Kinetic metals: reconstructing past cave drip rates using the “decay” of organic metal complexes (OMCs)

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Te Whare Wānanga o Waikato

Waikato Environmental Geochemistry

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Organic metal complexes (OMCs) in dripwaters

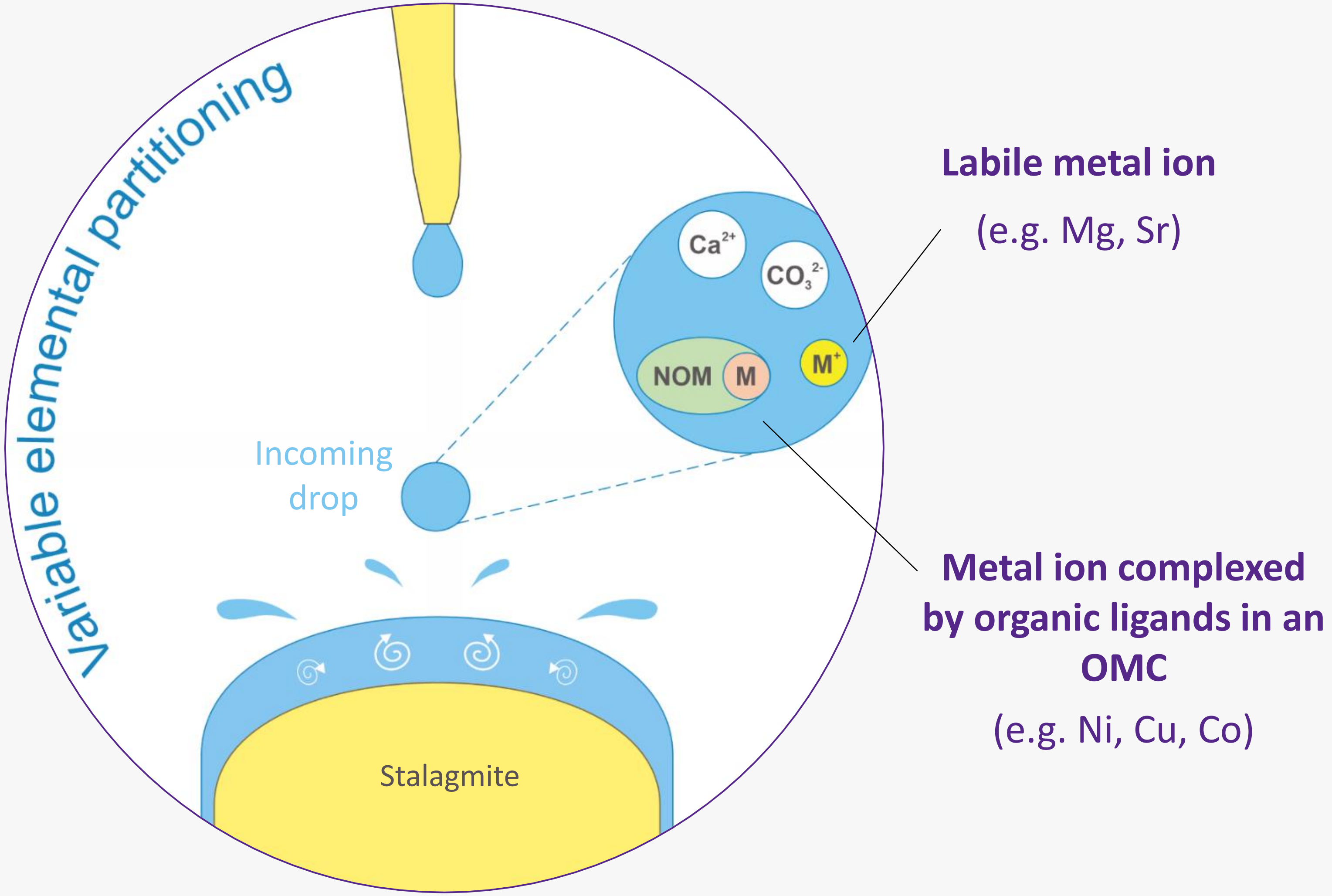
