# Mechanisms controlling circumneutral drainage generation at Antamina

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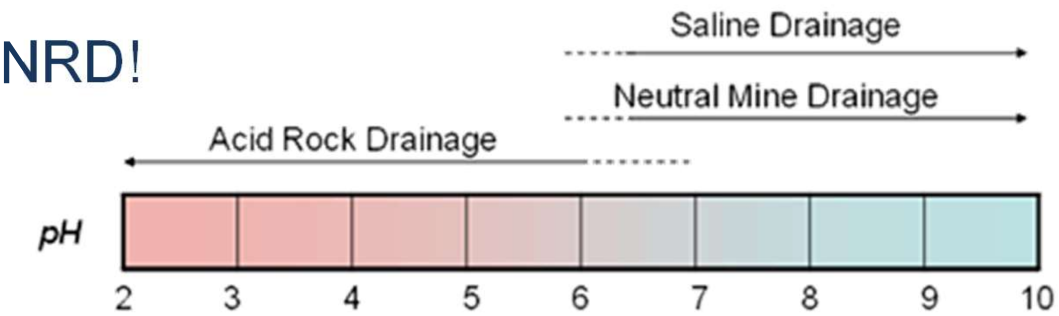
*BC MEND*
*ML/ARD*
*2020*

# The many faces of neutral rock drainage

- Everything that is *not* ARD?
  → No standardized definition of NRD!




- When can one encounter NRD:

  (i) Sulfide oxidation in the presence of sufficient acid-buffering
  (ii) Weathering of non-acid generating minerals (i.e., carbonates and silicates, dissolution of salts)
  (iii) Insufficient treatment of ARD: pH is increased to near-neutral but certain contaminants remain present at elevated concentrations

  - hardness (mostly Ca and Mg)
  - major ions (e.g., sulfate and chloride)
  - metal(oid)s (e.g., As, Se, Ni, Zn)
  - other contaminants (e.g., organics)

Vriens et al, 2020, Minerals

# Relevant solutes in NRD

Focus on 4 metal(oid) oxyanions: As, Se, Mo, Sb

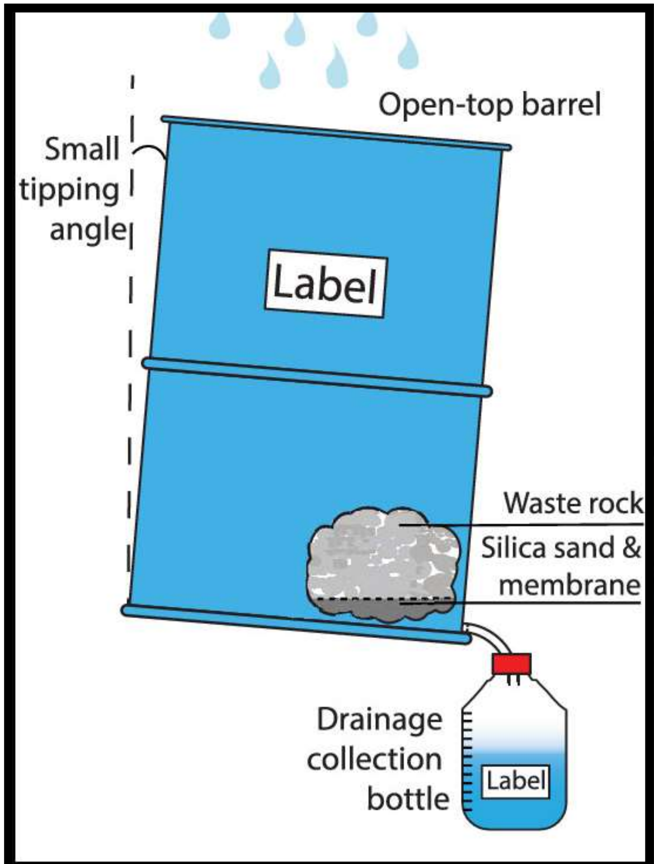
*Relatively* comparable aqueous biogeochemistry

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | | | | | | | | | | | | | | | | | He |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| Fr | Ra | Ac | Rf | Db | Sg | Bh | Hs | Mt | Ds | Rg | Cn | Uut | Fl | Uup | Lv | Uus | Uuo |

- What materials cause NRD with harmful levels of As, Se, Mo, Sb?
- Which processes and mechanisms control their mobility?

