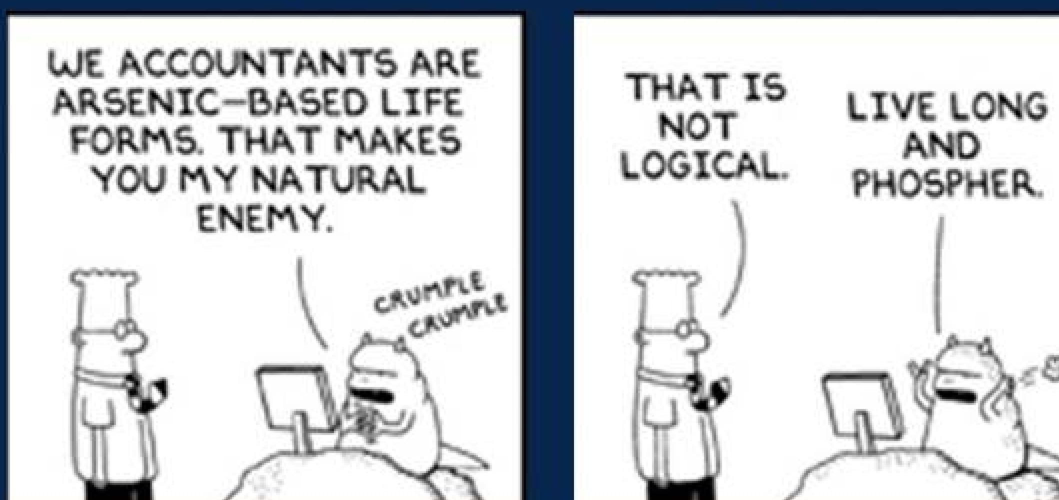
Arsenic, chromium, and uranium occurrence in California groundwater at the macro, well-bore, and micro scales

(Or: "More fun and interesting things than you ever cared to know about trace elements -- in 20 minutes or less")

By: John A. Izbicki, Michael T. Wright, Bryant C., Jurgens, and Loren F. Metzger



A little chemistry and a few factoids

	Arsenic	Chromium	Uranium
Form in water			
Reduced	As III ($HAsO_2^{o}$)	Cr III ($Cr_2O_{3(s)}$)	U IV ($U_4O_{9\,(s)}$)
Oxidized	As V ($H_2AsO_4^{2-}$)	Cr VI (CrO_4^{2-})	U IV | ($UO_2(OH)_2$) ($UO_2(CO3)_2^{2-}$)
Abundance in rock (milligrams per kilogram) (From Reimann and Caritat, 1998)			
Continental crust	2	130	1.7
Ultramafic rock	0.7	2,300	0.02
MCL (μg/L)	10	100 Cr(t) EPA 10 Cr(VI) CA prop.	30

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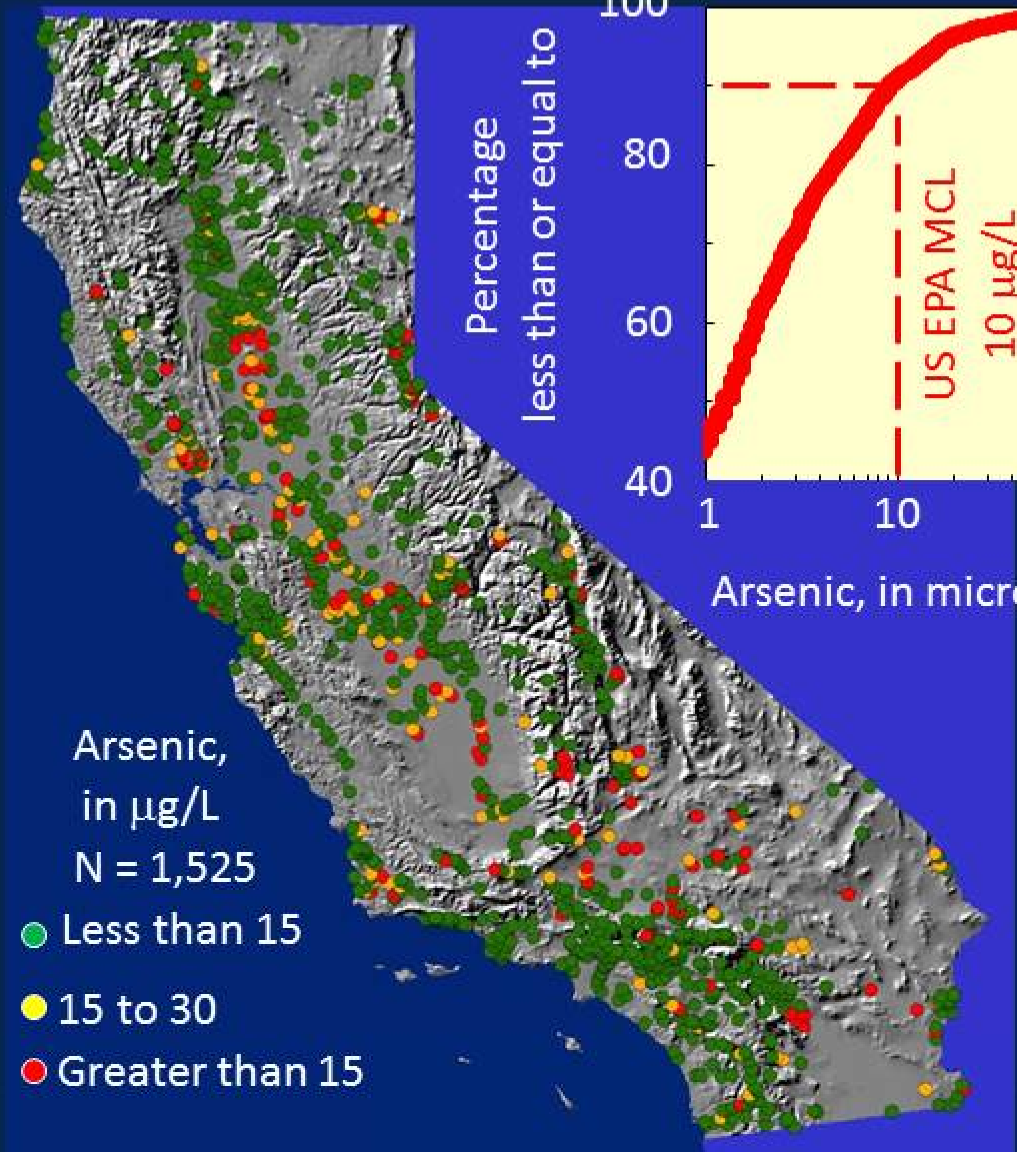
Arsenic in California's groundwater



About 10 percent of wells exceed US EPA Maximum Contaminant Level

Co-occurrence in groundwater from alluvial aquifers (US)

(From Ayotte, et al., 2011)

Humid climates	B, Si
Dry climates	Al, Si, U, PO_4, K

California WRCB/USGS GAMA data

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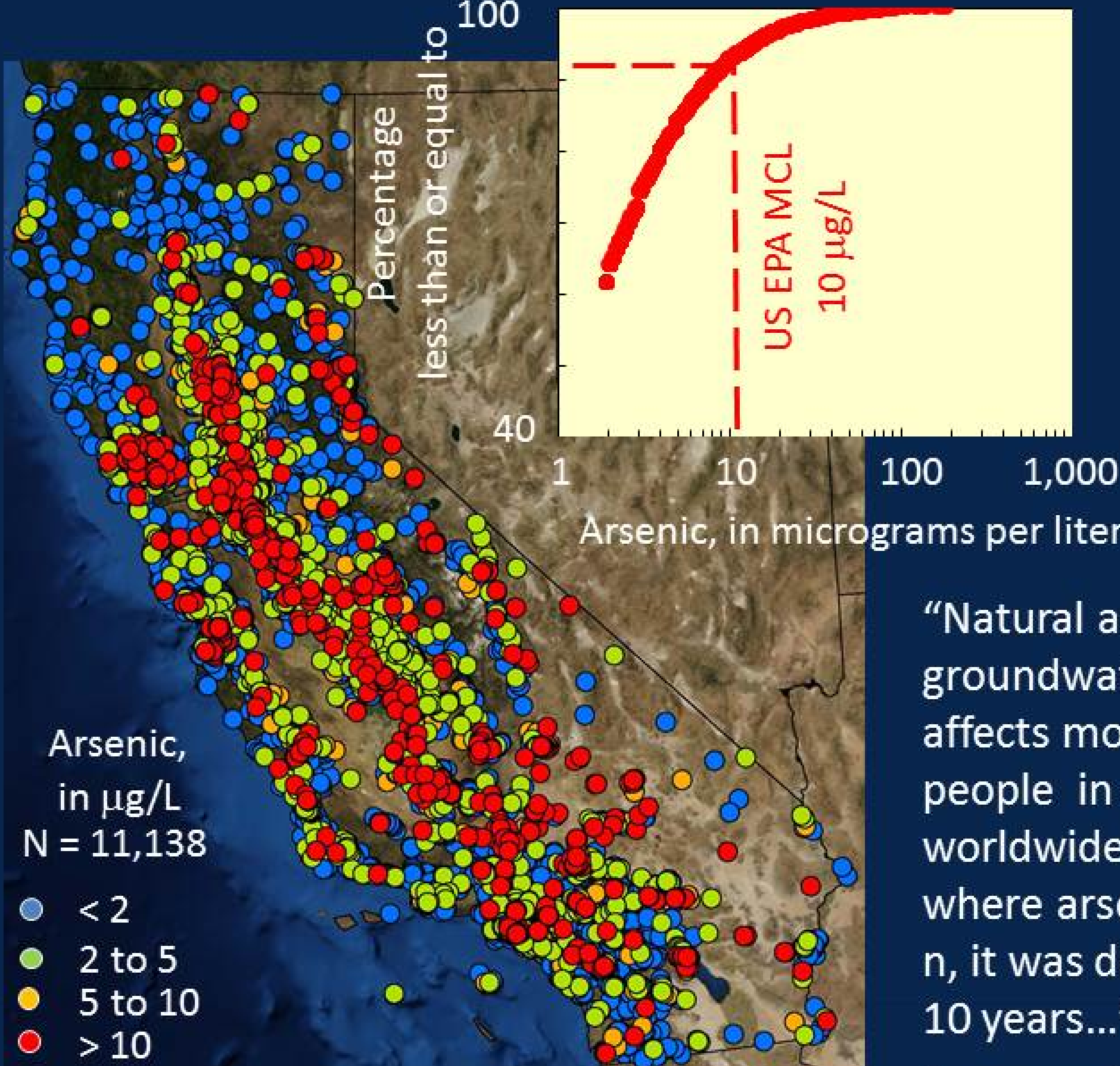
Arsenic in California's groundwater



California DPHS data

About 8 percent of wells exceed US EPA Maximum Contaminant Level

"Natural arsenic pollution of groundwater and surface water affects more than 140 million people in at least 70 countries worldwide. In half the countries where arsenic pollution is now know n, it was discovered within the last 10 years..."