Labile metals

- Hydrated or in simple *inorganic* complexes

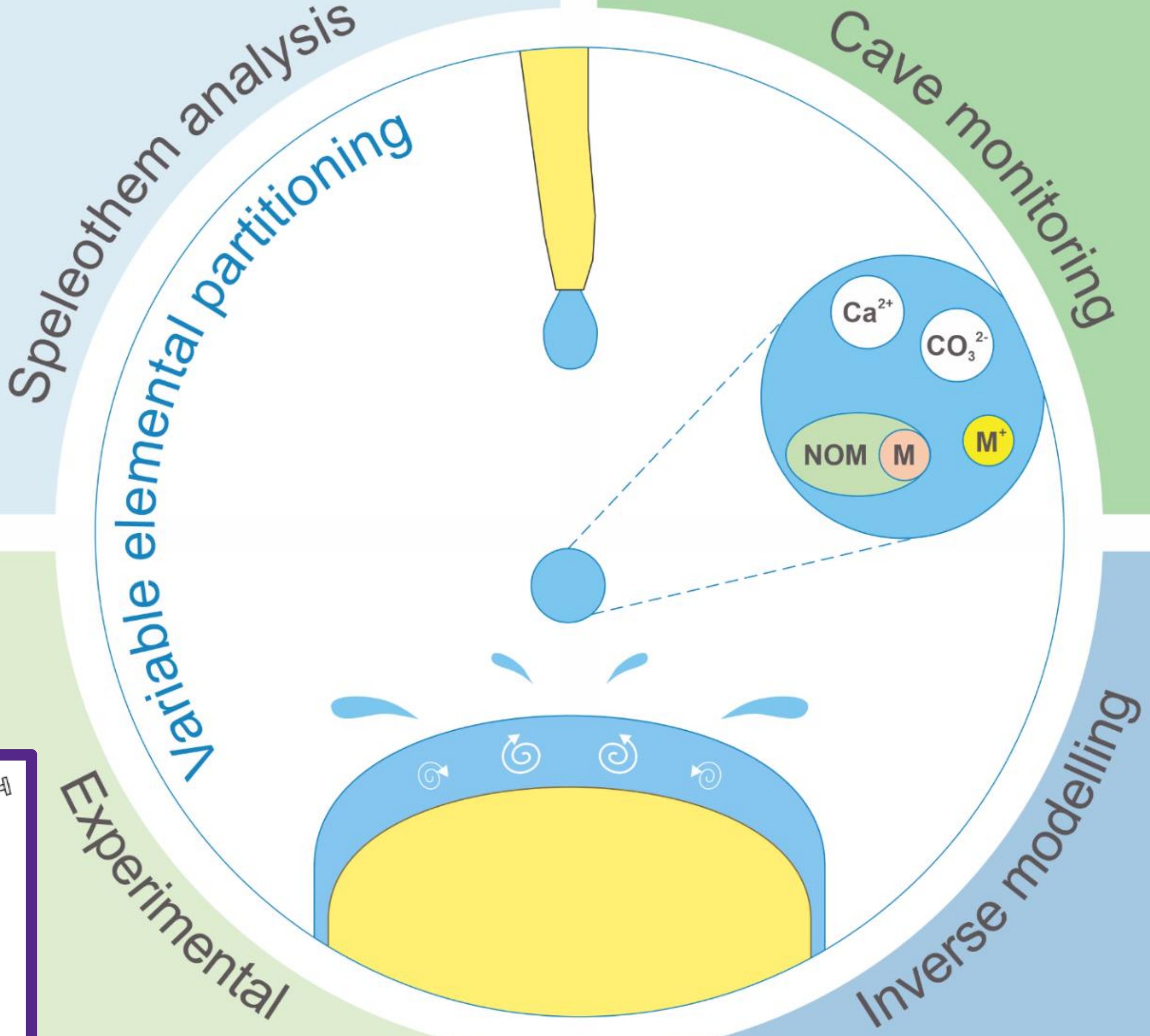
Kinetic metals

- >90% of transition metals are bound in OMCs
- OMCs transport metals to caves (e.g., Hartland et al., 2011, 2012)
- Release of metals to stalagmites is *time-sensitive*

Can we use OMC decay kinetics to extract a hydrological signal?

