Calcium Carbonate Minerals:
Scavengers of metals and radionuclides

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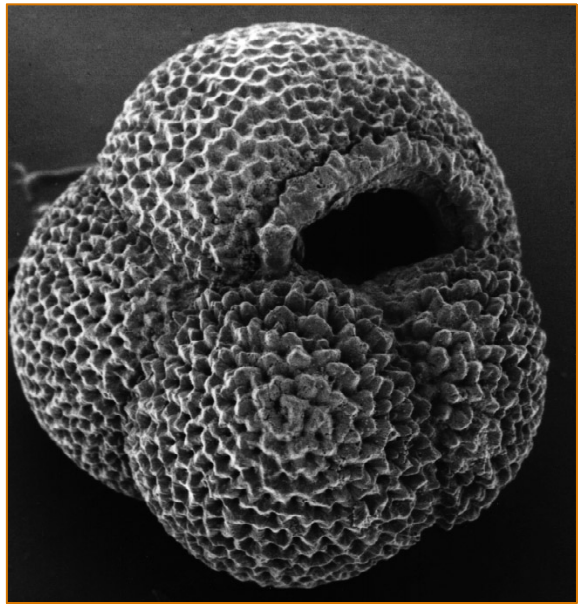
Calcium carbonate minerals

Abundance and Importance

- Limestone (mainly calcite) and sedimentary/metamorphic rocks (mainly dolomite) are exposed at about 20% of Earth surface
- Calcium carbonate minerals make up 4% of the Earth's crust
- In decreasing order of importance: calcite, dolomite, magnesium calcites, aragonite, and magnesite (Langmuir, 1997)

By Barry Deakin; https://commons.wikimedia.org/wiki/File:Limestone_cliffs_-_geograph.org.uk_-_1014071.jpg



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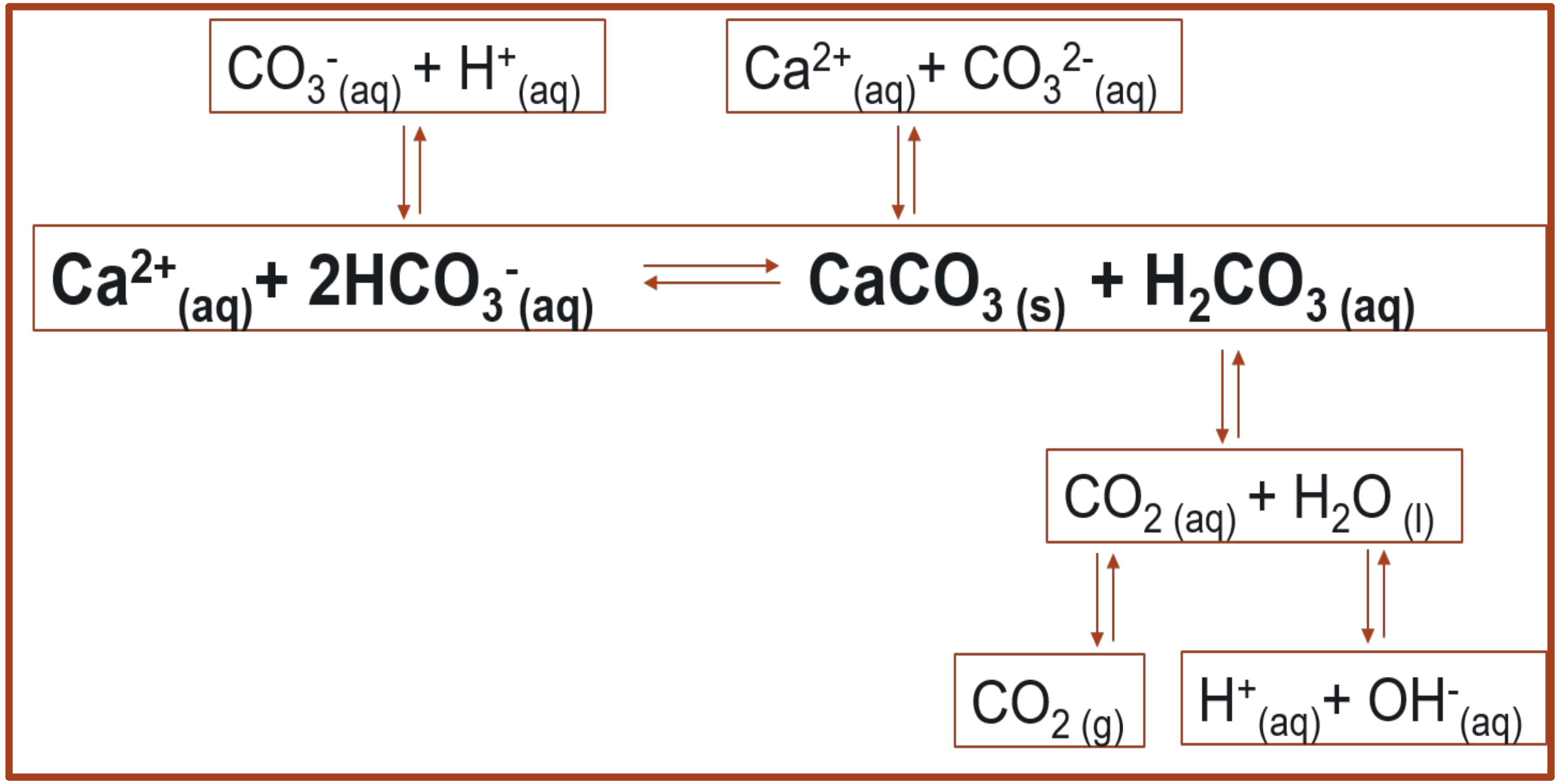
Calcium carbonate precipitation



$CO_3^-{}_{(aq)} + H^+{}_{(aq)}$

$Ca^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)}$

$Ca^{2+}{}_{(aq)} + 2HCO_3^-{}_{(aq)} \rightleftharpoons CaCO_{3\,(s)} + H_2CO_{3\,(aq)}$

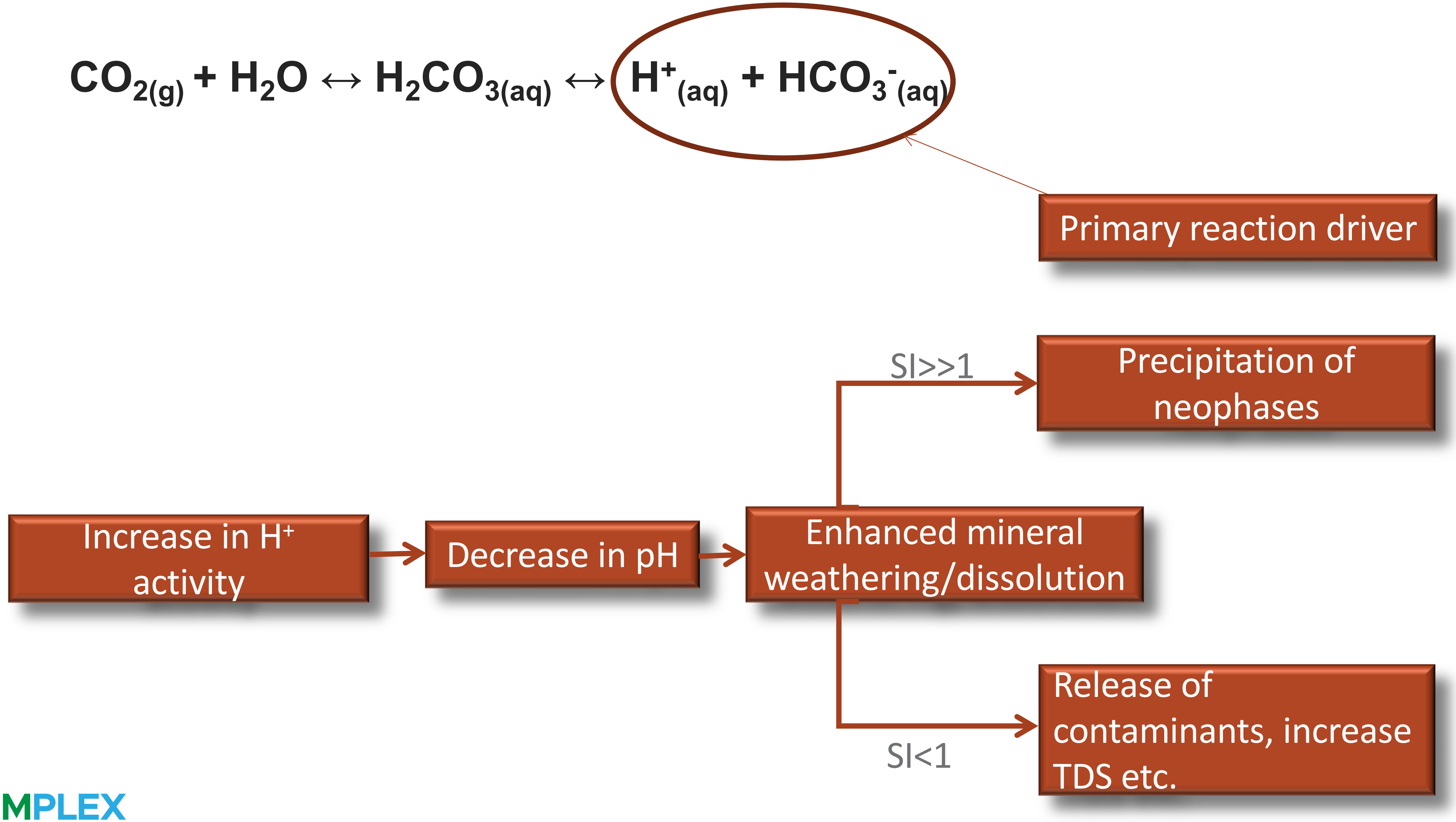
$CO_{2\,(aq)} + H_2O_{(l)}$

$CO_{2\,(g)}$

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

- Formation of $CaCO_3$ minerals
- Participating aqueous species
- Controlling chemical reactions (involving gas, aqueous and solid species)
- “The interface between minerals and aqueous solutions hosts globally important biogeochemical processes such as the growth and dissolution of carbonate minerals” (Laanait et al., 2015).

Strong buffers against pH changes



$$CO_{2(g)} + H_2O \leftrightarrow H_2CO_{3(aq)} \leftrightarrow H^+_{(aq)} + HCO_3^-{}_{(aq)}$$

Primary reaction driver

Increase in H^+ activity

Decrease in pH

Enhanced mineral weathering/dissolution

SI>>1

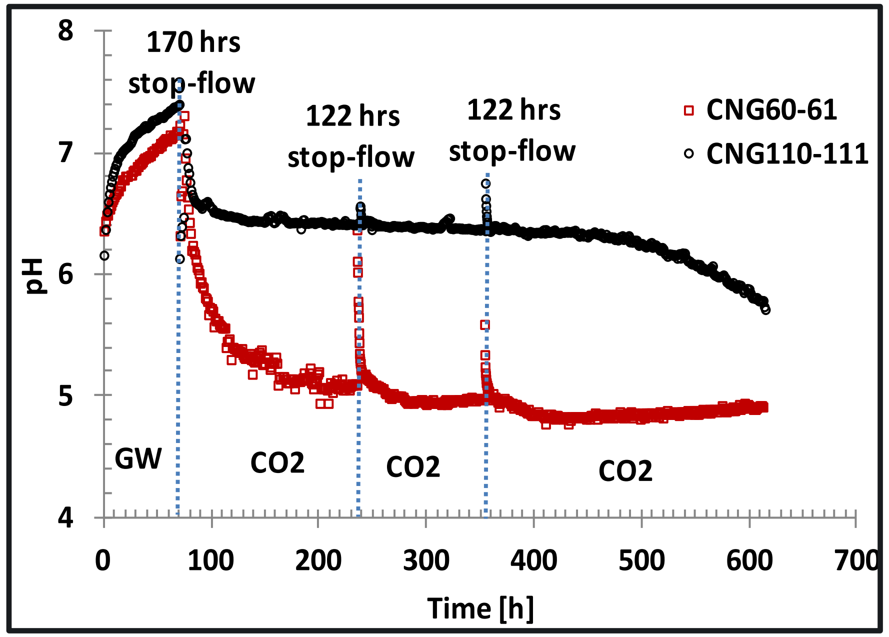
Precipitation of neophases

SI<1

Release of contaminants, increase TDS etc.

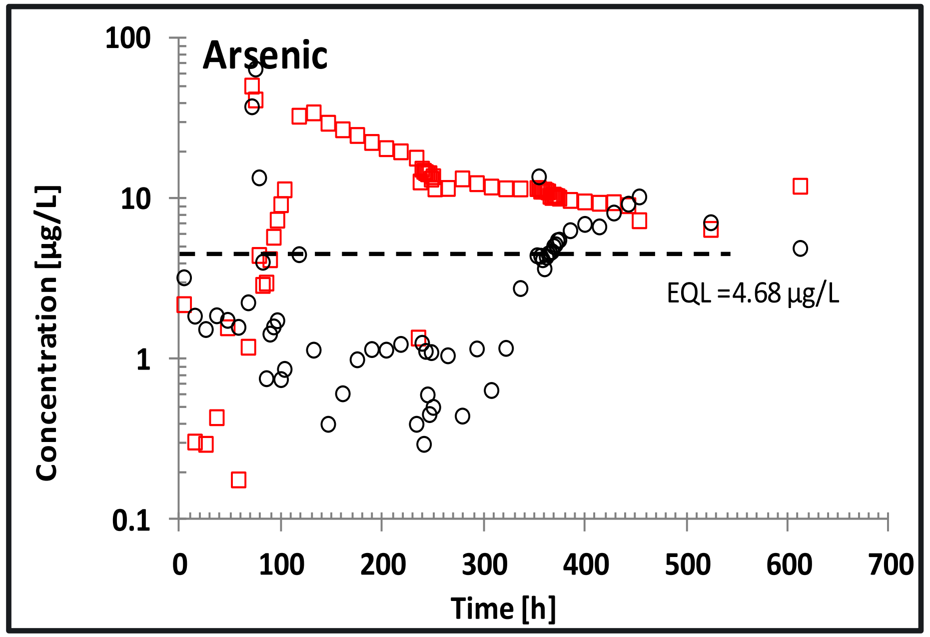
Harvey et al., 2013

Strong buffers against pH Changes



CNG 60
(No calcite)

CNG 110
(calcite)

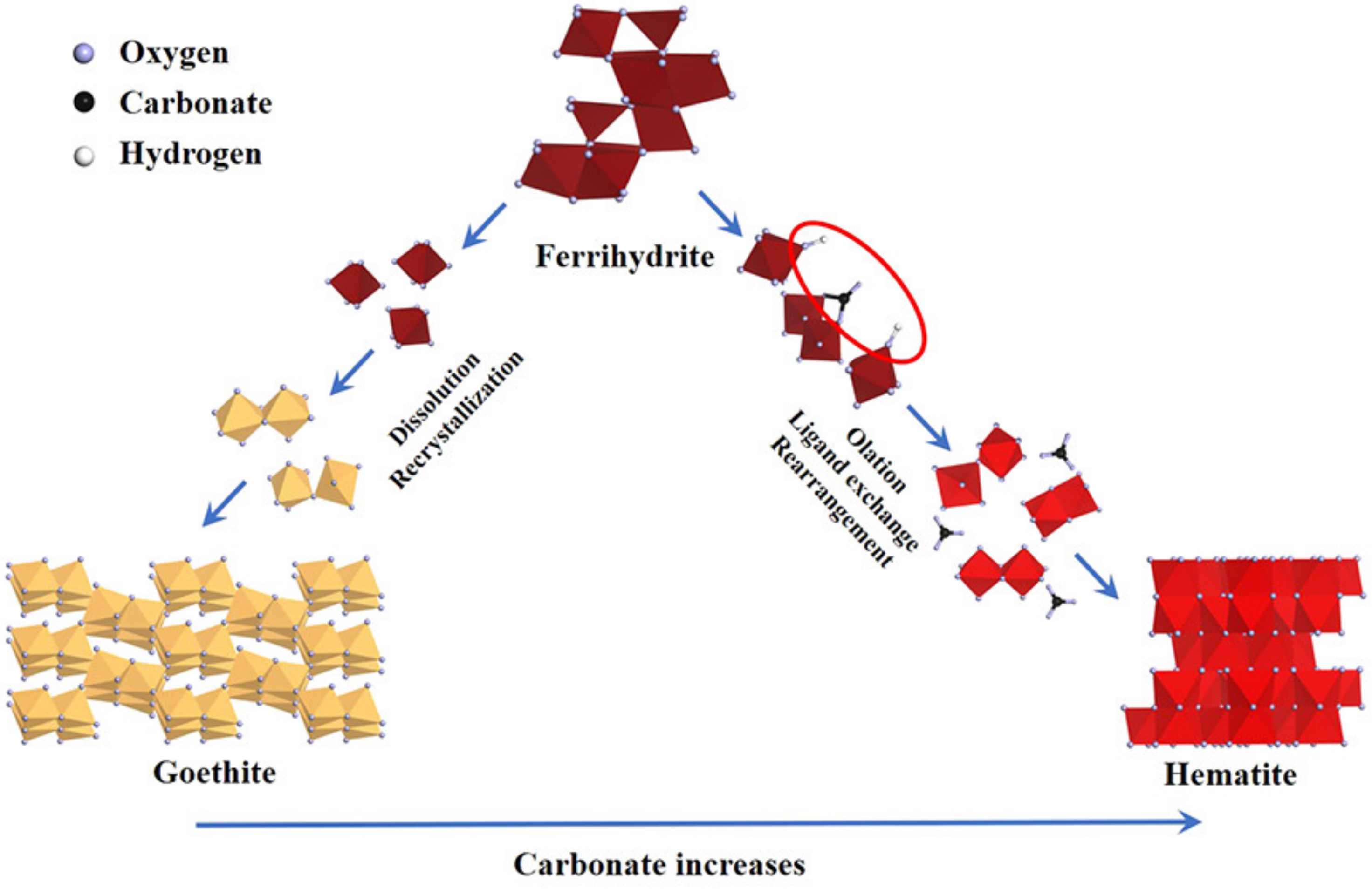


- **Well: CNG**
- **Depth: 60’ and 110’**
- **SGW: Kansas High Plains**
- **Gas: CO_2**
- **As MCL = 10 µg/L**

