Towards carbon storage in concrete - Mg-based binders

13.3.2024

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Inorganic circular materials group

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Professor
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Professor
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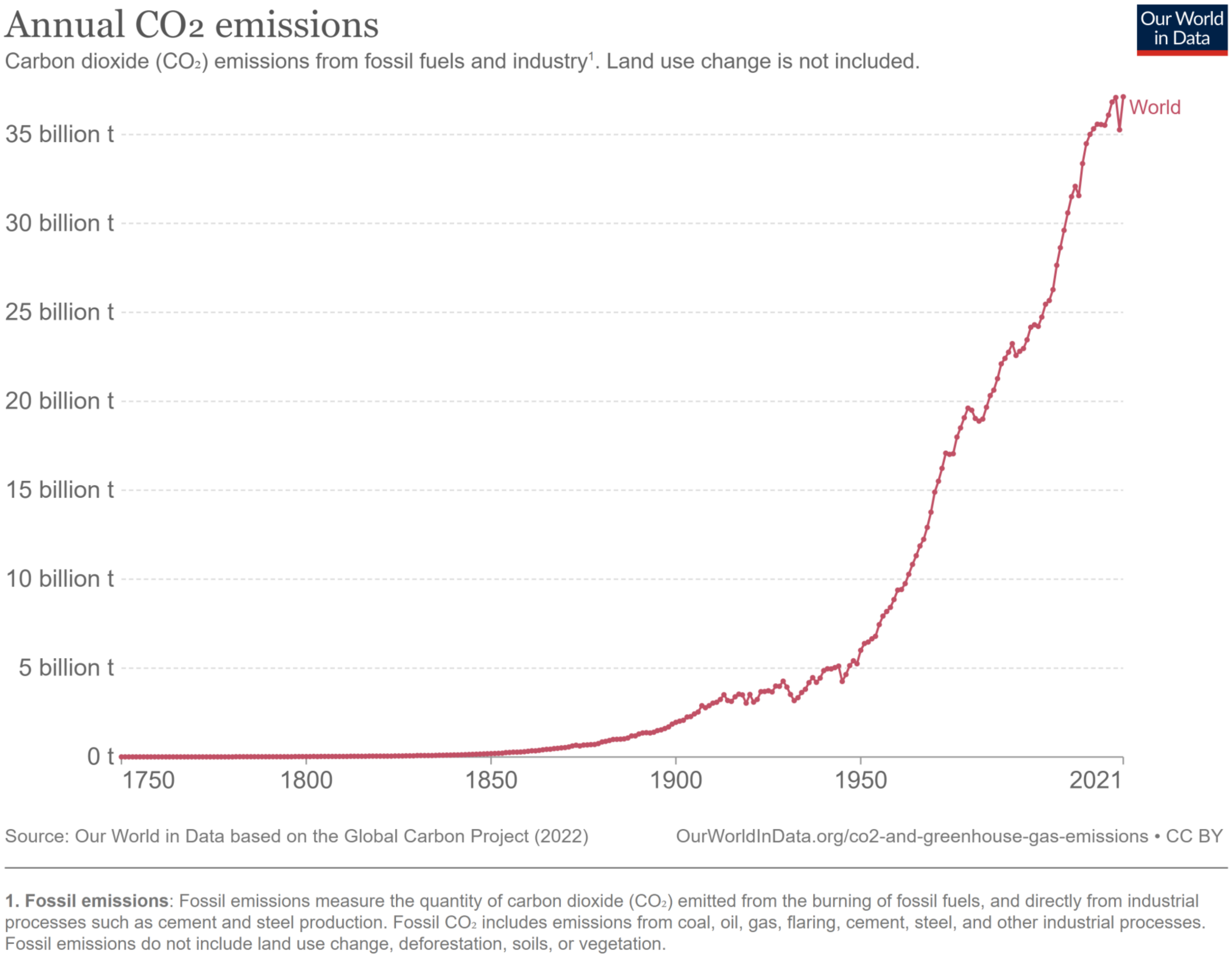
Senior research fellow
Katja Ohenoja

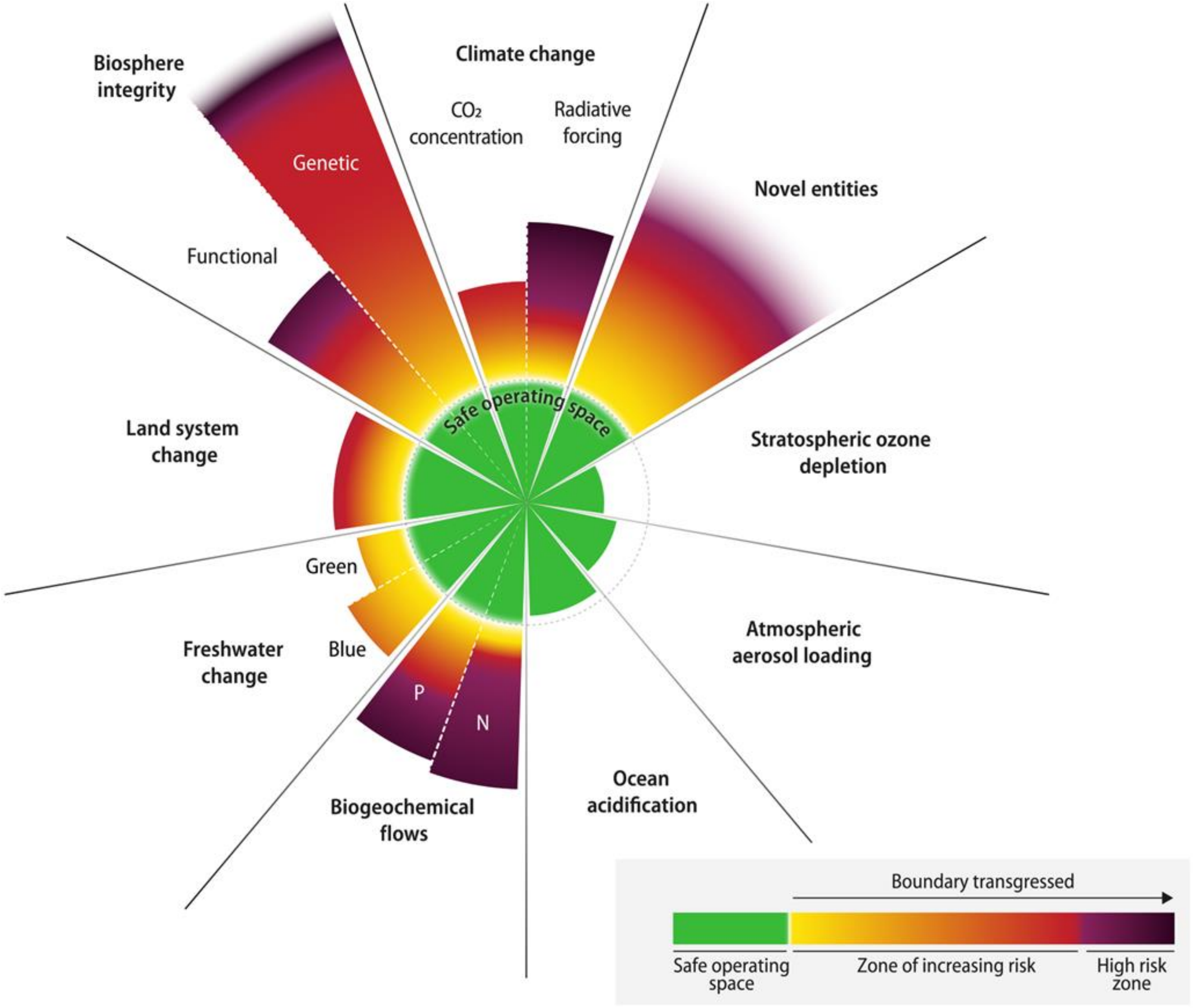
- **4 professors (2 associate/assistant), 2 senior research fellows**
- 8 postdocs, 28 doctoral researchers
  - Master students, trainees, laboratory technicians
- Budget: ~3 M€/year
- External funding: >80 %
  - EU Horizon, Business Finland, Academy of Finland, Private foundations, ERDF, direct company projects
- **Topics:**
  - Utilization, characterization, and processing of industrial inorganic side streams
  - Construction materials, aggregates
  - Magnesia-based binders, CO_2 capture storage & utilization (CCS/U)
  - Environmental applications, water purification
  - Materials chemistry, dissolution, surface interphase reactions

