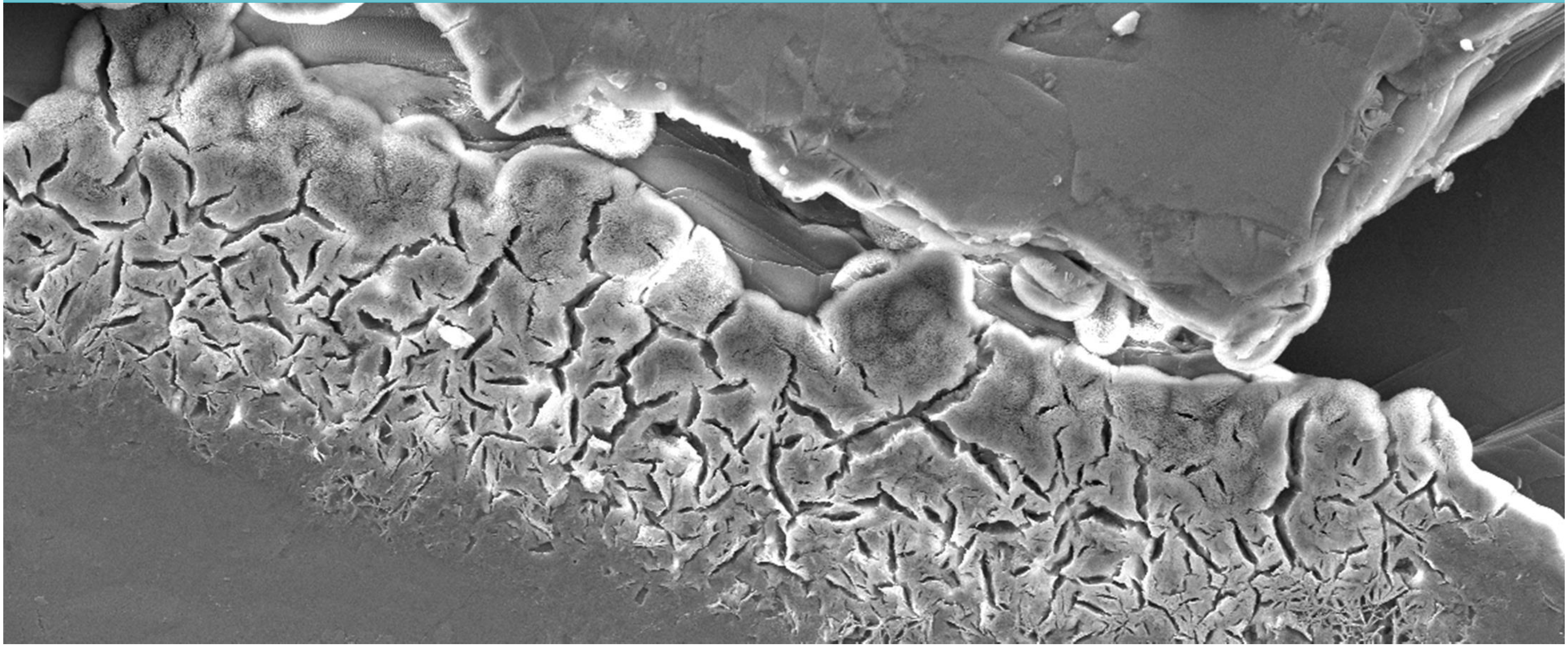
Probing the links between water availability and mineral reactivity

Anna Harrison, Sasha Wilson, Bree Morgan, Eric Oelkers



European Commission

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NSERC CRSNG

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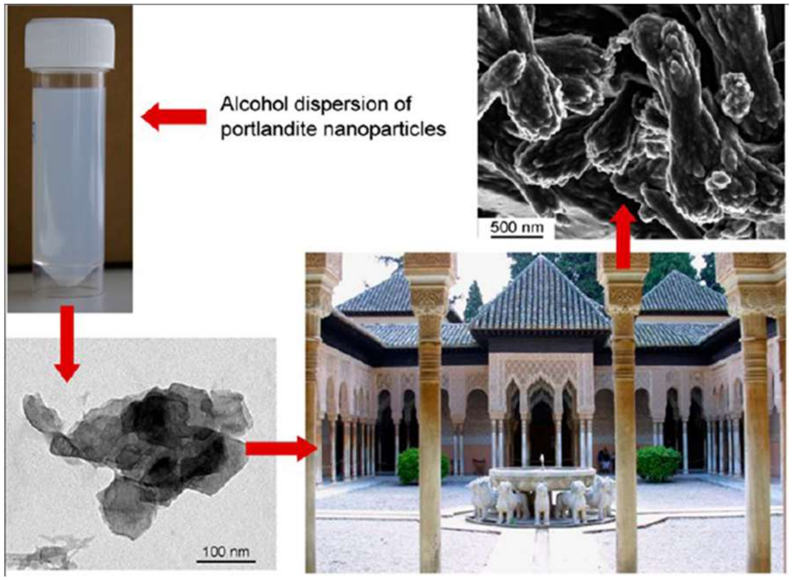
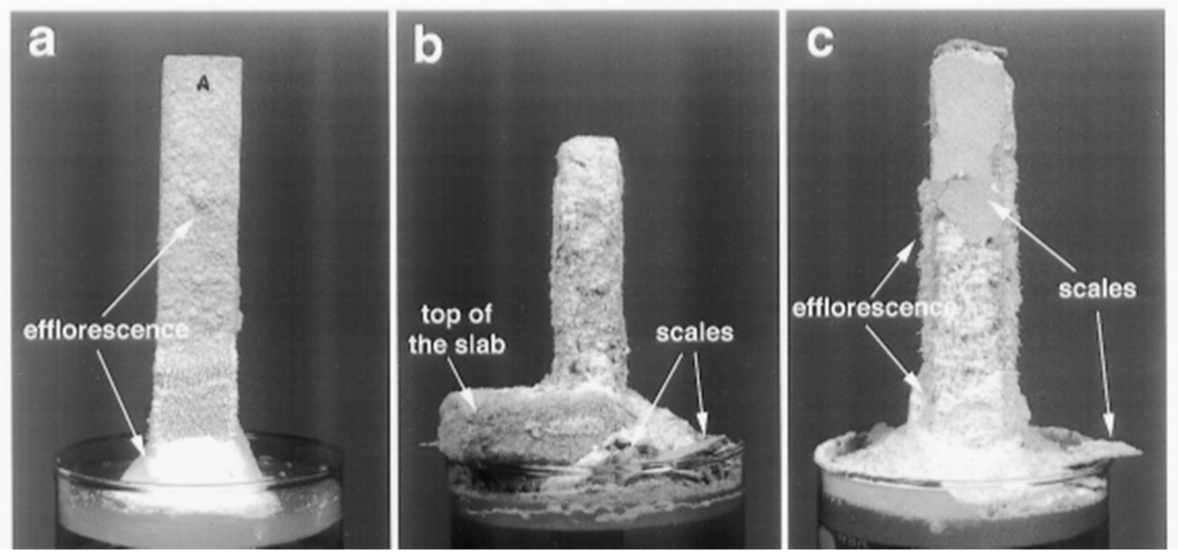
Where do we care?



Rodriguez-Navarro et al (2013)

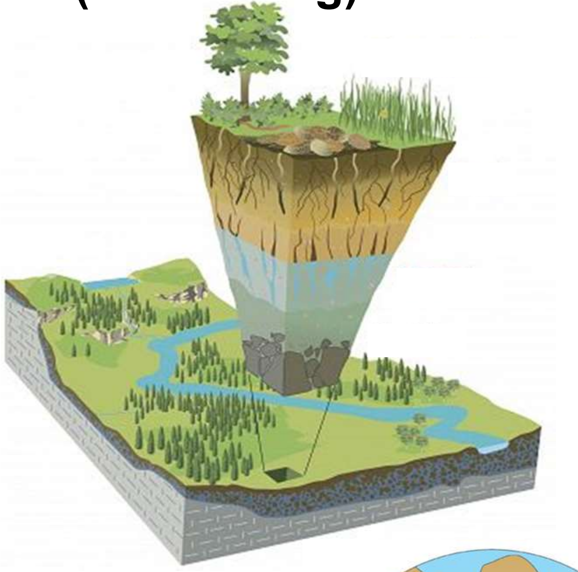
Building, concrete, and cultural heritage weathering and/or carbonation



Rodriguez-Navarro and Doehne (1999)

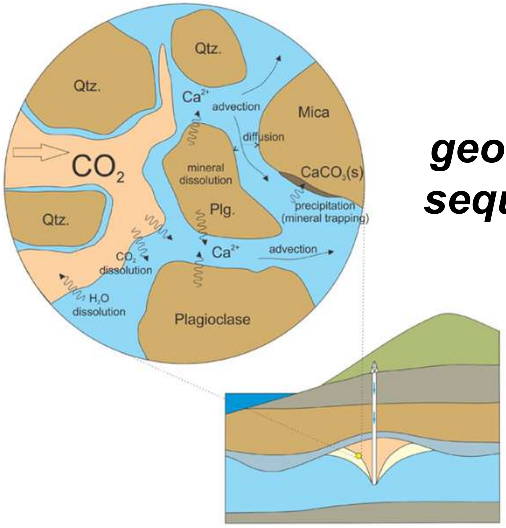
Where do we care?

Critical zone (weathering)



Mine waste management

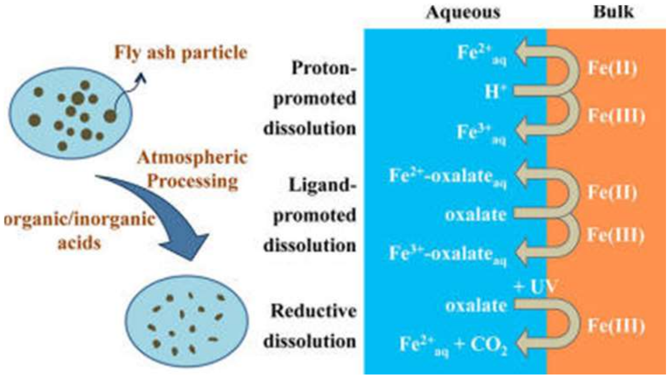
Wilson et al. (2006) *Am Mineral*



geologic CO_2 sequestration

Steefel et al. (2013) *Rev. Min. Geochem.*

Atmospheric particles



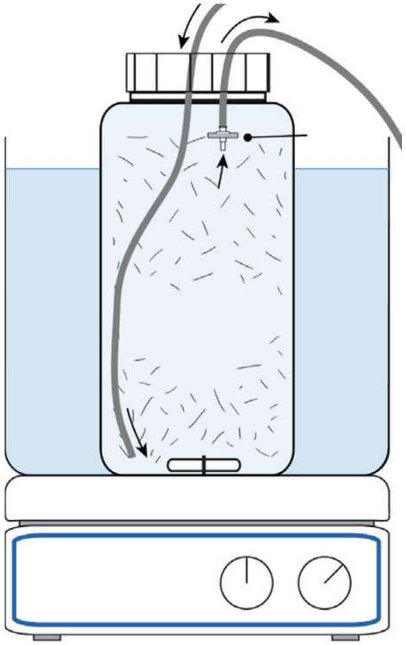
Chen and Grassian (2013) *EST*

Why does water matter?

- Reaction medium in which minerals dissolve and precipitate
- Transport medium
- Reactant that participates in reactions

Water unlimited vs water limited

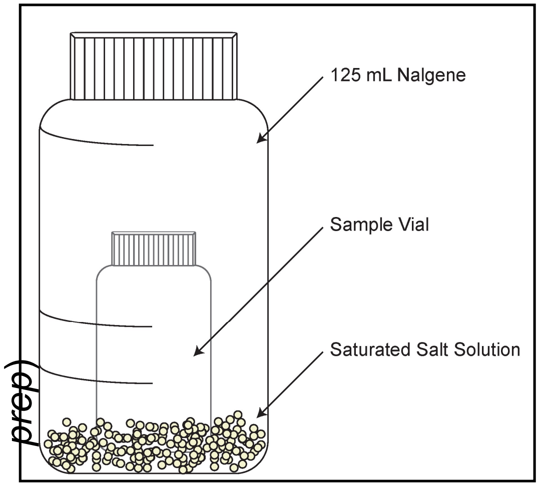
Water-unlimited



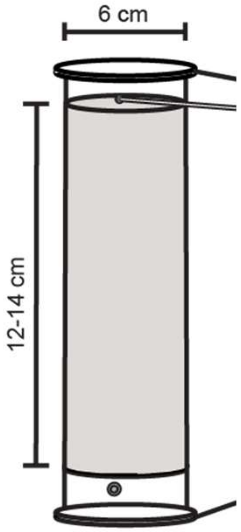
Thom et al. (2013)

- Unlimited fluid to sample
- Reaction rate measured based on changes in fluid composition

Water-limited



Wilson et al. *(in prep)*

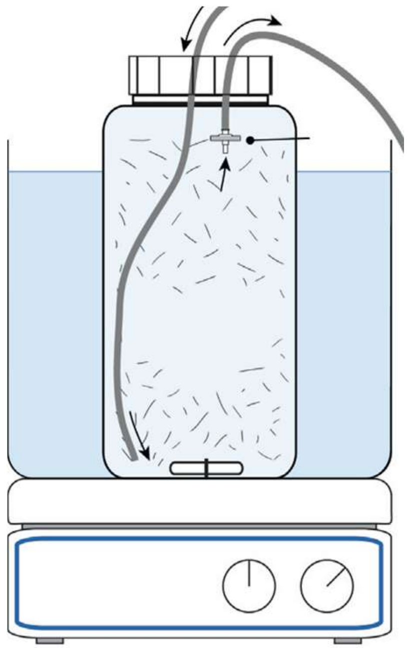


Harrison et al. (2015)

- Limited or no fluid to sample
- Reaction rate measured based on changes solid – requires greater extent of reaction
- Often a coupled dissolution-precipitation
- Density functional theory calculations

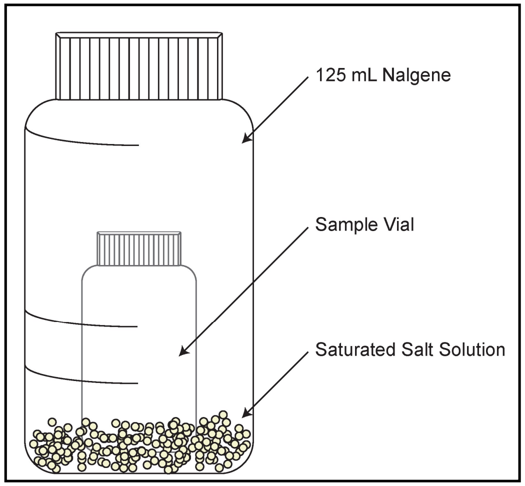
Water unlimited vs water limited

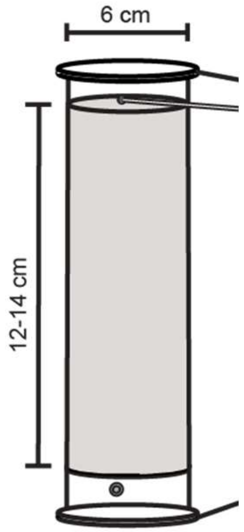
Water-unlimited



- Surface area
- Fluid composition
- Crystal chemistry and crystal structure
- Temperature
- Mass transfer

Water-limited





- Fast attainment of equilibrium in small water volume
- Limited volume in which precipitates can form
- Water impacts intrinsic rate
- Different water properties at dry conditions

What typically controls reaction rates?

- Surface area
- Fluid composition
- Crystal chemistry and crystal structure
- Temperature
- Mass transfer

What typically controls reaction rates?

- Surface area
- Fluid composition* - H_2O activity/partial pressure
- Crystal chemistry and crystal structure
- Temperature
- Mass transfer

Open questions

1) How much water is enough water for dissolution-precipitation reactions to proceed?
2) Does water availability impact dissolution/precipitation rates or just distribution of neo-formed minerals?
3) How can we incorporate water limitations in reactive transport models?

Test case: Carbon mineralization

Mineral Dissolution

Cation source
(Mg^2+, Ca^{2+})

