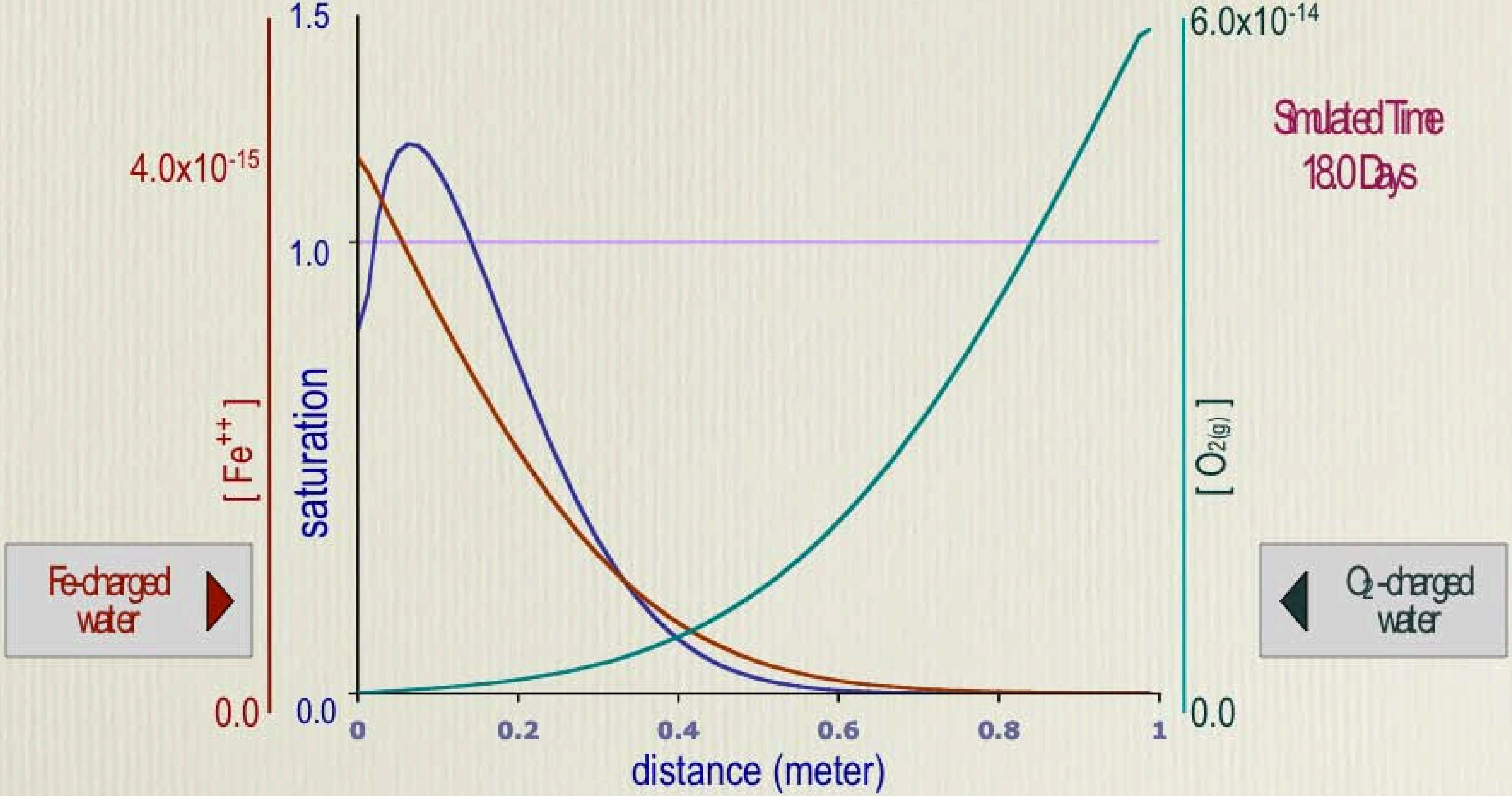

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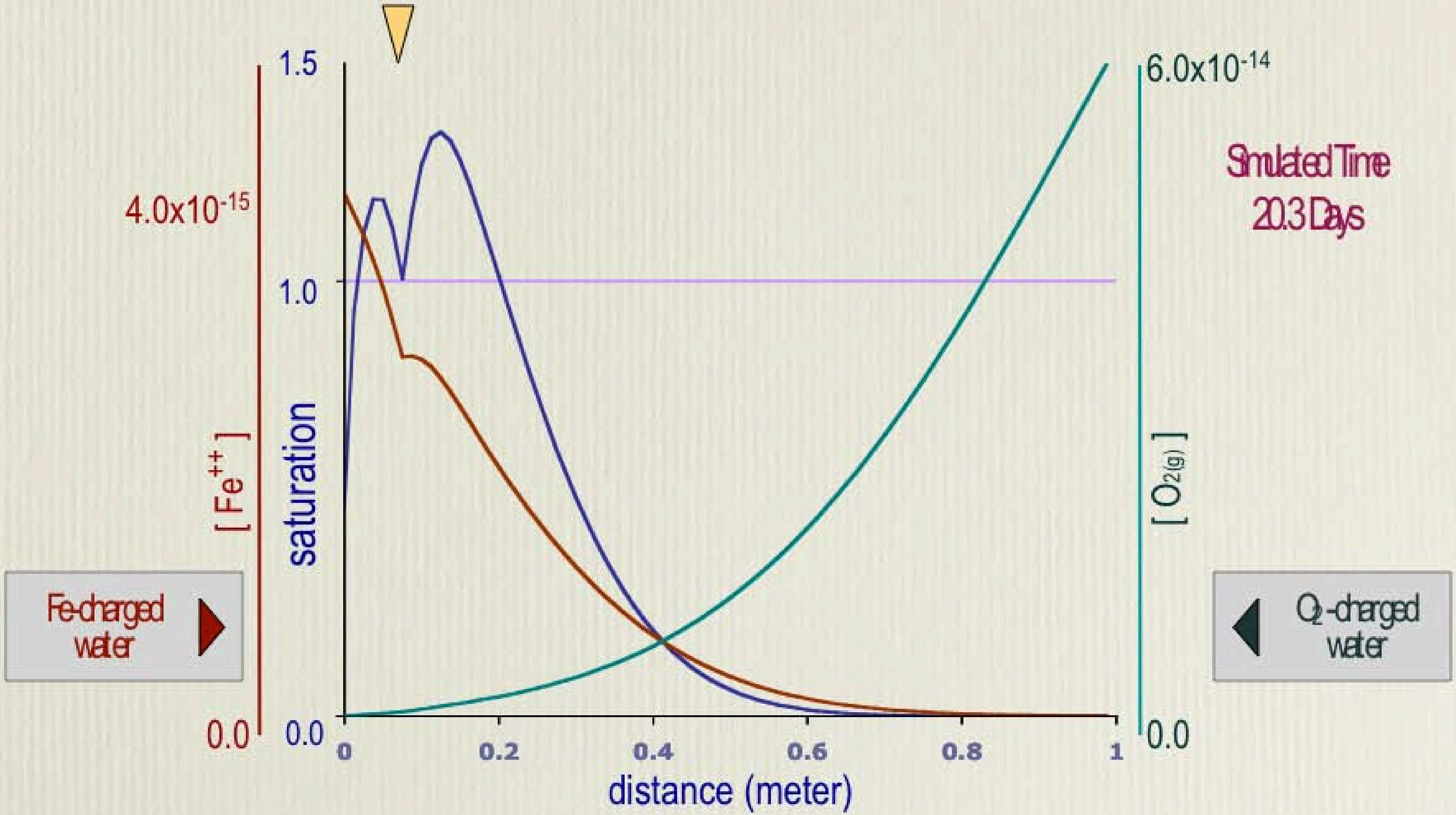

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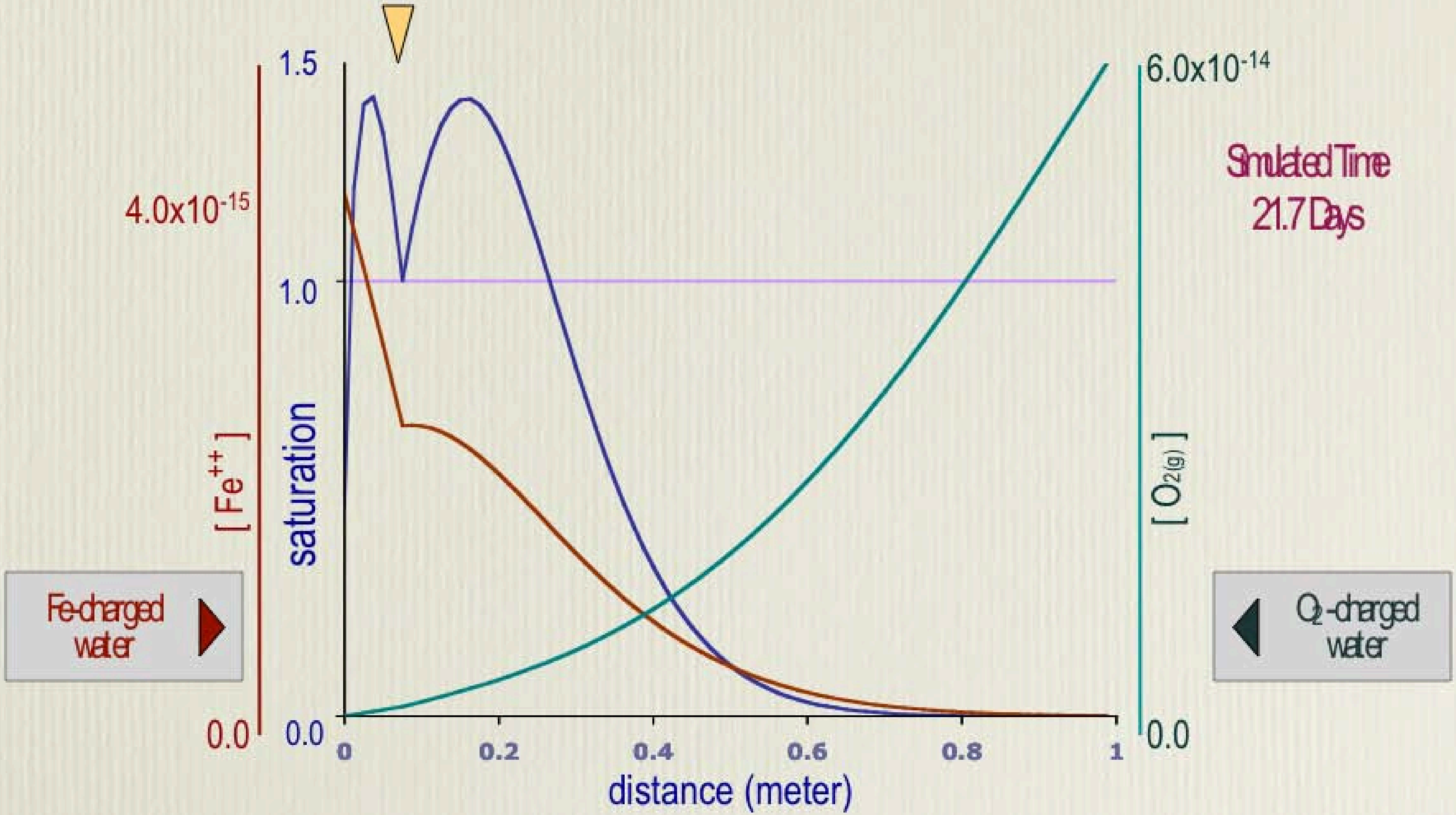

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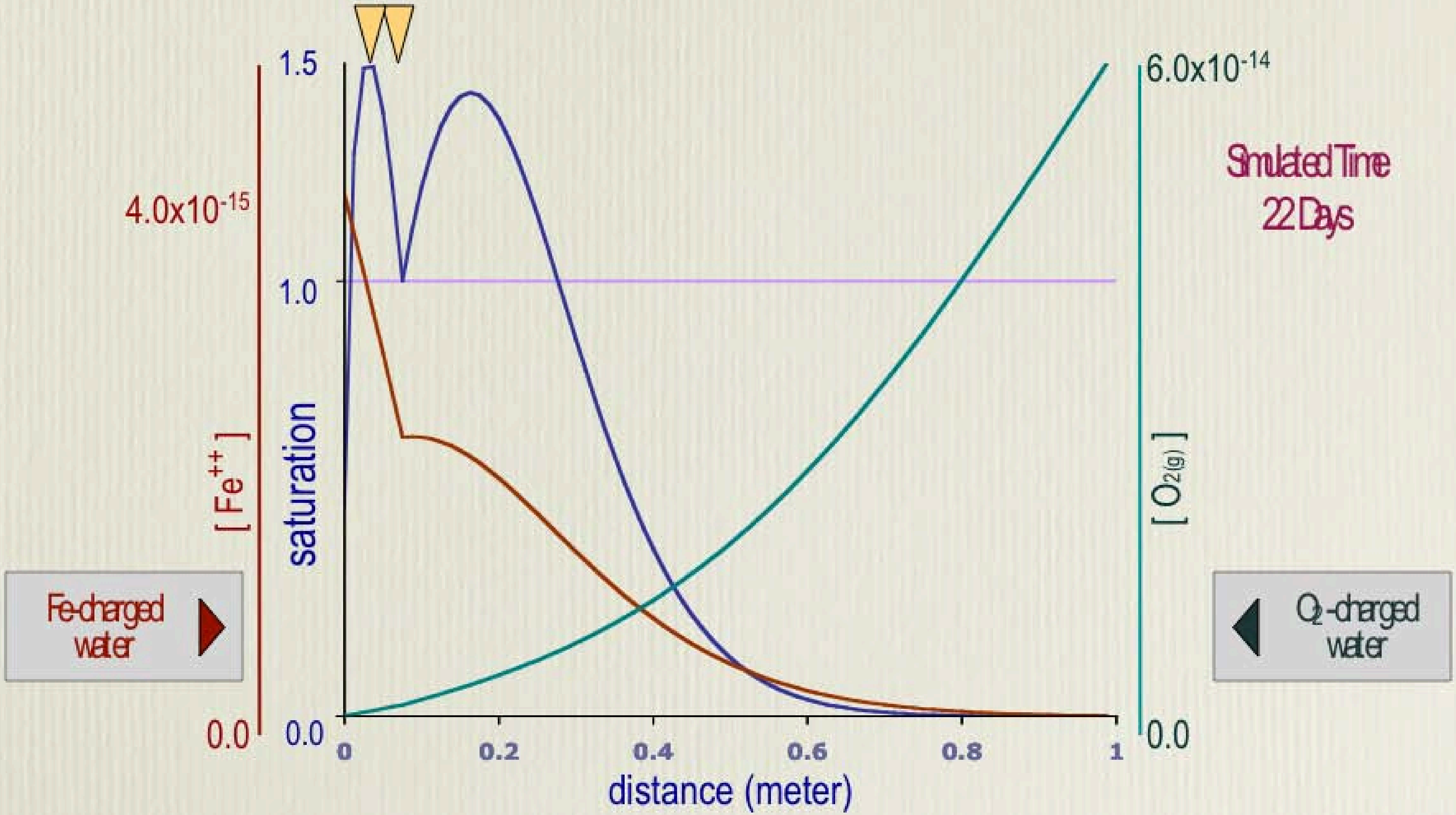

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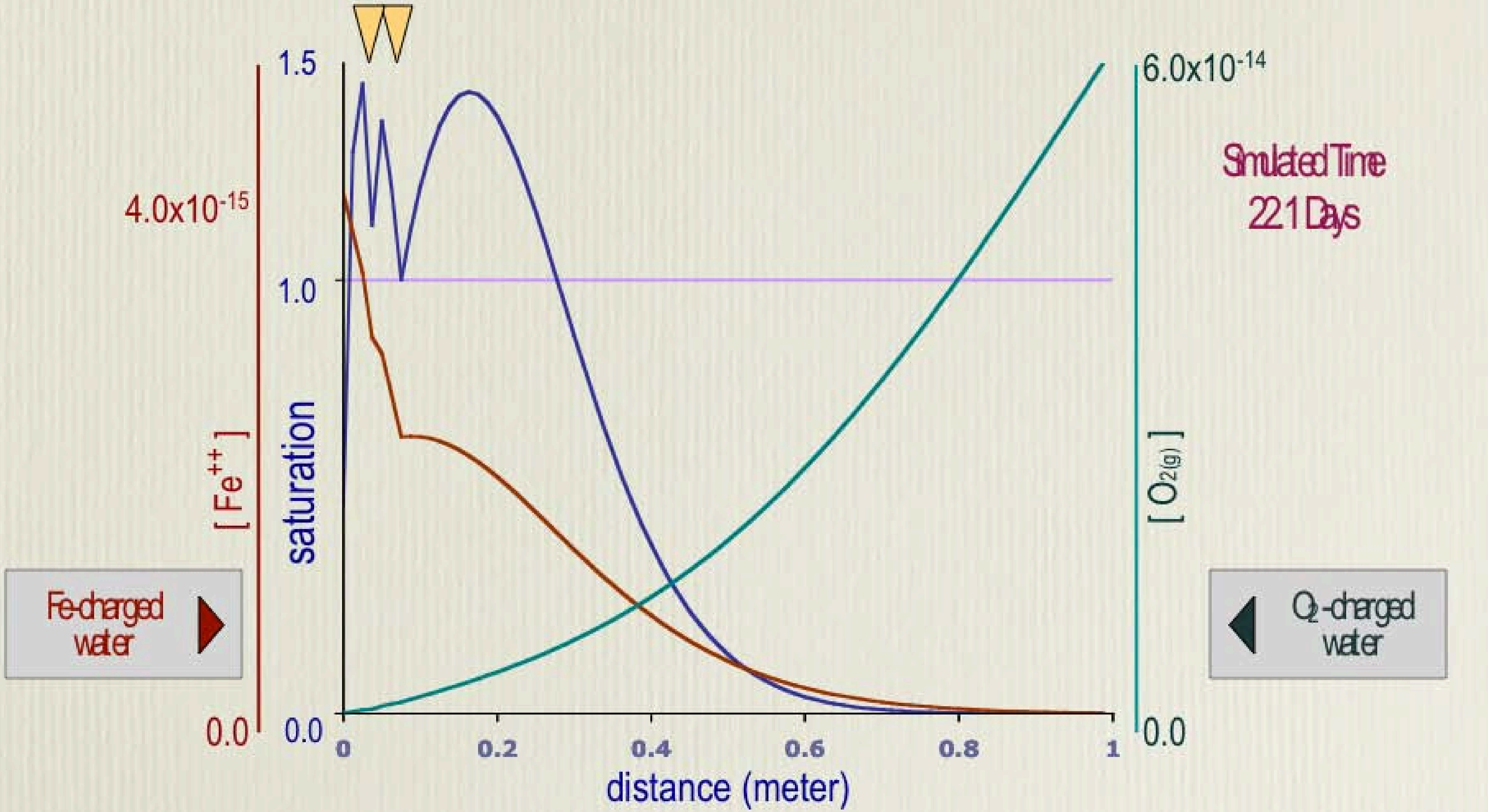

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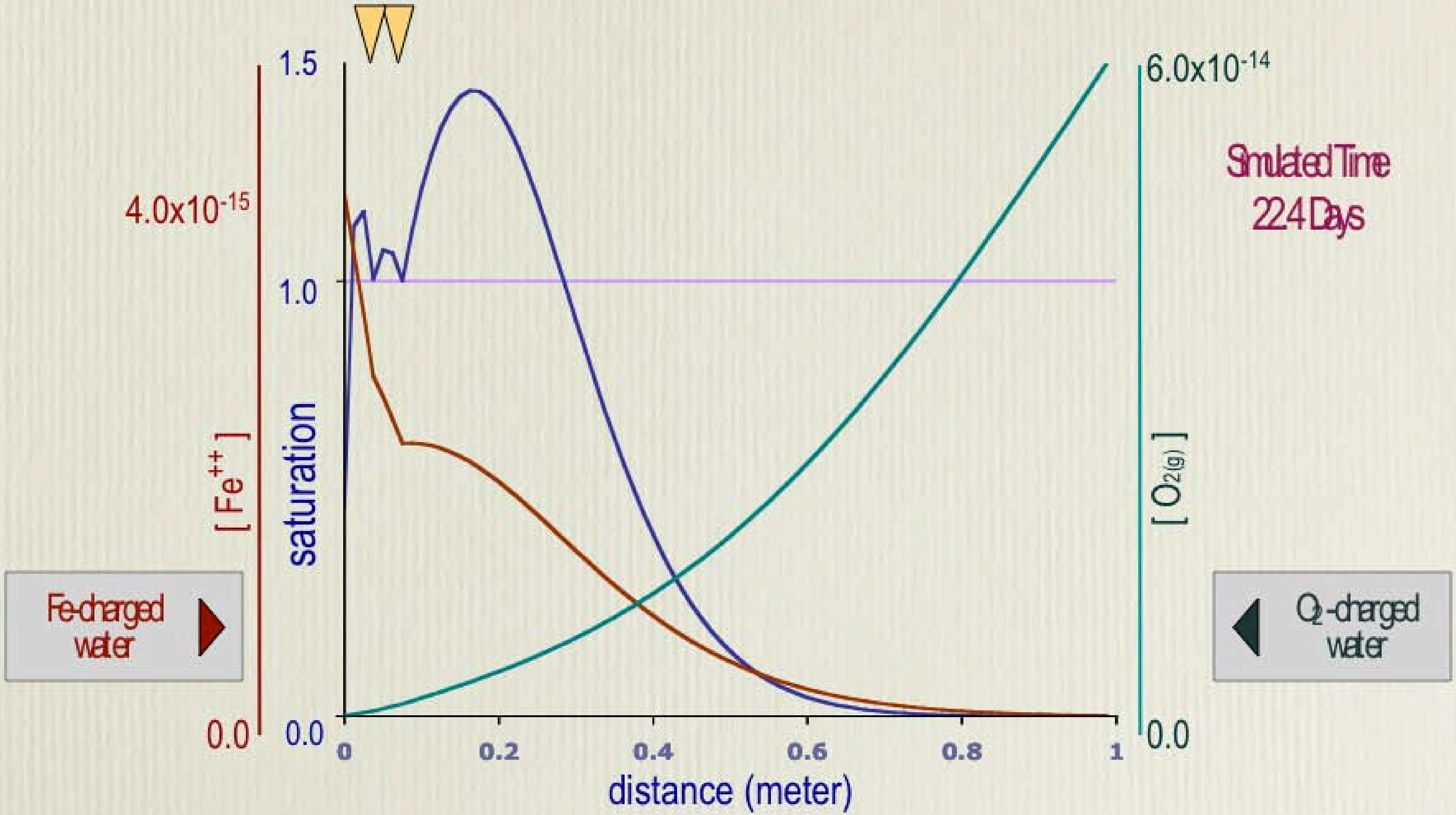