The issue at hand

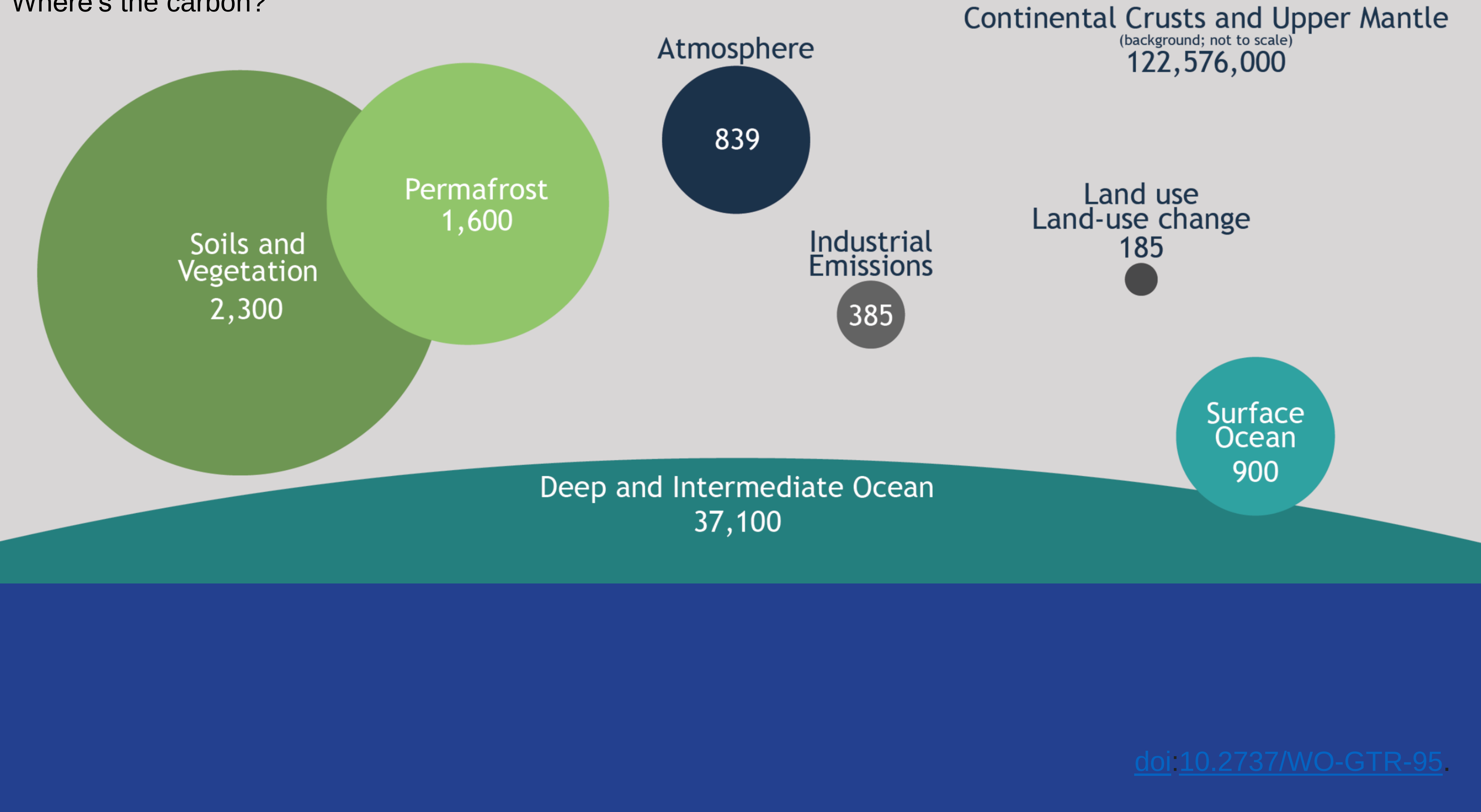


But…
all planetary boundaries should be considered

Planetary boundaries (situation 10/2023)