→ Monitor NRD generation from contrasting waste rock materials

# Field barrel experiments




~350 kg each




Vriens et al., 2019, ACS Omega

# Field barrel experiments

49 different experiments (+blanks) with different waste rock types

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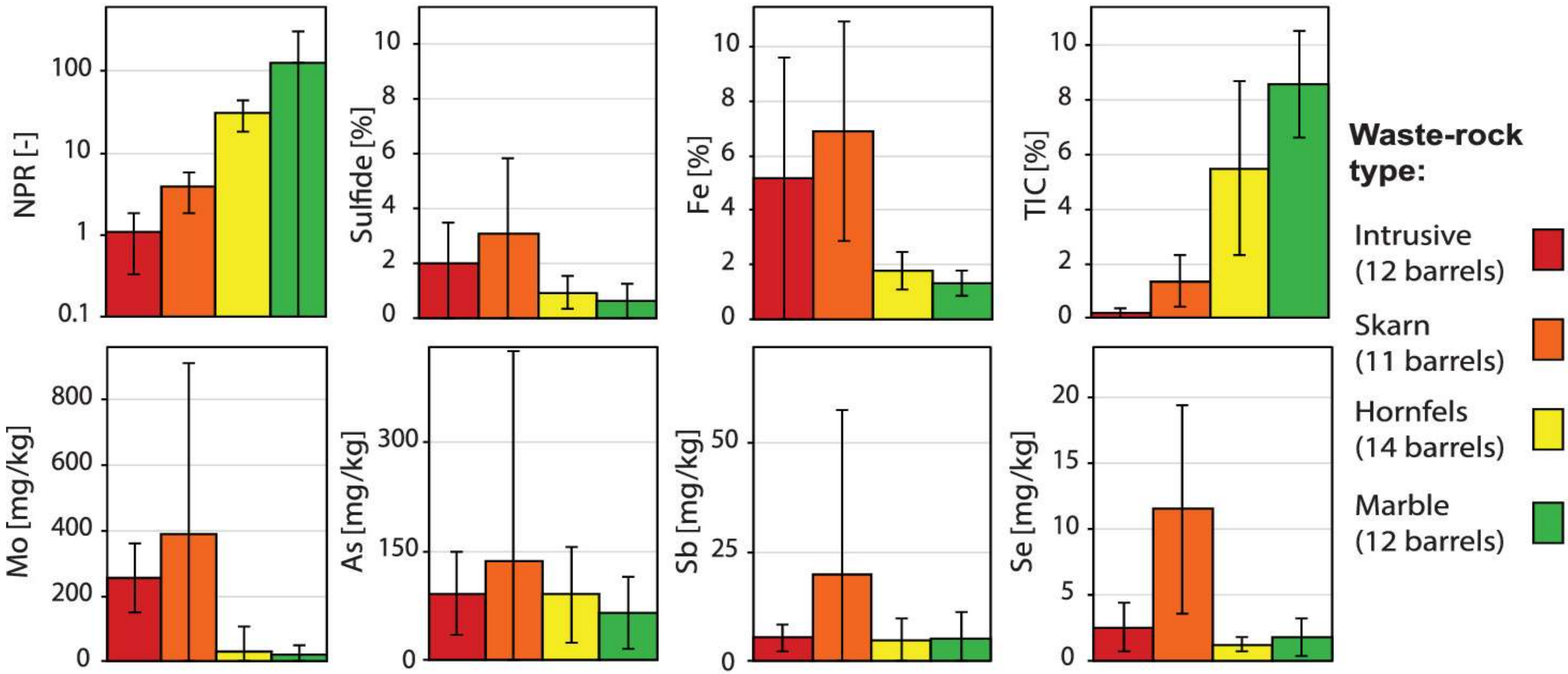
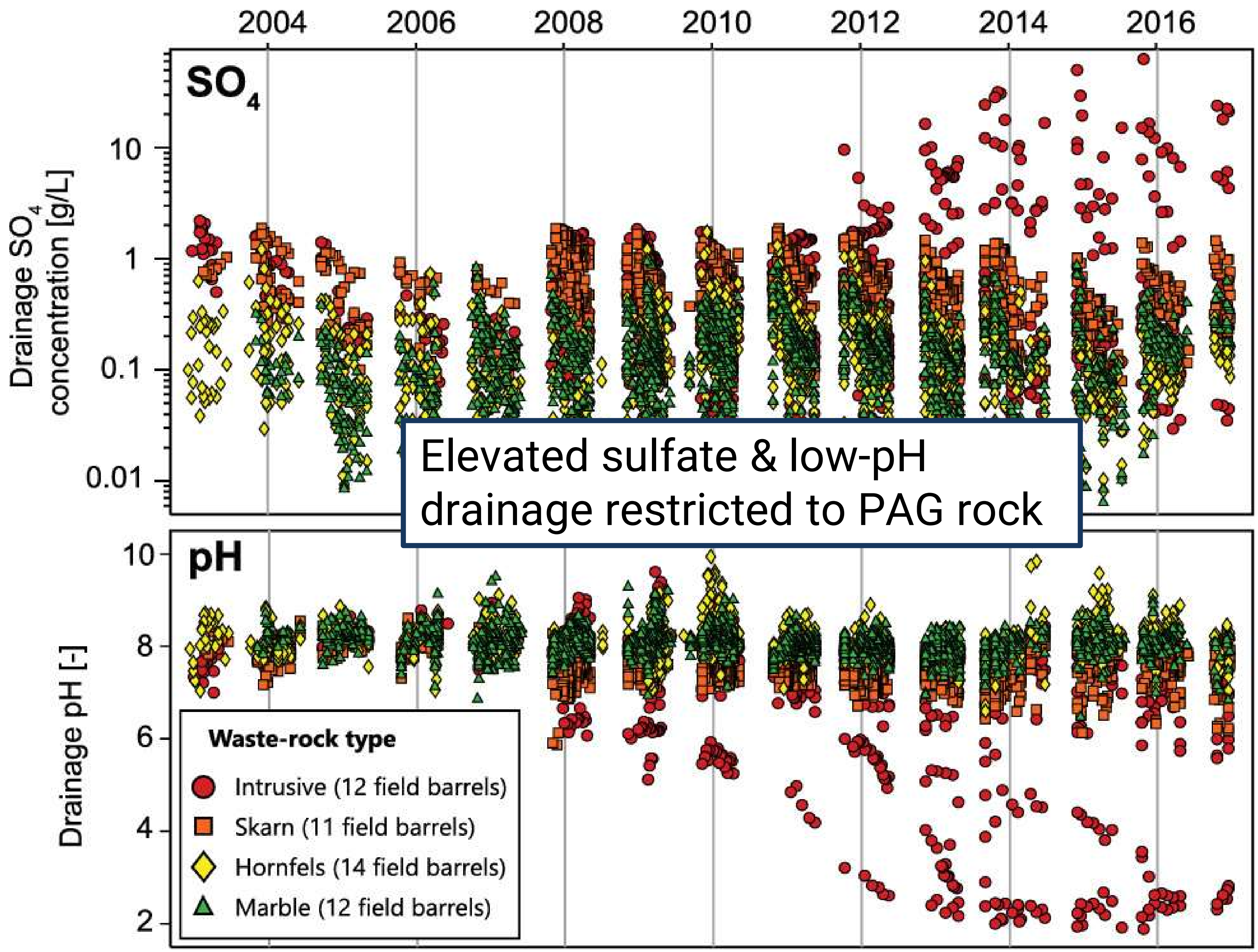
49 different experiments (+blanks) with different waste rock types:






Vriens et al., 2019, ACS Omega

# Long-term drainage dynamics




**5518 drainage samples!!**

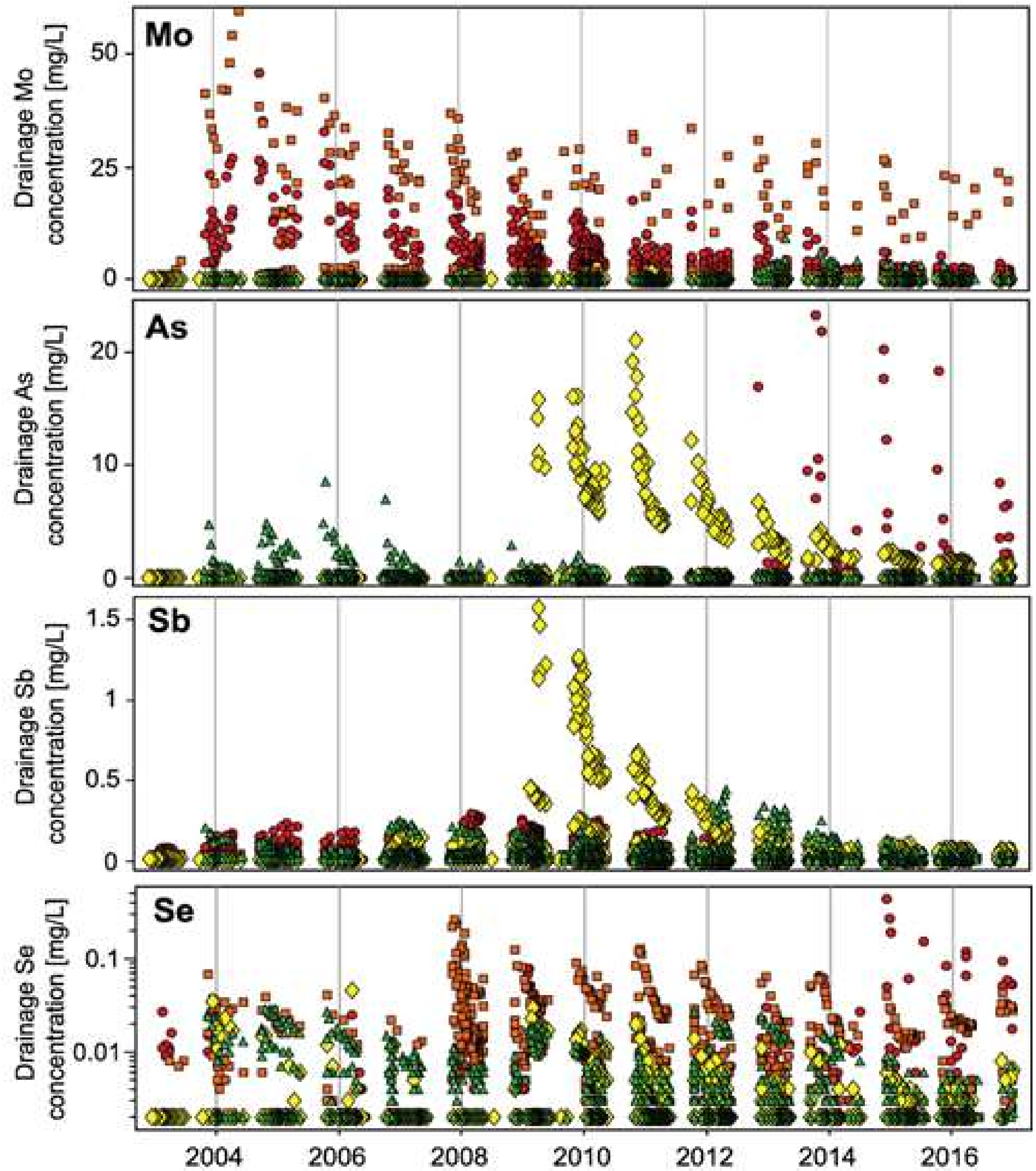
Vriens et al., 2019, ACS Omega

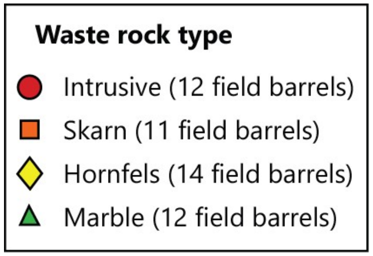
# Long-term drainage dynamics

Appreciable As, Mo, Sb, Se also in circumneutral to slightly alkaline drainage

from <u>both</u> NAG and PAG rock!