Lawter et al., 2016

Effects on Fe mineralogy

- Elevated carbonate/bicarbonate activity
- (Bi)carbonate ions promoted transformation of ferrihydrite to hematite
- Retarded goethite formation
- Strong control over Fe phase transformations/Fe cycling in oxic environments



Li et al., 2020

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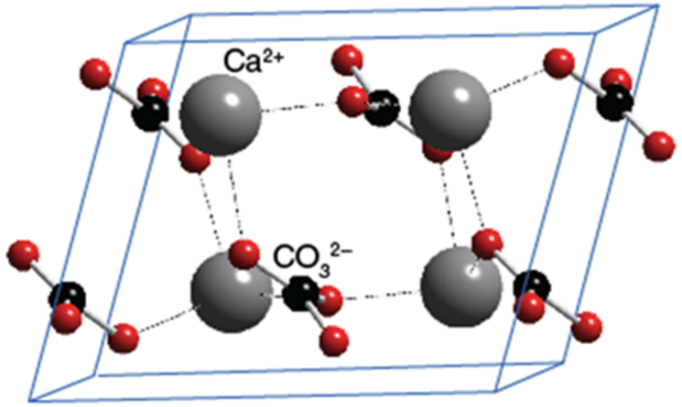
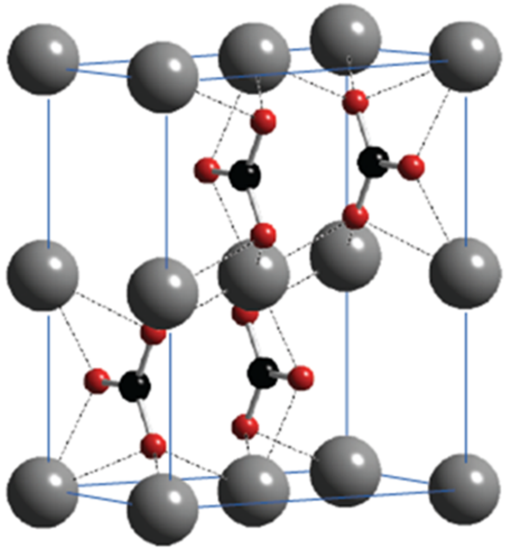
Calcium carbonate polymorphs

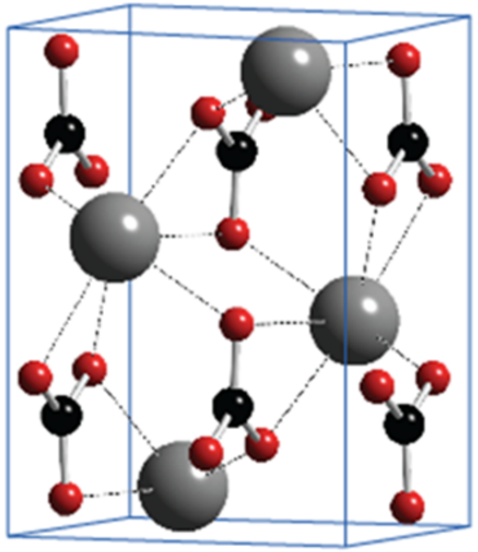
$CaCO_3$ Polymorph	Stability	Crystal Structure
Calcite	Stable at atm	rhombohedral
Vaterite	Metastable	hexagonal
Aragonite	Stable at high pressure	orthorhombic



Calcite



Vaterite

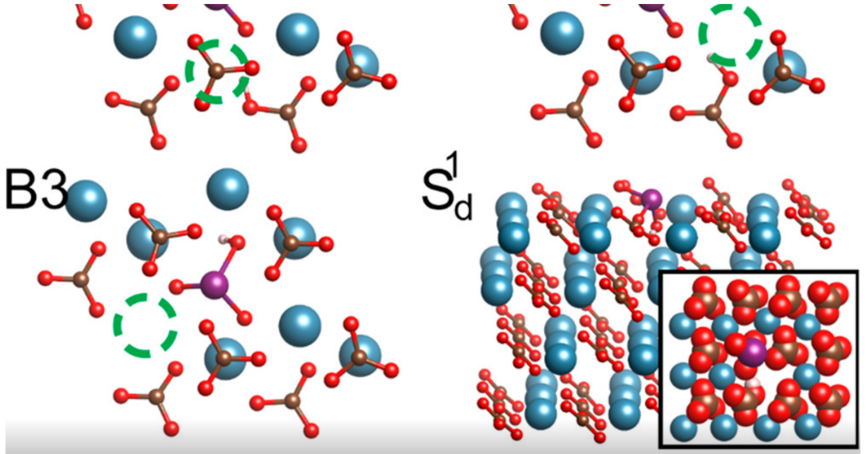


Aragonite

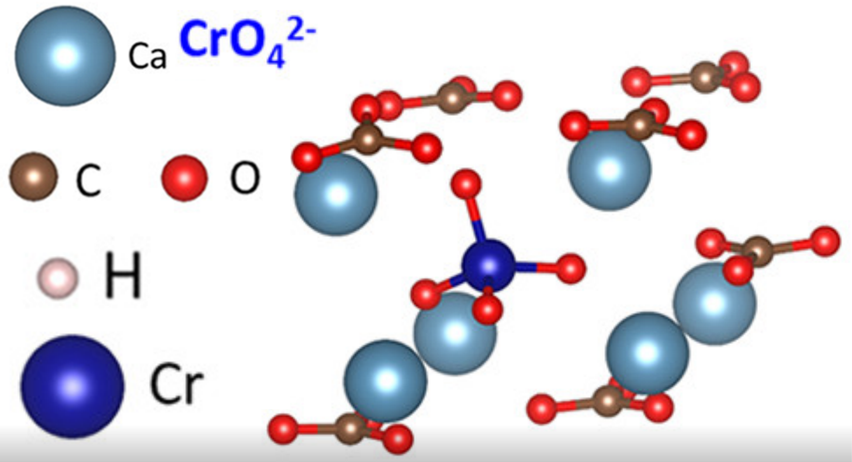
https://www.chemtube3d.com/ss-caco3/

Calcium carbonates

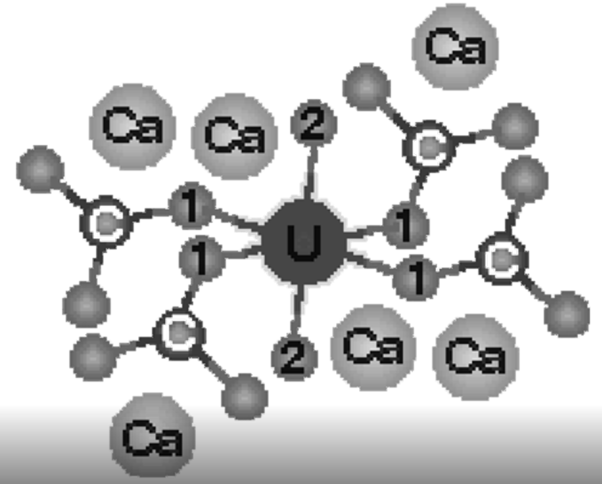
Hosts of Radionuclides, Metals, Metalloids



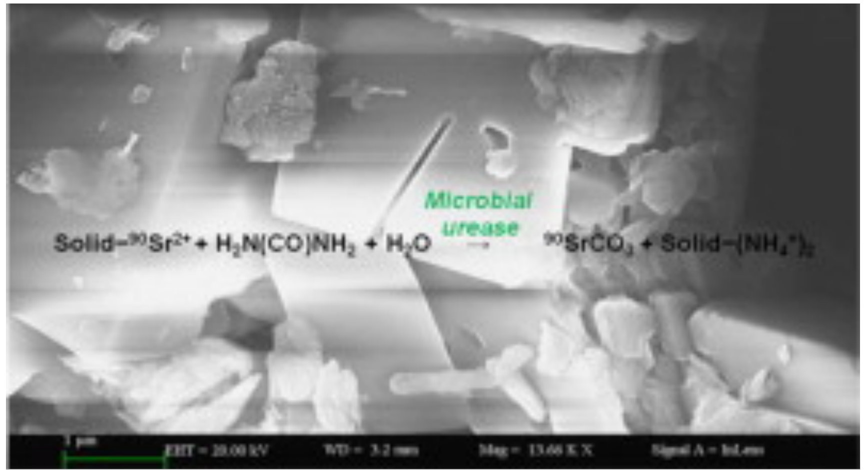
Iodine (Kerisit et al., 2018)



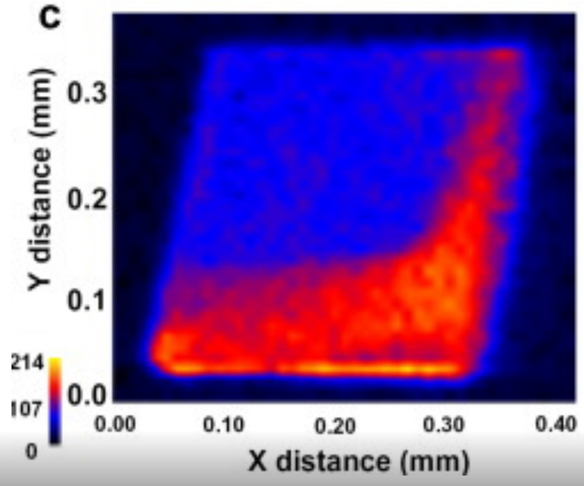
Chromium (Saslow et al., 2019)



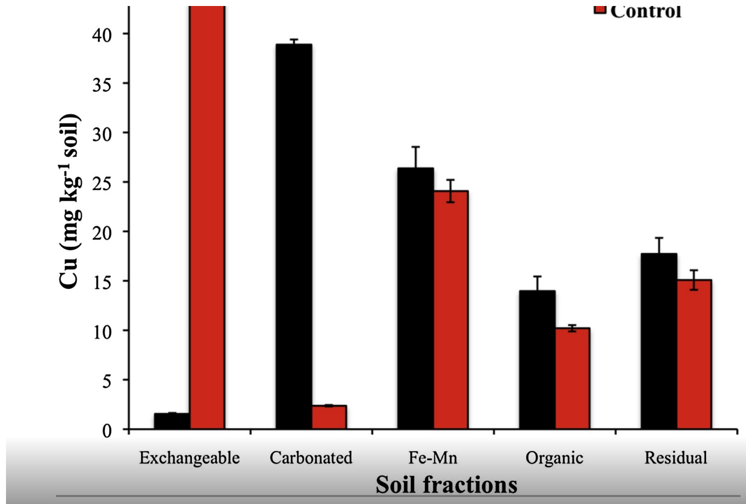
Uranium (Kelly et al., 2003)



Strontium (Achal et al., 2012)



Arsenic (Alexandratos et al., 2007)

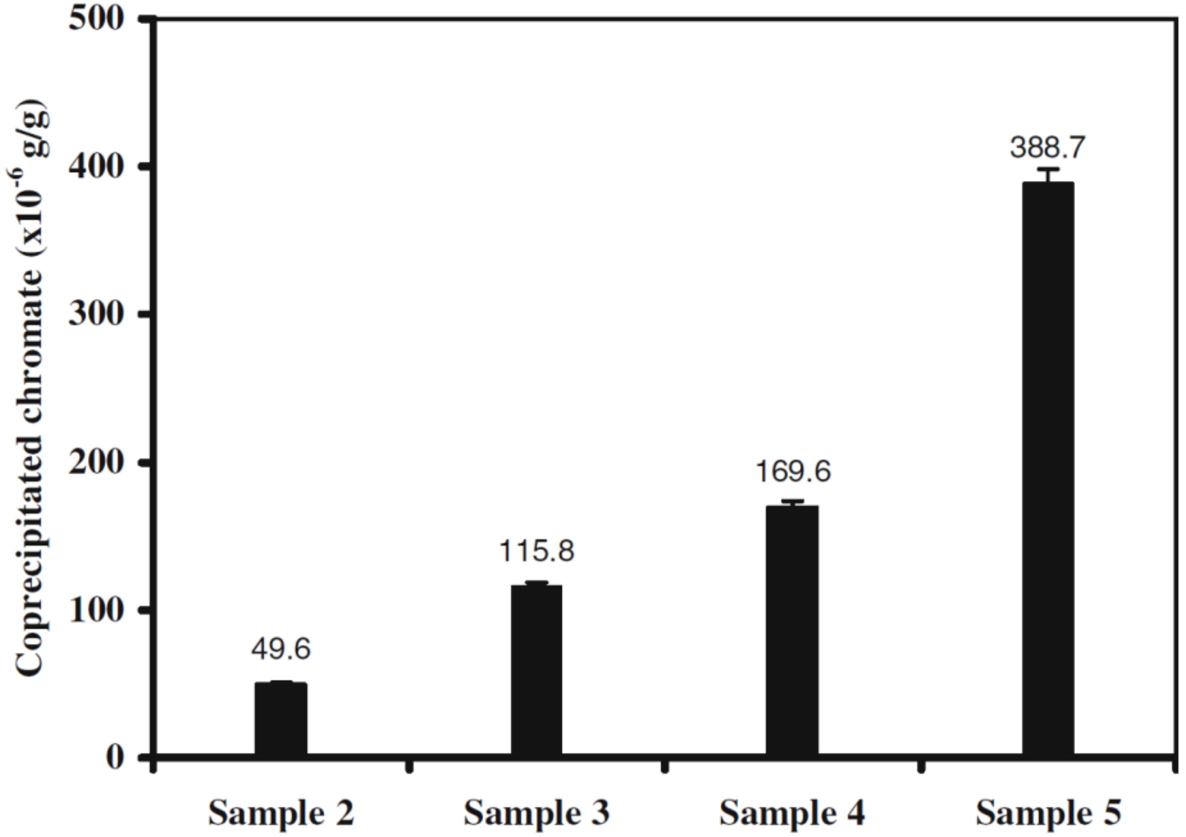


Copper (Chen et al., 2019)

Incorporation into $CaCO_3$: Chromium

- Found in naturally occurring carbonates as well as lab studies
- Positive correlation between Cr concentration in solution and Cr uptake
- CrO_4^{2-} substitutes for CO_3^{2-}