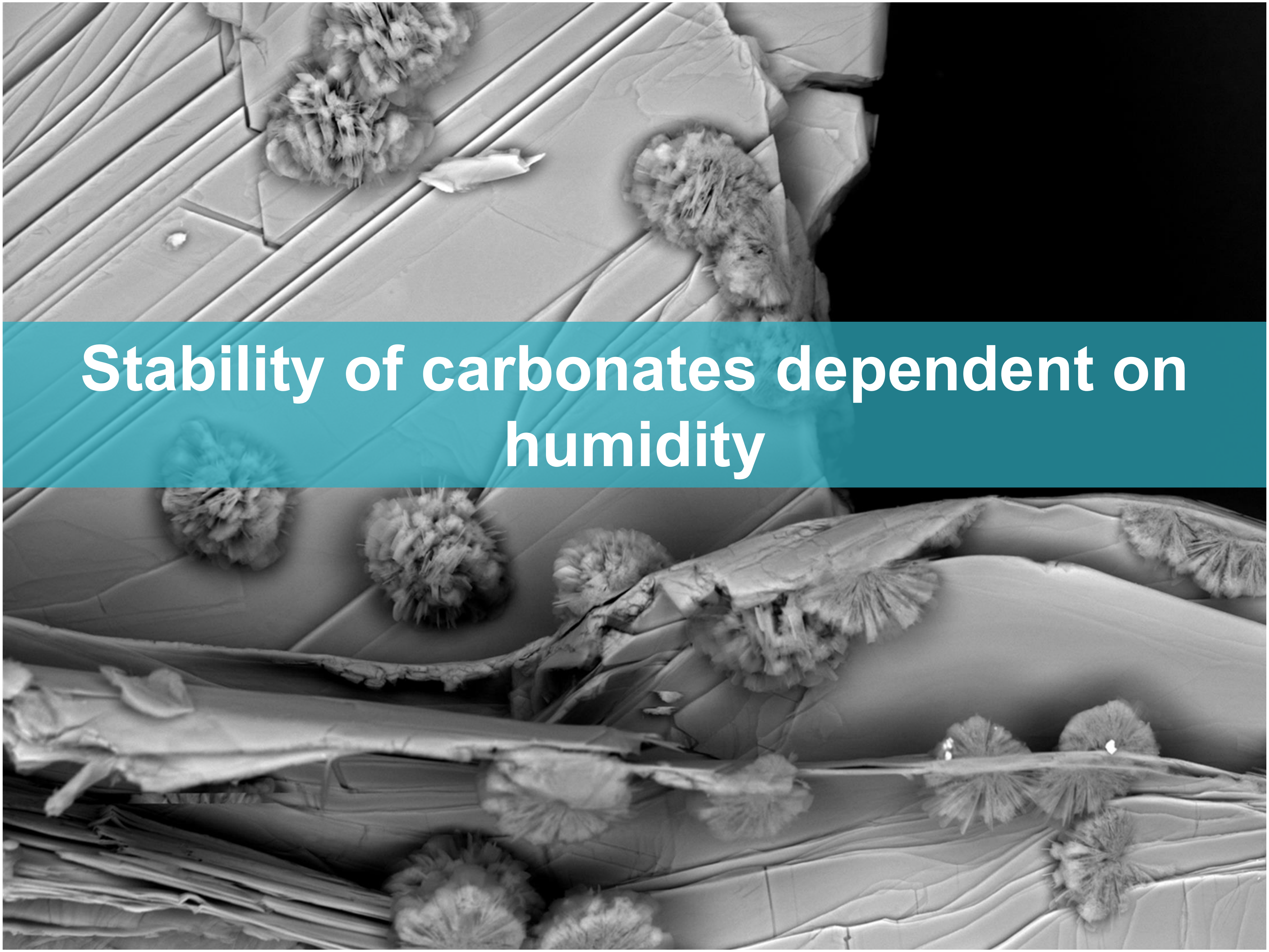
Stable sink for CO_2

Carbonate Precipitation

CO_2 Supply

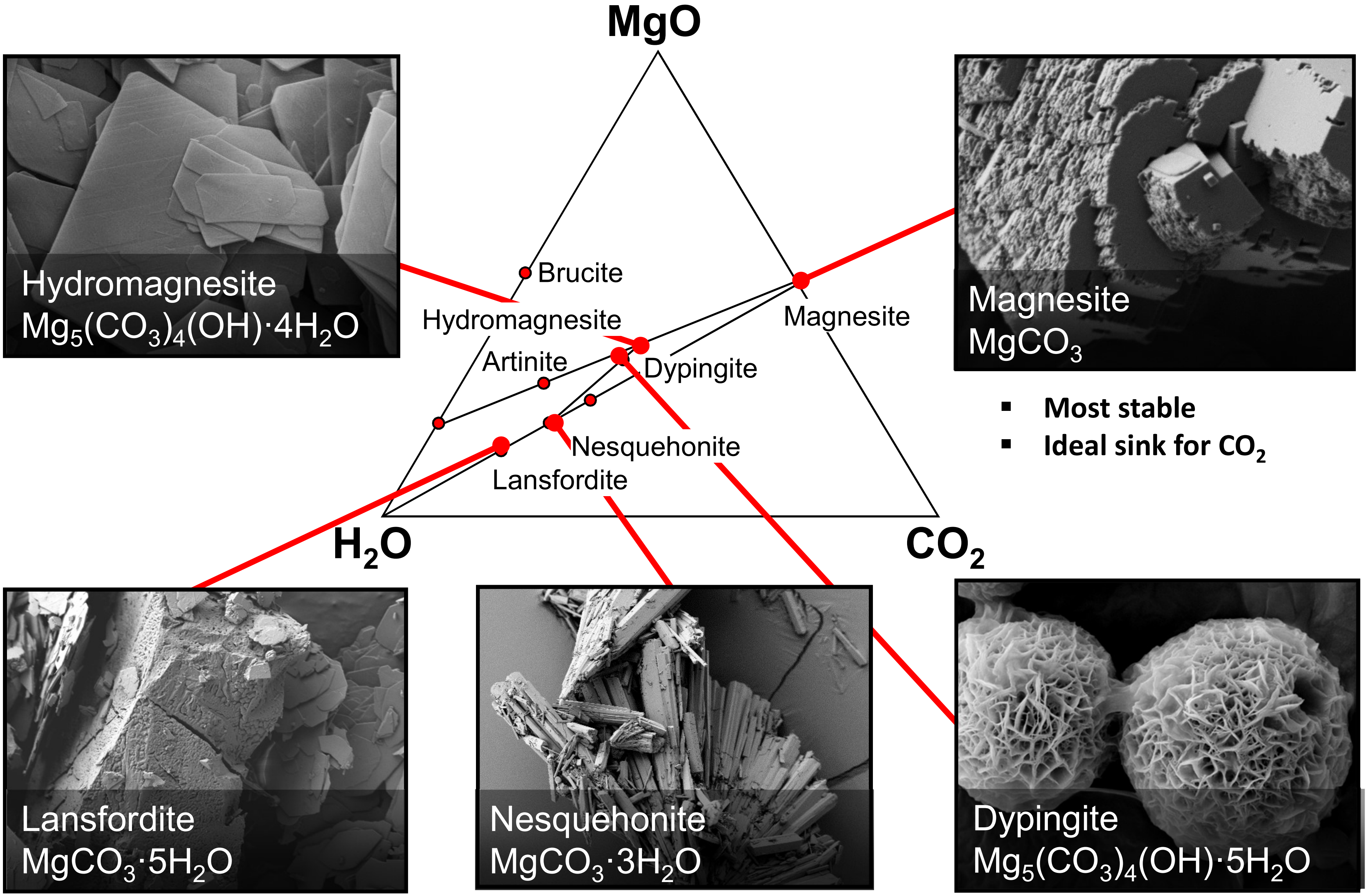
Source of CO_2

Water available



Stability of carbonates dependent on humidity

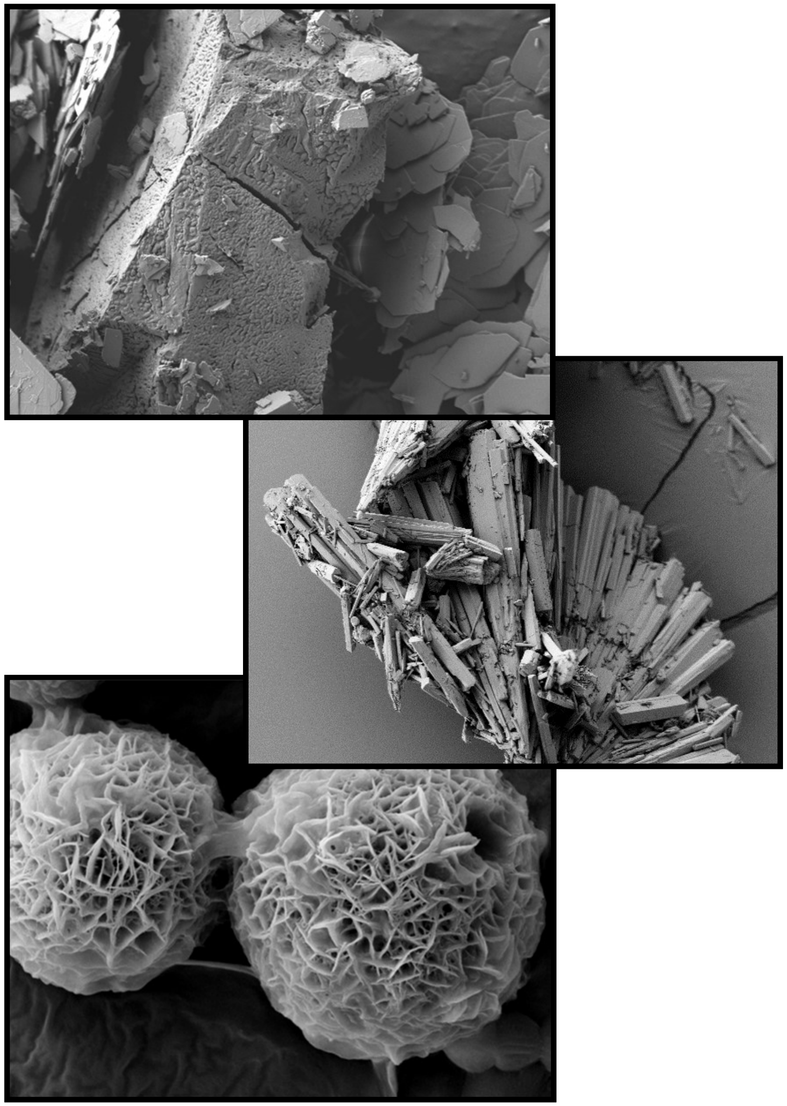
Humidity-dependent Mg-carbonate stability



- **Most stable**
- **Ideal sink for CO_2**

Slide courtesy of Ian Power

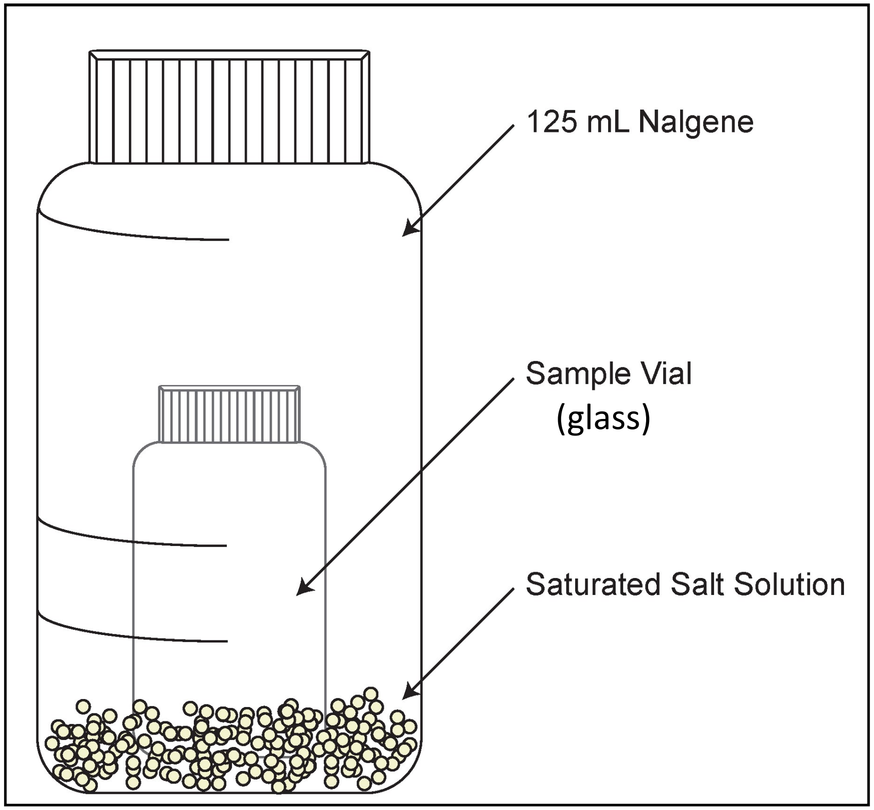
Pure phase T–RH stability experiments



Sasha Wilson (U of Alberta)

Bree Morgan (U of Sydn

Pure phase T–RH stability experiments



164+ long-term experiments:

- <75 µm grain size
- RH: 2 – 100%
- T: -25, 3, 23, 50, 75ºC
- *Nominally dry (unsaturated) systems*

- **T and relative humidity (RH) control the stability of many hydrous, hygroscopic phases**
- Phases: lansfordite, nesquehonite, dypingite, hydromagnesite (and magnesite)
- Constant RH and T
- Analysed at 2, 8 & 20 months and again at 3 years

$$RH = \frac{P_{H2O}}{P_{H2O,\max}} \cdot 100\%$$

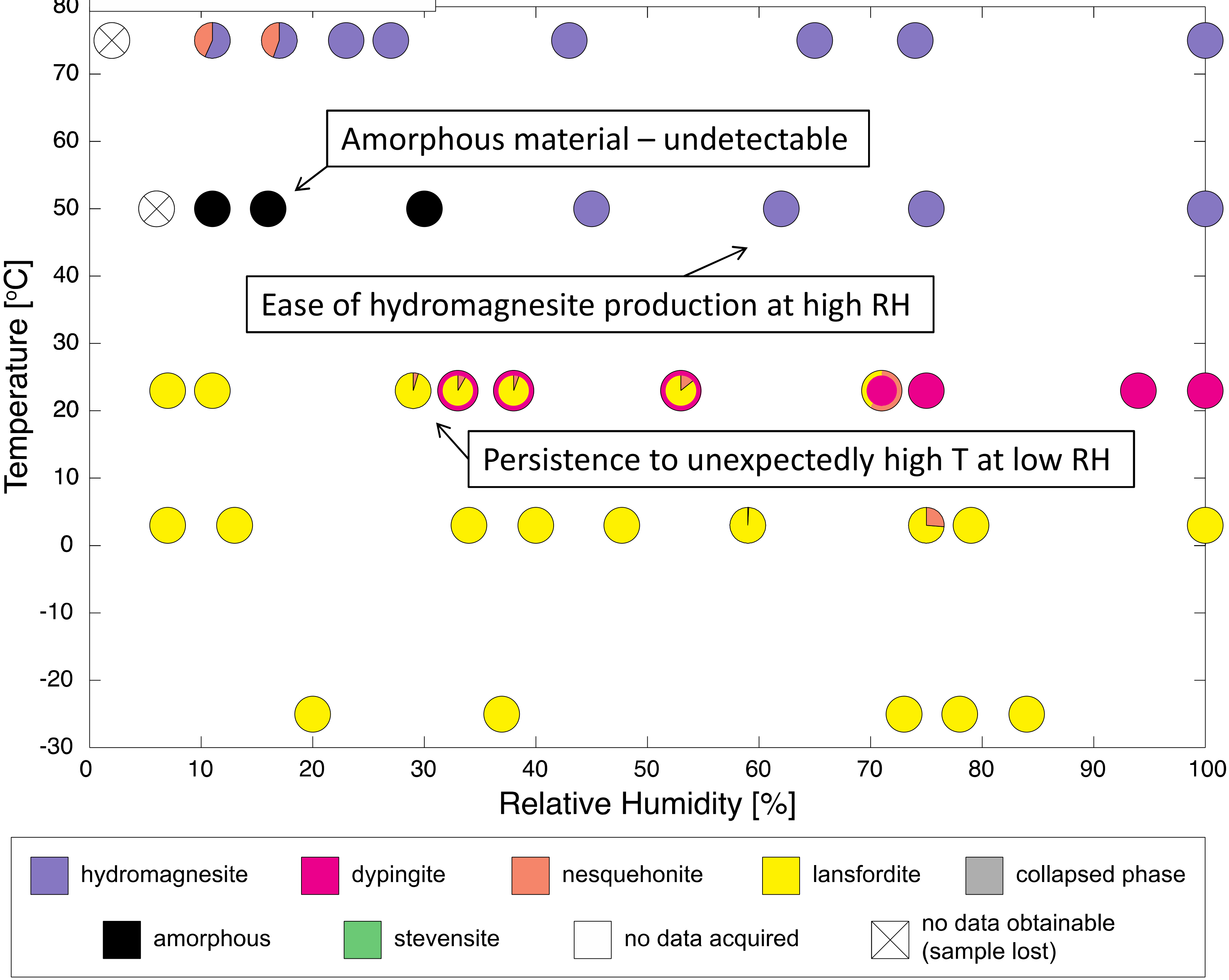
After Wilson & Bish (2012) GCA

Pure phase T–RH stability experiments

Wilson et al. *in prep*

Iansfordite – 8 months

$MgCO_3 \cdot 5H_2O$

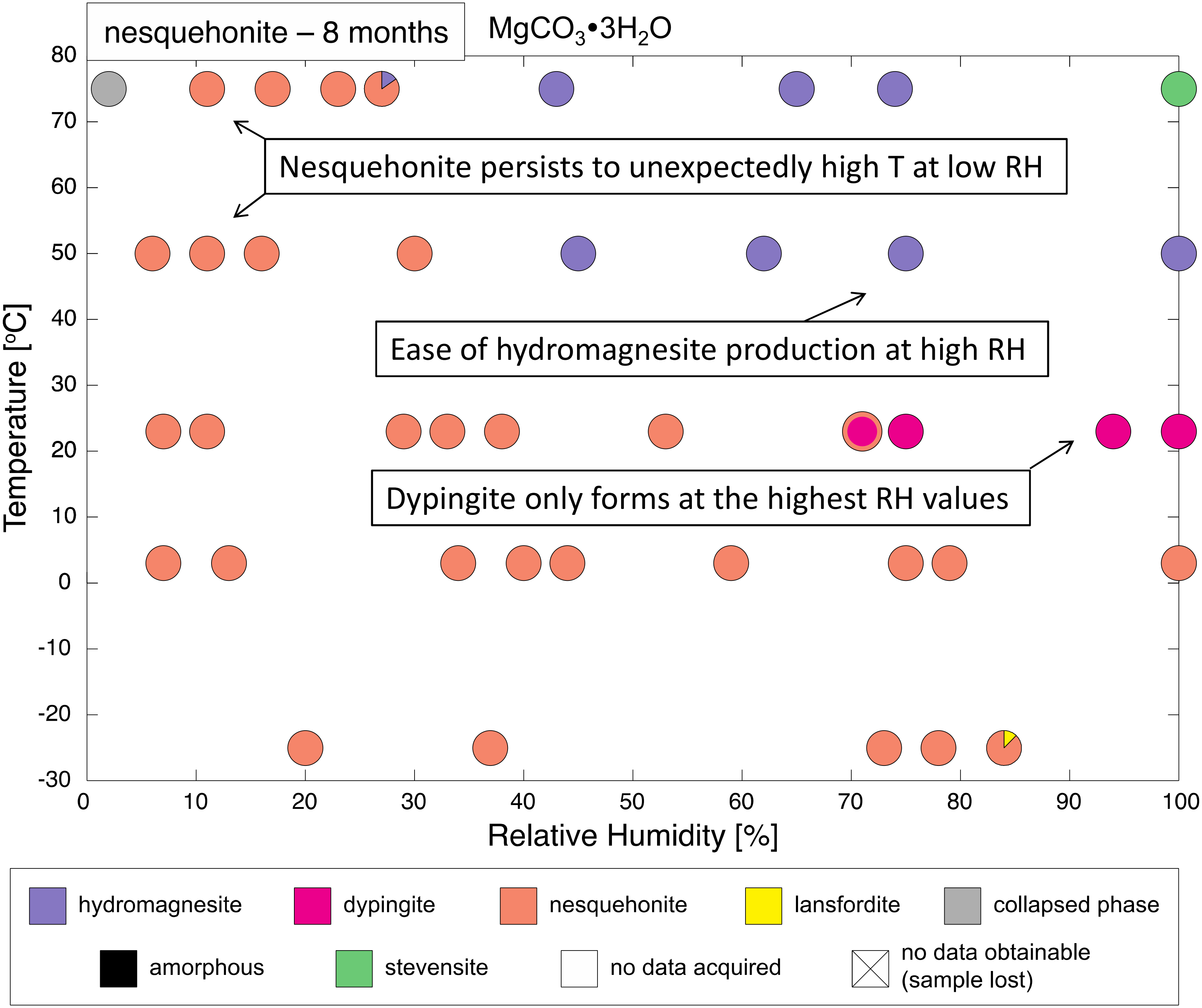


Amorphous material – undetectable

Ease of hydromagnesite production at high RH

Persistence to unexpectedly high T at low RH

Wilson et al. *in prep*



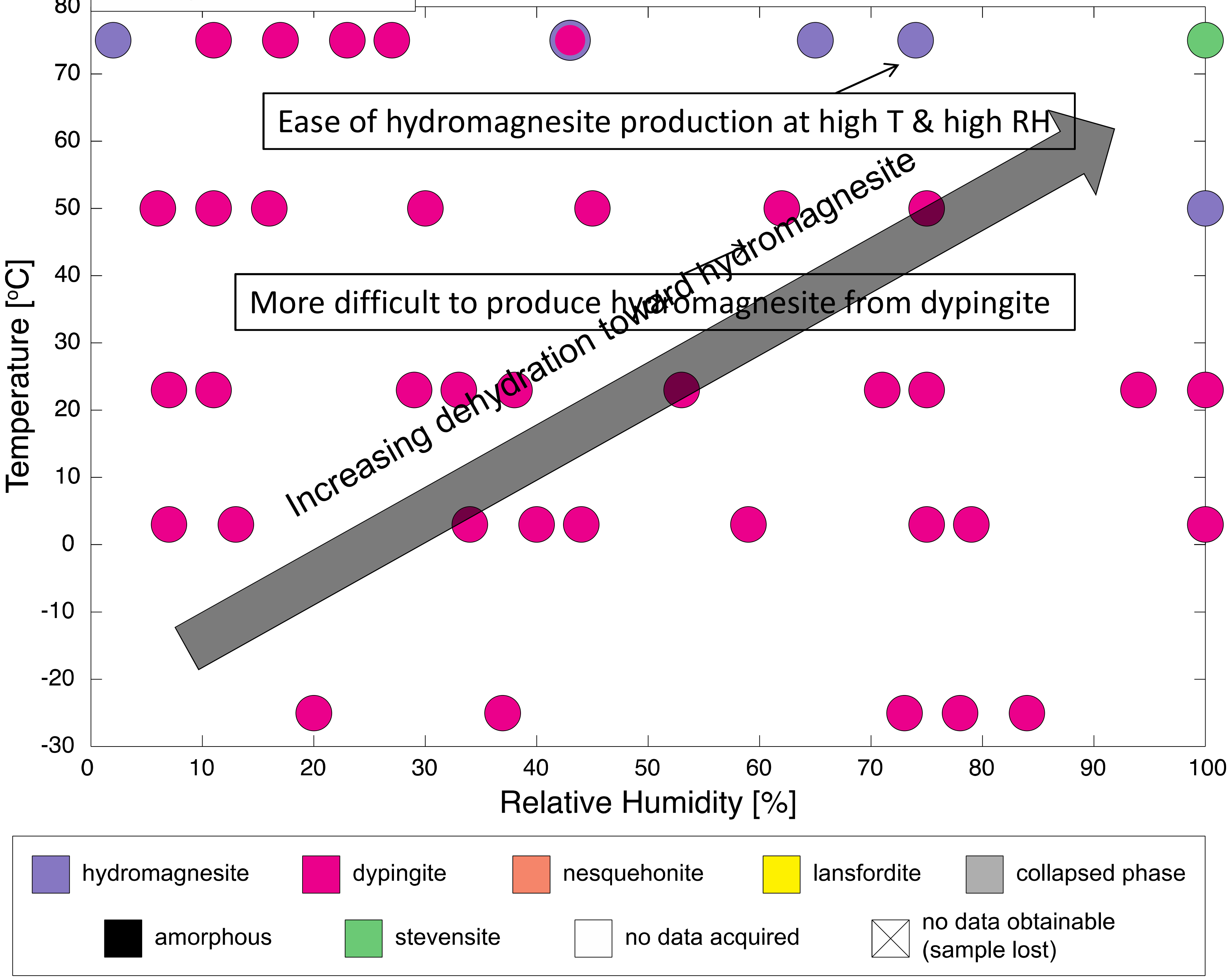
Nesquehonite persists to unexpectedly high T at low RH

