Antimony in the New Zealand environment

Antimony minerals and Sb environmental mobility

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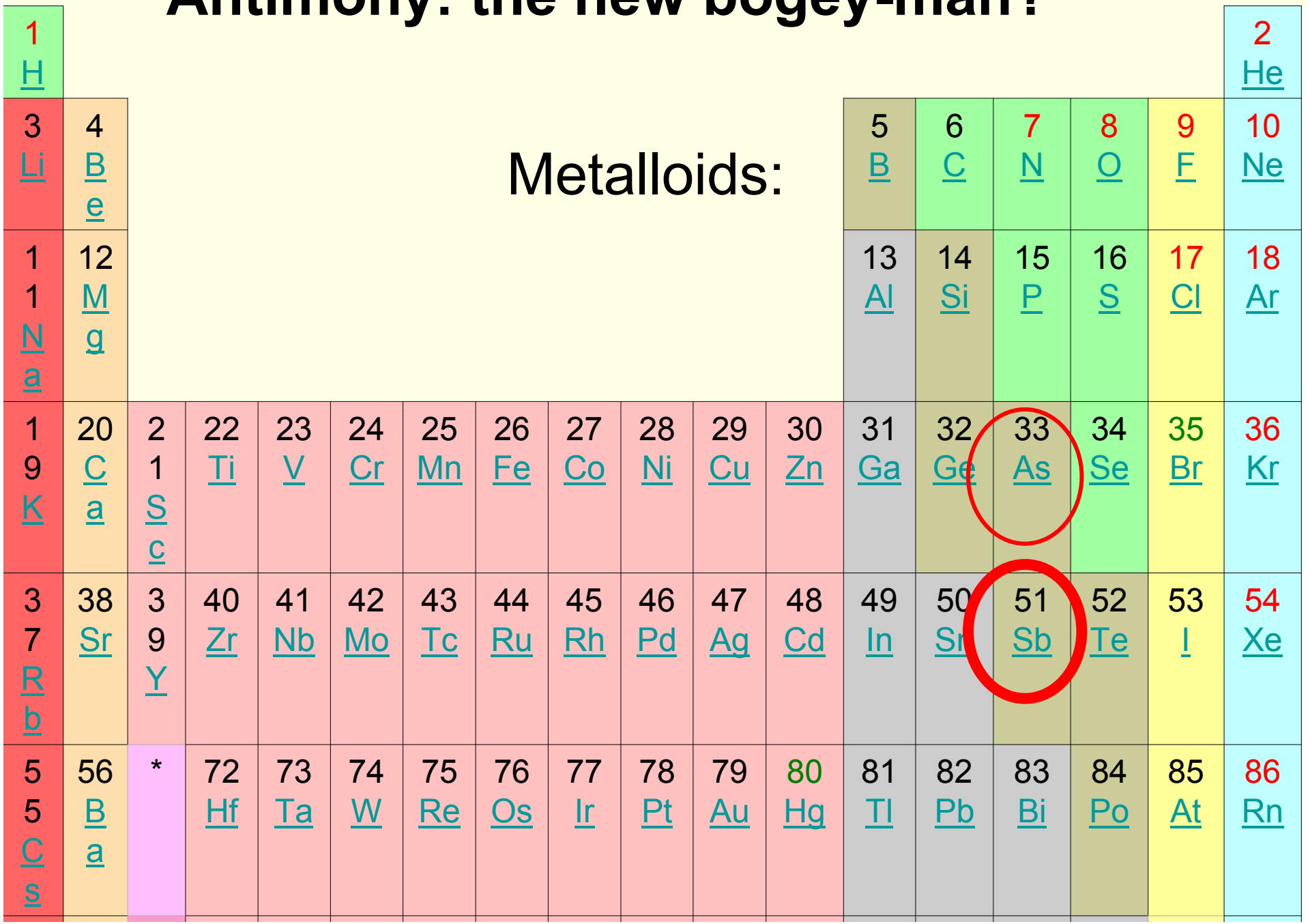
Principal topics

- Introduction to Sb
- Point sources: geothermal and mines
- Sb minerals and solubility
- Sb mobility in the environment
- Arising Sb environmental issues

Antimony: the new bogey-man?

Metalloids:



Chemical behaviour

Antimony

- Sb^{3+}, Sb^{5+}
- Forms oxyanions
- Widely used historically
- No nutritional use in humans
- Highly toxic to humans (mimics P)

Arsenic

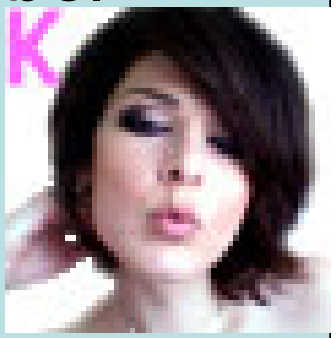
- As^{3+}, As^{5+}
- Forms oxyanions
- Widely used historically
- No nutritional use in humans
- Highly toxic to humans (mimics P)

Historic usage

- Water containers in Ancient Egypt
- Cosmetics, especially eye-shadow

  Ancient Egyptians, Queen of Sheba, Jezebel

  Still used in Middle East (="kohl", Pb-rich)



- Black pigment for paint

  (cf As in wallpaper pigments)
- Medical, e.g., Tartar emetic (K-Sb tartrate)

  (cf As widely used for skin conditions etc)
- Alchemy

  (As was a more common reagent)

Current usage

- Flame retardants in plastics etc:
  Sb_2O_3 (2-3%) with halogens
  (about 50% of total Sb production)
- Catalysts in plastic production
  (e.g., Sb-triacetate for PET)
- Alloys, especially with Pb: hardens metals
  (e.g., batteries; solder)
- Electronics (pure Sb metal)

Sb in global human environment

- Drinking water limit set very low:

  WHO and NZ: 20 ppb

  US EPA: 6 ppb (As = 10 ppb)
- Mining areas: up to 100 ppb
- Leach Sb, Pb from plumbing: MoH recommends running off first 500 mls
- PET bottles: leach up to 1 ppb Sb
- Stibine (SbH_3) from mattresses implicated in cot deaths (controversial)

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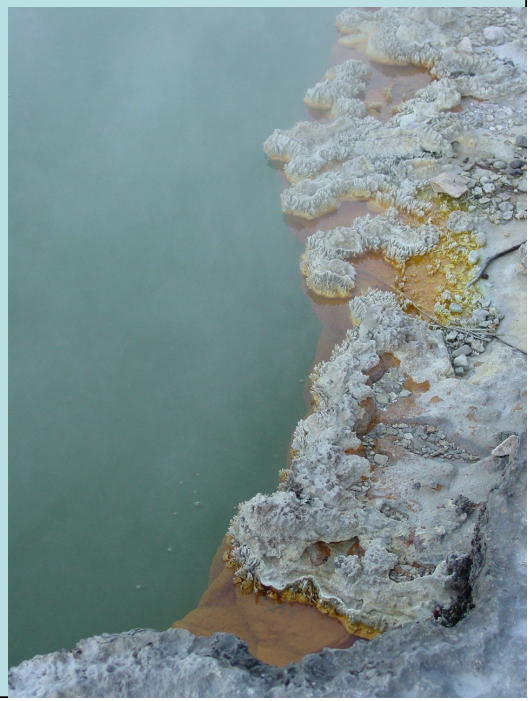
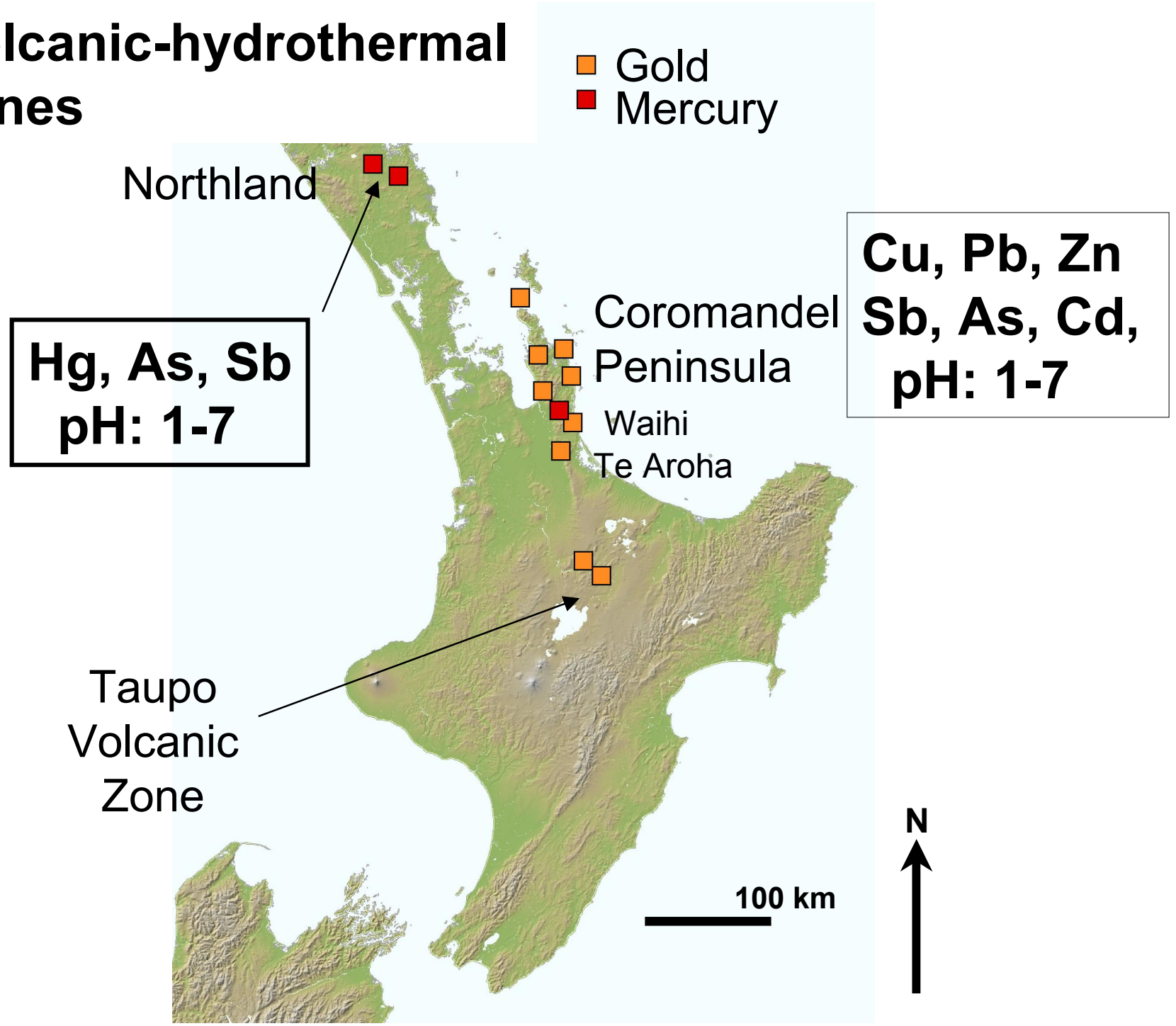
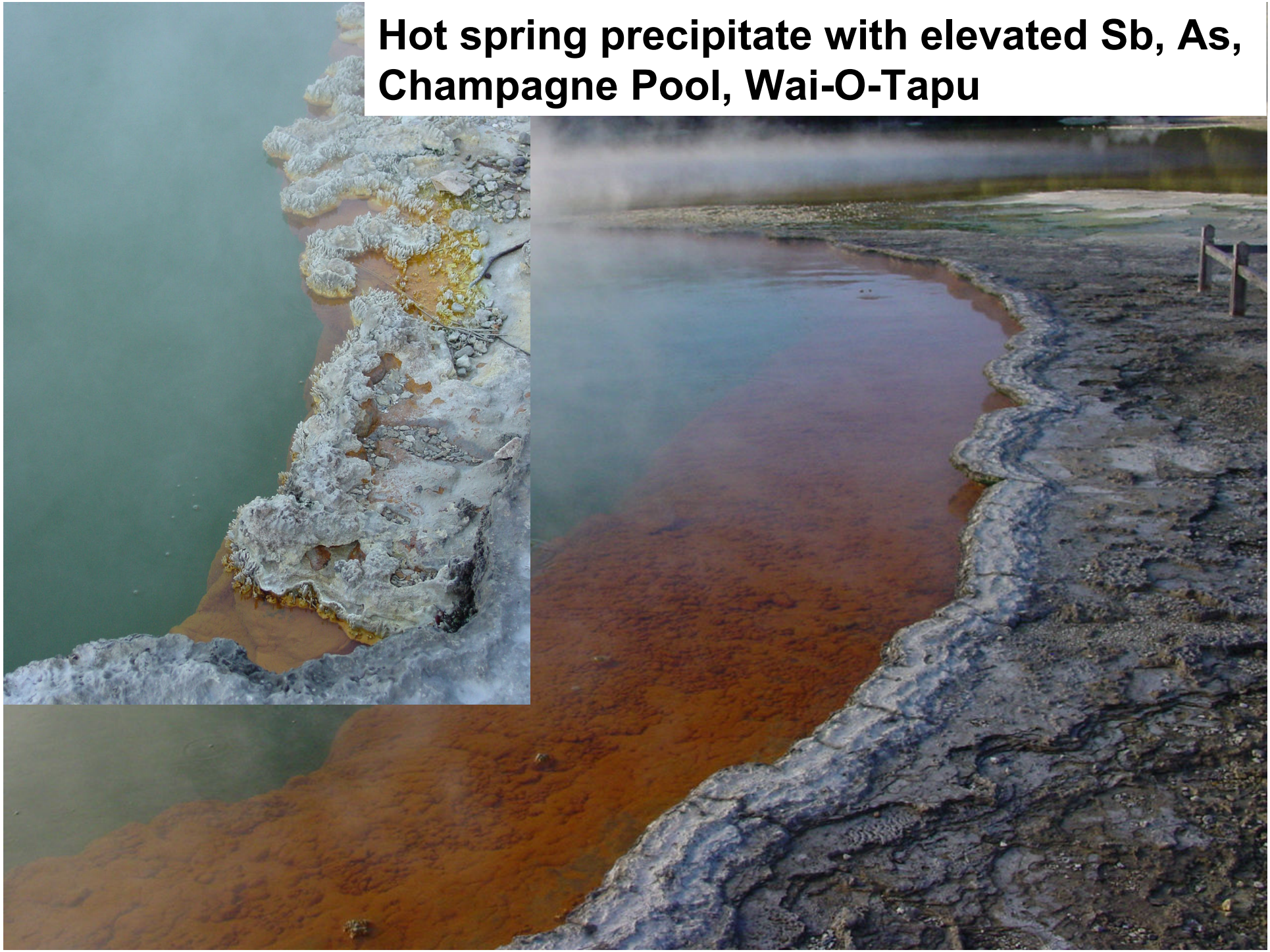
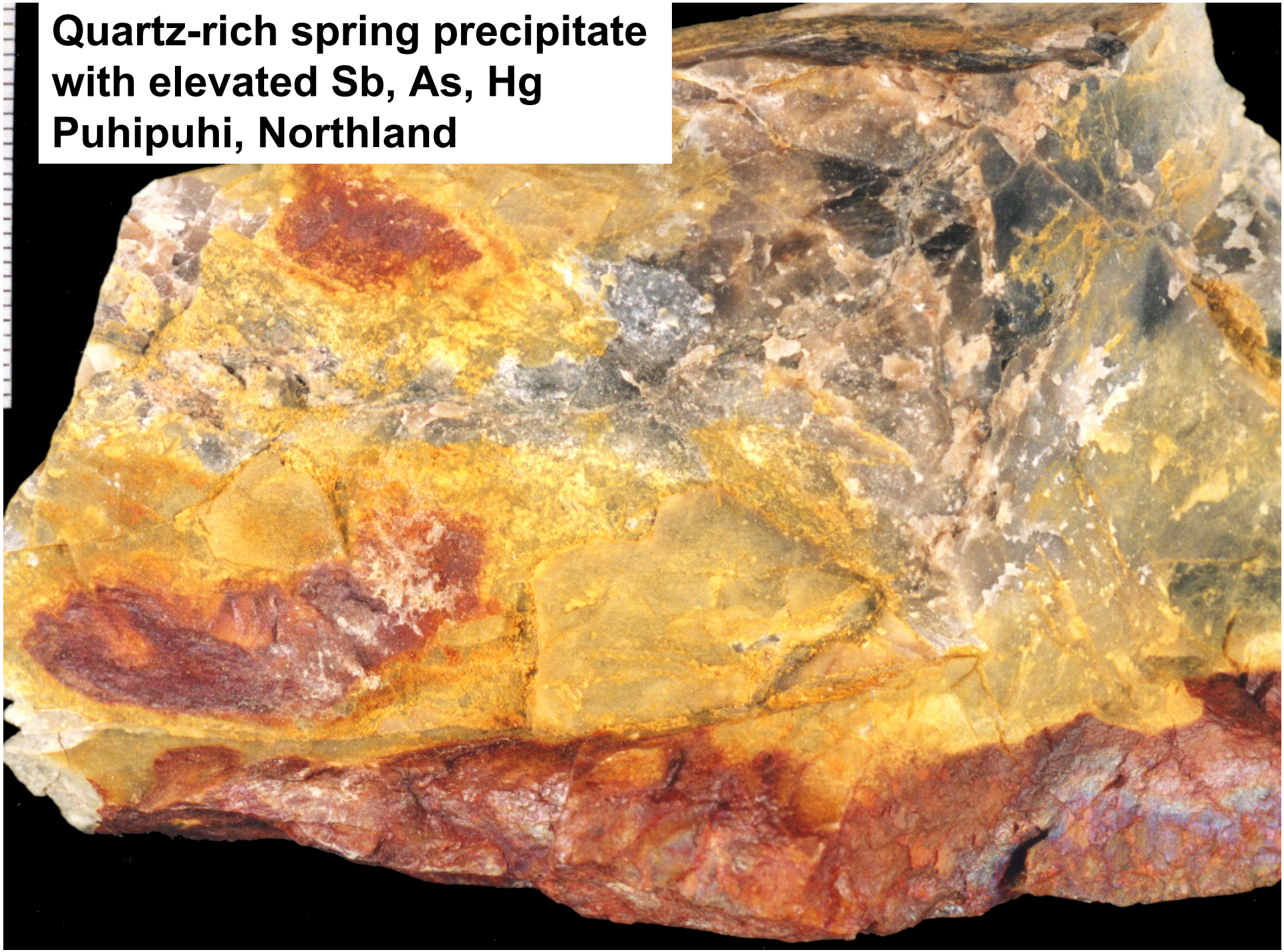