Ravenscroft, 2007

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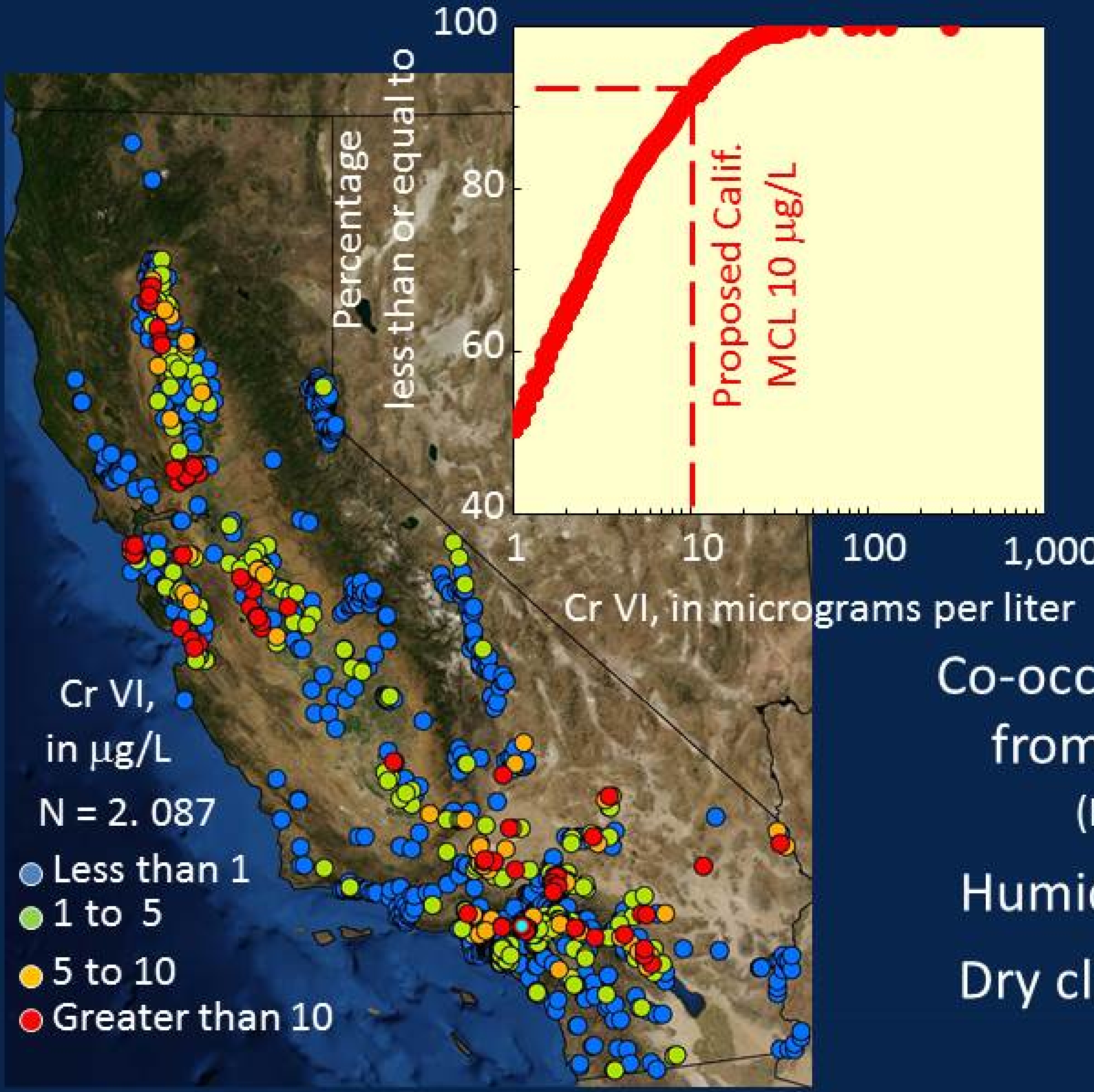
Chromium (Cr VI) in California's groundwater



California DPHS data

About 9 percent of wells exceed proposed California Maximum Contaminant Level

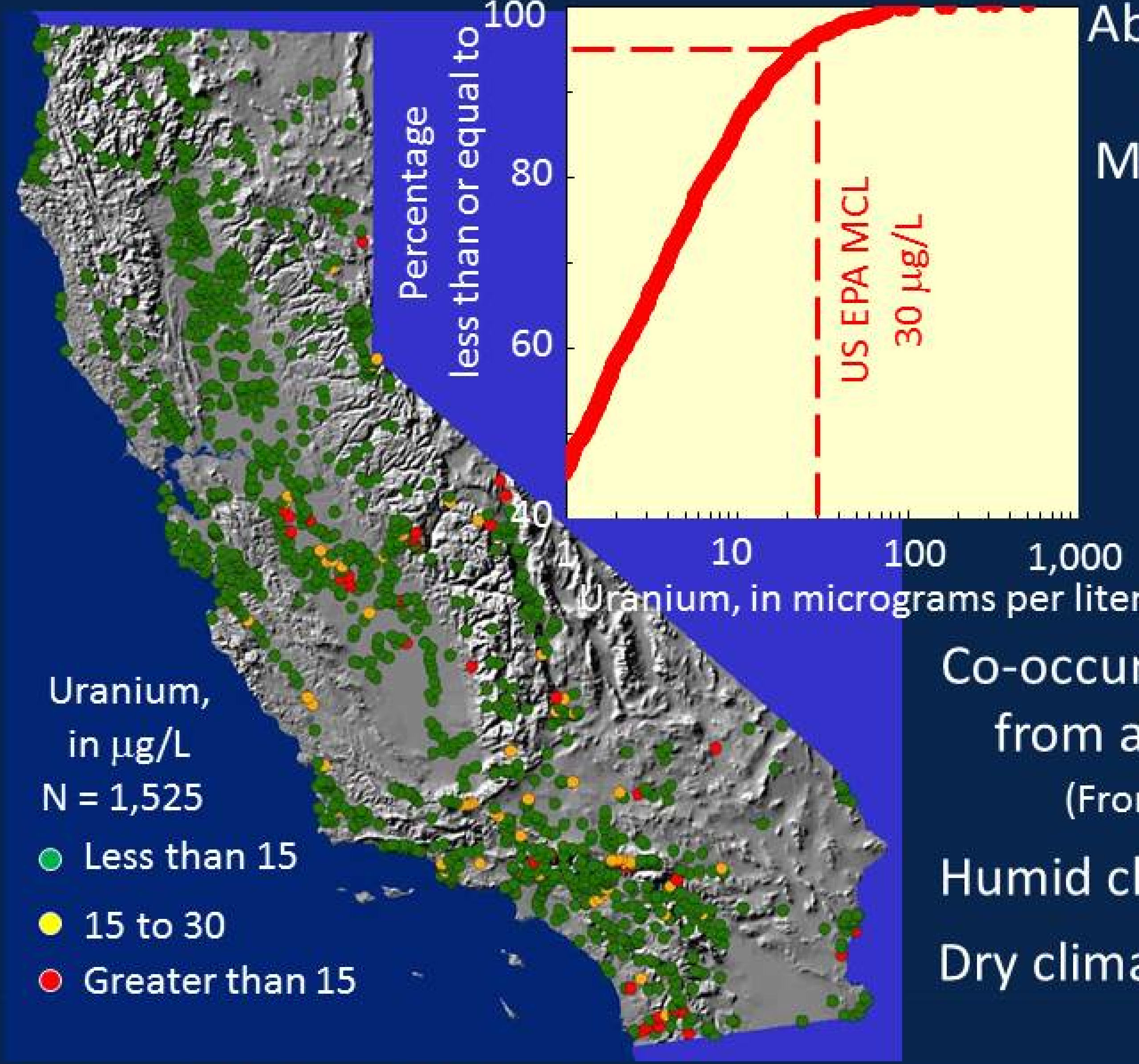
Co-occurrence in groundwater from alluvial aquifers (US)

(From Ayotte, et al., 2011)

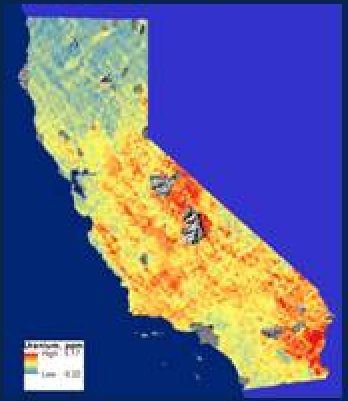
Humid climates U

Dry climates Ni

Uranium in California's groundwater



About 4 percent of wells exceed the US EPA Maximum Contaminant Level



Co-occurrence in groundwater from alluvial aquifers (US)