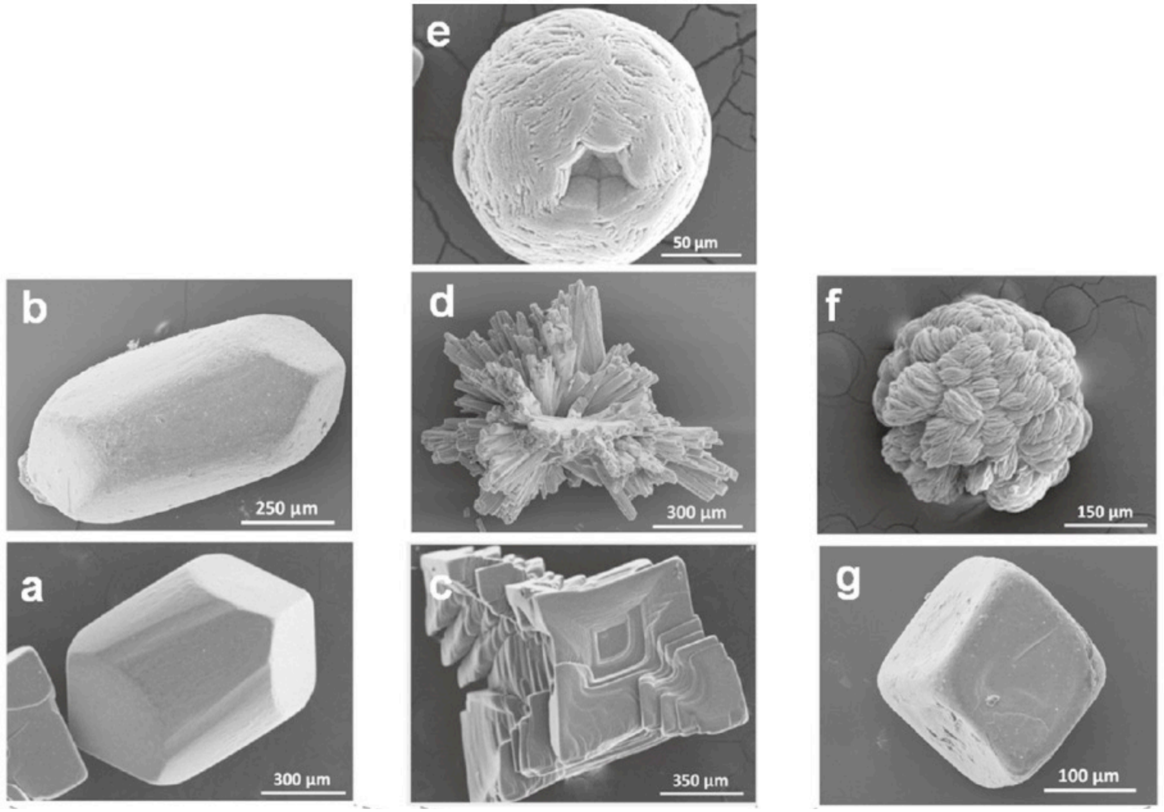
Modified from Hua et al., 2007



Increasing initial Cr concentration

Cr in $CaCO_3$: effect on crystal growth

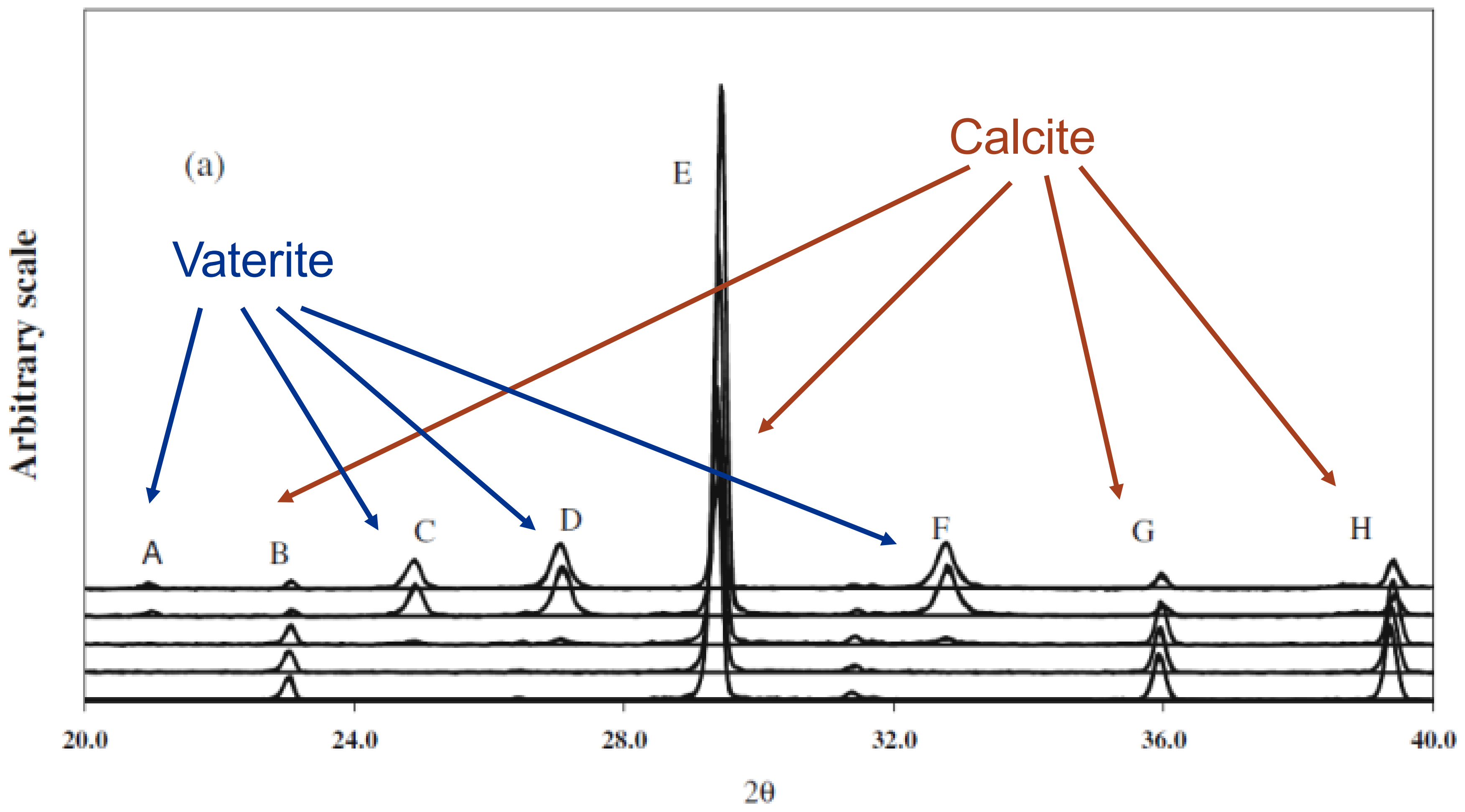
- Incorporation of Cr changes nucleation density, size, and the ratio of precipitating polymorphs
  - Up to 50% size reduction with Cr(VI) present
  - Results in enrichment of heavy Cr isotopes in the solid vs. solution
- Increasing Cr concentrations results in increased vaterite to calcite ratios; promotes aragonite formation



Sánchez-Pastor et al., 2011

Cr in $CaCO_3$: calcite polymorphs

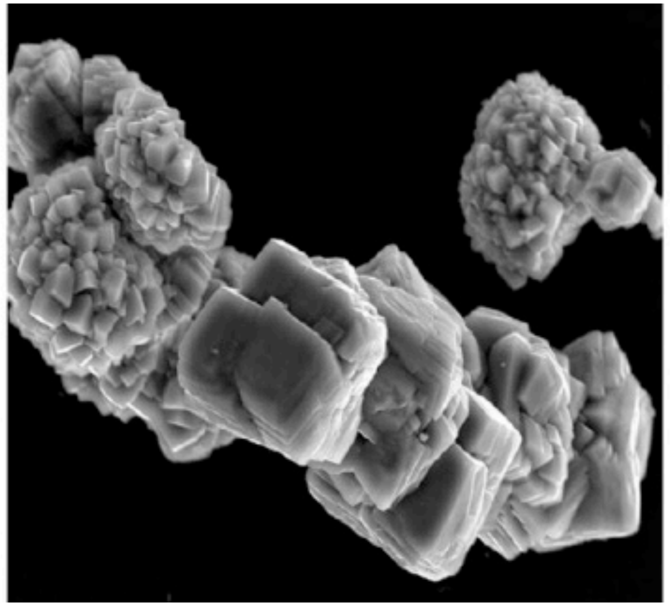
- Cr(VI) doped $CaCO_3$ experiments showed increased amounts of vaterite and aragonite
- Presence of Cr in the $CaCO_3$ can delay or prevent transformation to calcite

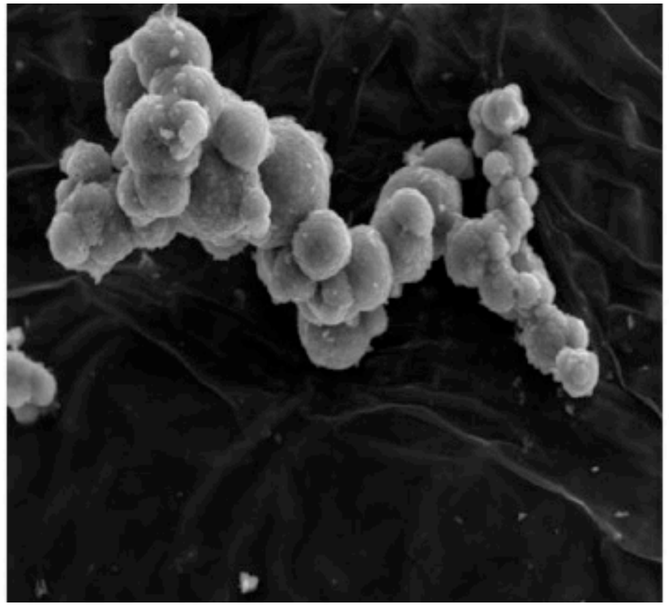


Modified from Hua et al., 2007

Cr in $CaCO_3$: calcite polymorphs

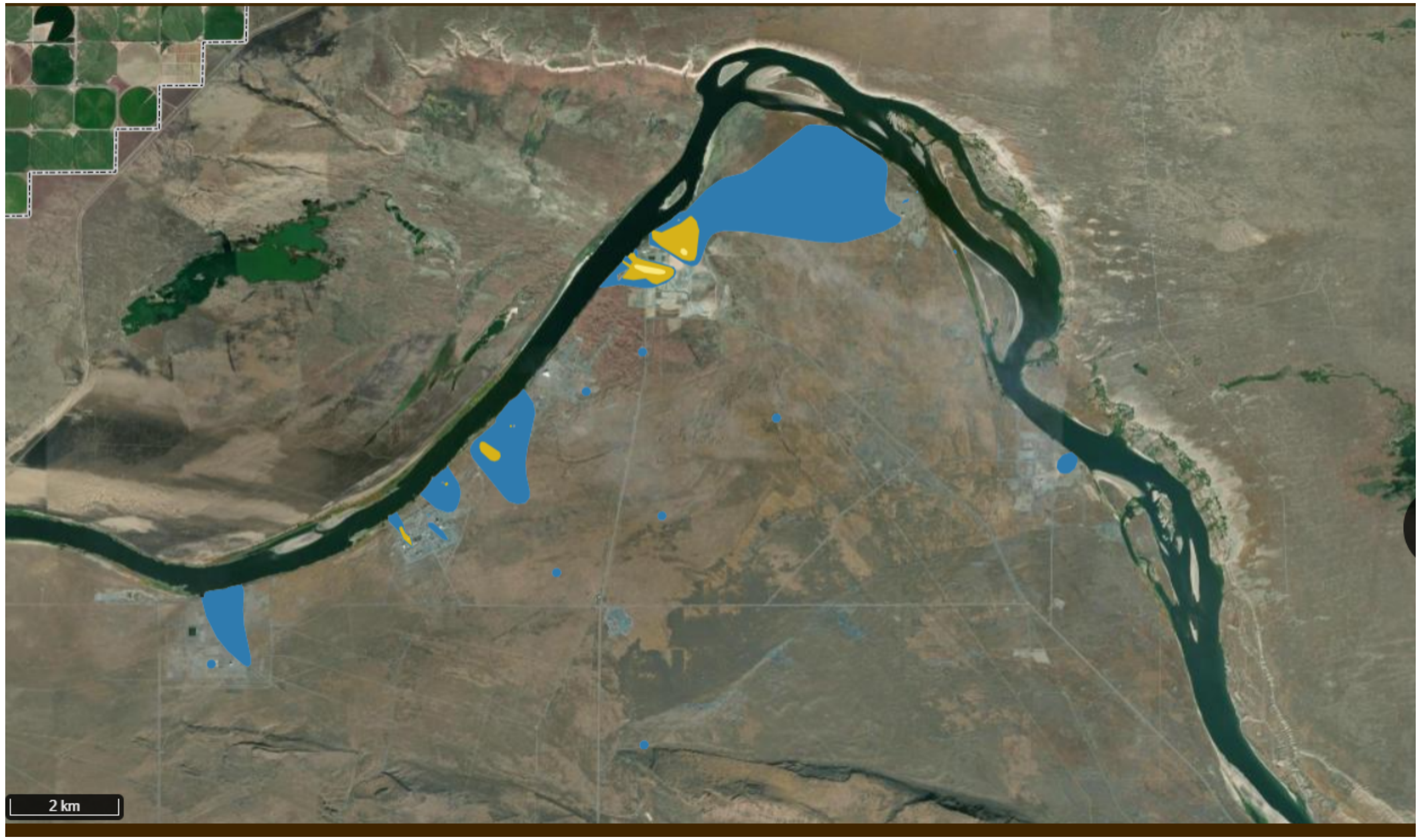
- As previous studies showed, vaterite was more likely to form in these studies than calcite
  - Calcite from 0 Cr test (left); vaterite from 100 ppm Cr(VI) test (right)





Chromium contamination at Hanford

- Chromium was used as an anti-corrosive in coolant water
  - Cr contamination is found around the reactor sites
- Cr(VI) plumes as of 2008
  - *phoenix.pnnl.gov*



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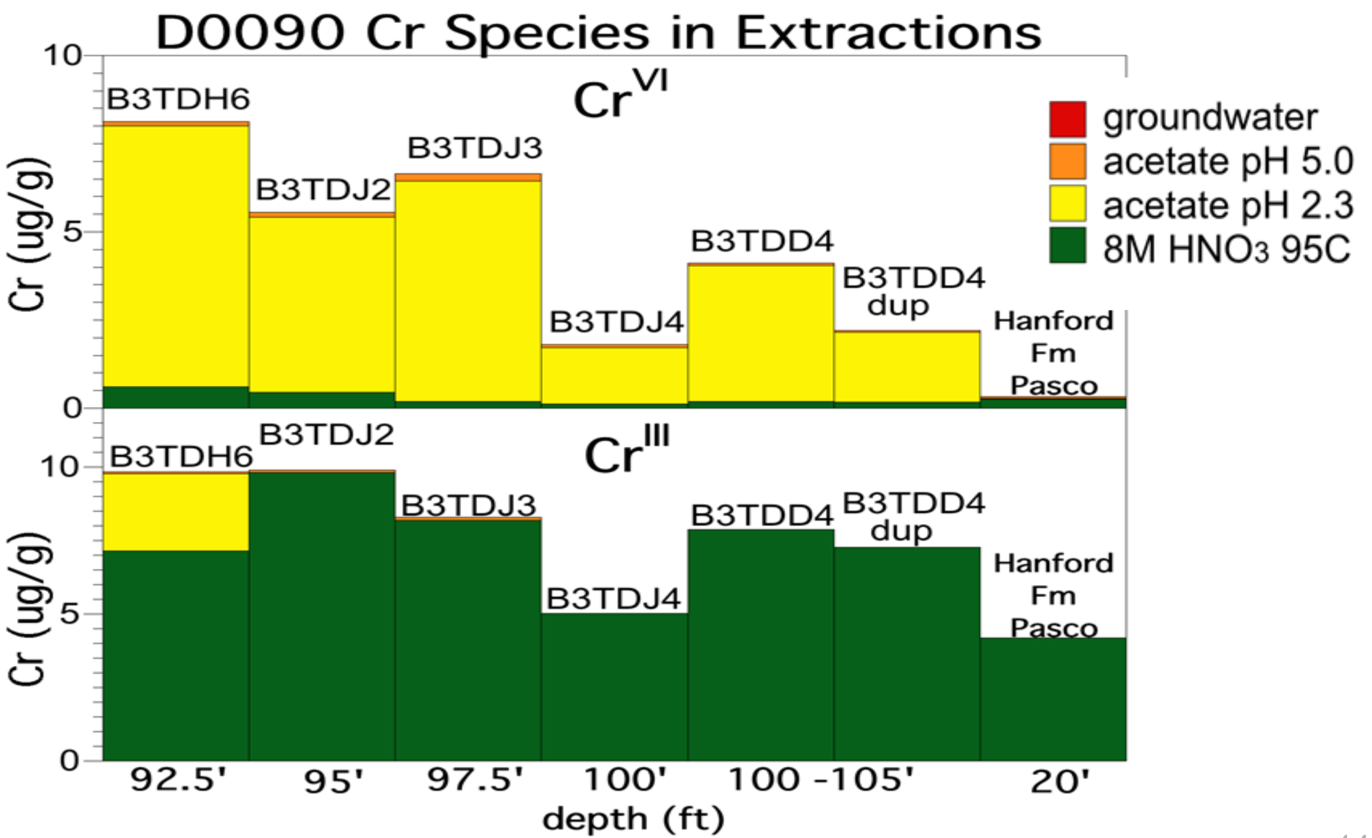
Chromium and $CaCO_3$ at Hanford

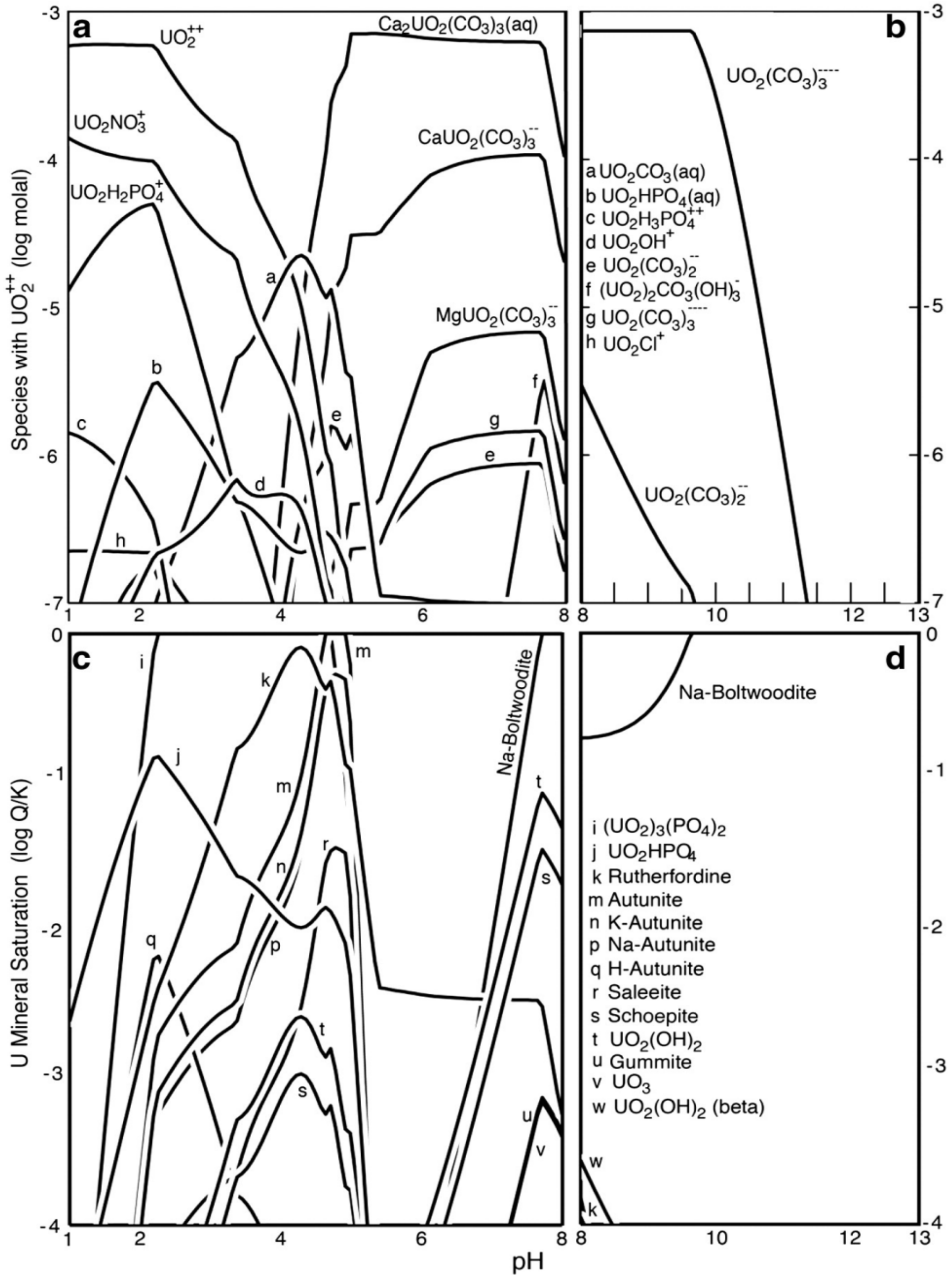
- Cr(VI) association with calcium carbonates has been shown through sediment characterization
- Mobile Cr is mostly Cr(VI) and anthropogenic
  - Pasco sediment shows natural Cr)
- Cr(VI) is mostly associated with highly soluble carbonates and/or Fe-oxides (yellow)