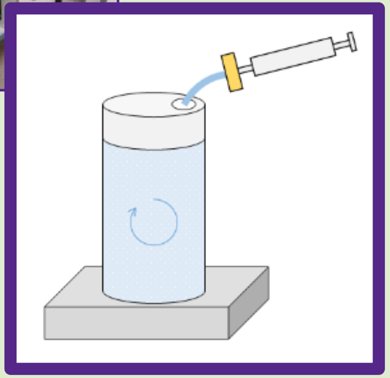


Time-series of transition metal concentrations

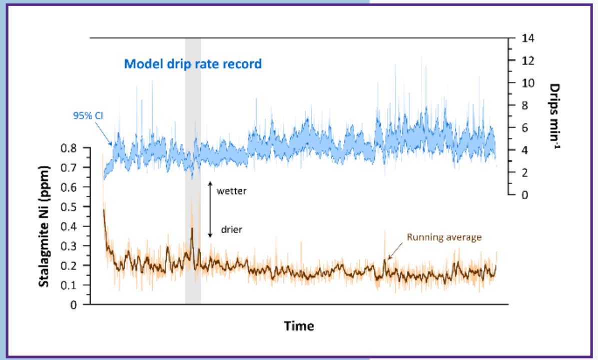


New Zealand & South Pacific

Cave-analogue



Kinetic studies



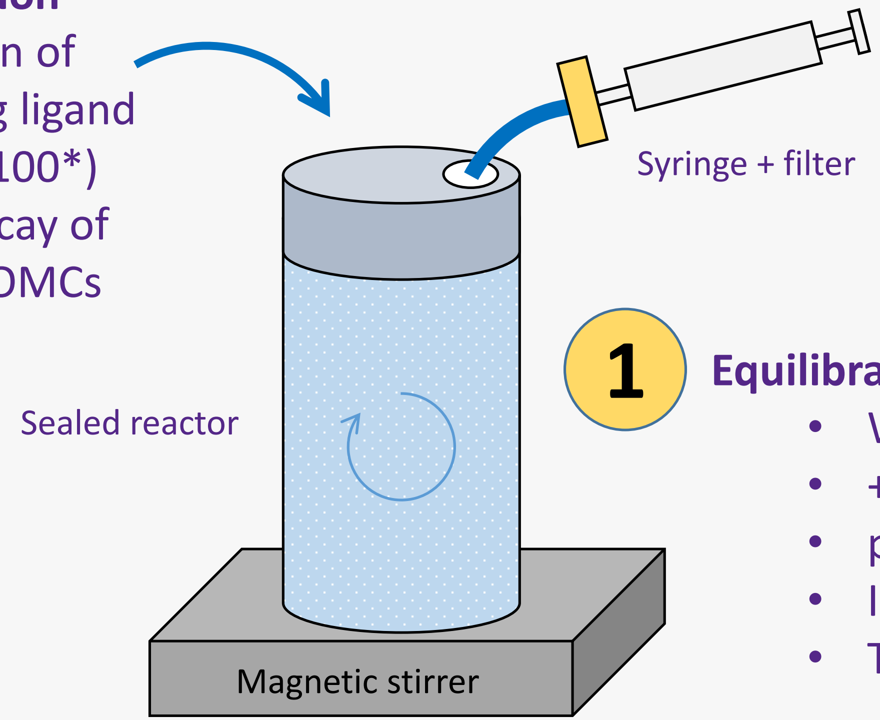
(Semi-)quantitative rainfall record

Measuring the decay of OMCs

Competitive ligand exchange

2

Initiation
addition of
competing ligand
(Chelex-100*)
drives decay of
natural OMCs



3 **Sub-sampling** for ICP-MS
(10 s → 2 h from initiation)

1 **Equilibration of sample solution**

- Waters from 8 NZ caves
- + 5 ppb Ni, Cu, Co
- pH 8.5
- Ionic strength
- Temperature

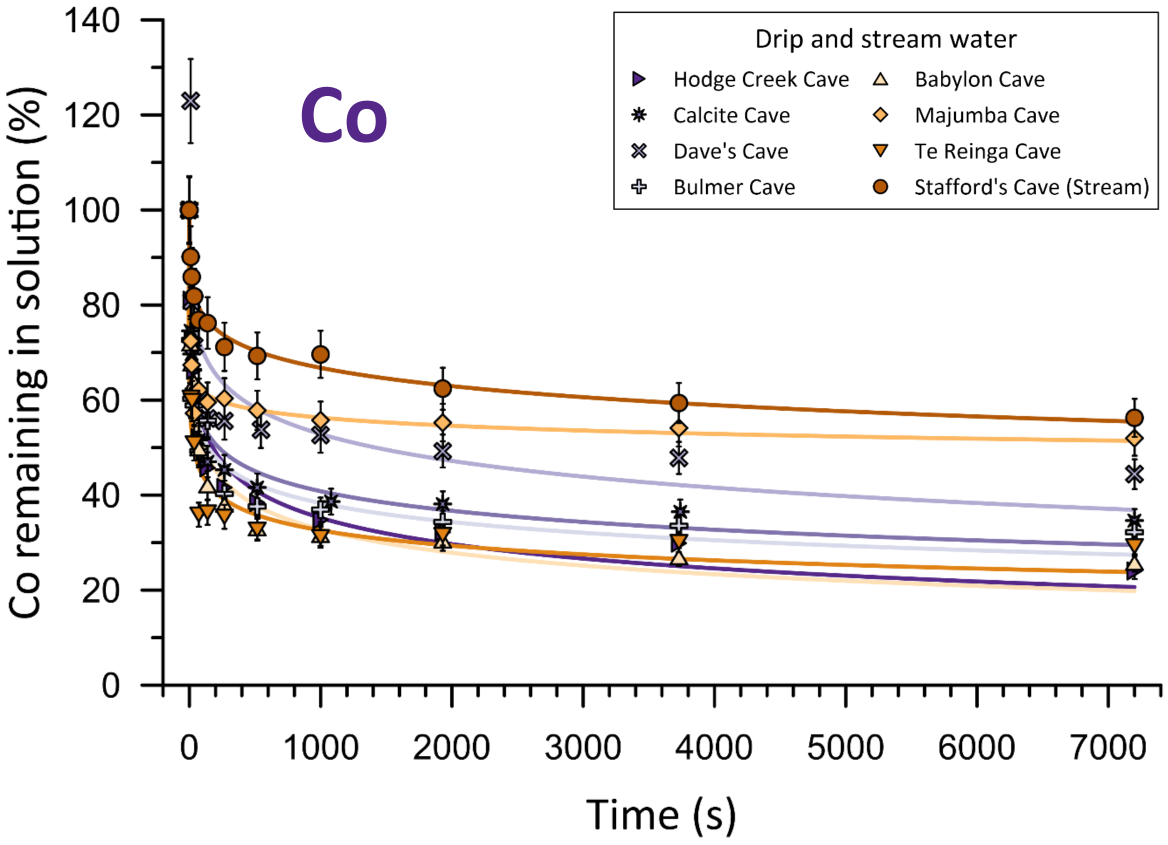
Note:
Kinetics are highly sensitive to method: strictly *conditional*

Objective here:
How does kinetic limitation vary between caves?