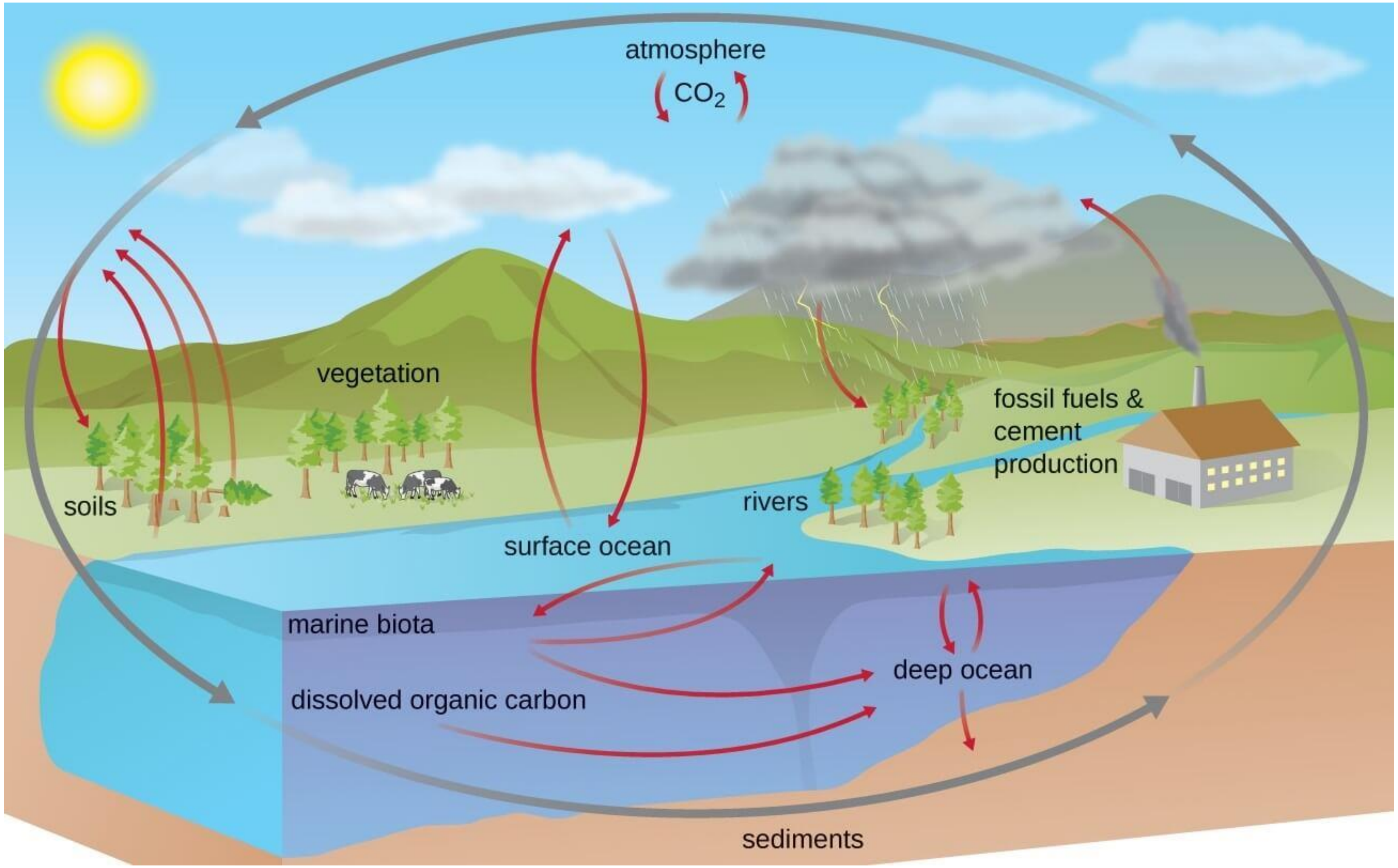


Where’s the carbon?

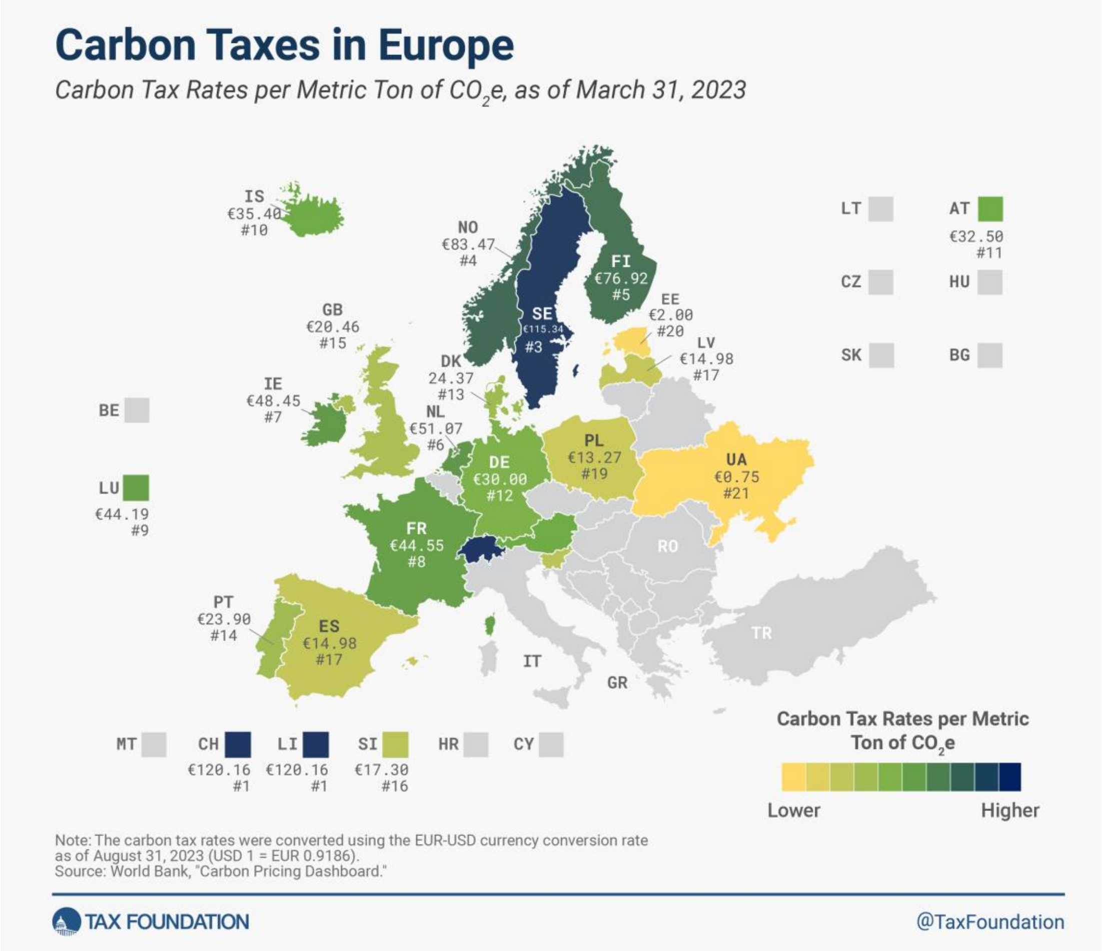


doi:10.2737/WO-GTR-95.

Slow and fast carbon cycles



Carbon Tax across Europe and global Carbon price trend



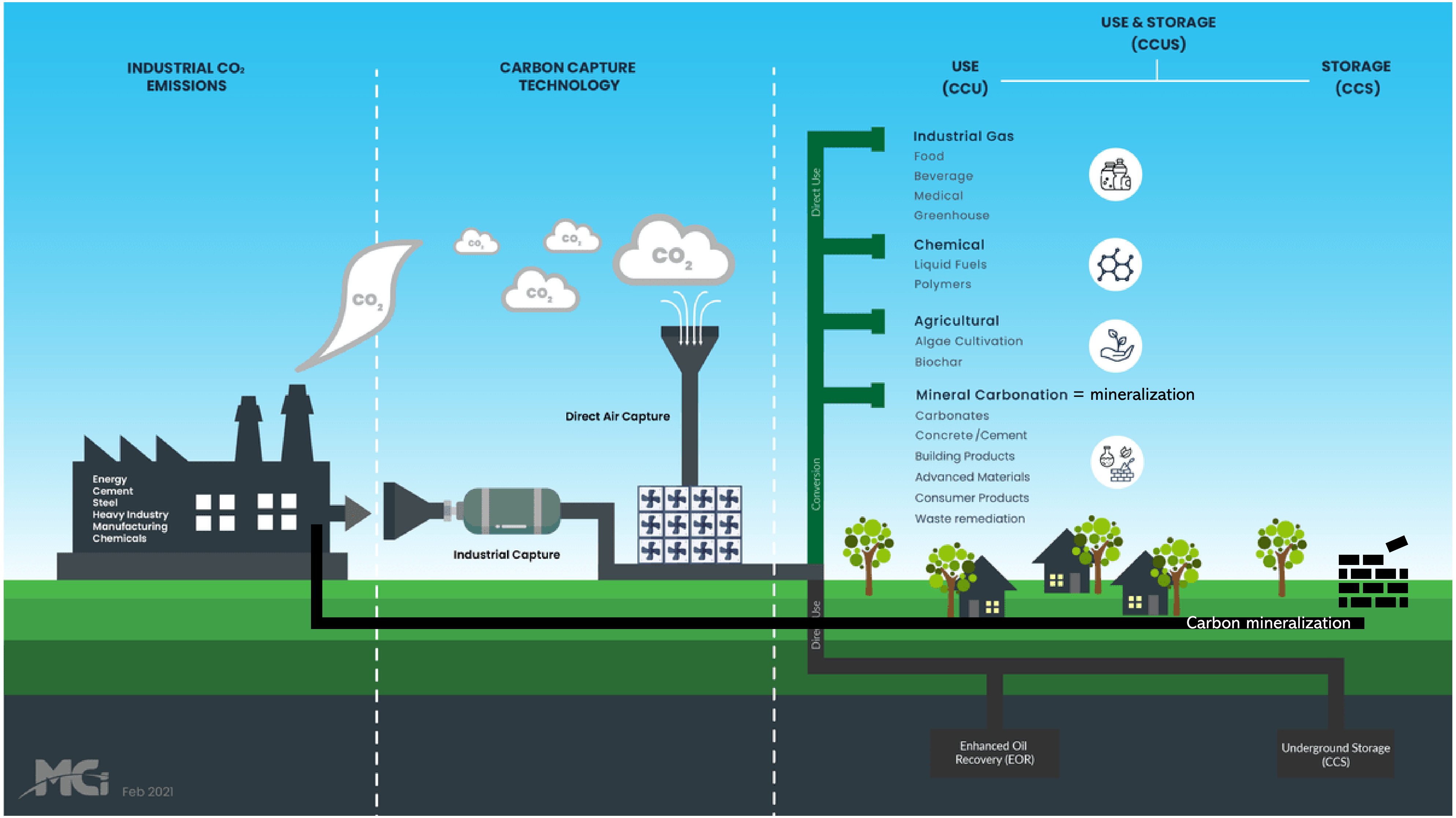
In 1990, Finland was the world's first country to introduce a carbon tax.