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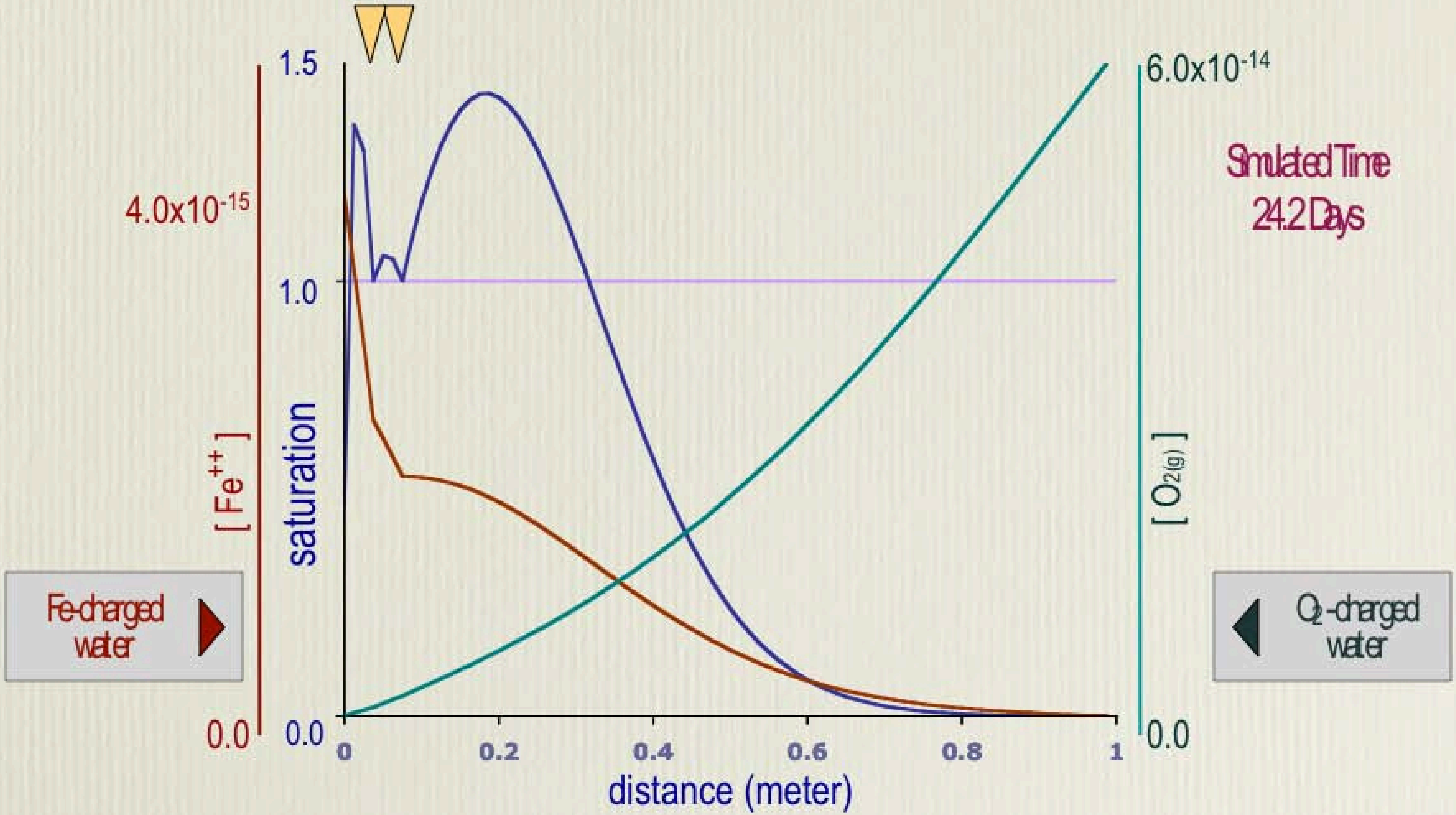

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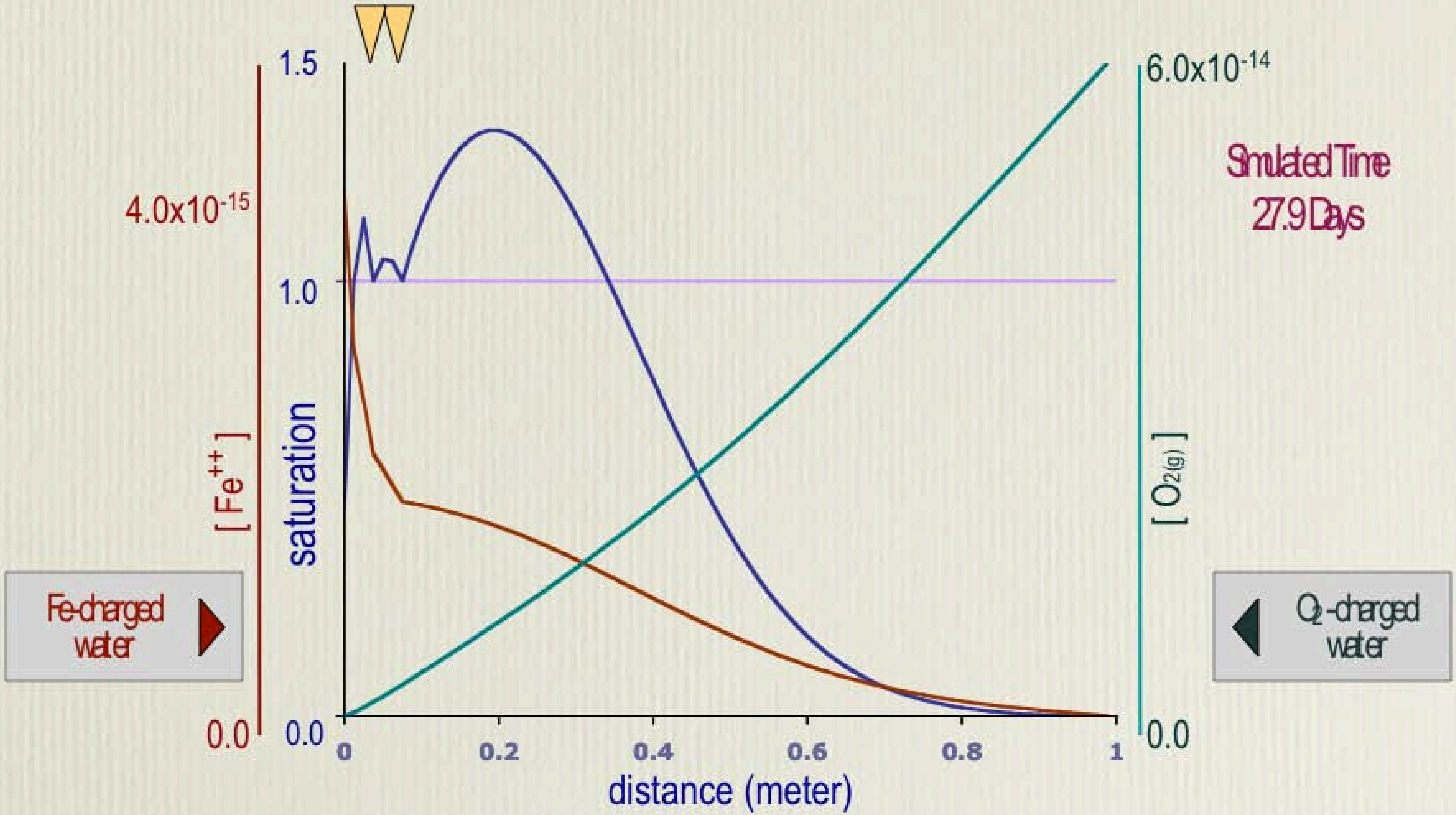

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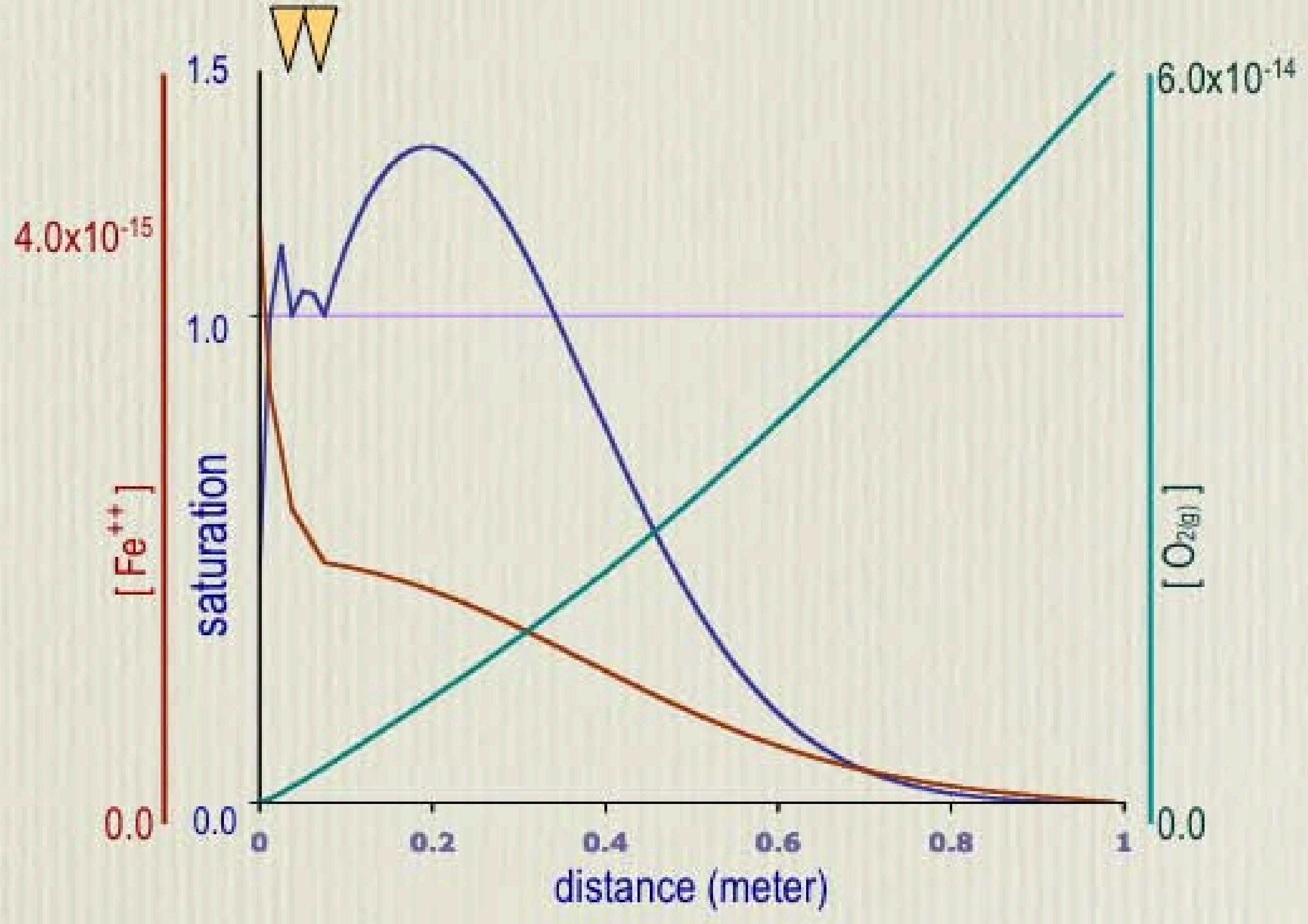
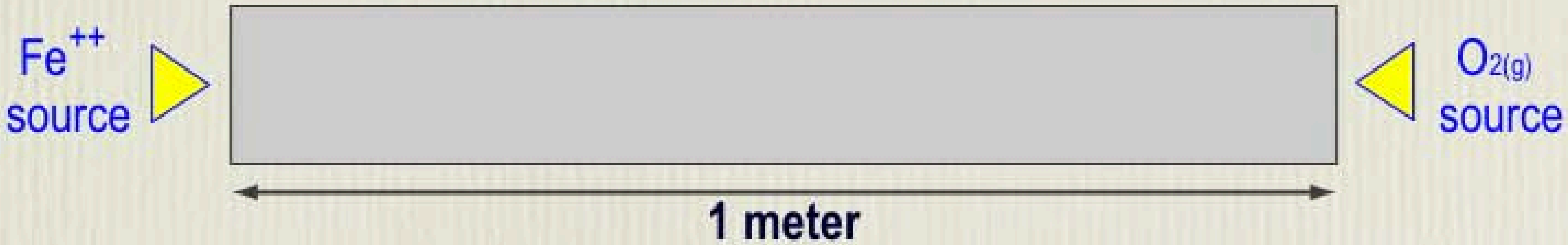


Diffusive infiltration only:

limited infiltration into country rock results in formation of Liesegang Bands

Reaction-Diffusion (Liesegang) Process



Simulation Parameters

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Concentrations (moles/L)

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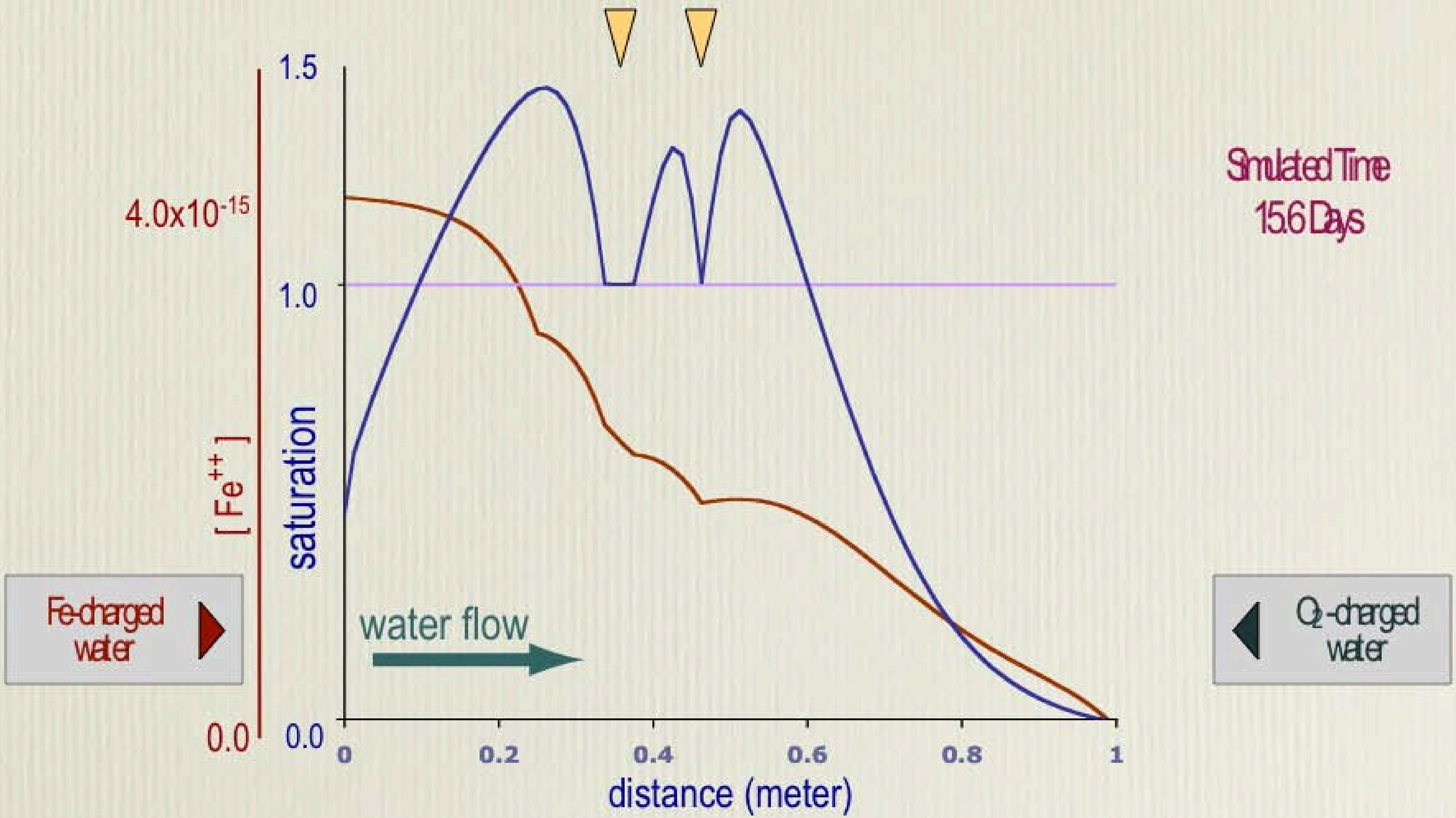
System length 1.0 m

Numerical grid resolution 1 grid / cm

Variation: Imposed advection (2.6 cm/yr) of Fe-charged water

Reaction-Diffusion (Liesegang) Process



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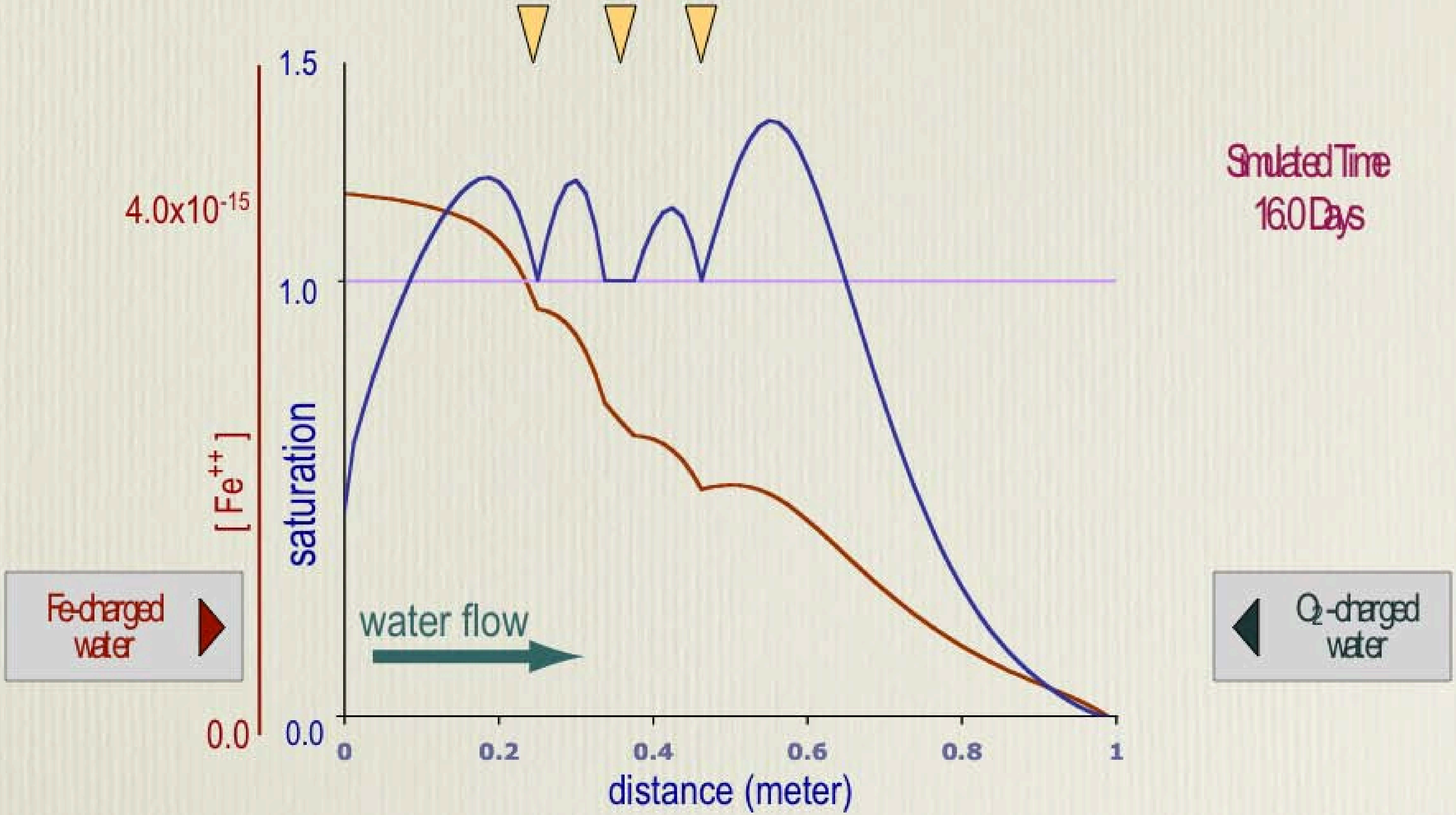