Volcanic-hydrothermal zones



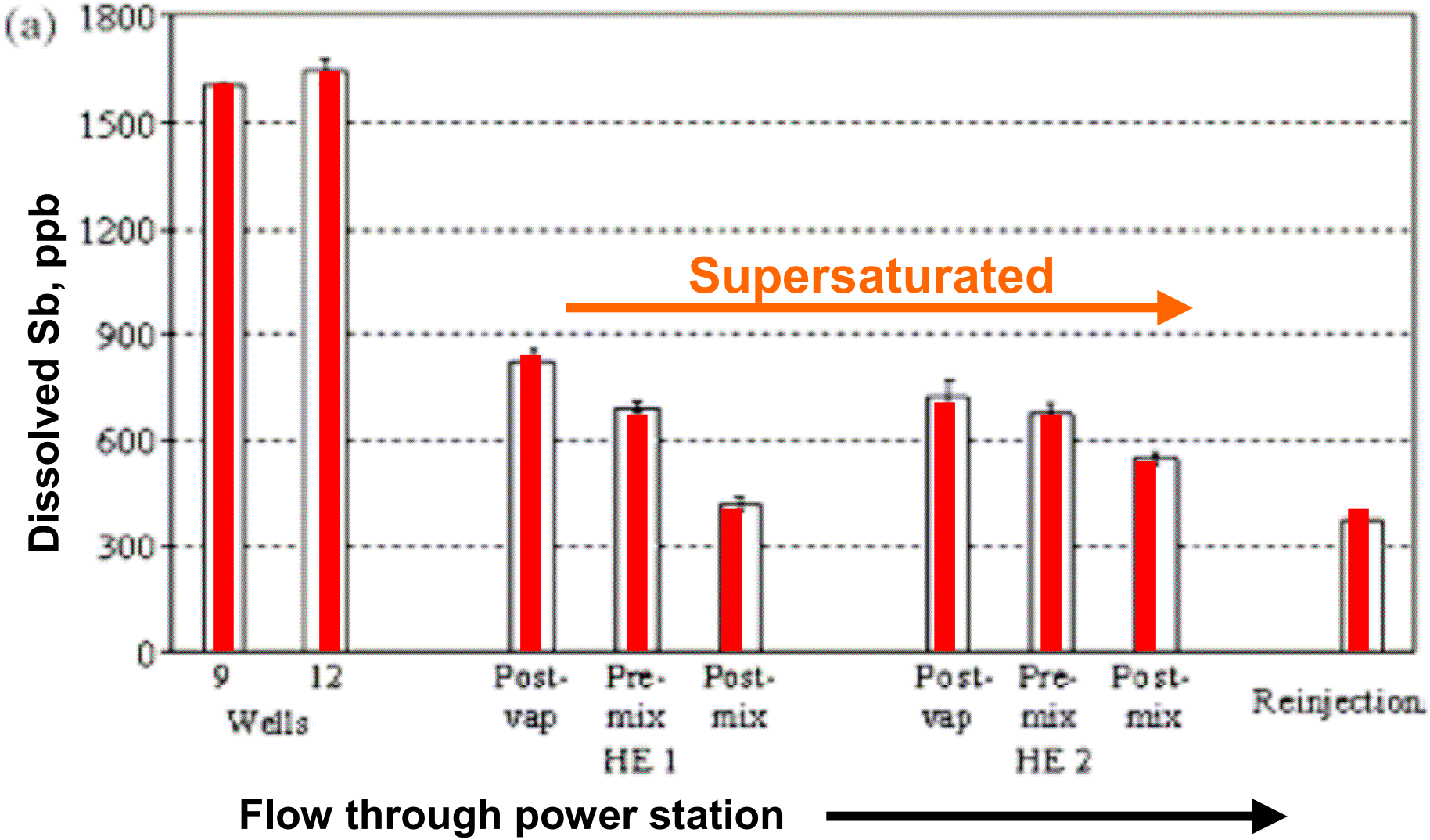
Hot spring precipitate with elevated Sb, As, Champagne Pool, Wai-O-Tapu



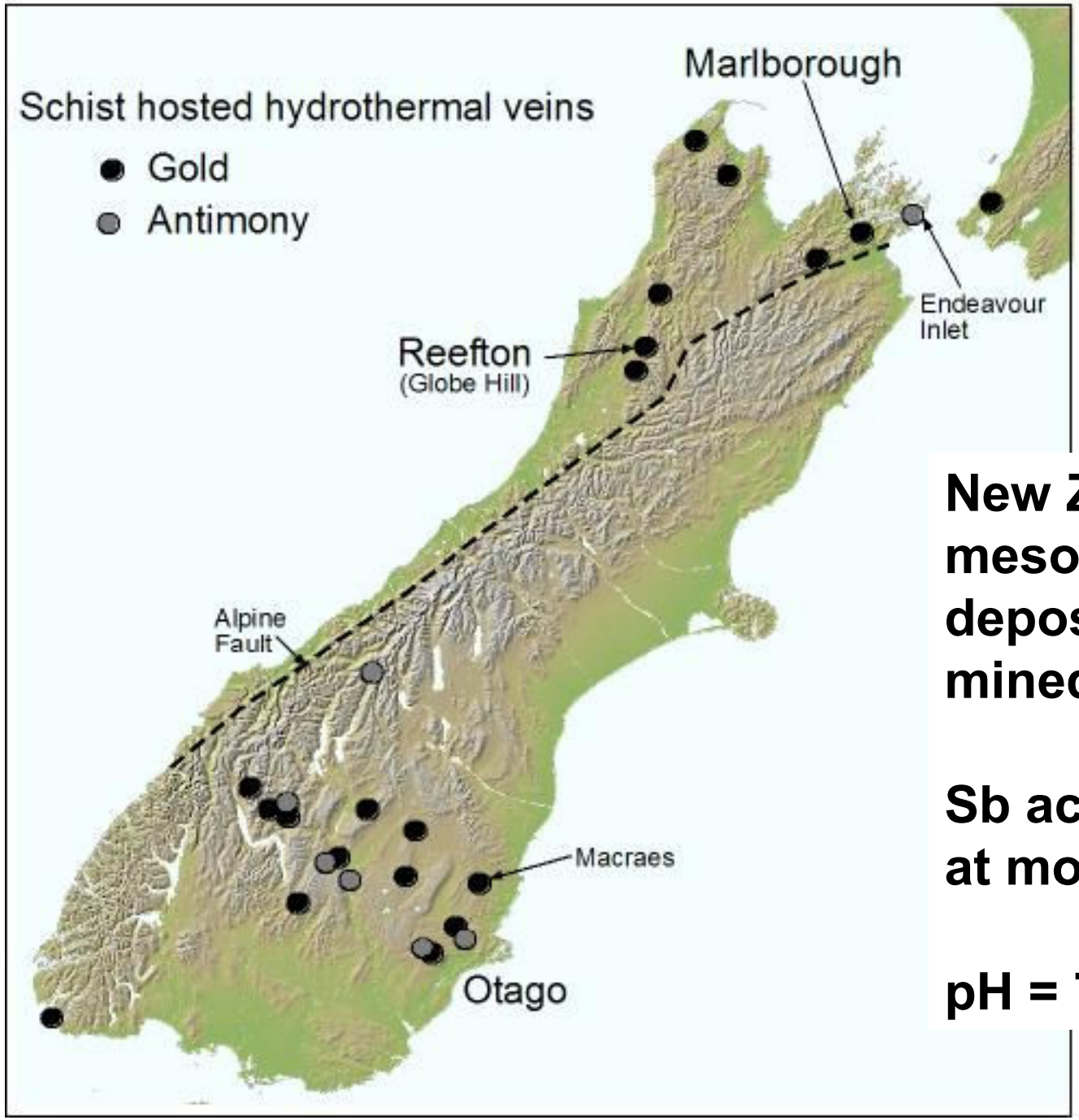

Quartz-rich spring precipitate
with elevated Sb, As, Hg
Puhipuhi, Northland

Hot spring depositing Hg,Sb,As in sediments, Ngawha, Northland

Dissolved Sb through Ngawha geothermal power station



Wilson, Webster-Brown & Brown 2007



New Zealand mesothermal Sb deposits, some mined historically

Sb accompanies Au at most sites

pH = 7

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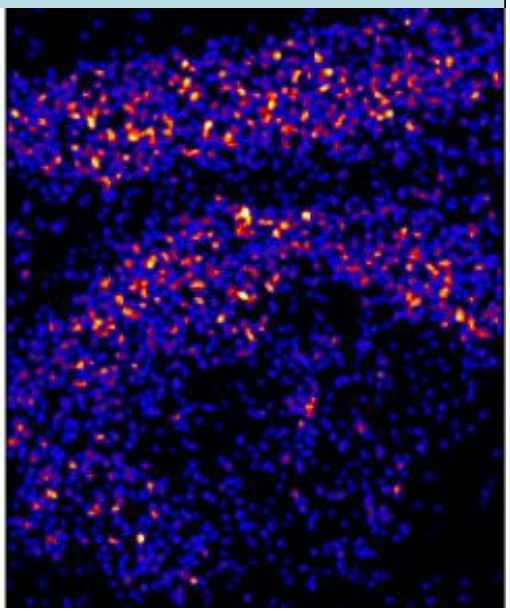
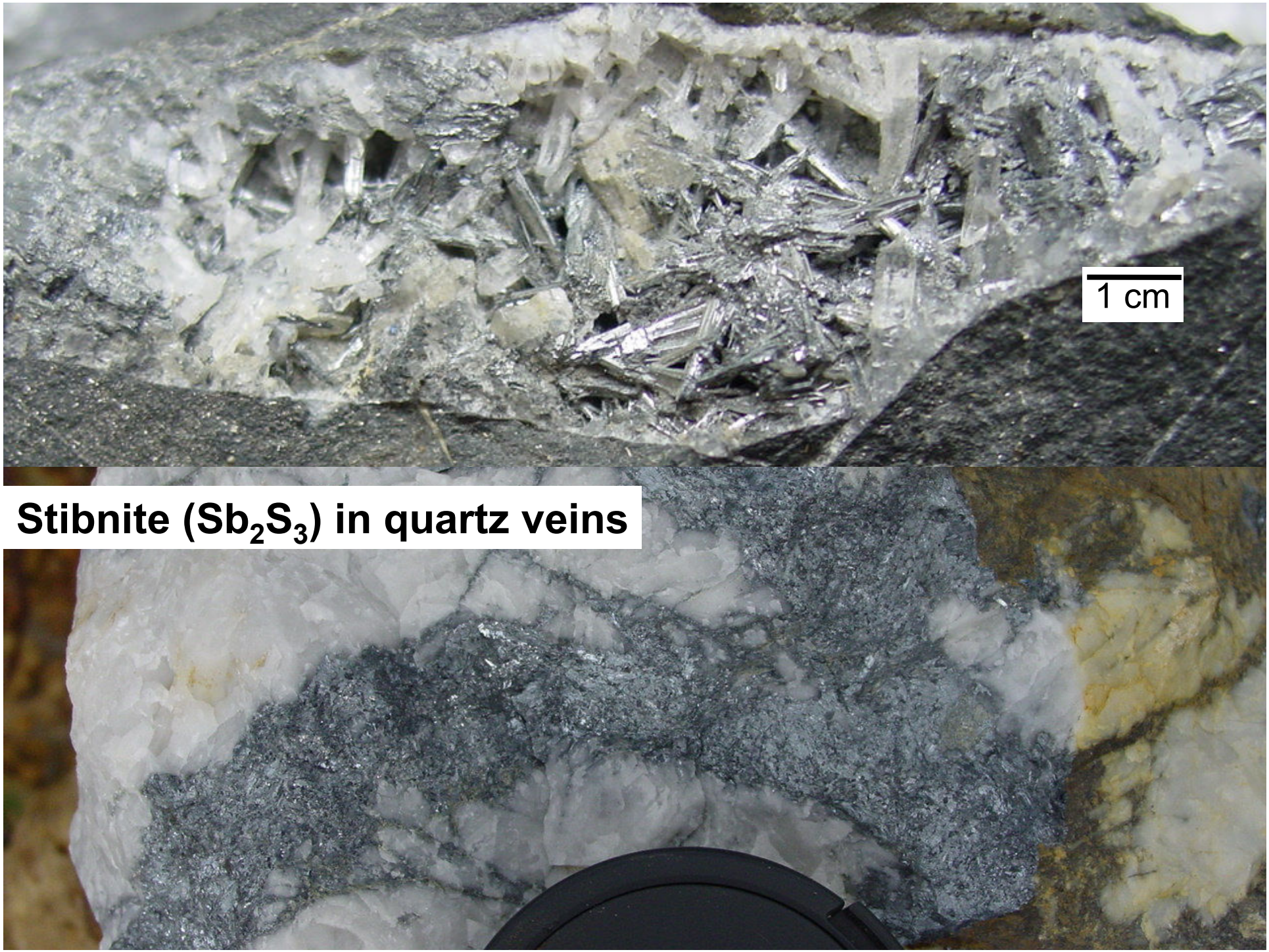
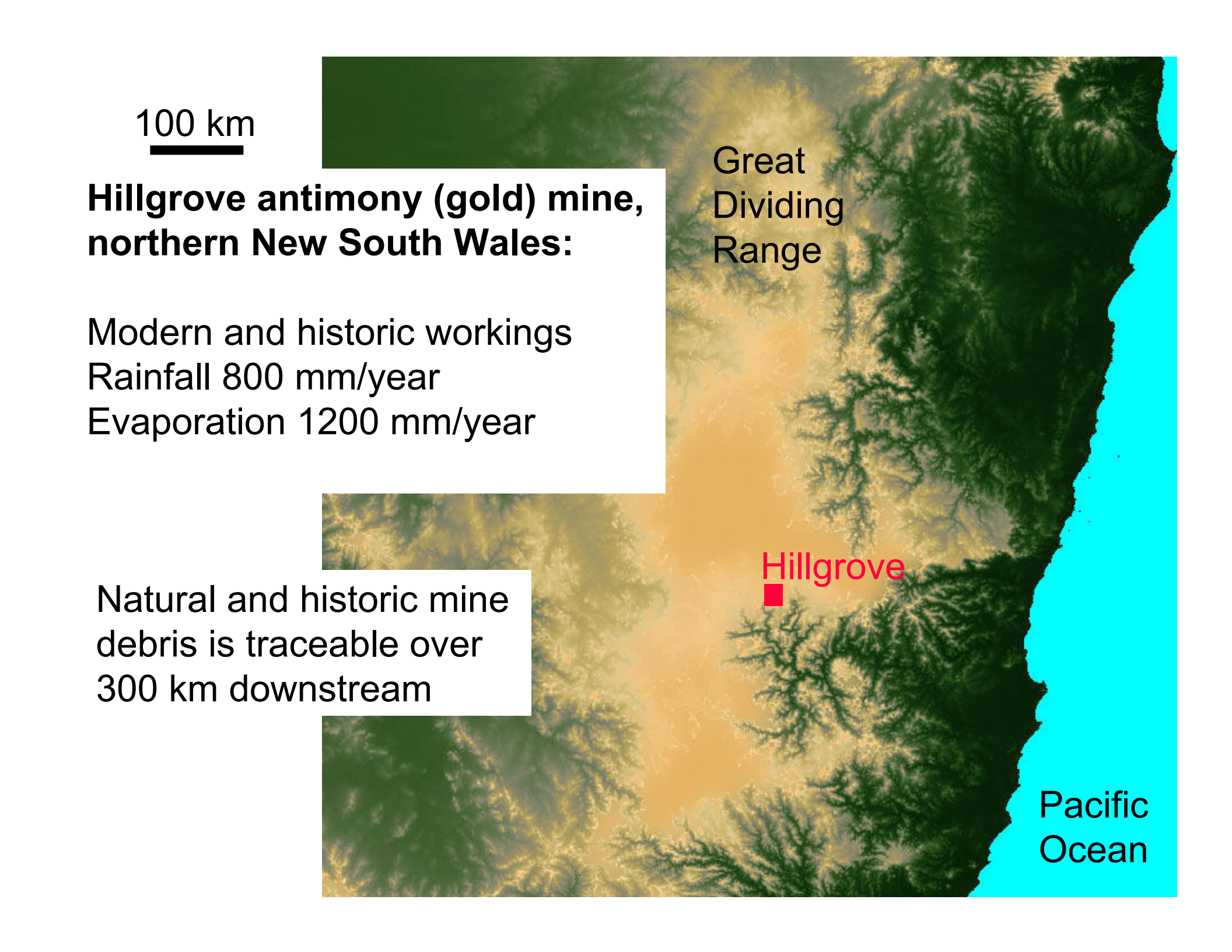