Now 20 EU countries have, €1-100€ /ton

Double taxation in Finland

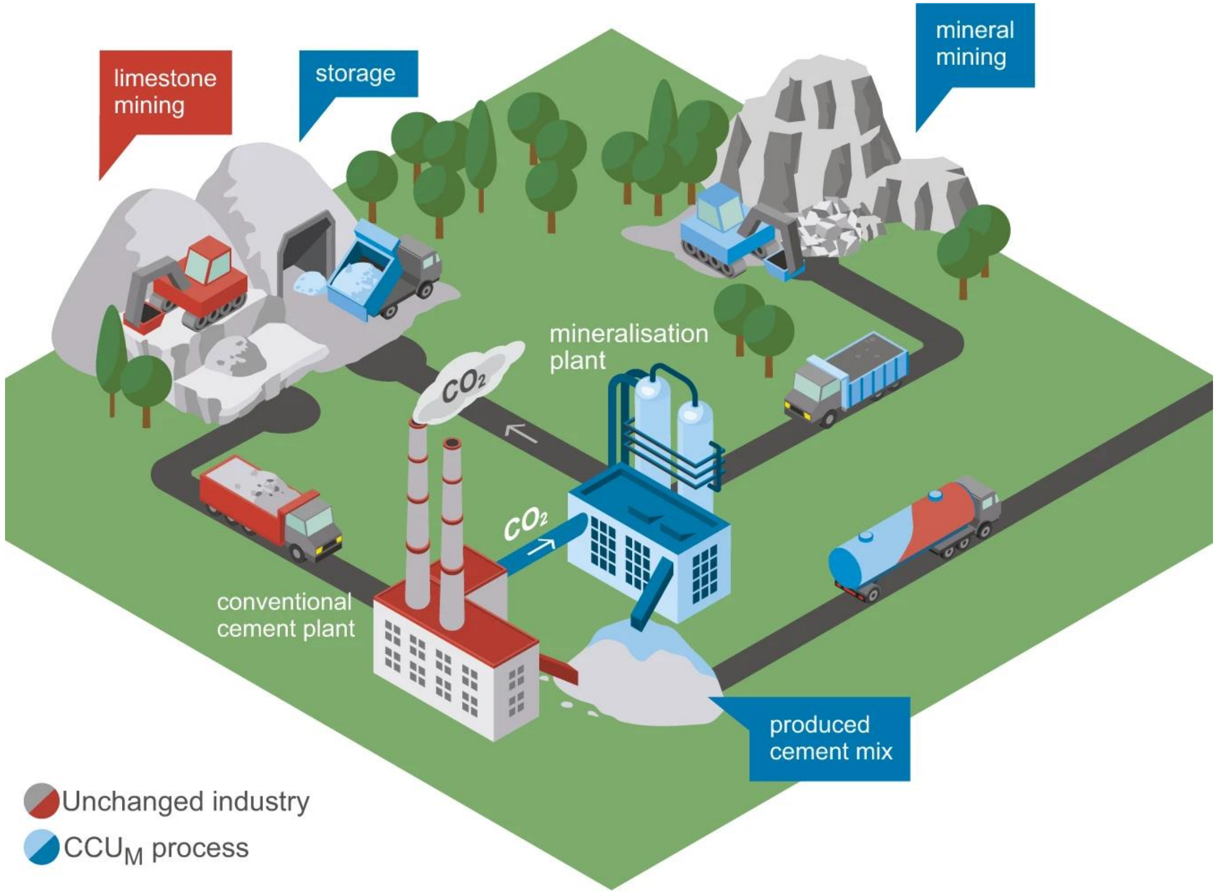
CCS vs. CCU

CCUS – Carbon capture utilization and storage



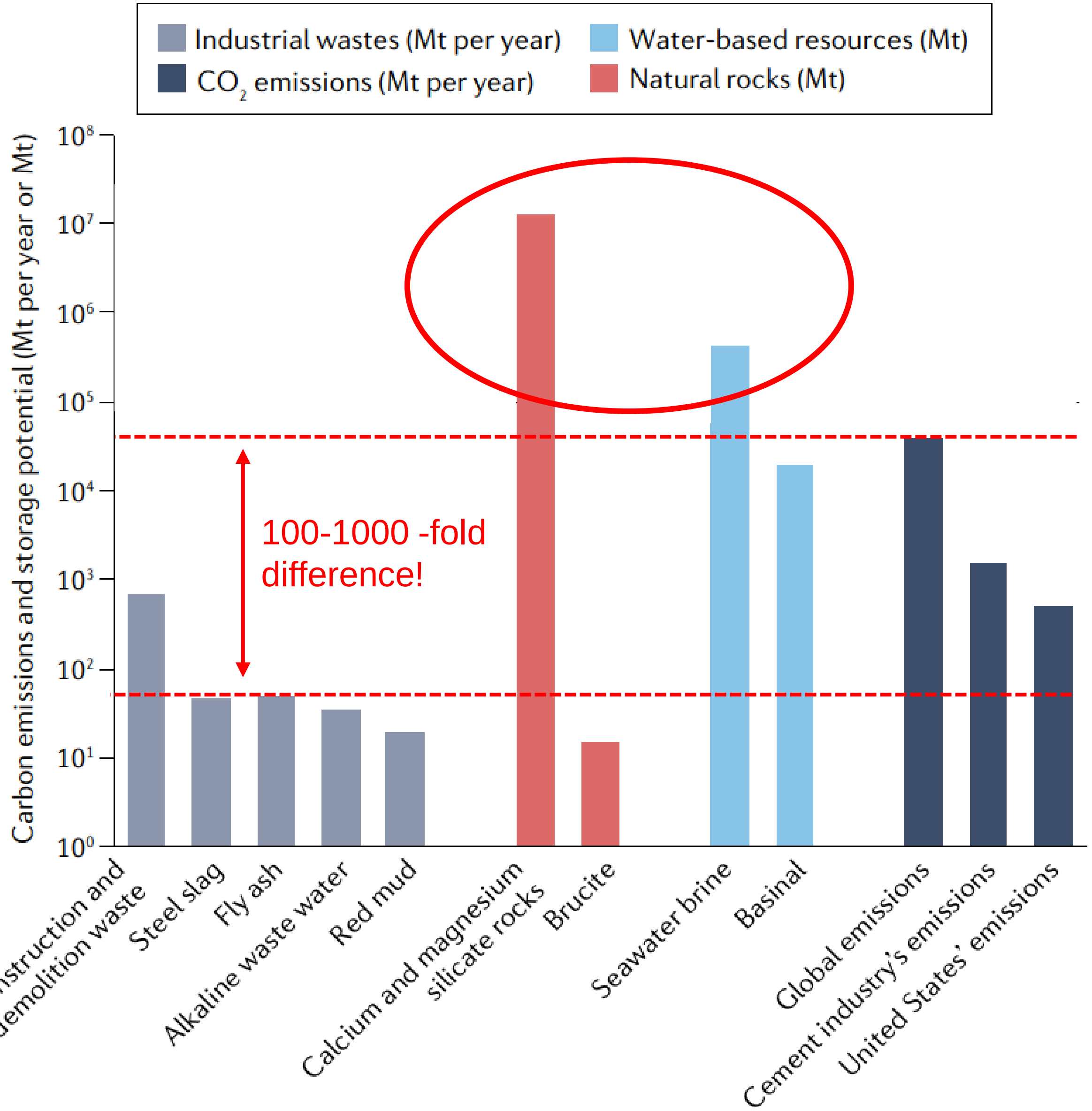
https://www.mineralcarbonation.com/mineral-carbonation

CO_2 capture and utilisation through mineralisation



https://www.nature.com/articles/s43247-022-00390-0

Availability of minerals?



 14.3.2024 https://www.nature.com/articles/s41570-022-00418-1#citeas

Abundance

Abundance	CaO	MgO
Earth’s crust	5%	2.9%
Earth’s upper mantle	3%	38%
Slags, ashes etc.	Up to 50%	Usually <10%
Seawater	0.04%	0.13%

– **CaO**

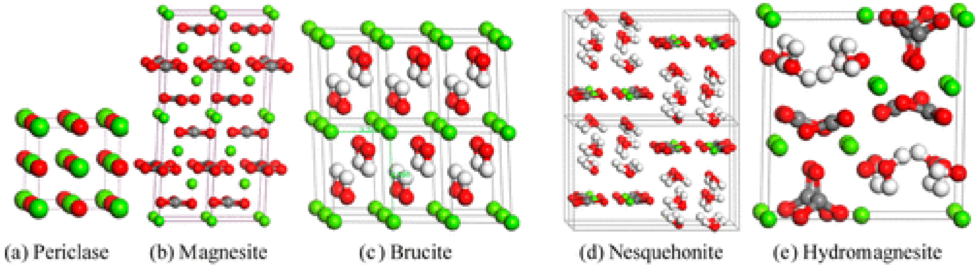
- Available primarily as $CaCO_3$
- Also in industrial side streams

– **MgO**

- Available primarily as Mg-silicates
- Not as widely distributed around the globe as $CaCO_3$
- MgO is currently listed as critical mineral in EU (!)

Available chemistries for MgO-based cements

https://pubs.acs.org/doi/10.1021/jp500271n



- **Different chemistries being considered**
  - **Magnesium silicate hydrate (MSH)**
  - Mg oxychloride (MOC) / -sulfate (MOS)
  - Mg phosphate cement
    - Competes with fertilizer feedstock (P)
  - $MgCO_3$
    - Needs high pressure/temperature
    - Not cohesive (cubic mineral)
  - **HCB –cement (Hydrous carbonate-containing brucite)**
  - **Hydrated magnesium carbonates (HMC's)**
    - Potential for carbon capture
    - Reaction rate and durability need to be improved

Hydrated magnesium carbonates

Nesquehonite	$MgCO_3{\cdot}3H_2O$
Hydromagnesite	$4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O$
Dypingite	$4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$

Magnesium silicate hydrate (MSH) cements

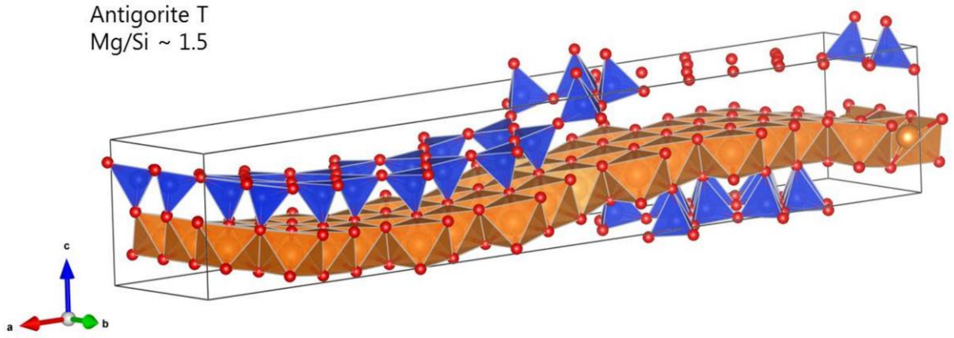


Figure 25: Schematic sketch of the structure of antigorite T (T:O structure phyllosilicate) from (Dódony et al., 2002).

- Forms by mixing MgO and SiO2
- Somewhat similar to CSH
- TRL 8-9 (?)