Truex et al., 2015
Szecsody et al., 2019
Szecsody et al., 2020

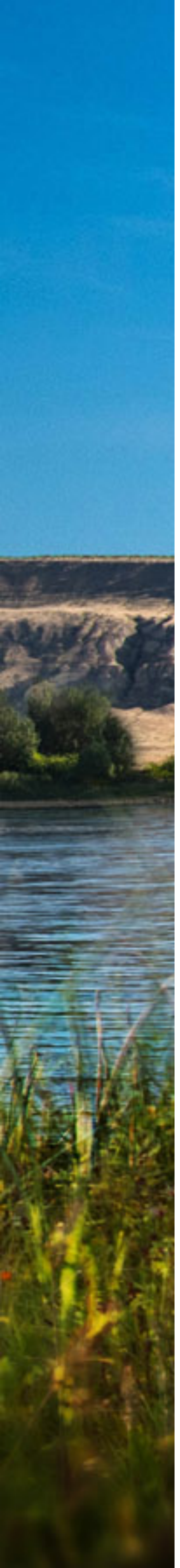


Calcium carbonates interaction with uranium

- Important contaminant
    - In many natural environments and contaminated sites around the globe
- Both U(VI) and U(IV) can be incorporated into calcite
- Two main mechanisms: adsorption or co-precipitation
    - Other relevant (calcium carbonate mediated) reactions
        - ✓Facilitate sequestration of aqueous U
        - ✓Hinder U interactions with minerals
- Complex aqueous and solid phase speciation



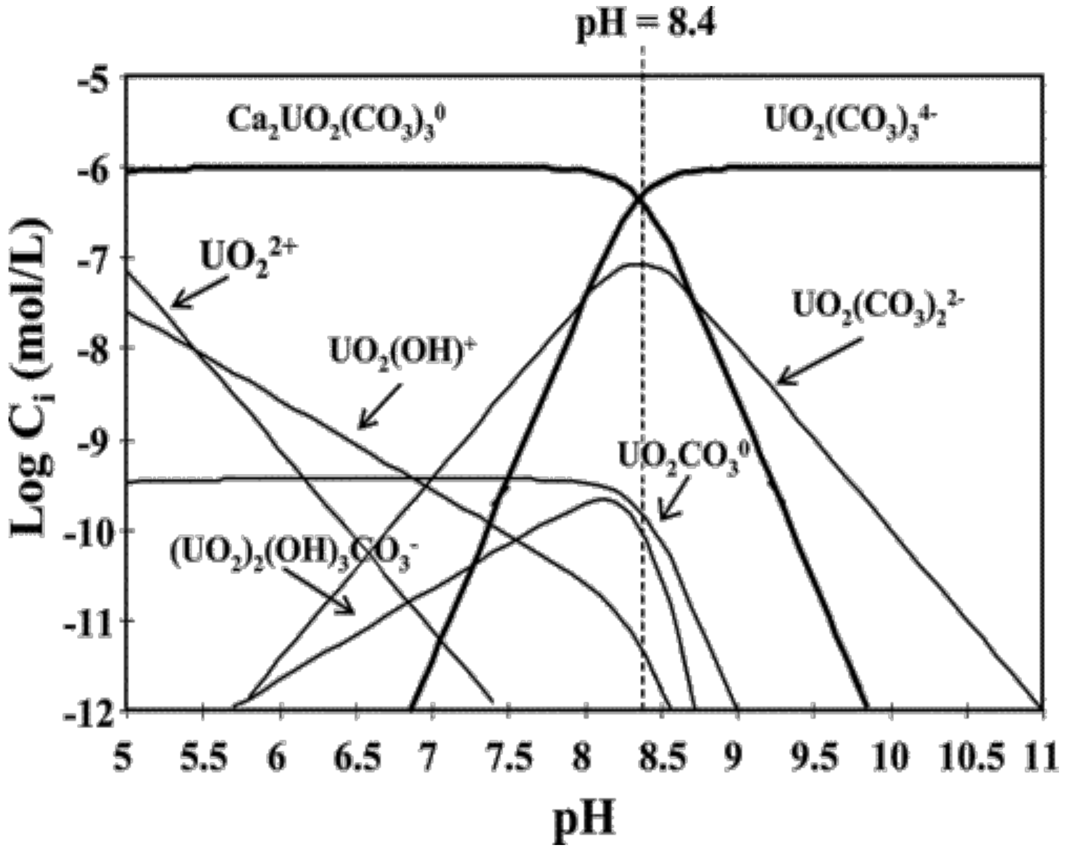
Szecsody et al., 2013

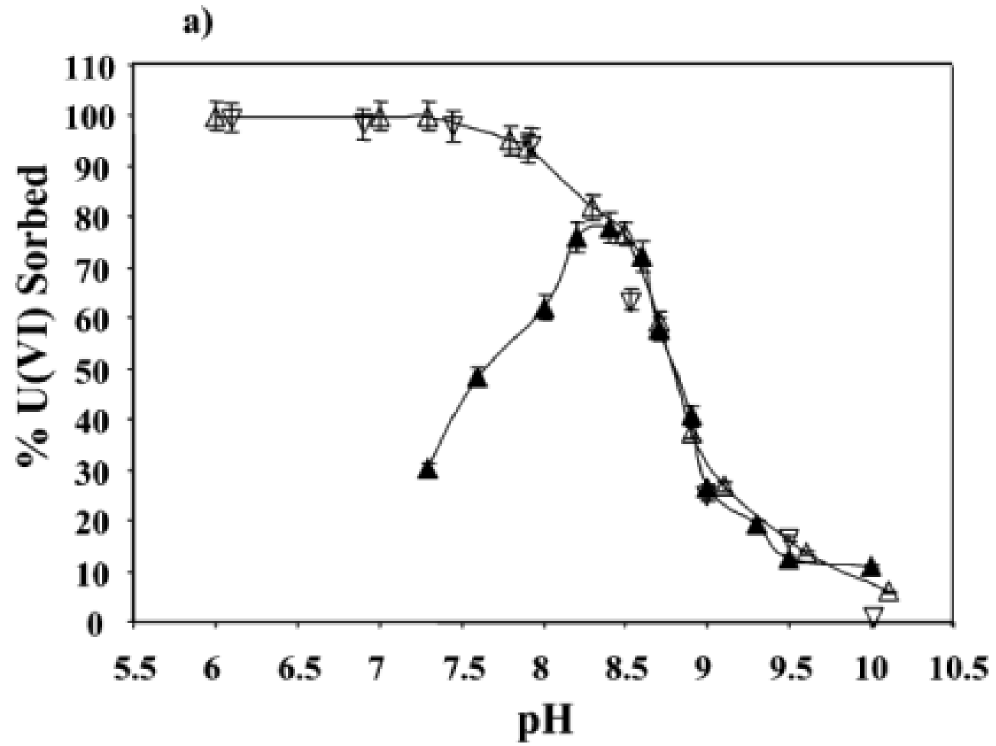


Calcium carbonates

Uranium Adsorption

- Factors that control U(VI) sorption to calcium carbonates
    - U(VI) loading (multiple uranium species)
    - Ca concentration
    - pH
- Importance of aqueous speciation





Dong et al., 2005

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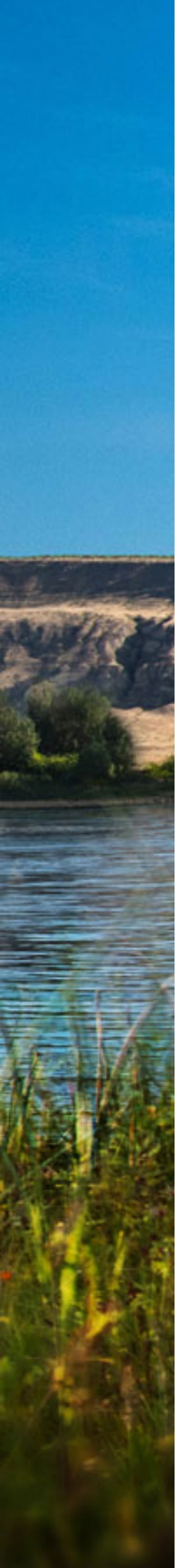
Uranium aqueous speciation at Hanford



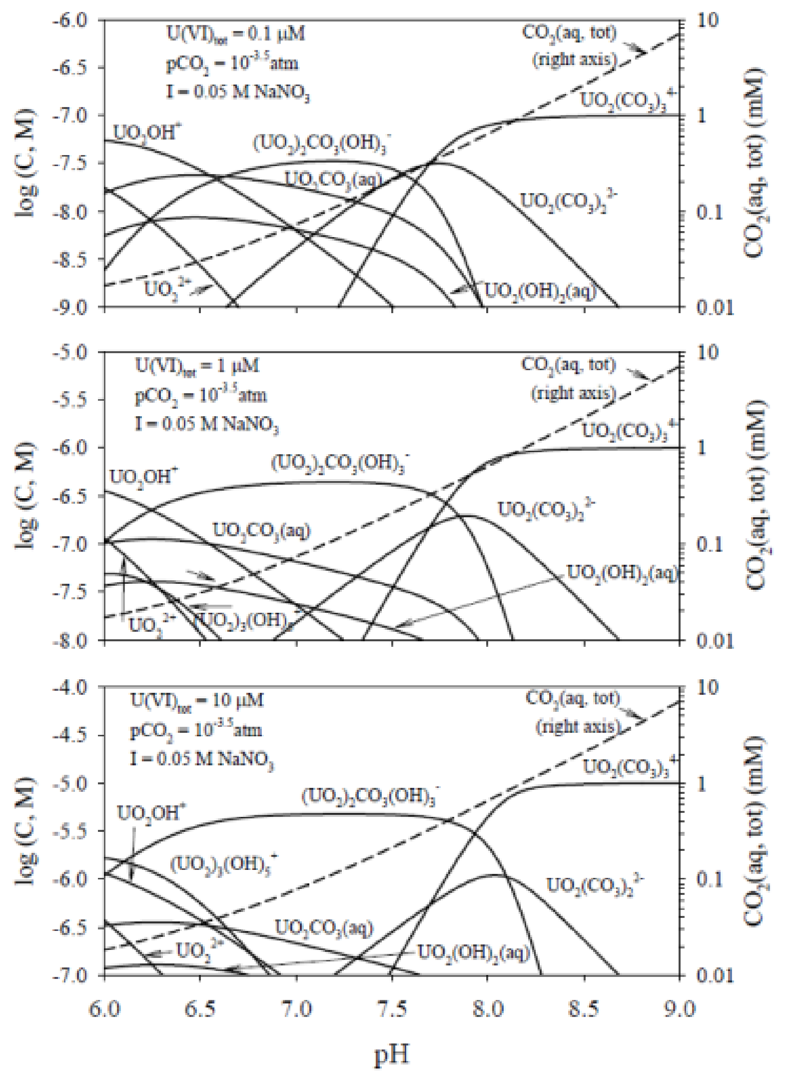


Figure 4-1. Aqueous U(VI) speciation as a function of pH, total aqueous U(VI) and carbonate concentrations. The carbonate concentration is in equilibrium with CO$_2$(g) pressure of $10^{-3.5}$ atm.

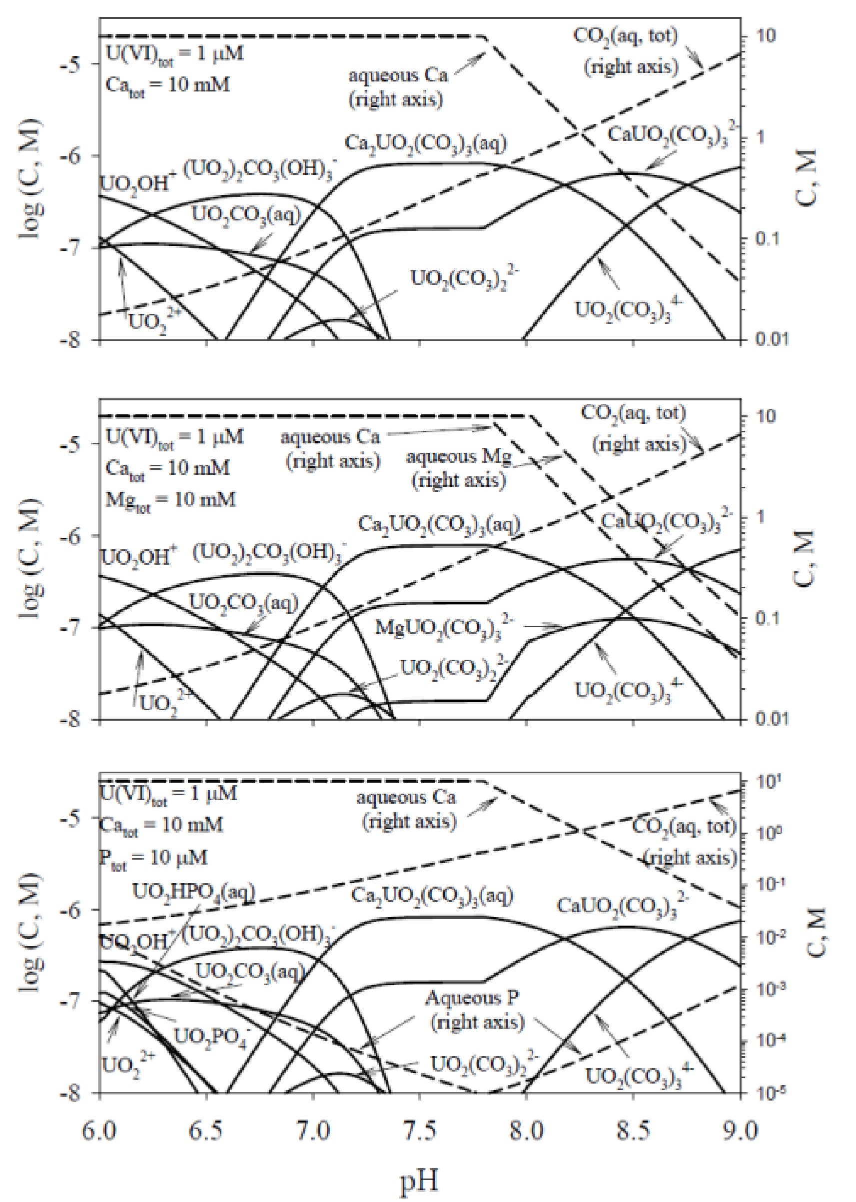


Figure 4-2. Aqueous U(VI) speciation in presence of Ca, Ca and Mg (middle panel), and Ca and phosphate (bottom panel). The total concentration of Ca was 10 mM including both aqueous and solid phases in equilibrium. The solid calcium was represented by calcite. Total Mg concentration was 10 mM including both aqueous and solid phase dolomite in equilibrium. The phosphate concentration was in equilibrium with mineral hydroxyl apatite.