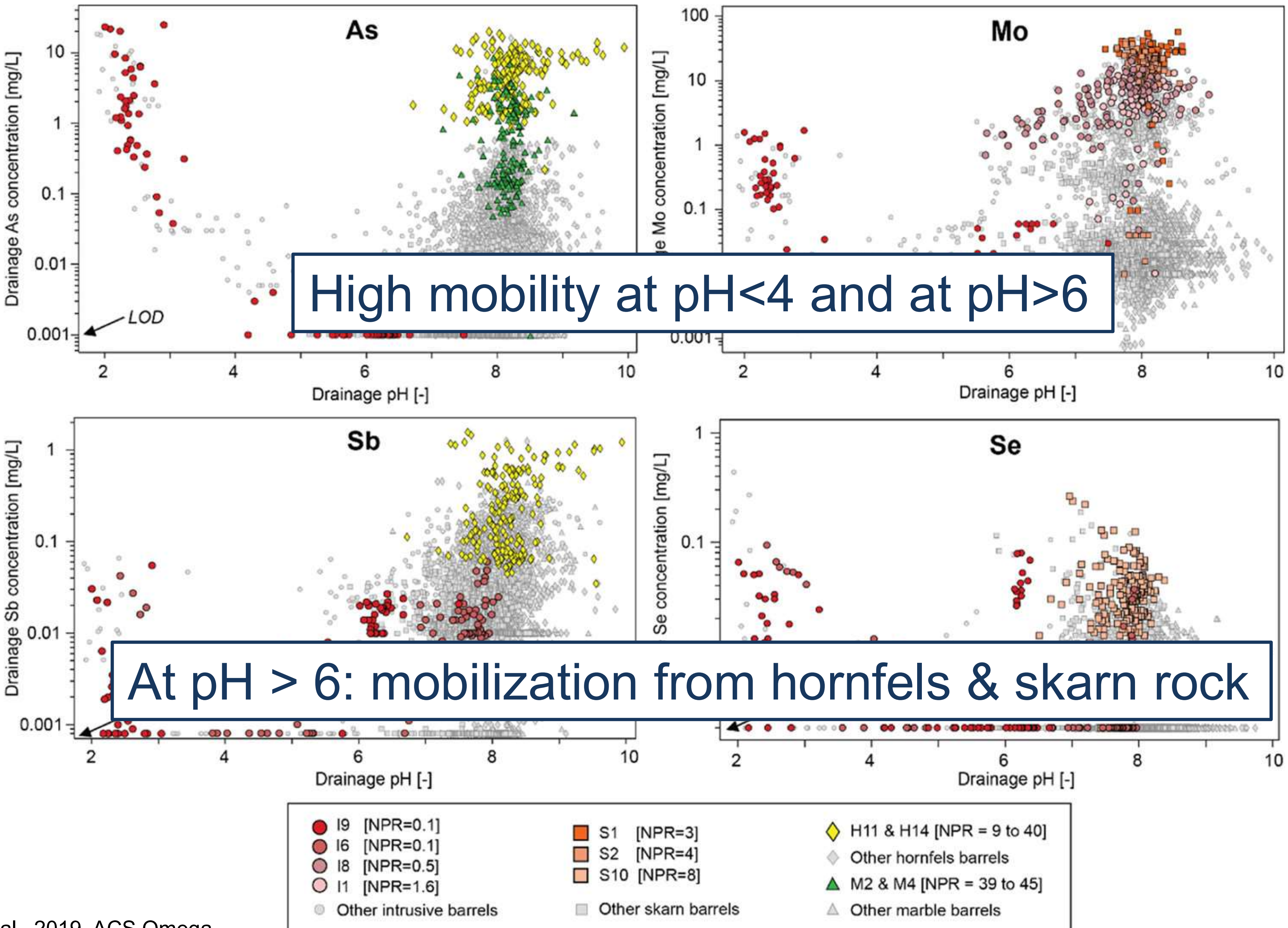
Timing of release: distinct reactivity between various waste-rock types ?




<u>Vriens</u> et al., 2019, ACS Omega

# pH-dependent metal(oid) mobilization:




High mobility at pH<4 and at pH>6

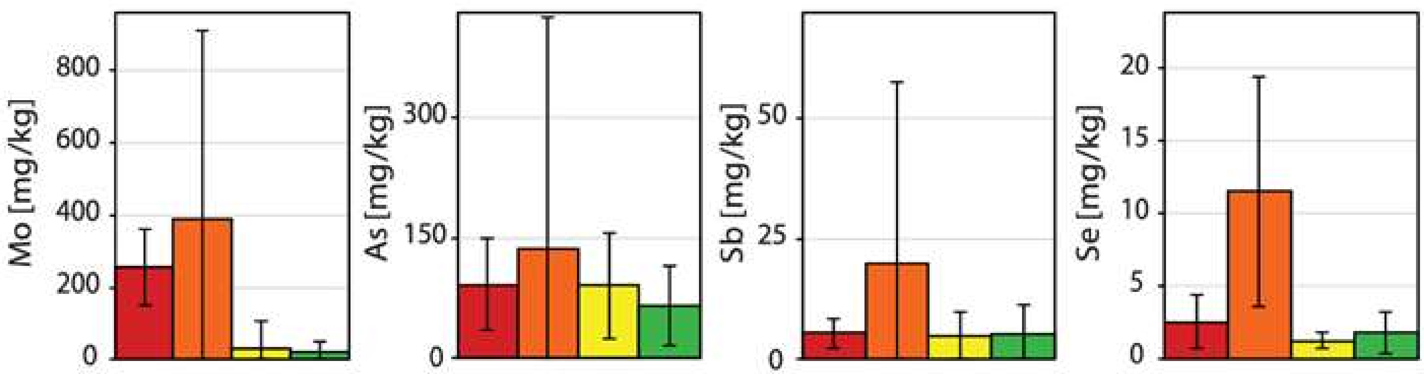
At pH > 6: mobilization from hornfels & skarn rock

Vriens et al., 2019, ACS Omega

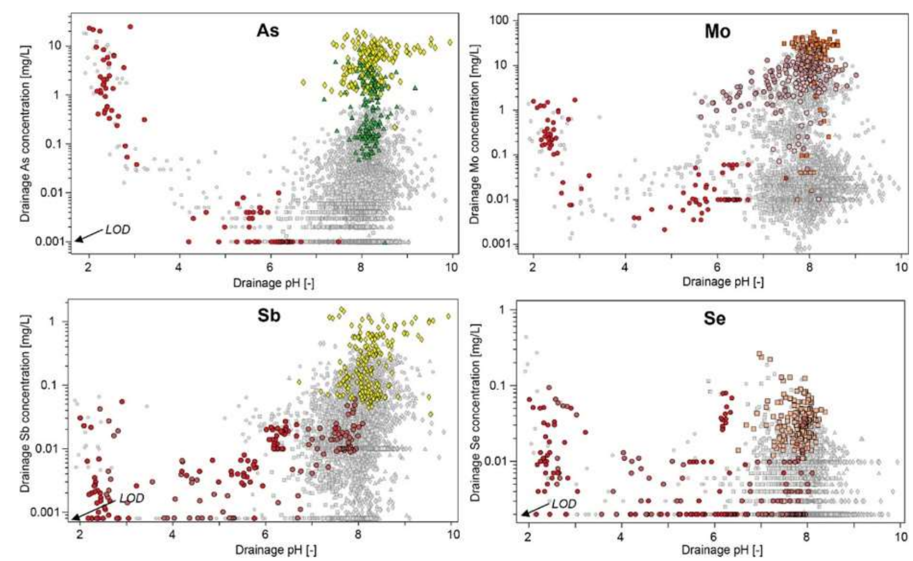
# Drainage chemistry vs. bulk composition

Highest NRD Se & Mo mobilization in skarn materials?