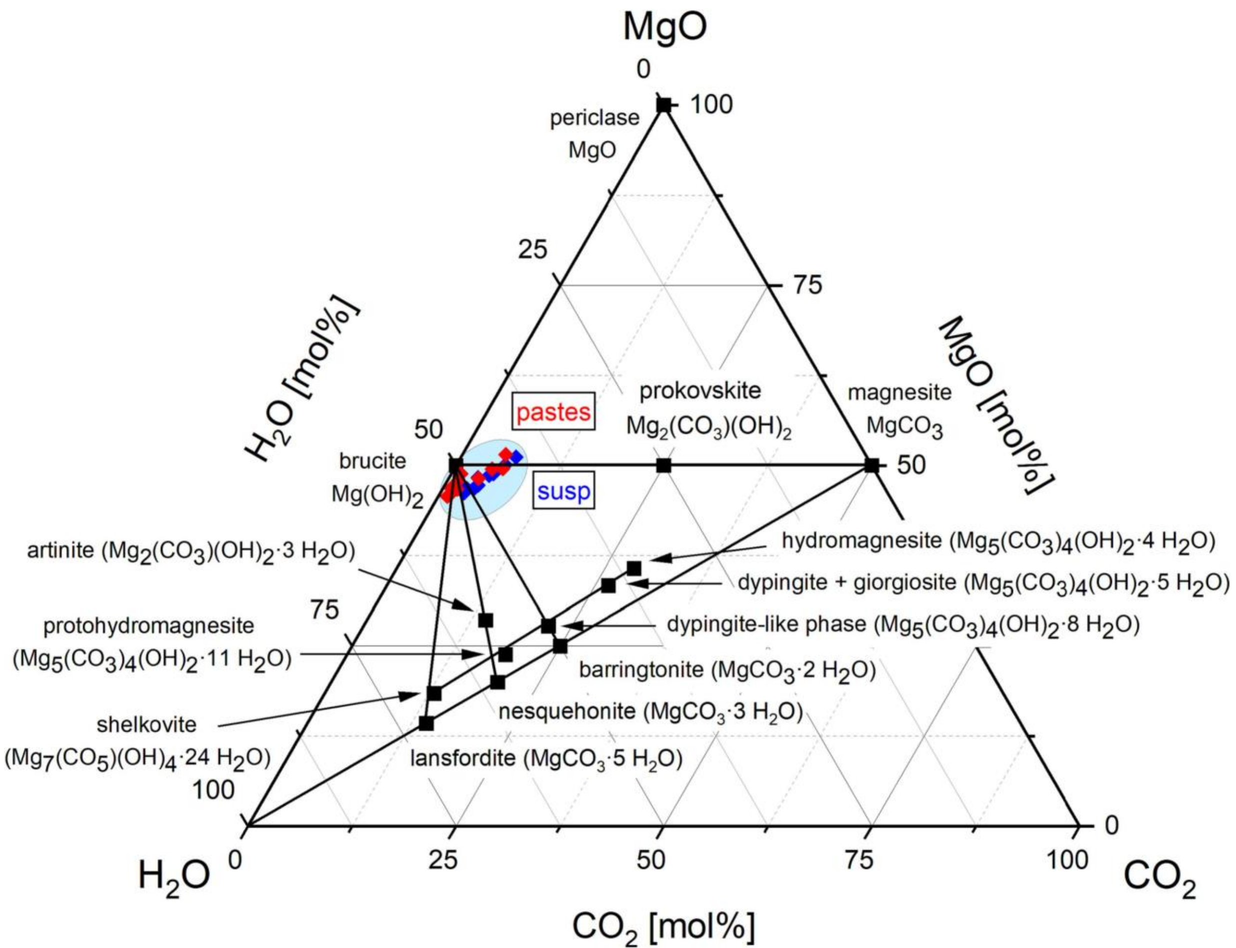
- **Advantages**

- Carbon-neutral feedstocks avalaible
- Low pH compared to OPC
- Highly durable e.g. in marine environments
- Does not carbonate (?)

- **Challenges**

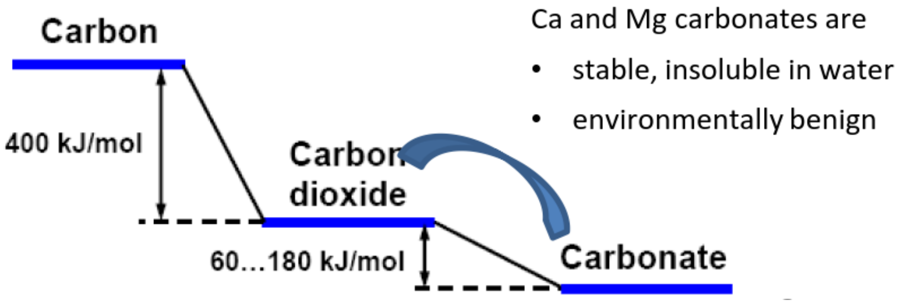
- High water demand
- No admixture development yet
- Compatibility issues with steel reinforcement
- MgO market/recovery technologies undeveloped

Mg-carbonate binders



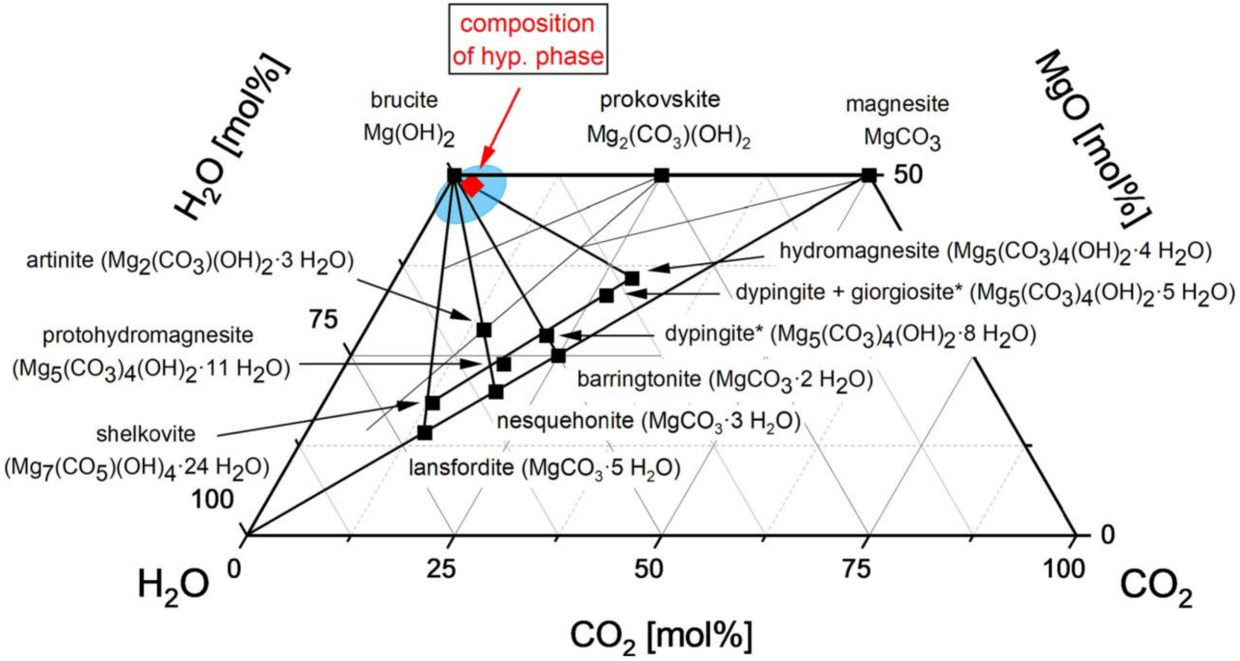
- Only magnesite (MgCO3) thermodynamically stable, but kinetically hindered