Zachara et al., 2007

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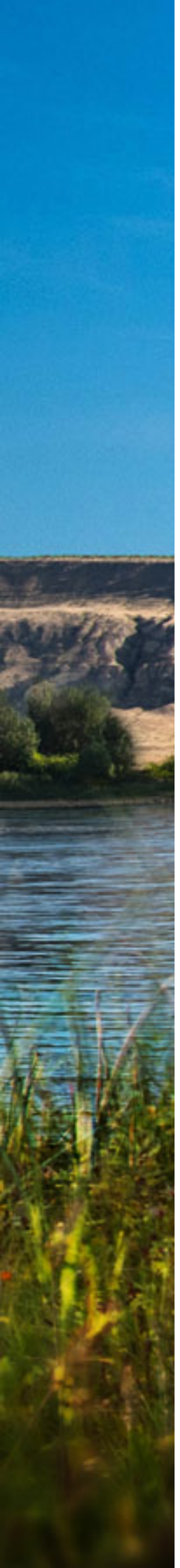
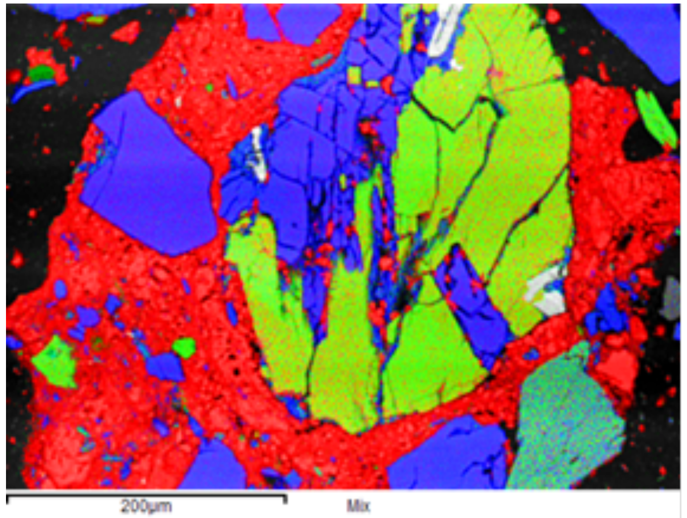
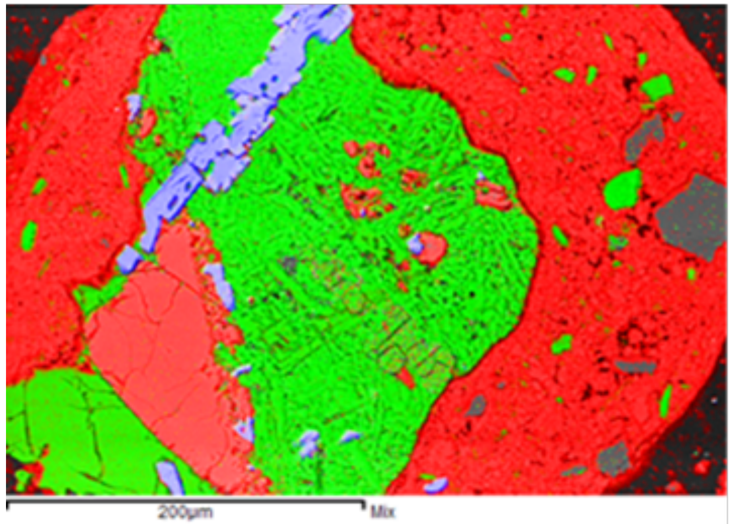
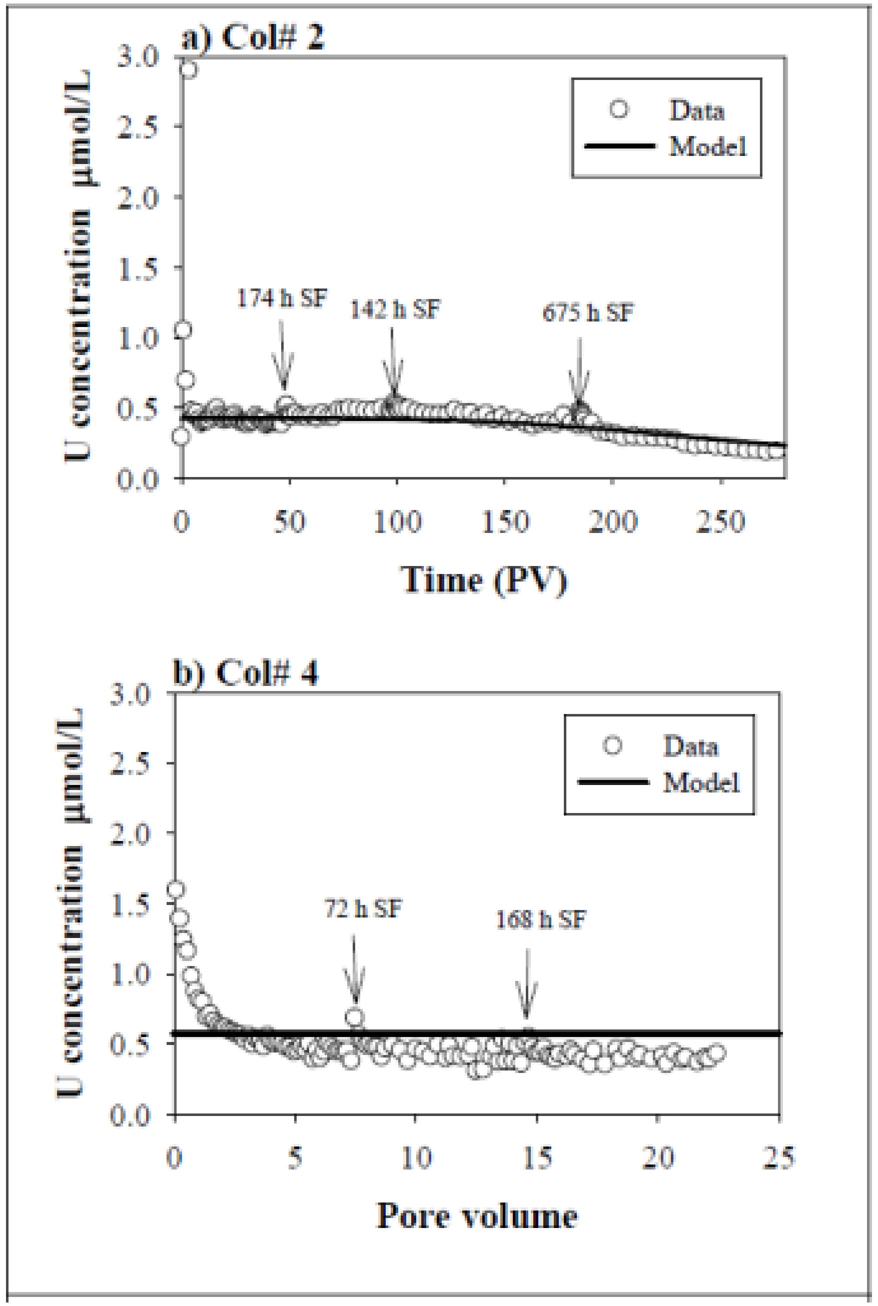


Hanford sediments

Role of $CaCO_3$ in Uranium Transport

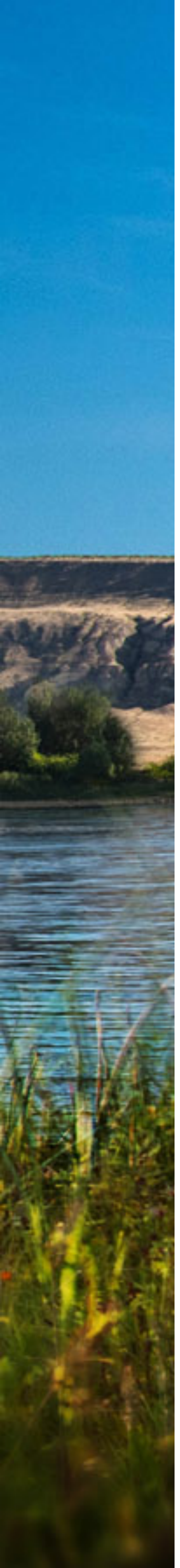






- Sediment 110, Cold Creek Paleosol, TX Tank Farm (caliche layer)
- Calcite content ~33%
- Effluent U(VI) (FRT of 1 and 6.5 h)
- $CaCO_3$ minerals (Ca red, Fe blue and Al green)
- Spectroscopic measurements: adsorbed U(VI)

Zachara et al., 2007; Qafoku and Icenhower, 2008



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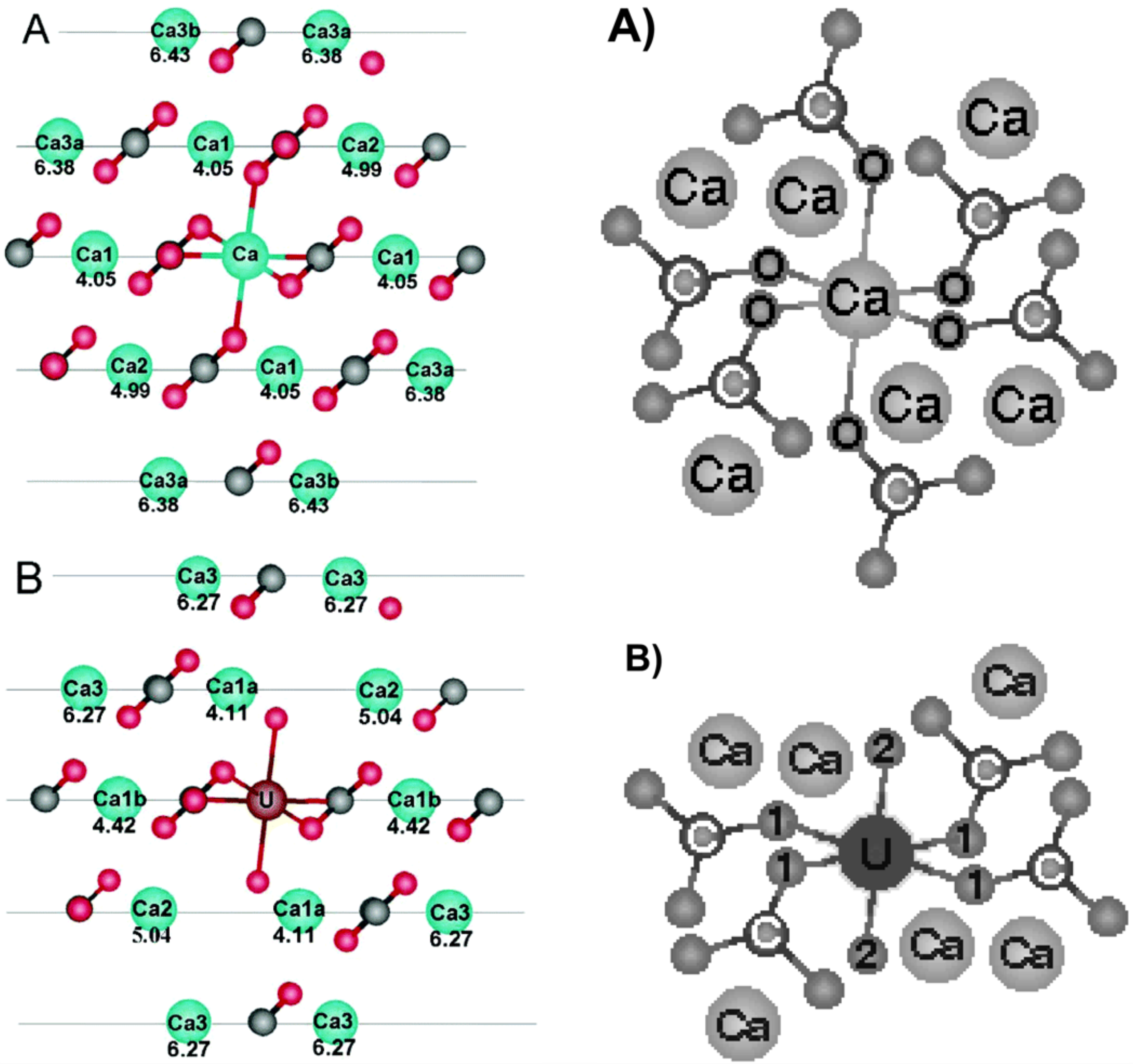
Uranium incorporation into $CaCO_3$

- In calcite, time may increase incorporation into the structure
- Comparison between different aged samples show increased calcite-like structure and stability as time increased



A: Calcite structure; B (left): 298-Ma uranyl-calcite (Kelly et al. 2006); B (right) 13.7-ka uranyl calcite (Kelly et al. 2003)

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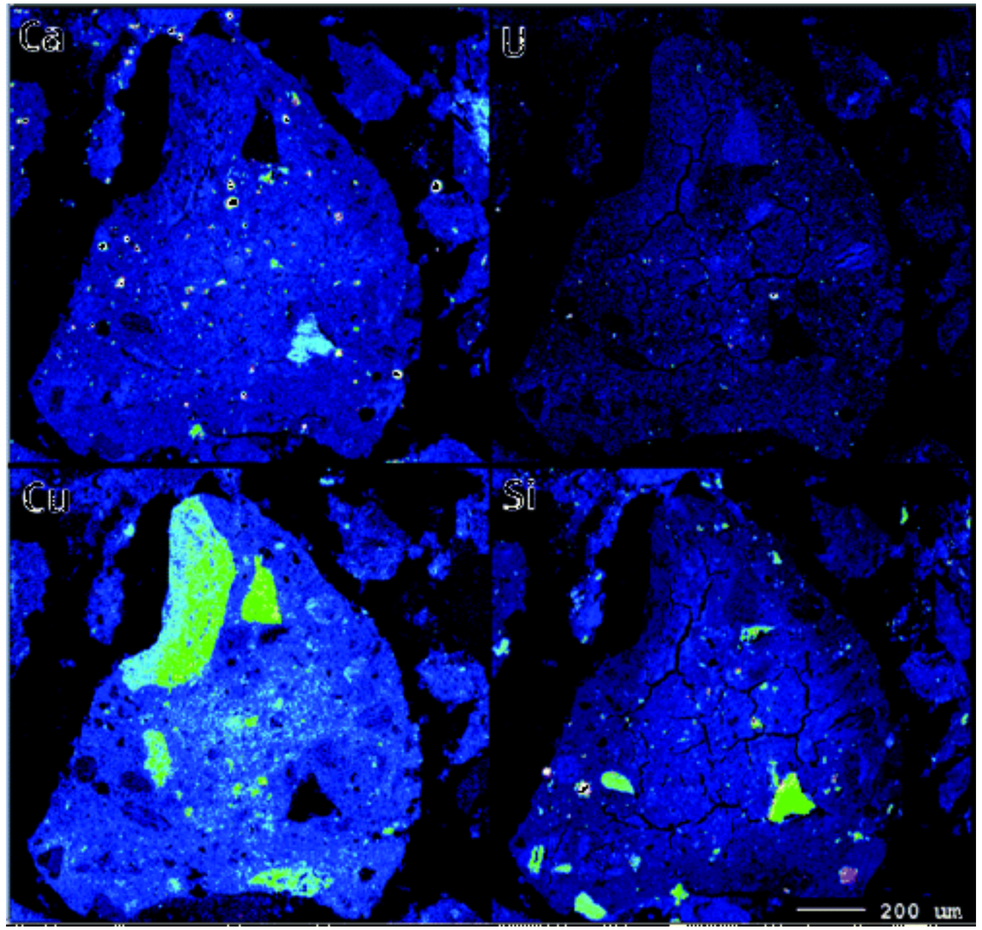
Uranium and $CaCO_3$ at Hanford

- Found sediments with U(VI) substituted into calcite
  - Substitution sites showed local aragonite-like structure
  - Predominant formation of U in the sediment despite low $CaCO_3$ content (1-3.2 wt%)
  - False-color elemental abundance map from a Hanford sediment show Ca inclusions and a U-rich phase, but also low concentrations of U and Ca throughout
  - *Wang et al., 2005*



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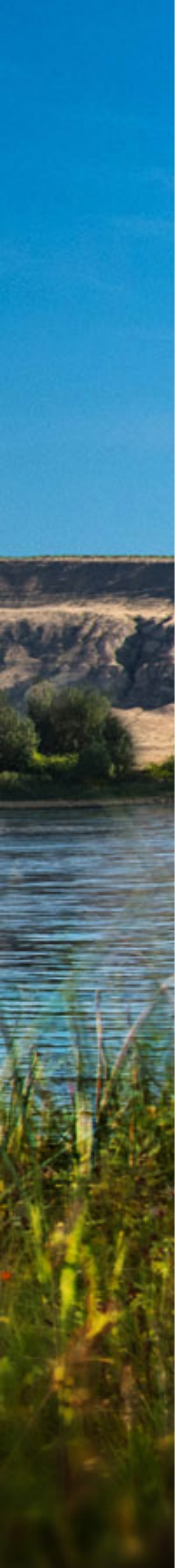