*very strong synthetic ligand used to bind trace metals

Measuring the decay of OMCs

Competitive ligand exchange



undissociated after 2h
(stable complexes)

Exponential decay determined by k_d (s^{-1})

OMC equilibria

$$M + L_i \underset{k_{d,i}}{\overset{k_{f,i}}{\rightleftarrows}} ML_i$$

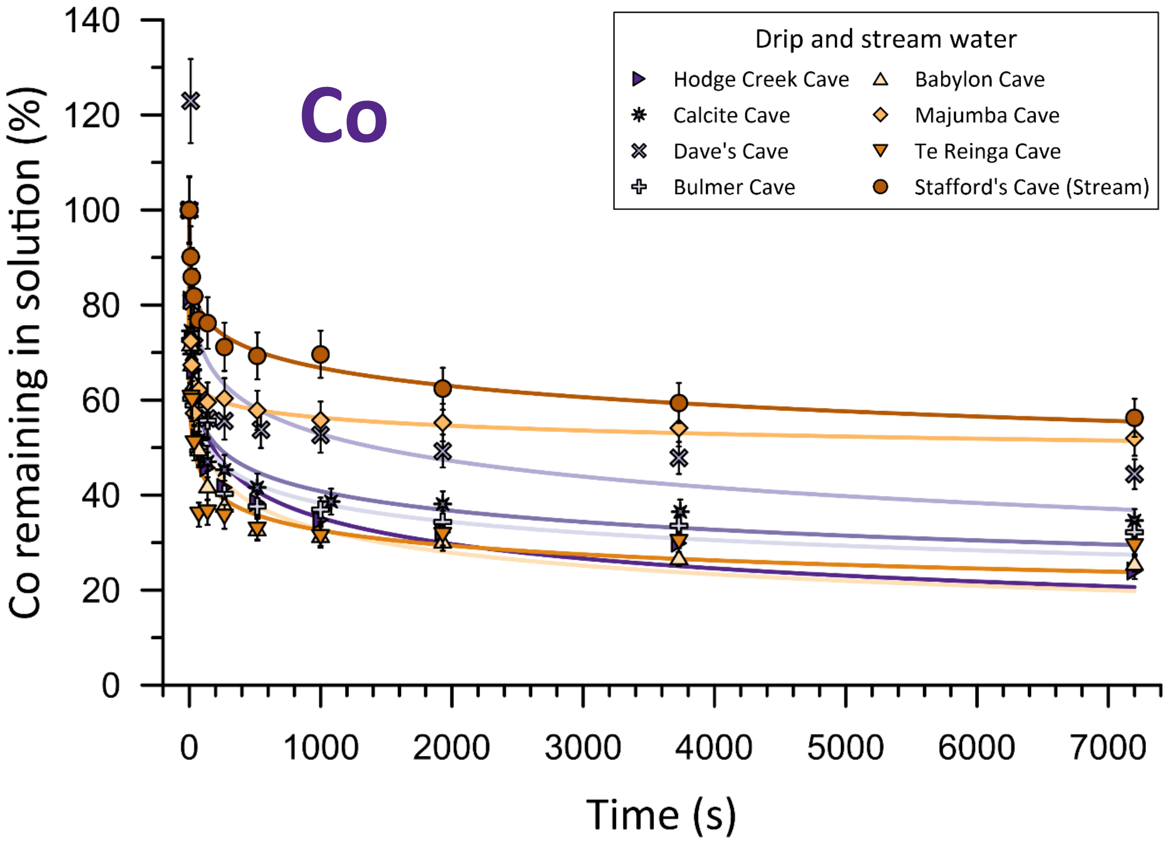
OMCs

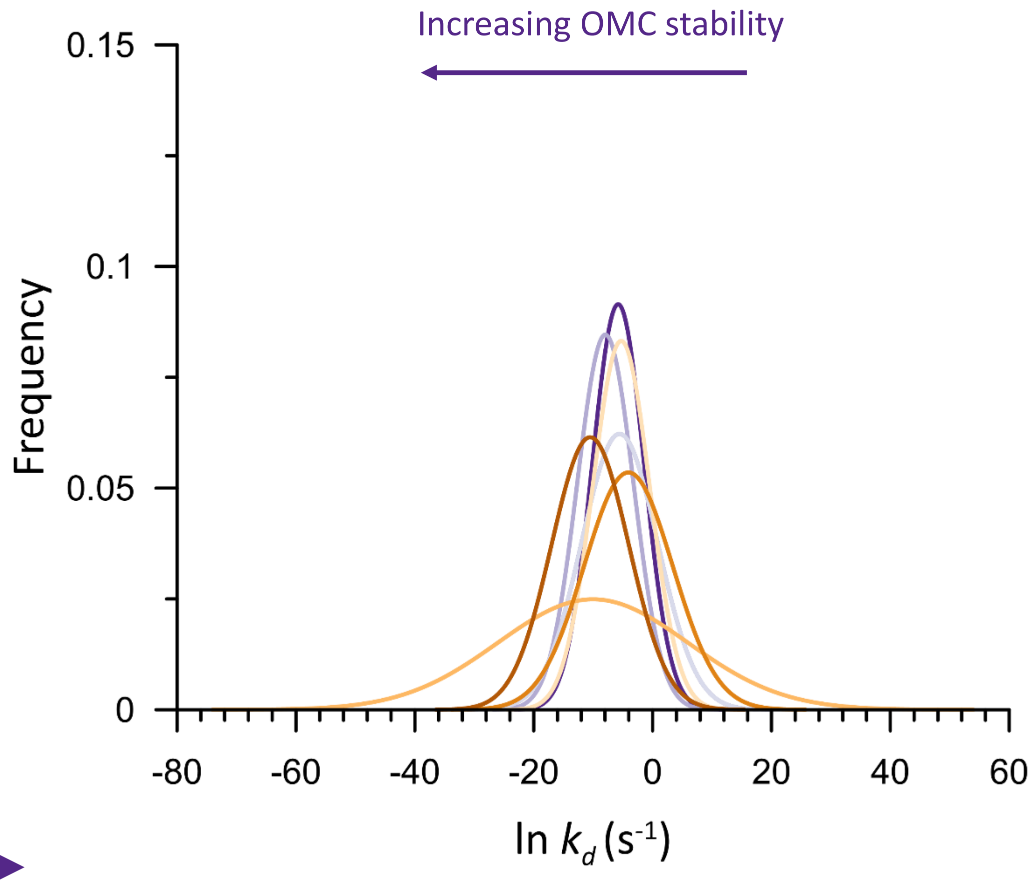
$$k_{d,i} = \frac{k_{f,i}}{K_i}$$

k_d: dissociation rate constant

Measuring the decay of OMCs

Competitive ligand exchange





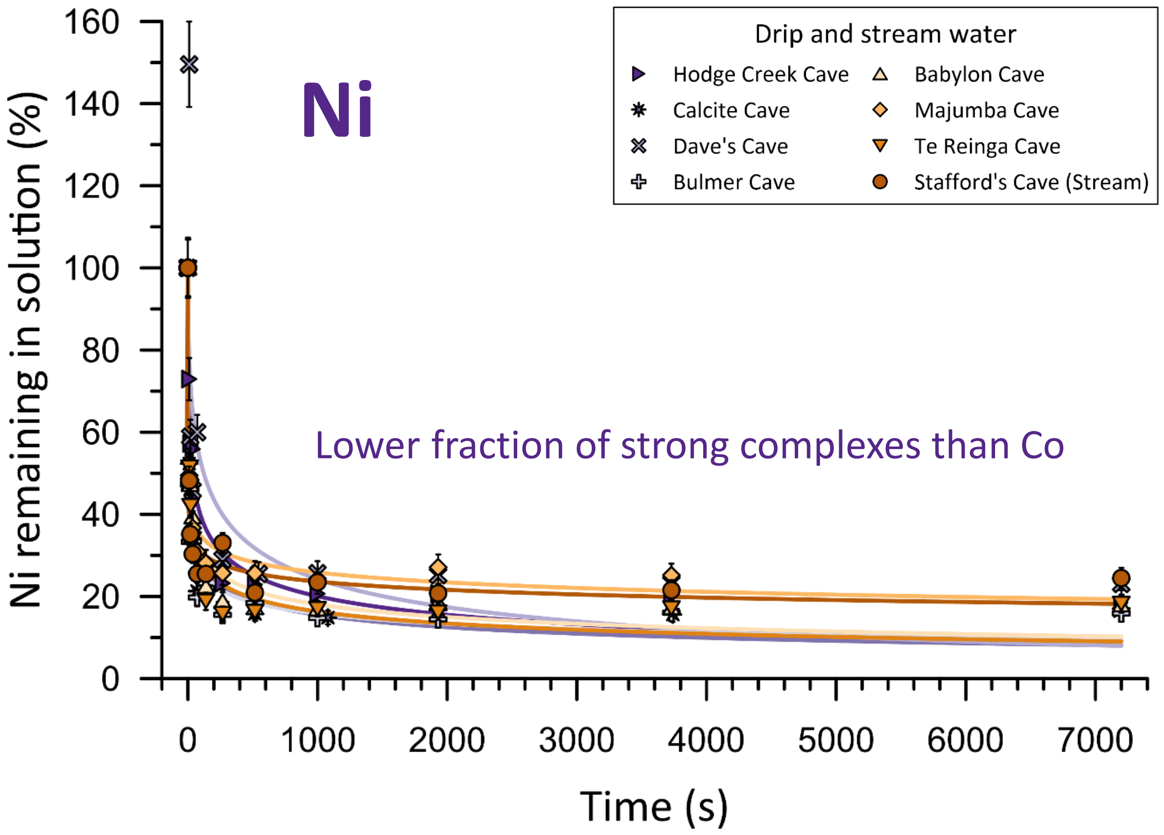
Exponential decay determined by k_d (s^{-1})