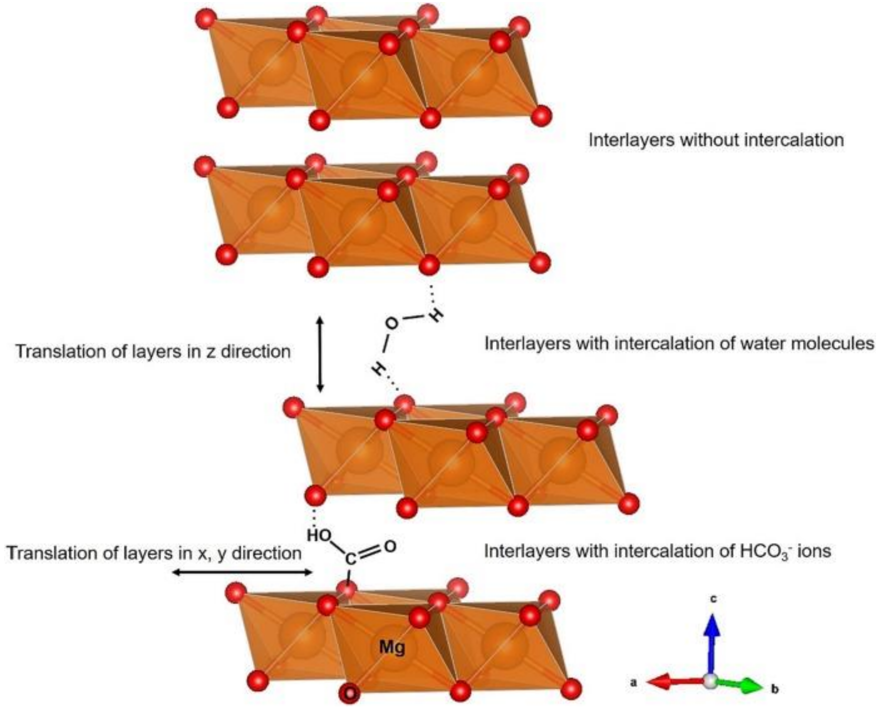
- Brucite (HCB) cement
- Hydrated magnesium carbonate (HMC's) binders



HCB –cement
(Hydrous carbonate-containing brucite)

- Forms with MgO + CO2 (5-10%)
- Distorted brucite [Mg(OH)2] structure
- Promising results from first concrete experiments in EMPA
- TRL 5 (?) – active area of research