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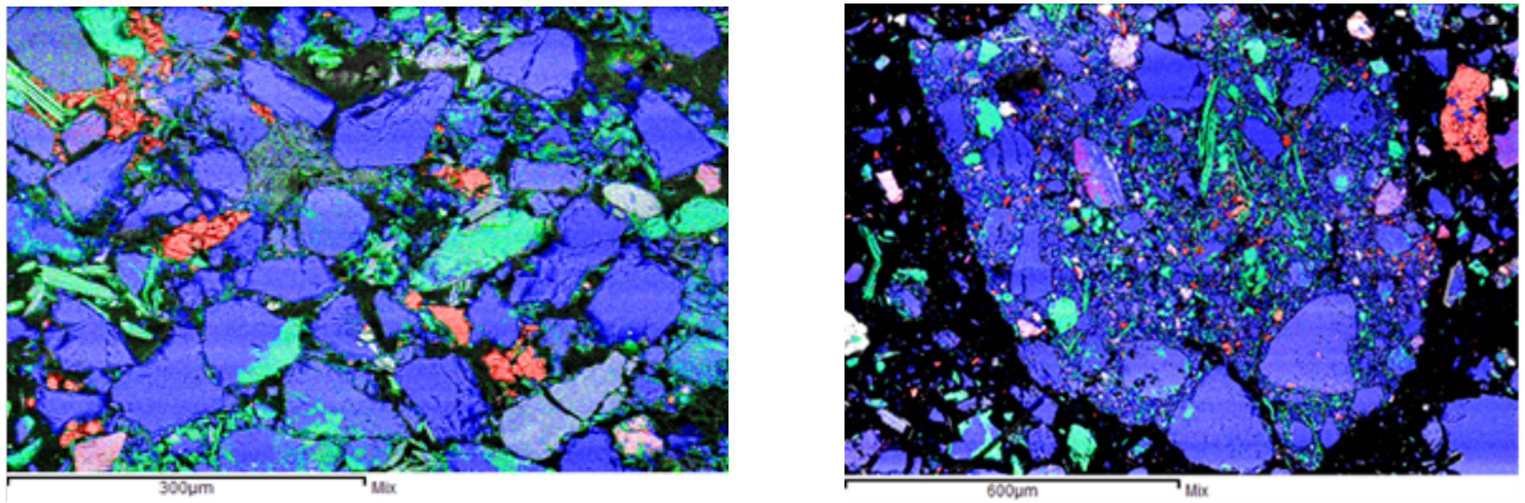
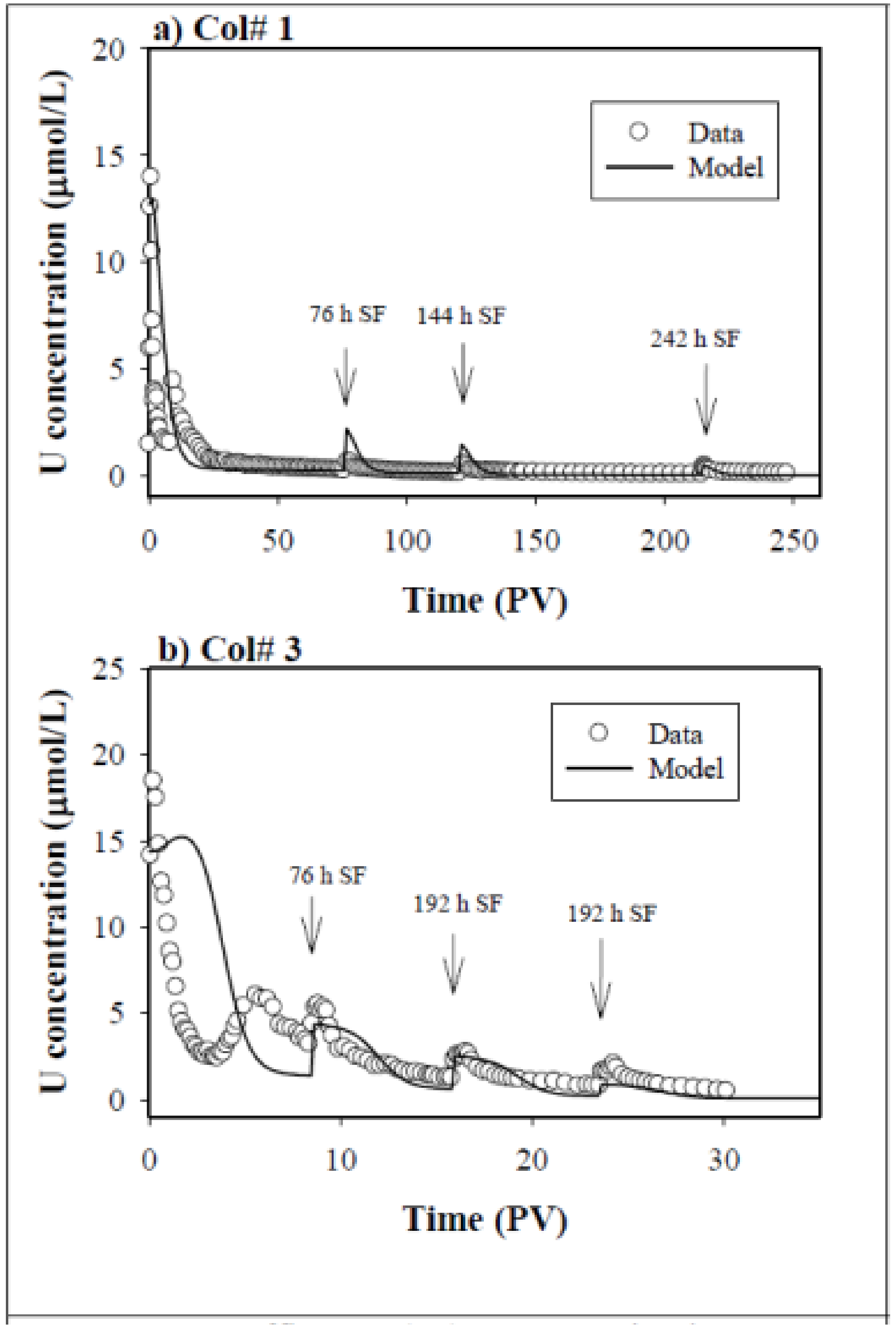
Hanford sediments

Role of $CaCO_3$ in Uranium Transport



- Sediment 69, Hanford formation, TX Tank Farm
- Calcite content 2.4% (small particles)
- Effluent U(VI) (time-dependent, FRT of 1 and 6.5 h)
- $CaCO_3$ minerals (Ca red, Si blue and K green)
- Spectroscopic measurements confirmed U(VI) incorporated in calcite



Zachara et al., 2007; Qafoku and Icenhower, 2008

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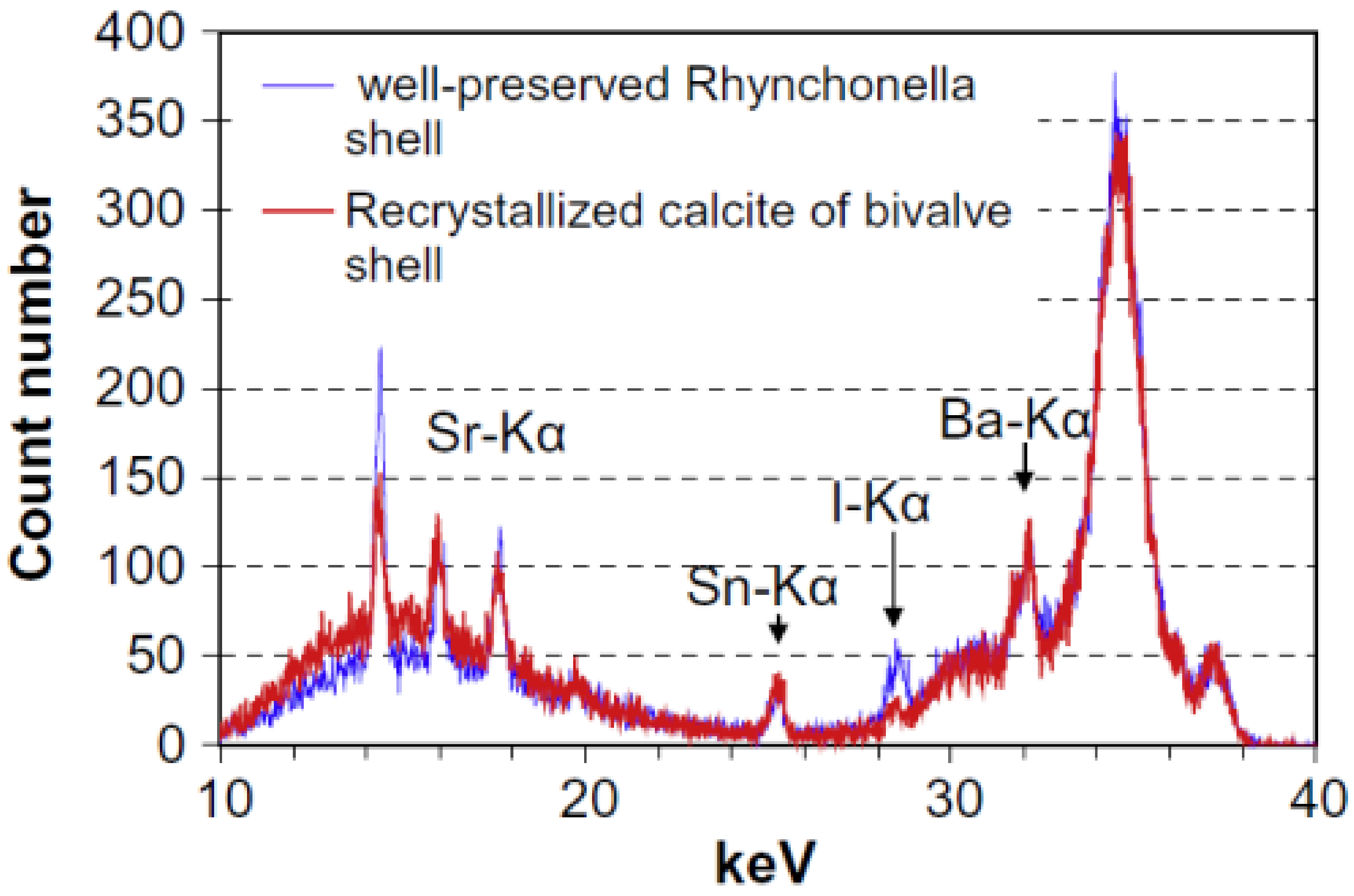
Incorporation into $CaCO_3$: Iodine

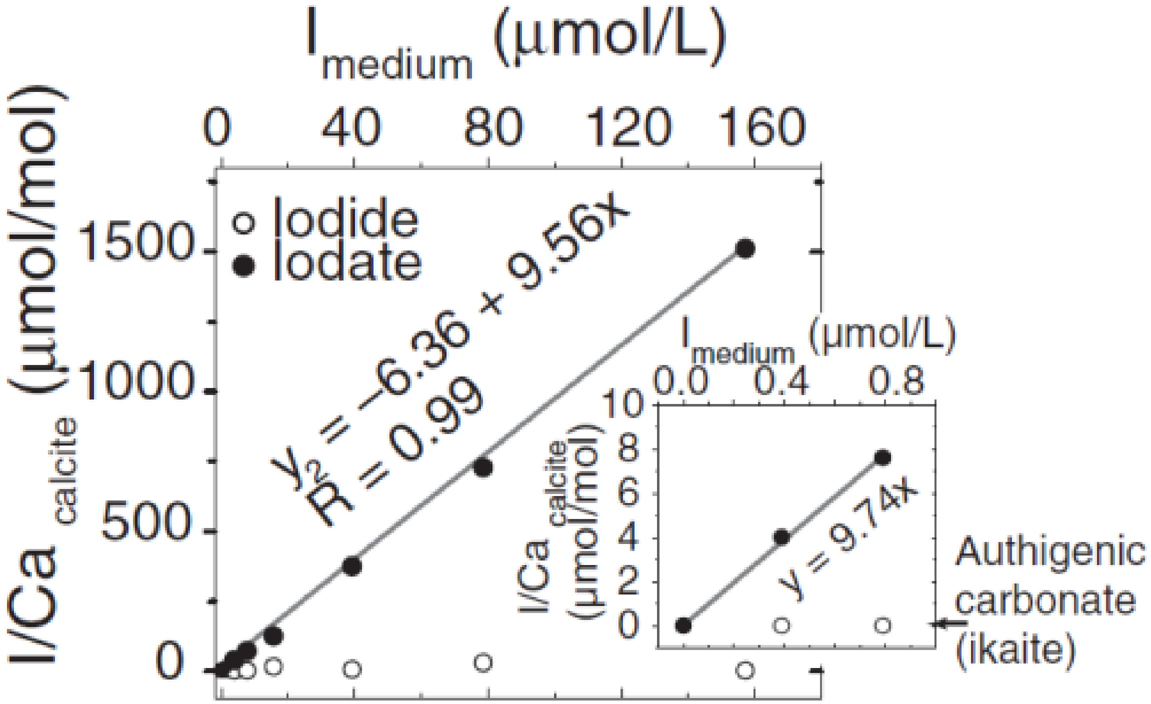
- Many laboratory studies have shown I incorporation into calcite
- Naturally occurring
  - Found in speleothems and in carbonate shells
  - Lost during recrystallization bio-calcite shell



Lerouge et al., 2010

Incorporation into $CaCO_3$: Iodine Speciation

- Positive correlation between iodate concentrations in solution vs. in the solid;
  - an increase in iodide concentrations did not result in more iodide in the solid
- Iodate can incorporate into the calcite structure; iodide does not
- I/Ca ratios in shells can indicate oceanic anoxic events



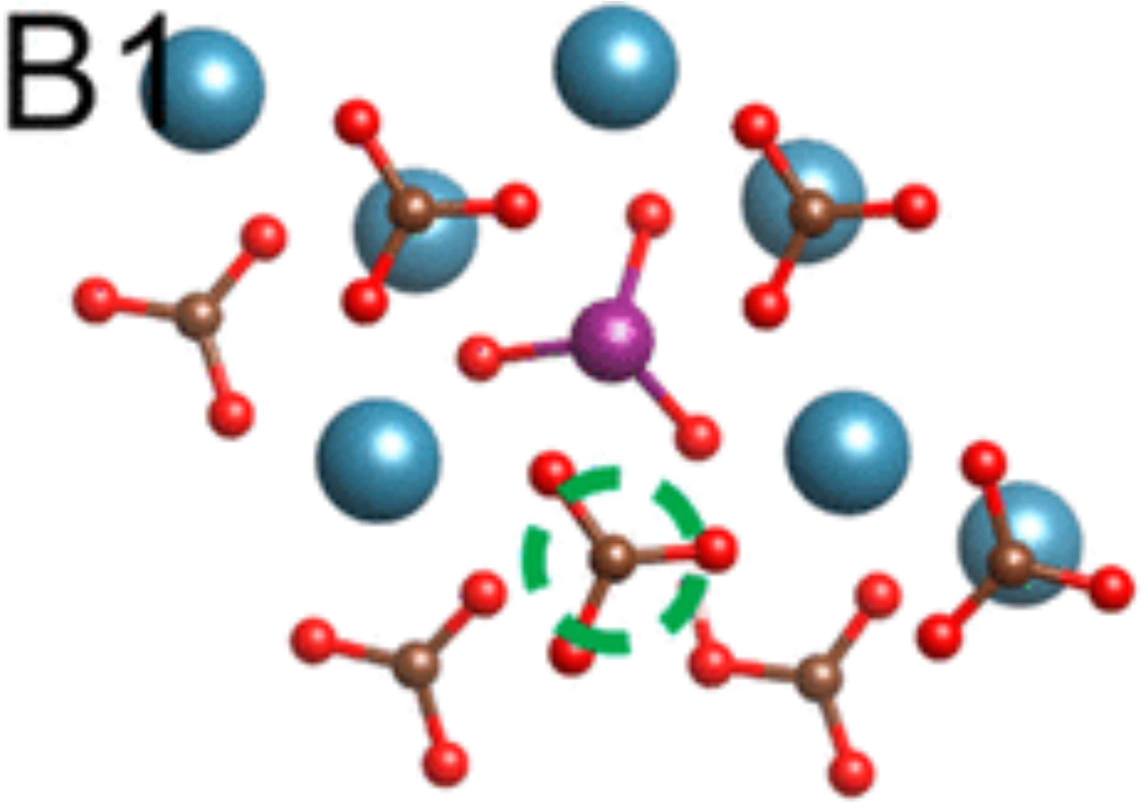
Lu et al., 2010

Incorporation into $CaCO_3$: Iodine

- Conducted *ab initio* molecular dynamics modeling
  - IO_3^- substitutes for CO_3^{2-} with Na^+ or H^+ for charge balance
  - Substitution of iodine (purple) in one nearest neighbor scenario, with charge compensation by H^+ (white) and Ca vacancy in green
- Co-contaminants can have an effect on iodate removal
  - Reduction in I removal with Cr present