Highest mobility of As & Sb in NRD from hornfels / marble?







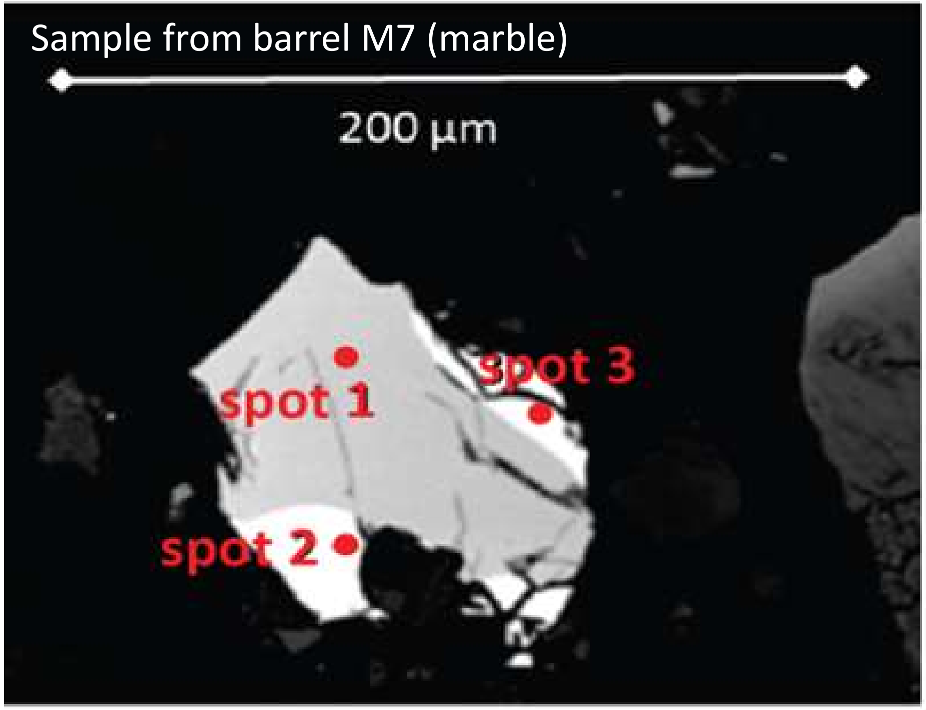

Vriens et al., 2019, ACS Omega

# Mineralogical composition; As-Sb

| | | **intrusive (I9)** | **skarn (S10)** | **hornfels (H14)** | **marbles (M7)** |
|---|---|---|---|---|---|
| | elem. content (mg/kg) | 228 | 1050 | 289 | 73 |
| arsenopyrite | FeAsS | 23 | 11 | <0.1 | <0.1 |
| realgar/orpiment | $As_4S_4/As_2S_3$ | <0.1 | <0.1 | 3 | 4 |
| enargite/tennantite | $Cu_3AsS_4$ $Cu_{12}As_4S_{13}$ | 15 | 19 | **31** | **39** |
| watanabeite | $Cu_4(As,Sb)_2S_5$ | 6 | 22 | 14 | 10 |
| As–Fe-(oxy)sulfates | $(Fe,Cu,Pb,As)O(SO_4)$ | 59 | 24 | 45 | 33 |
| As–Fe-carbonates | $(Fe,Mn,As,Cr,Cu)CO_3$ | <0.1 | <0.1 | 6 | 7 |
| As-fornacite | $(Ca,Cu,Cr)(AsO_4)(OH)$ | <0.1 | 35 | 1 | 7 |
| | *total* | *100* | *100* | *100* | *100* |
| | | **intrusive (I9)** | **skarn (S10)** | **hornfels (H14)** | **marbles (M7)** |
| | elem. content (mg/kg) | 13 | 20 | 11 | 13 |
| stibnite | $Sb_2S_3$ | 36 | 43 | 23 | 17 |
| watanabeite | $Cu_4(As,Sb)_2S_5$ | 61 | 54 | 77 | 89 |
| (Bi)stibiconite | $(Bi,Fe)Sb_3O_6$ | <0.1 | <0.1 | 3 | 3 |
| | *total* | *100* | *100* | *100* | *100* |

# Oxidation of primary As/Sb-sulfides

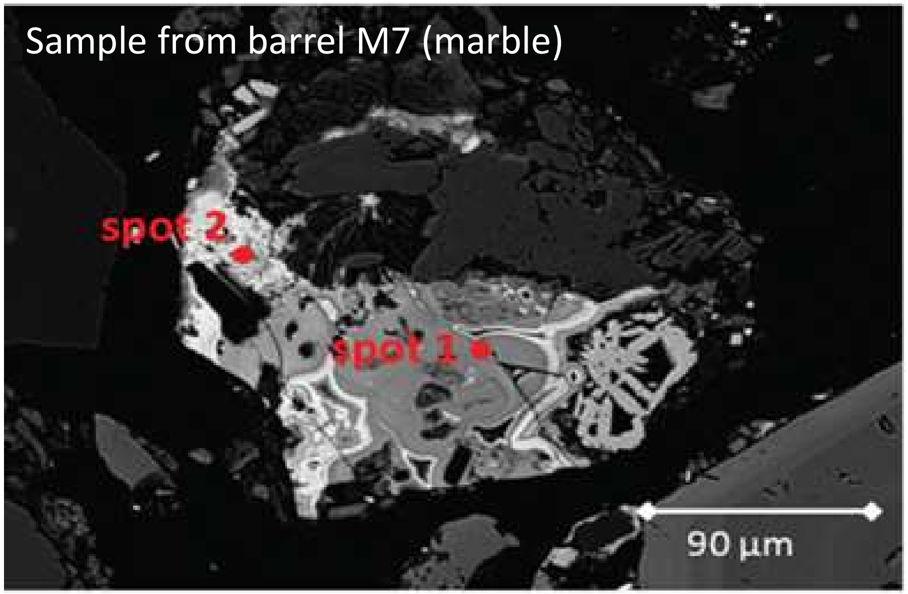
ΔG°$_f$ for oxidative dissolution
Realgar and orpiment : −31 to −84 kJ/mol
Arsenopyrite: −141 kJ/mol
Enargite: −206 kJ/mol




| | Spot 1 | Spot 2 | Spot 3 |
|---|---|---|---|
| As | <0.1 | 10 | 7 |
| C | <0.1 | 47 | 56 |
| Ca | 19 | 0.2 | 0.2 |
| Cu | 29 | 20 | 16 |
| Fe | 26 | 2 | 2 |
| O | 1 | 8 | 8 |
| S | 26 | 10 | 7 |
| Sb | <0.1 | 0.6 | 0.7 |
| Si | <0.1 | 0.4 | 0.1 |
| Zn | <0.1 | 2 | 2 |
| Total: | 100 | 100 | 99.8 |

**Faster dissolution of more labile sulfides in marble and hornfels?**

# Identification of relevant secondary phases




| | Spot 1 | Spot 2 |
|---|---|---|
| S | <0.1 | 3 |
| Fe | 1 | 2 |
| O | 26 | 21 |
| Si | 12 | 3 |
| Cu | 18 | 20 |
| Zn | 13 | 6 |
| Mn | 4 | 21 |
| As | <0.1 | 7 |
| C | 23 | 16 |
| Ca | 0.3 | 1 |
| Al | 1 | <0.1 |
| Mg | 1 | <0.1 |
| Total: | 100 | 99 |