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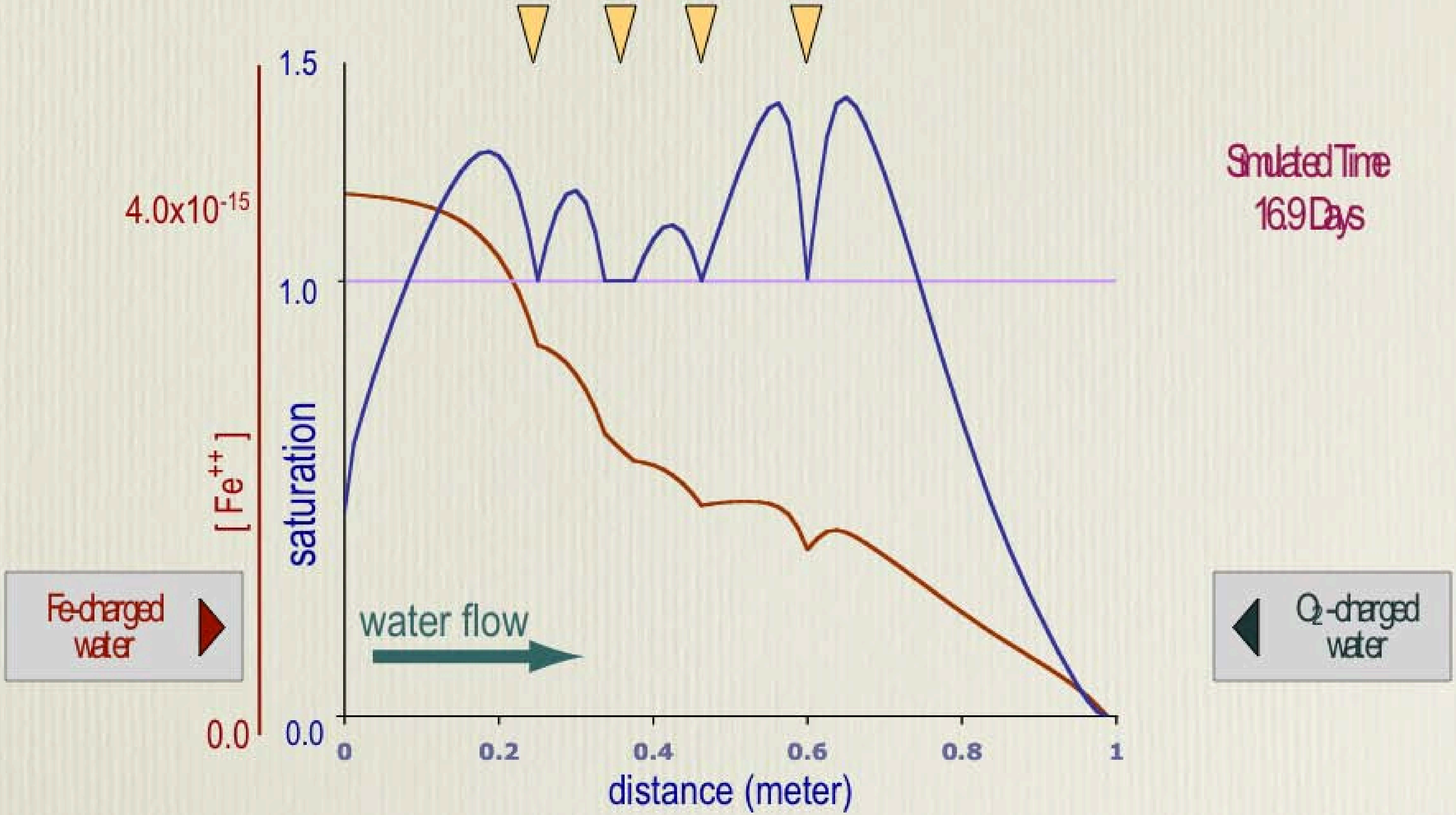

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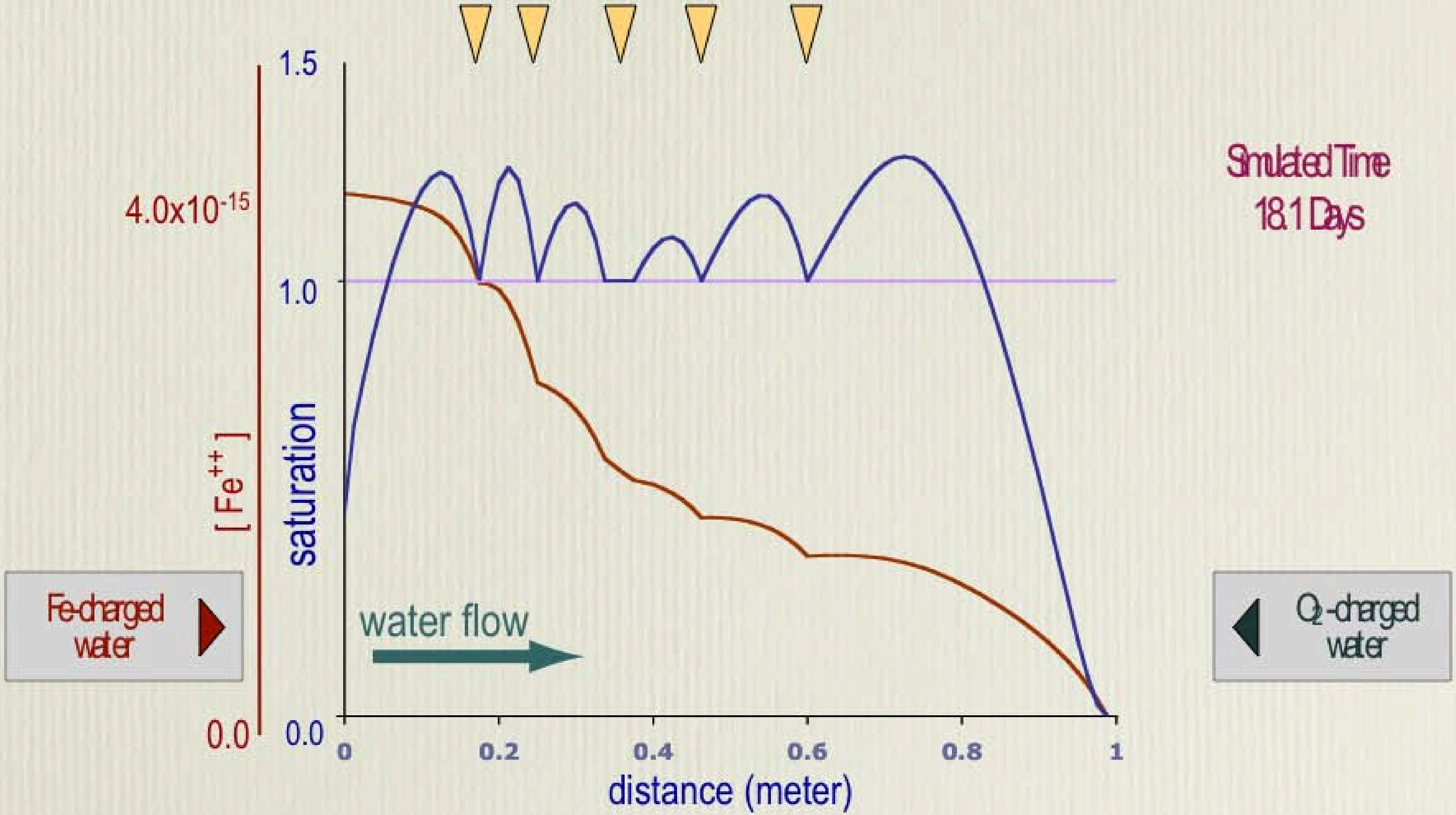

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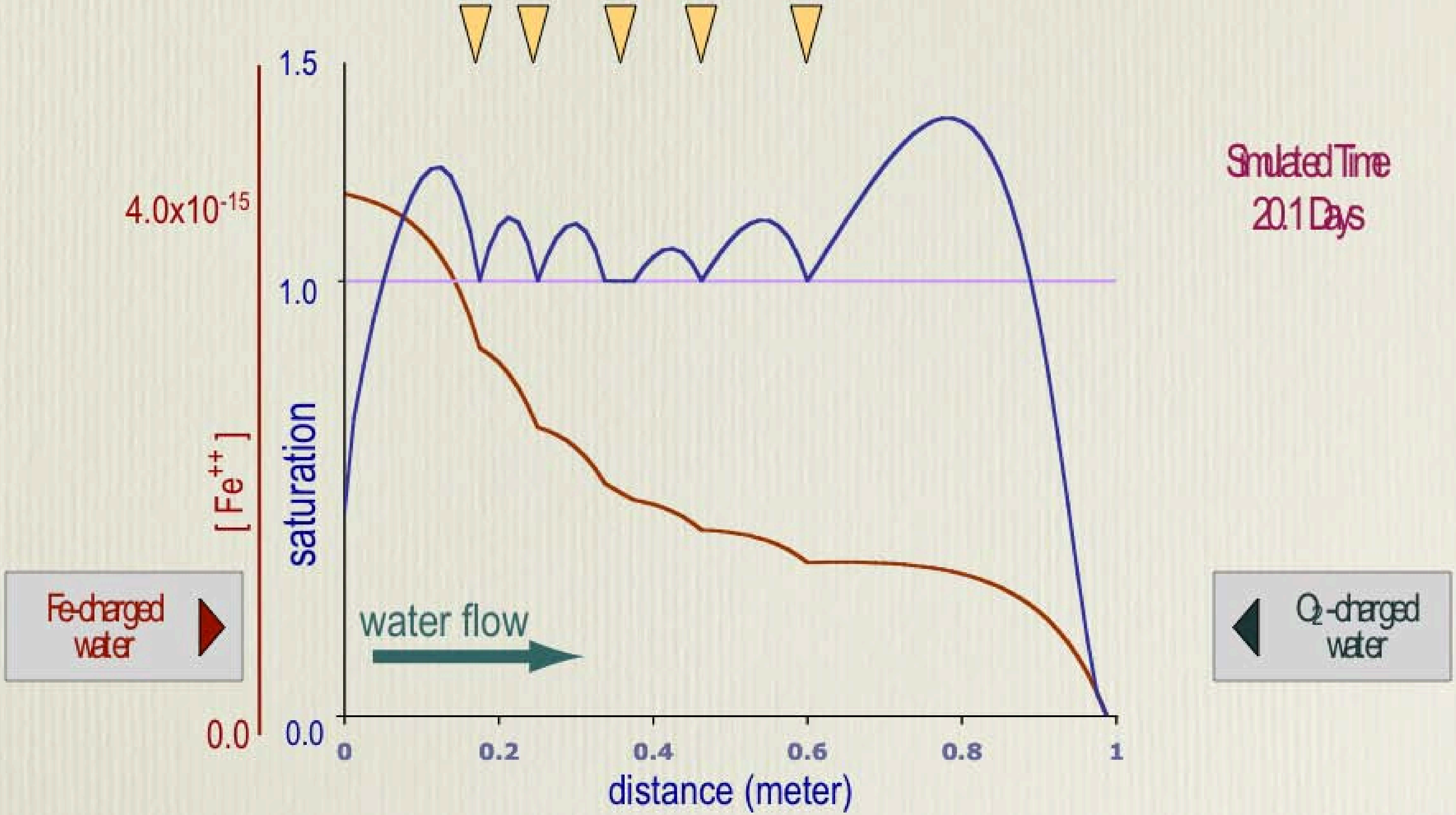

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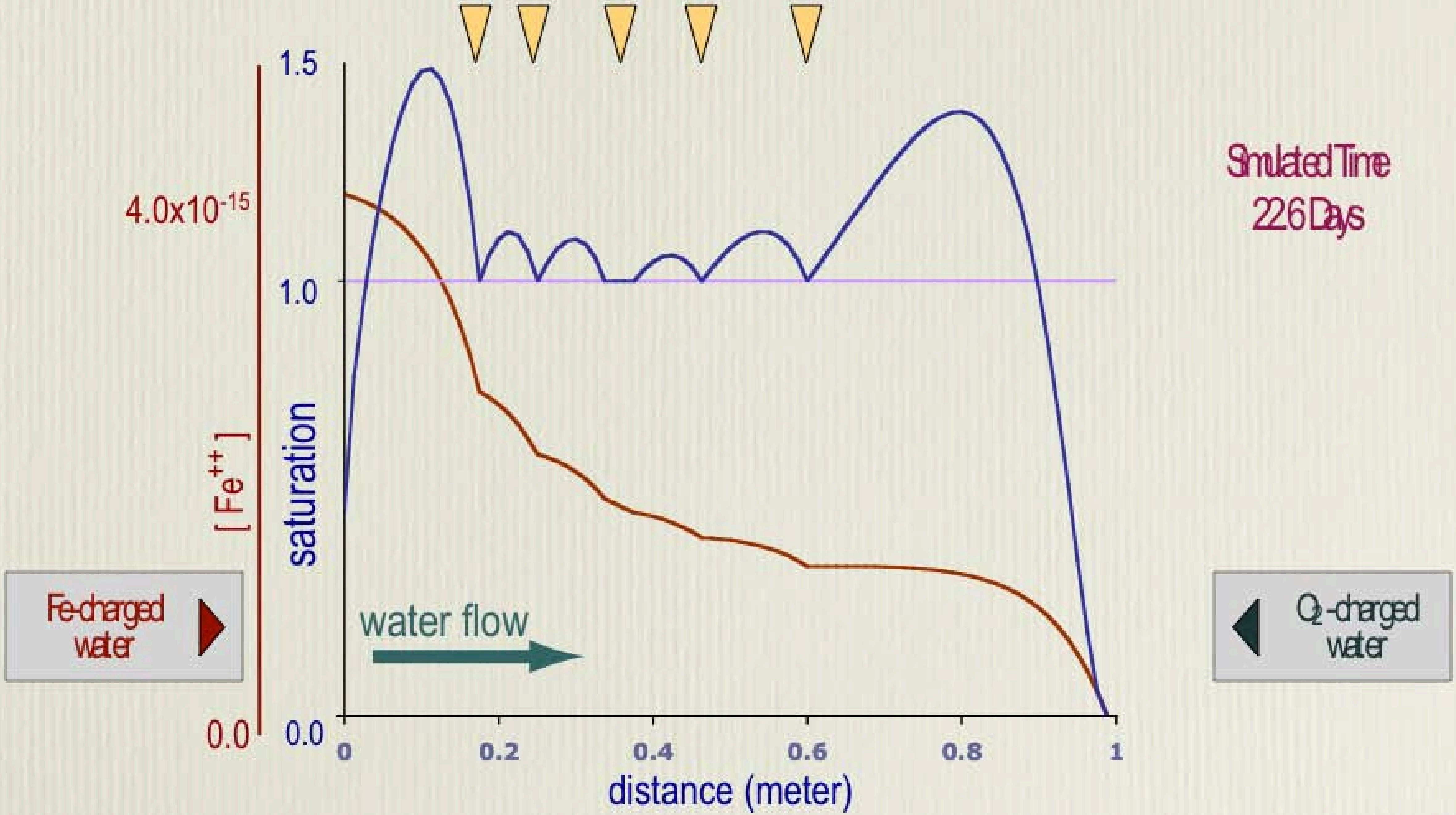

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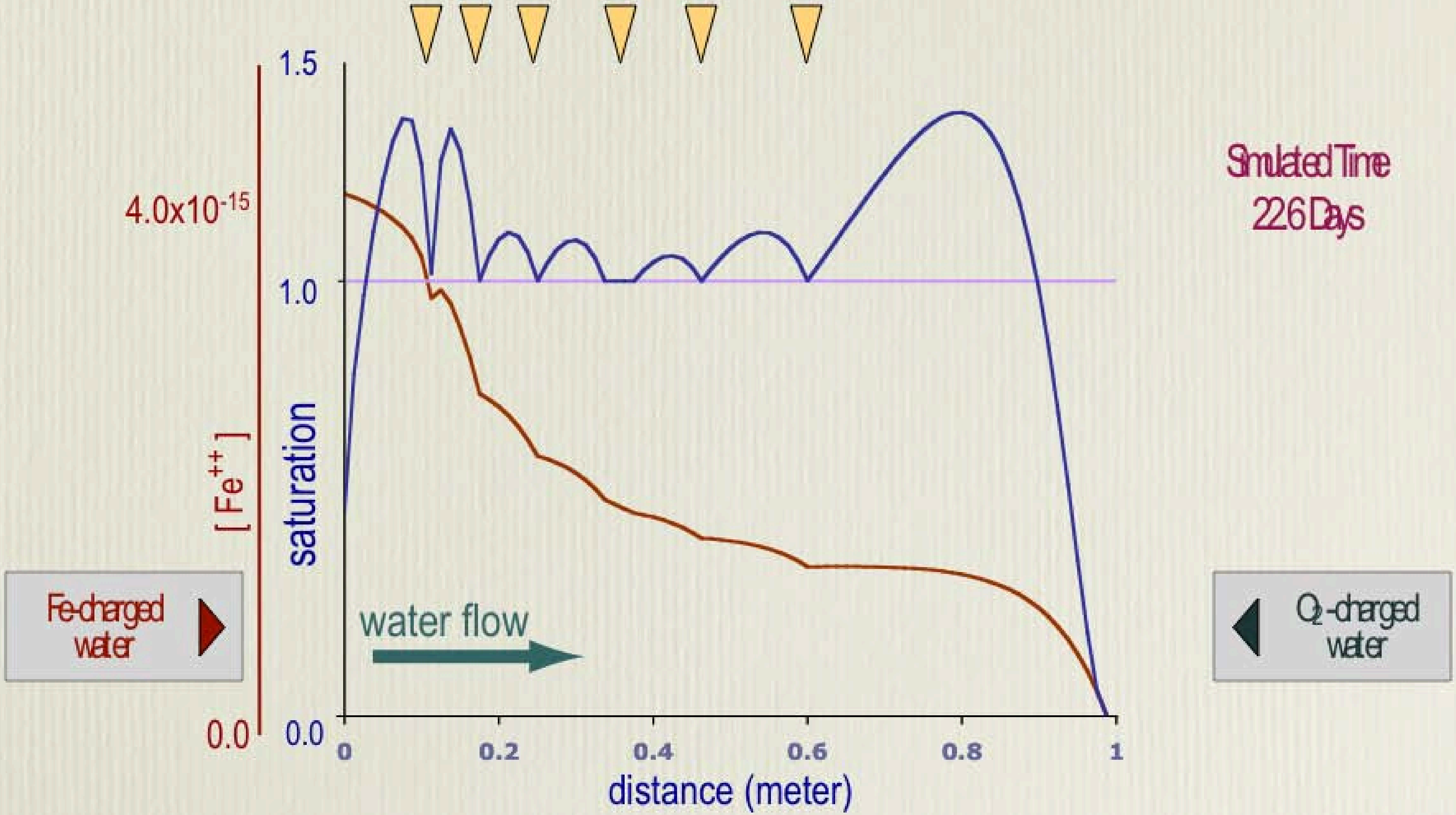

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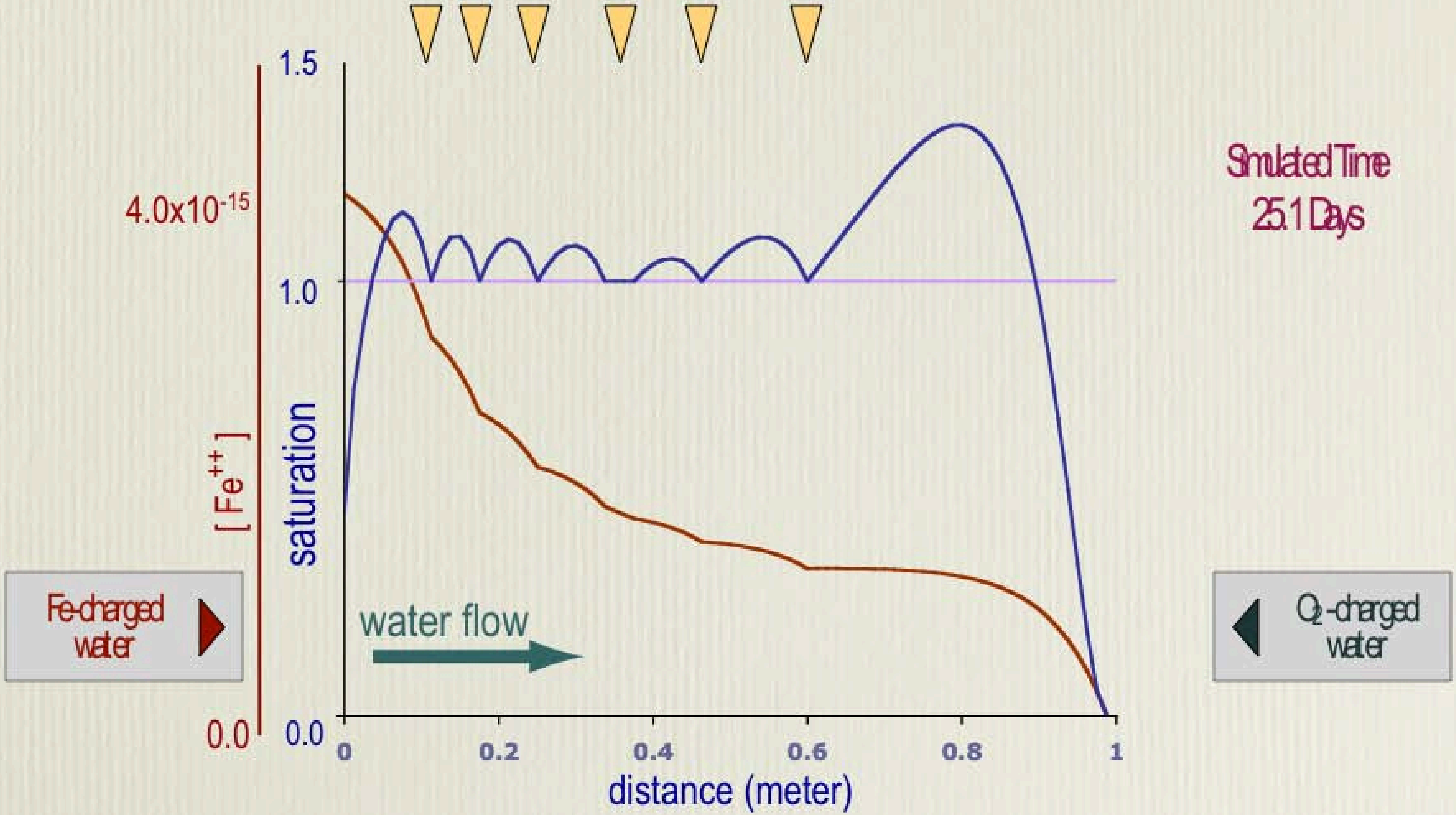