Kerisit et al., 2018

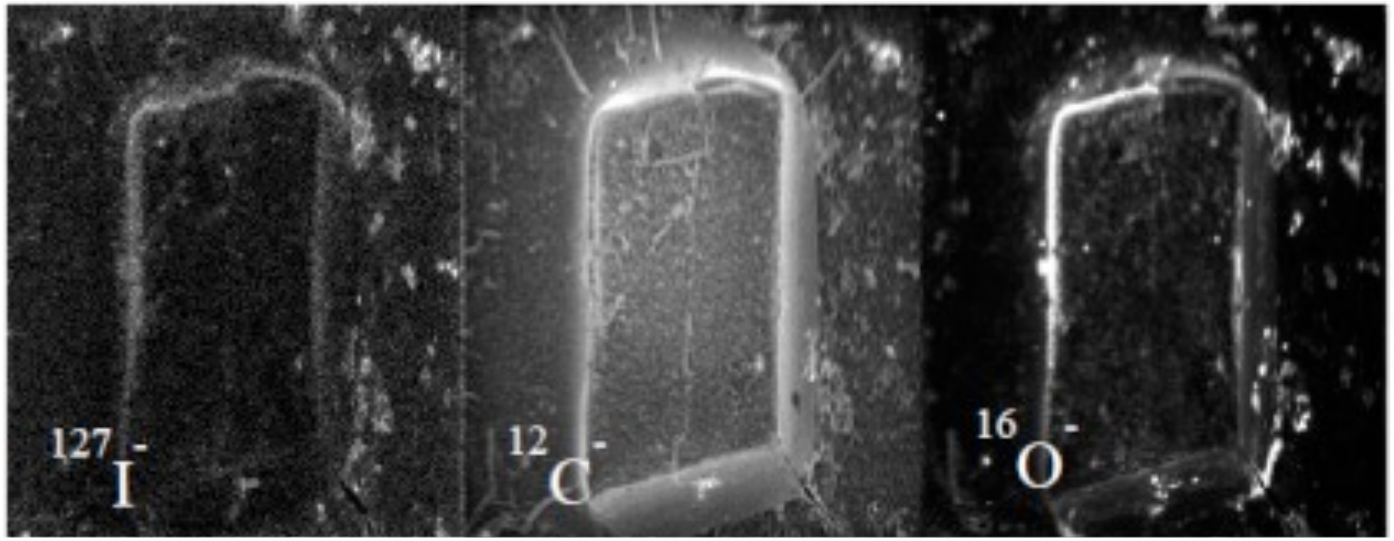
Saslow et al., 2019

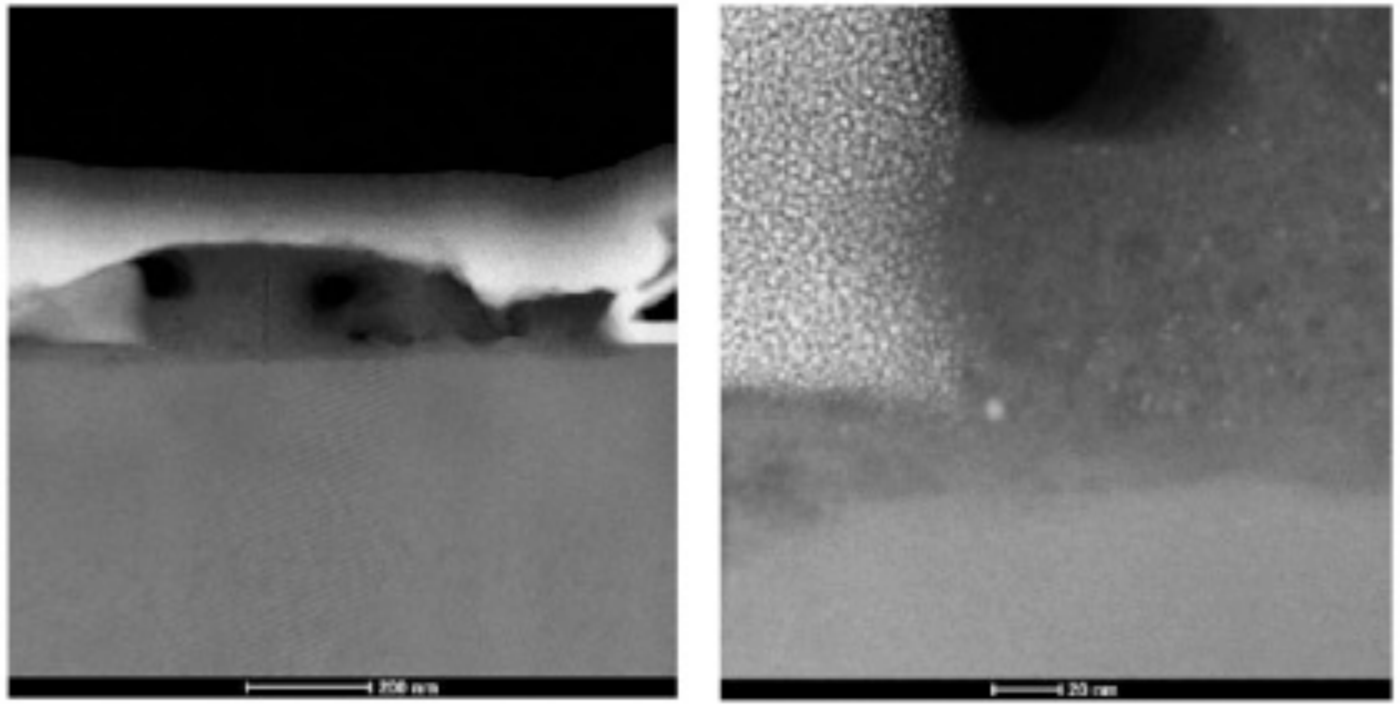


Incorporation into $CaCO_3$: Iodine

- NanoSIMS (top) showing iodine along the surface of calcite
- TEM/EDS (bottom) also showed iodine likely near the surface of the calcite particles

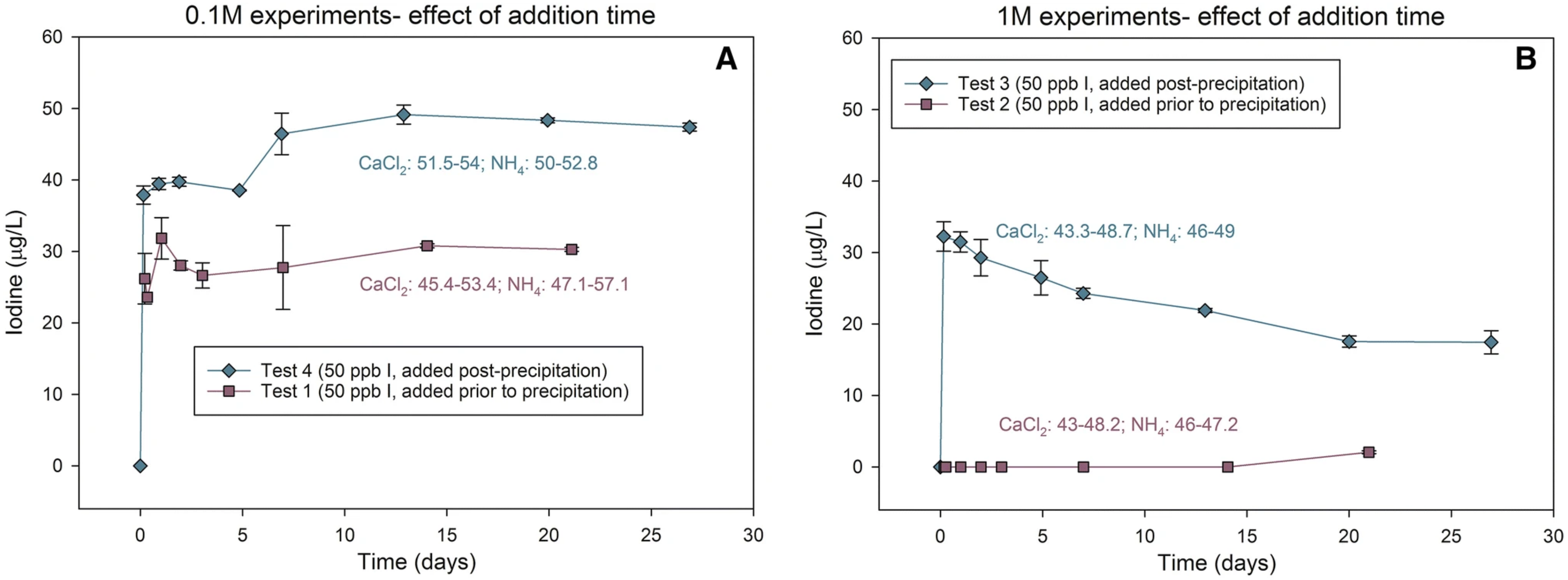
Truex et al., 2017





Incorporation into $CaCO_3$: Iodine

- Iodine can be incorporated into the calcite structure, or adsorbed onto the surface



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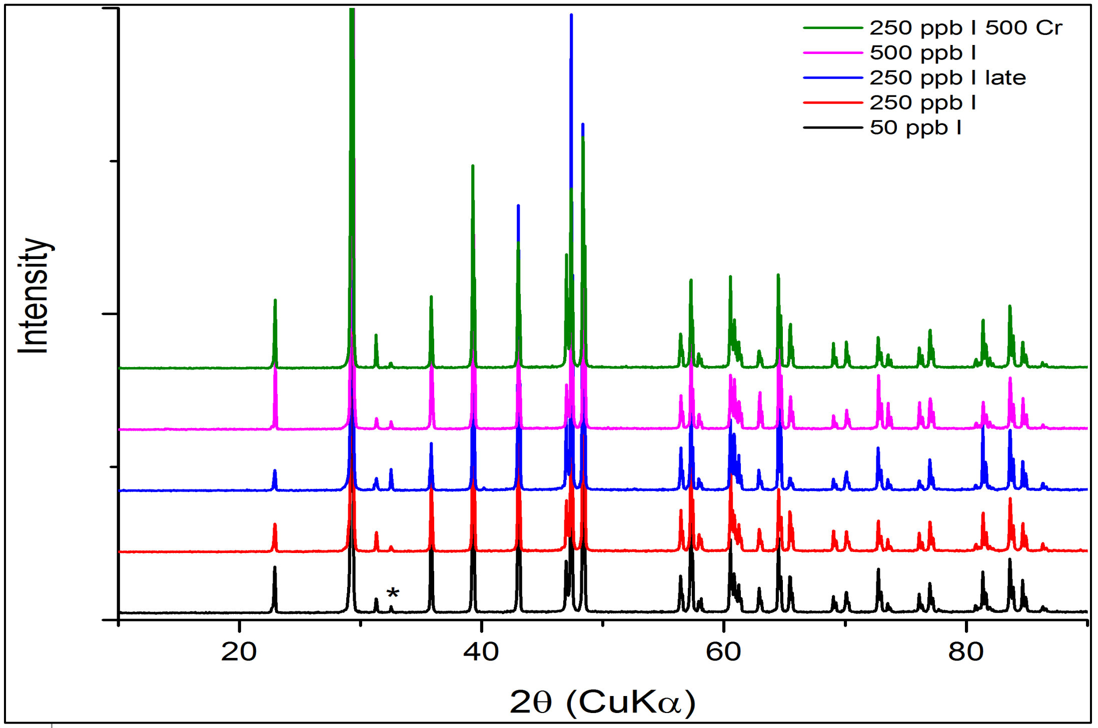
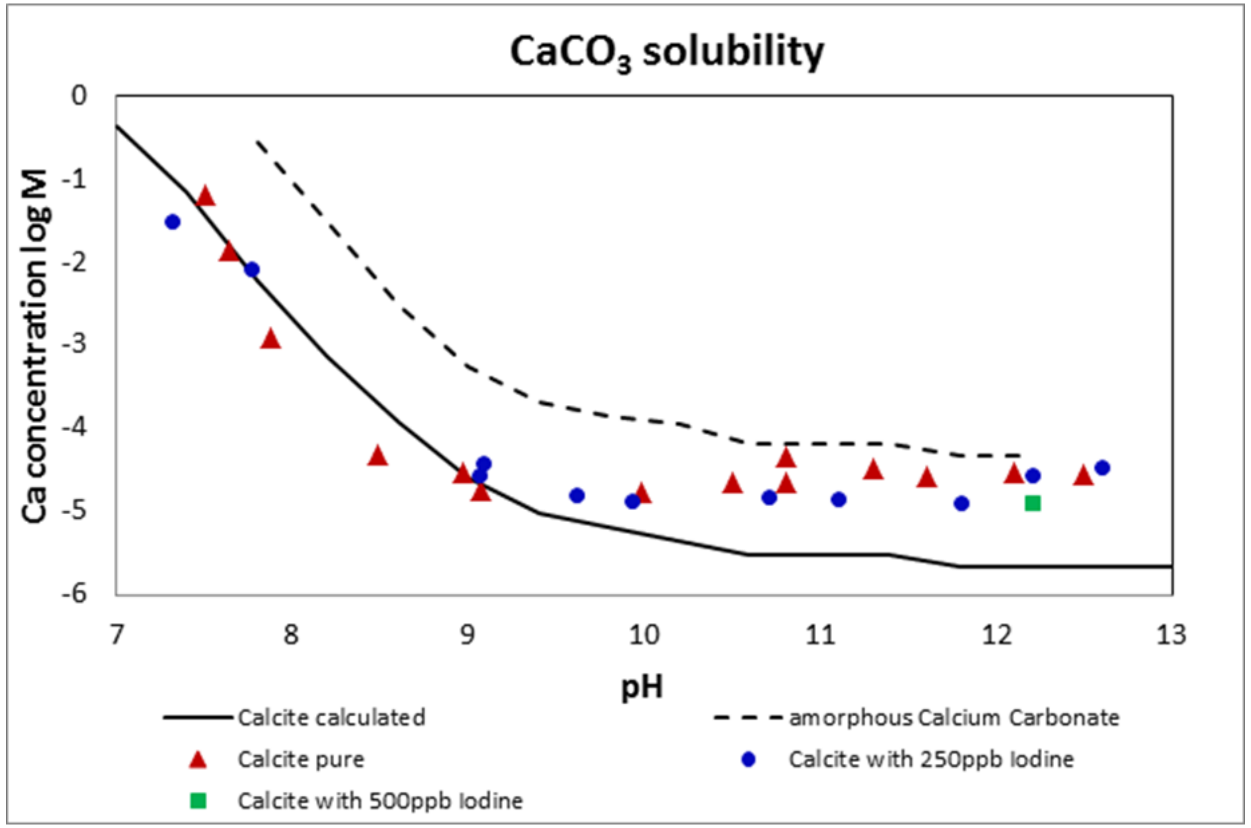
Stability of I-substituted calcite

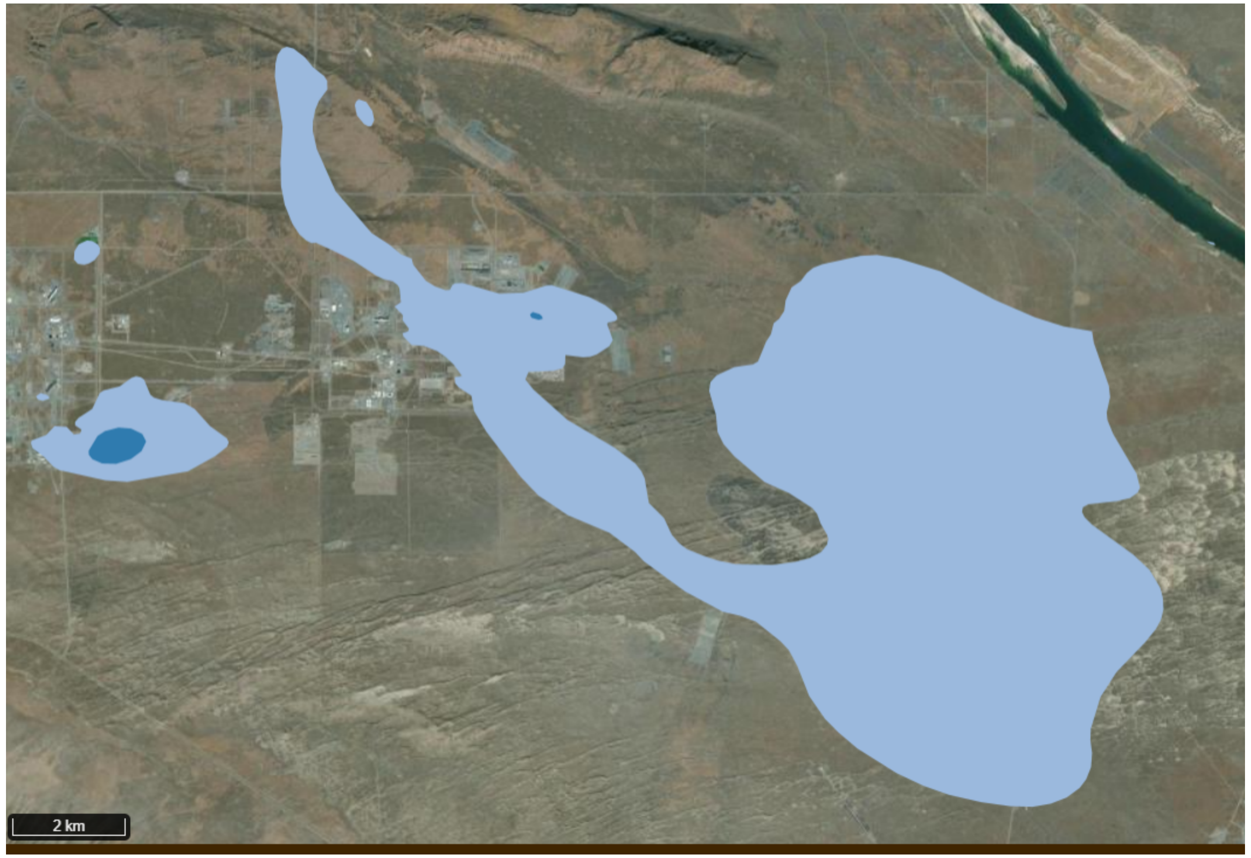
- In a PNNL lab study, only calcite was found in iodine incorporation experiments
- Mineral stability was not affected by incorporation of iodine





Iodine contamination at Hanford

- Iodine plume as of 2018
    - *phoenix.pnnl.gov*
- ^{129}I is a by-product of plutonium production
    - Long half life (1.57 x 10^7 years)
    - Low drinking water standard (1 pCi/L)
- Large, dilute plumes make remediation a challenge



