

**University of Stuttgart** 

Institute for Modelling Hydraulic and Environmental Systems Department of Hydromechanics and Modelling of Hydrosystems



### What is the Scope of the Model?

Subsurface biogeochemical gold (Au) mobilization, transport, and precipitation



### **Reactions and Processes in the Simplified Model**



### **Model Scale and Primary Variables**

- Large spatial scales of interest in applications → modelling on REV scale using volume averaged quantities:
  - Mole fractions  $x_{w}^{\kappa}$  (mobile components)
  - Volume fractions  $\phi_{\lambda}$  (solids)



# Mass Balance Equations

$$\sum_{\alpha} \frac{\partial}{\partial t} \left( \phi \rho_{\alpha} x_{\alpha}^{\kappa} S_{\alpha} \right) + \nabla \cdot \left( \rho_{\alpha} x_{\alpha}^{\kappa} \mathbf{v}_{\alpha} \right) - \nabla \cdot \left( \rho_{\alpha} \mathbf{D}_{\alpha, \text{pm}}^{\kappa} \nabla x_{\alpha}^{\kappa} \right) = q^{\kappa}$$

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• Mass balance equation of components exclusively in the water phase:

$$\frac{\partial}{\partial t} \left( \phi \rho_{\mathbf{w}} x_{\mathbf{w}}^{\kappa} S_{\mathbf{w}} \right) + \nabla \cdot \left( \rho_{\mathbf{w}} x_{\mathbf{w}}^{\kappa} \mathbf{v}_{\mathbf{w}} \right) - \nabla \cdot \left( \rho_{\mathbf{w}} \mathbf{D}_{\mathbf{w}, \mathrm{pm}}^{\kappa} \nabla x_{\mathbf{w}}^{\kappa} \right) = q^{\kappa}$$

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• Mass balance for the immobile components / solid phases:

$$\frac{\partial}{\partial t} \left( \rho_{\lambda} \phi_{\lambda} \right) = q^{\lambda}$$

#### **Sources and Sinks: Reactions**





$$r_{\text{growth}}^{\text{bio}} = \mu \cdot \phi_{\text{bio}} \rho_{\text{bio}}$$
$$\mu = \mu_{\text{max}} \cdot \frac{C_{\text{w}}^{\text{substrate}}}{K_{\text{substrate}} C_{\text{w}}^{\text{substrate}}}$$

$$\begin{array}{lll} r_{\rm decay}^{\rm bio} &=& k_{\rm d} \cdot \phi_{\rm bio} \rho_{\rm bio} \\ k_{\rm d} &=& k_{\rm d,0} + k_{\rm d,Au} \left( c_{\rm w}^{\rm Au} - c_{\rm crit}^{\rm Au} \right) \end{array}$$

$$r_{\text{Substrate}} = rac{r_{\text{growth}}^{\text{diss,bio}} + r_{\text{growth}}^{\text{prec,bio}}}{Y_{ ext{bio,substrate}} M_{ ext{substrate}}}$$



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$$r_{\rm CN} = Y_{\rm CN} r_{\rm growth}^{\rm diss,bio}$$

$$r_{\rm Citrate} = Y_{\rm Citrate} r_{\rm growth}^{\rm diss,bio}$$

# **Gold Dissolution and Precipitation**



$$r_{\rm diss}^{\rm Au_{\rm large}} = k_{\rm diss} c^{\rm Mn^{\rm III/IV}} A_{\rm Au_{\rm large}} \phi_{\rm Au_{\rm large}} c_{\rm w}^{\rm CN}$$
$$r_{\rm diss}^{\rm Au_{\rm NP}} = k_{\rm diss} c^{\rm Mn^{\rm III/IV}} A_{\rm Au_{\rm NP}} \phi_{\rm Au_{\rm NP}} c_{\rm w}^{\rm CN}$$

# **Gold Dissolution and Precipitation**



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$$r_{\rm diss}^{\rm Au_{NP}} = k_{\rm diss} c^{\rm Mn^{III/IV}} A_{\rm Au_{NP}} \phi_{\rm Au_{NP}} c_{\rm w}^{\rm CN}$$

$$r_{\rm prec} = k_{\rm prec}^{\rm bio} \phi_{\rm prec, bio} c_{\rm w}^{\rm Au_{complex}}$$

$$+ k_{\rm prec}^{\rm clay} \rho_{\rm soil} (1 - \phi_0) R_{\rm soil}^{\rm clay} c_{\rm w}^{\rm Au_{complex}}$$

$$+ k_{\rm prec}^{\rm OM} \rho_{\rm soil} (1 - \phi_0) R_{\rm soil}^{\rm CM} c_{\rm w}^{\rm Au_{complex}}$$



Gold NP Mobility and Aggregation

$$r_{\rm d,NP} = k_{\rm d,NP} c_{\rm w}^{\rm Citrate} \phi_{\rm Au_{NP}}$$

$$r_{\mathrm{a,NP}} = +k_{\mathrm{a,NP}}^{\mathrm{clay}}\rho_{\mathrm{soil}}\left(1-\phi_{0}\right)R_{\mathrm{soil}}^{\mathrm{clay}}c_{\mathrm{w}}^{\mathrm{Au_{NP}}} \\ +k_{\mathrm{a,NP}}^{\mathrm{OM}}\rho_{\mathrm{soil}}\left(1-\phi_{0}\right)R_{\mathrm{soil}}^{\mathrm{CM}}c_{\mathrm{w}}^{\mathrm{Au_{NP}}}$$



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$$r_{\rm agg} = k_{\rm agg} \rho_{\rm mol,Au} \phi_{\rm Au,NP}$$

### **Test Setup**

- Bronze Age settlement in Bavaria: Gold artifacts real or fake?
- Boundary and initial conditions relatively well known



no flow

sides: Dirichlet BC = initial conditions, no gold species or substrate







### **Conclusions and Outlook**

• The developed model qualitatively reproduces expected behaviour.



• Future work: Calibrate and validate the model using a variety of experiments at different scales

 $\rightarrow$  Combined modeling and experimental investigations will improve the model, the experiments and the understanding of gold cycling



## Thank you!







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