Ease of hydromagnesite production at high RH

Dypingite only forms at the highest RH values

dypingite – 8 months

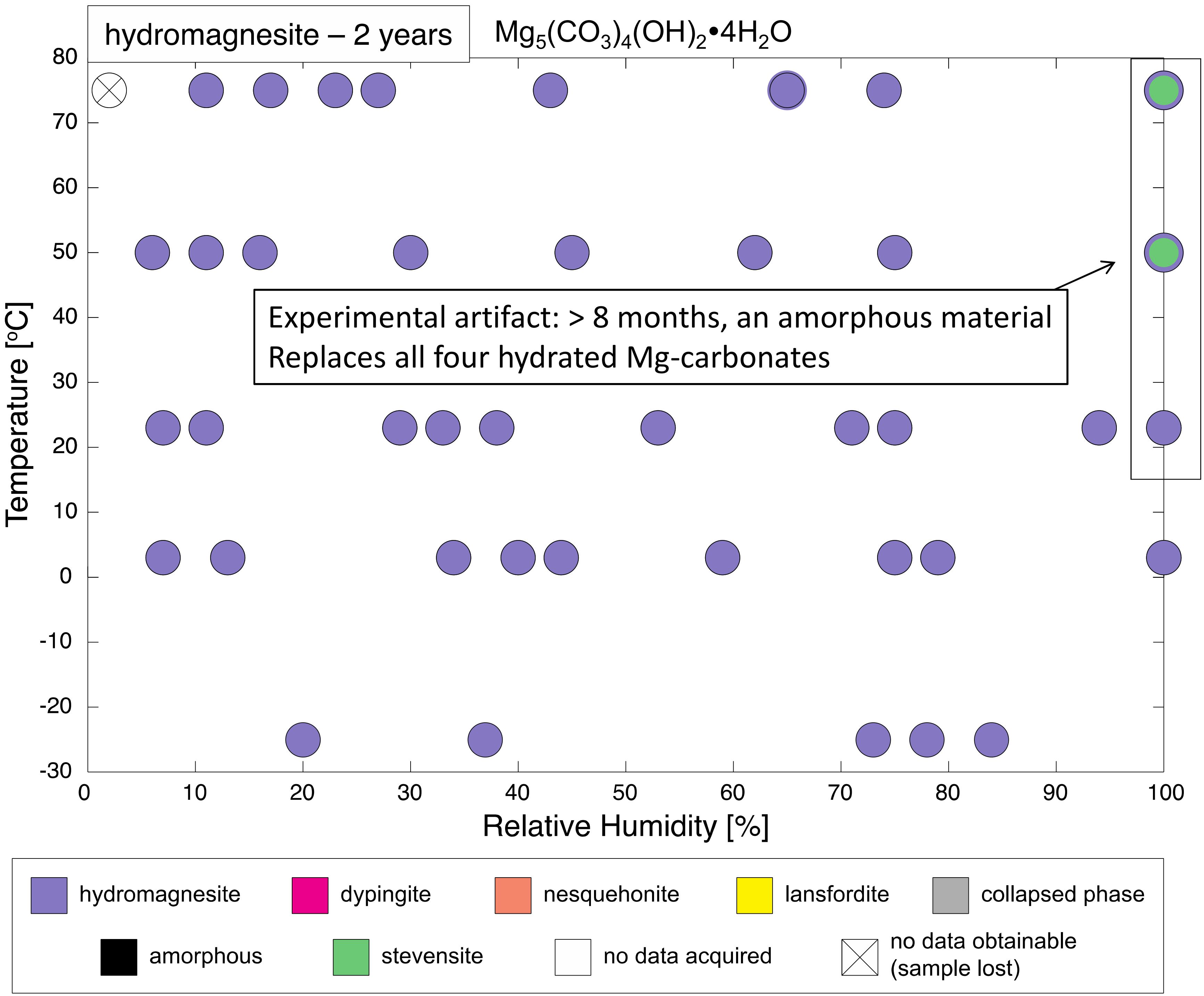
$Mg_5(CO_3)_4(OH)_2 \bullet \sim 5H_2O$



Ease of hydromagnesite production at high T & high RH

Increasing dehydration toward hydromagnesite

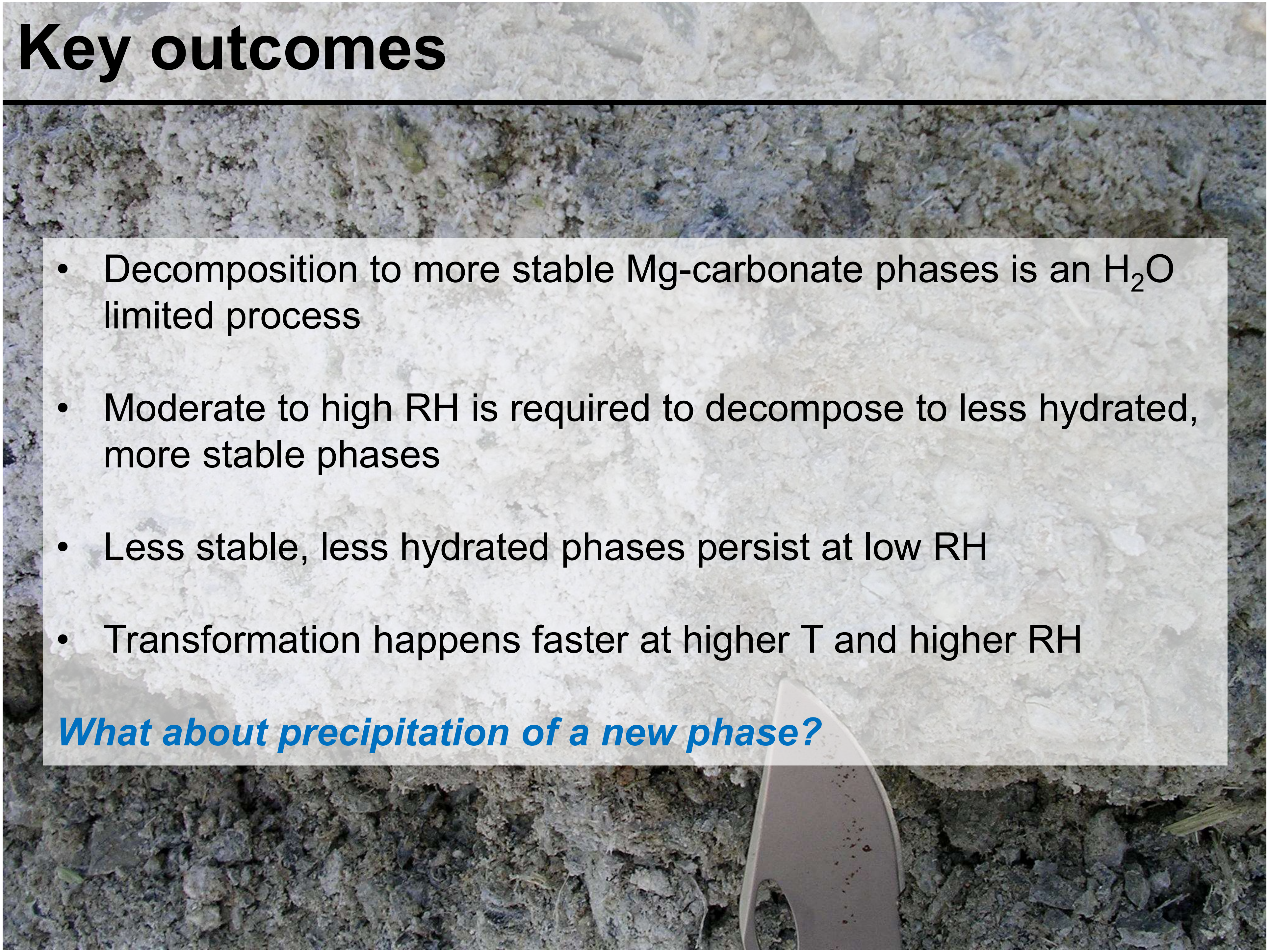
More difficult to produce hydromagnesite from dypingite


hydromagnesite – 2 years

$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$

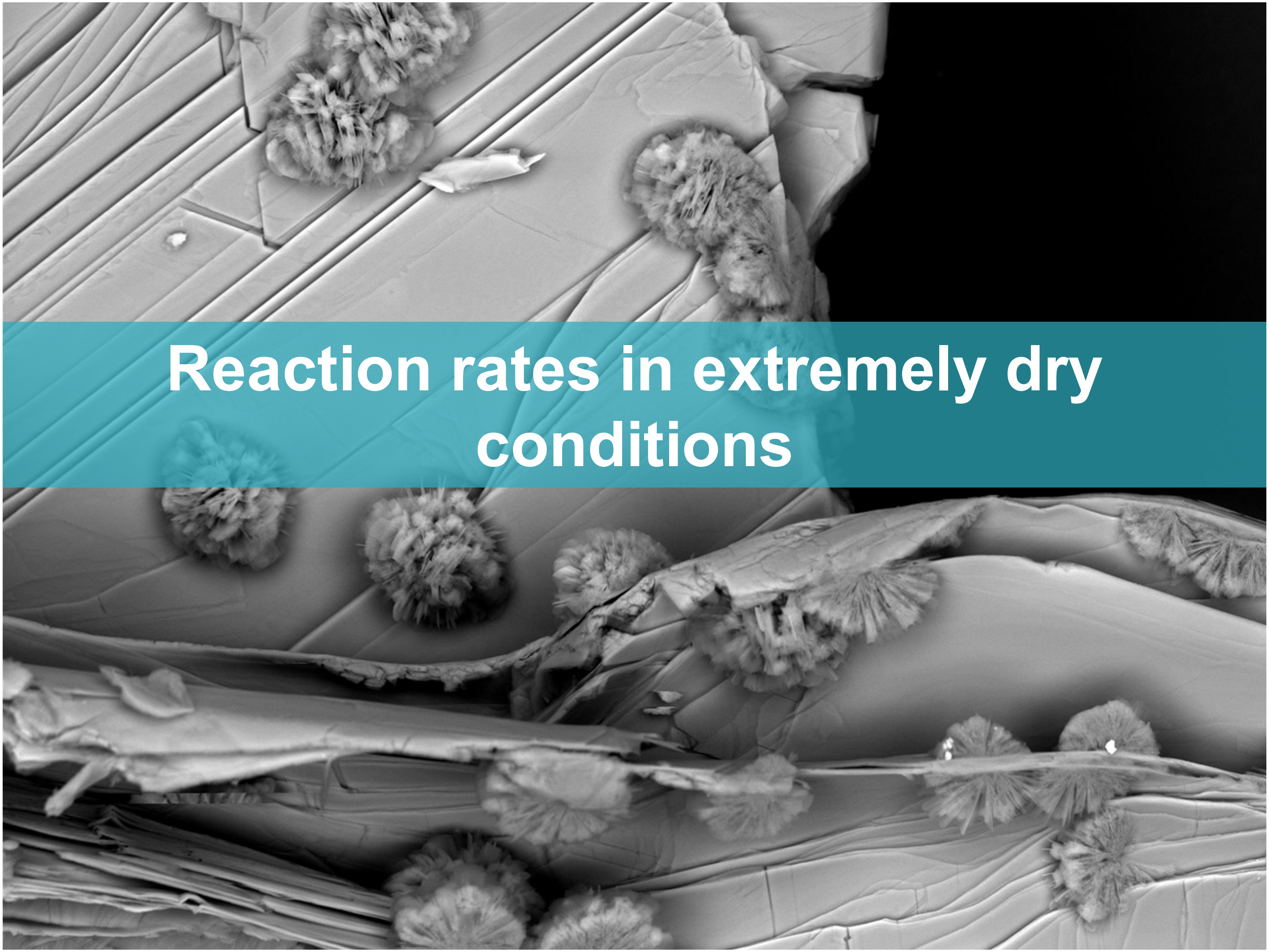
Experimental artifact: > 8 months, an amorphous material Replaces all four hydrated Mg-carbonates

Key outcomes



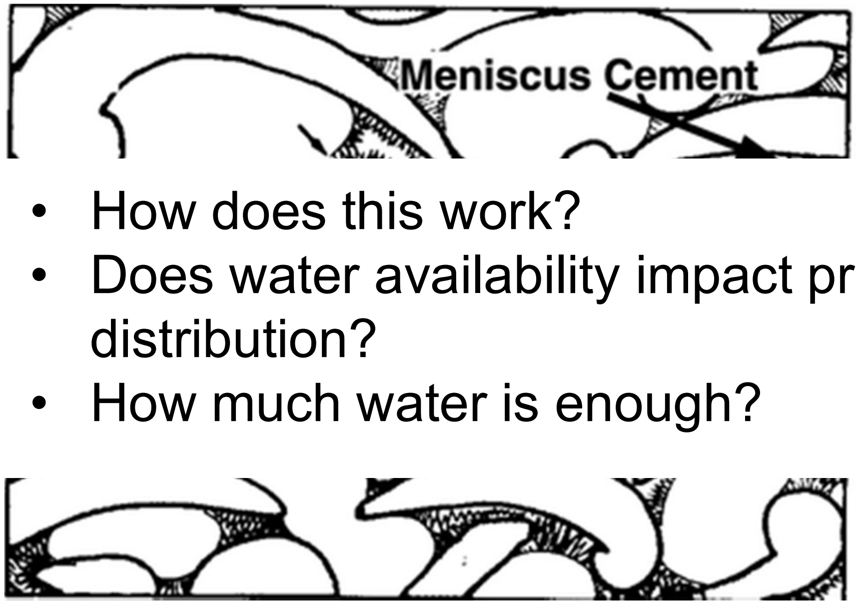
- Decomposition to more stable Mg-carbonate phases is an H_2O limited process
- Moderate to high RH is required to decompose to less hydrated, more stable phases
- Less stable, less hydrated phases persist at low RH
- Transformation happens faster at higher T and higher RH

What about precipitation of a new phase?



Reaction rates in extremely dry conditions

How does precipitation work?



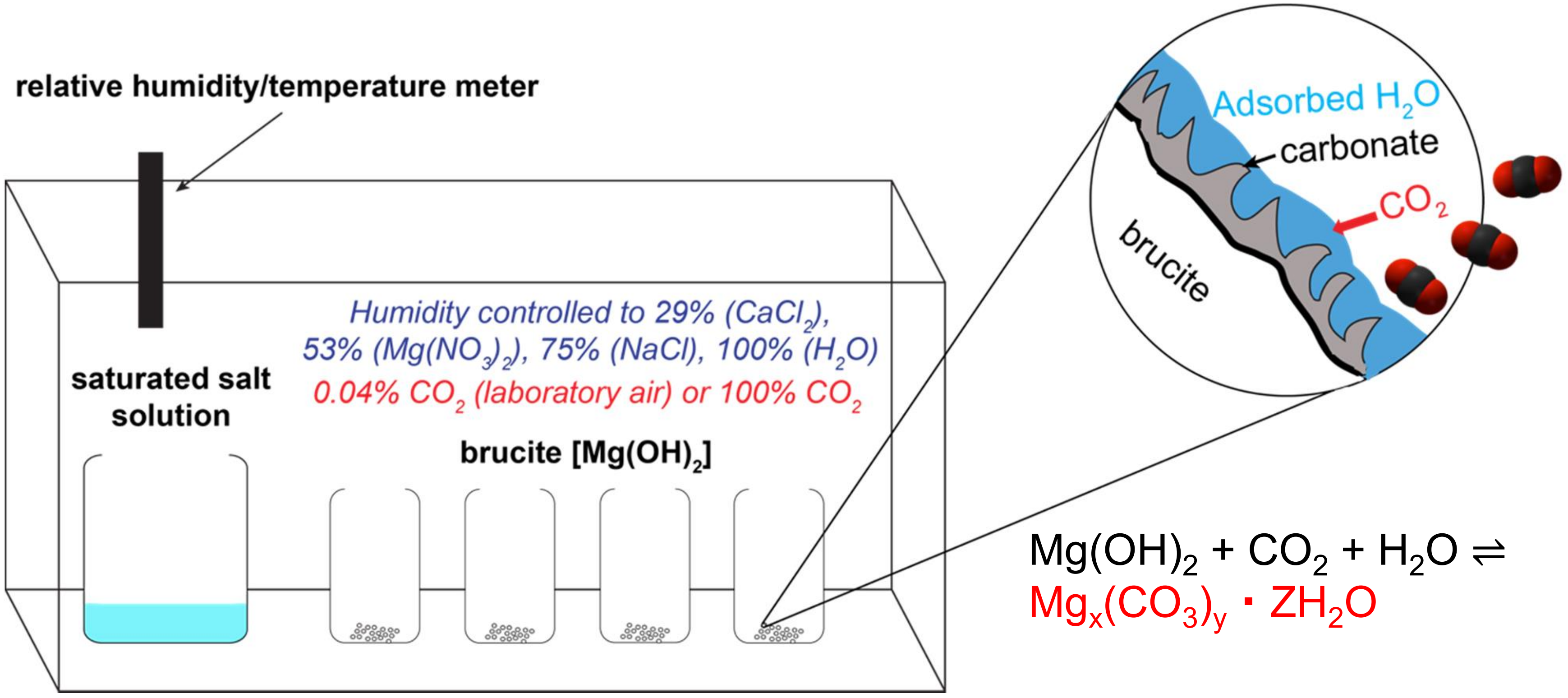
Purser (1978) *J. Petrol. Geol.*

This study

- How does this work?
- Does water availability impact precipitation rates or just distribution?
- How much water is enough?

- ”meniscus” cements often taken as evidence of precipitation in the unsaturated zone, leading to patchy and variable carbonate distribution

Water-limited carbonate growth experiment



Humidity controlled to 29% ($CaCl_2$), 53% ($Mg(NO_3)_2$), 75% ($NaCl$), 100% (H_2O)

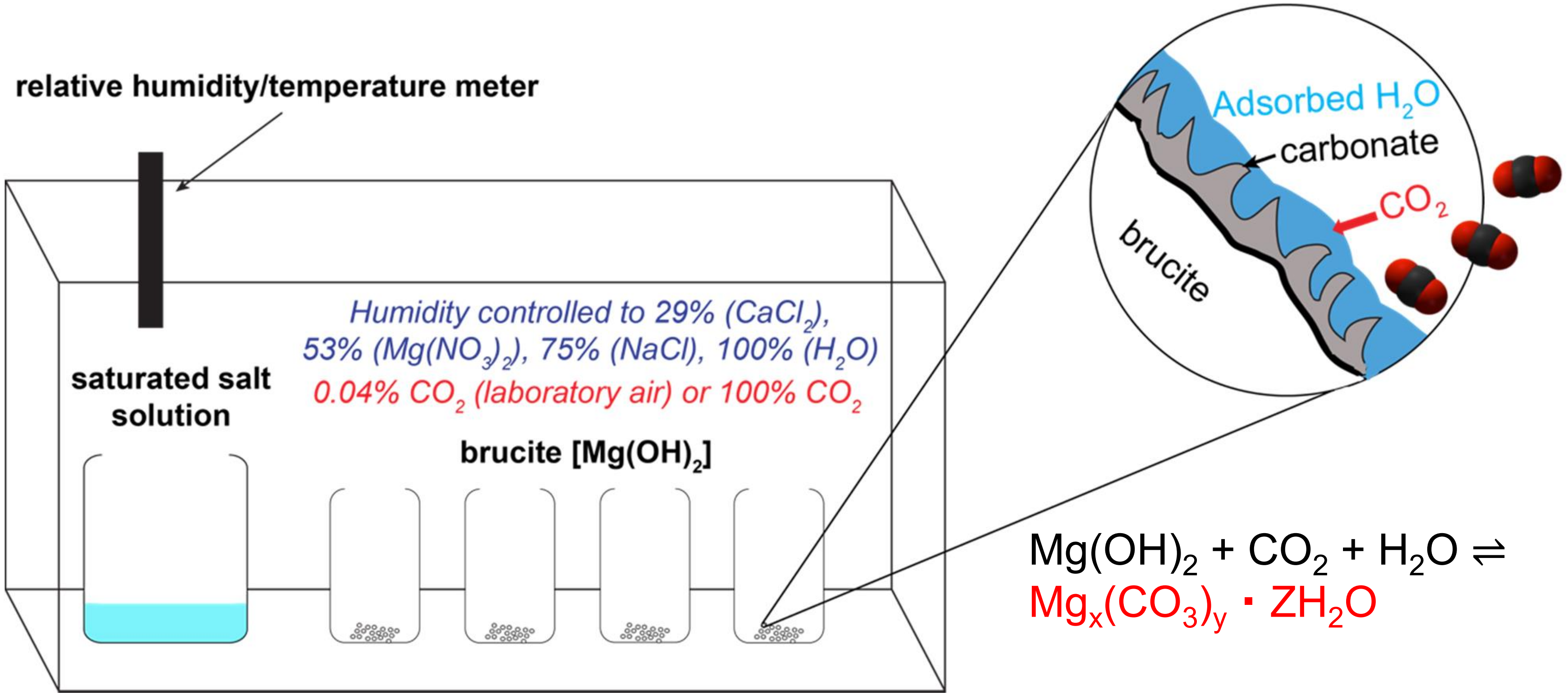
0.04% CO_2 (laboratory air) or 100% CO_2

$$Mg(OH)_2 + CO_2 + H_2O \rightleftharpoons Mg_x(CO_3)_y \cdot ZH_2O$$

- Brucite $[Mg(OH)_2]$, a common accessory mineral in ultramafic rock, was exposed to atmospheres of varied humidity (29%-100%) as controlled with saturated salt solutions at 25°C
- Two types of brucite:
  1) massive, polycrystalline brucite (200 - 400 μm)
  2) freshly cleaved crystalline sheets (millimetre-scale)
- Pure and atmospheric pCO_2

Harrison et al. *in*

Water-limited carbonate growth experiment

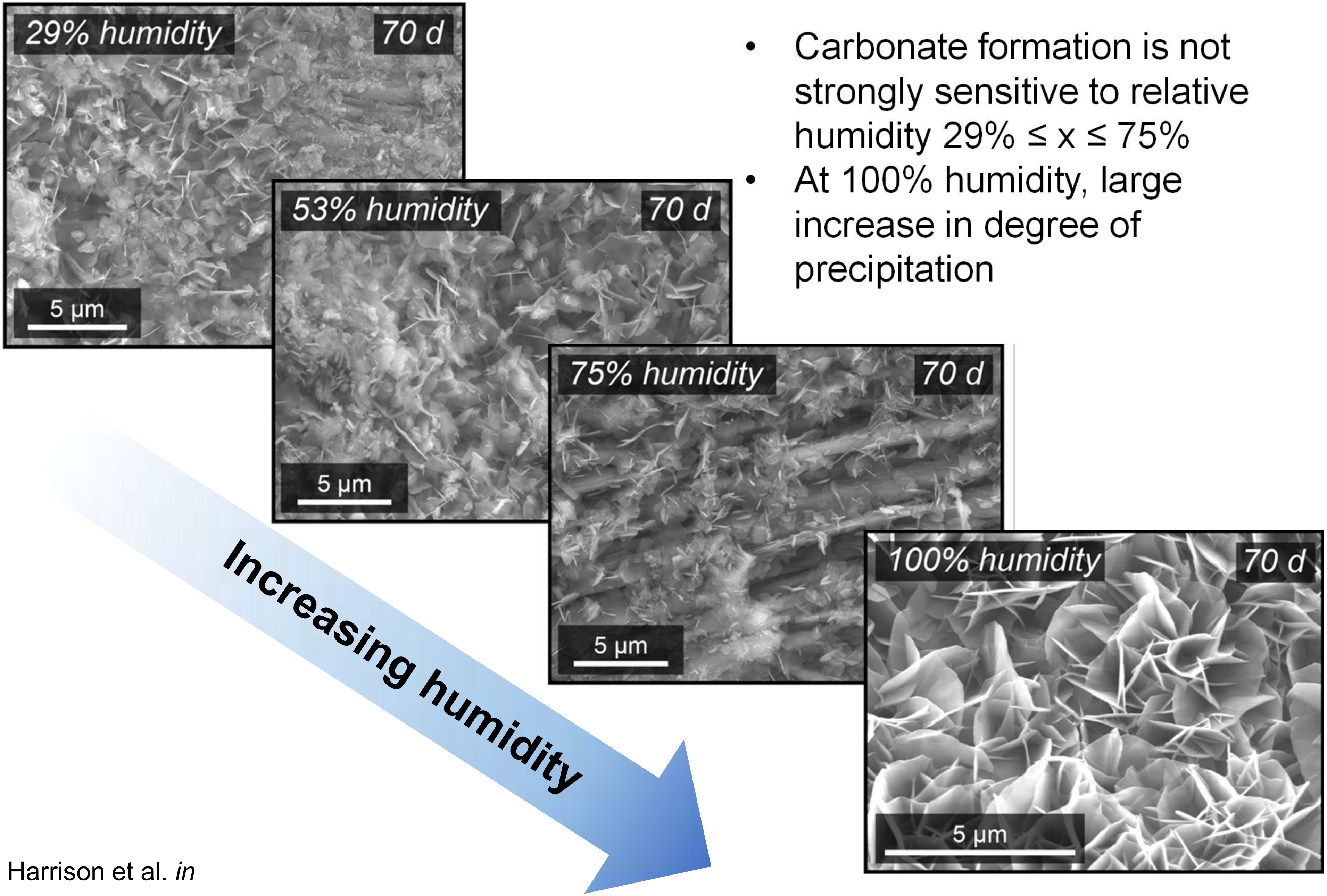


$$Mg(OH)_2 + CO_2 + H_2O \rightleftharpoons Mg_x(CO_3)_y \cdot ZH_2O$$

- Masses tracked before and after reaction (CO_2 and H_2O gain)
- Reaction products examined using scanning electron microscopy (SEM), infrared spectroscopy (FTIR), and synchrotron-based X-ray computed micro-tomography, total carbon quantified