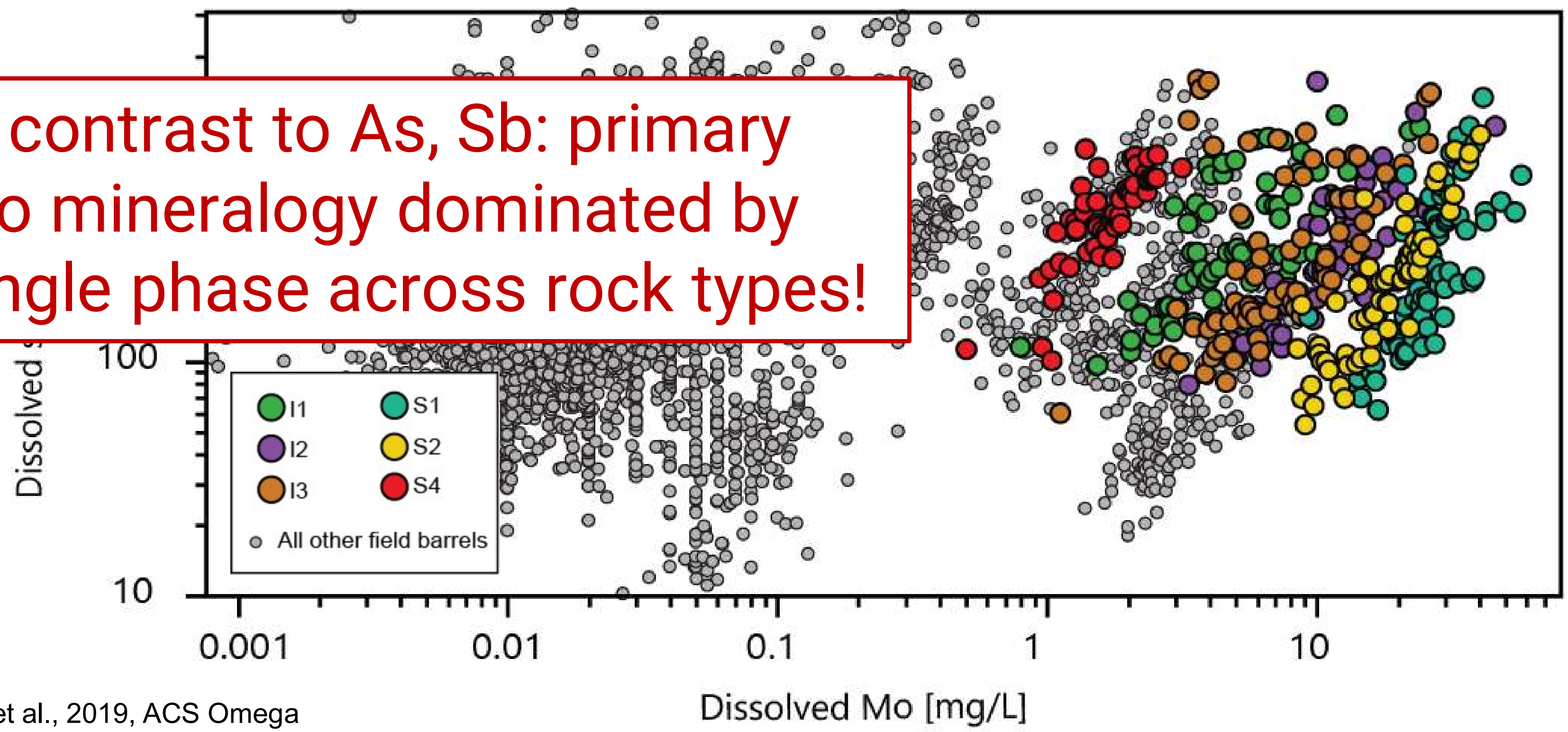
| | | intrusive (I9) | skarn (S10) | hornfels (H14) | marbles (M7) |
|---|---|---|---|---|---|
| | elem. content (mg/kg) | 228 | 1050 | 289 | 73 |
| As–Fe-(oxy)sulfates | (Fe,Cu,Pb,As)O($SO_4$) | 59 | 24 | 45 | 33 |
| As–Fe-carbonates | (Fe,Mn,As,[illegible],Cu)$CO_3$ | <0.1 | <0.1 | 6 | 7 |
| As-fornacite | (Ca,Cu,Cr)($AsO_4$)(OH) | <0.1 | 35 | 1 | 7 |
| | *total* | *100* | *100* | *100* | *100* |

?

# Mineralogical composition; Mo

| | | intrusive | skarn | hornfels | marble |
|---|---|---|---|---|---|
| | elem. content (mg/kg) | 250 | 948 | 289 | 104 |
| molybdenite | $MoS_2$ | **97** | **91** | **98** | **86** |
| Mo–Fe–(oxy)sulfates | $(Fe,Cu,Mo,Zn,As)O(SO_4)$ | 3 | 4.8 | 0.3 | 6.2 |
| Mo–fornacite | $Pb_2((Mo,Cr)O_4)(AsO_4)(OH)$ | <0.1 | 2.6 | 0.4 | 0.9 |
| powellite | $CaMoO_4$ | <0.1 | 0.2 | <0.1 | 1.6 |
| wulfenite | $PbMoO_4$ | <0.1 | 0.2 | <0.1 | 2.1 |
| Mo–oxides | (Pb,Ca,Mo)O | <0.1 | 1.2 | <0.1 | 3.1 |
| | *Total* | *100* | *100* | *100* | *100* |

In contrast to As, Sb: primary Mo mineralogy dominated by single phase across rock types!