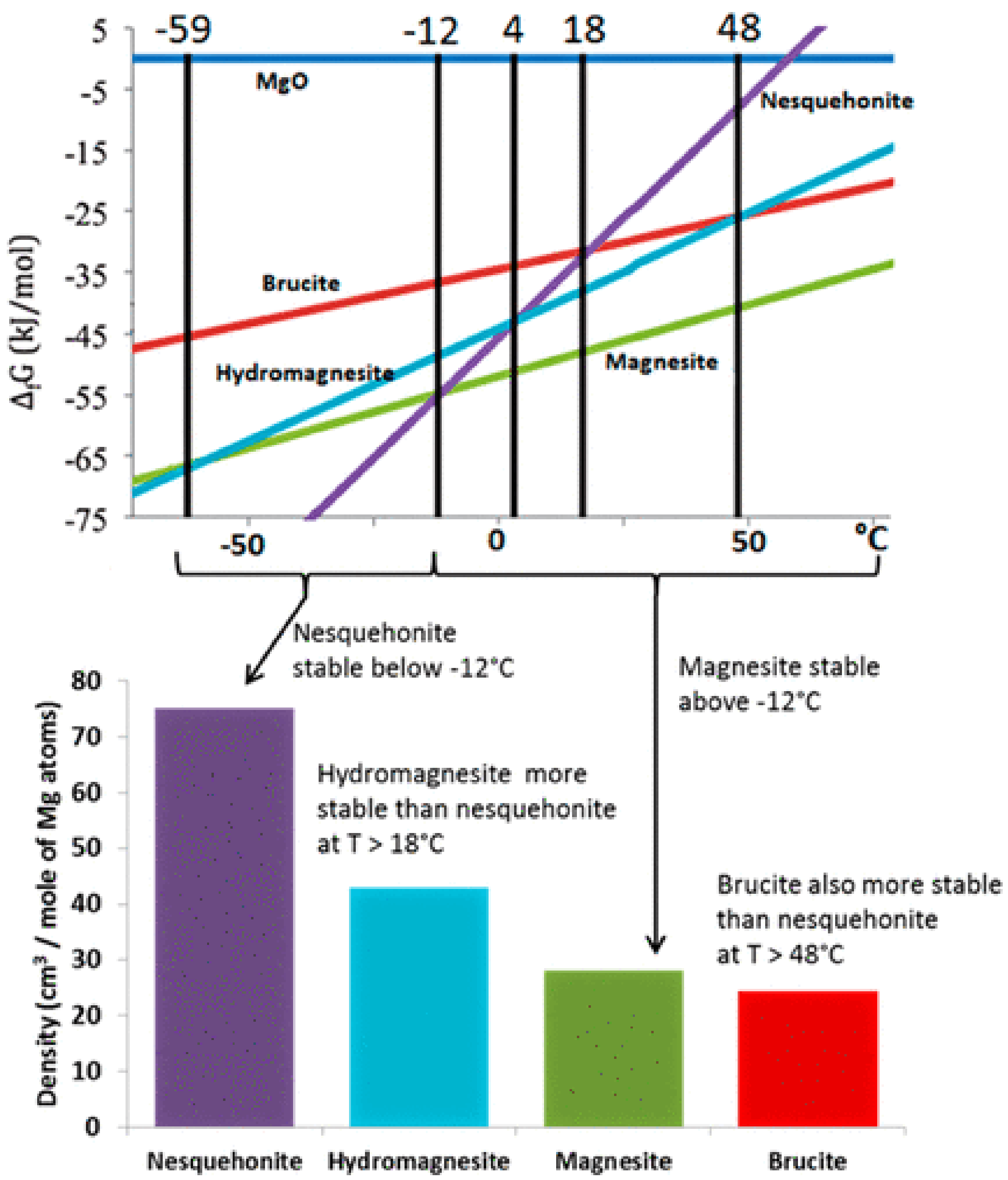




https://doi.org/10.1016/j.cemconres.2023.107304

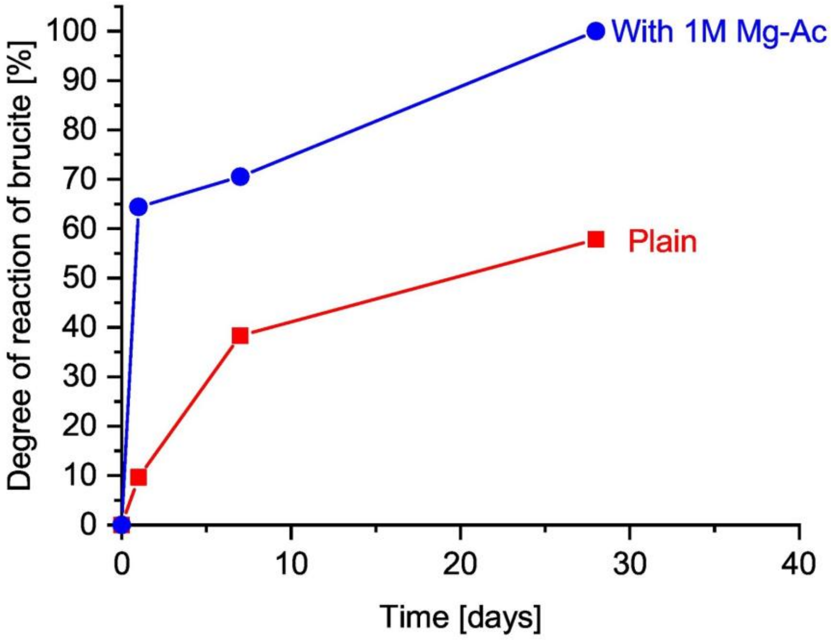
HMC binders

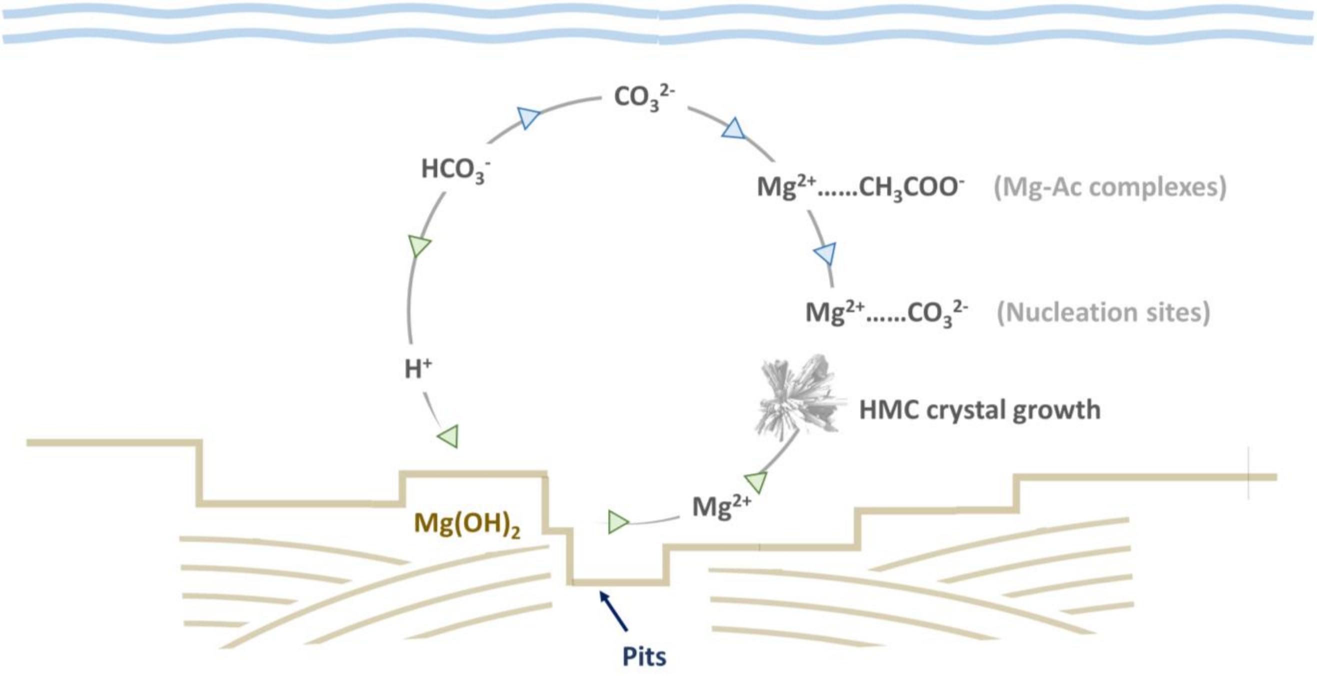
- **Nesquehonite/hydromagnesite most promising**
- **However, not possible to use in conventional concrete due to low water durability**
- **Dehydrated nesquehonite functions much like gypsum**
  - Dry powder that hardens when mixed with water
  - Volumetrically stable
  - Low water durability (better than gypsum)



Magnesia-Based Cements: A Journey of 150 Years, and Cements for the Future?