(From Ayotte, et al., 2011)

Humid climates Mo, Se, Cr, Cu, TDS

Dry climates Mo, As, NO_3, Cr, Cu, TDS

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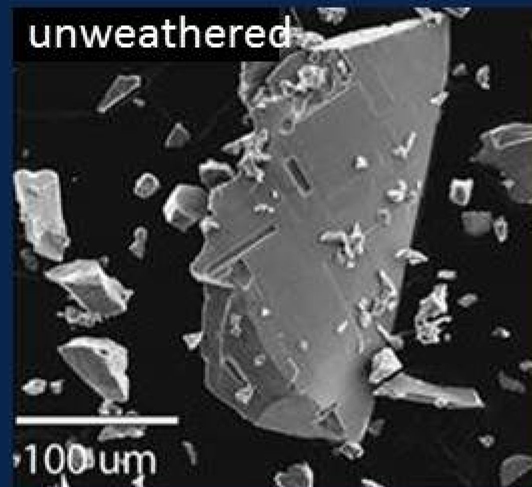
California WRCB/USGS GAMA data

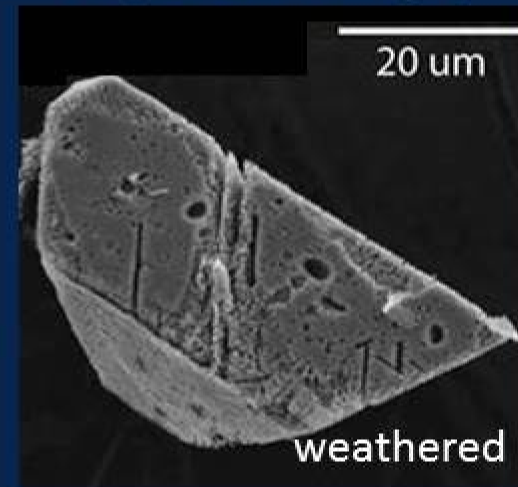
Geology and selected mineralogy

Very simplified geology

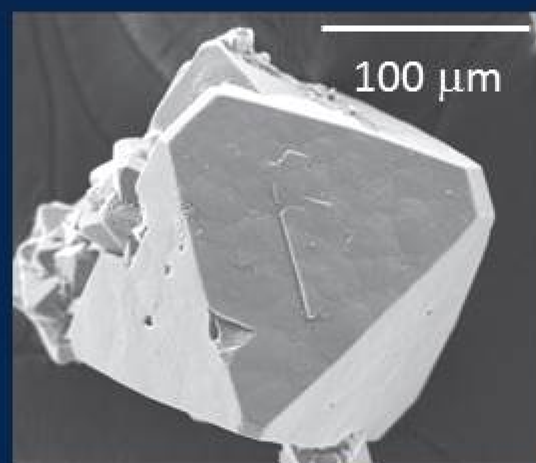
- Alluvium
- Volcanics
- Franciscan
- Granites
- Metamorphic/mafic

1. Chromium in chromite (Coast Range)

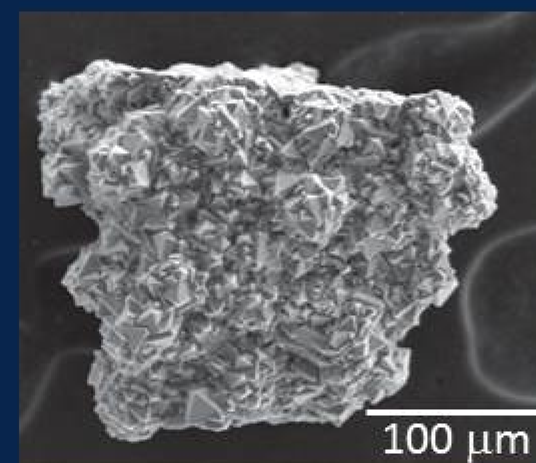




2. Arsenic in pyrite (Sierran alluvium)



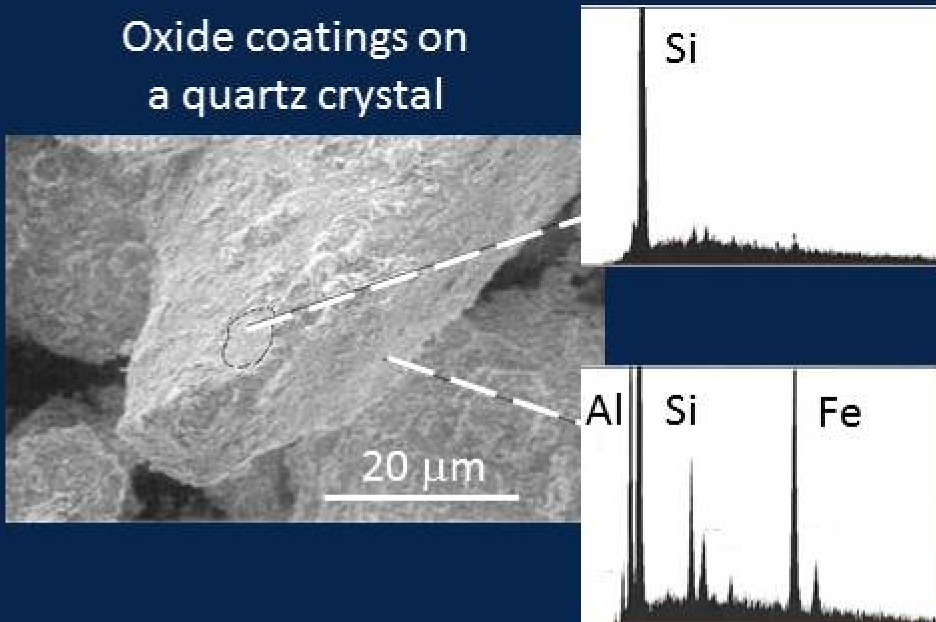
Octahedral crystal
4 percent arsenic



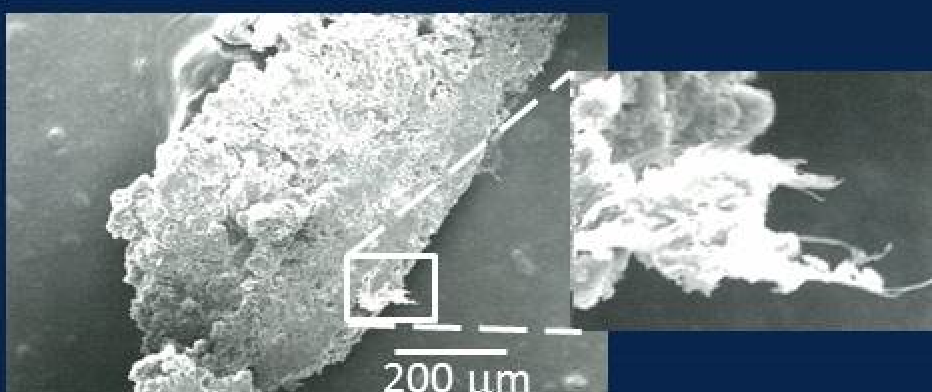
Twinned-pyritohedron crystal
0 percent arsenic

Sorption on the surfaces of mineral grains

Oxide coatings on
a quartz crystal



Iron oxide on the
surface of a mineral grain



Iron oxide rich paleosols
in unsaturated alluvium

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Sorption on the surfaces of mineral grains