Harrison et al. *in*

Precipitation occurs in adsorbed water film



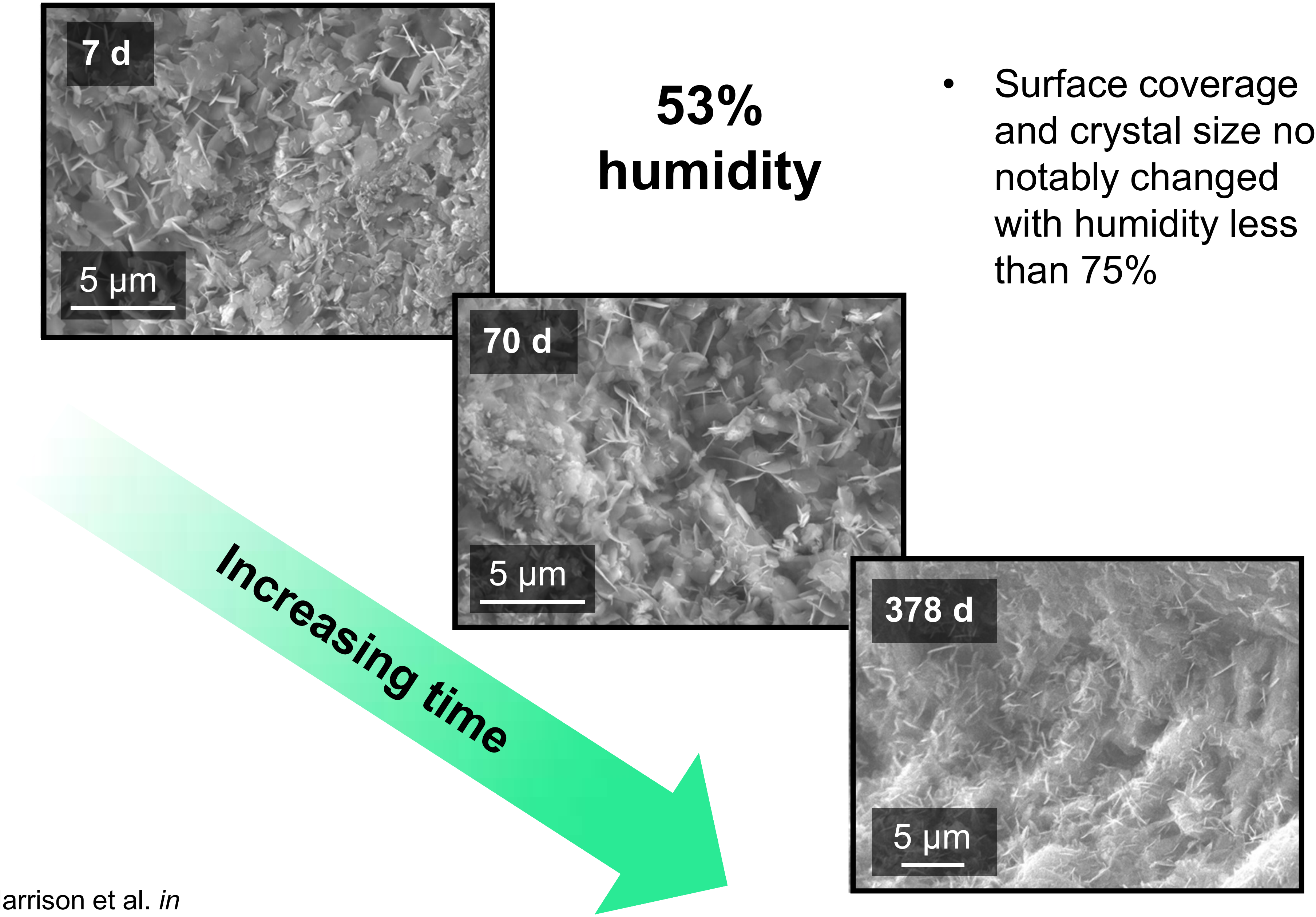
- Carbonate formation is not strongly sensitive to relative humidity 29% ≤ x ≤ 75%
- At 100% humidity, large increase in degree of precipitation

Harrison et al. *in*

Limited precipitation at low humidity

53% humidity

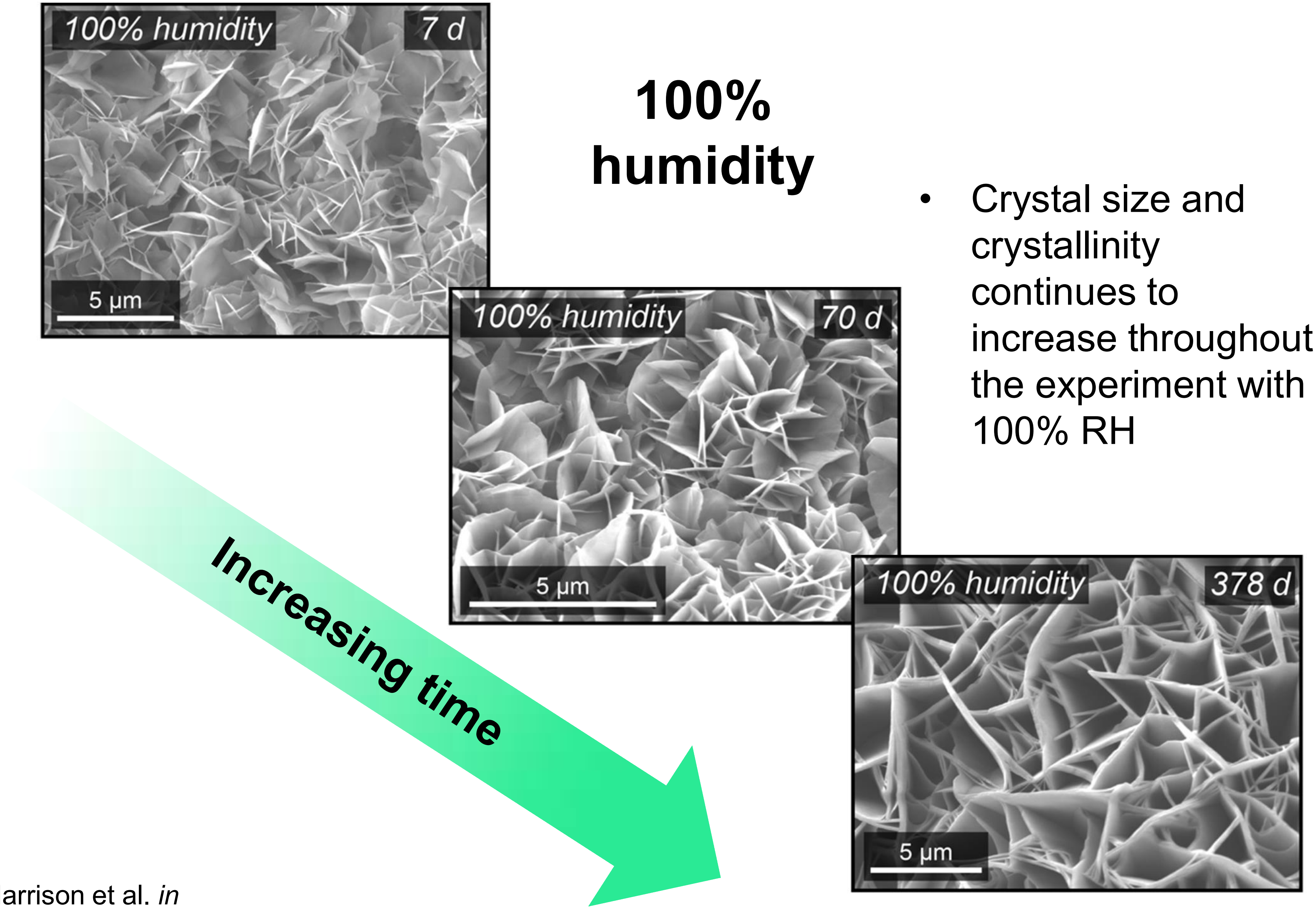
- Surface coverage and crystal size not notably changed with humidity less than 75%



Harrison et al. *in*

Carbonate growth at high humidity

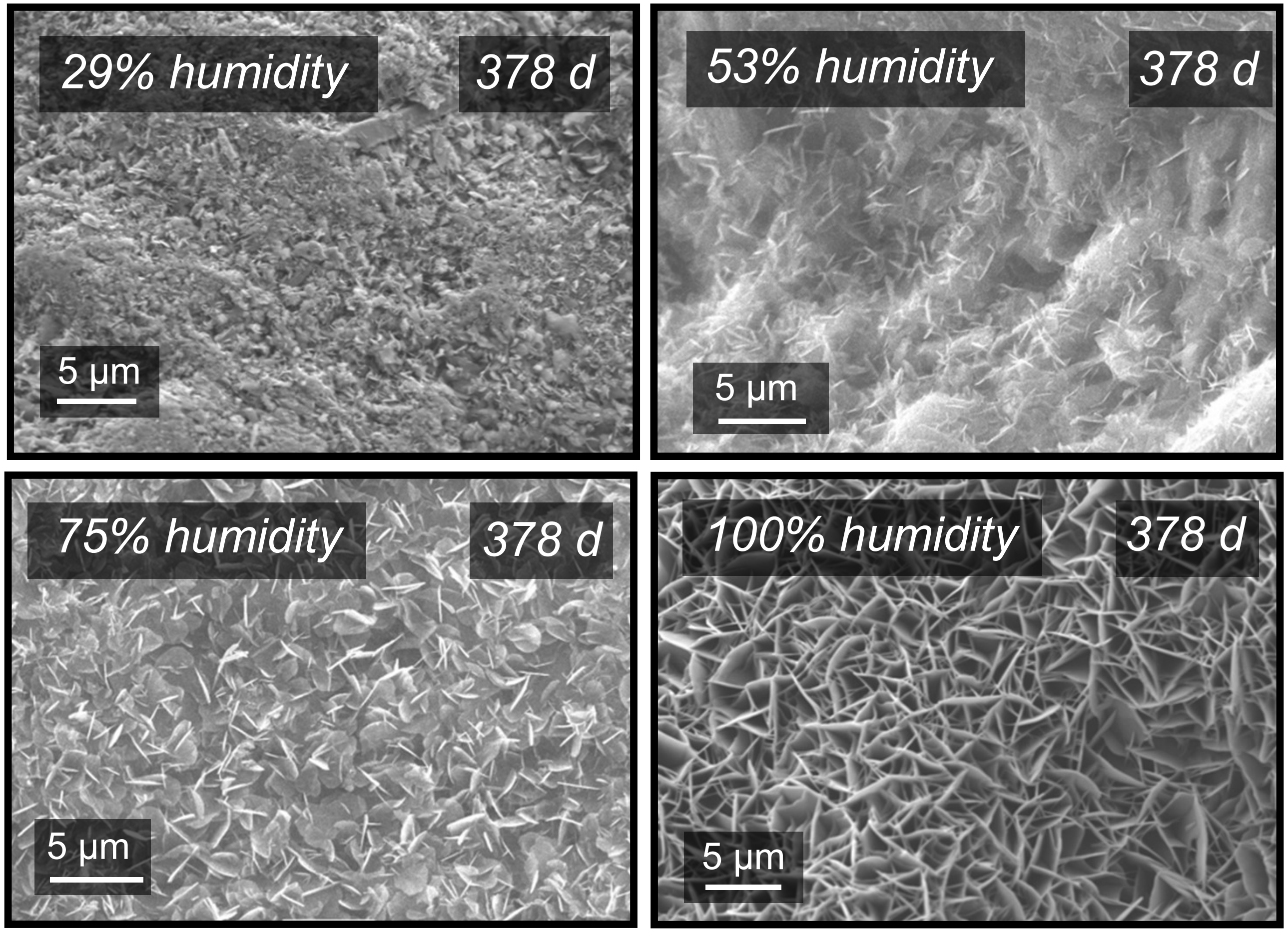
100% humidity



- Crystal size and crystallinity continues to increase throughout the experiment with 100% RH

Harrison et al. *in*

Precipitation depends on humidity



- A **threshold value** of relative humidity (film thickness?) required to facilitate or **enhance rate of precipitation**

Harrison et al. *in*

Crystal face or topographic control

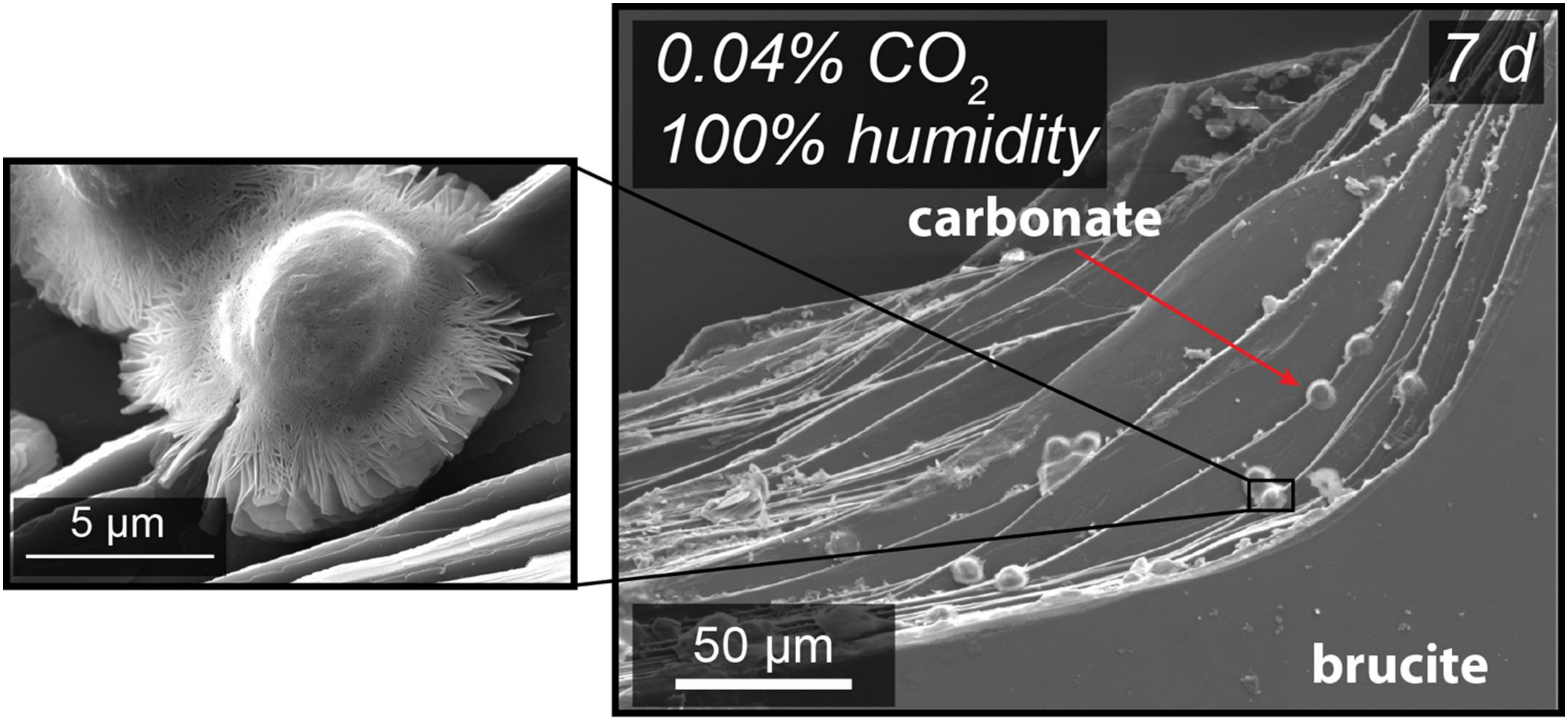
75% RH, pure CO_2 (cleaved brucite)

- Precipitates were associated with topography (*e.g.*, sheet edges) on cleaved brucite crystals

Harrison et al. *in*

Crystal face or topographic control

(cleaved brucite)

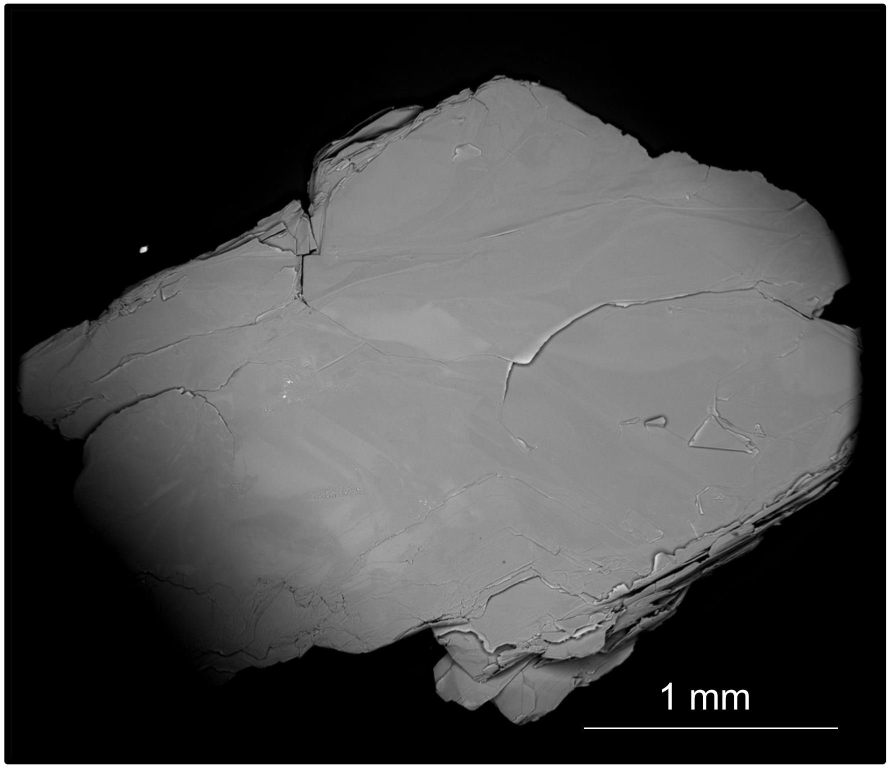


- **Precipitation is controlled either by presence of thicker water films at these locations OR crystal structure of substrate**