Stibnite (Sb_2S_3) in quartz veins

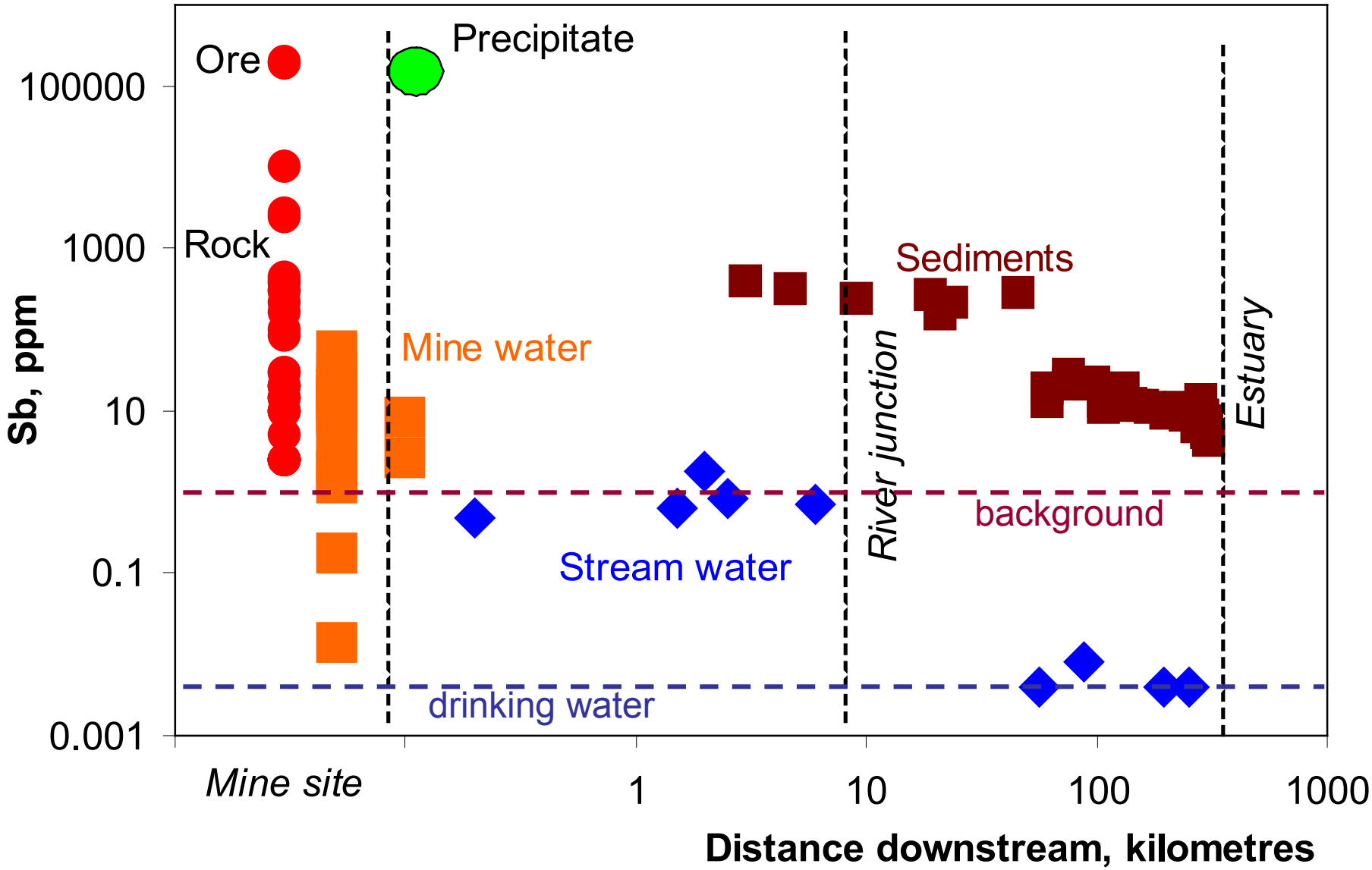


Hillgrove antimony (gold) mine, northern New South Wales:

Modern and historic workings
Rainfall 800 mm/year
Evaporation 1200 mm/year

Natural and historic mine debris is traceable over 300 km downstream

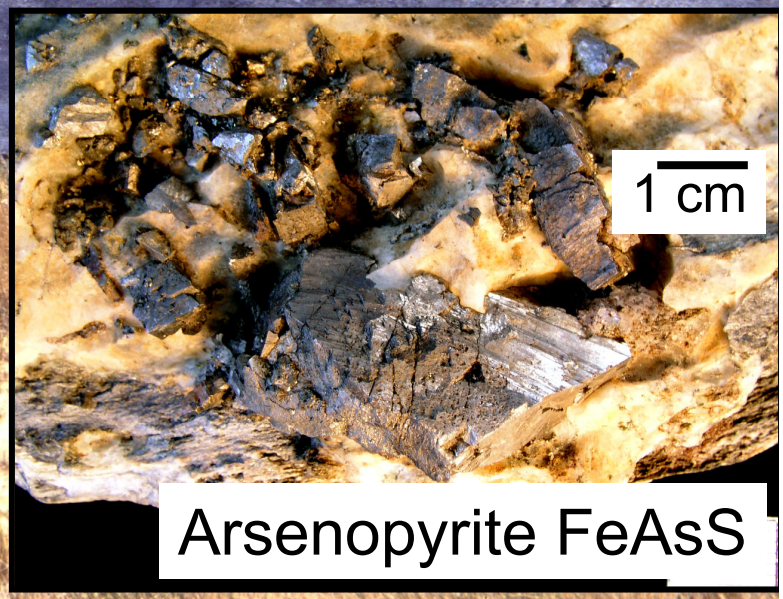
Downstream of Hillgrove mine site: elevated Sb in sediments and waters