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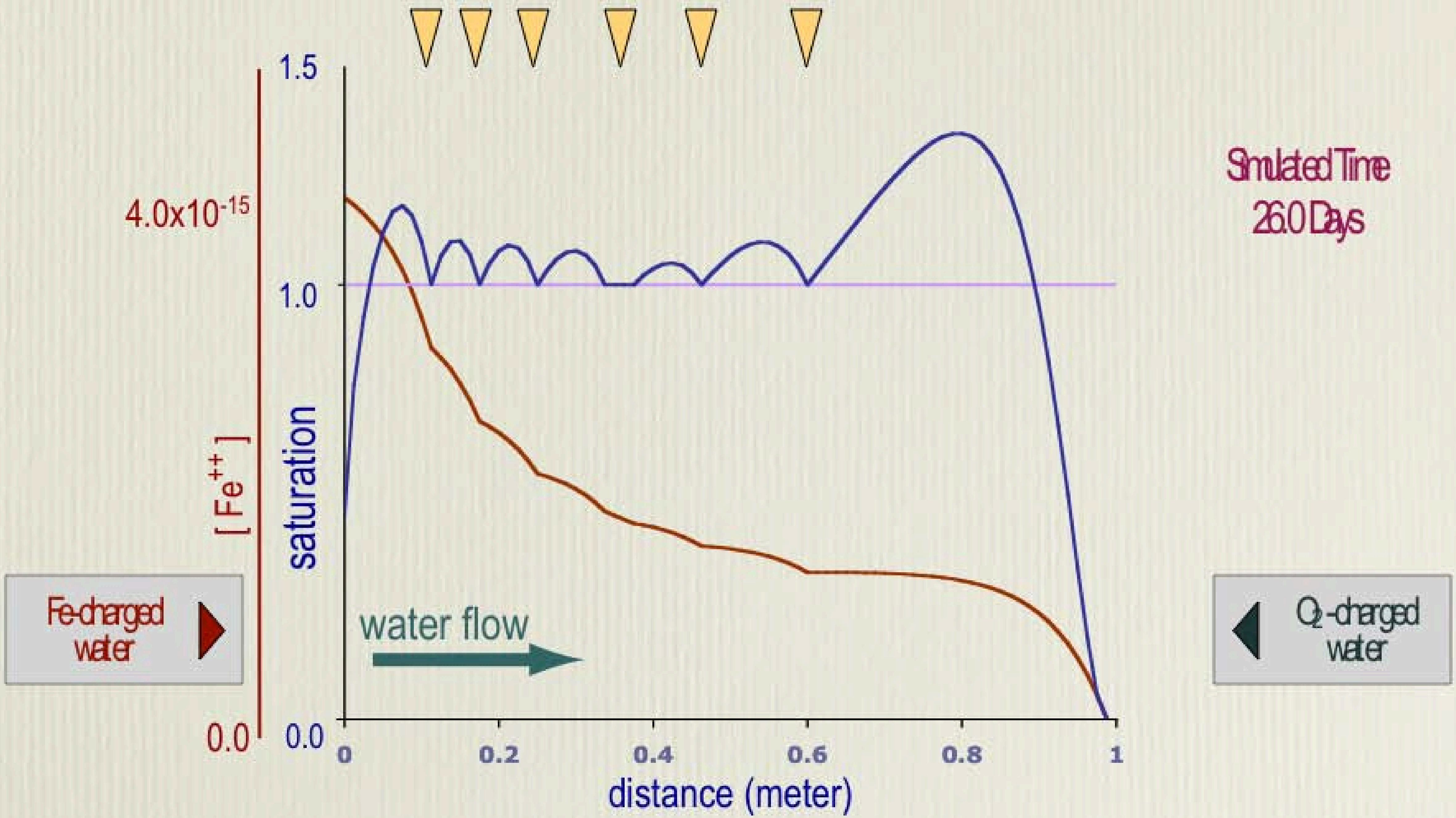

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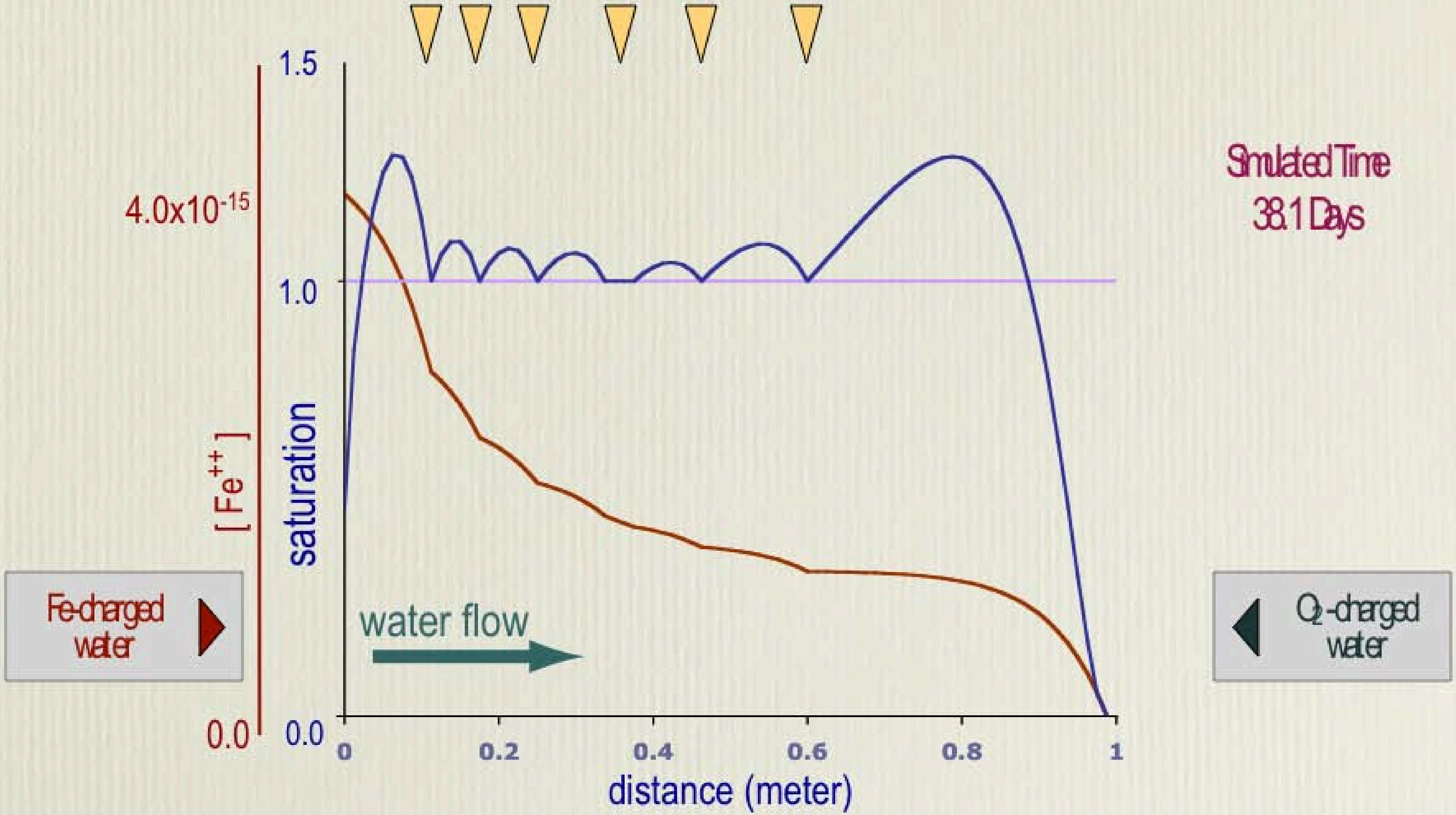

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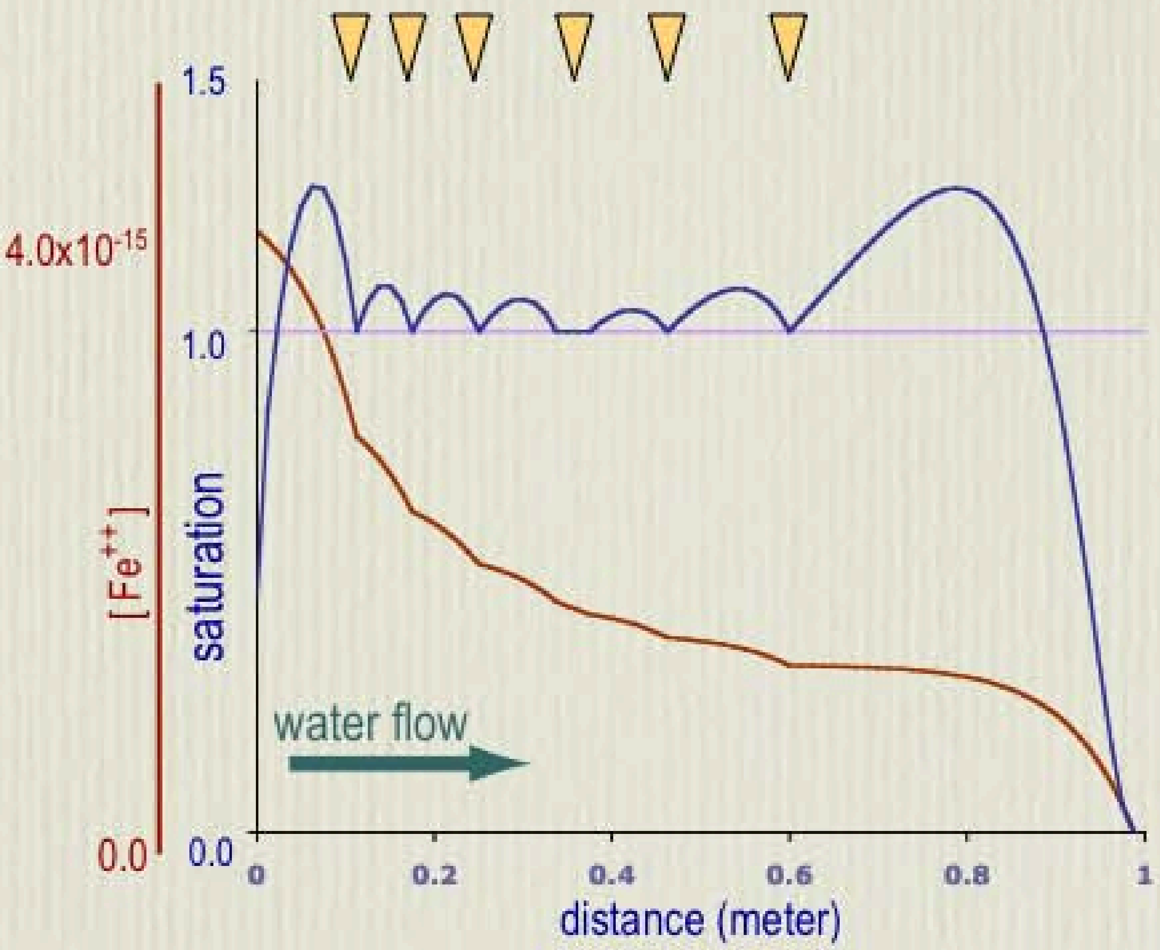
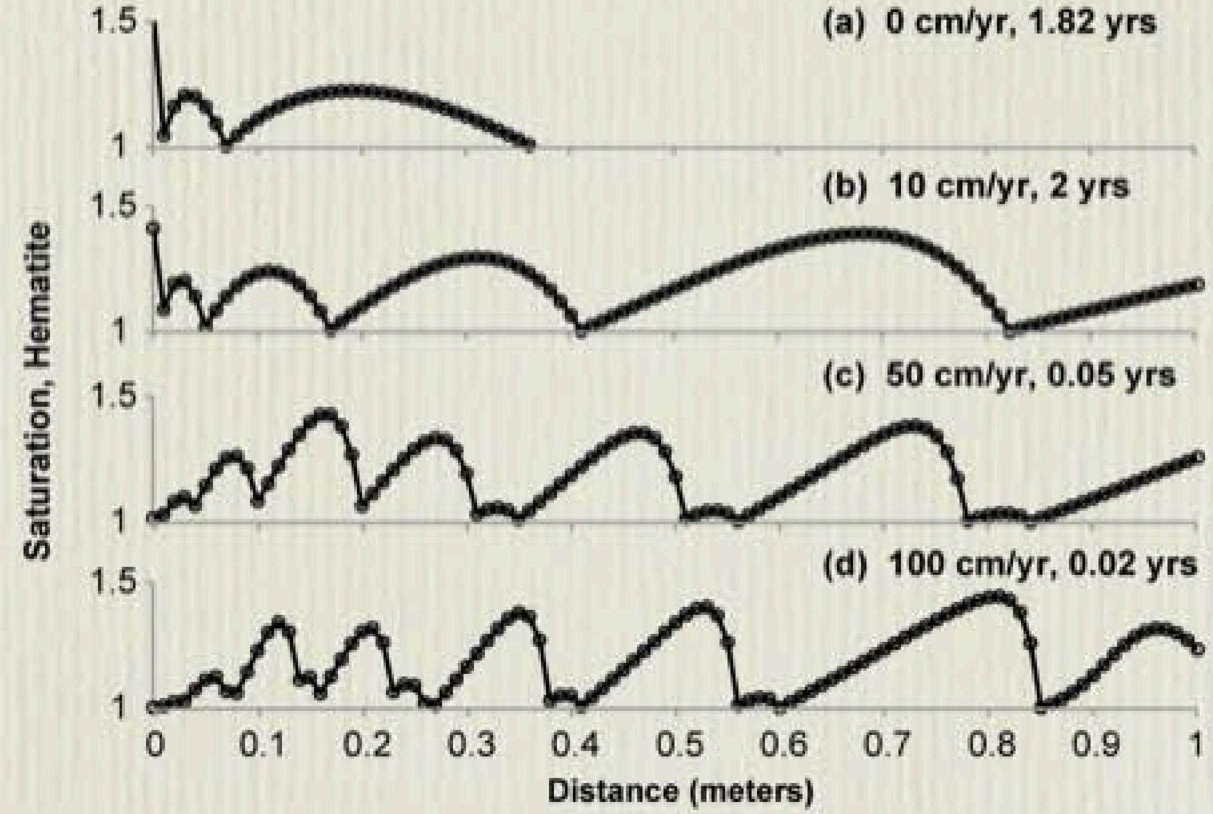


Diffusive infiltration assisted with advective influx:

Distributed nodule precipitation
Pattern depends on solute supply rate

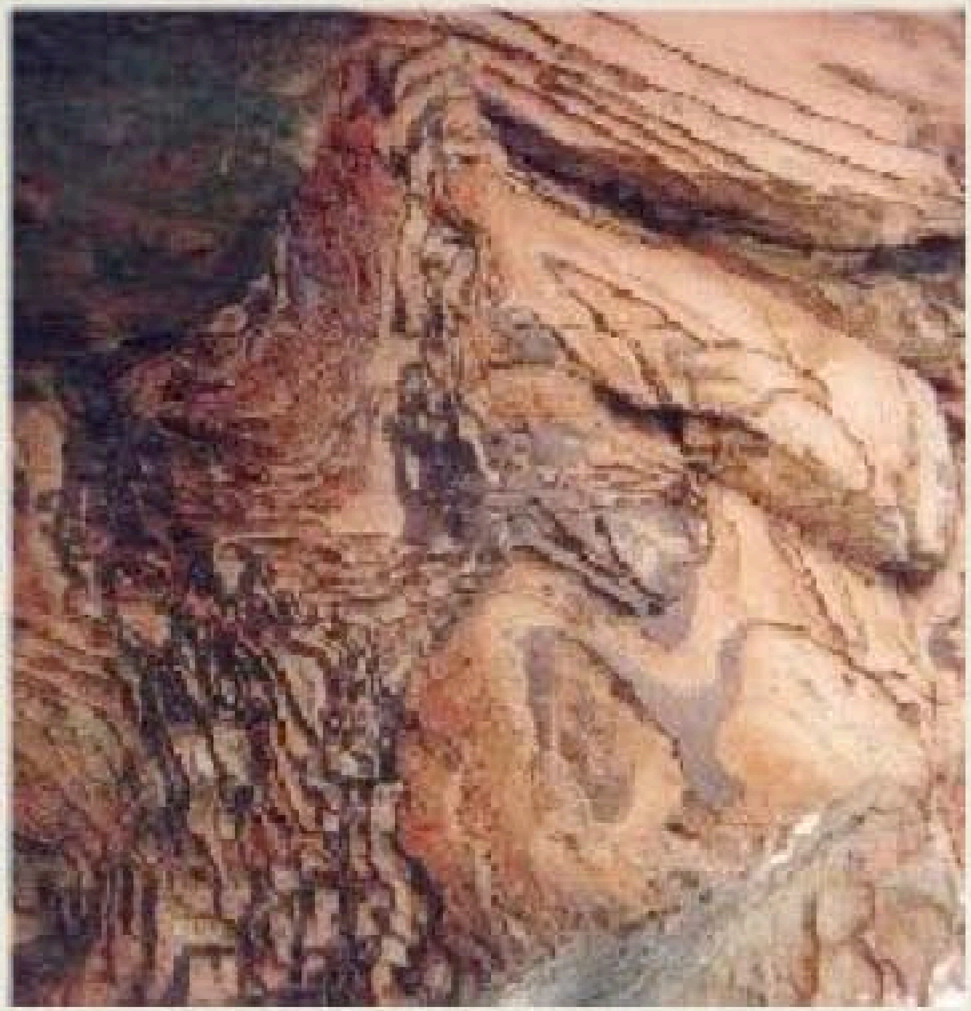
Horseshoe Canyon and Colorado River, Page, Arizona



Greater abundance of oxygen results in greater complexity of the pattern

Given time, nucleates form throughout the sediment

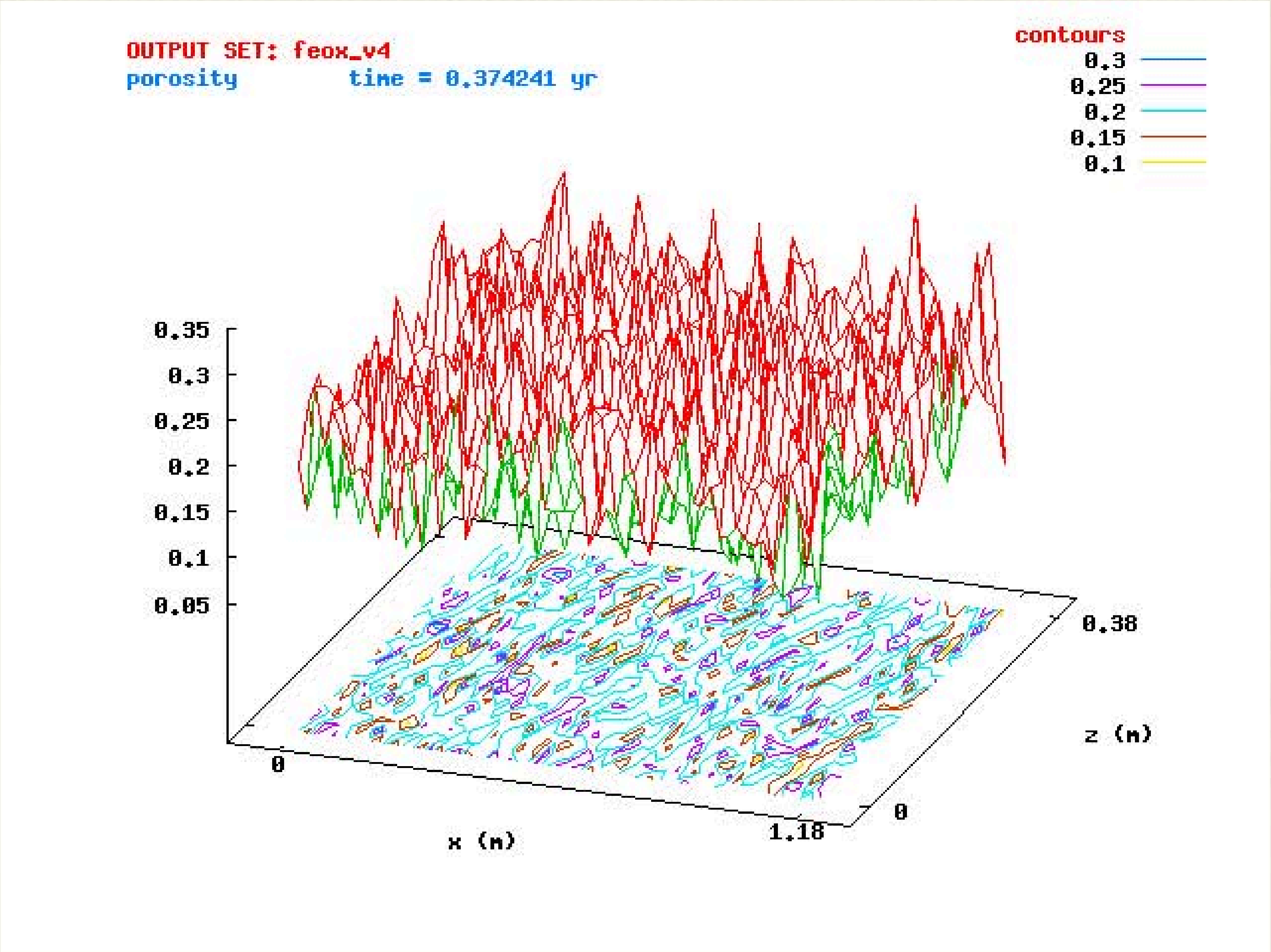
Iron-Oxide "Liesegang" Bands in Sandstones



Red River Gorge, Cumberland Falls, Natural Bridge and Cumberland Gap areas. The source of the iron is the carbonate mineral siderite. But when siderite weathers, it oxidizes forming the yellow-brown mineral limonite as well as hematite and goethite. Kentucky Geological Survey, http://www.uky.edu/KGS/rocksmn/liesegang.htm

Liesegang Banding is used to describe the morphological similarity between iron-oxide reaction front bands and the patterns observed in lab experiments. Lab experiments impose only 1D variability.