Oxide coatings on
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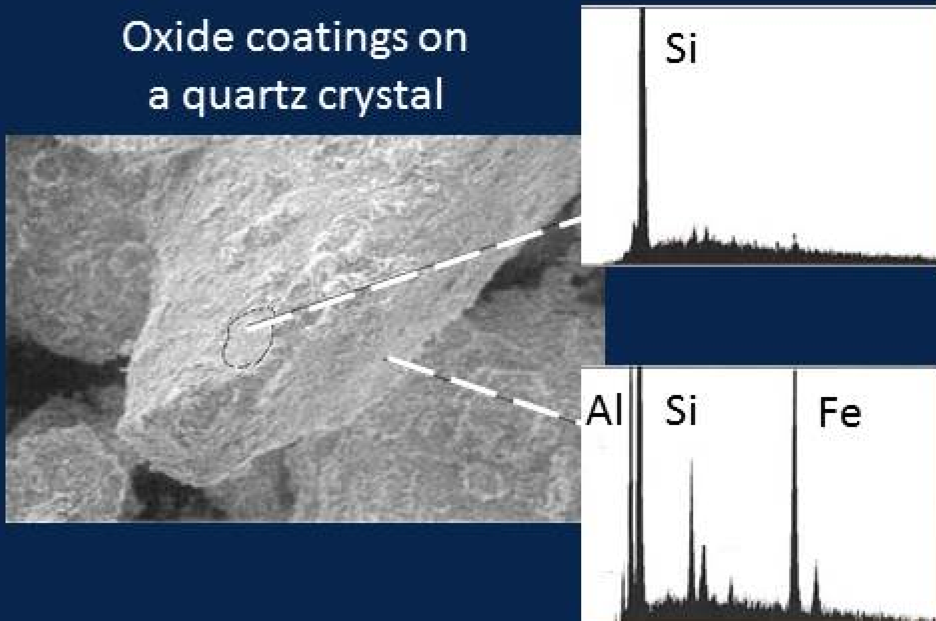
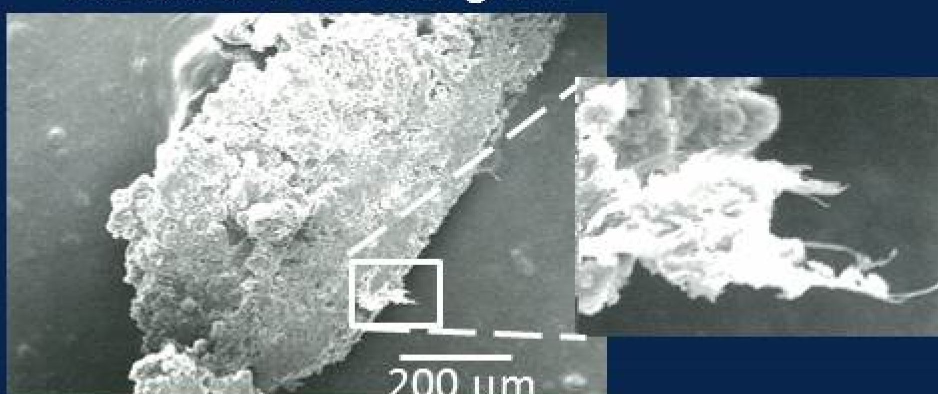
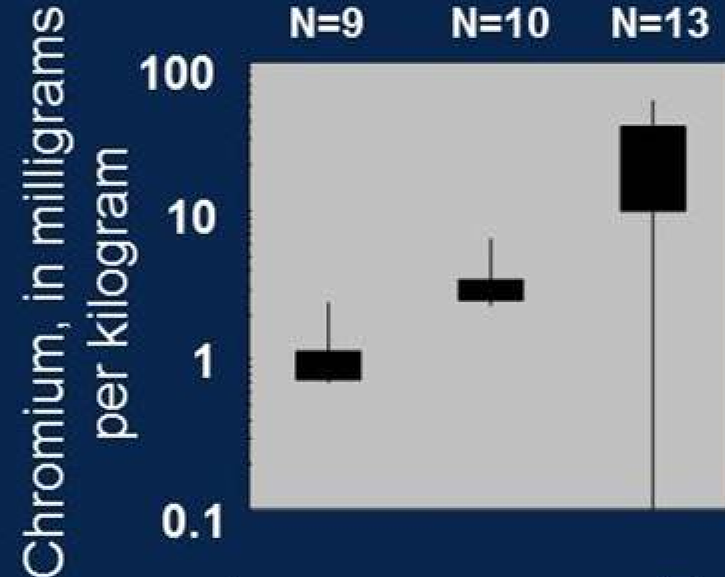


Iron oxide on the
surface of a mineral grain



Acid-extraction data



Sorption on the surfaces of mineral grains

Sorption of selected anions

Strongly sorbed ↑

OH^-

$H_2AsO_4^-$

F^-

SO_4^{-2}

CrO_4^{-2}

HCO_3^-

Cl^-

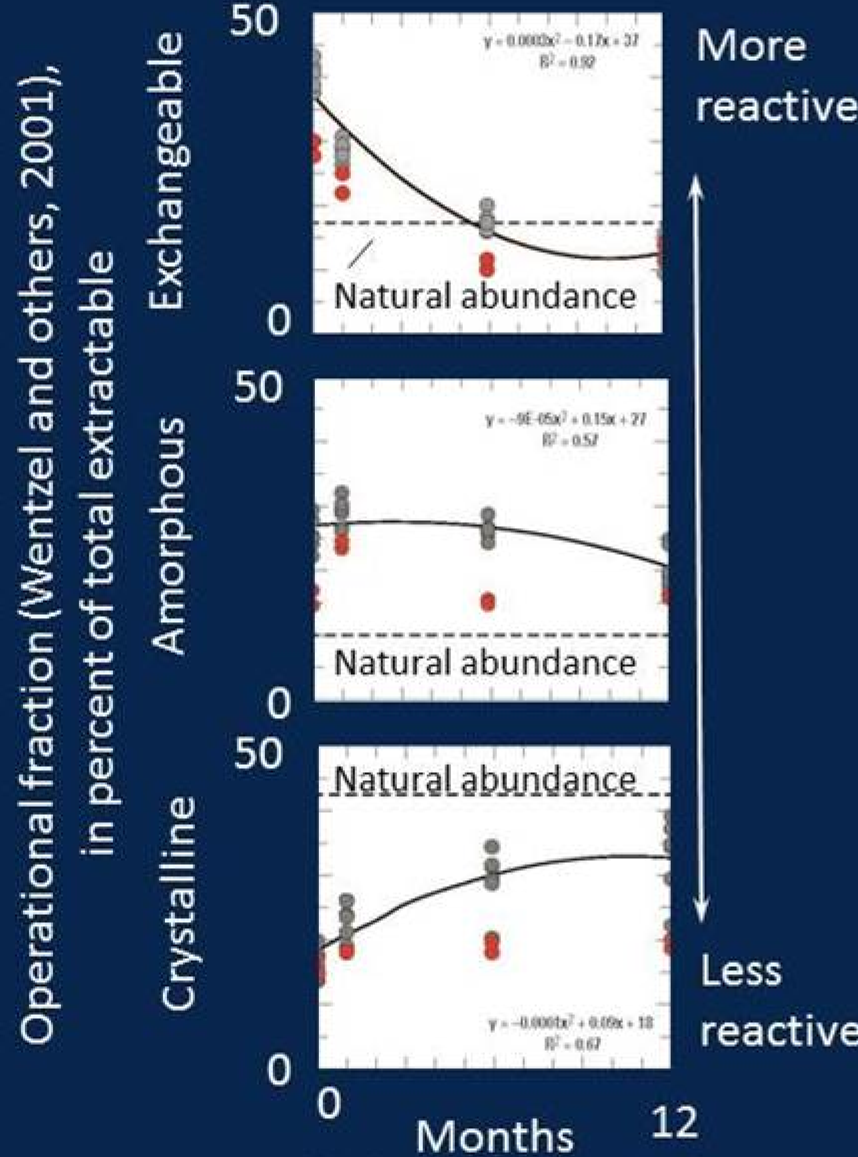
NO_3^-

Weakly sorbed ↓

(From Clifford, 1999; Trussell et al., 1980)

Sorption is pH dependent

Arsenic -73



(Izbicki and others, in review)

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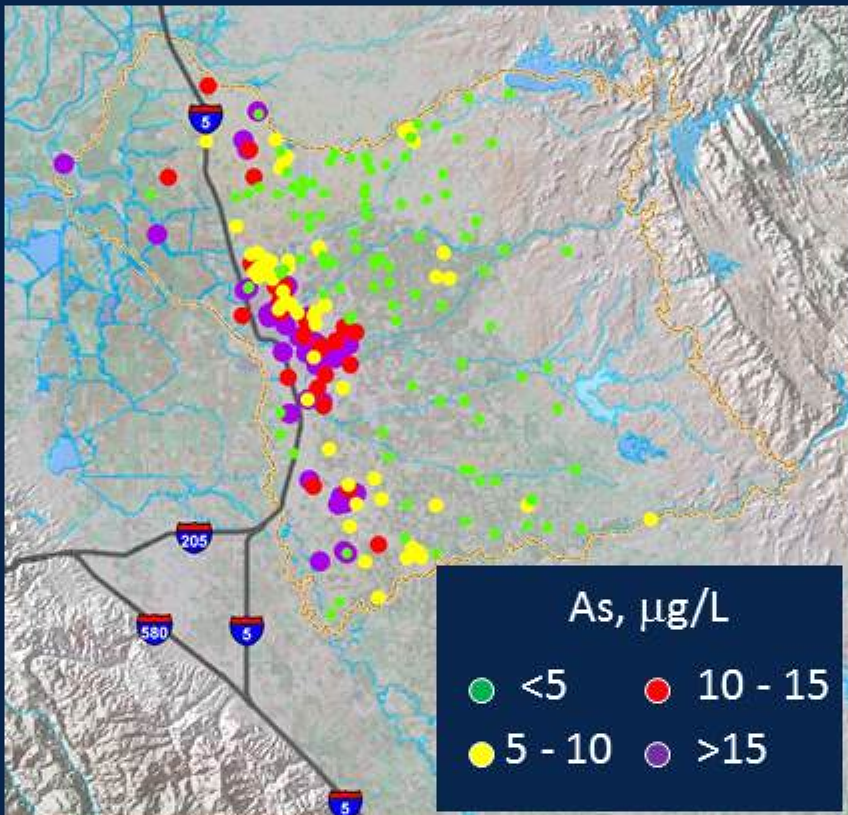
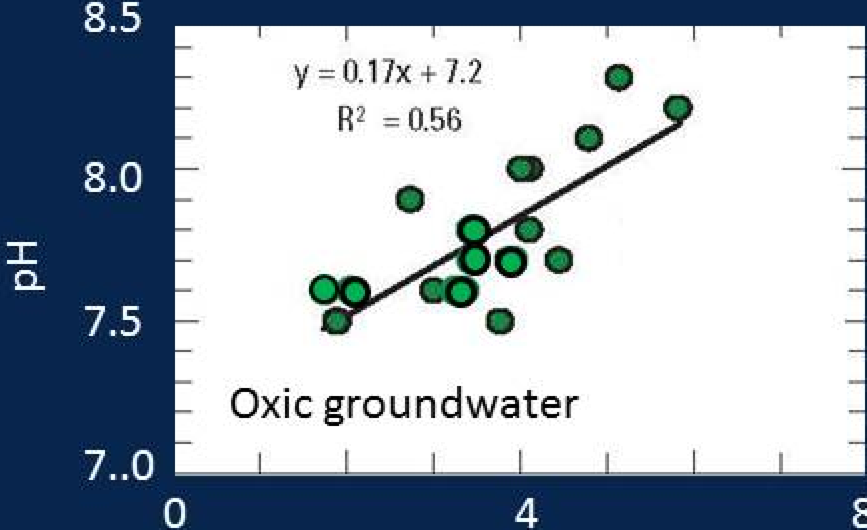
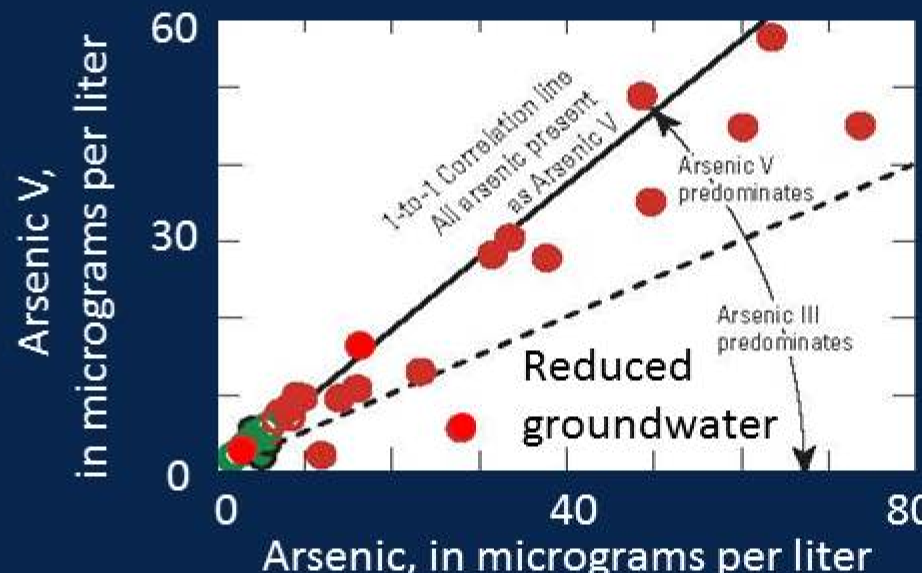
Groundwater flow, redox, and pH