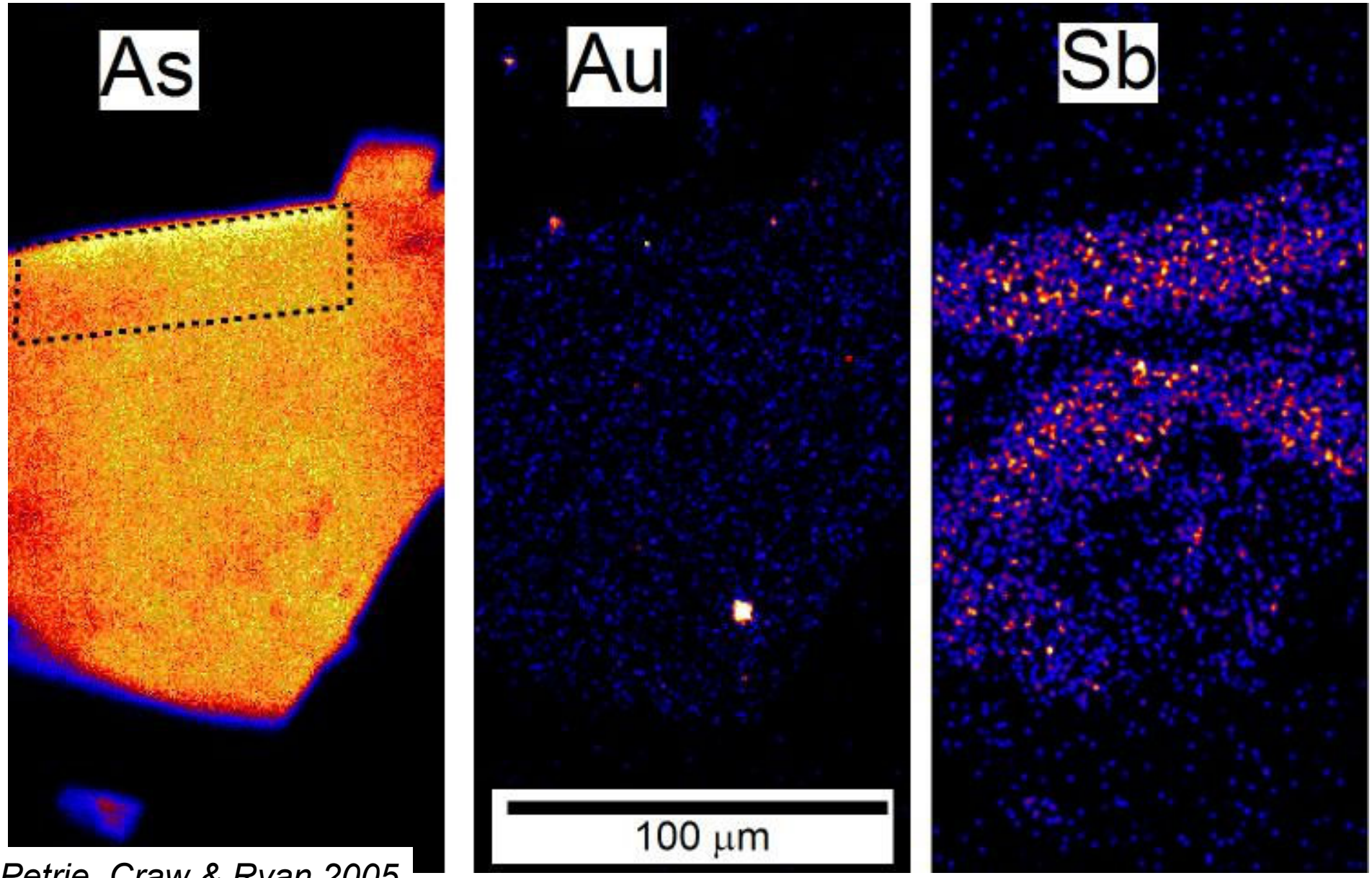
Ashley, Craw, Graham & Chappell 2003

Macraes gold mine, Otago, New Zealand

Rainfall c. 600mm/year
Evaporation c. 700 mm/year

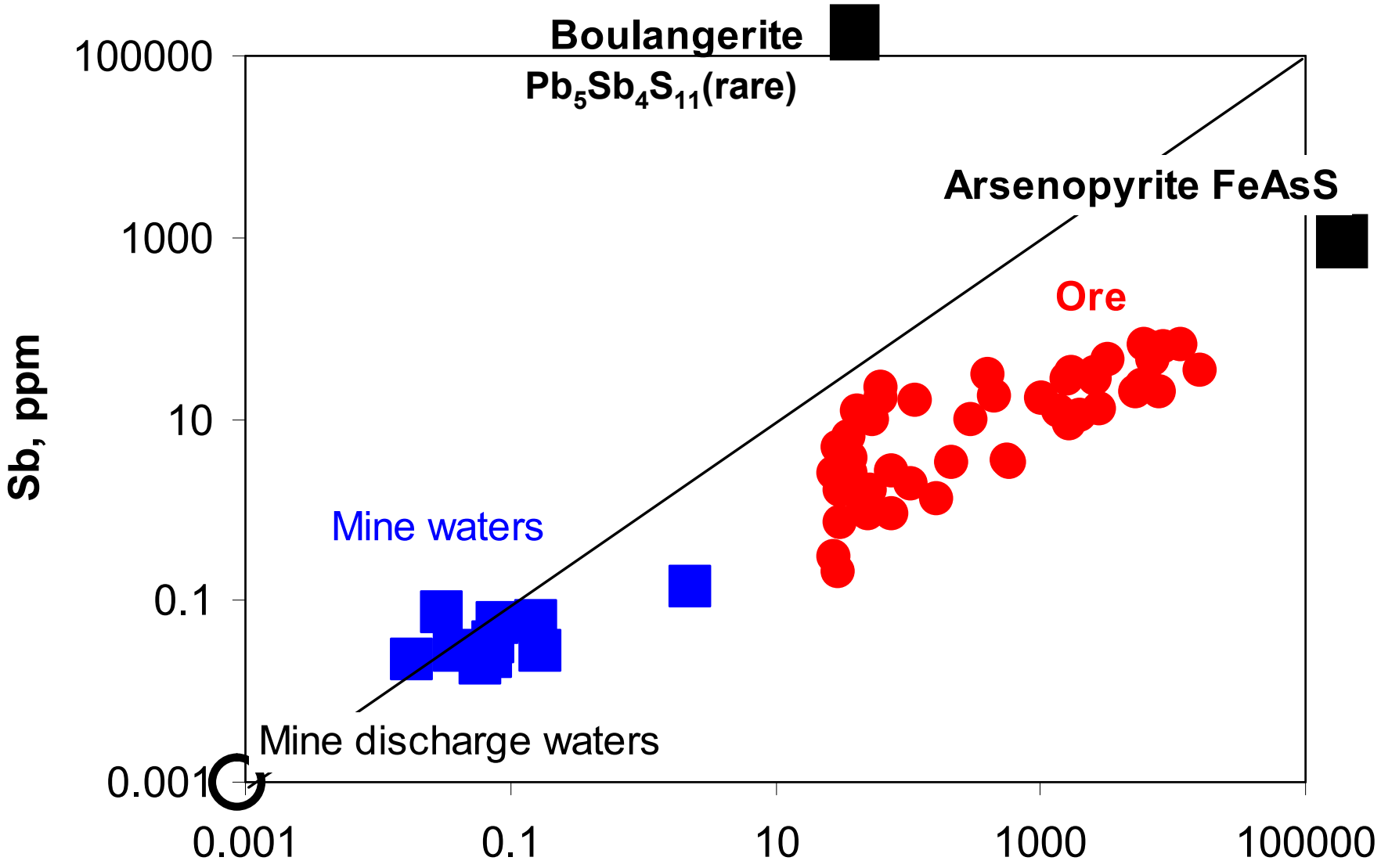


PIXE image of Macraes arsenopyrite with 2000 ppm Sb

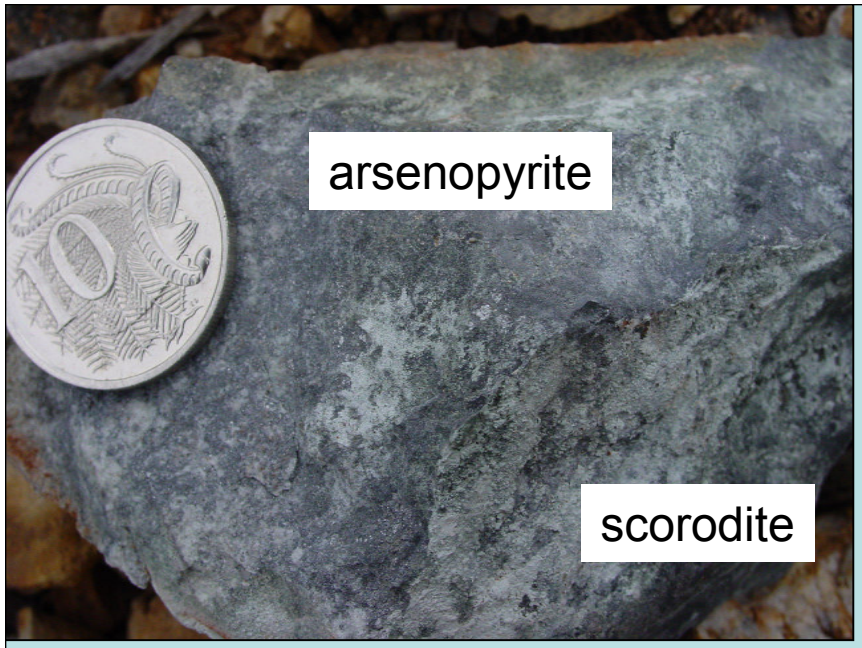


Petrie, Craw & Ryan 2005

Macraes mine: high evaporation in mine pits



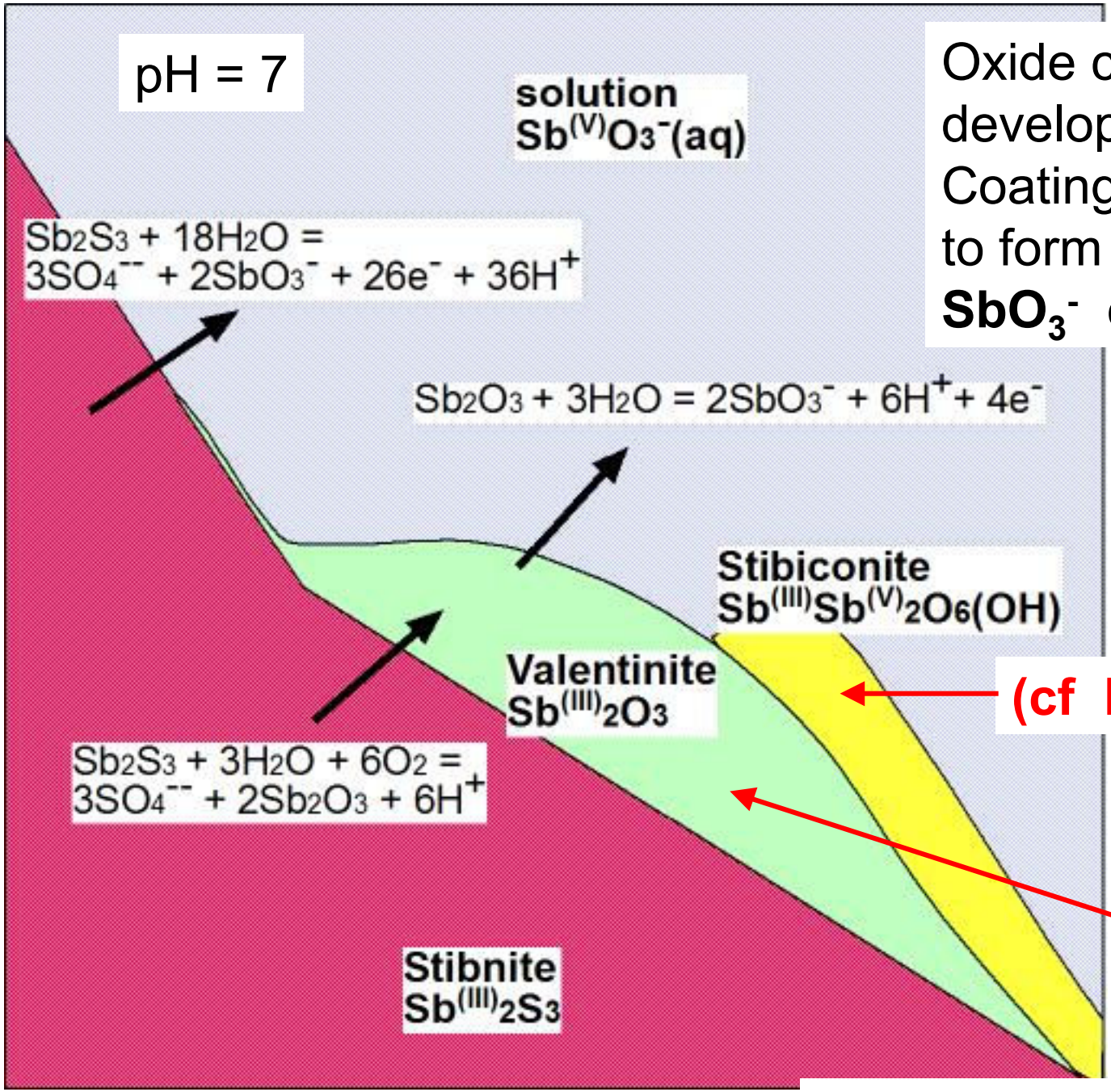
Craw, Ashley, Wilson & Hunter 2004



Oxidised arsenopyrite forms scorodite ($FeAsO_4.2H_2O$),

Oxidation of sulphide minerals

Stibnite (Sb_2S_3):
oxidises to various Sb oxides,
which are very soluble
(up to 50 mg/L)



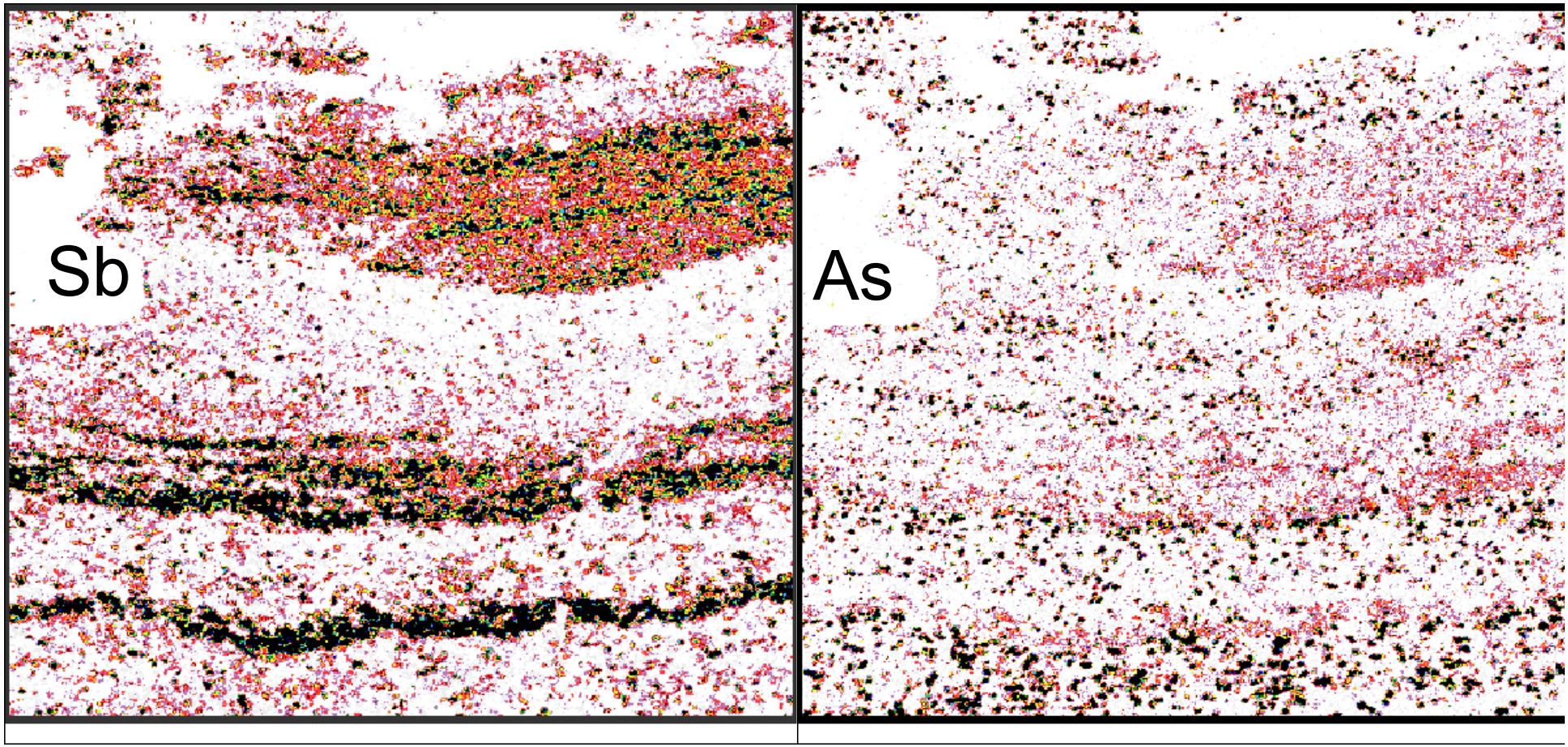
Oxide coating develops on stibnite. Coating dissolves readily to form Sb(V) oxyanion **SbO_3^-** or **$Sb(OH)_6^-$**

(cf $HAs^vO_4^{2-}$)

(cf $FeAs^{(V)}O_4 .nH_2O$)

(cf $As^{(III)}_2O_3$)

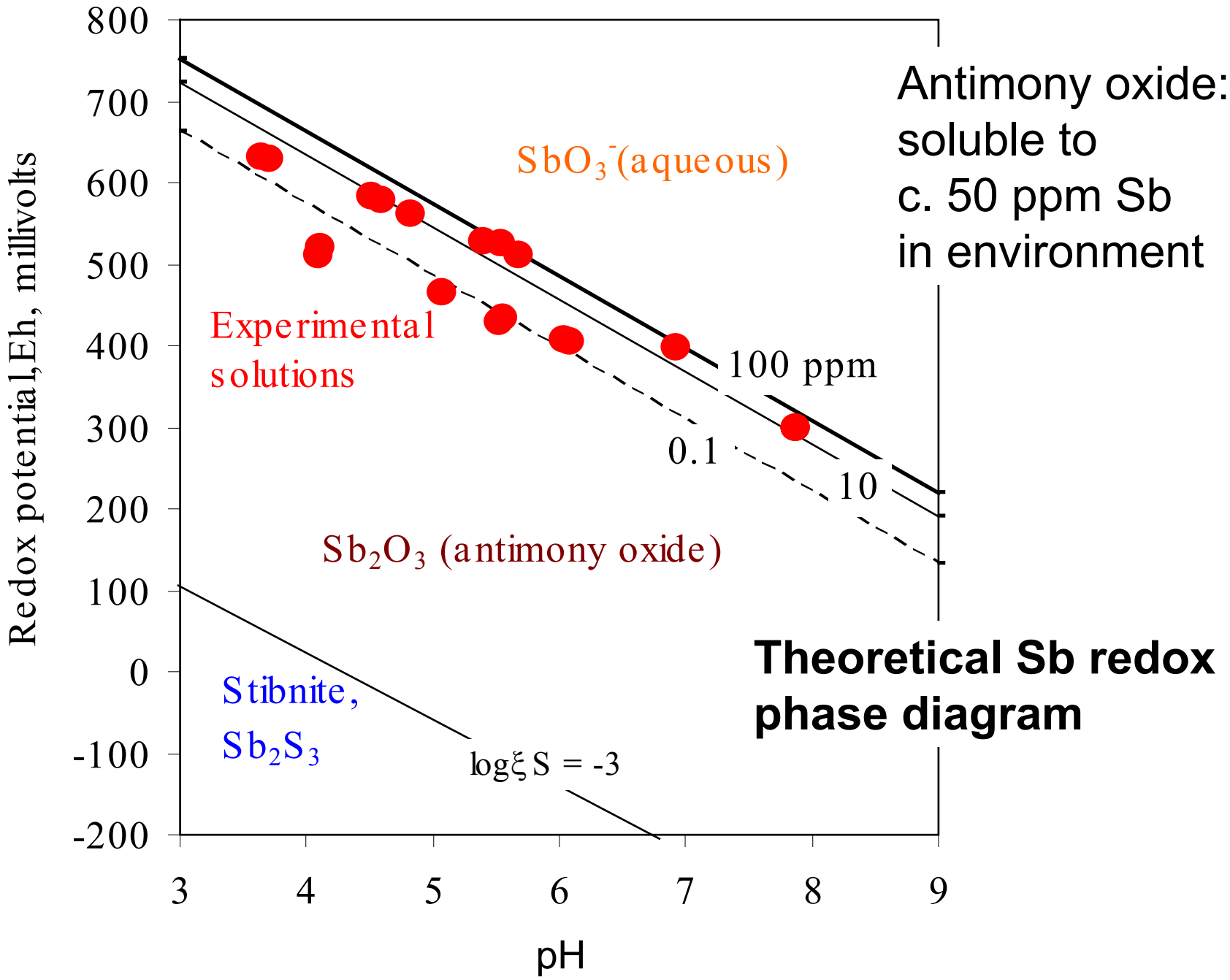
Ashley, Craw, Graham & Chappell 2003



1 mm

Hillgrove mine tailings, c. 1 month old
Dry, high evaporation conditions
Layering is bedded stibnite and arsenopyrite
Incipient antimony oxide formation and cementation

Ashley, Craw, Graham & Chappell 2003



Antimony oxide: soluble to c. 50 ppm Sb in environment

Theoretical Sb redox phase diagram

Ashley, Craw, Graham & Chappell 2003

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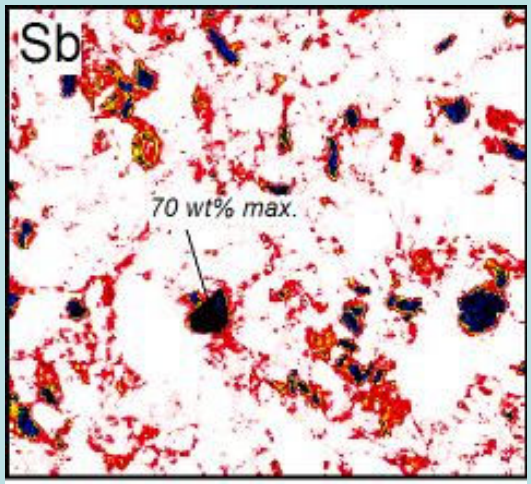
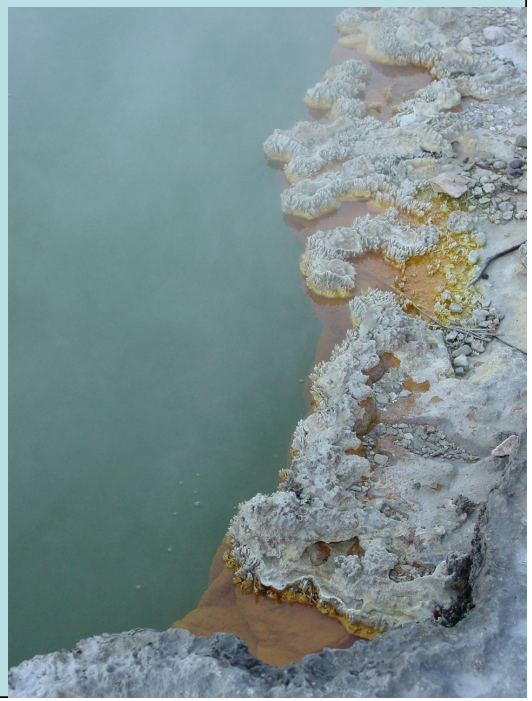
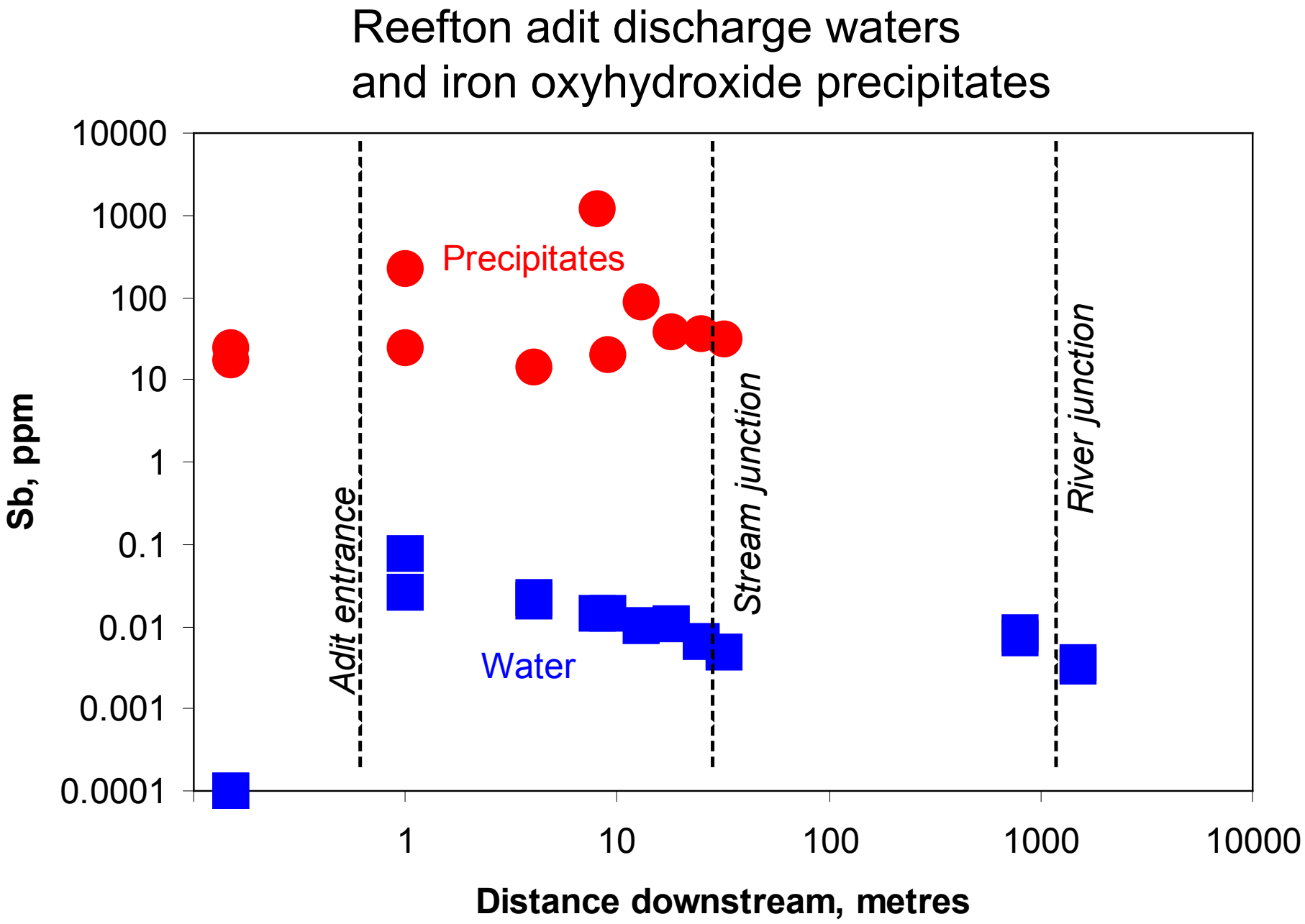