Harrison et al. *in*

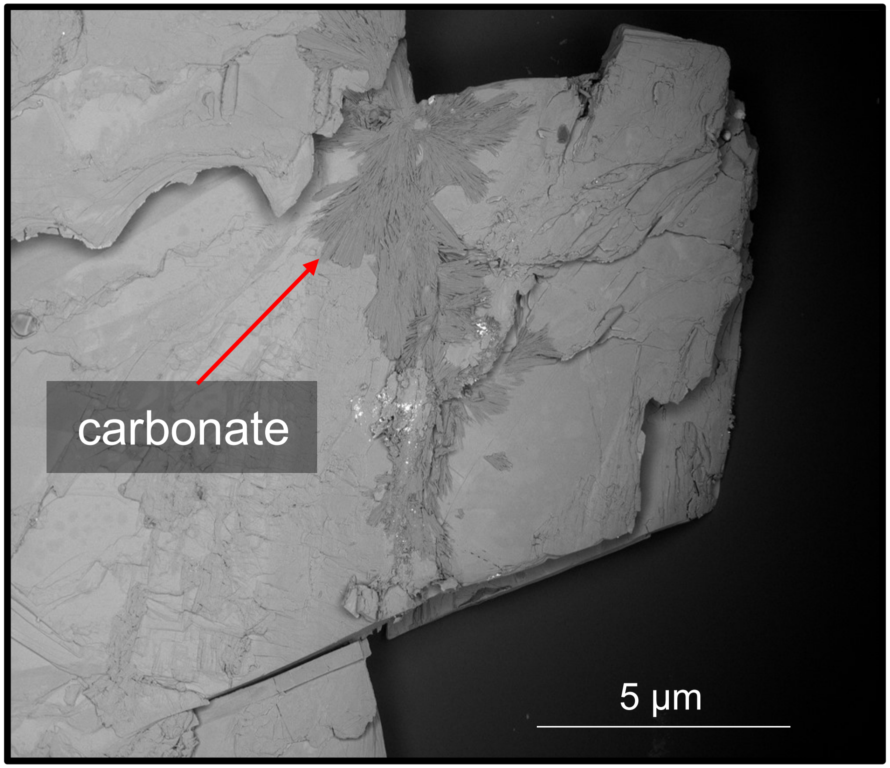
RH-dependent growth on both substrates

4% RH



Pure CO$_2$, 24 h

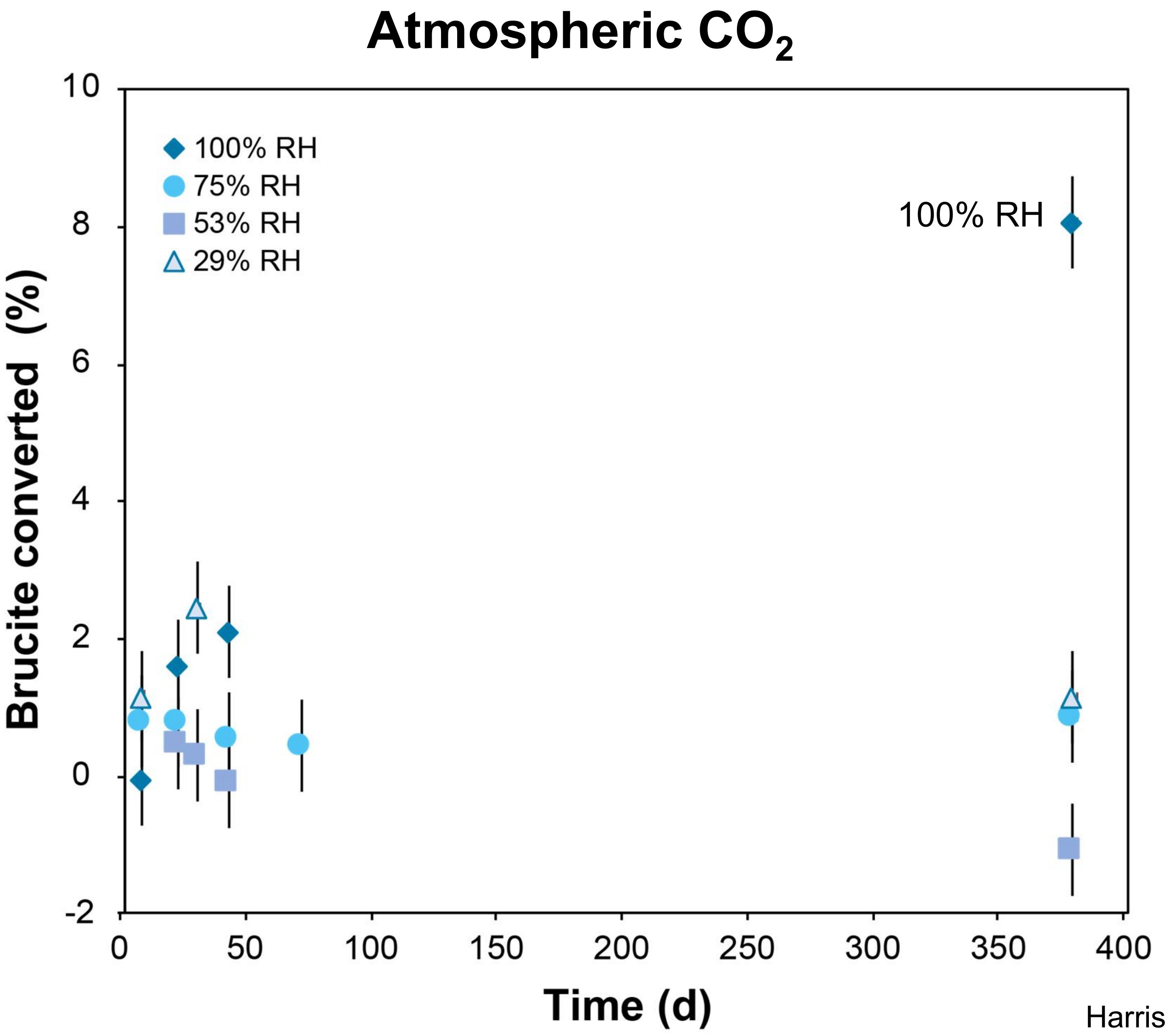
100% RH



Pure CO$_2$, 24 h

Harrison et al. *in*

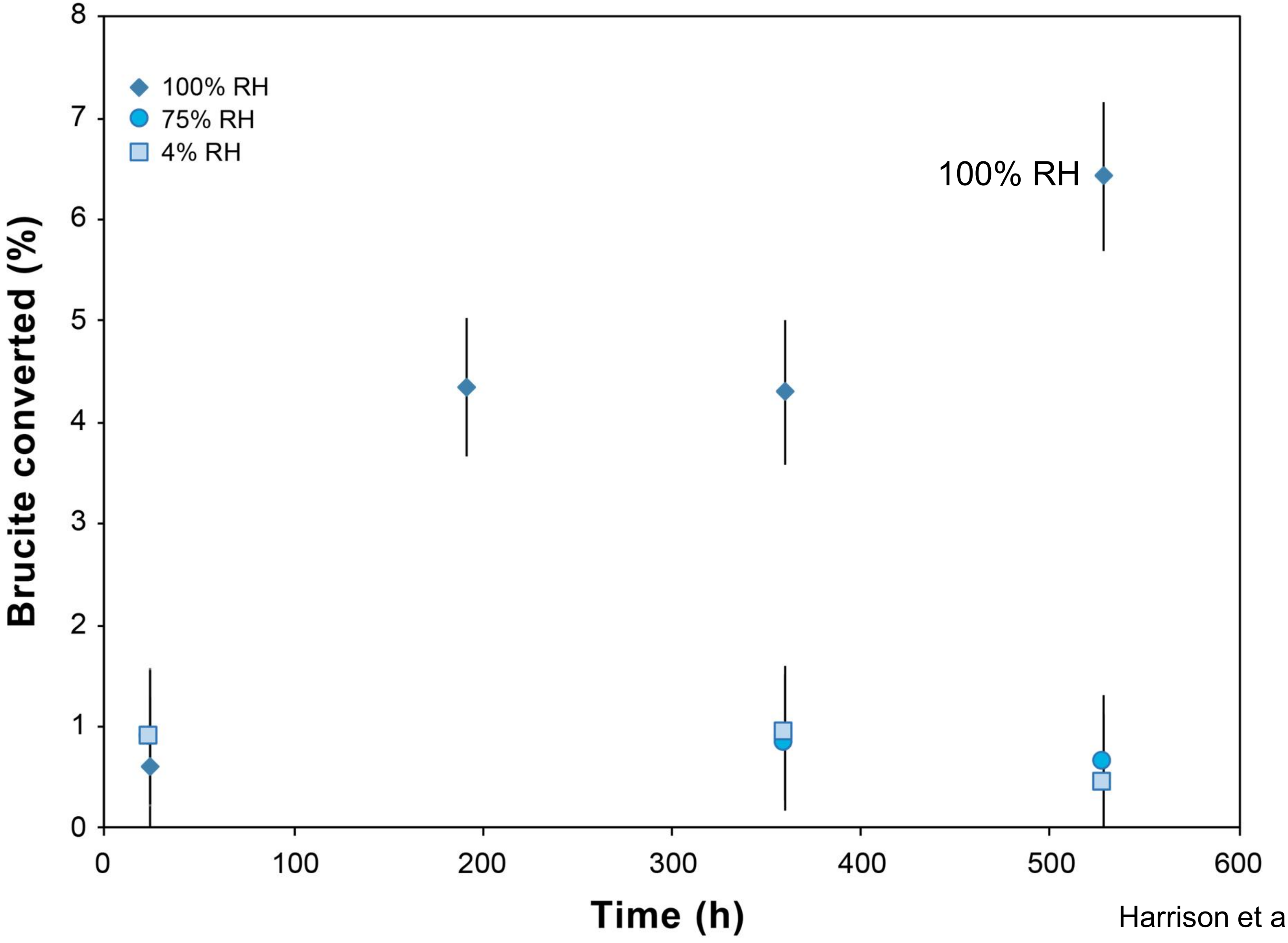
Quantifying the reactions



Harrison et al. *in*

Quantifying the reactions

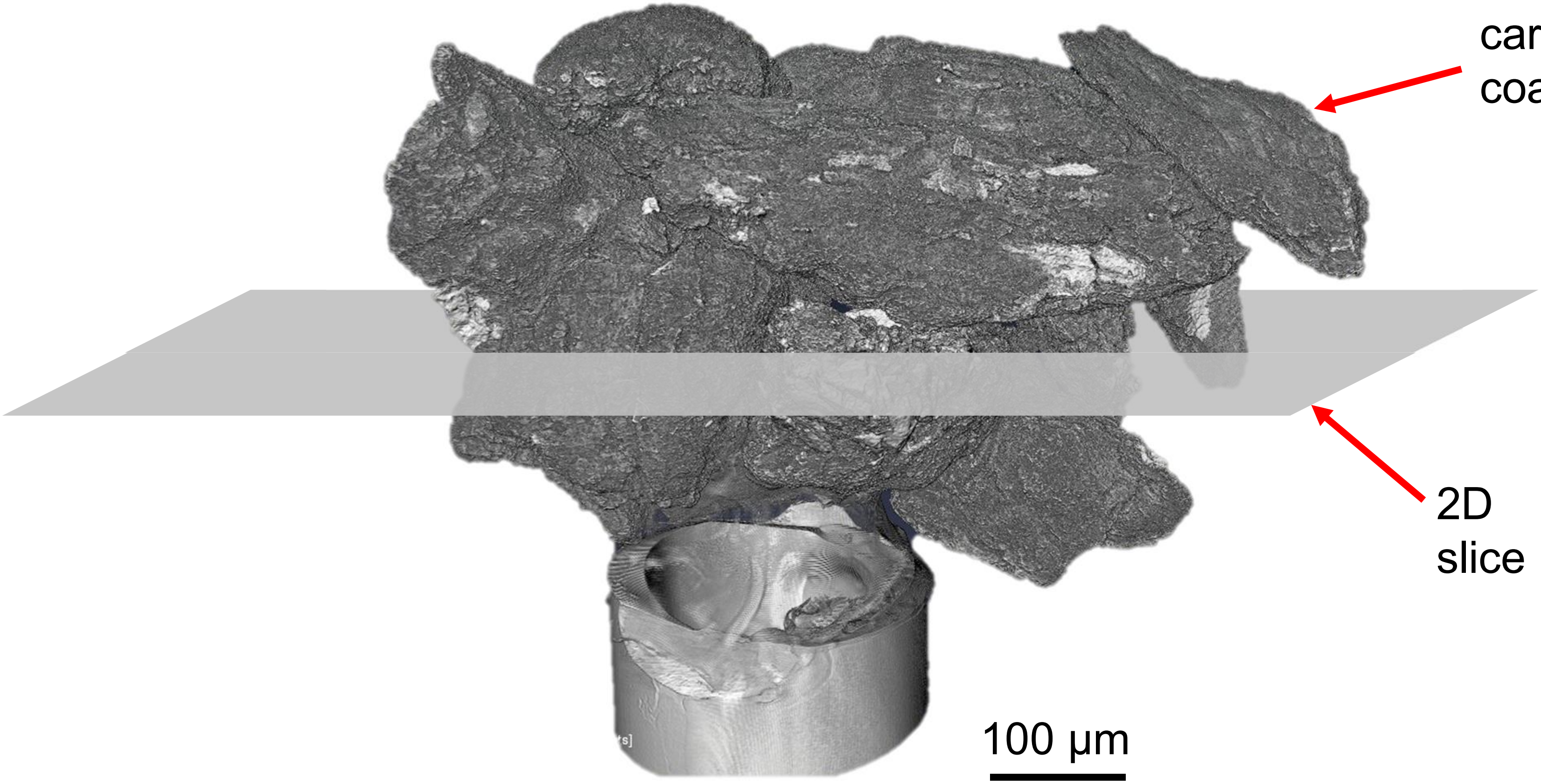
Pure CO_2



Harrison et al. *in*

Extent of precipitation: 3D imaging

100% RH, 378 days



Flakey carbonate coating

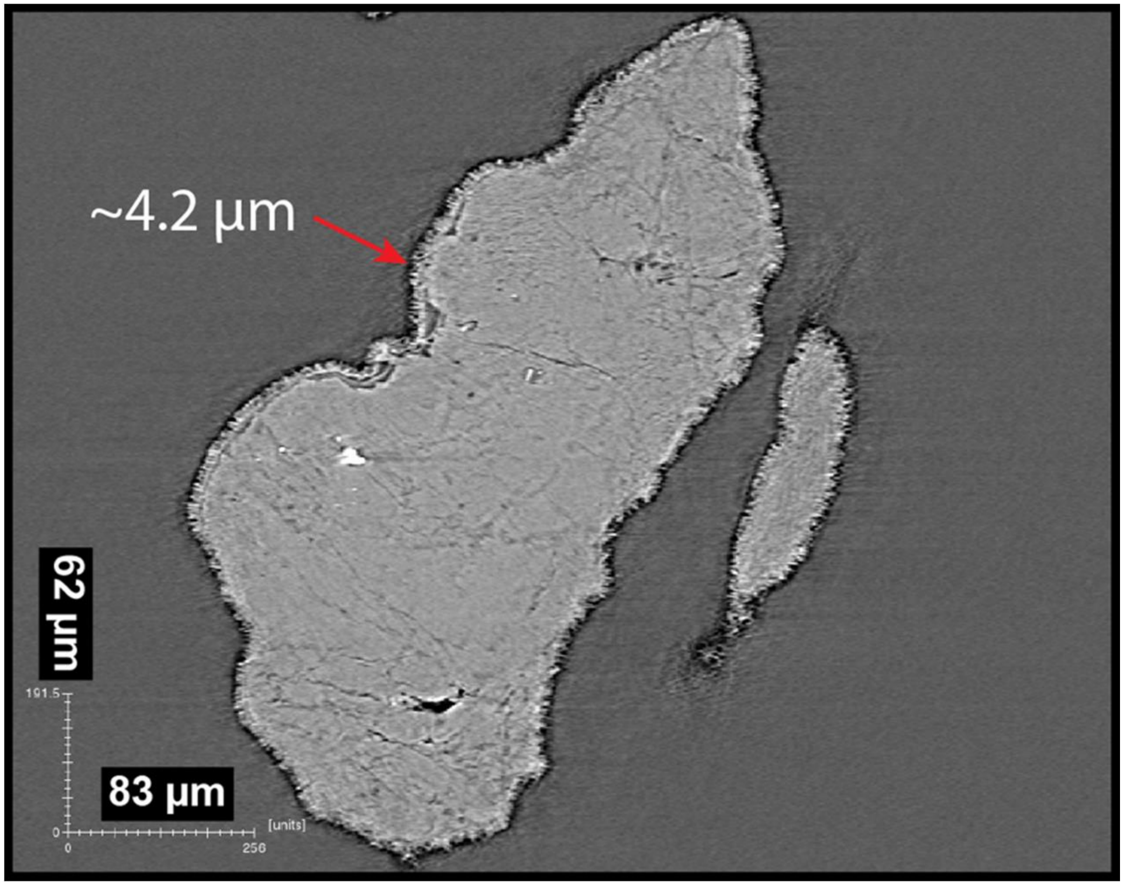
2D slice

100 µm

Harrison et al. *in*

Extent of reaction

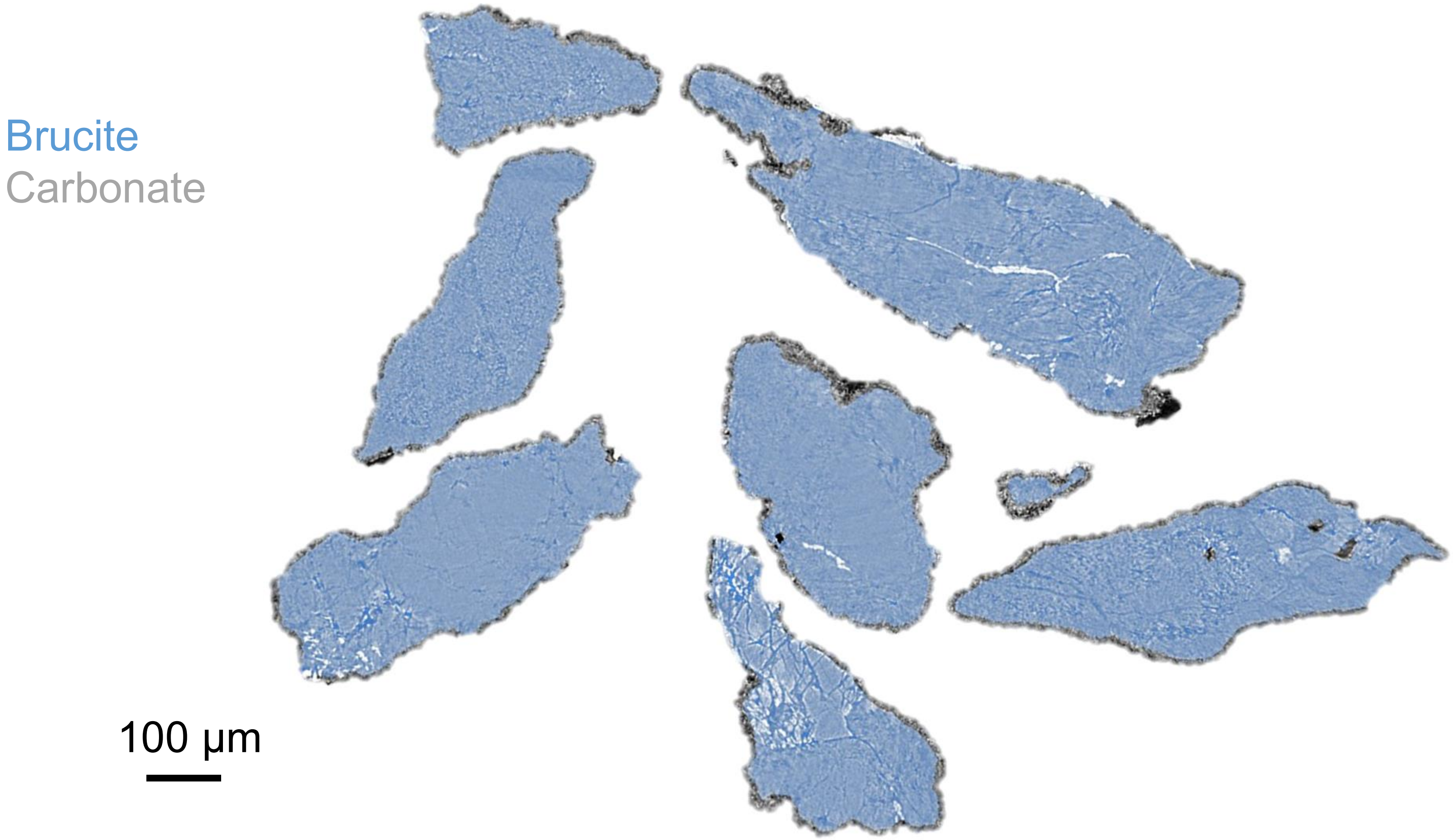
100% humidity, 378 days



- Carbonate rind thickness exceeds typical adsorbed water film thickness (e.g., 15 Å on calcite; Bohr et al., 2010, *GCA*; 10s-100s nm $Mg(NO_3)_2$ rinds on MgO; Al-Abadleh et al., 2003, *J. Phys. Chem.)*

Harrison et al. *in*

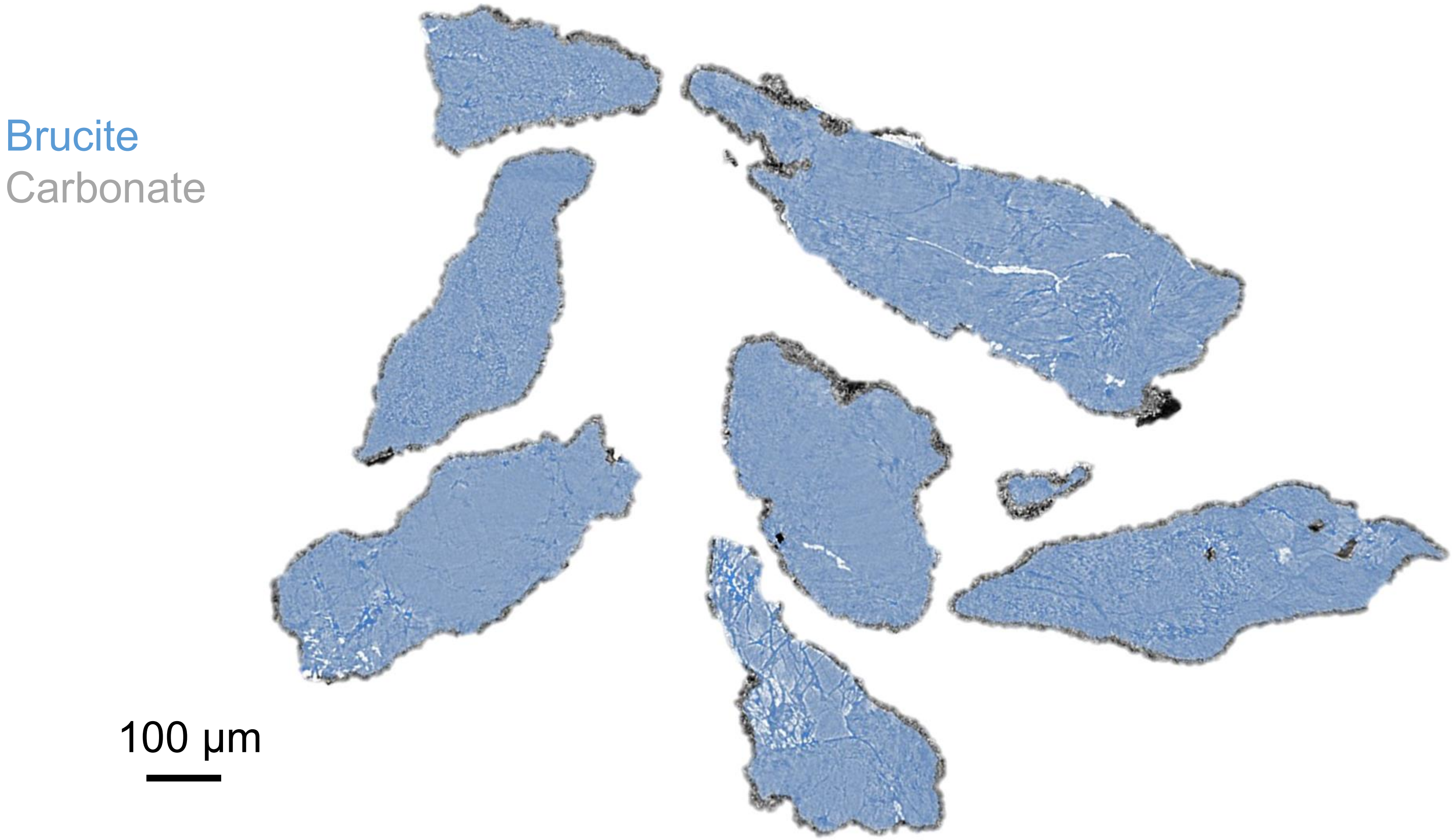
Calculating carbonate volume



- Carbonate precipitates homogeneously distributed and near-constant thickness (~4 µm) around all brucite grains
- Volume of carbonate determined by application of erosion filter to separate rind from bulk, followed by difference in volume of entire grain and unreacted (bulk) brucite