Northeastern San Joaquin Groundwater Subbasin







Changes in dissolved oxygen and redox affect spatial and depth distribution of trace elements

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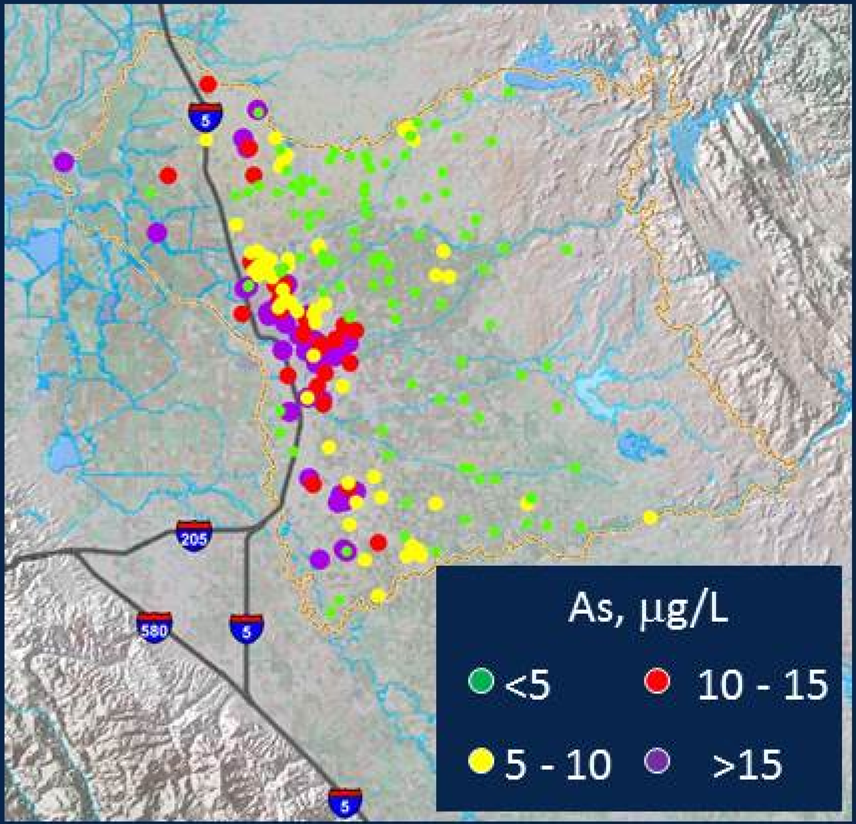
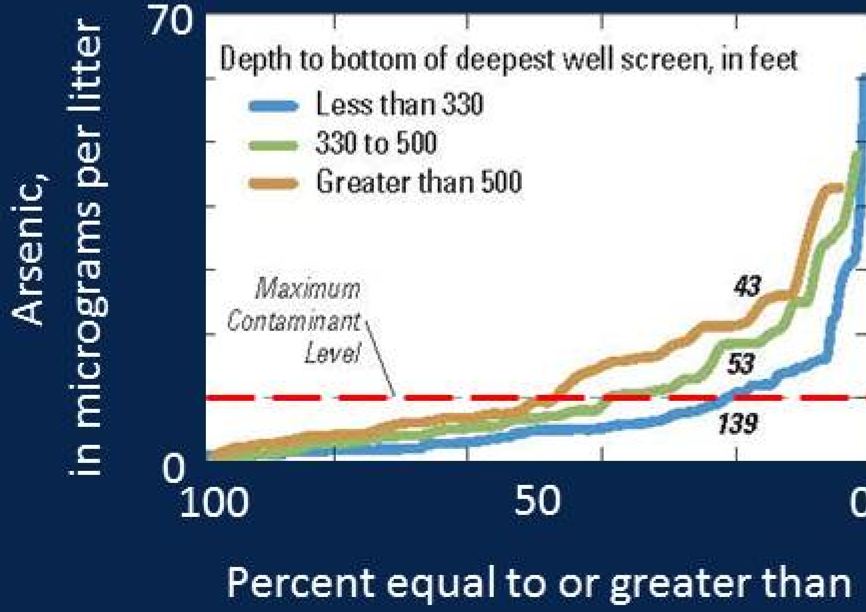


Changes in dissolved oxygen and redox affect spatial and depth distribution of trace elements

Arsenic concentrations with depth



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Groundwater flow, redox, and pH

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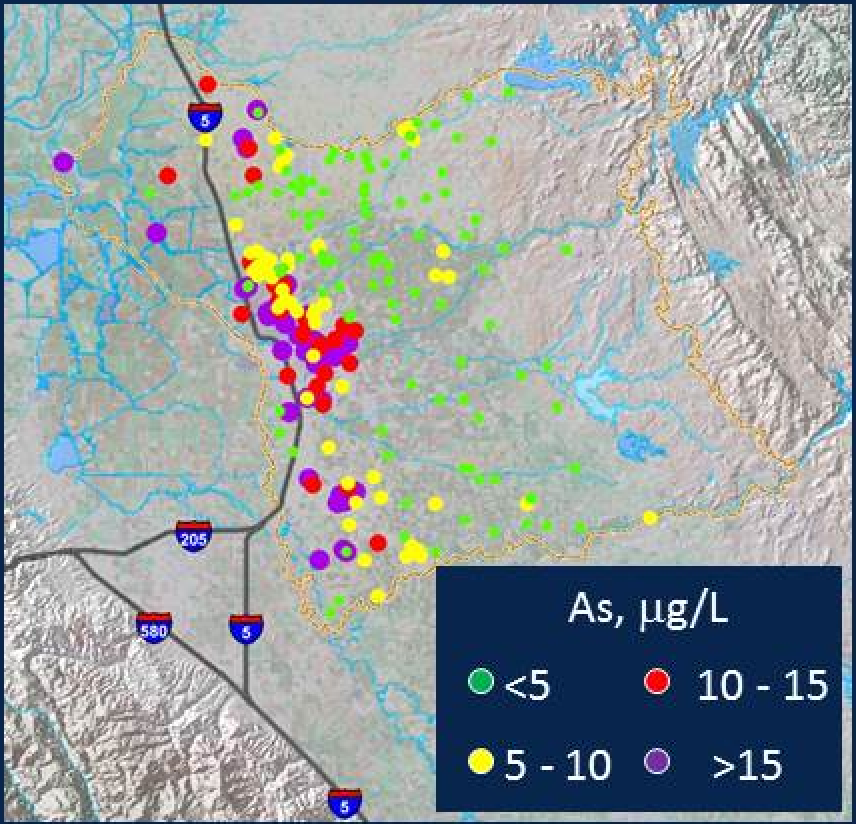
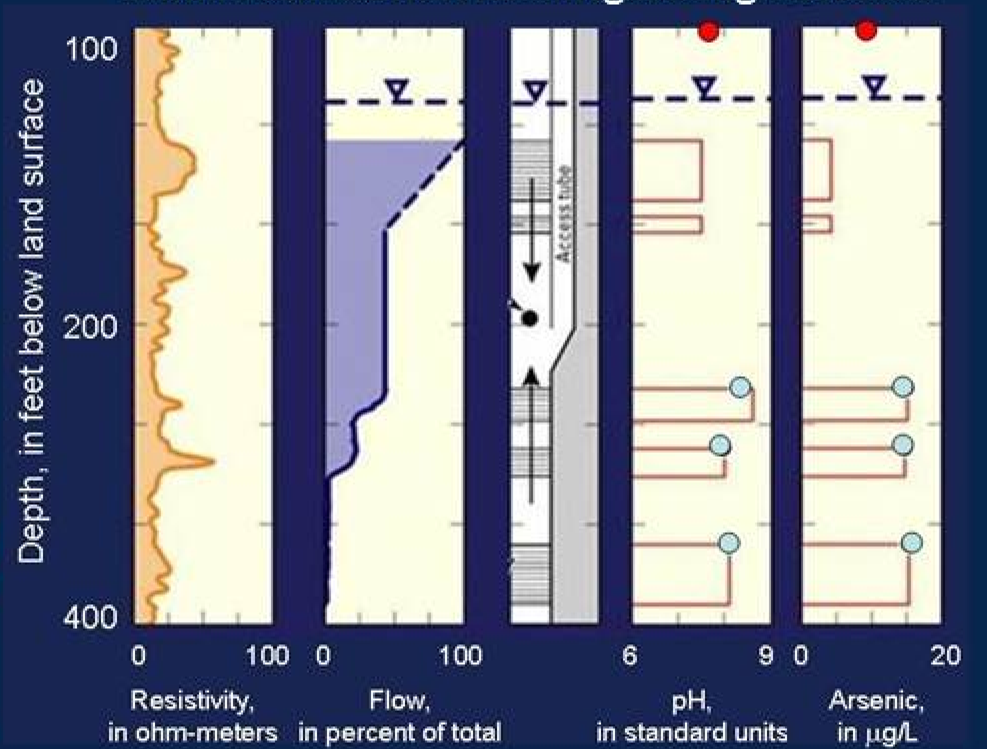
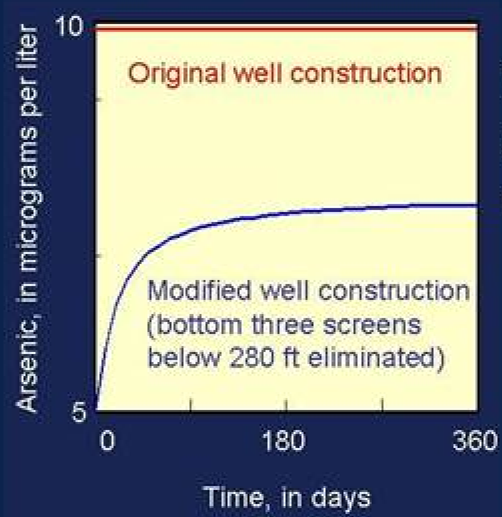