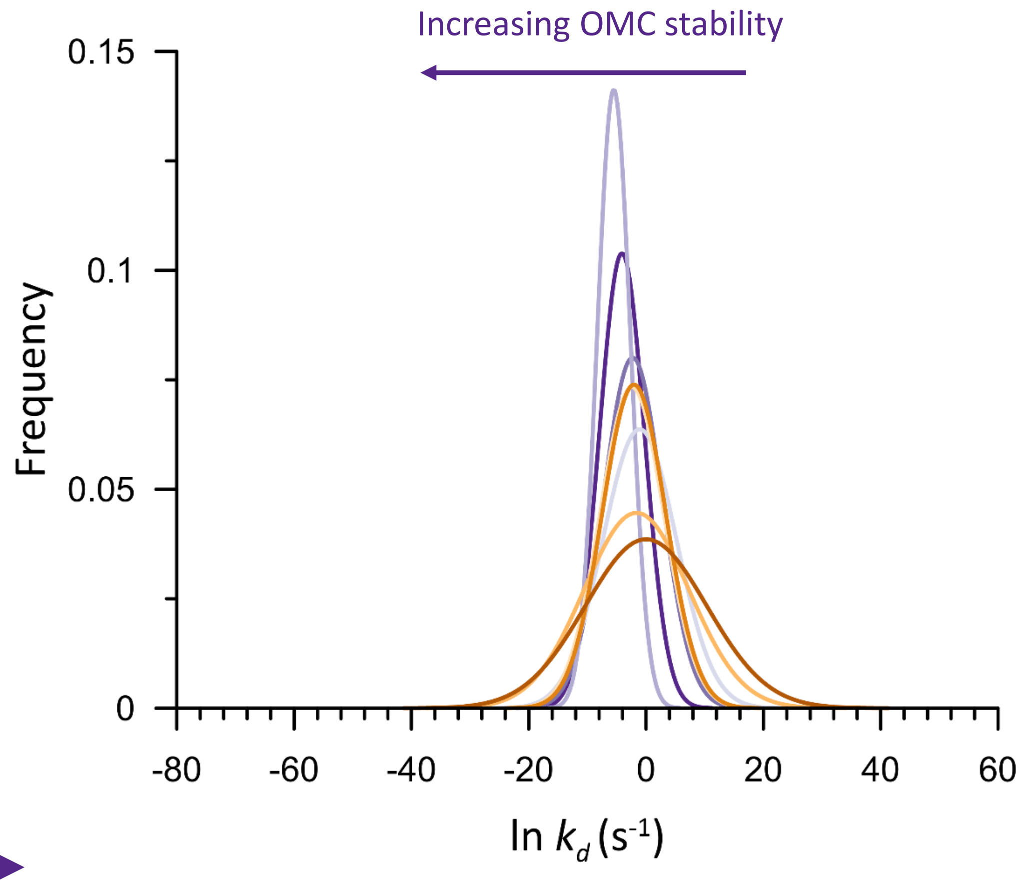
Fit kinetic data to lognormal model (Rate et al., 1992)

Continuous distribution of ln k_d (s^{-1}) with μ and σ

Measuring the decay of OMCs

Competitive ligand exchange





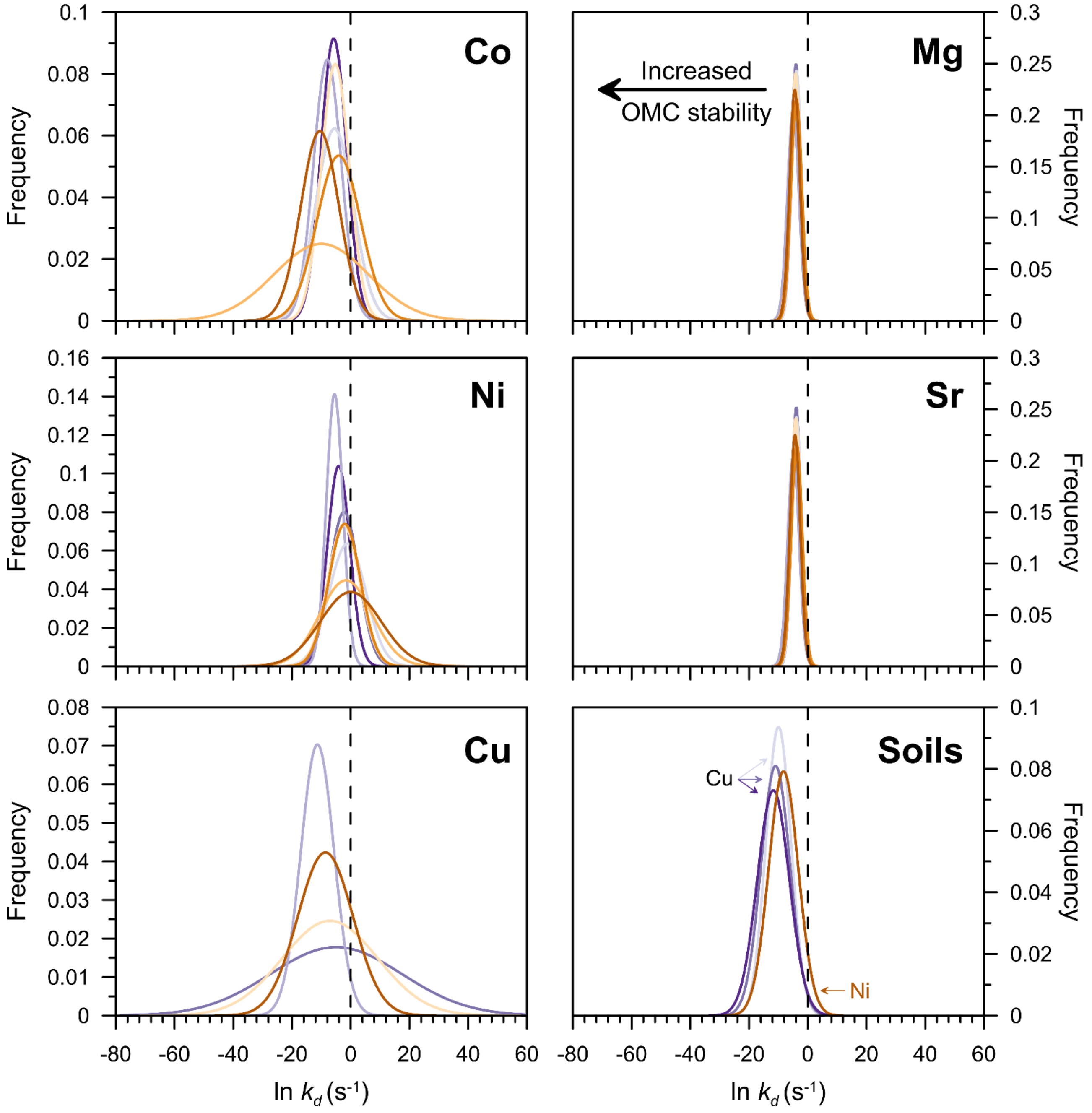
Exponential decay determined by k_d (s^{-1})