Reaction-Diffusion Process: 2D Heterogeneity



2D: flow-reaction feedback, between naturally occurring sedimentological heterogeneity (variation in grain size and porosity) and imposed fluid flow

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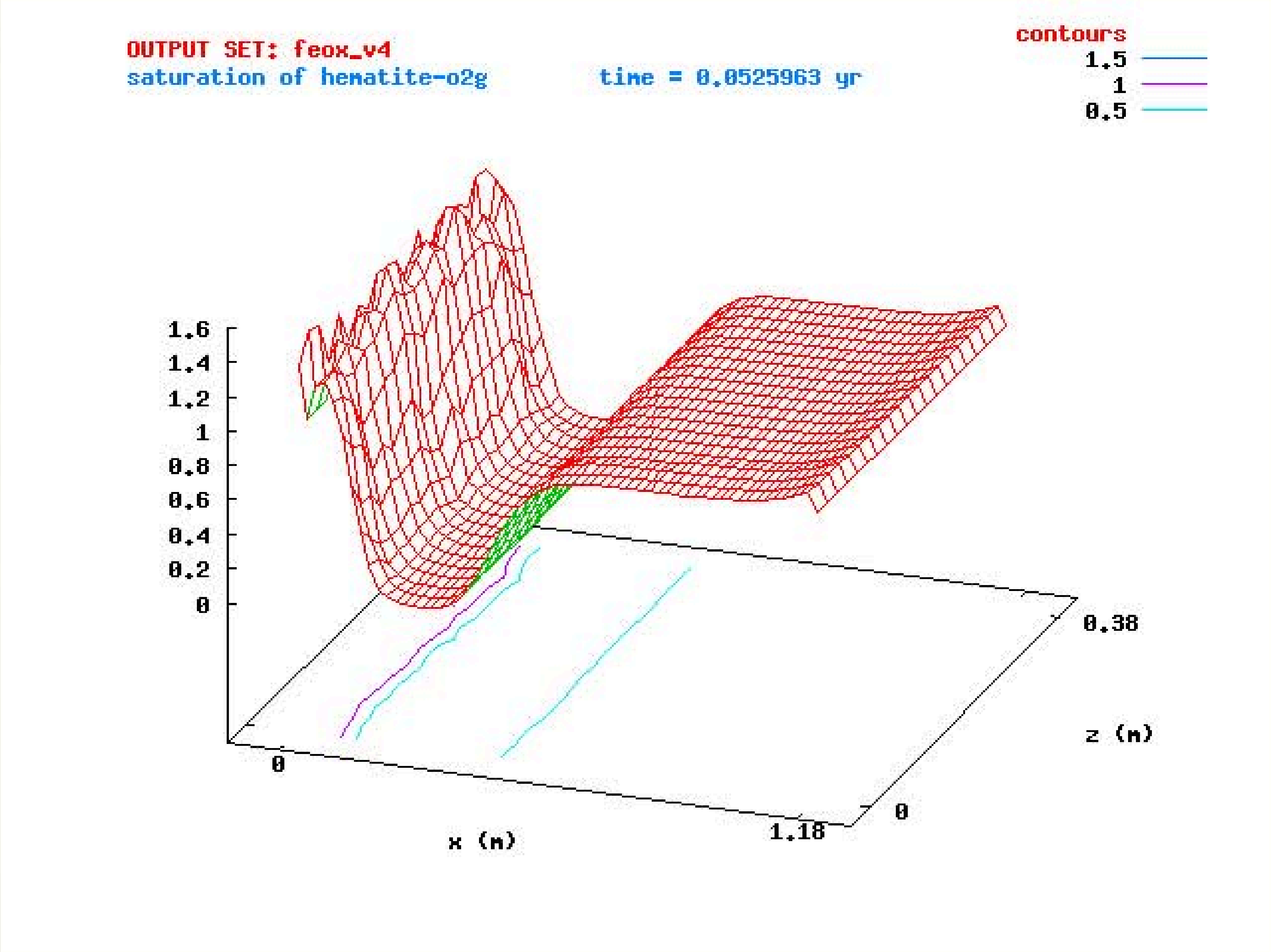

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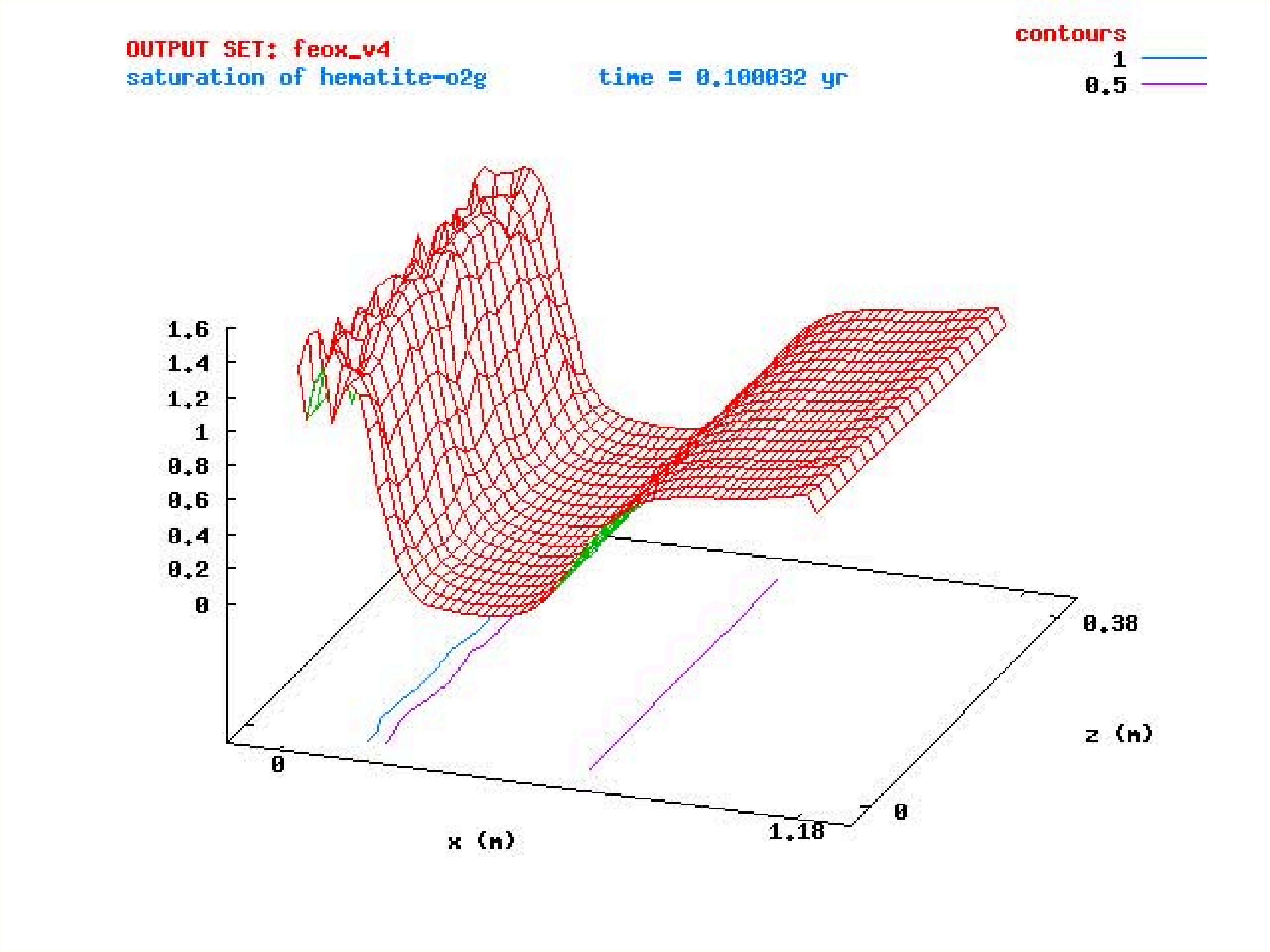

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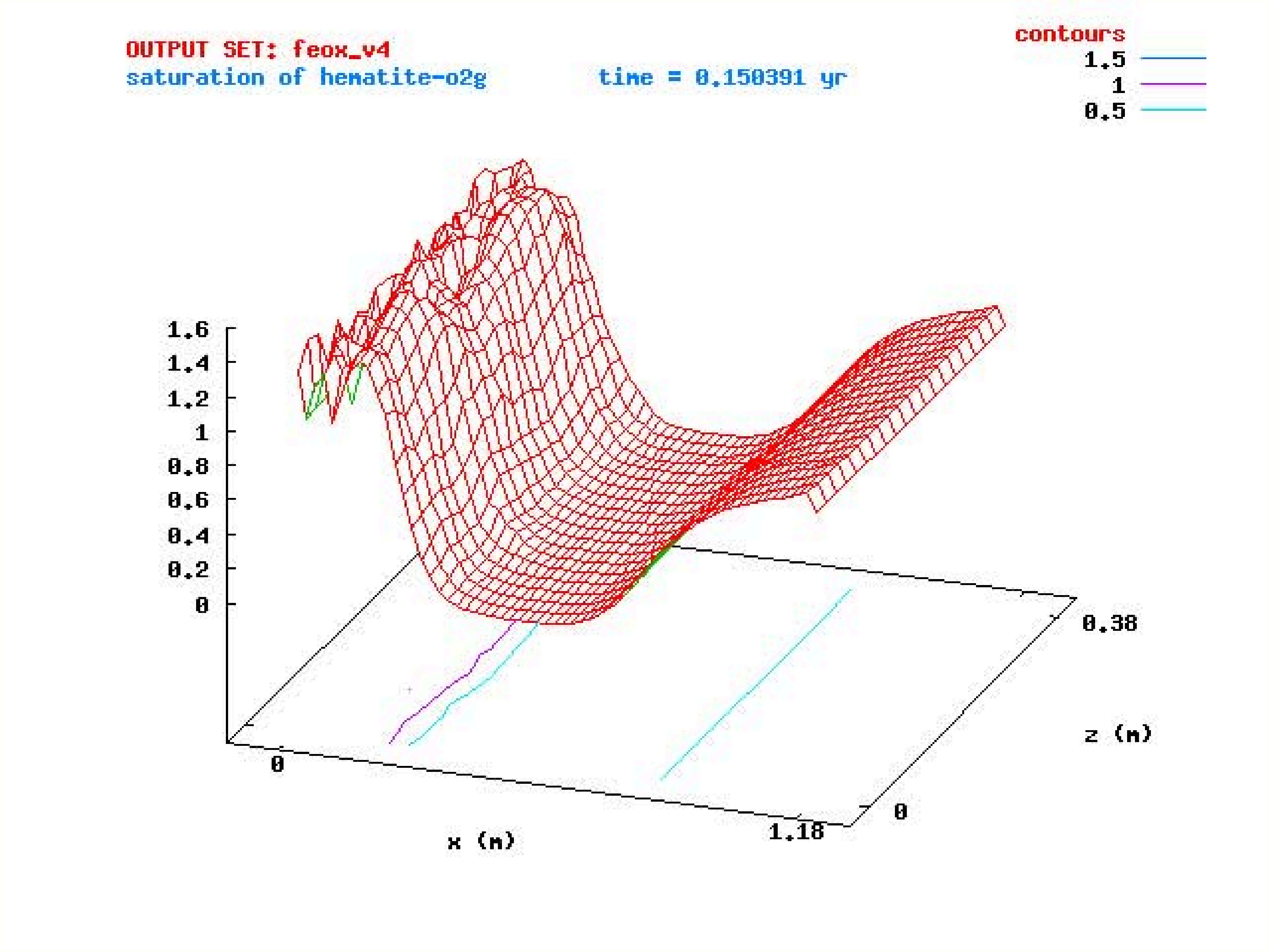

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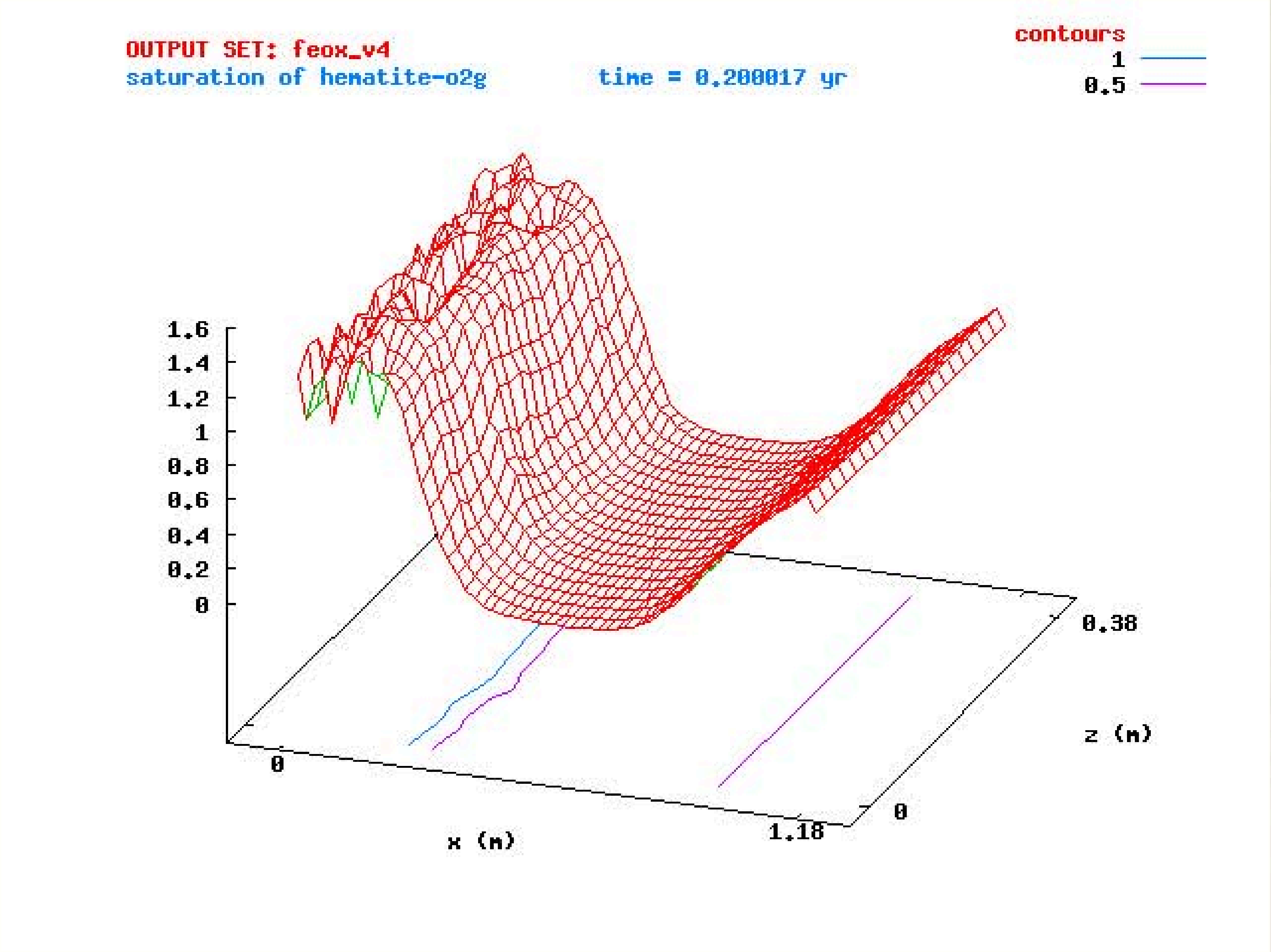

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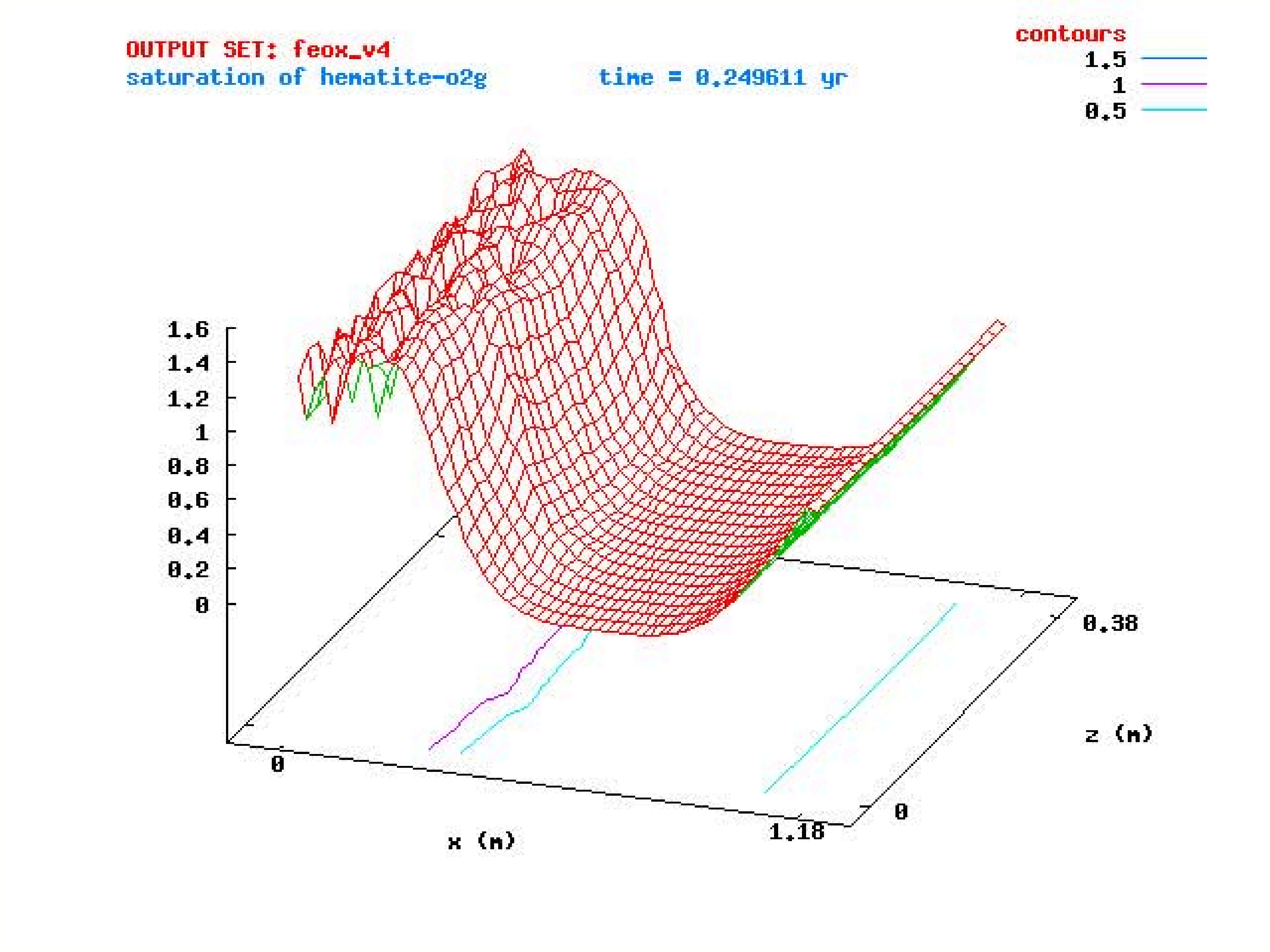