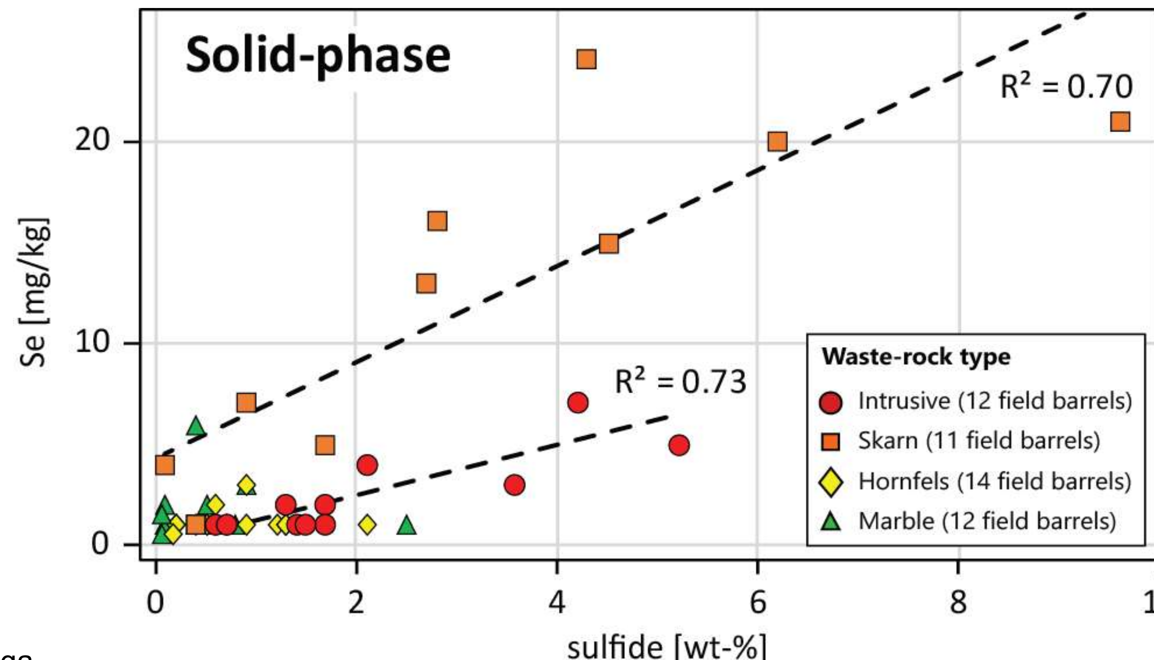

Vriens et al., 2019, ACS Omega

# Mineralogical composition; Se

## Idem to Mo: consistent Se phases across rock types

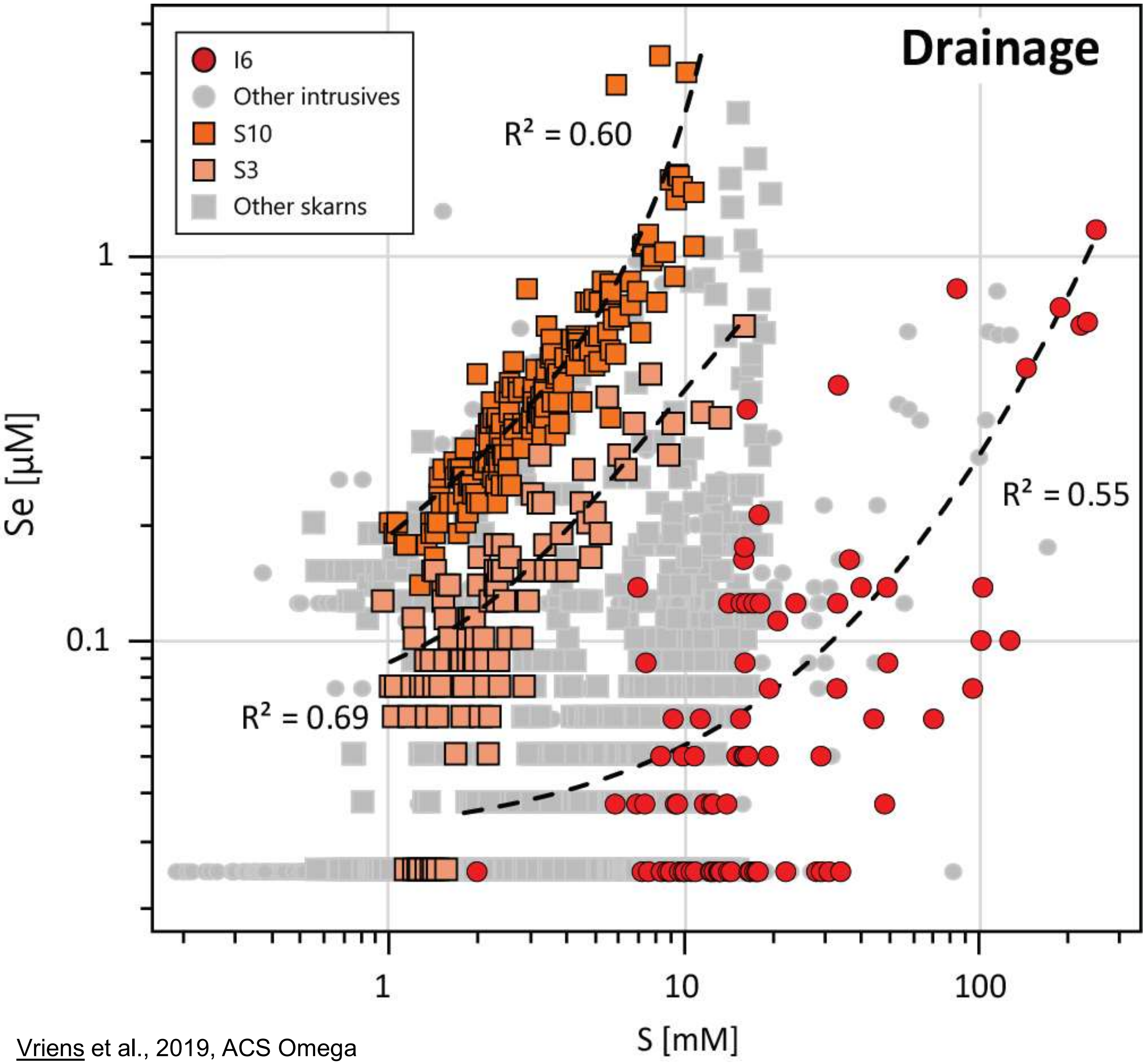
| | | intrusive | skarn | hornfels | marble |
|---|---|---|---|---|---|
| | elem. content (mg/kg) | 5 | 13 | <2 | 3 |
| Se–galena | Pb(Se,S) | **99** | **99** | **100** | **100** |
| Se-pyrite | $Fe(Se,S)_5$ | 0.4 | <0.1 | <0.1 | <0.1 |
| Se–sulfosalts | (Cu,Pb,Fe)SeS | 0.4 | 1 | <0.1 | <0.1 |
| | *total* | *100* | *100* | *100* | *100* |

Clausthalite [PbSe] or ferroselite [$FeSe_2$]?




Vriens et al., 2019, ACS Omega

# Drainage composition: Se versus S




Waste rock S over Se :
**10k-23k**

Drainage S over Se:
**30k-200k**

→ Preferential retention of Se?

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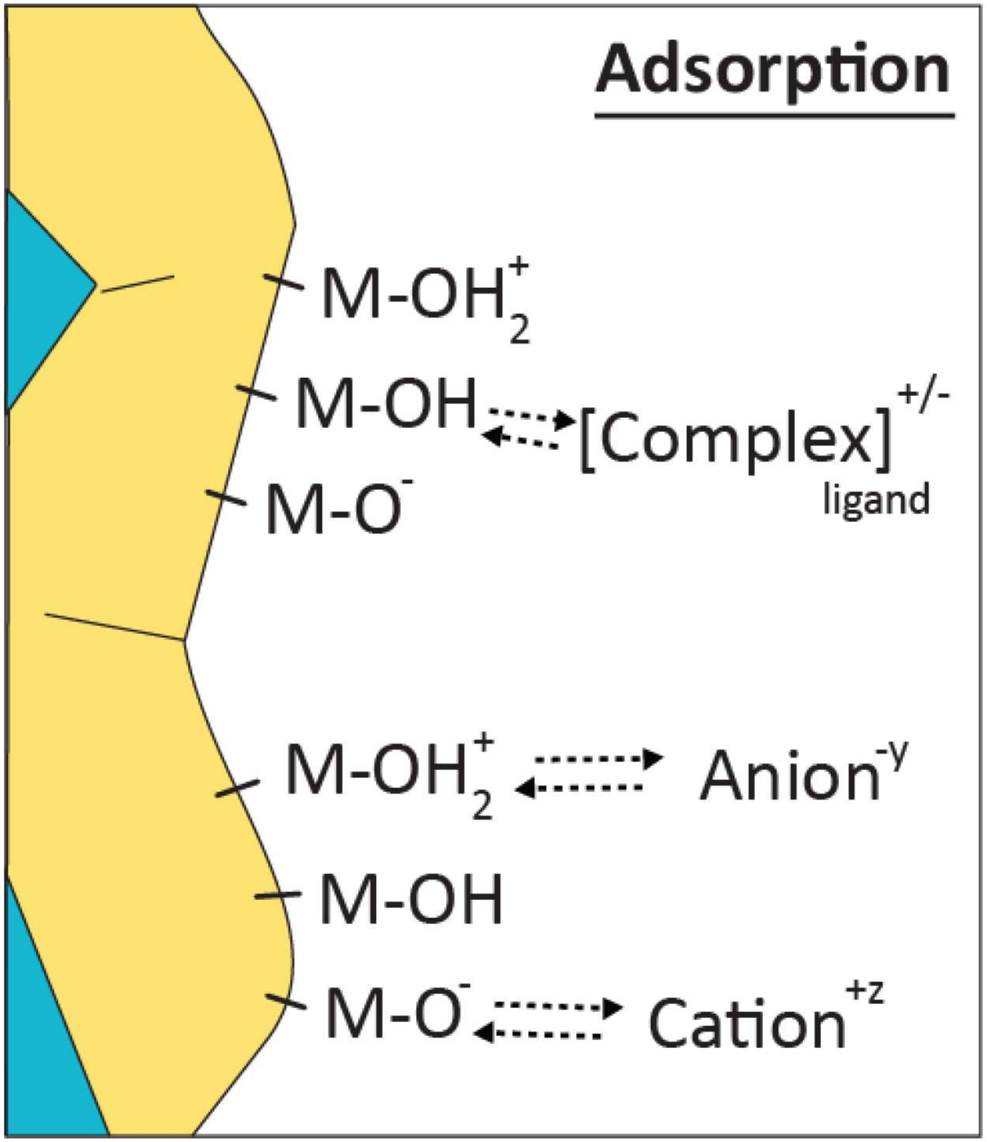
# pH dependent mobility: adsorption