Changes in dissolved oxygen and redox affect spatial and depth distribution of trace elements

Well modification to mitigate high arsenic





Numerical simulations at the well-bore scale to predict results

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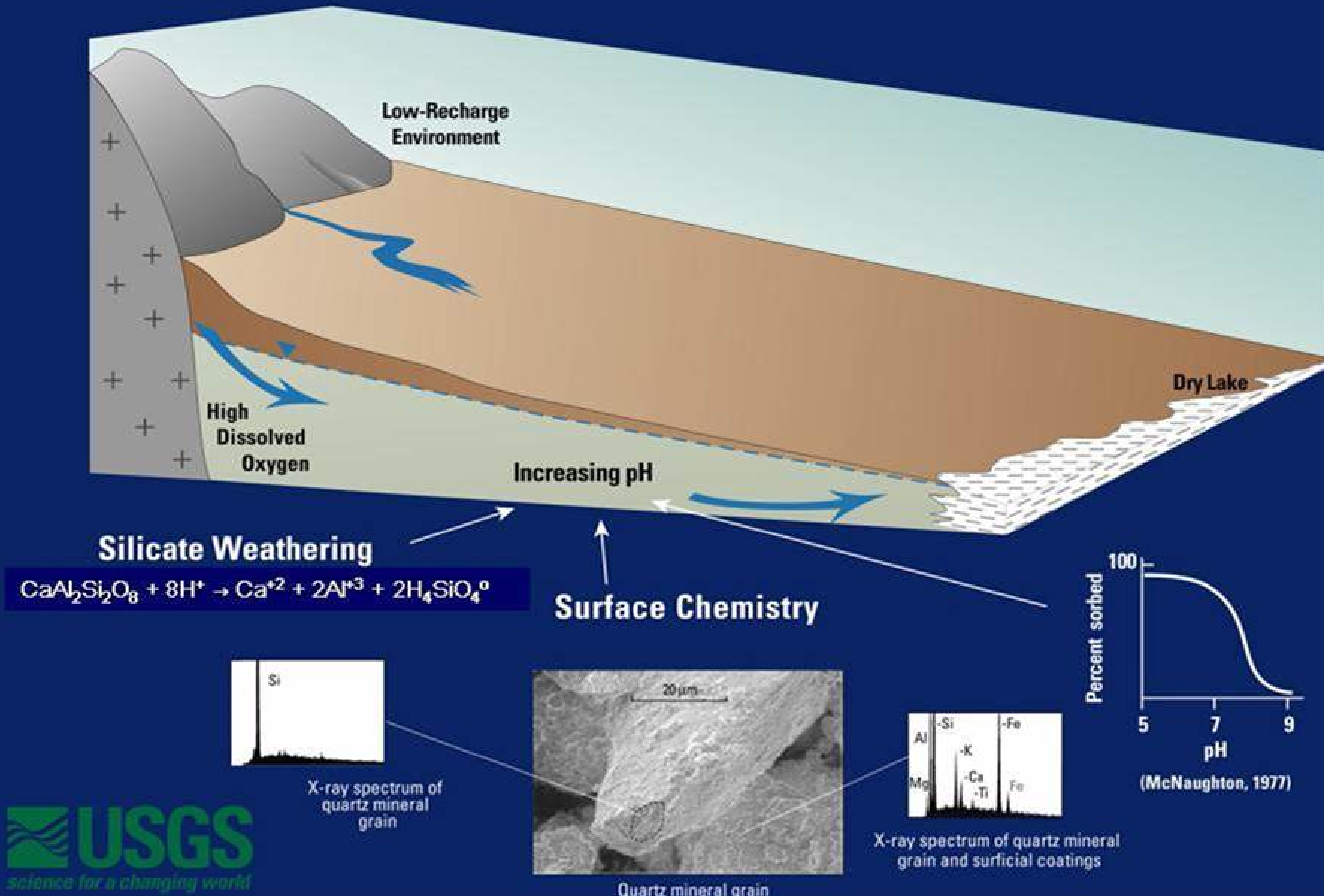
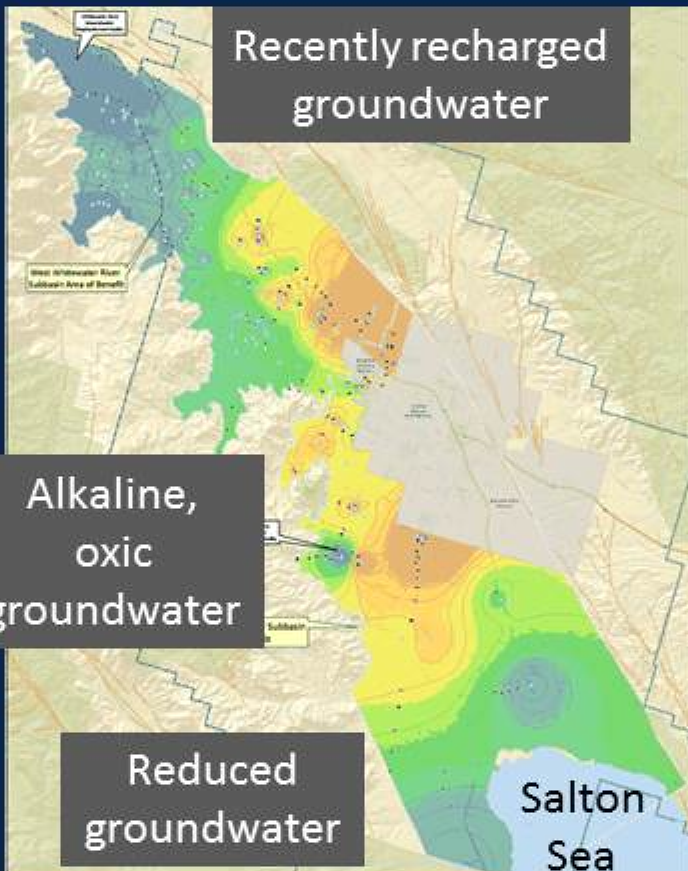
Groundwater flow, redox, and pH



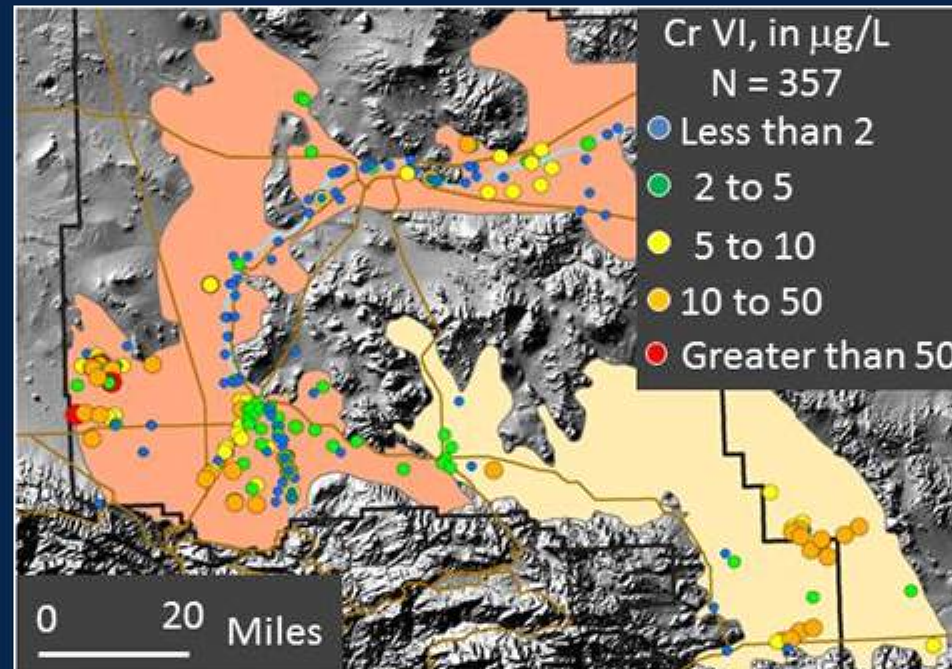
Groundwater flow, redox, and pH

Simpler regional flow systems



Coachella Valley
Groundwater Basin
(From Coachella Valley Water District)