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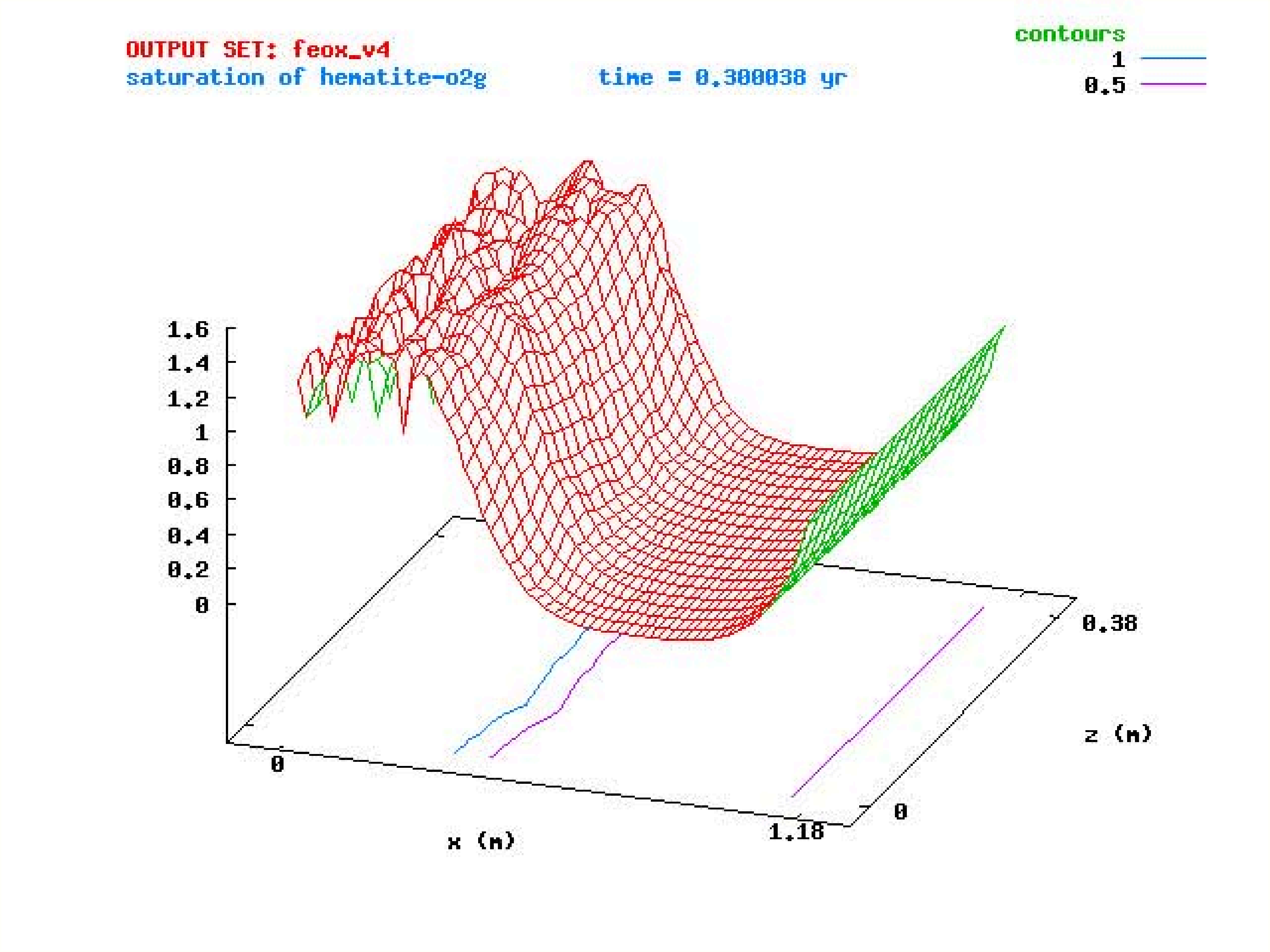

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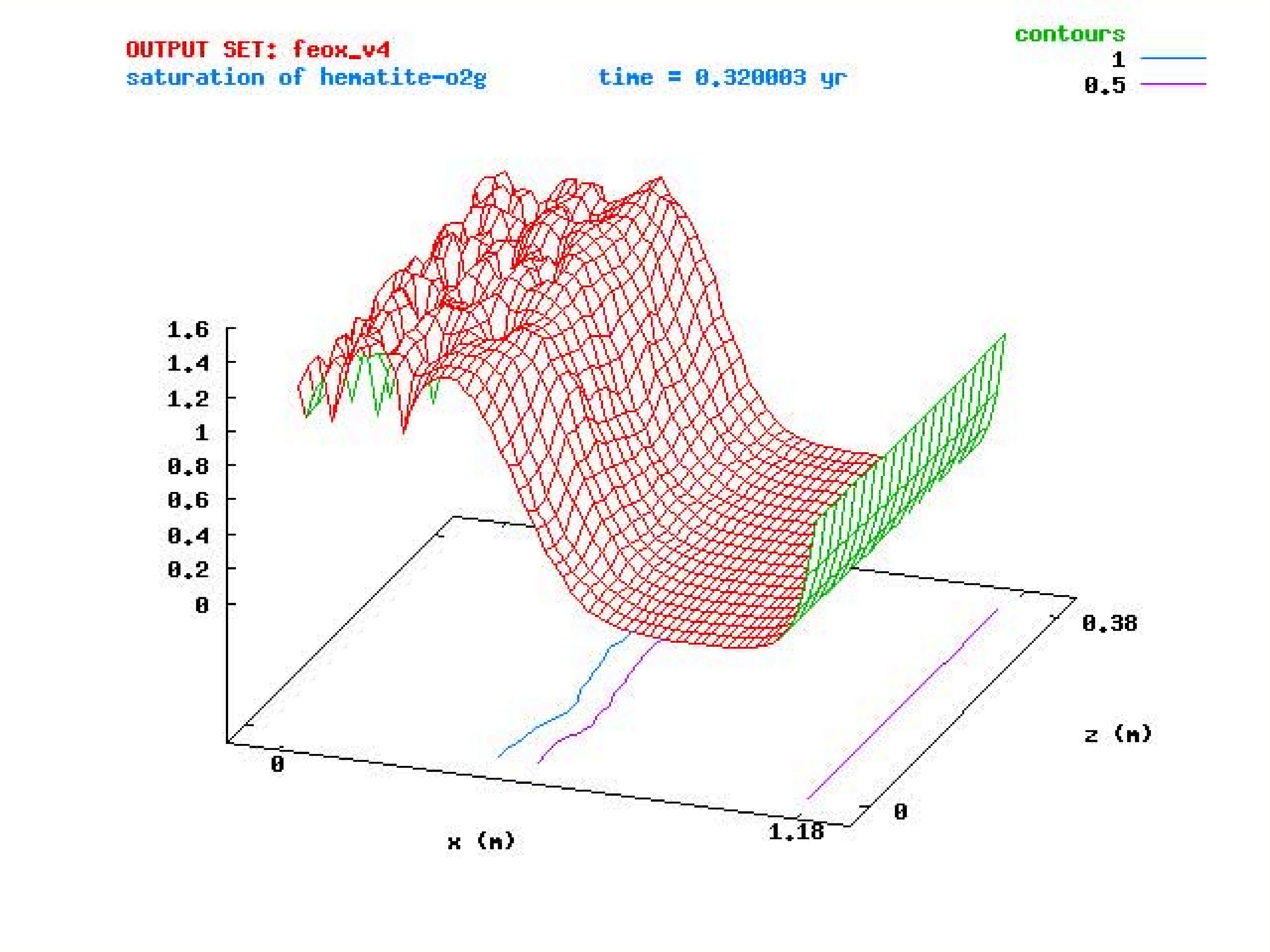

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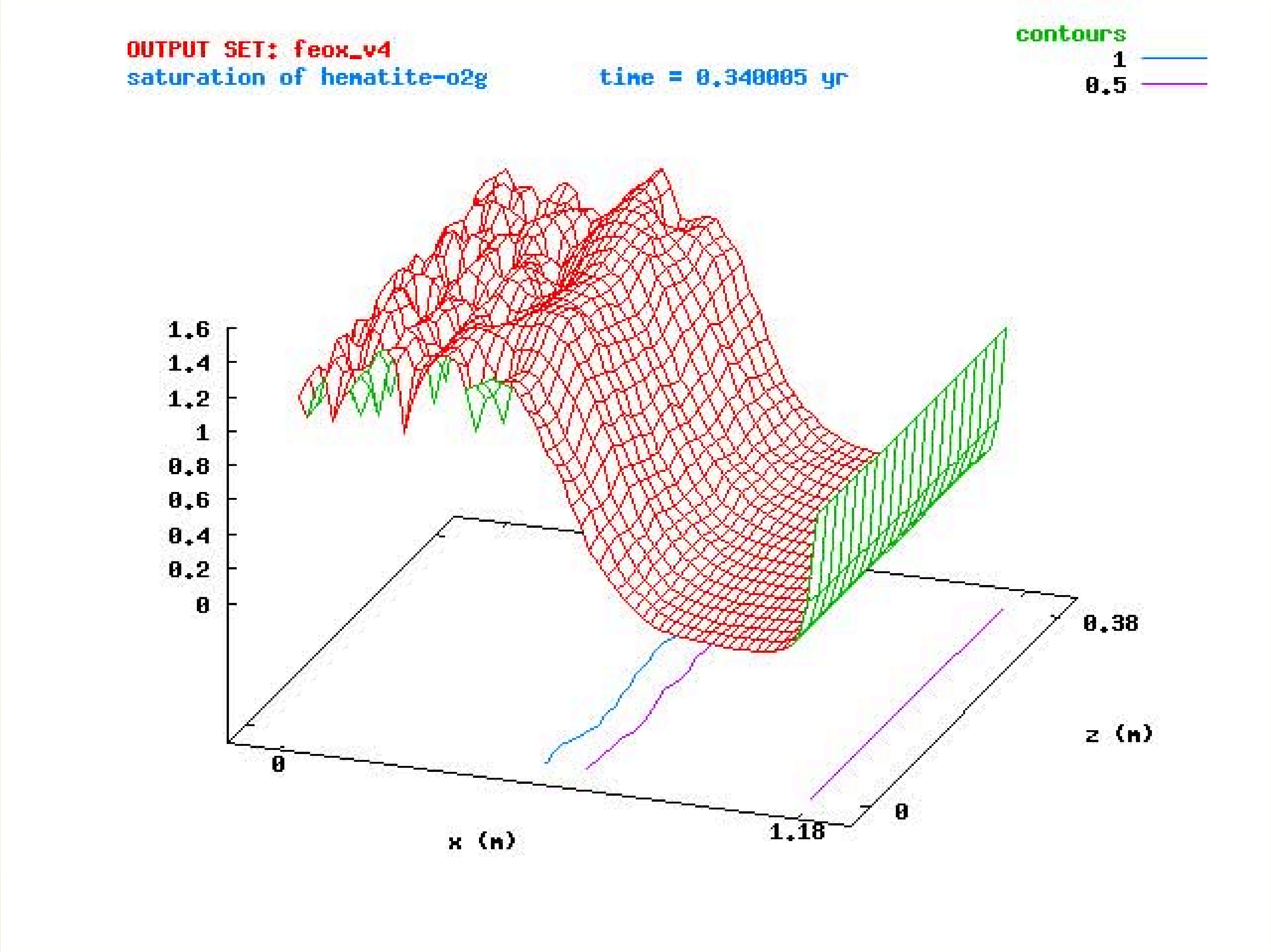

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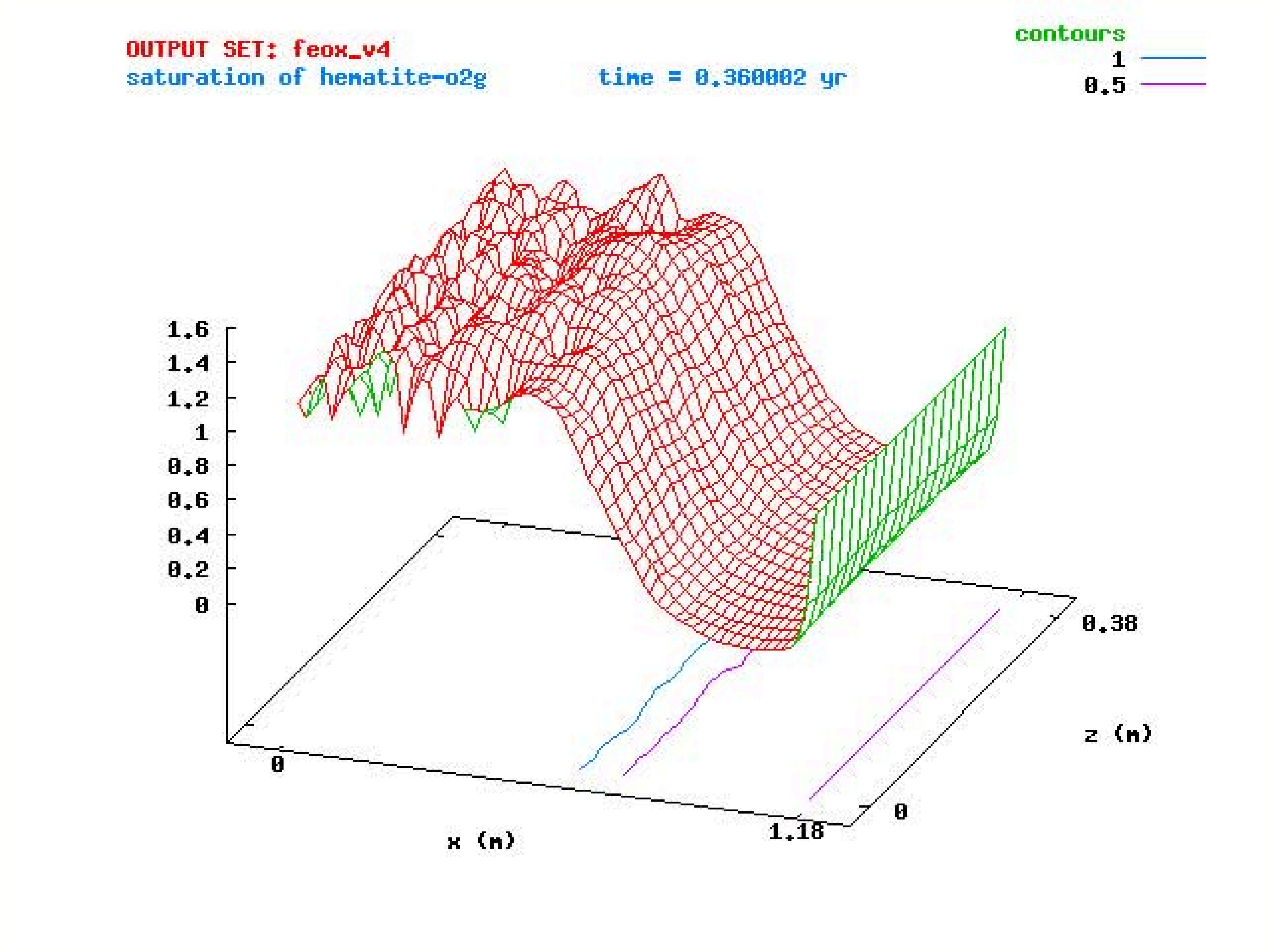

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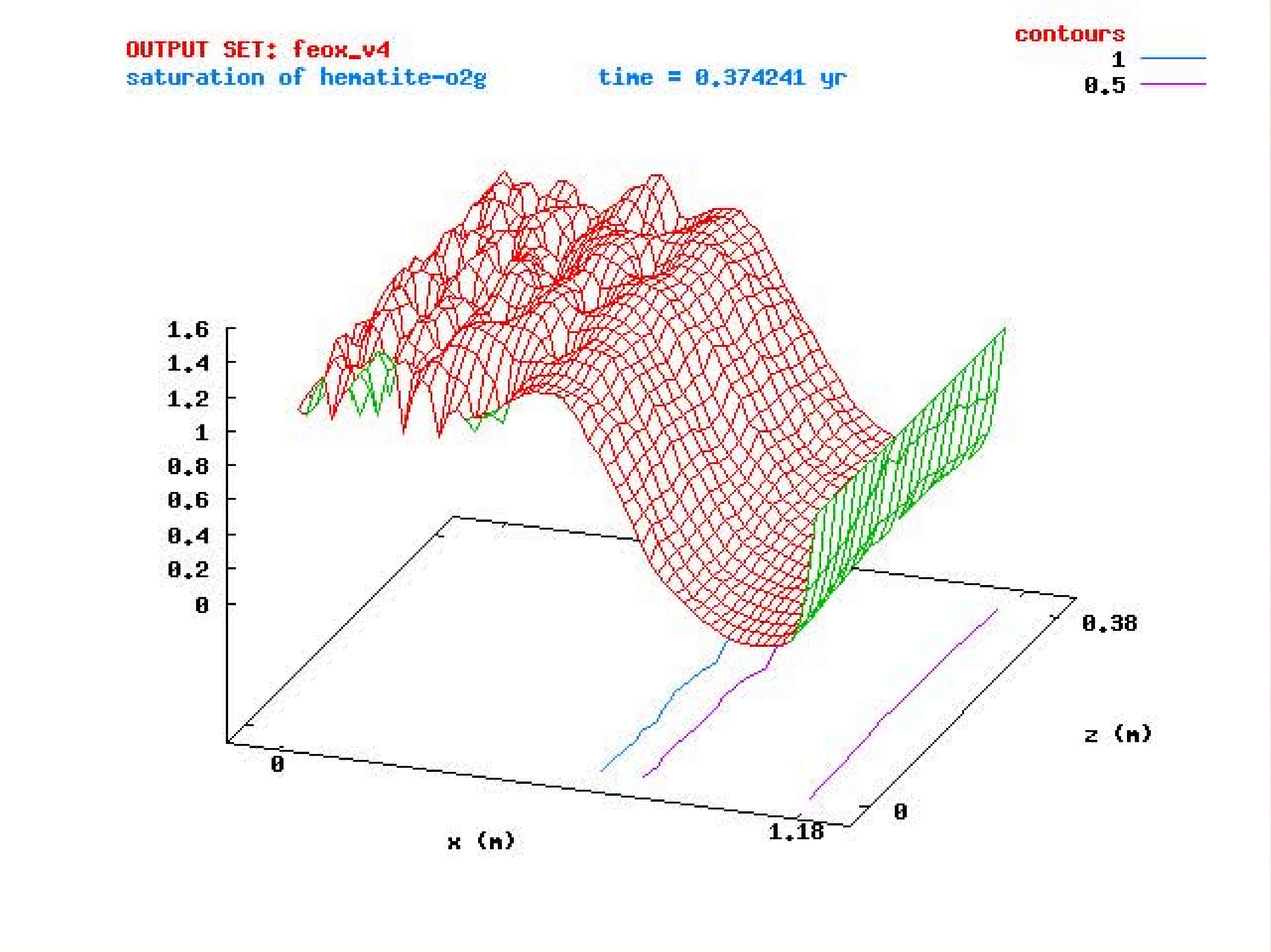