Electrostatic interaction between charged surface and charged ions/complexes

Various sorption models: diffuse/Stern layers on sorbent; inner- or outersphere complexation as f(hydration)

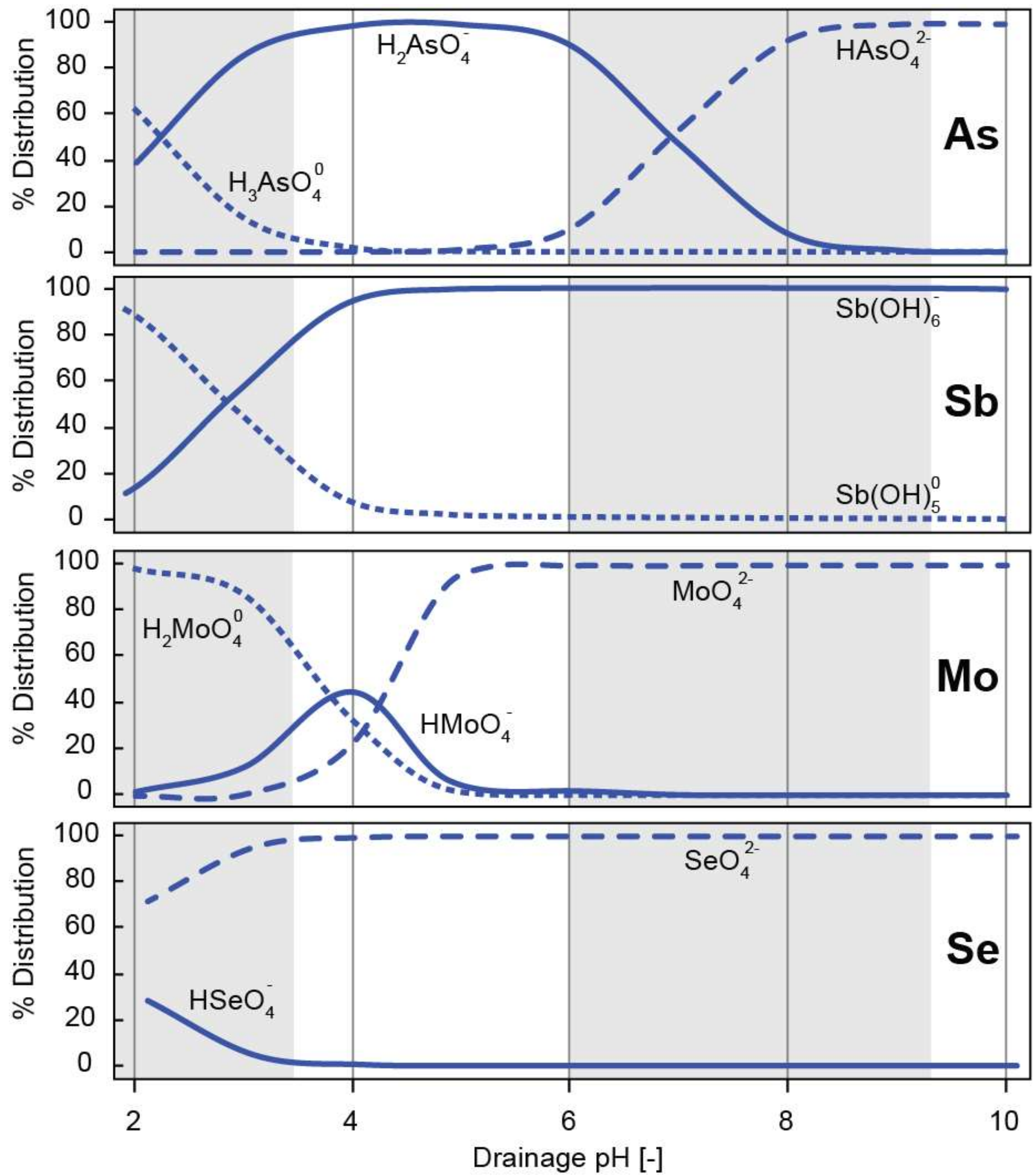
- **Need to know aqueous speciation!**
- **Need to know mineral surface properties!**

**Vriens** et al, 2020, Minerals

# Adsorption of metal(oid)s

Protonation and redox equilibrium constants, stability constants for aqueous complexes are well-known!

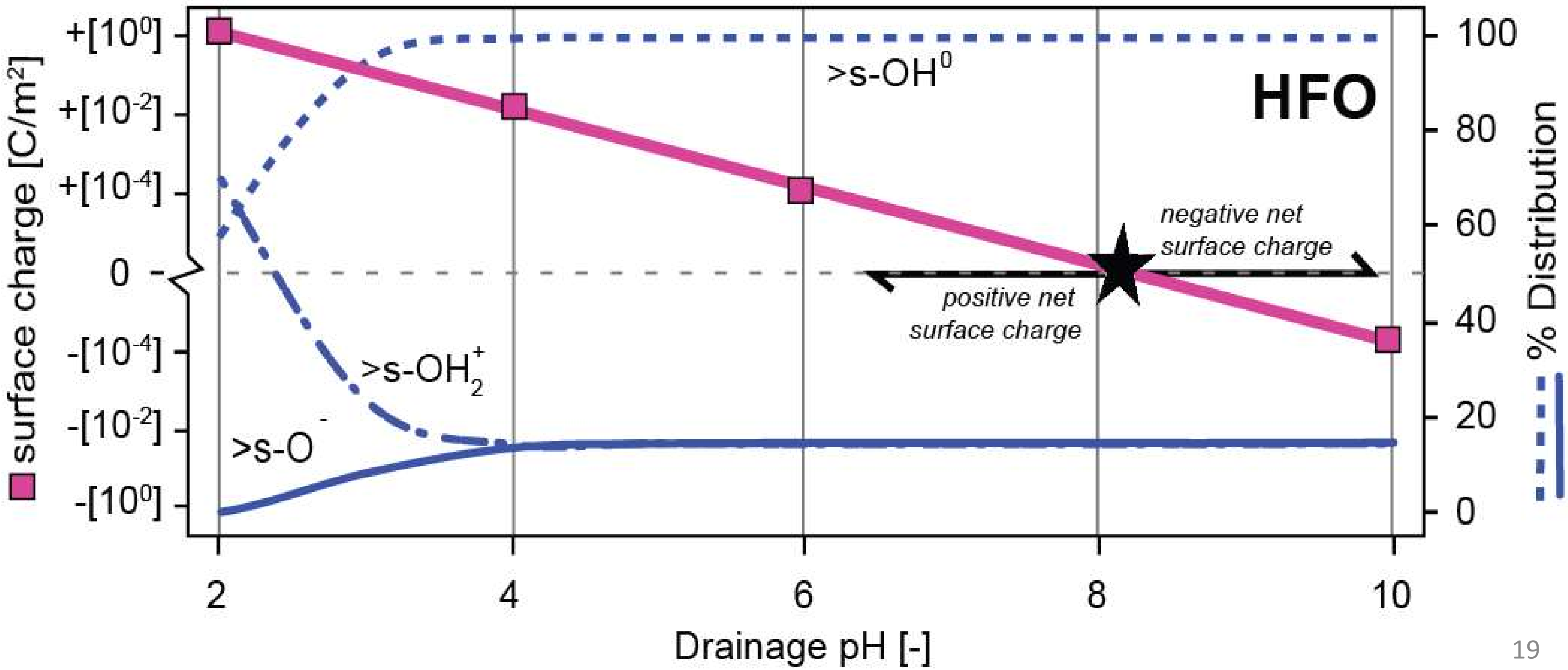
In our case, the long-term drainage chemistry is also known! (*competition*)