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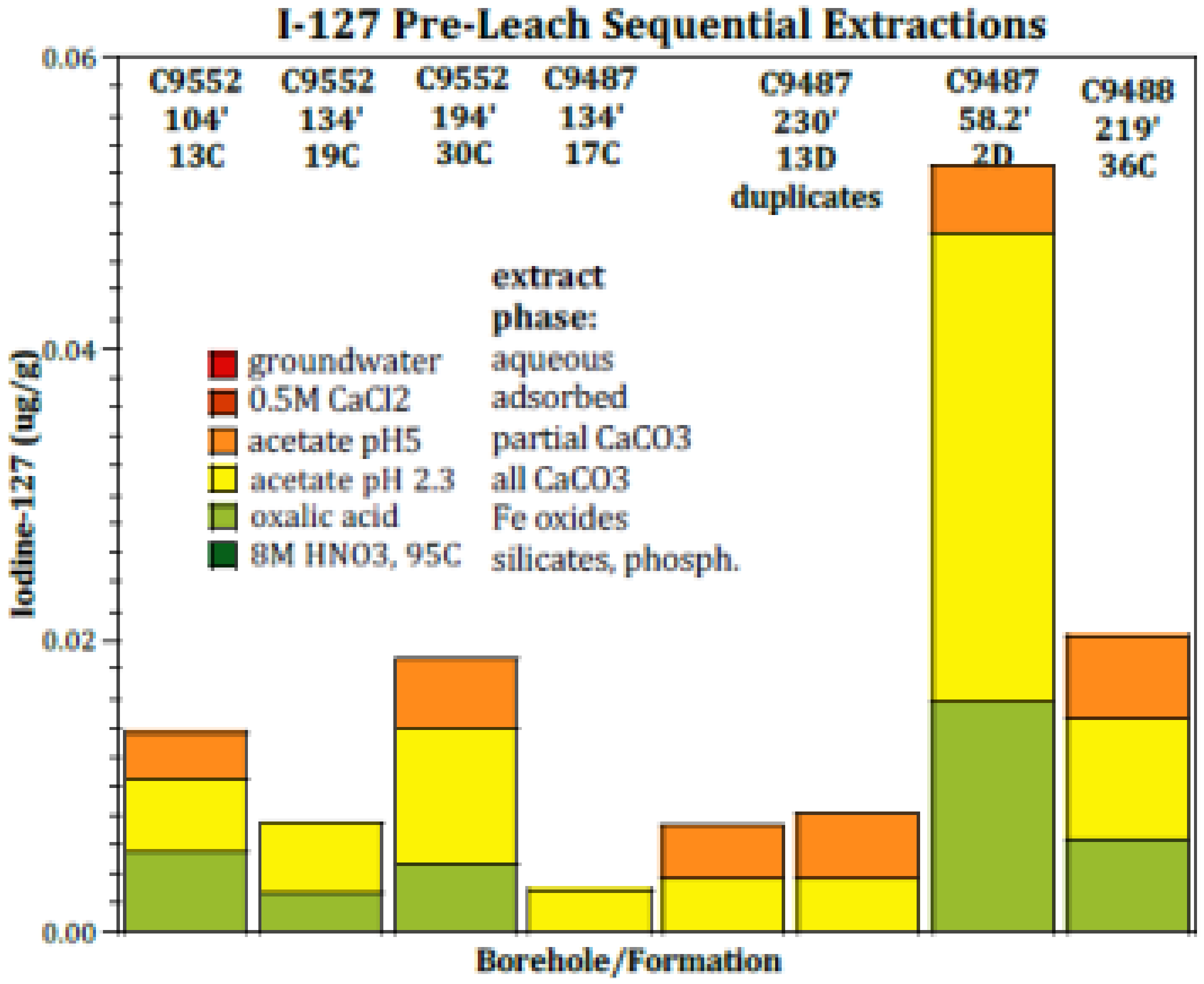
Iodine and $CaCO_3$ at Hanford

- The majority of iodine found in Hanford sediments is associated with $CaCO_3$
- Groundwater samples also show iodine association with calcite
  - CO_2 degassing during groundwater sampling resulted in calcite precipitation
  - 7-40% of iodine was removed due to coprecipitation

Zhang et al., 2013



Szecsody et al., 2017

Summary: Cr, U, and I in carbonates

Contaminant	Incorporation into $CaCO_3$
Chromium	Can delay or prevent transformation of vaterite to calcite; CrO_2^{4-} is substituted for CO_3^{2-}
Uranium	U(VI) can incorporate into calcite but uranium speciation is very complex
Iodine	Incorporated when in the oxidized iodate form, at the surface of calcite

https://www.chemtube3d.com/ss-caco3/

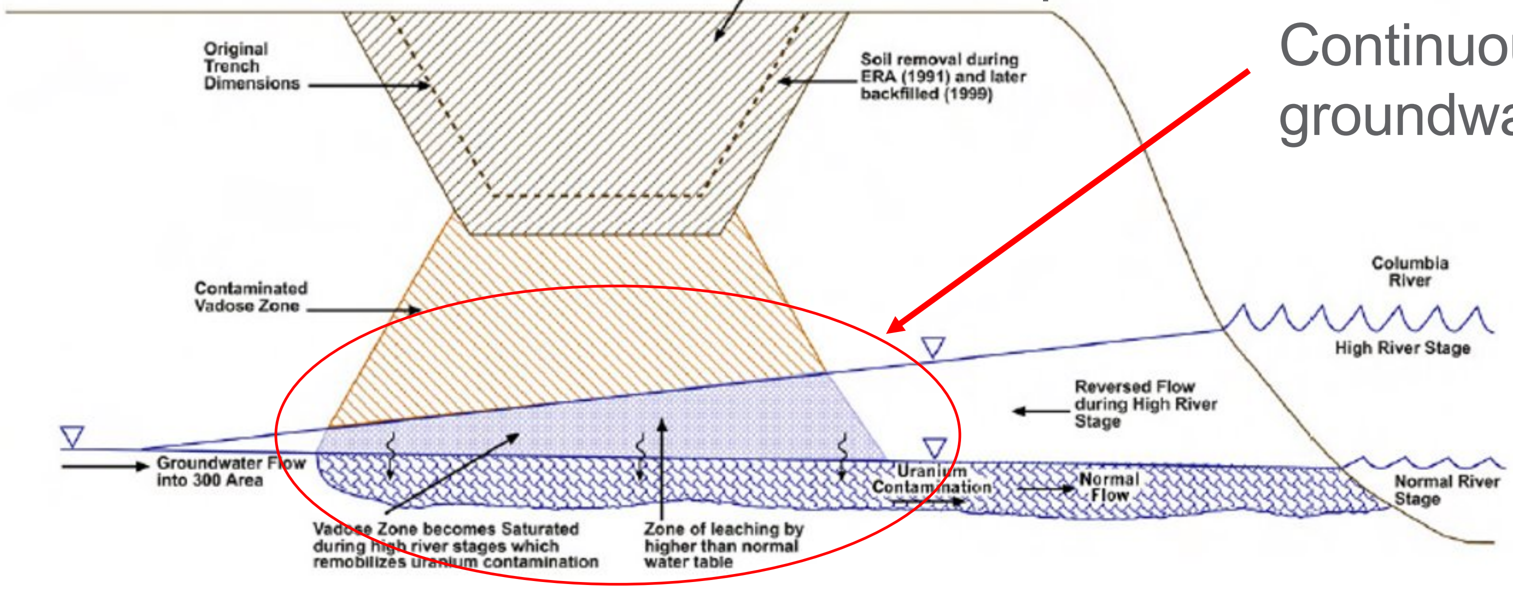
Role of calcium carbonates

- Calcite-induced contaminant attenuation/release pathways at complex contaminated sites
  - Adsorption of contaminants to calcium carbonates
  - Co-precipitation of contaminants with calcium carbonate that act as a solubility-controlled partitioning interaction with respect to slowing contaminant transport (e.g., within the plume especially at the distal portions)
  - Co-precipitation with calcium carbonate that provide a continuing source of contaminants (e.g., for the tail of a plume or near former source areas),
  - Low-solubility compounds that are formed as a result of calcium carbonate dissolution

- Important components of the conceptual models
- Incorporated in managed natural attenuation (MNA) evaluations
- Part of the remediation strategy

Continuous source identification

- Periodic re-wetting of sediments can cause carbonate dissolution
- In the 300 Area of the Hanford Site, changes in the river stage resulted in release of uranium from carbonates
  - Understanding of carbonates and their role in U mobilization helped determine the continuing source of U in this area

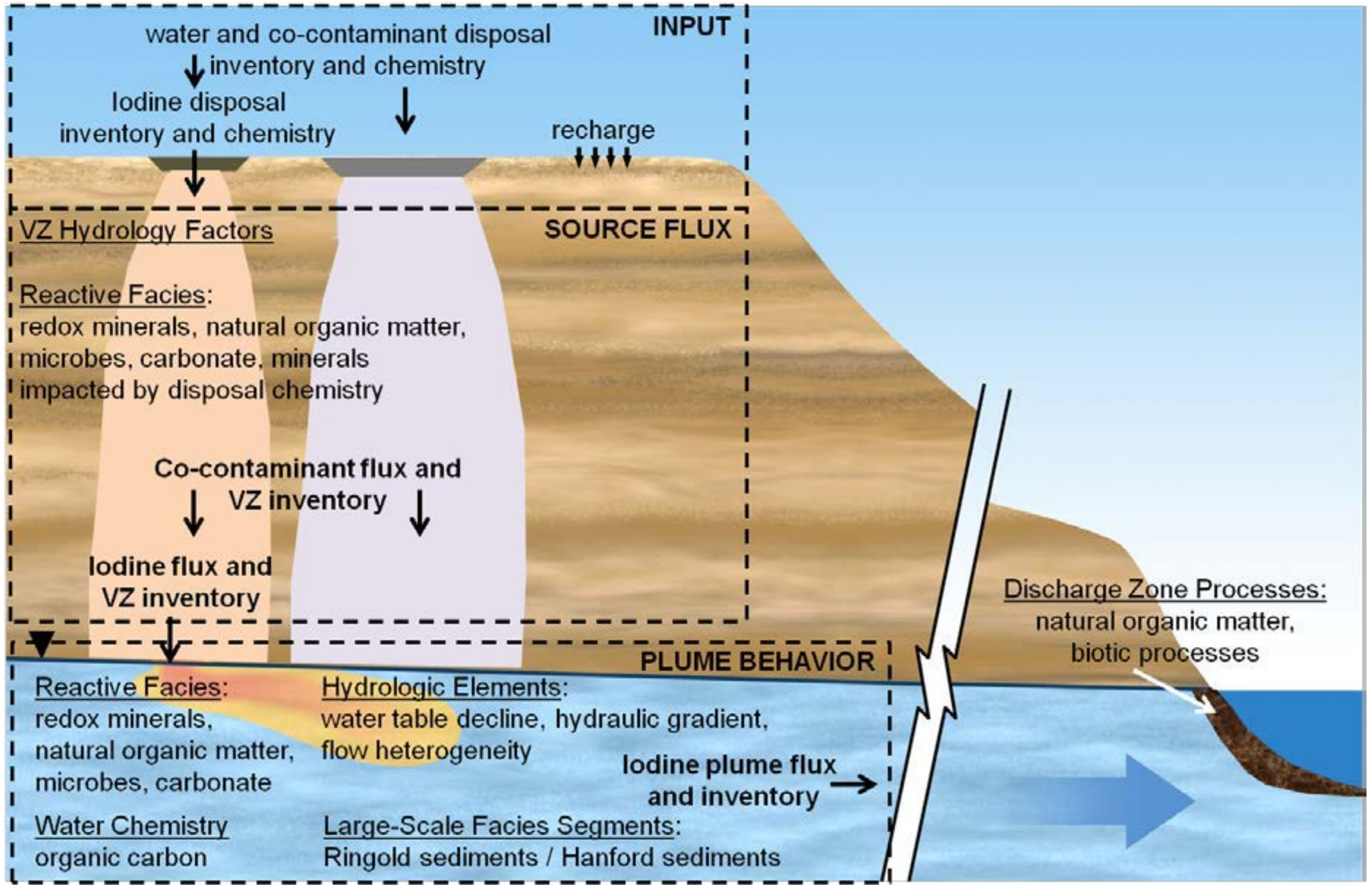


Uranium disposal trench

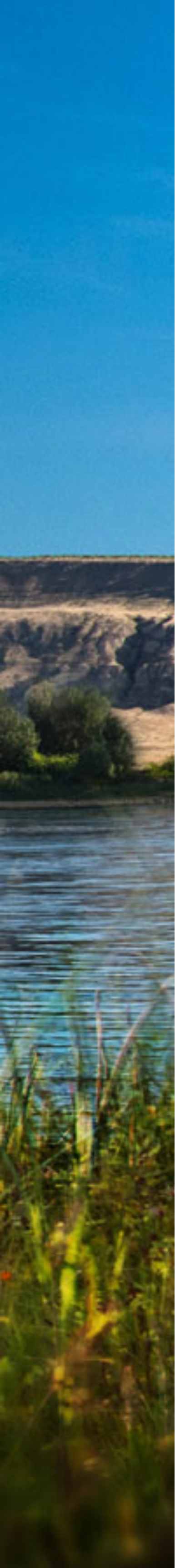
Continuous source to groundwater

Conceptual site model

- CSMs are an essential first step for creating remedial plans for complex sites
    - From Interstate Technology & Regulatory Council (ITRC): "…a thorough conceptual site model (CSM) can best represent site complexities, (and) define remediation potential based on site complexities…"
- Complex sites where calcium carbonates are present, should include carbonates in the CSM



Truex et al., 2007



Monitored natural attenuation

- MNA as an alternative to direct remediation interventions
  - Relies on natural processes that will reduce the mass, toxicity, mobility, and/or volume of the contaminants
  - Part of a carefully designed, controlled and monitored site-specific remediation strategy
  - Provides an effective knowledge-based remedy alternative
    - ✓ Sites difficult to access, with high degree of heterogeneities, and traditional remediation techniques are difficult to apply
  - Usually combined with long-term monitoring

- Calcite-based processes provide a MNA pathway for U, I, Cr and others

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Carbonate system under field conditions

- Groundwater and vadose zone pore water may have elevated CO_2 levels
  - Resulting in CO_2 partial pressures 10-100 times above atmospheric levels
  - Hanford groundwater samples undergo significant CO_2 outgassing when brought to the surface
  - Elevated CO_2 partial pressures are the result of:
    - ✓ decomposition of OM or deposited OM
    - ✓ As infiltration passes through sediments, it dissolves CO_2 and carries it down
- These circumstances provide a means to induce calcite precipitation in the subsurface:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3(s) + CO_2(g)\uparrow + H_2O$$

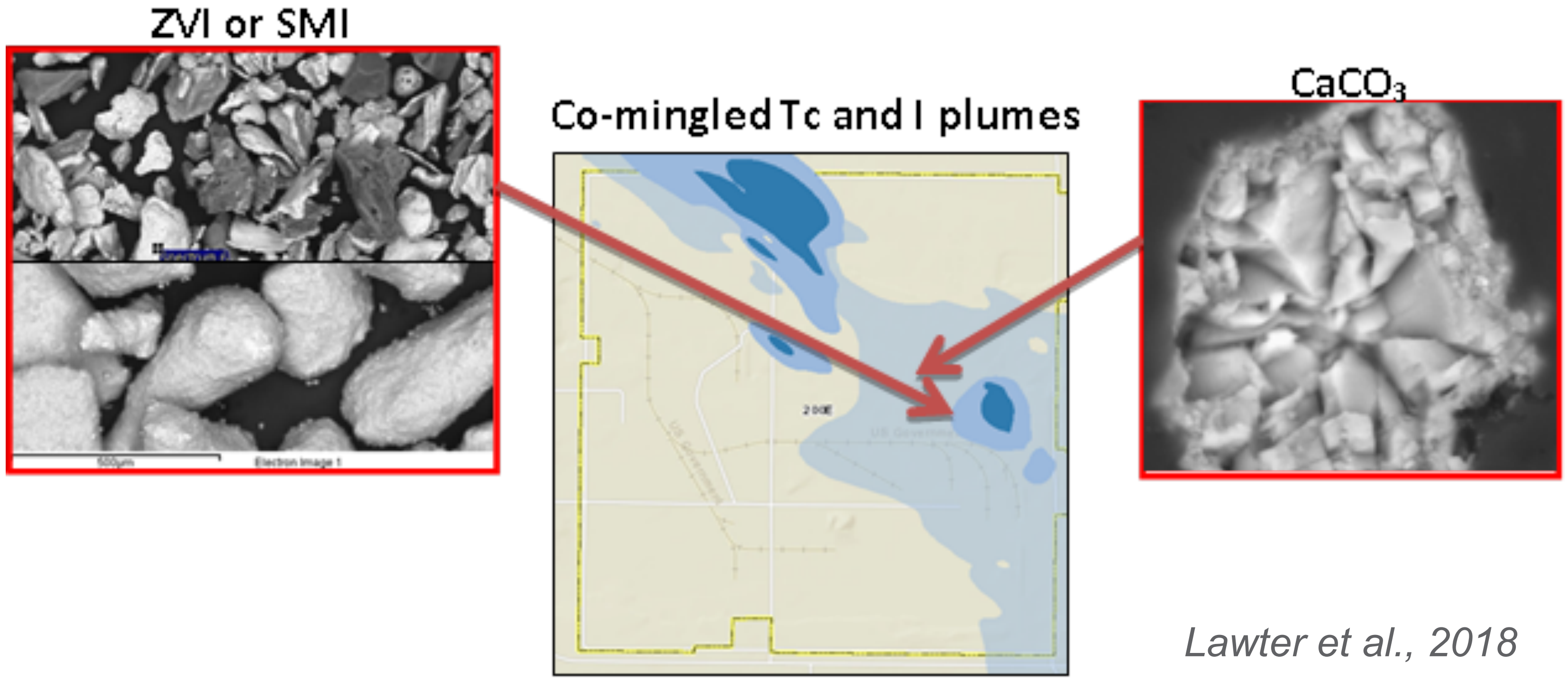
  - Inducing CO_2 outgassing from solution will result in calcite precipitation

Remediation through induced $CaCO_3$ precipitation

- One way to reduce the CO_2 partial pressure in the subsurface is through barometric pumping
  - Could be used to reduce CO_2 partial pressures in the vadose zone and groundwater to induce calcite precipitation and remove contaminants from solution
- If necessary and effective implementation approaches can be developed, calcite processes could be applied as an active in situ remediation approach to enhance attenuation
  - These active approaches could involve formation of calcium carbonate in the subsurface
  - Perturbing the subsurface geochemical system by injecting CO_2 gas in the subsurface to induce mineral dissolution, release of Ca, and subsequent precipitation of carbonates

Remediation at complex sites

- Co-located contaminants present a unique set of challenges
  - Multiple contaminants can be incorporated in Ca-carbonate minerals
  - However, effects of co-contaminants would need to be understood to evaluate these mixed contaminant applications



Map produced using PHOENIX (phoenix.pnnl.gov)

Lawter et al., 2018

Thank you