More complex
regional flow systems



Mojave River
Groundwater basin
(From USGS and Mojave Water Agency data)

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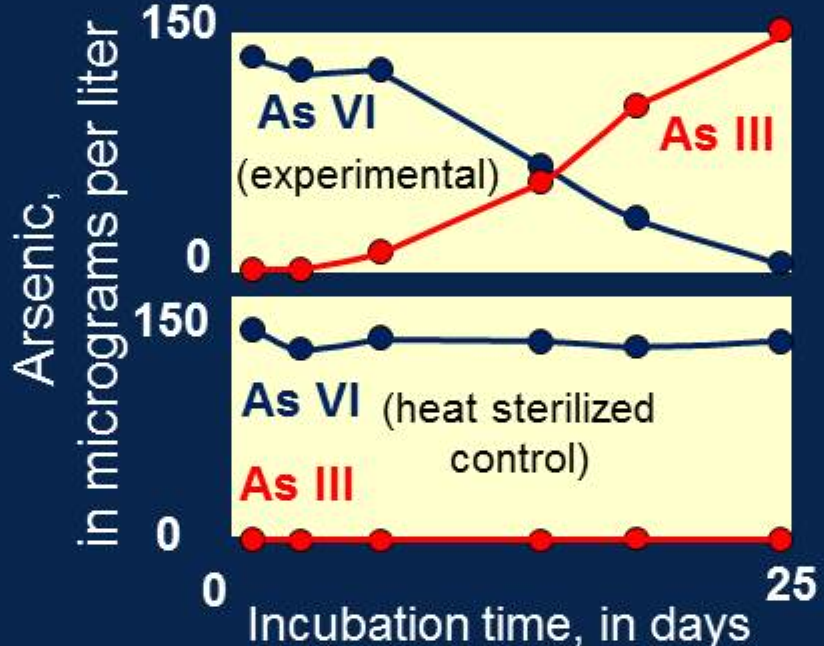
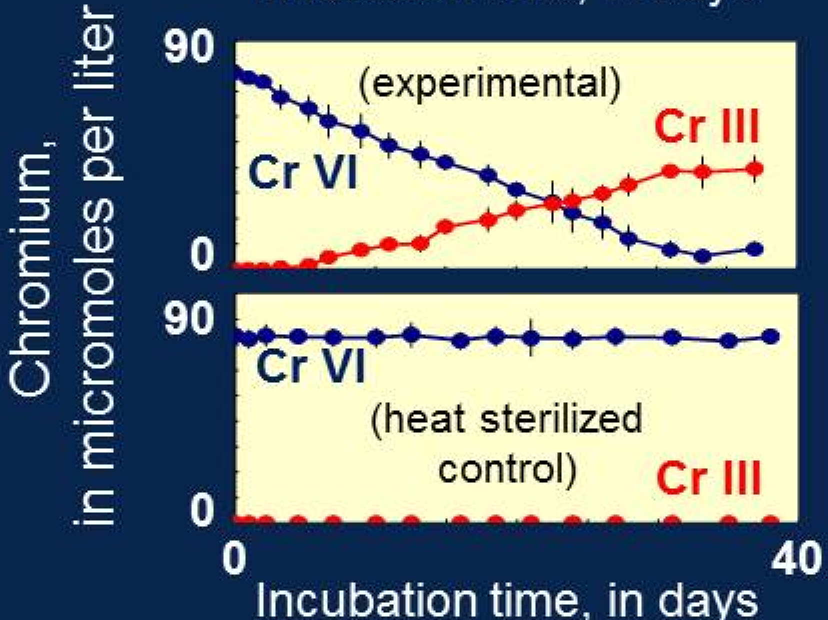
Microbiology—reduction of oxidized forms



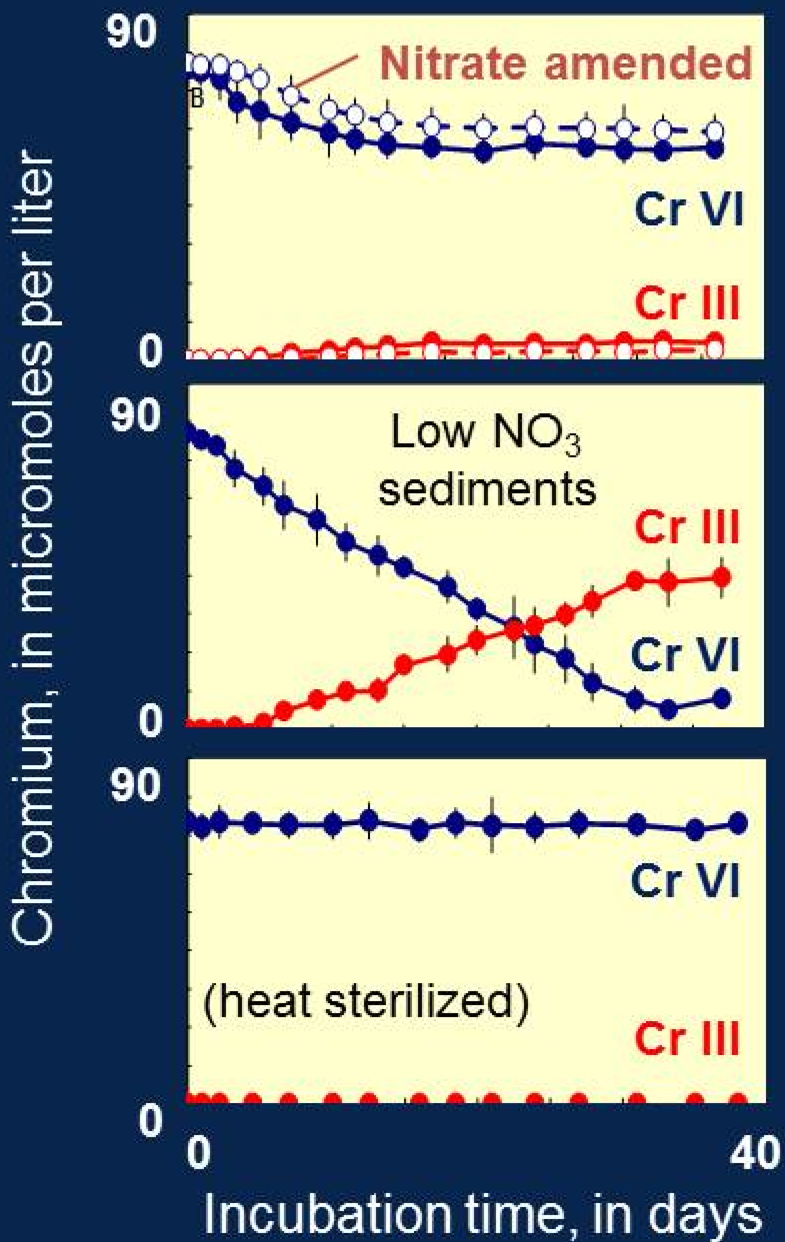


Gibbs free energy (ΔG^o)
coupled to hydrogen oxidation

Reaction	ΔG^o (kJ/mol e^-)
Manganese reduction	-94.06
Nitrate reduction	-86.44
Chromate reduction	-45.02
Iron reduction	-43.89
Arsenate reduction	-36.98
Sulfate reduction	-0.42
Methanogenesis	+0.67

(From Ahmann, 1997; Thauer, 1977; Nordstrom and Archer, 2003)

Microbiology—reduction of oxidized forms



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(From Ahmann, 1997; Thauer, 1977; Nordstrom and Archer, 2003)

Isotope geochemistry

- No naturally occurring isotopes of arsenic
- Four naturally occurring-stable isotopes of chromium
  - Best suited for process-oriented work
- There is no silver-bullet that will allow you to dispense with sound hydrology and geochemistry