# Adsorption onto *messy* mineral phases

Surface properties of amorphous secondary mineral phases not known! (*RSA, sorption site density*)

Assumption: hydrous ferric oxide (Fe-OOH; model phase):



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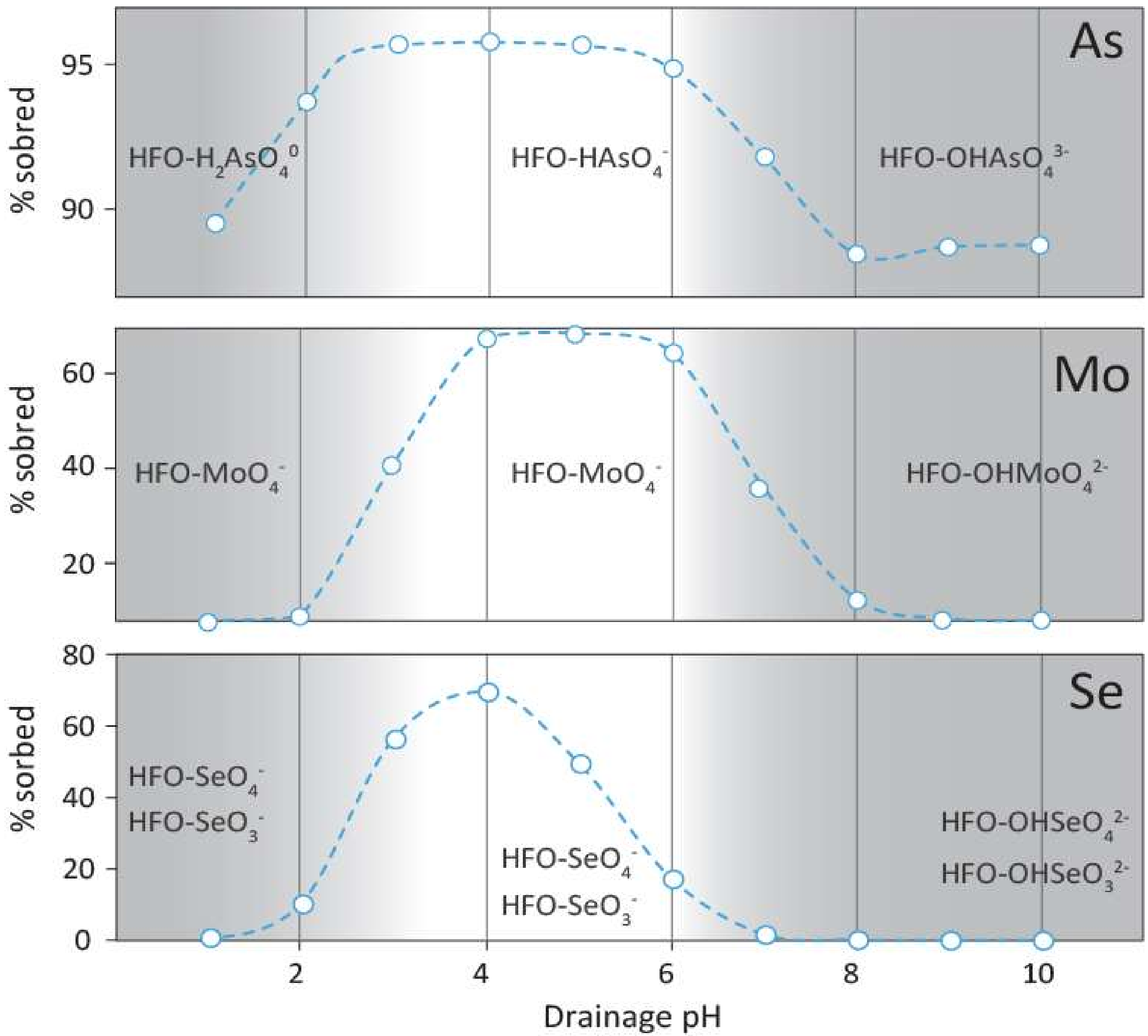
# Adsorption modeling



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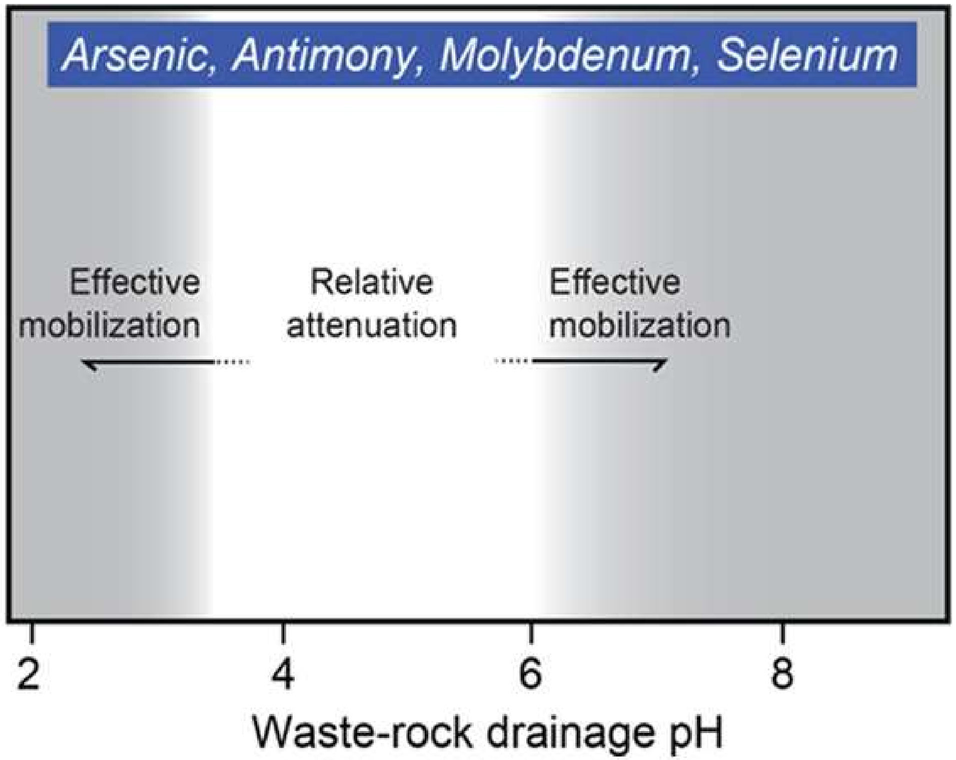
# Three different 'mobility' regimes:

1. Acidic (pH<3.5): <u>elevated</u> As, Sb, Mo, and Se mobility due to negligible adsorption and dissolution of Fe-oxides
2. Slightly acidic (3.5<pH<6): <u>low</u> As, Sb, Mo, and Se mobility due to effective retention by adsorption
3. Circumneutral to slightly alkaline (6<pH<9): <u>elevated</u> As, Sb, Mo, and Se mobility due to negligible retention by adsorption and little secondary precipitation



# What else can adsorption explain?

Fe-content in hornfels and marble lower than in intrusive and skarn → lower abundance of potential sorption sites

High-alkalinity drainage from carbonate-rich rock enhances As mobility due to competitive occupation of sorption sites

Sorption edges of As, Mo, Sb, and Se appear similar despite different adsorption modes → mobility controlled by surface properties rather than aqueous speciation

# Practical implications

- Oxyanion-forming trace elements As, Sb, Mo, and Se can be released in the mg/L range from both NAG and PAG rock
- Their mobility is highest under circumneutral to slightly alkaline (6<pH<9) drainage conditions
- In addition to bulk content and waste rock reactivity, element-specific mineralogy and adsorption phenomena provide clues to drainage dynamics

Different drainage types from a single rock lithology / class

# Open questions:

- Quantitative importance of sorption under oxygen-depletion?
  → Adsorption of reduced solutes completely different…
- Material heterogeneity: e.g., small-scale acidic zones under bulk-alkaline drainage pH
  → Kinetics of precipitation and adsorption relative to drainage?

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# Thank you!

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