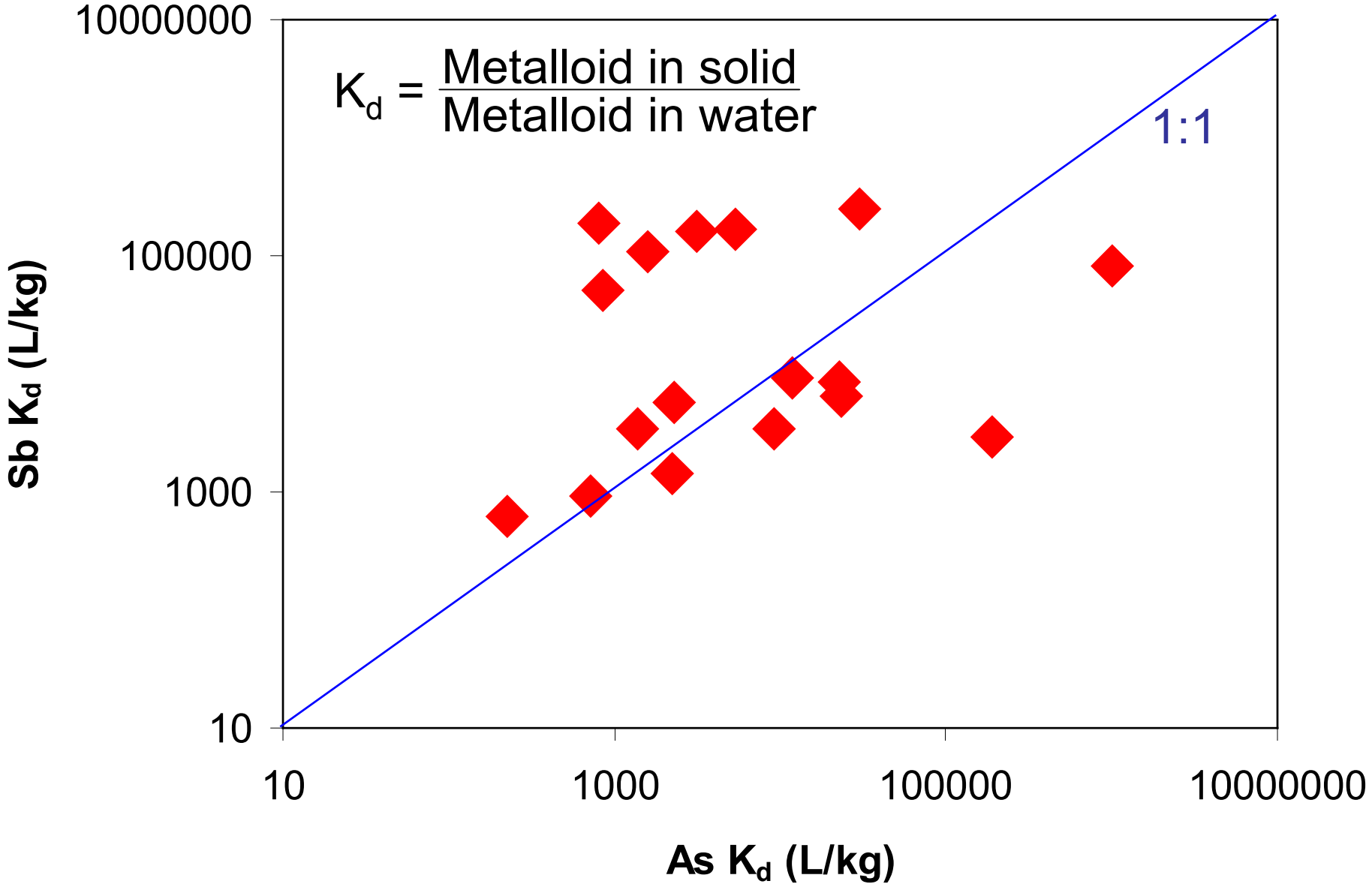


Reefton gold mine, New Zealand: rainfall c. 3000 mm/year
Arsenopyrite, pyrite, stibnite; discharges have HFO precipitates



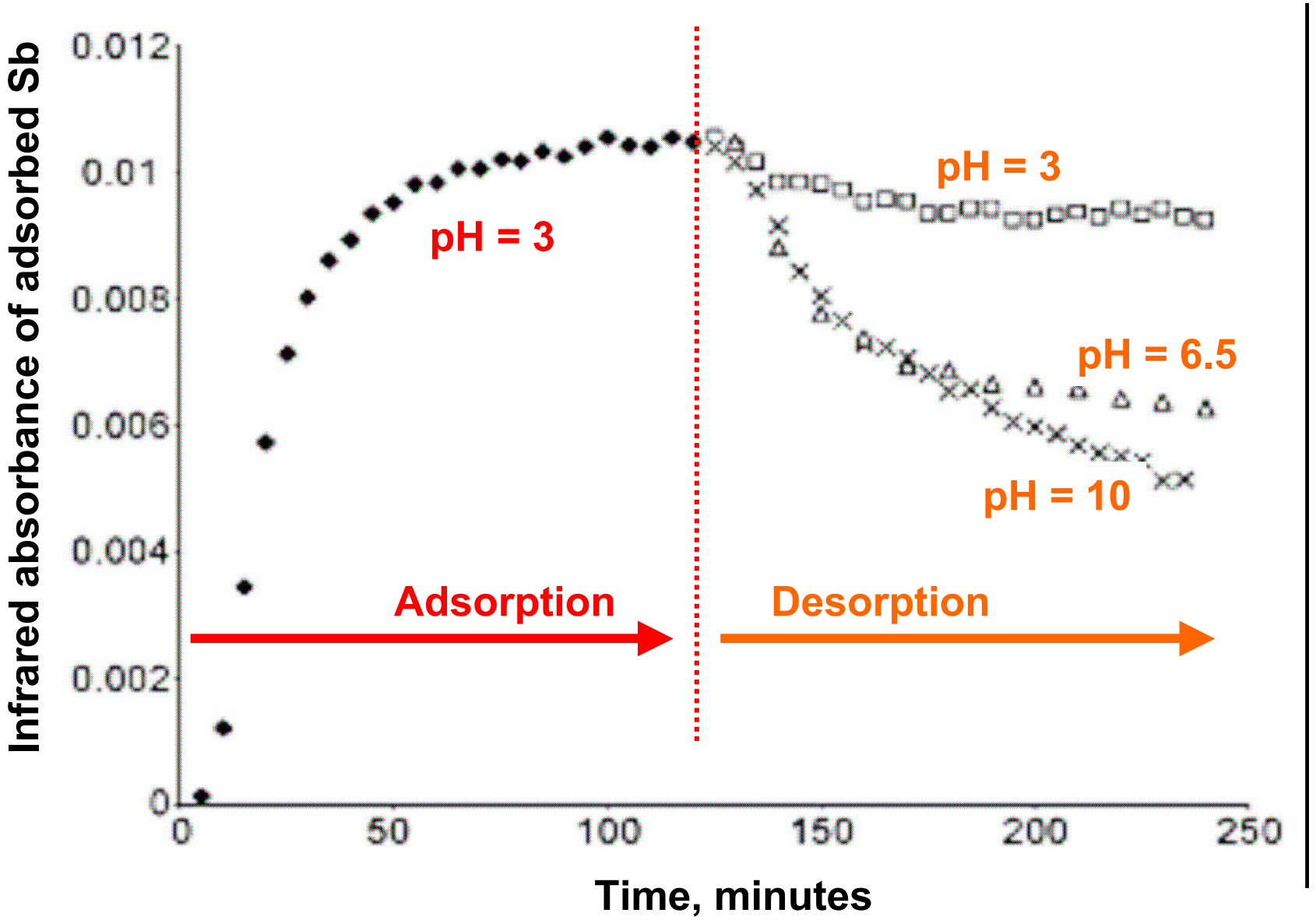
Craw, Wilson & Ashley 2004

Bulk distribution constants for arsenic and antimony in Reefton iron oxyhydroxide/water