Harrison et al. *in*

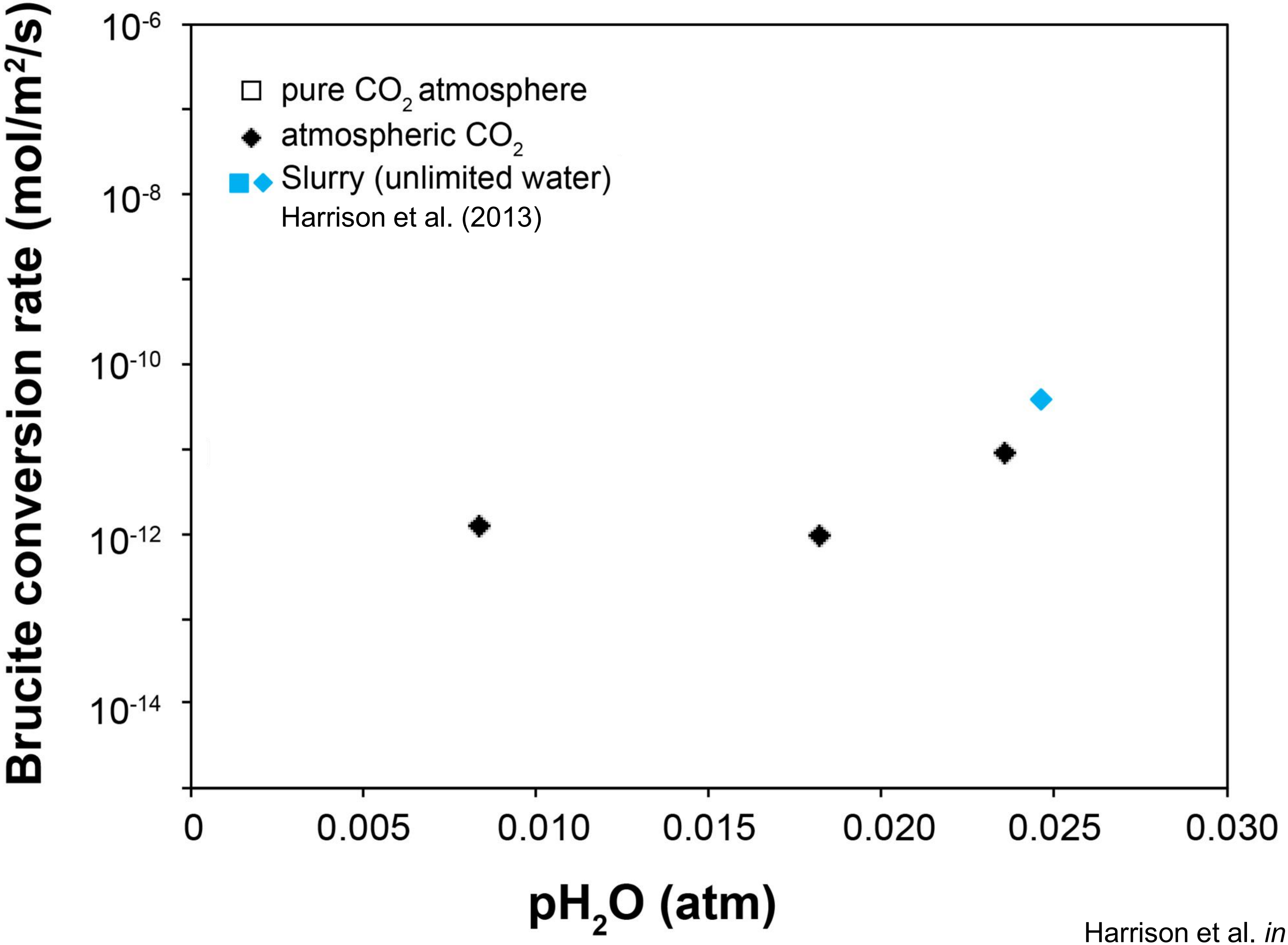
Calculating carbonate volume



- **14%** of solid is carbonate
- **8% brucite conversion** to dypingite [$Mg_5(CO_3)_4(OH)_2 \cdot \sim 5H_2O$]
- Distributed as a thin rind on the surface of the mineral

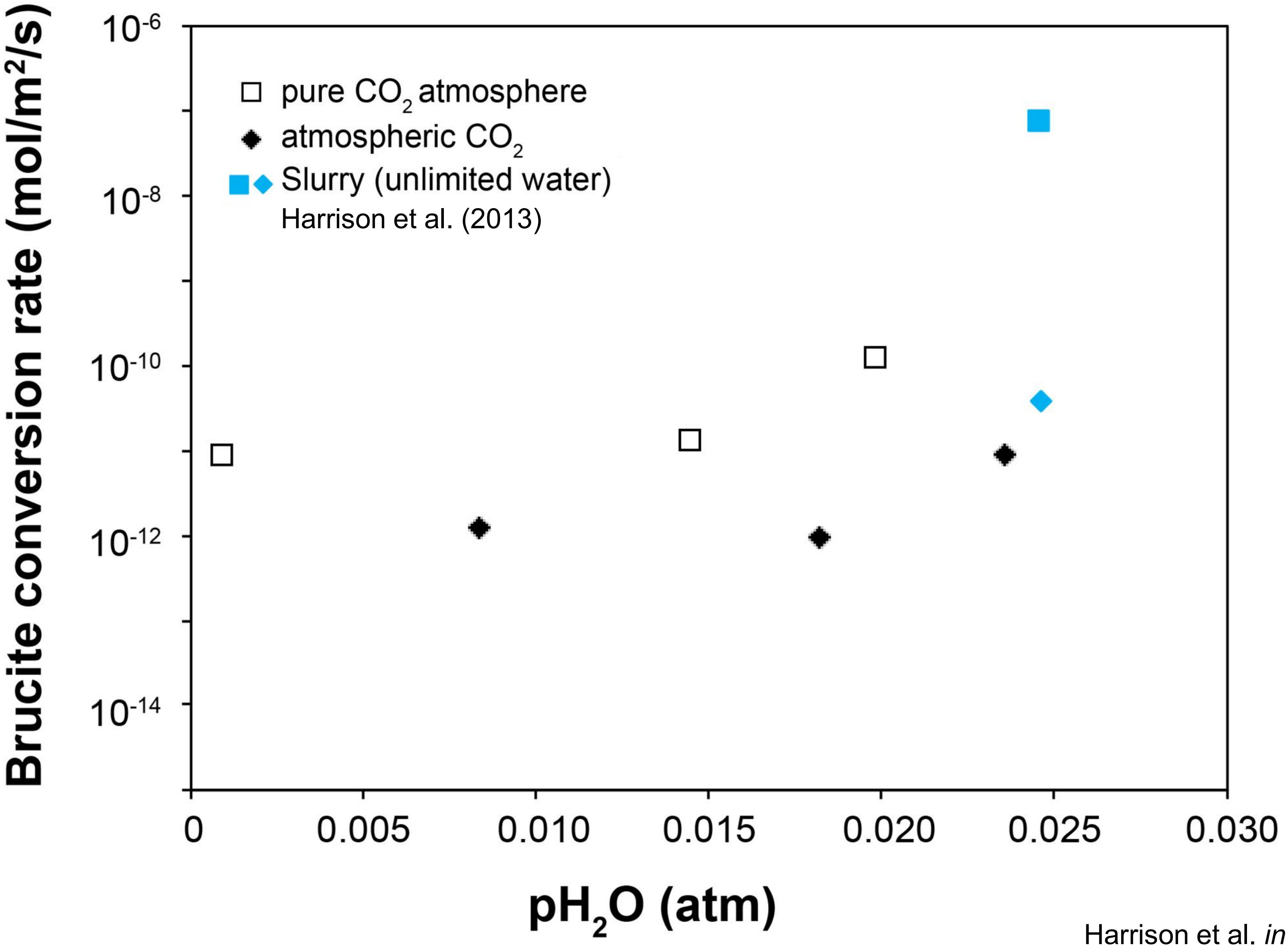
Harrison et al. *in*

Rates are water content dependent



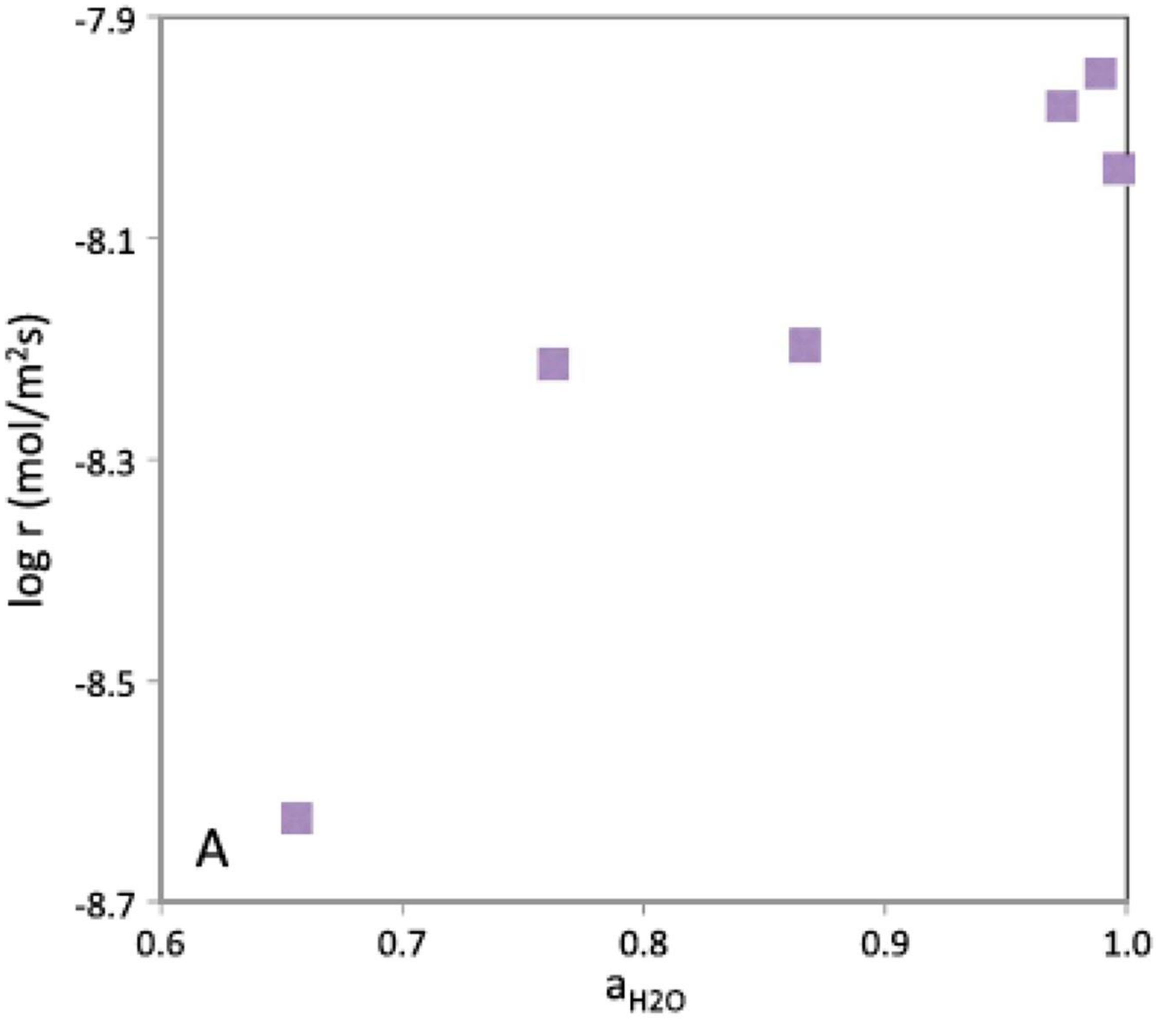
Harrison et al. *in*

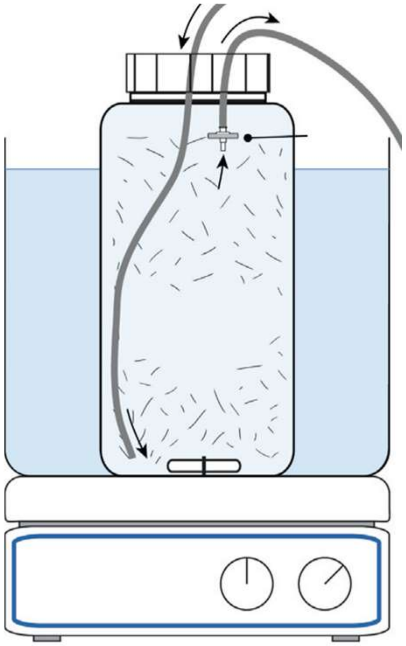
Rates are water content dependent



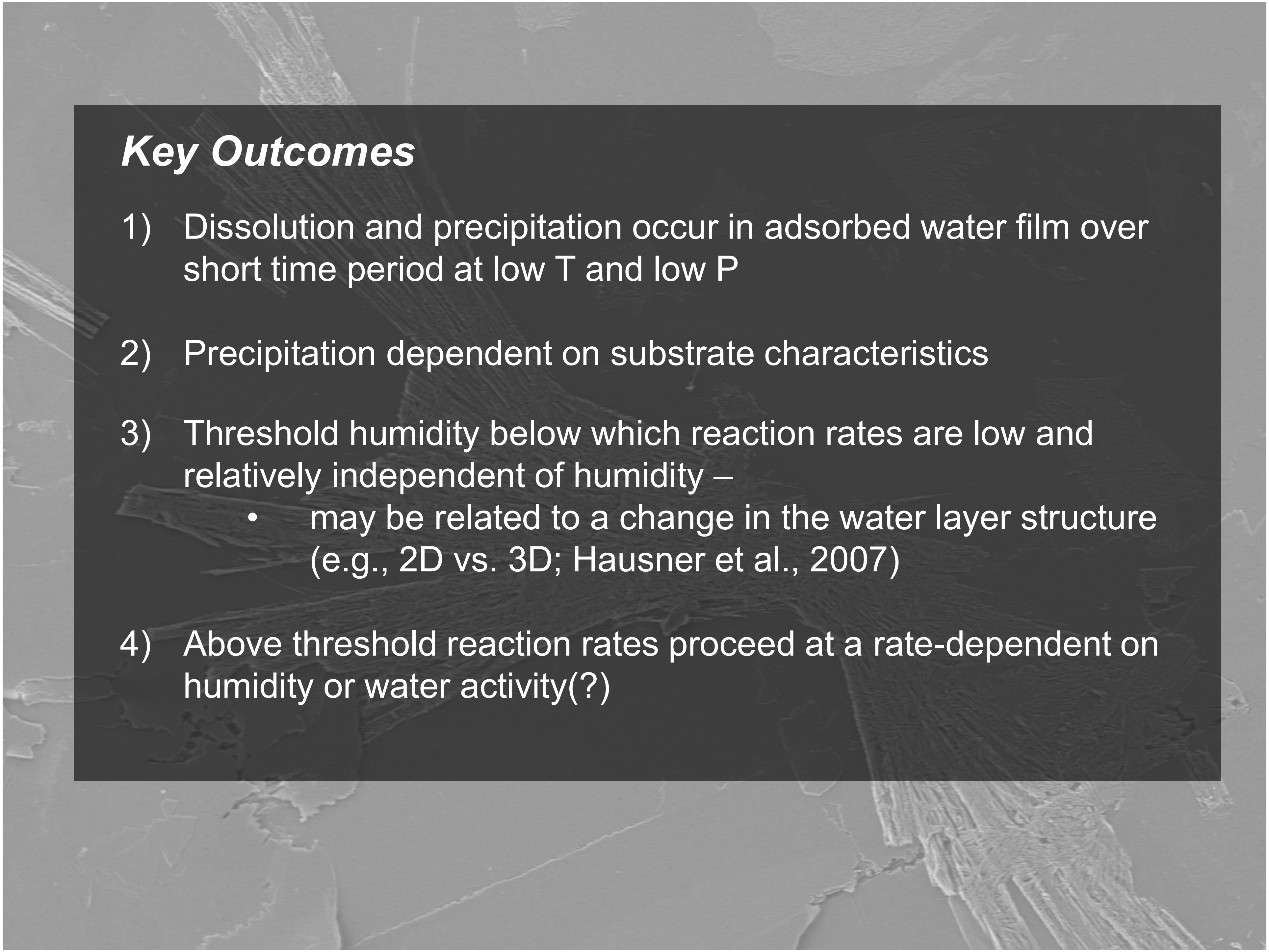
Harrison et al. *in*

Rates impacted by water activity





Olsen et al. (2014) *JGR Planet*



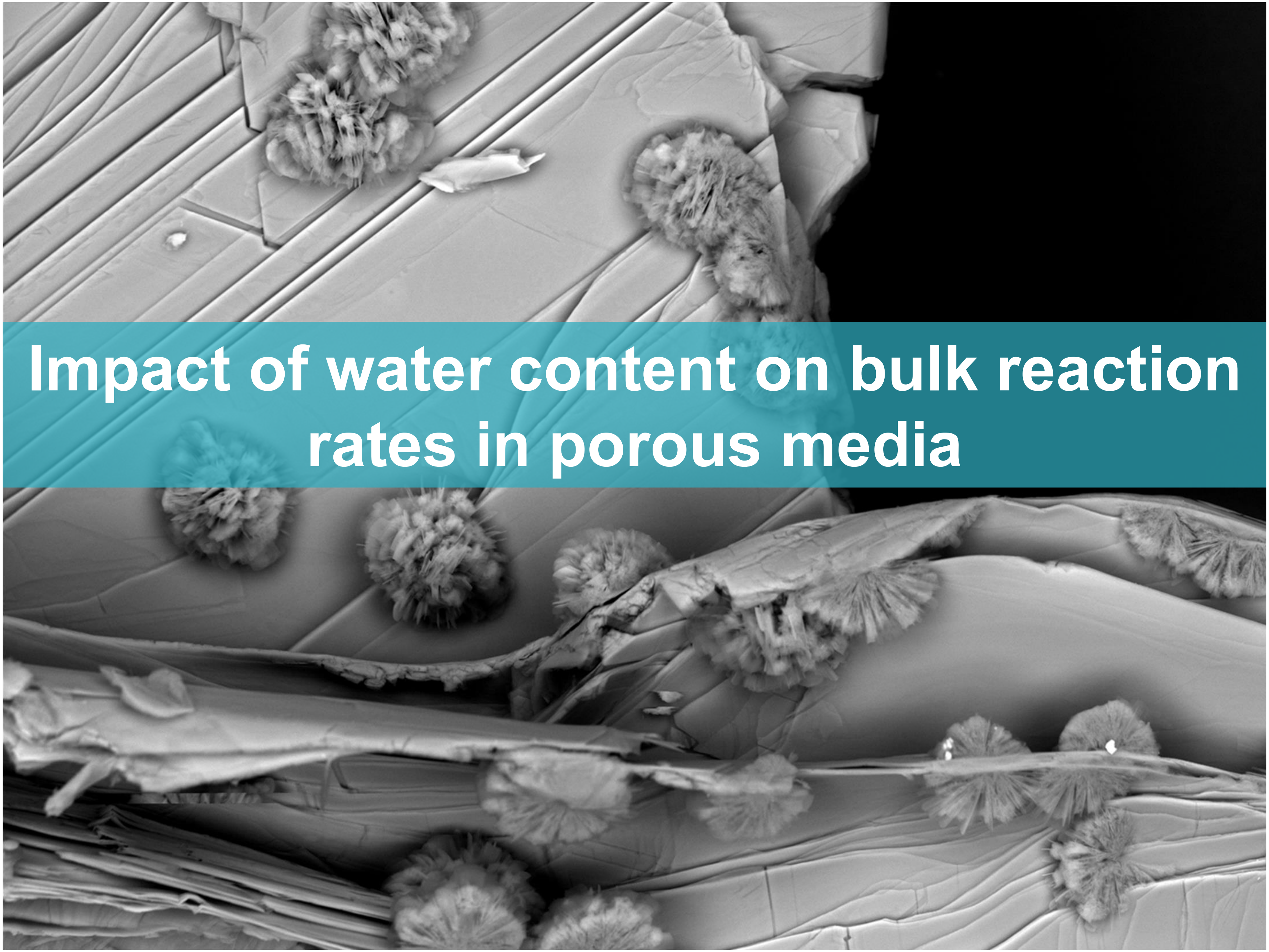
Key Outcomes

1) Dissolution and precipitation occur in adsorbed water film over short time period at low T and low P

2) Precipitation dependent on substrate characteristics

3) Threshold humidity below which reaction rates are low and relatively independent of humidity –
    - may be related to a change in the water layer structure (e.g., 2D vs. 3D; Hausner et al., 2007)

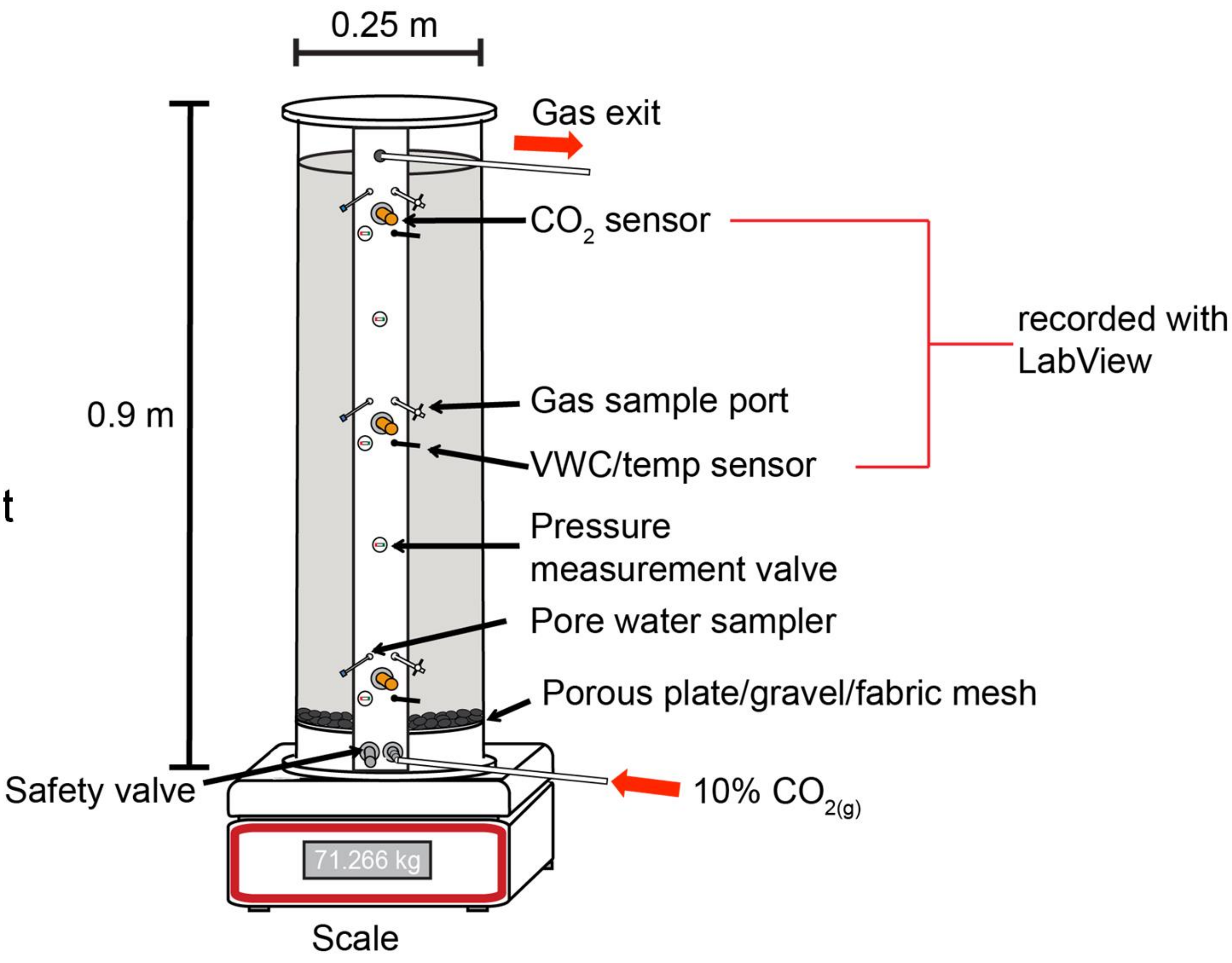
4) Above threshold reaction rates proceed at a rate-dependent on humidity or water activity(?)