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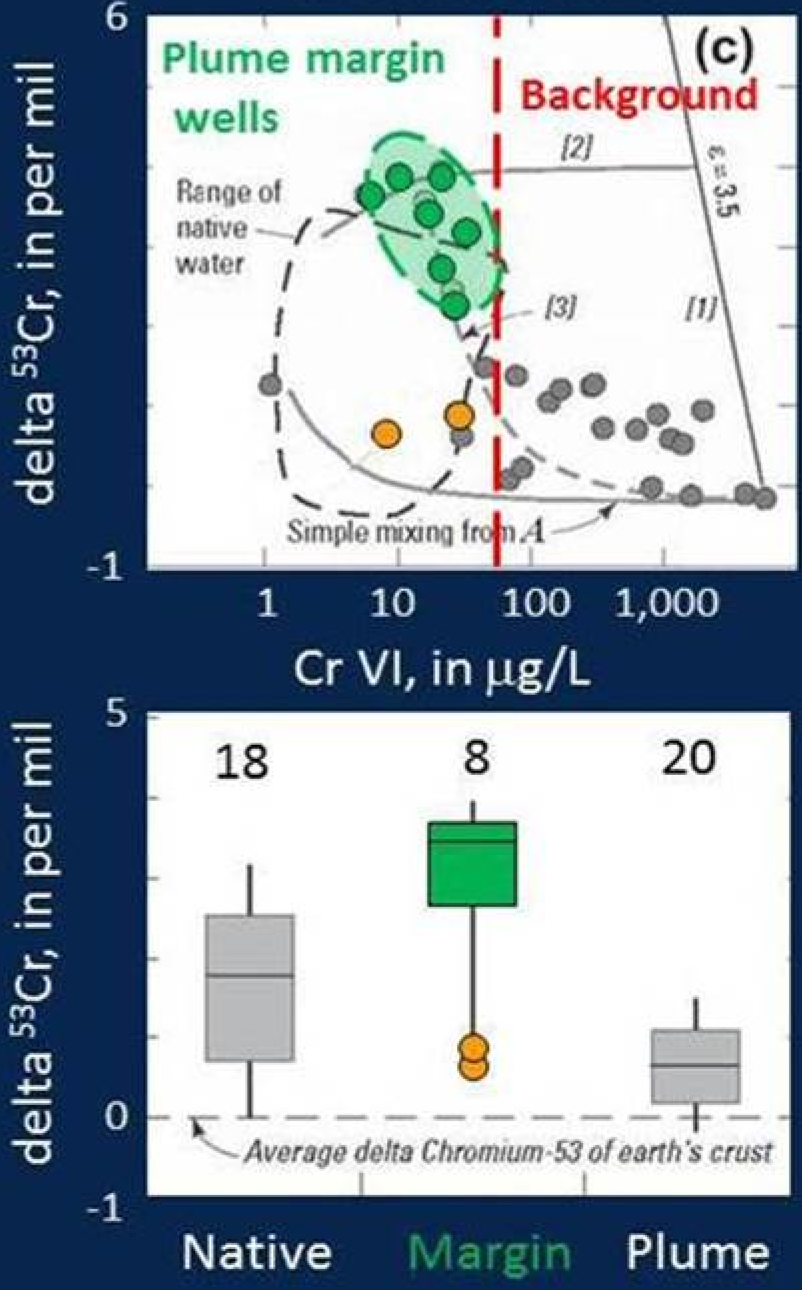
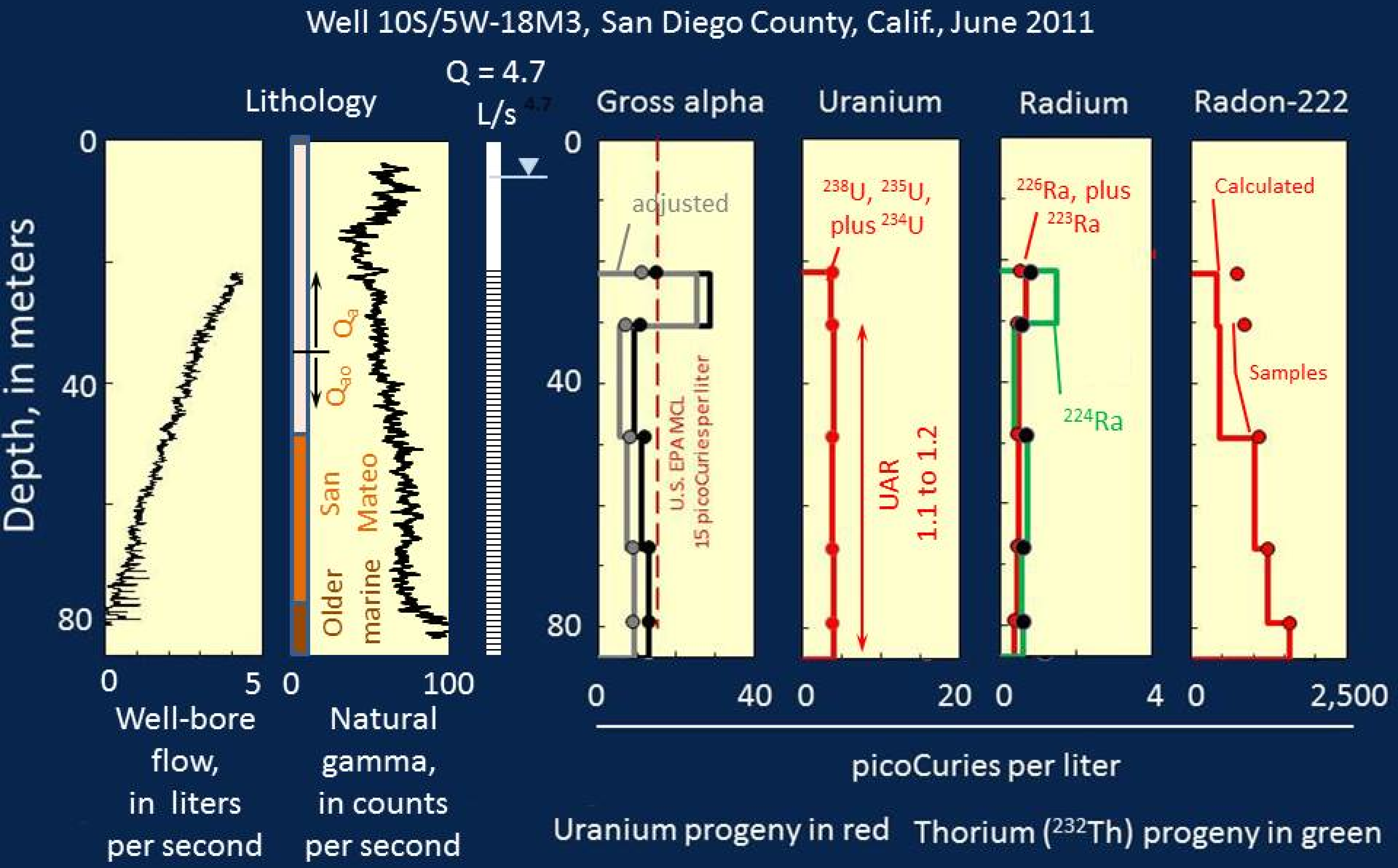
Topock, CA
(Izbicki and others, 2012)

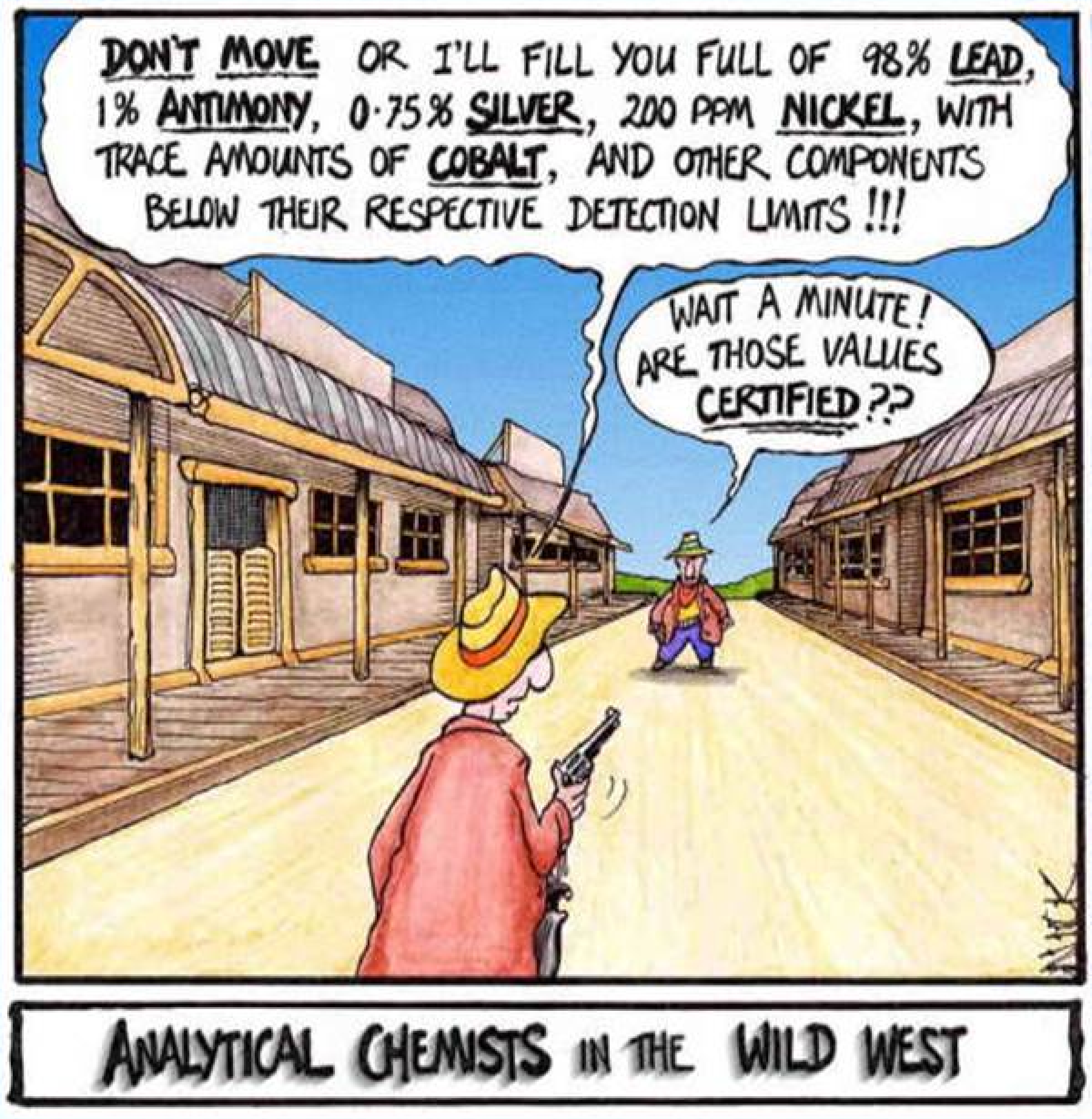


Isotope geochemistry

"All that glitters is not gold" and all that is radioactive is not uranium



Just a little more fun with trace elements



High frequency of occurrence of trace elements in California's groundwater with respect to MCL's and other health-based standards

U.S. EPA CCL-3
(Contaminant Candidate List)

- Cobalt
- Molybdenum
- Strontium
- Vanadium

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