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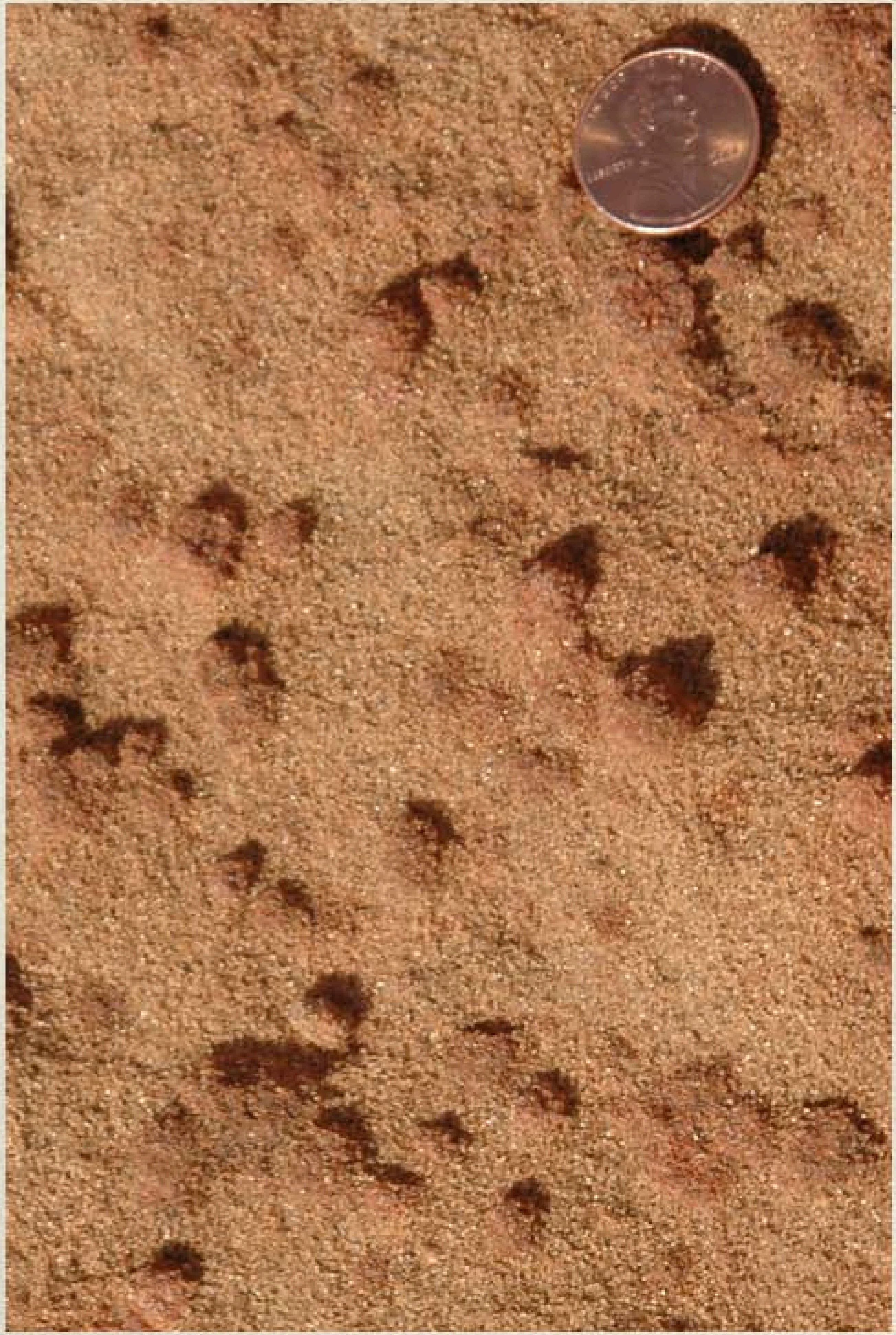
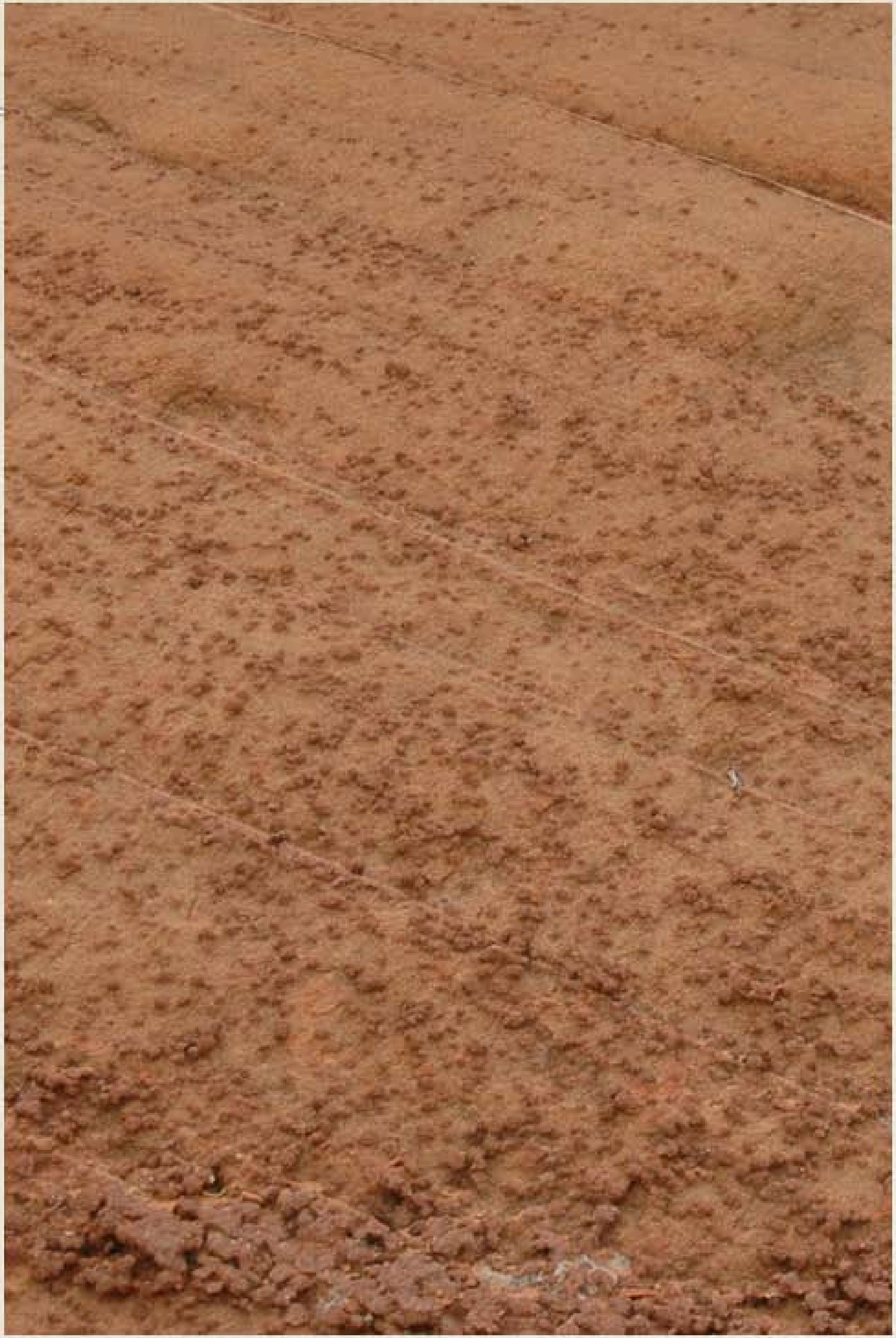
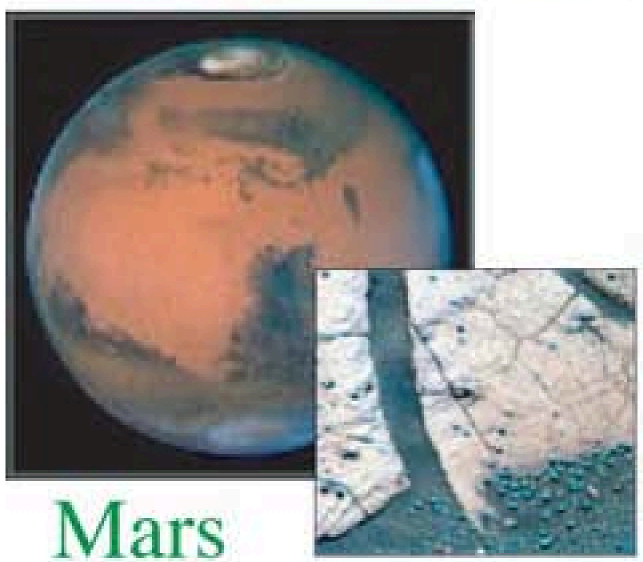


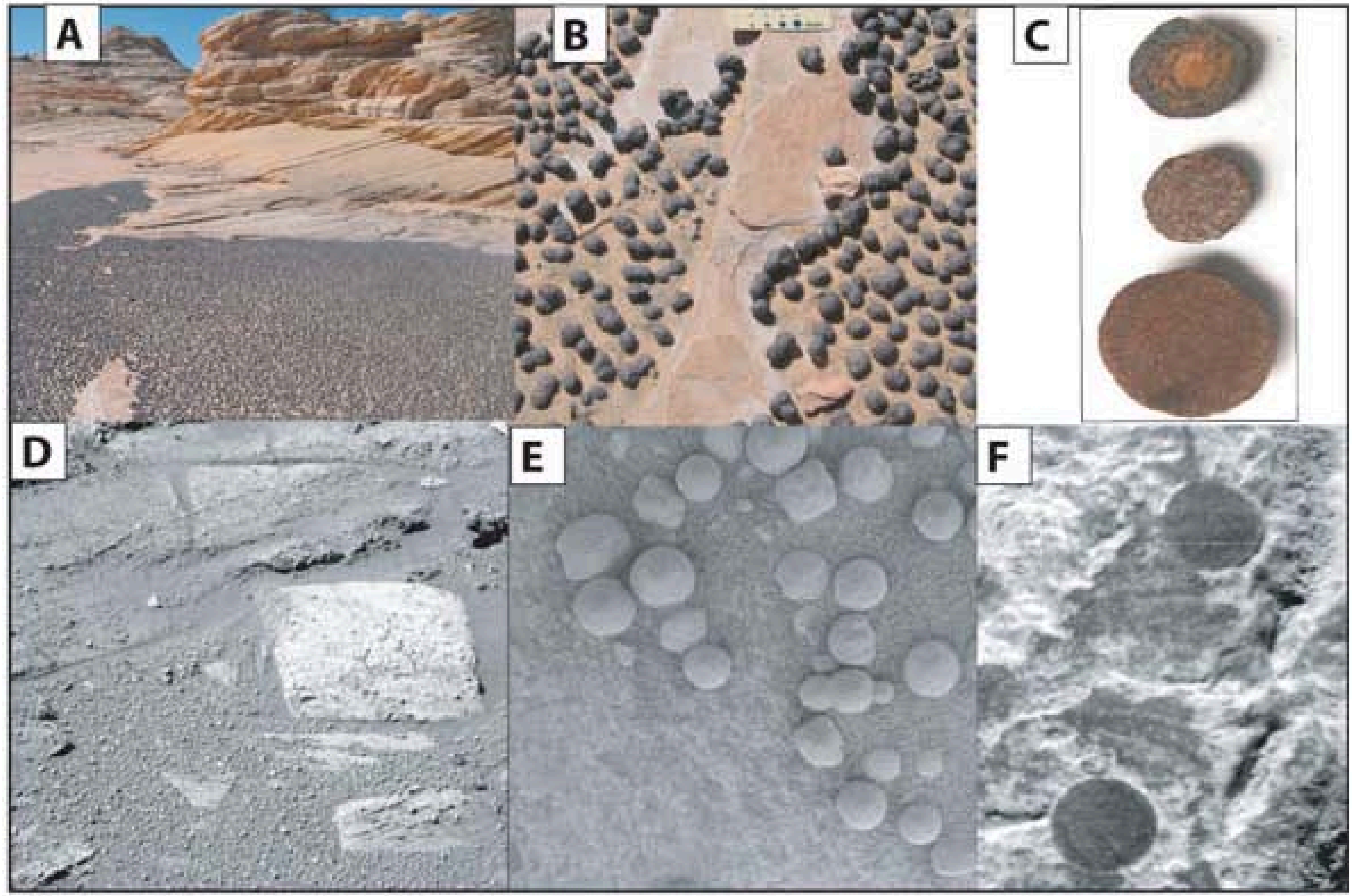


Comparison, Terrestrial and Marsian Spherules

Utah

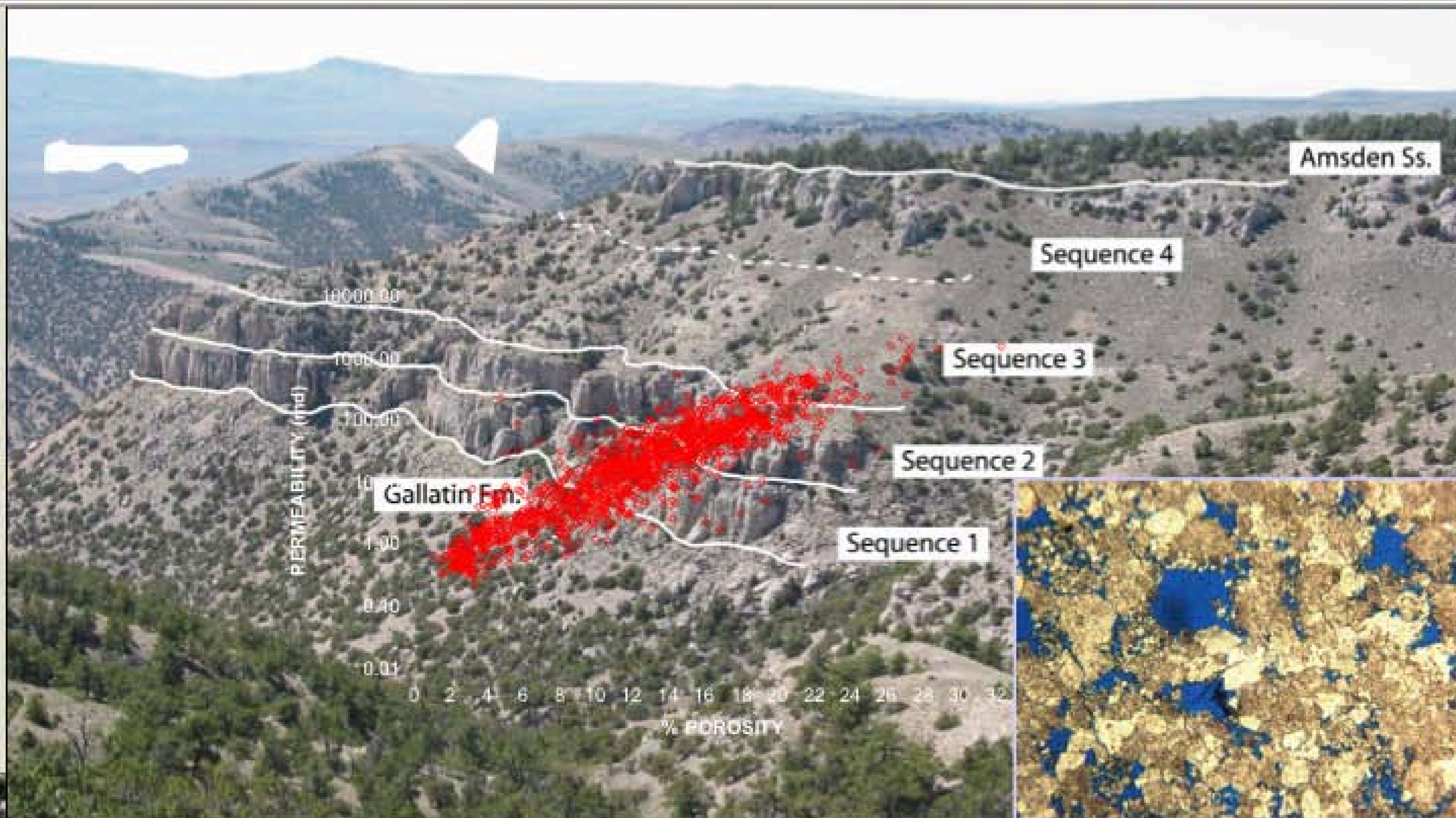


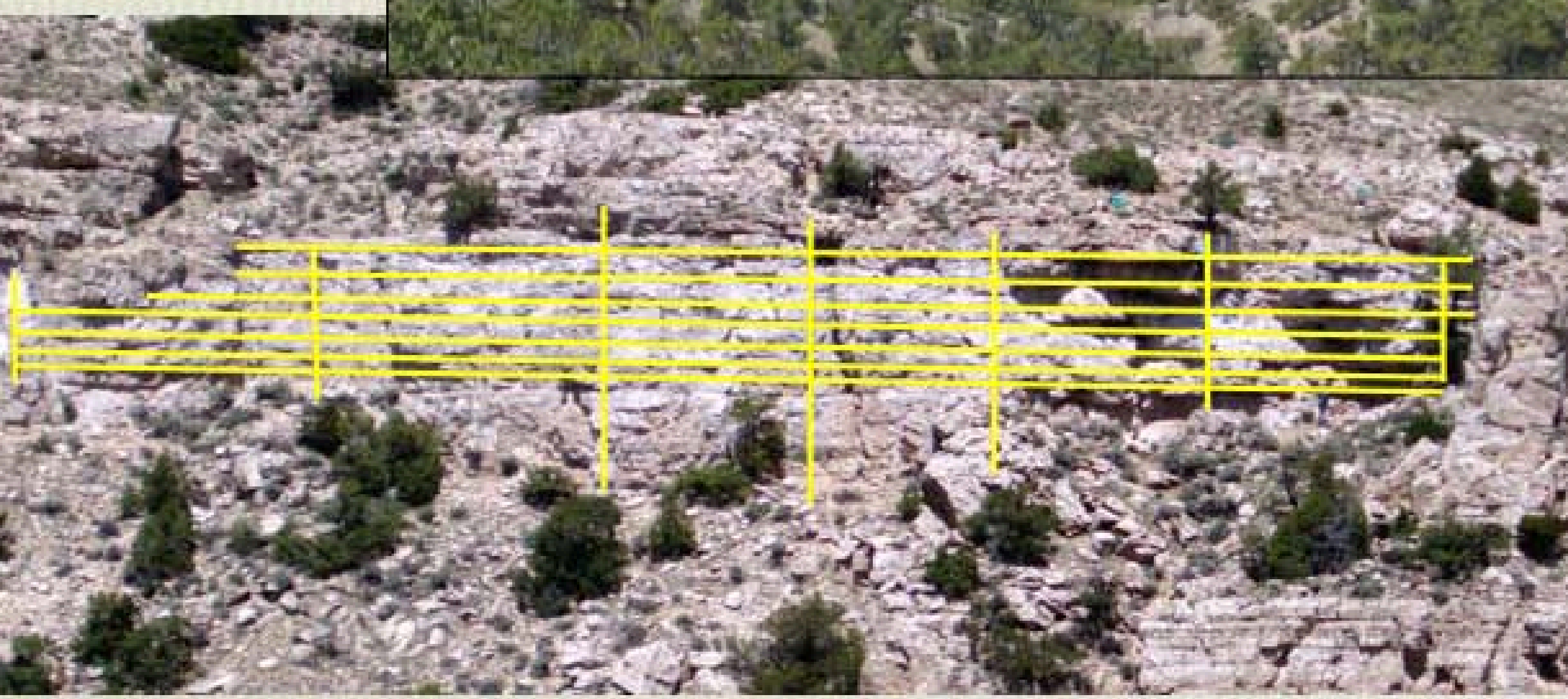
Mars



Terrestrial iron oxide concretions (A-C) with comparable images from Mars (D-F).
Terrestrial concretions shown are ~1-2 cm diameter. Mars concretions <0.5 cm diameter.

Dolomitization: 2D Pattern-Forming Process



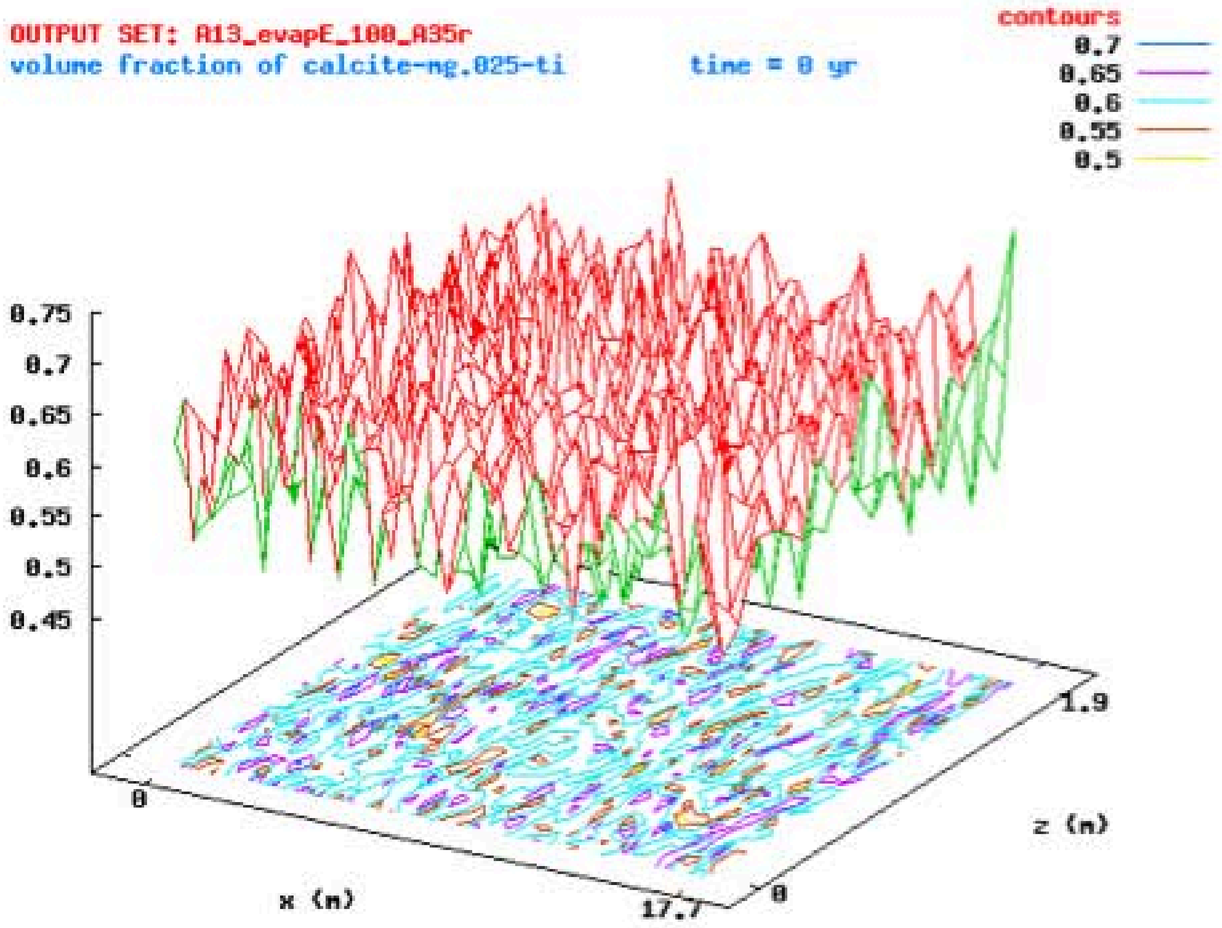


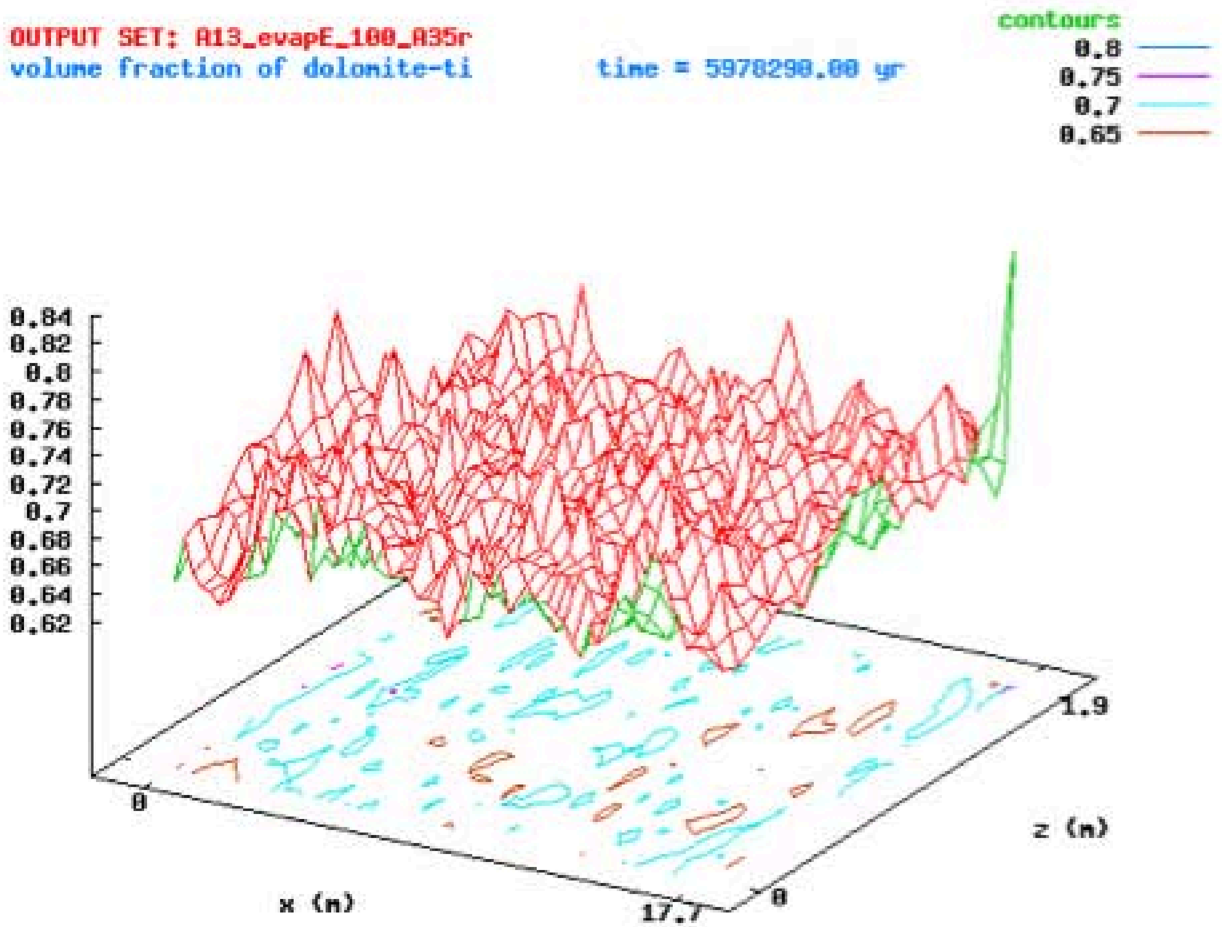
from AVID consortium report, Prof. David Budd, Univ. of Colorado Boulder