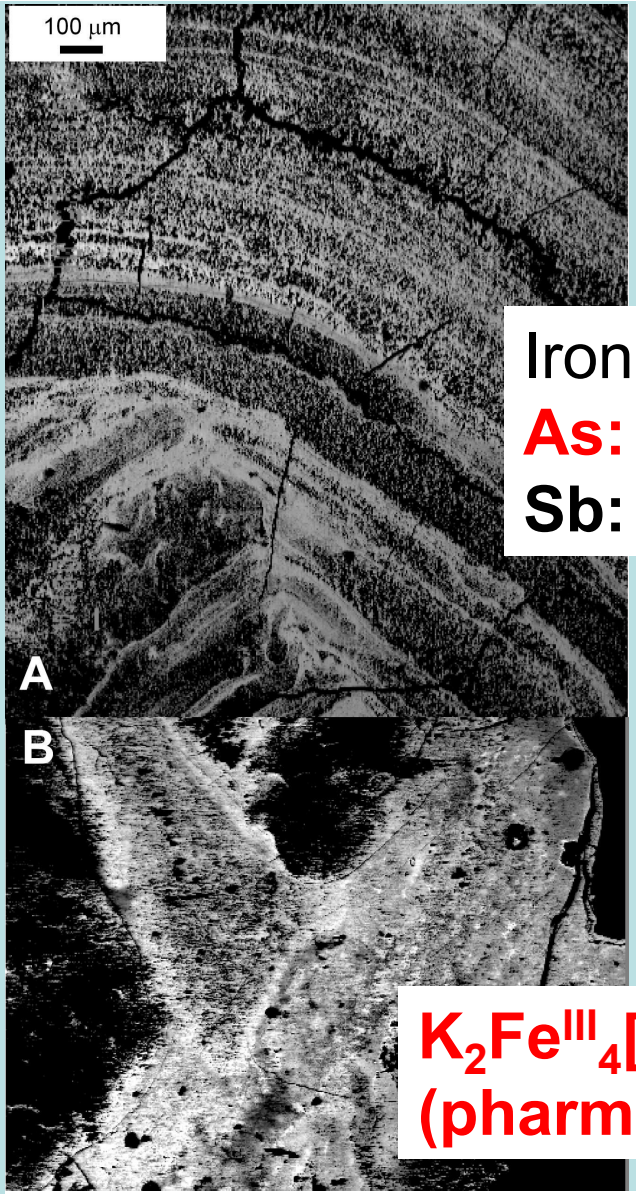
Craw, Wilson & Ashley 2004

Antimony adsorption/desorption on iron oxyhydroxide



McComb, Craw & McQuillan 2007

Electron backscatter images:
pale zones = As-rich

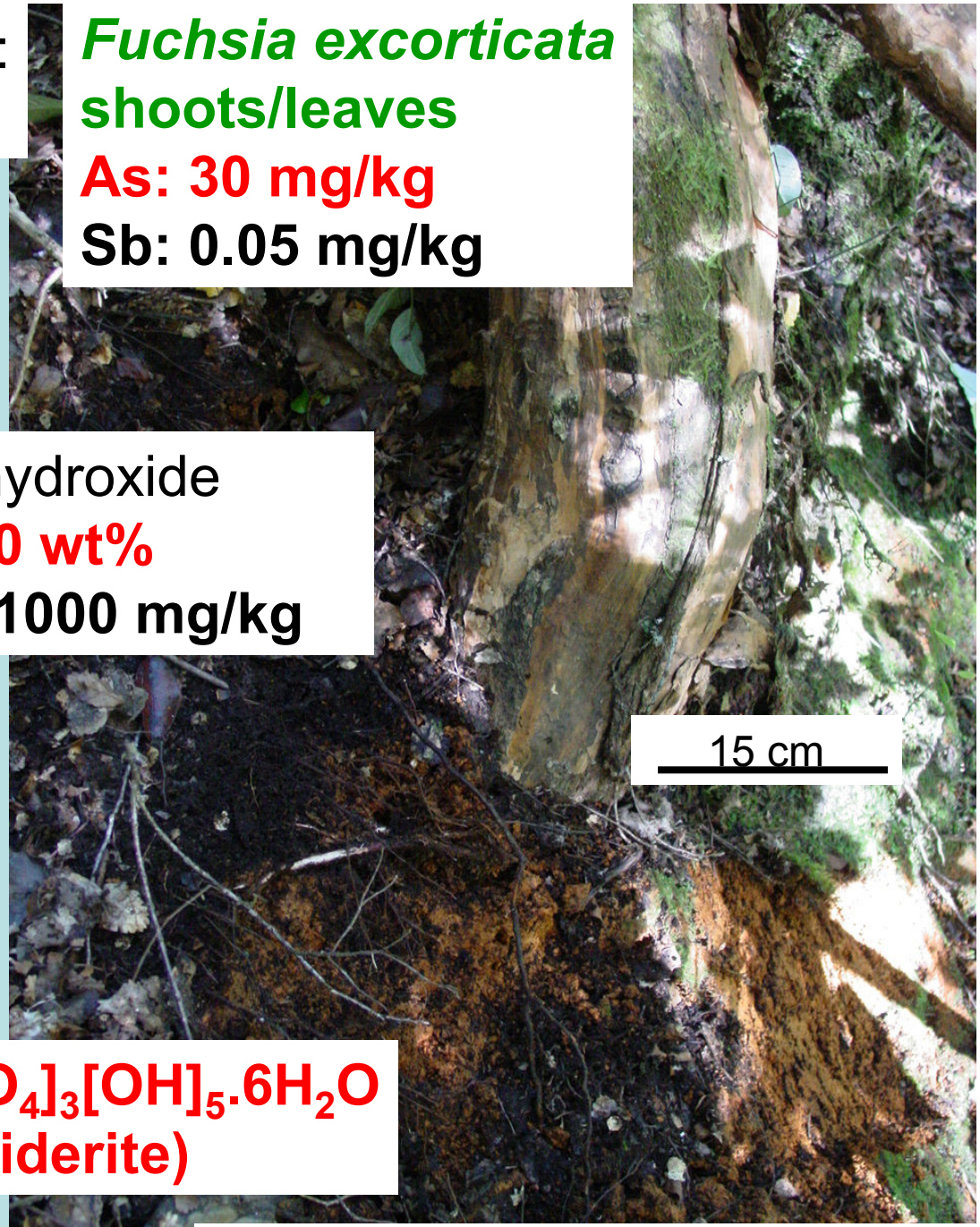


Hewlett, Craw & Black 2005

***Fuchsia excorticata* shoots/leaves**
As: 30 mg/kg
Sb: 0.05 mg/kg

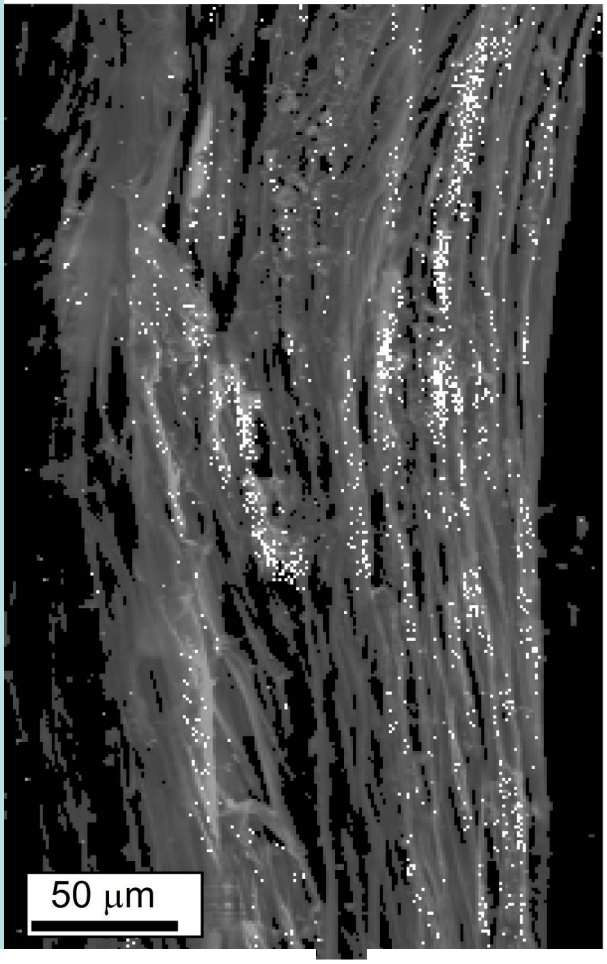
Iron oxyhydroxide
As: 10-20 wt%
Sb: 100-1000 mg/kg

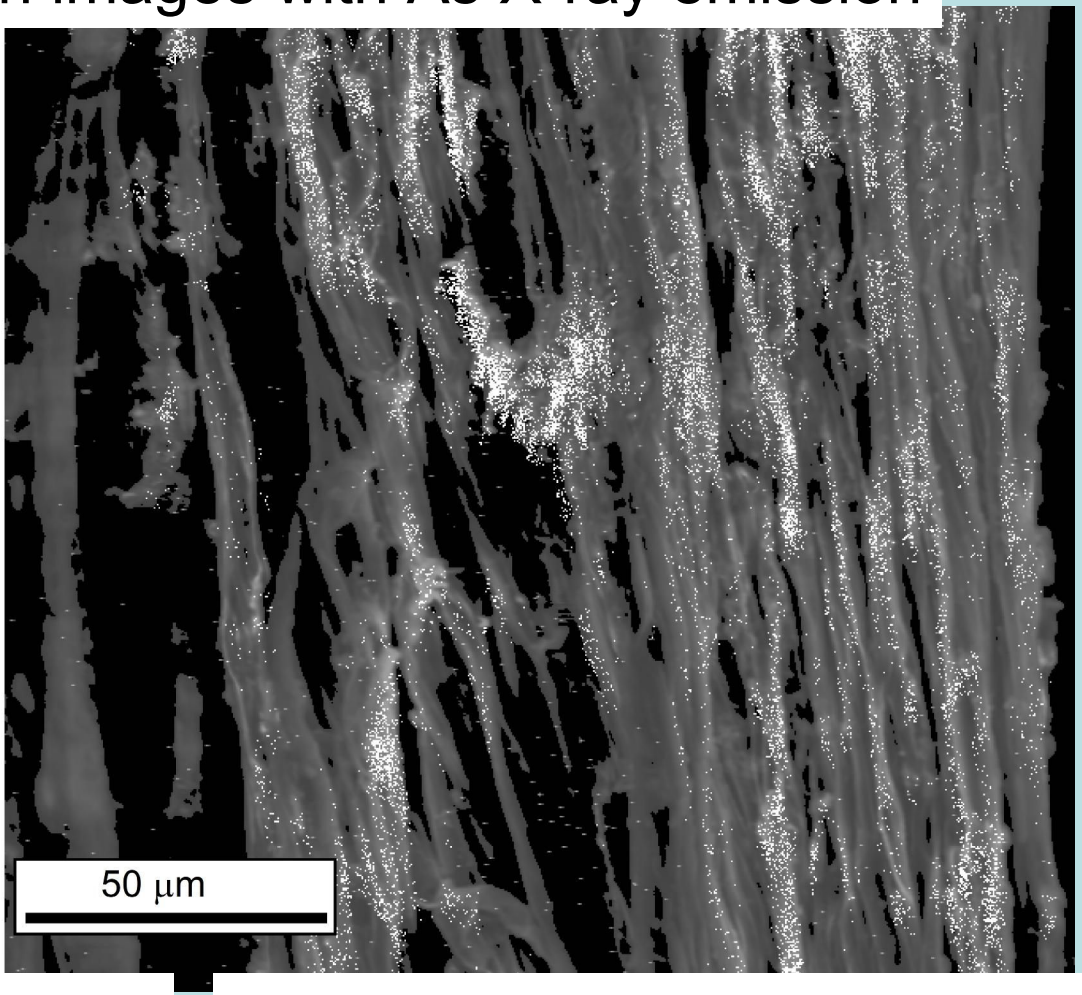
$K_2Fe^{III}_4[As^VO_4]_3[OH]_5.6H_2O$
(pharmacosiderite)



Craw, Rufaut, Haffert & Paterson 2007

Moss, *Pohlia wahlenbergii*
secondary electron images with As X-ray emission





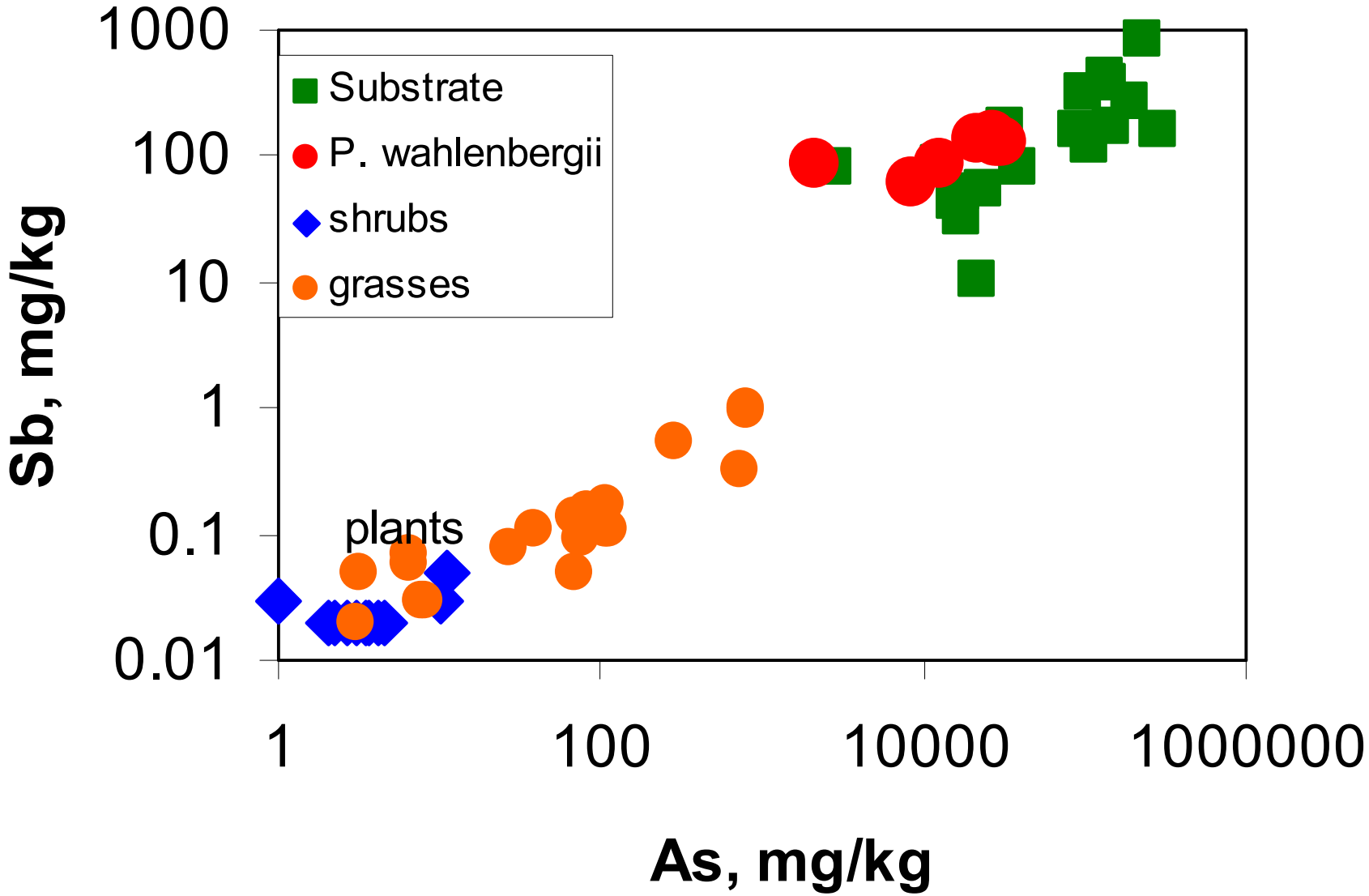
Moss As: 0.8-3 wt%

Moss Sb: 90-200 mg/kg

Substrate As: 3-16 wt%
Sb: 10-1000 mg/kg

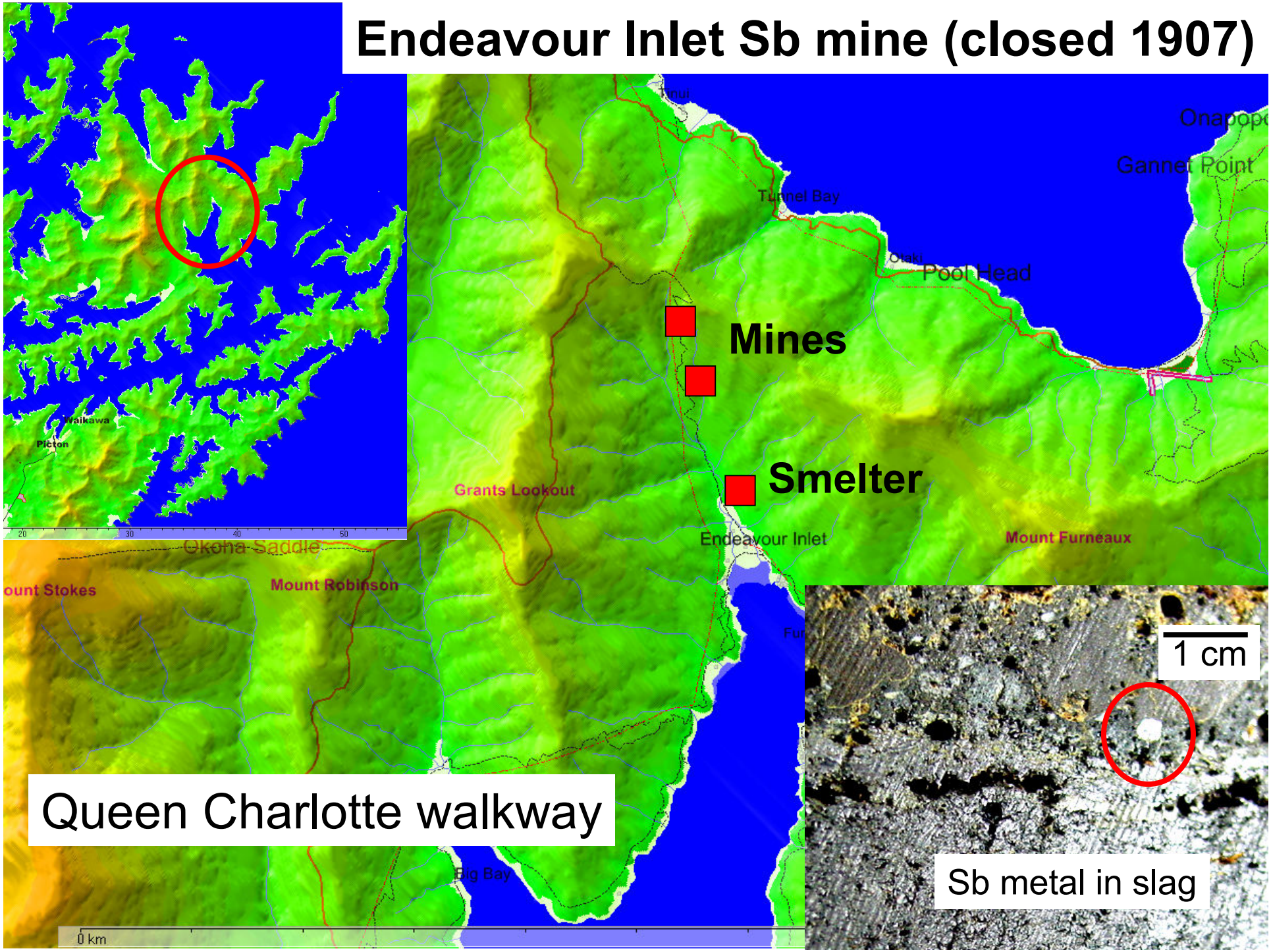
Craw, Rufaut, Haffert & Paterson 2007

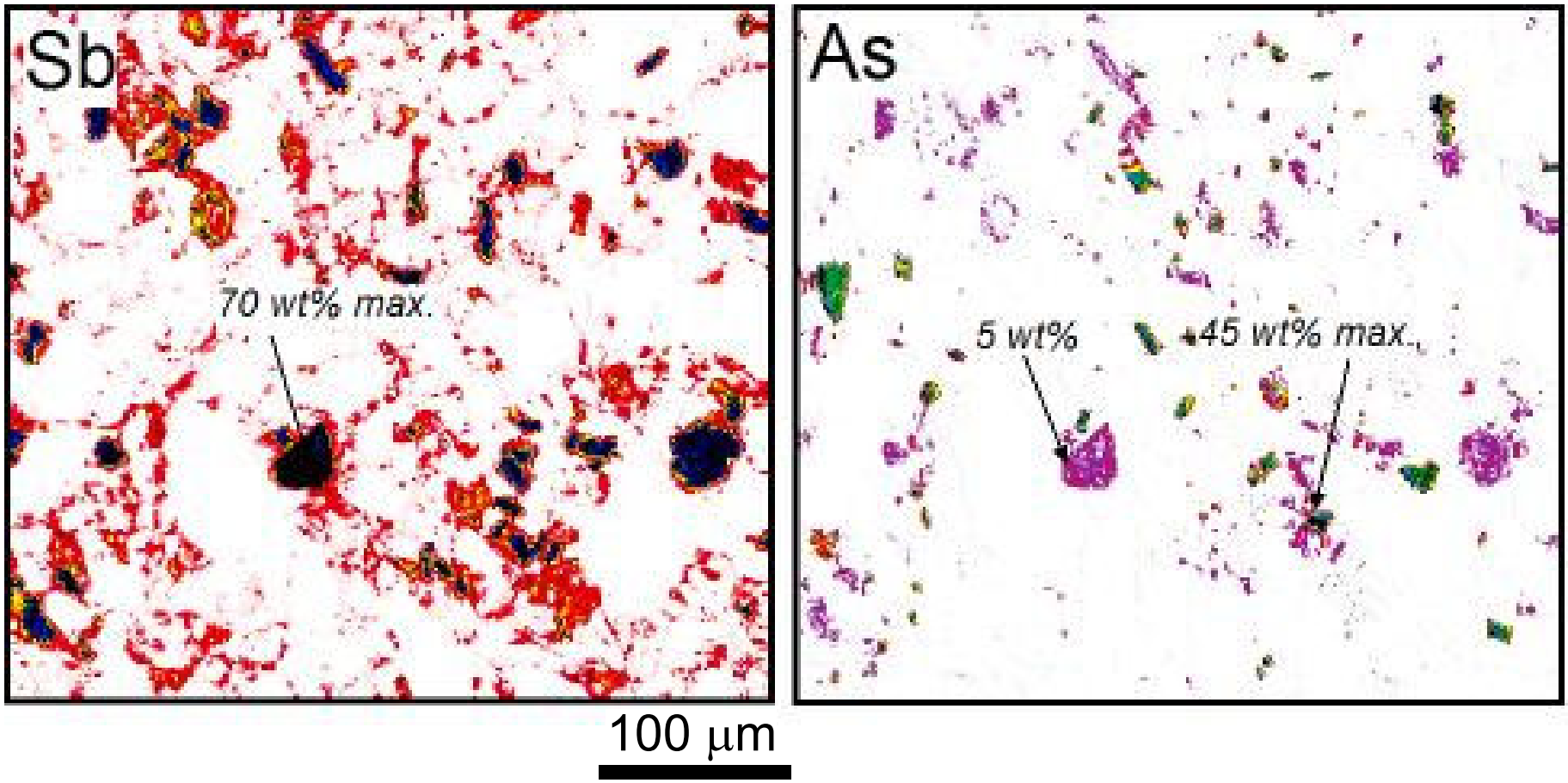
As/Sb ratio of plants reflects As/Sb ratio of substrates