Fit kinetic data to lognormal model (Rate et al., 1992)

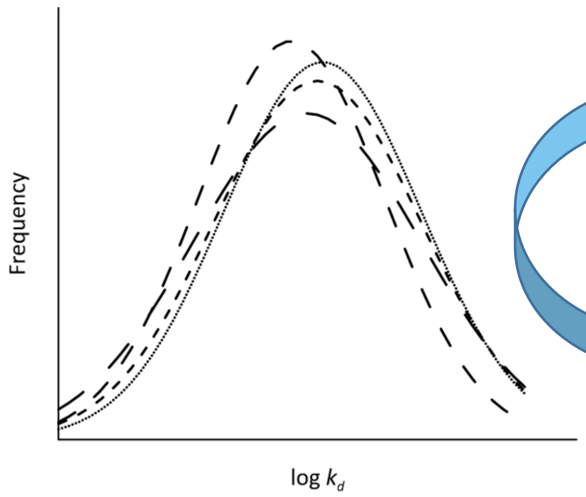
Continuous distribution of ln k_d (s^{-1}) with μ and σ

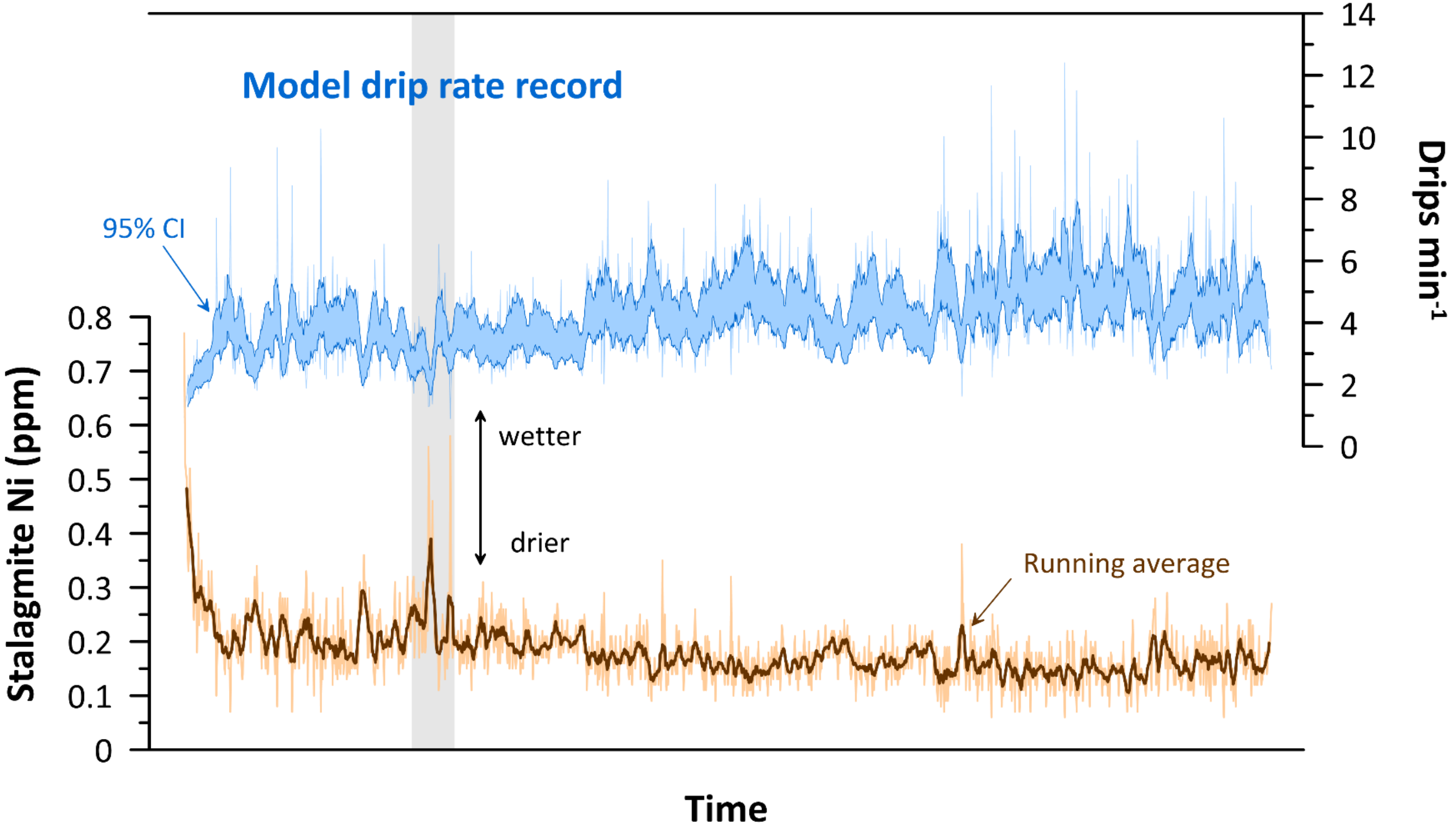
OMC decay in cave waters and soil extracts