Geologic time-scale process

Takes millions of years to replace deposited carbonate mineral with dolomite

Influx of hypersaline water as the chemical driving force





Dolomitization

Initial calcite distribution pattern:

based on extensive and thorough field sampling study

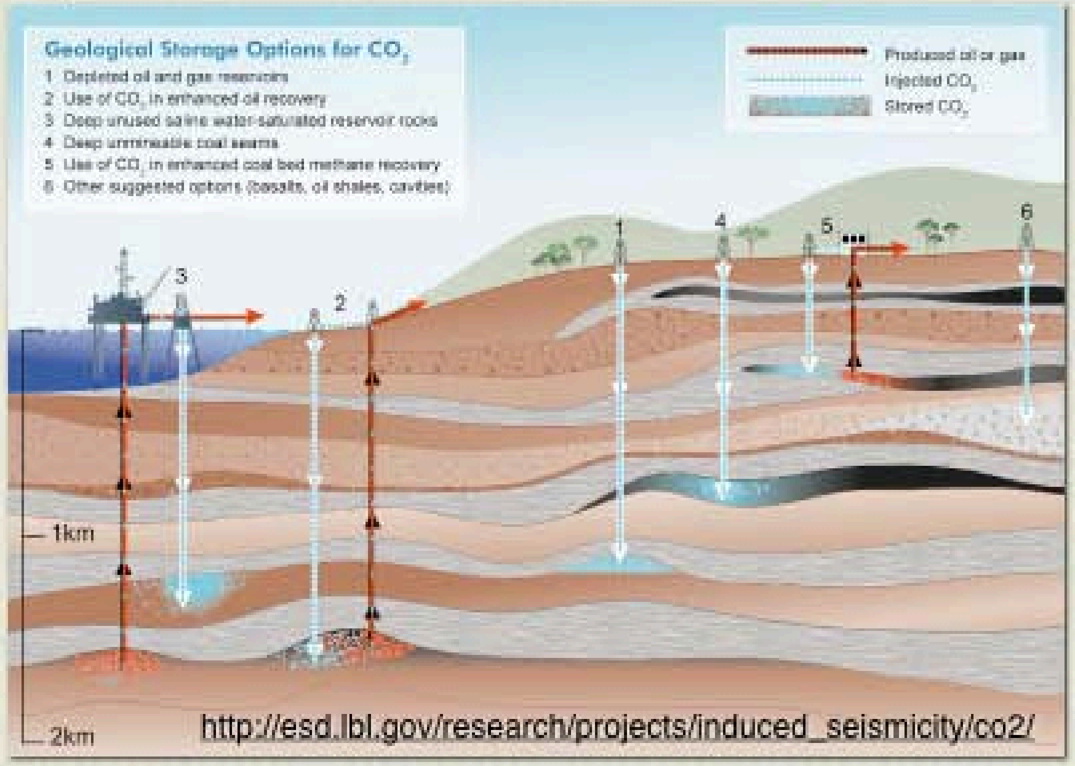
shows statistical normal calcite abundance variation of 60% +/- 15%

dolomite $CaMg(CO_3)_2$ replaces calcite ($CaCO_3$) when hypersaline water with high (but variable) Mg content enters the sediment

water flow rate of 1 m/yr approximated

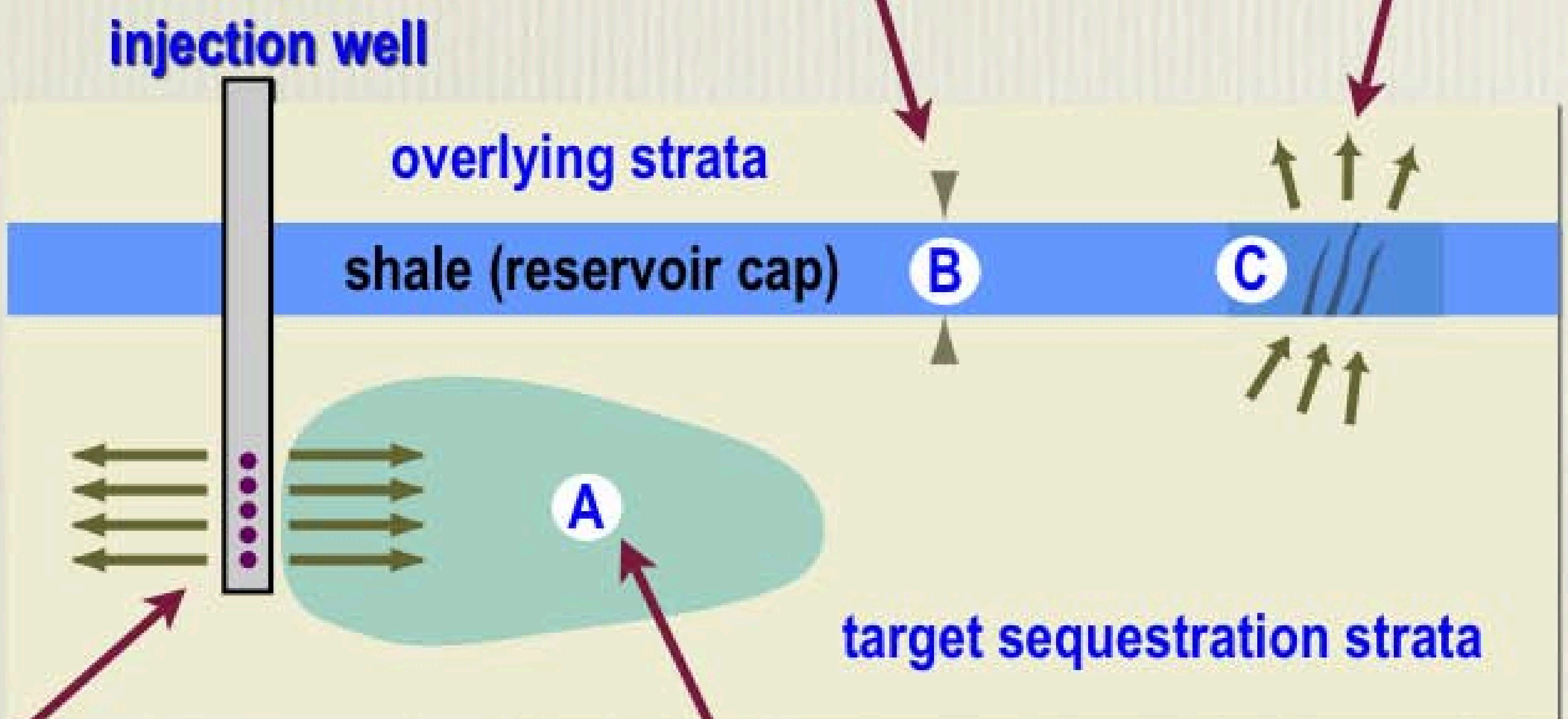
advection-reaction coupling produces a pattern of dolomite abundance that does not correlate with initial calcite abundance

Carbon Capture and Storage (CCS) Simulator



interaction of CO_2 with sediments
concern: alteration of the confining strata integrity

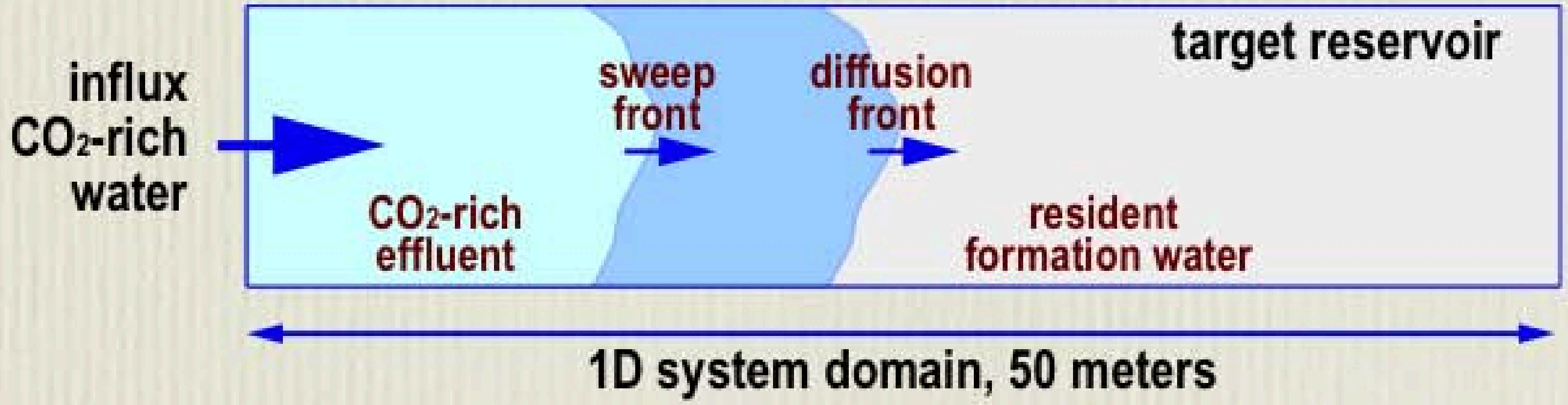
leakage through naturally occurring permeability paths (fracture network, interlayered high-perm sediments)

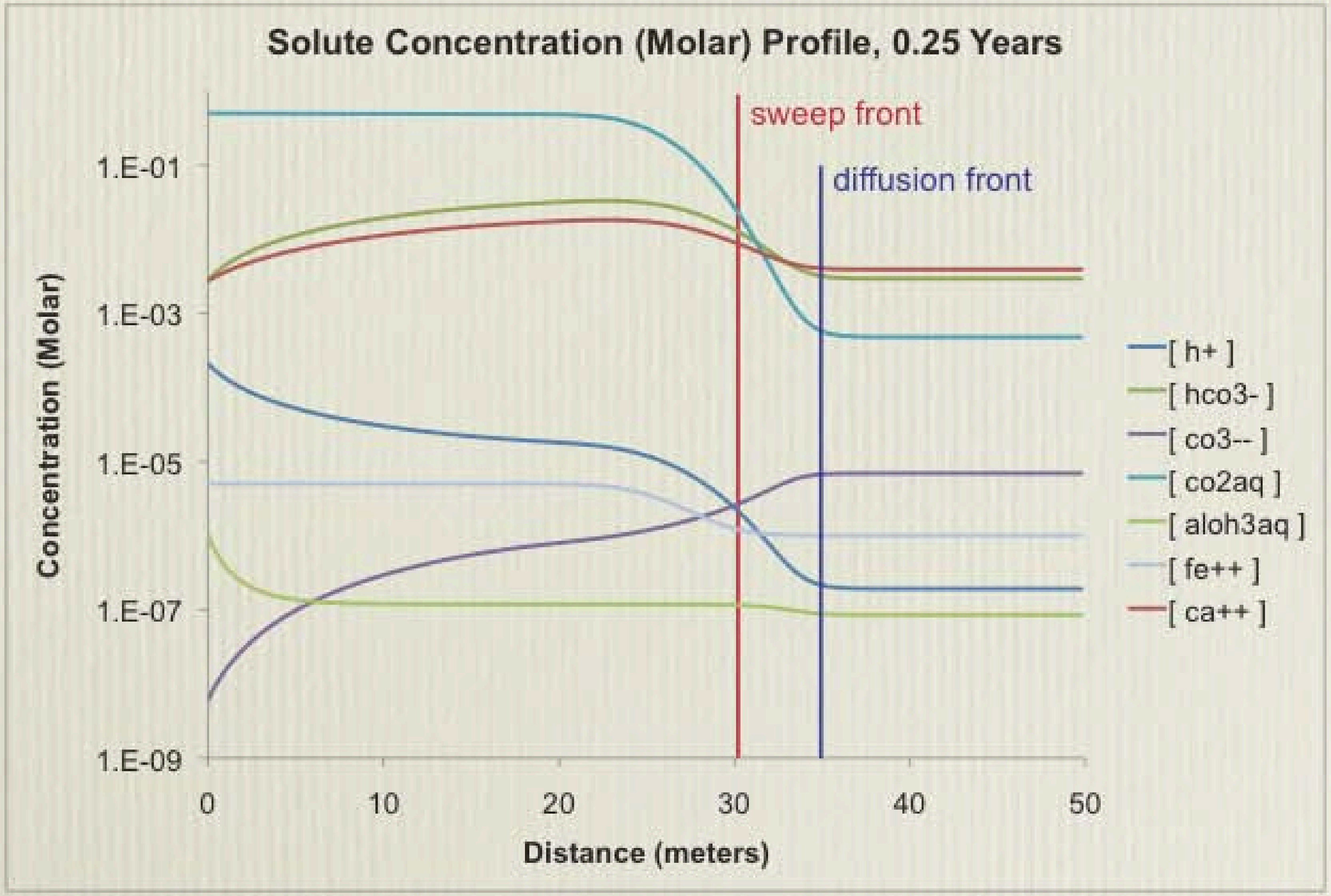


injection of super-critical CO_2

transition: super-critical to liquid form?
reaction-front instability: fingering, flow self-focusing

Preliminary CCS Simulation, 1D





Objective

characterize interaction between CO2-rich water and resident formation water and sediment

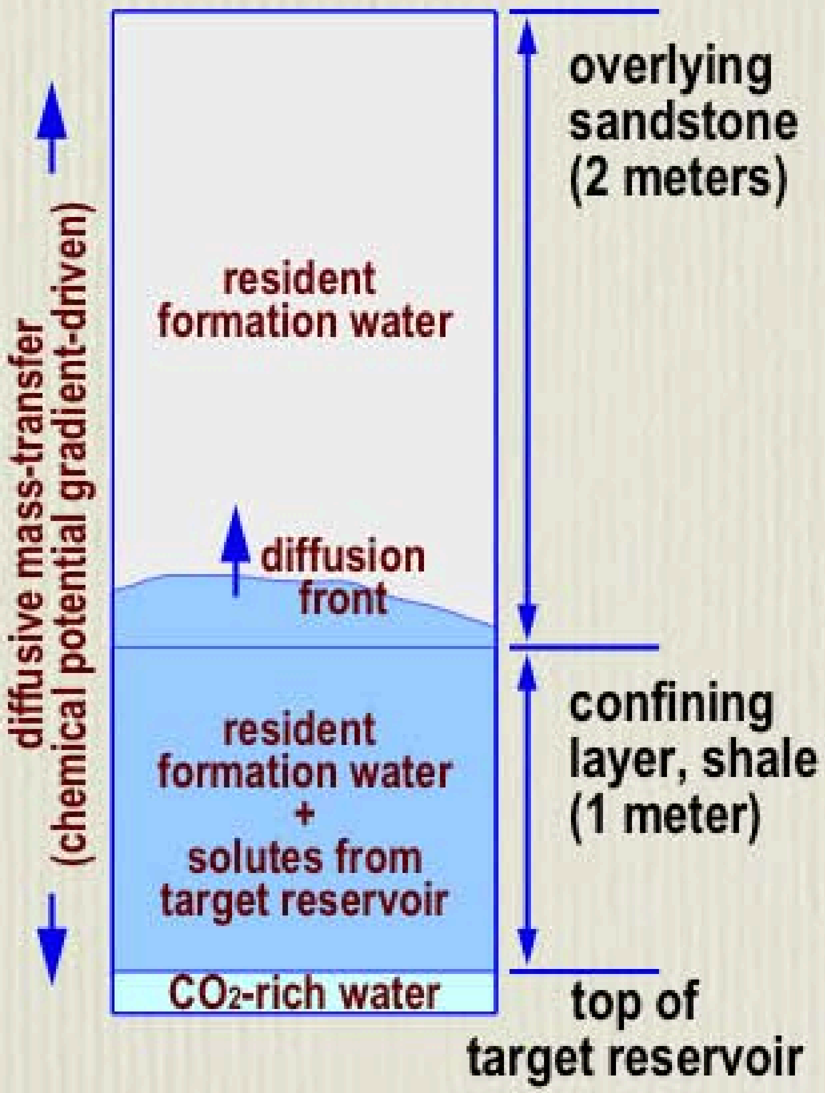
Finding

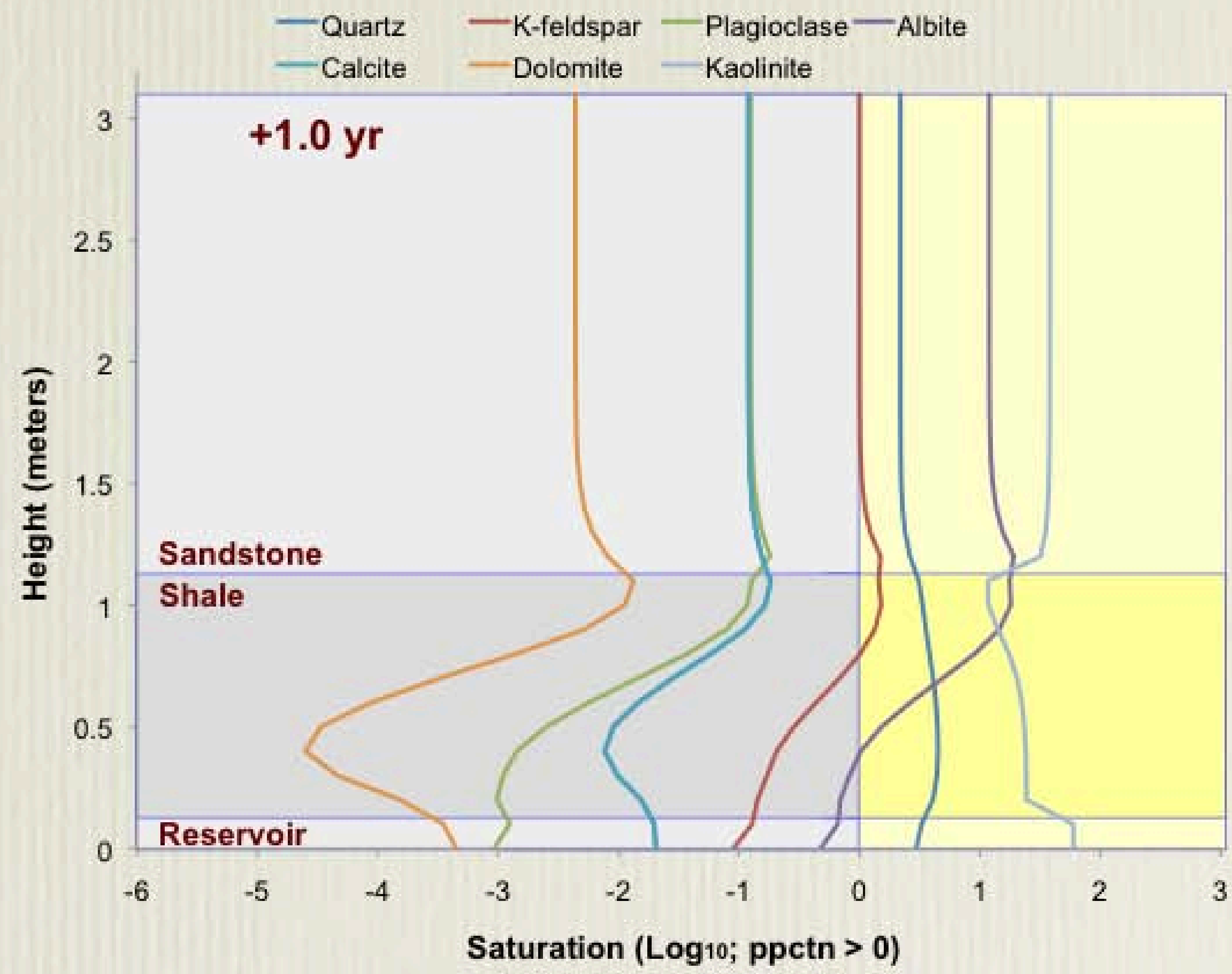
varying diffusivities of solutes result in formation of multiple fronts

diffusion front of H and bicarbonates preced the sweep front

extent of mineral alteration is minor, but suggest significant leakage of solutes through diffusion

Preliminary CCS Simulation, 1D





Total diffusive leakage of solutes through confining sediments may be significant

Important consequence of the alteration of the sediment property: mineral dissolution/precipitation may make the sediment more brittle or ductile

Result in formation of secondary reaction zones surrounding the target reservoir

Applications of Reactive-Transport Models

Characterize

Movement of reactive chemicals through sediments and rocks

Interaction among the chemicals, and with the resident material

Carbon Capture and Storage

Nuclear Waste Disposal Site Management

Contaminant Fate and Transport in Groundwater

Mine Tailing Assessment

Uranium Roll-Front Deposits

Reactive Permeability Barriers

Cellular/Biological Models

Petroleum Reservoir Characterization

And so on ...