Impact of water content on bulk reaction rates in porous media

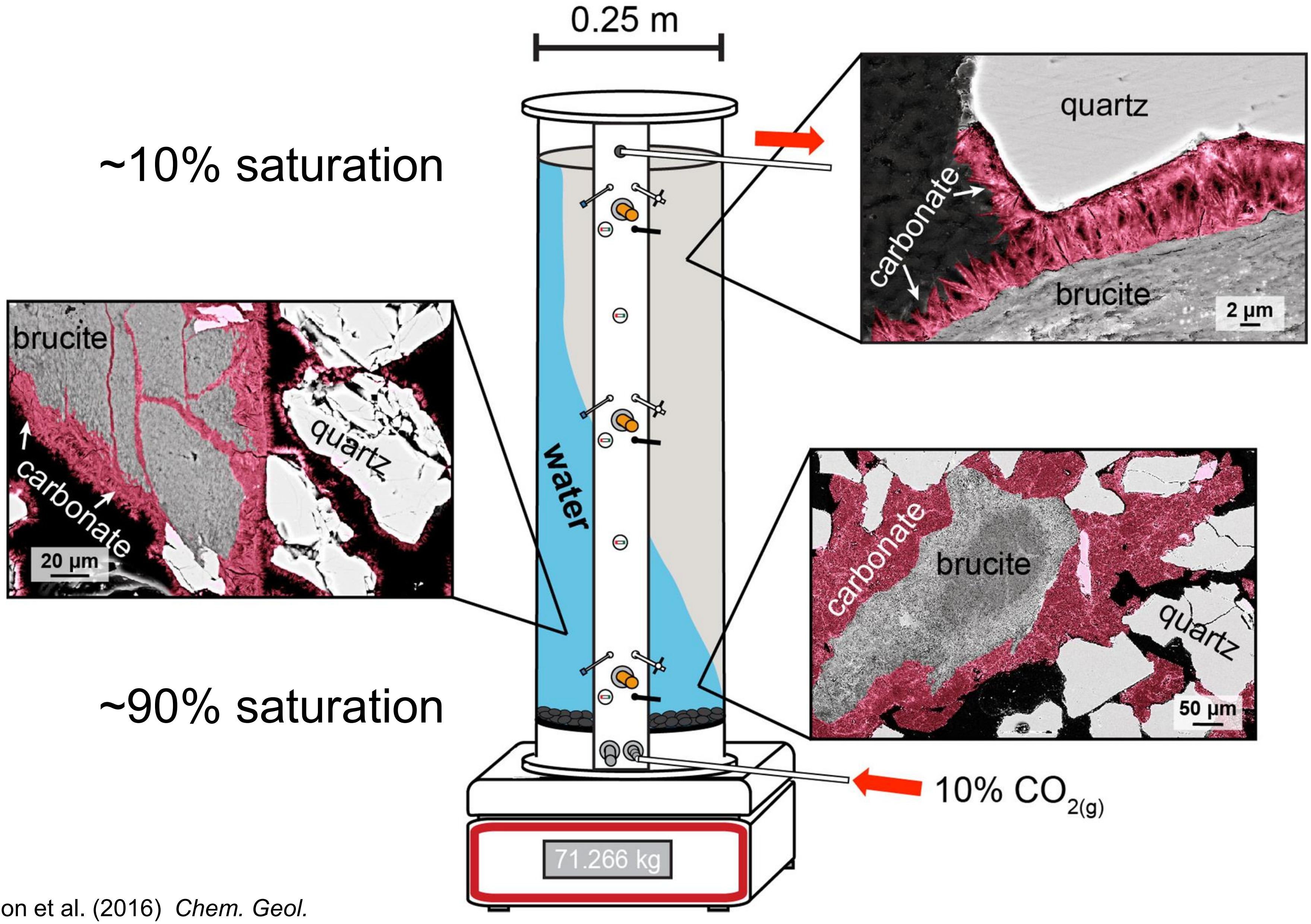
Unsaturated column experiments

- 10 wt.% brucite [$Mg(OH)_2$], 90 wt.% [SiO_2]
- Bulk water saturation: 35% or 60%
- Gradient in water content from ~10-90%
- Reaction rate monitored by measurement of CO_2 flux and mass gain of columns



Harrison et al. (2016) *Chem. Geol.*

Carbonate precipitation dictated by water

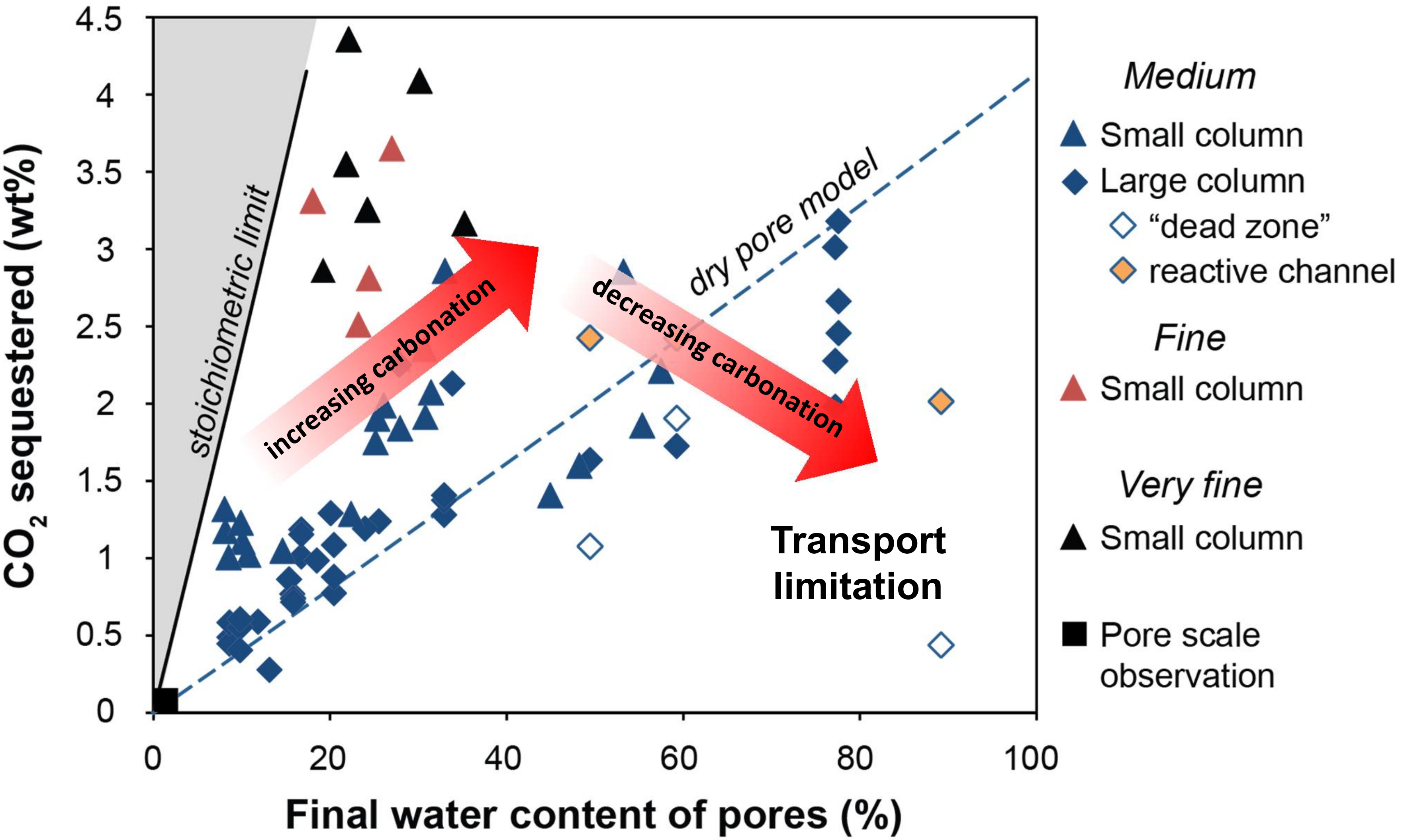


~10% saturation

~90% saturation

Harrison et al. (2016) *Chem. Geol.*

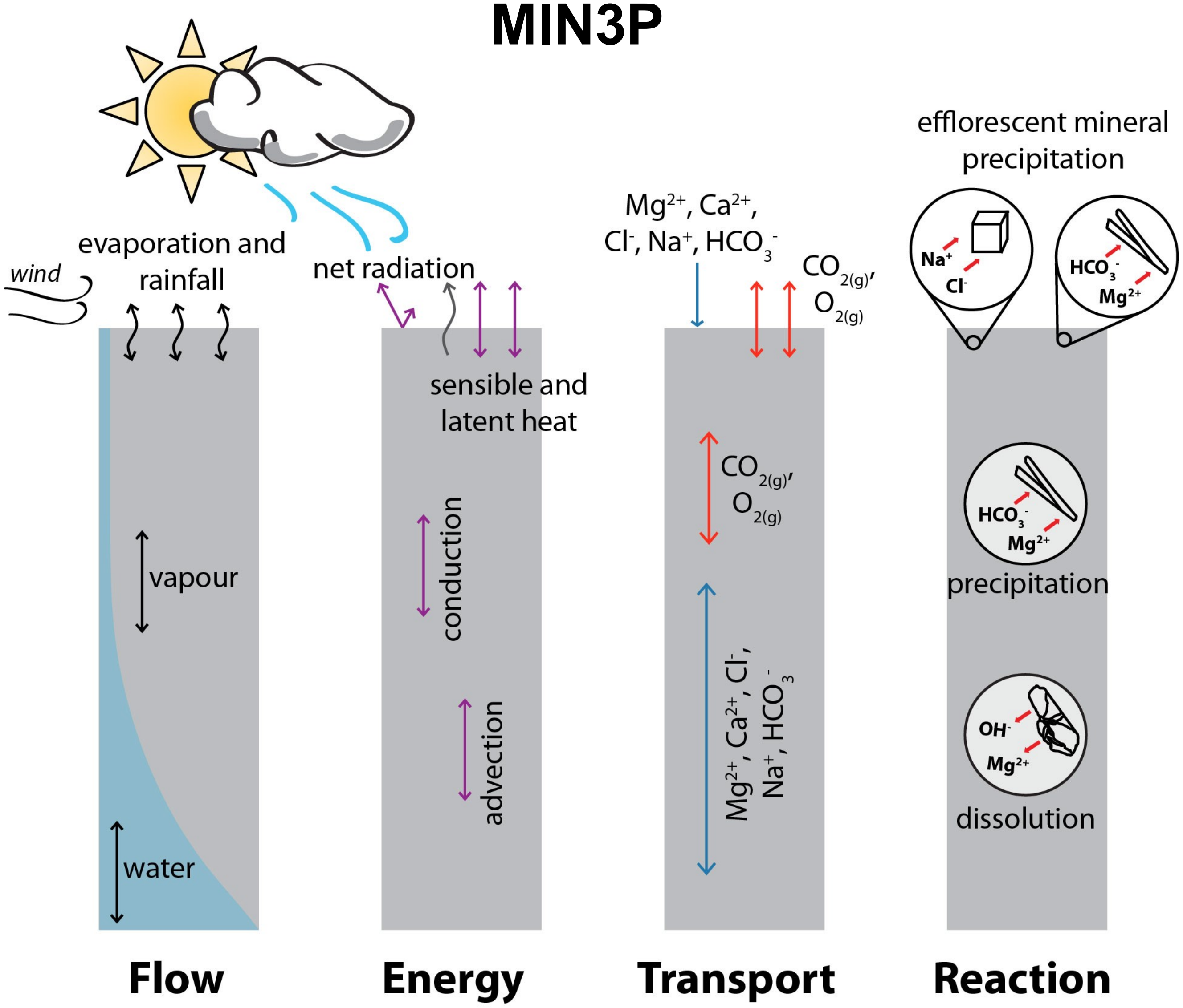
Reaction extent dictated by water content



Harrison et al. (2016) *Chem. Geol.*

Reactive transport modelling

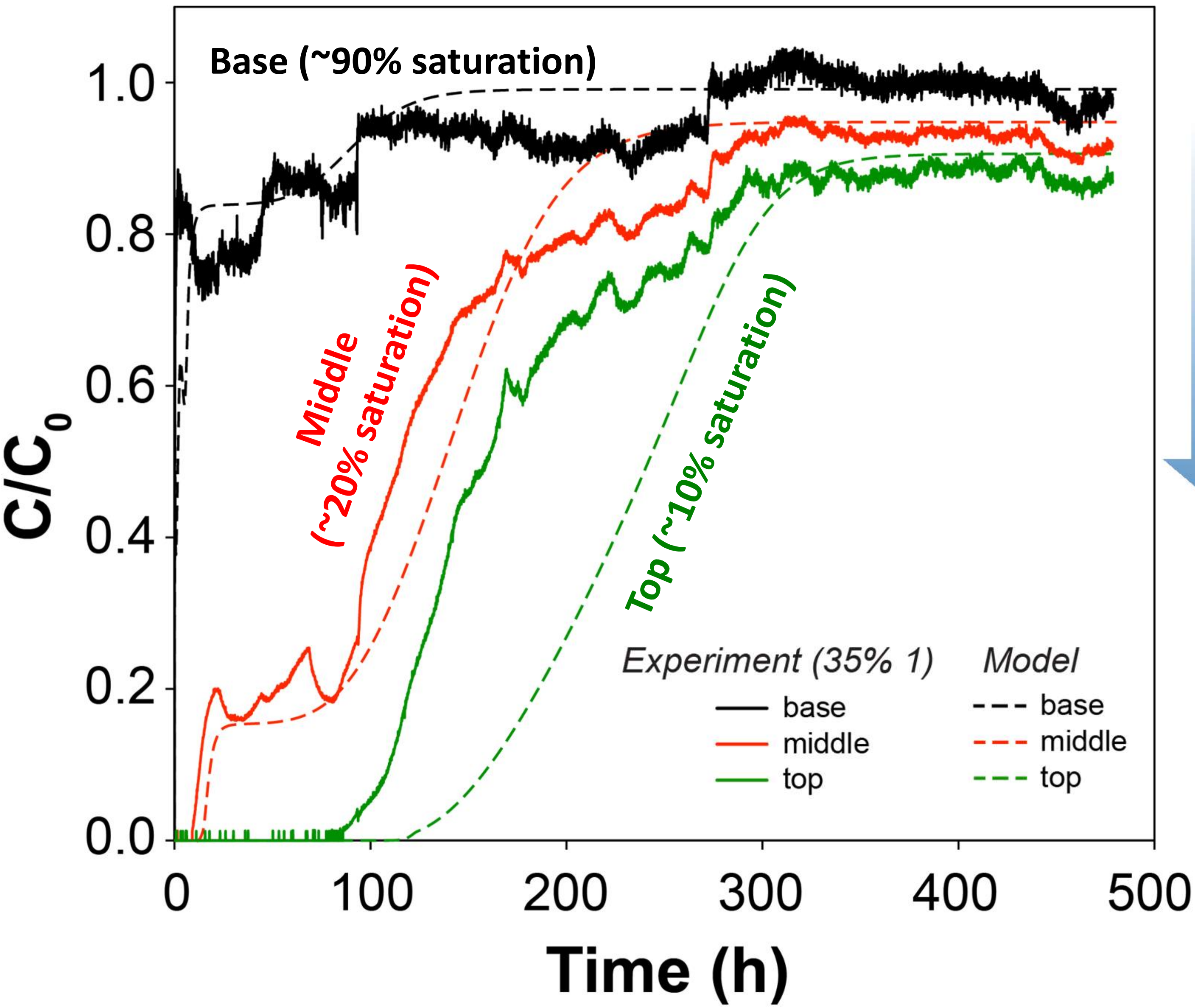
MIN3P

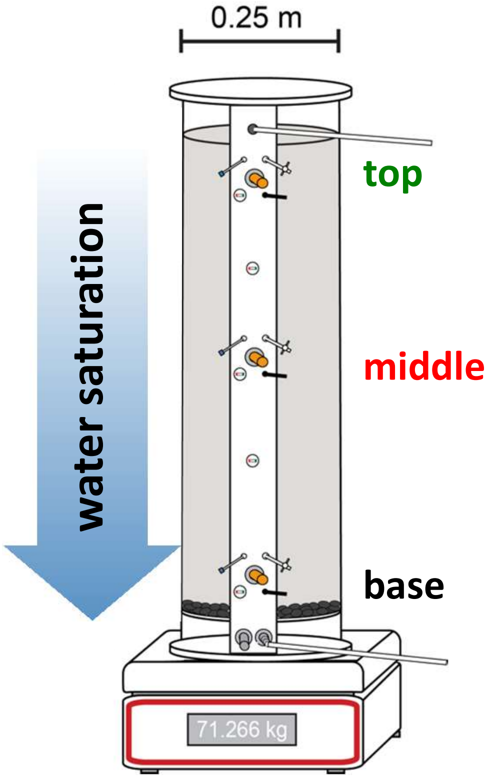


Transport via diffusion and advection in aqueous and gaseous phases

Mayer et al. (2002) *Water Resour. Res.;* Molins and Mayer (2007) *Water Resour. Res.*; Bea et al. (2012) *Vadose*