- 8 cave water samples + 3 soil extracts ($CaCl_2$)
- Exponential decay evident in all
- k_d distributions to be better constrained (smaller σ) – ignore absolute values!
- Kinetics vary between transition metals and water samples (consistent for soils)
  - No obvious relationships with NOM quality/quantity
- Mg and Sr kinetics highly consistent:
  - Primarily weak aquo-metal complexes
  - No kinetic limitation
  - Inorganic partitioning



Estimating drip rate from selected ln k_d distributions





Notes & assumptions:

- Partitioning of Ca and labile Ni into calcite occurs at ca. the same rate (Lindeman et al., 2022)
- Residence time (and drip rate) based on supplied $[Ni]_{labile}$ from water thin-film
- Currently not calibrated against monitoring data

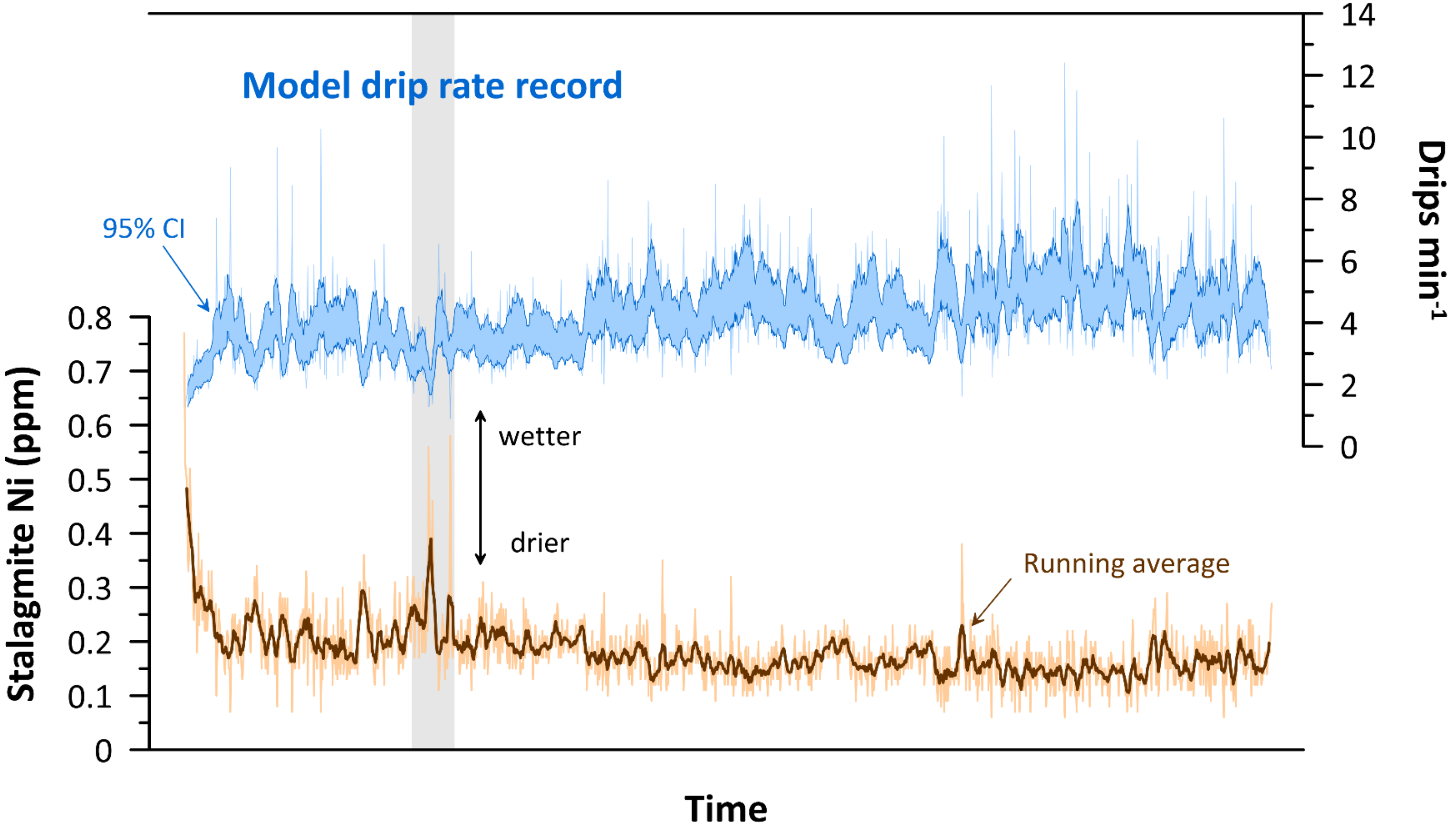
Estimating drip rate from selected ln k_d distributions

Ongoing work:

- Improvement of current fitting routine to constrain distributions
- Sensitivity study

Cave monitoring:
- Responsivity and magnitude of aqueous [M] variability
- Drip rate – rainfall relationship

- Elaboration and calibration of model in relation to other proxies



Thank you!

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