Craw, Rufaut, Haffert & Paterson 2007

Endeavour Inlet Sb mine (closed 1907)





Endeavour Inlet, Marlborough, historic mine tailings:
Arsenic up to 5 wt% in stibnite
Minor arsenopyrite, pyrite
Antimony adsorbed on to iron oxyhydroxides
from oxidation of iron minerals; more mobile than As

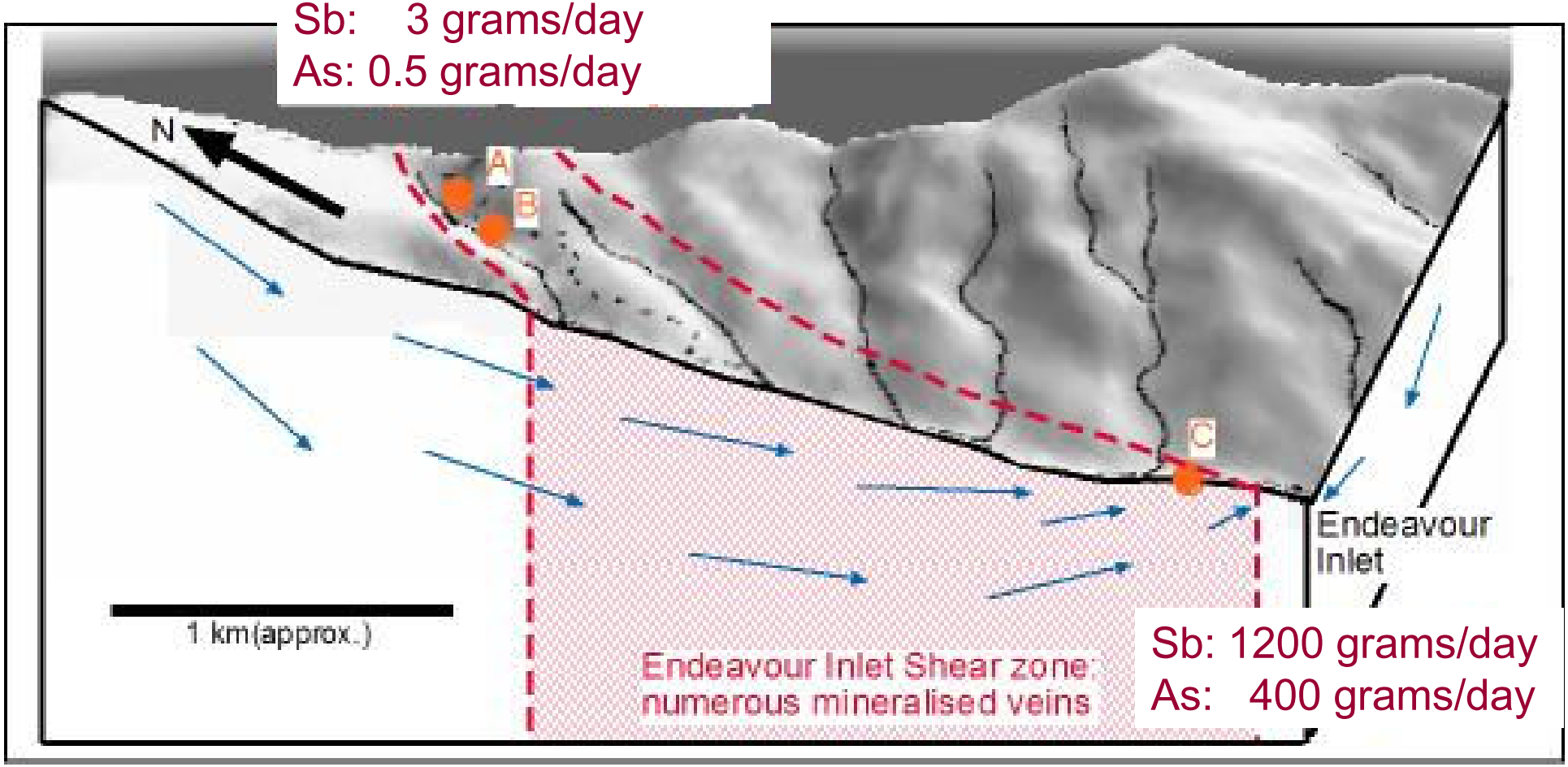
Wilson, Craw & Hunter 2004

Endeavour Inlet, Marlborough, historic antimony mines

No iron oxyhydroxide at adits

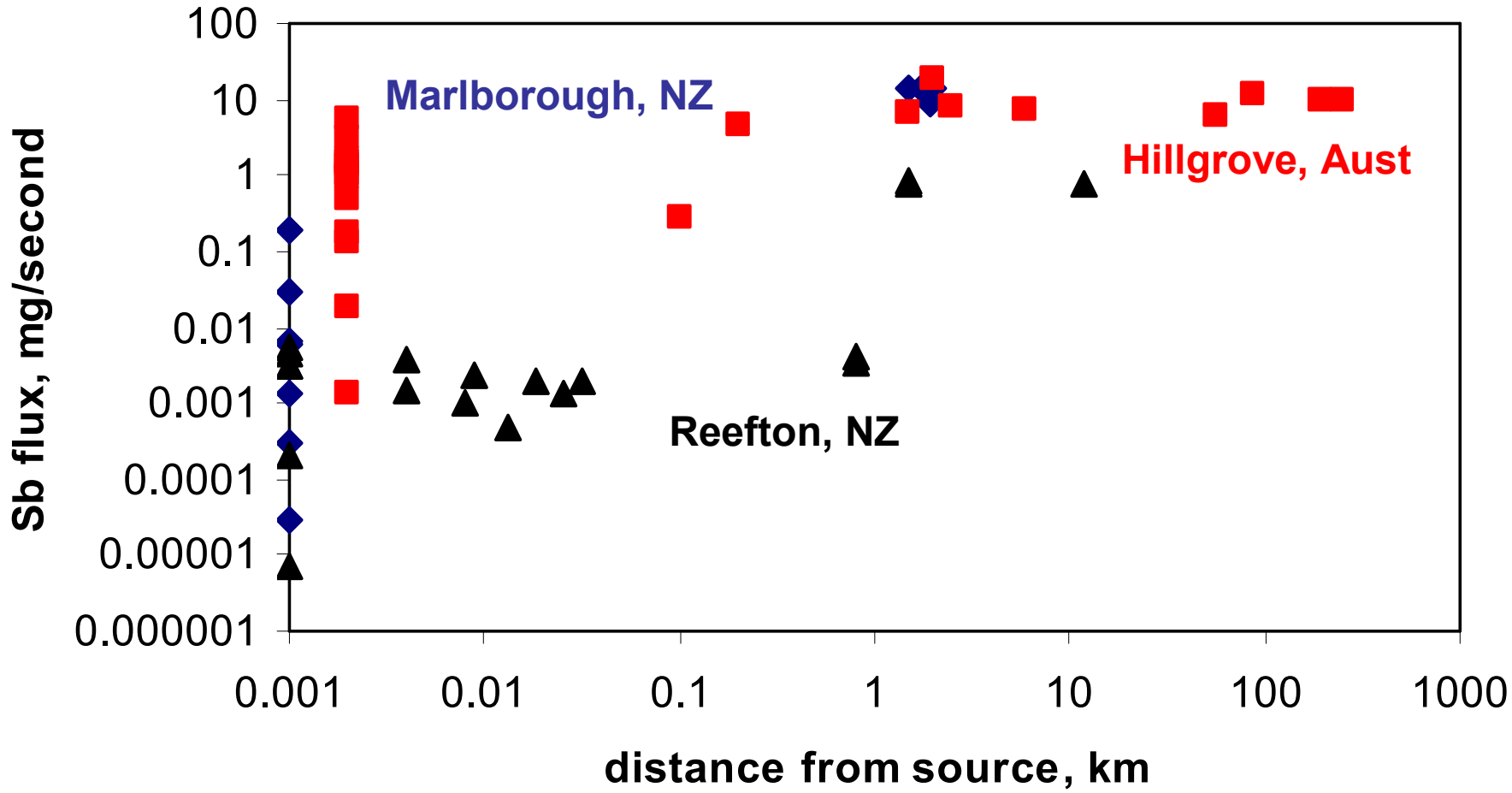
c. 1000 mm rainfall/year

Ground and surface water carries Sb for kilometres



Wilson, Craw & Hunter 2004

Flux of Sb from mine sites at neutral pH



Ashley, Craw, Tighe & Wilson 2006

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Metalloids in rocks and soils

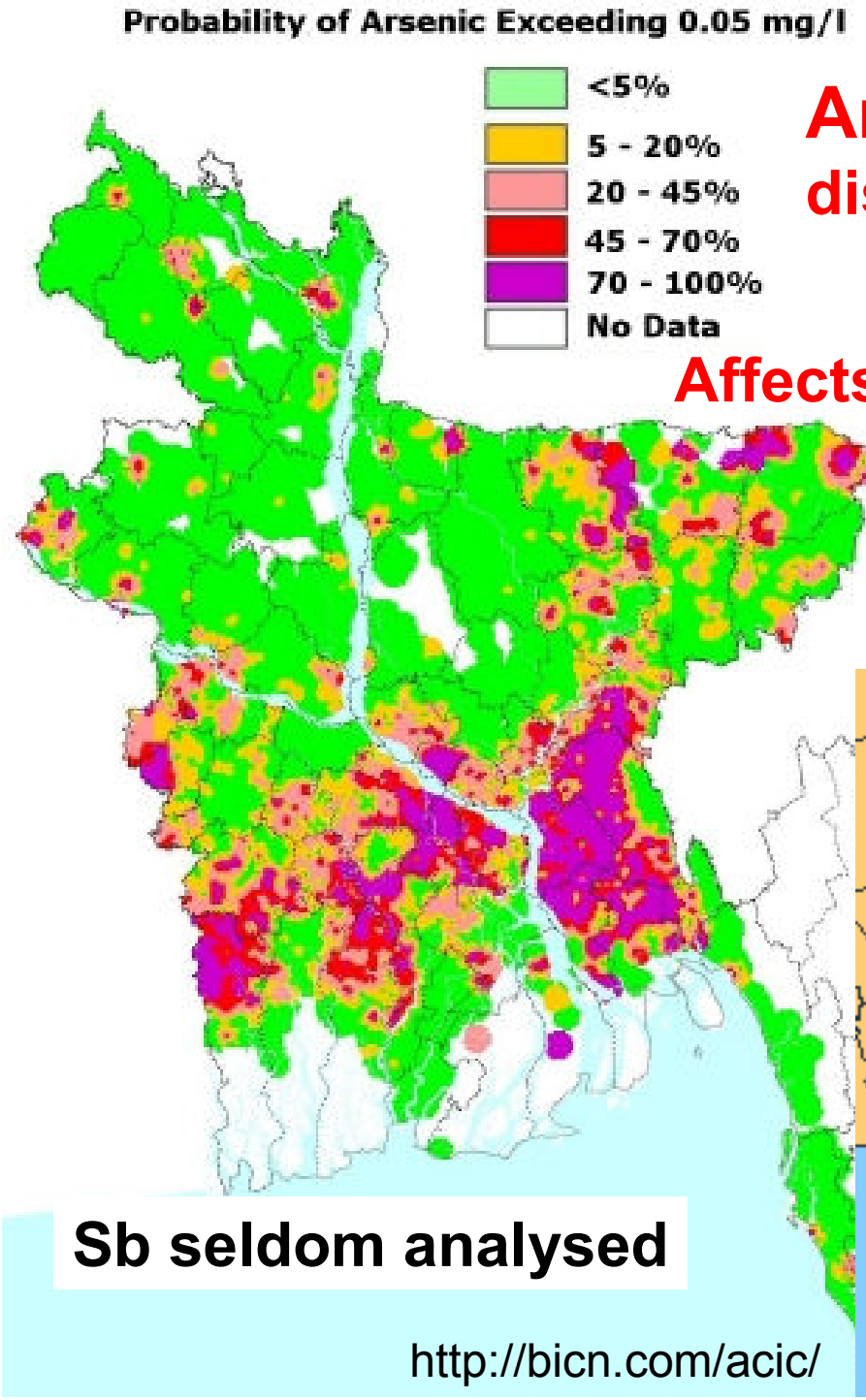
Antimony

- Background rocks: 0.01- 0.1 ppm
- Background soils: <0.1 ppm
- "Contaminated" (ANZECC) 2 ppm trigger value

Arsenic

- Background rocks: 2-20 ppm
- Background soils: 0.1-5 ppm
- "Contaminated" (ANZECC) 20 ppm trigger value

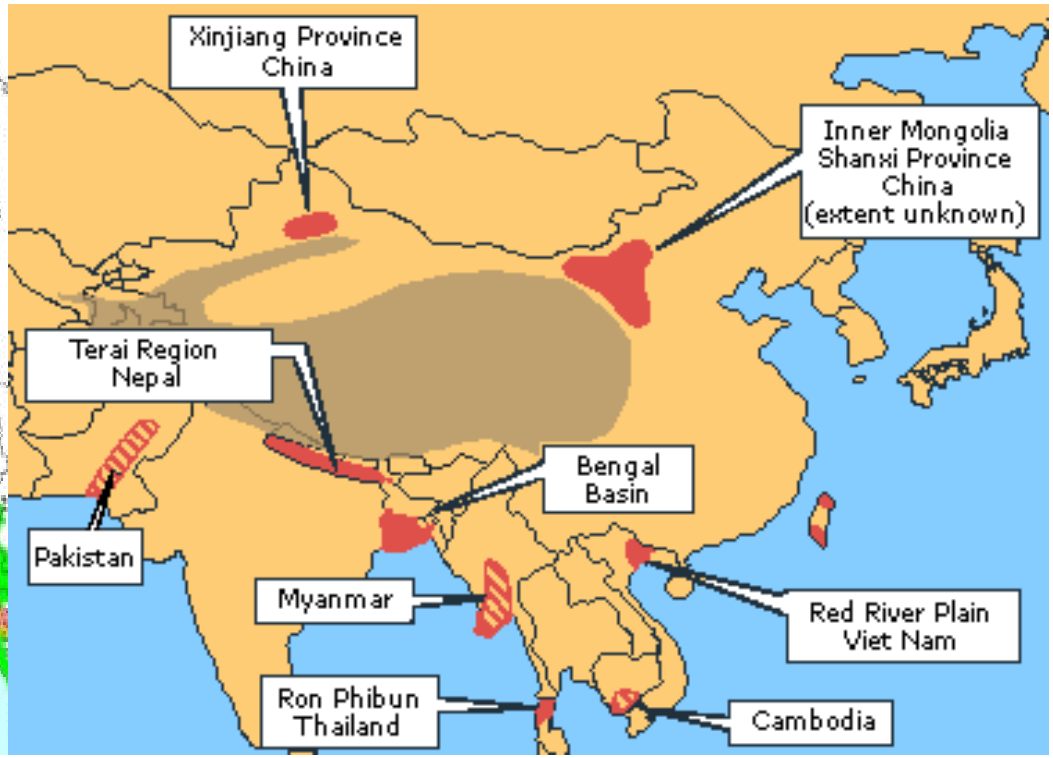
Background rock As is near "contaminated" As level;
Background rock Sb is <one tenth of "contaminated"