Model fails at low water saturation

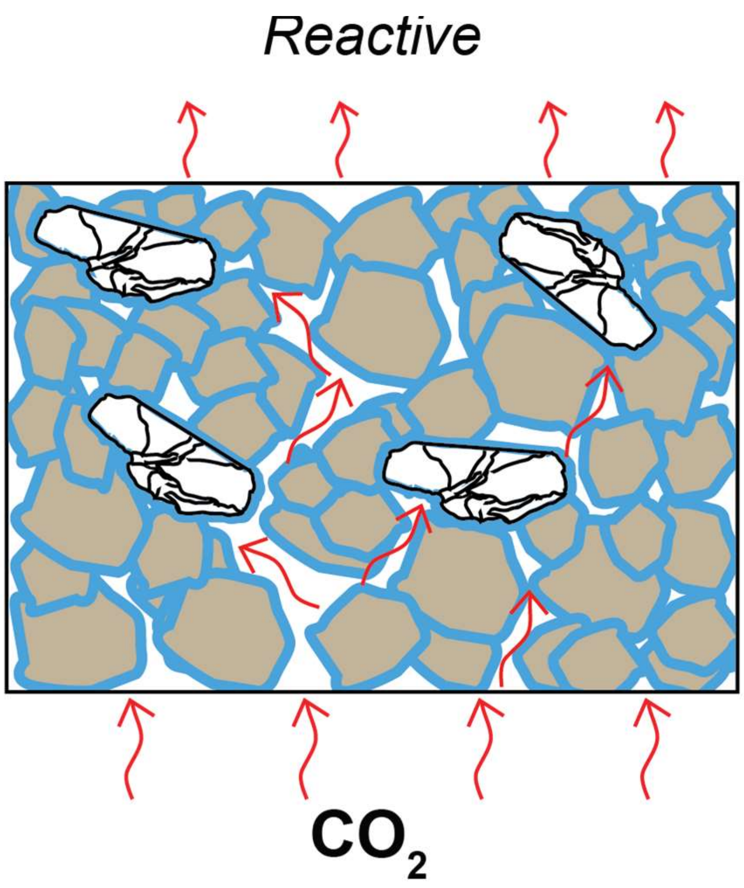




Harrison et al. (2016) *Chem. Geol.*

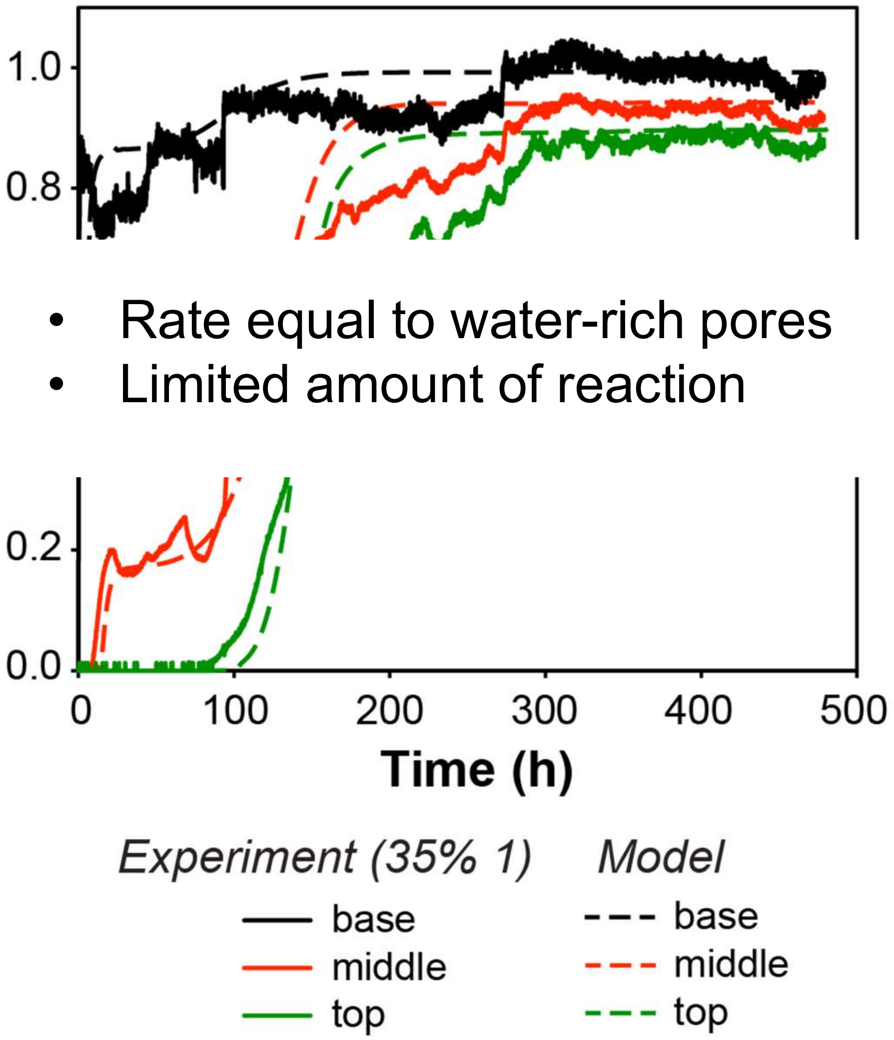
“End-member” conceptual models

Damp pore

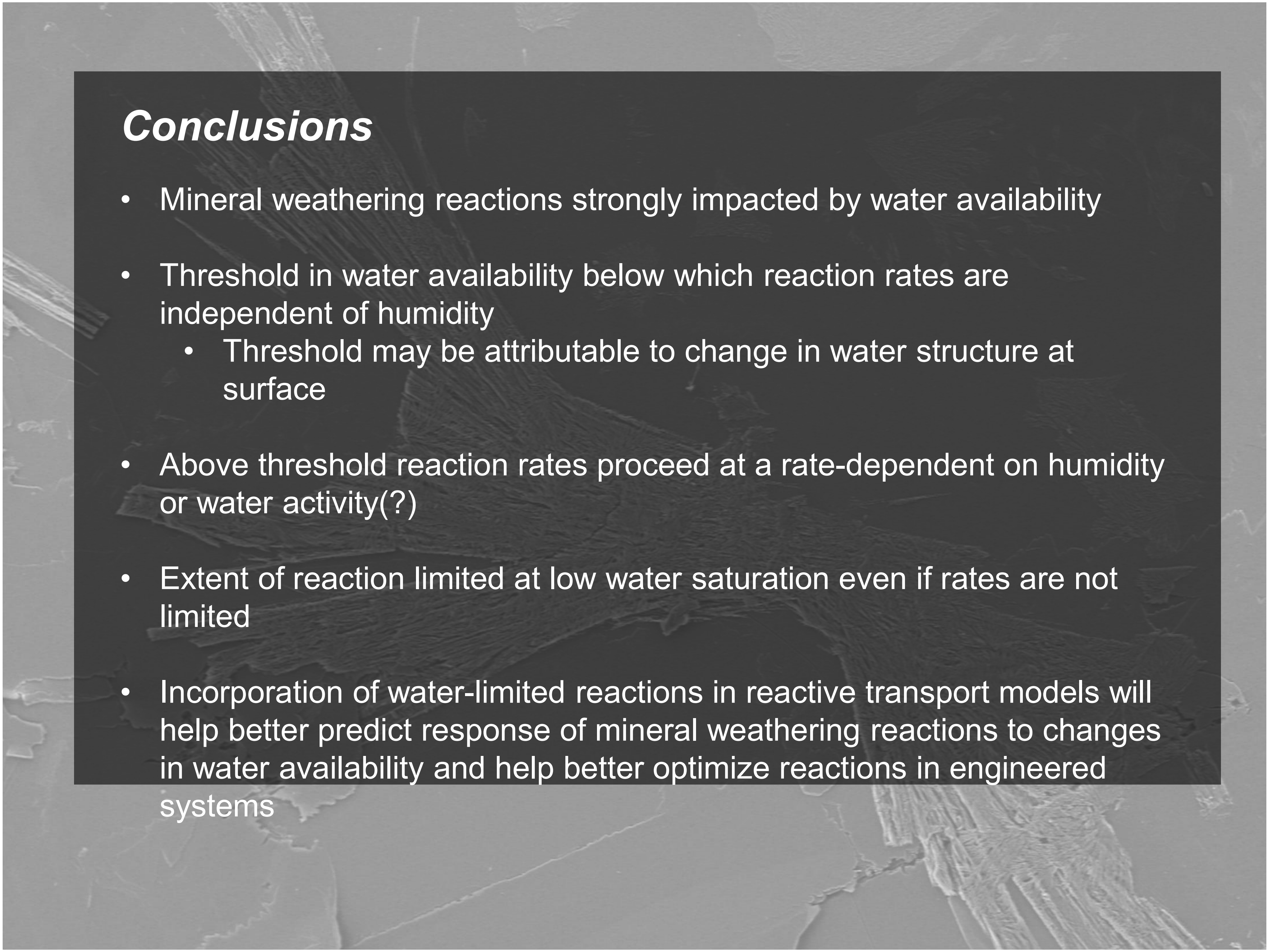


Surface area maintained
Reduced reactive capacity

- Rate equal to water-rich pores
- Limited amount of reaction



Harrison et al. *in prep*



Conclusions

- Mineral weathering reactions strongly impacted by water availability
- Threshold in water availability below which reaction rates are independent of humidity
  - Threshold may be attributable to change in water structure at surface
- Above threshold reaction rates proceed at a rate-dependent on humidity or water activity(?)
- Extent of reaction limited at low water saturation even if rates are not limited
- Incorporation of water-limited reactions in reactive transport models will help better predict response of mineral weathering reactions to changes in water availability and help better optimize reactions in engineered systems

Collaborator acknowledgements

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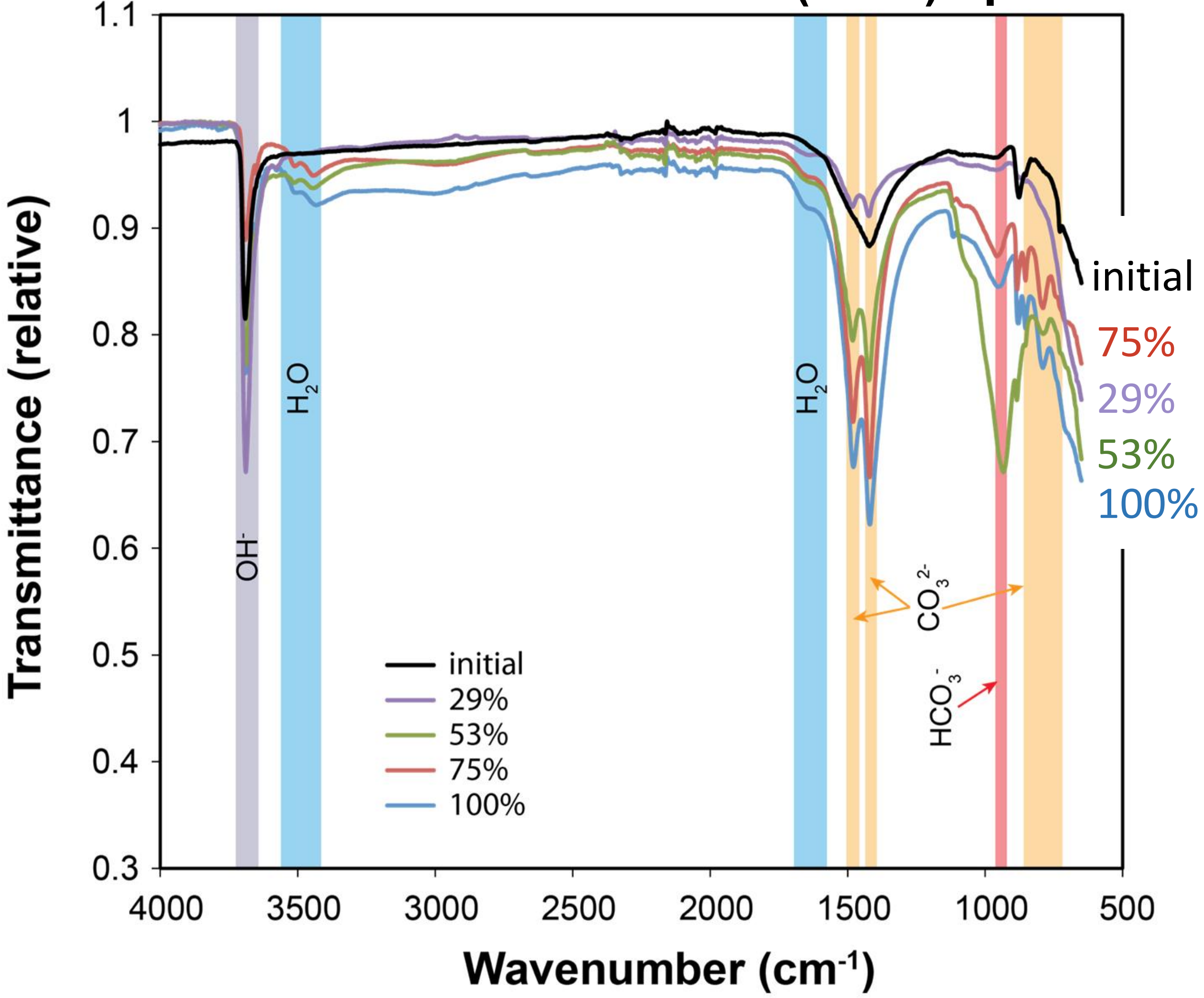
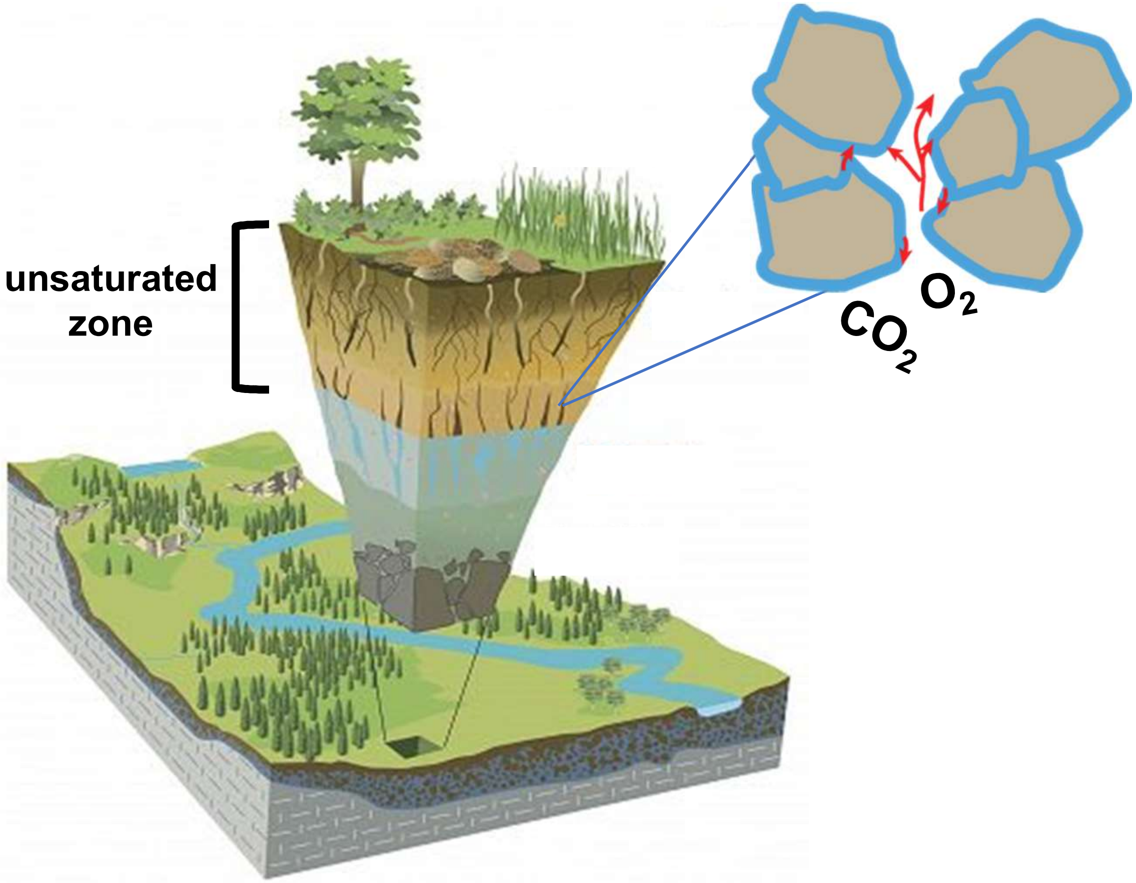
Hydrated Mg-carbonates at all humidities

Fourier transform infrared (FTIR) spectra



- Hydrated hydroxy-Mg-carbonates (dypingite or hydromagnesite) form within one week at all RHs and atmospheric *p*CO_2 and within 24 h with pure CO

Gas-driven reactions



- Reactions that store C are dependent on exposure to CO_2
- Exposure to gas is important driver of reactions and their kinetics
- Water may be limiting for these important gas-driven reactions
- Water limitations in reactive transport models will help predictions and optimizing reactions

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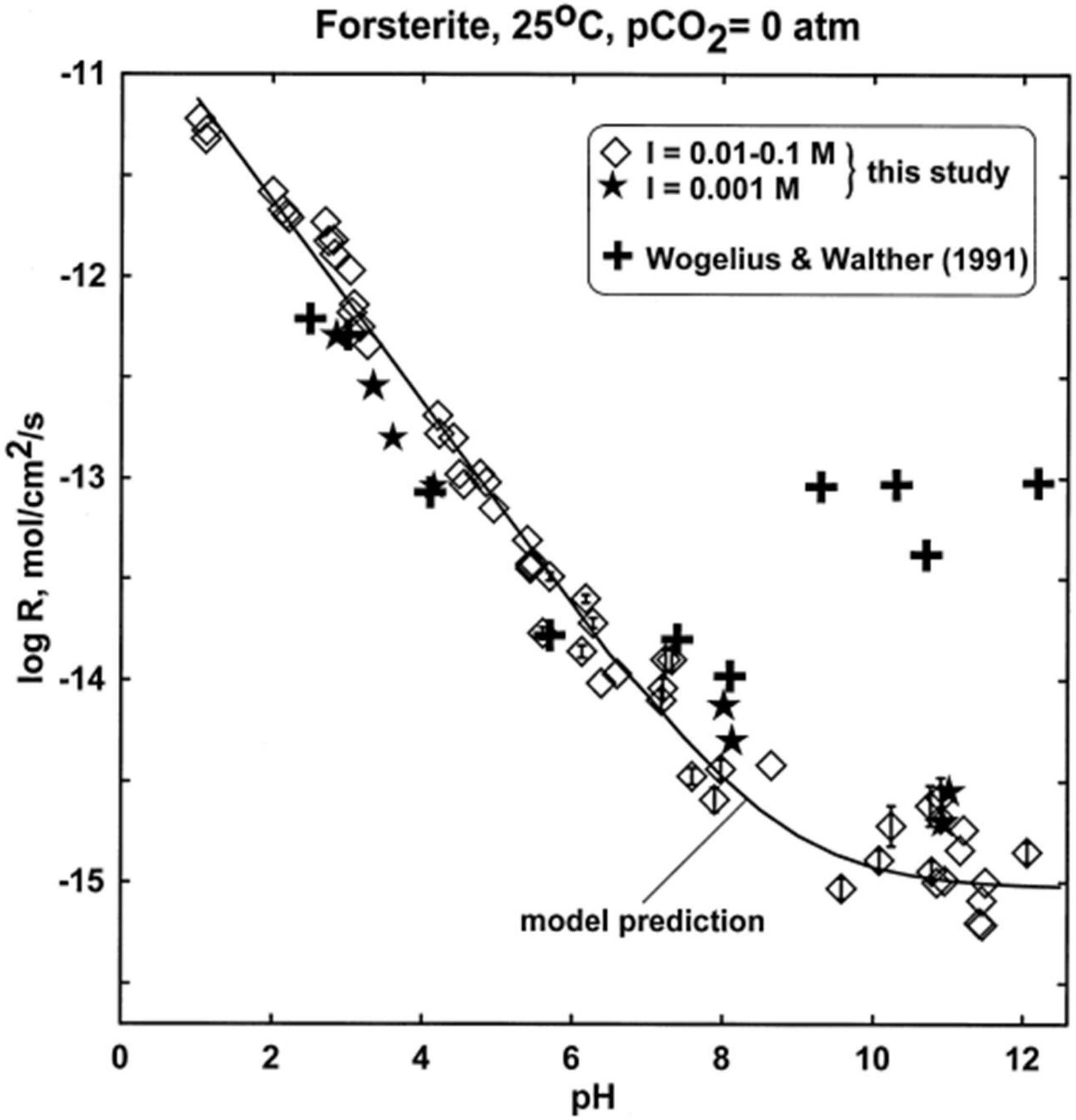
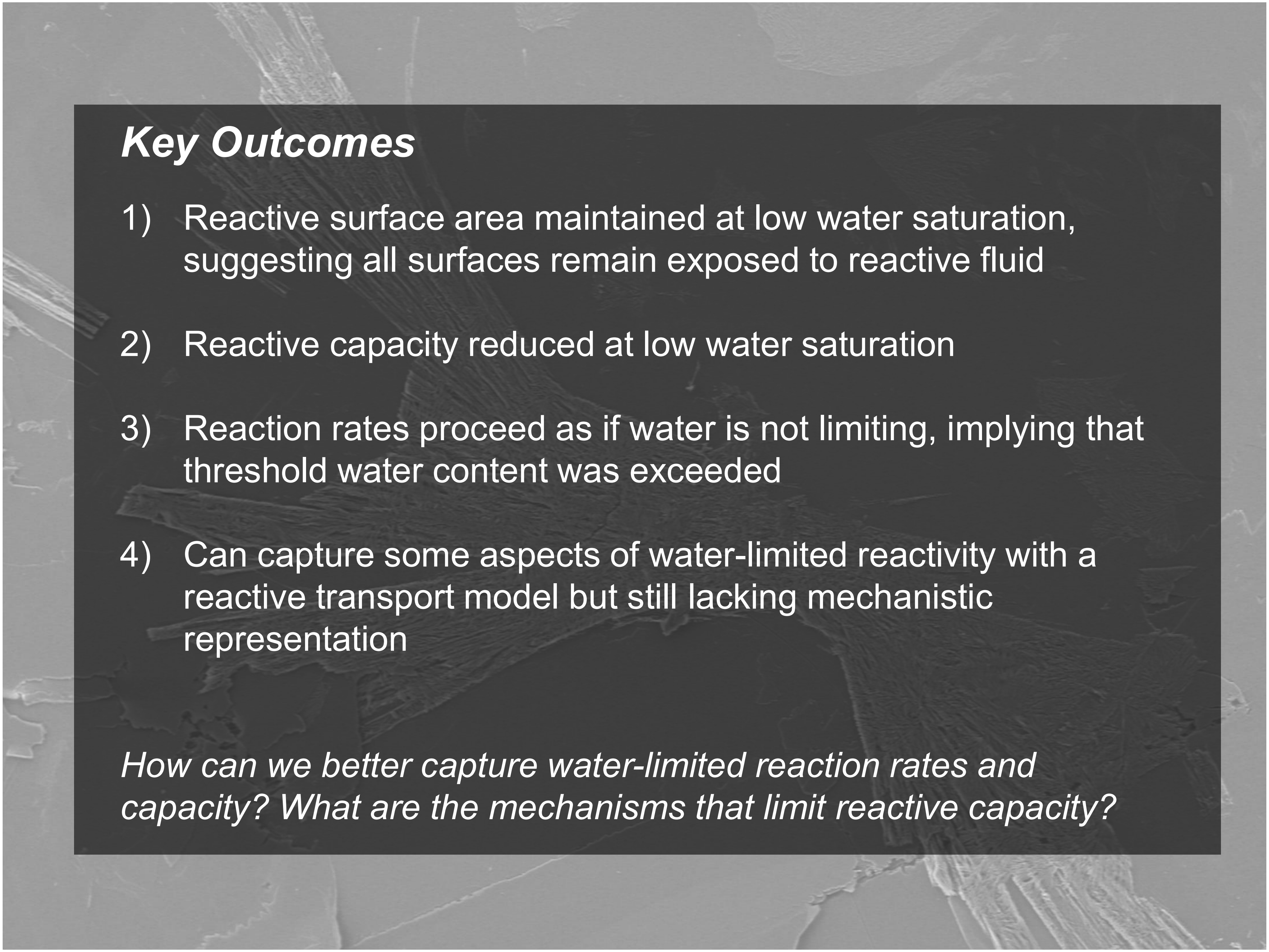
Fluid composition



Pokrovsky and Schott (2000) *GCA*



Key Outcomes

1) Reactive surface area maintained at low water saturation, suggesting all surfaces remain exposed to reactive fluid

2) Reactive capacity reduced at low water saturation

3) Reaction rates proceed as if water is not limiting, implying that threshold water content was exceeded

4) Can capture some aspects of water-limited reactivity with a reactive transport model but still lacking mechanistic representation

How can we better capture water-limited reaction rates and capacity? What are the mechanisms that limit reactive capacity?