Arsenic in groundwater:
dissolved from background rocks

Affects 30 million people in Bangladesh

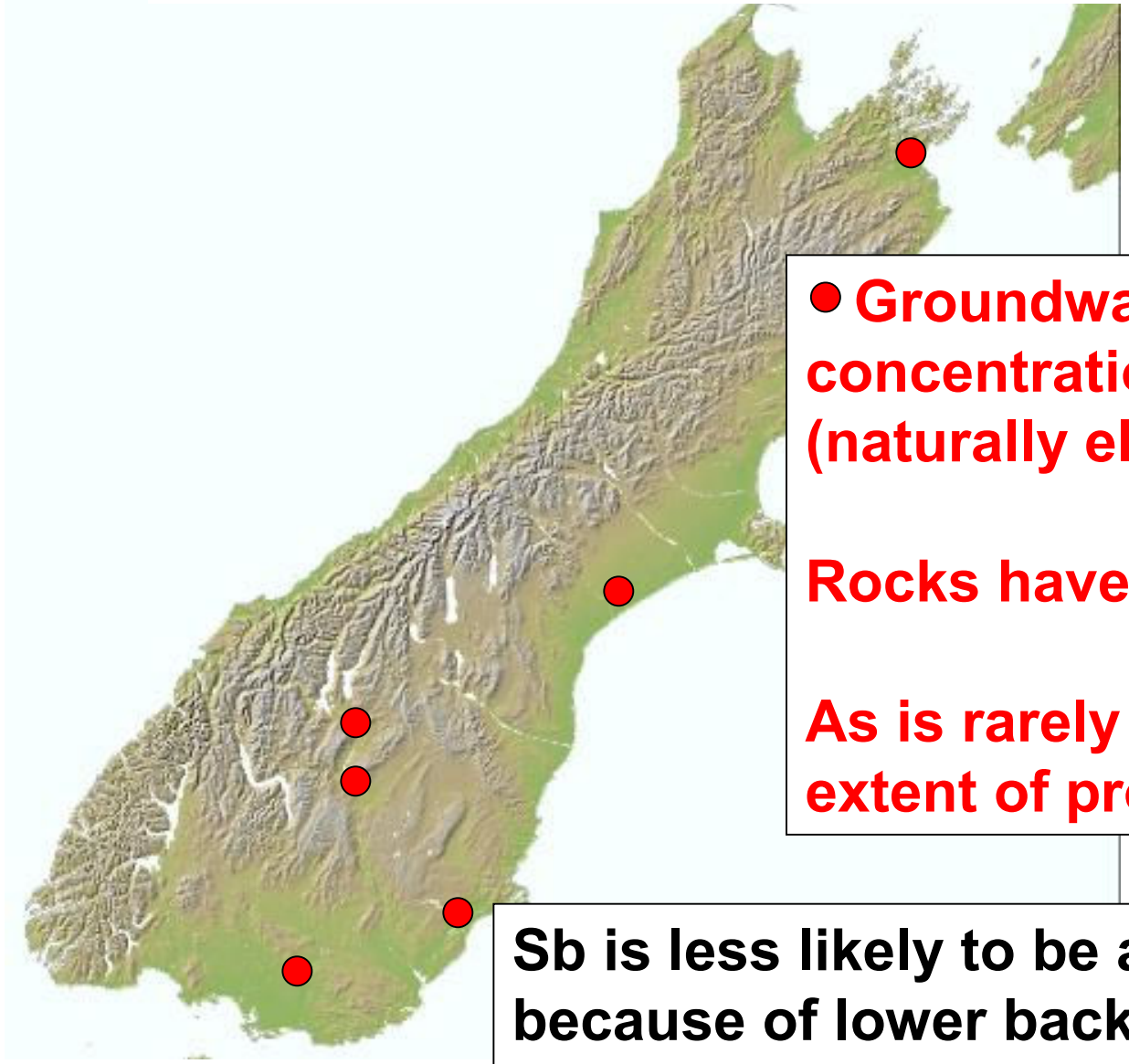
A regional problem:



Sb seldom analysed

http://bicn.com/acic/

New Zealand has potential As issues in deeper, slower-flowing groundwater aquifers



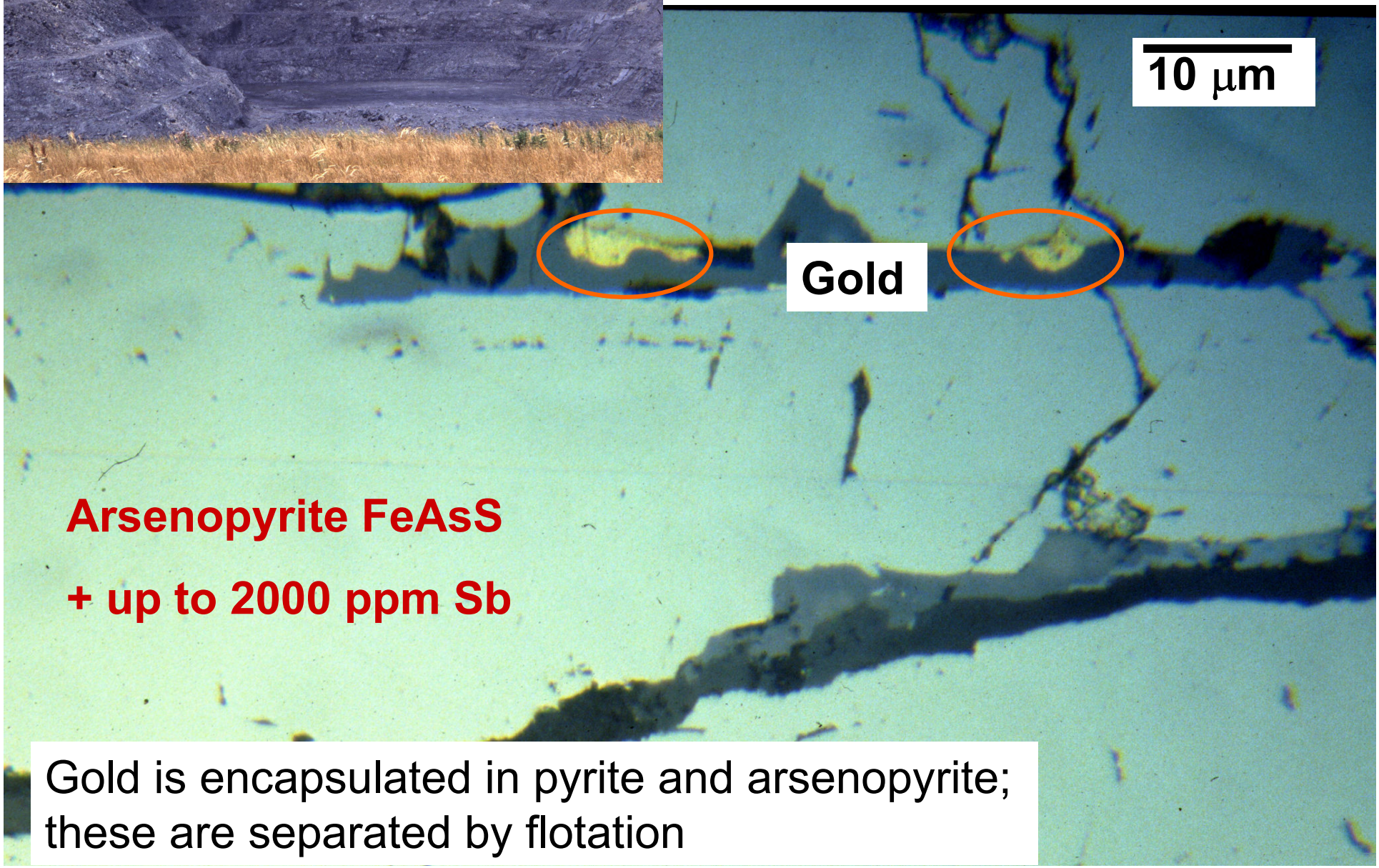
● Groundwater with arsenic concentrations >WHO limit (naturally elevated arsenic)

Rocks have high As background

As is rarely analysed, so extent of problem is unknown

Sb is less likely to be an issue because of lower background Sb in rocks. No data are available

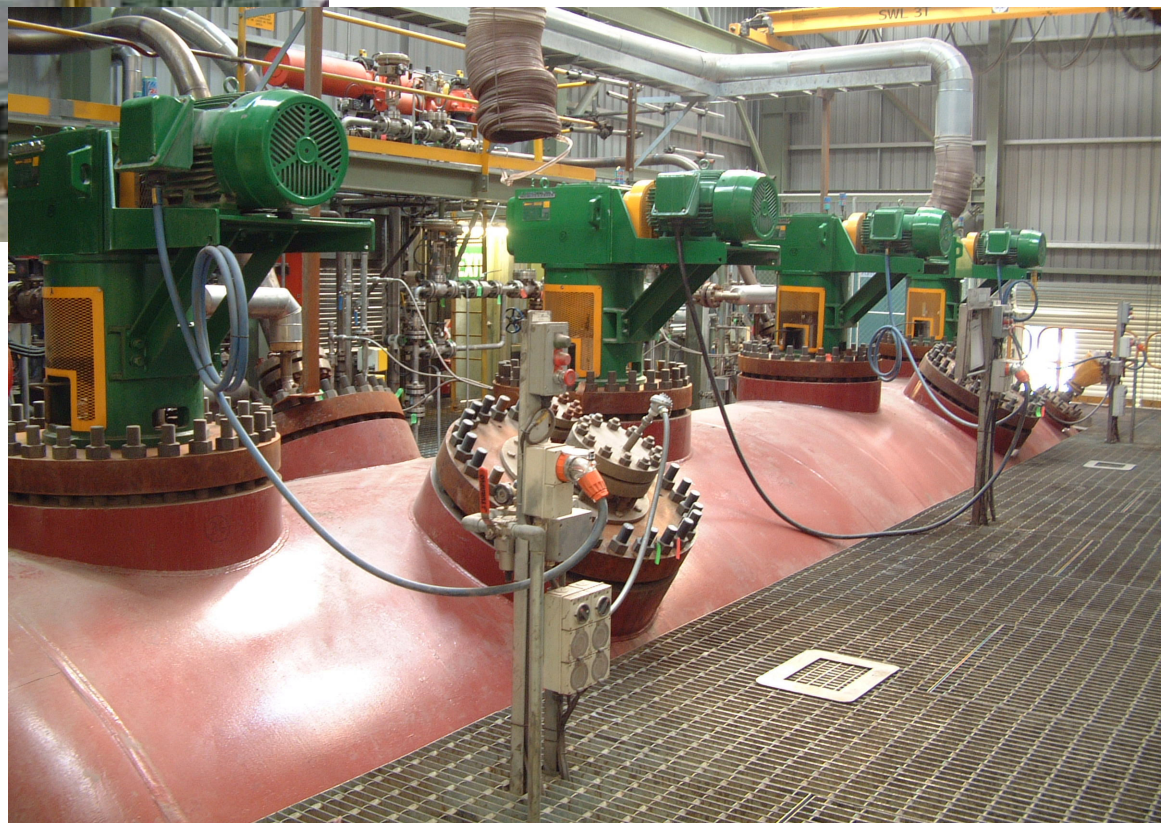
Macraes mine, Otago



Gold is encapsulated in pyrite and arsenopyrite; these are separated by flotation

Pressure-oxidation autoclave

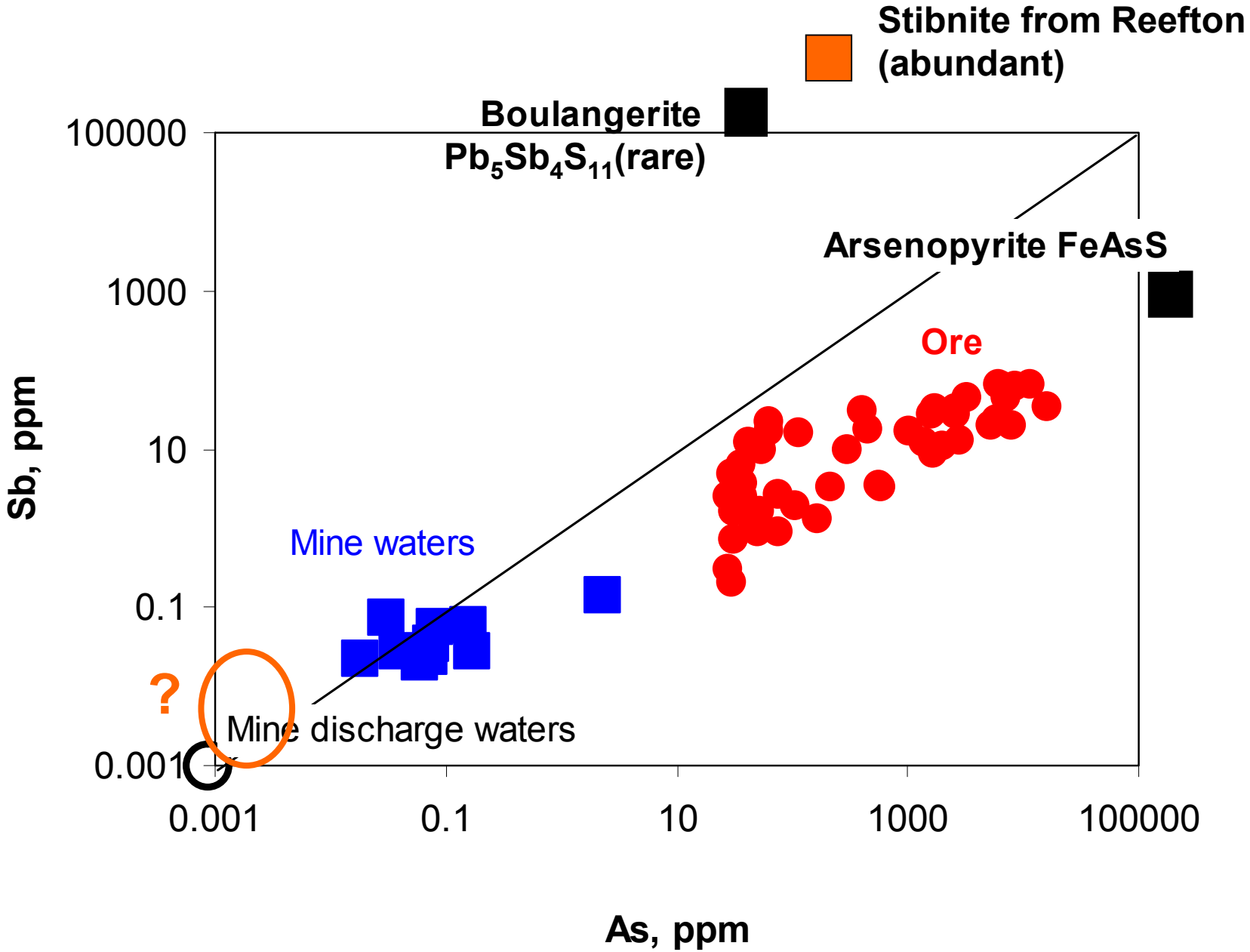
Concentrate slurry is roasted in oxygen atmosphere at 225°C



Results in acid solution (pH =1)
pH raised to 10.5 for cyanidation

Mobilises As and Sb in solution

Macraes mine Sb increase from oxidation and addition of Reefton ore?



Waiuta gold mine site, Westland
As condensate was byproduct

Condenser

Solids: **As: 11-40 wt%**
Sb: 50-1000 mg/kg

Arsenolite As_2O_3
+ Sb impurity

Lead arsenate spray for e.g., codling moth in apples (discontinued in 1970s)

Preparation:

$Pb(NO_3)_2(aq) + H_3AsO_4(aq)$
$=$**$PbHAsO_4$(solid)** $+2HNO_3(aq)$

Dissolved As obtained from commercial **As_2O_3 (soluble)**

Much commercial **As_2O_3** has **Sb** impurity (1%)

Sprayed orchards have elevated As in soils
Expect **Sb** as well; As/Sb = 100

Conclusions

- **Sb is chemically similar to As, but present at lower levels in most rocks**
- **Natural Sb point sources are found throughout New Zealand**
- **Sb minerals are soluble and dissolved Sb can be transported for kilometres**
- **Dissolved Sb is readily attenuated by iron oxyhydroxide, if present**
- **Levels of Sb in our environment are poorly known because Sb is commonly not on the analysis list**