https://pubs.acs.org/doi/full/10.1021/acs.chemrev.5b00463

Steering the carbonation kinetic and degree of $Mg(OH)_2$ using organic additives



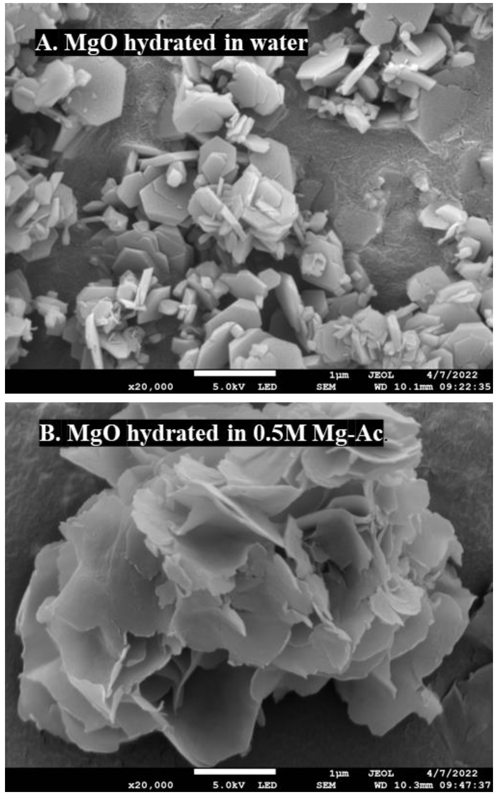


Brucite reached ca. 100% in reaction degree with the presence of Mg-acetate

https://doi.org/10.1016/j.cemconres.2021.106696

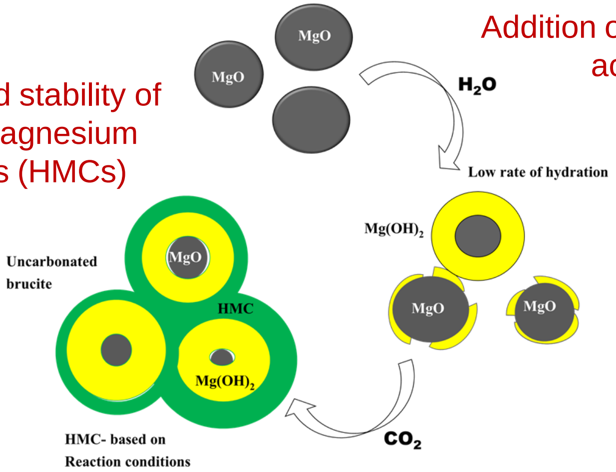
An additive to influence hydration and carbonation of MgO

Hydration



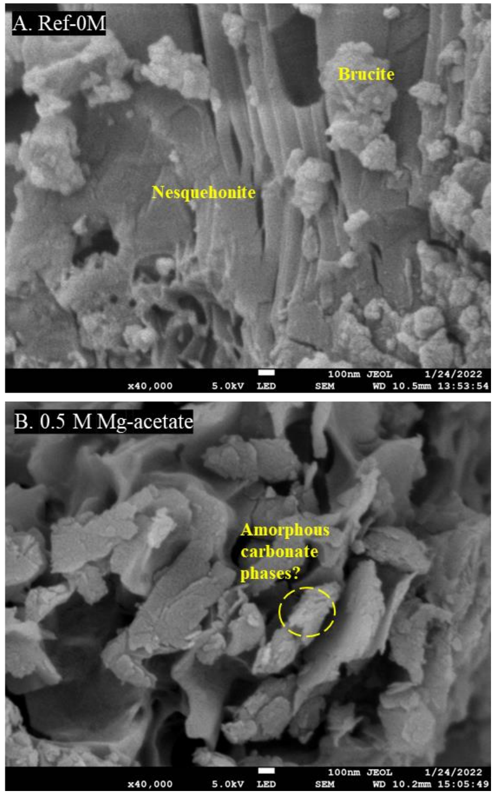
Durability and stability of hydrated magnesium carbonates (HMCs)

Addition of Magnesium acetate



Schematic representation of hydration and carbonation of MgO

Carbonation



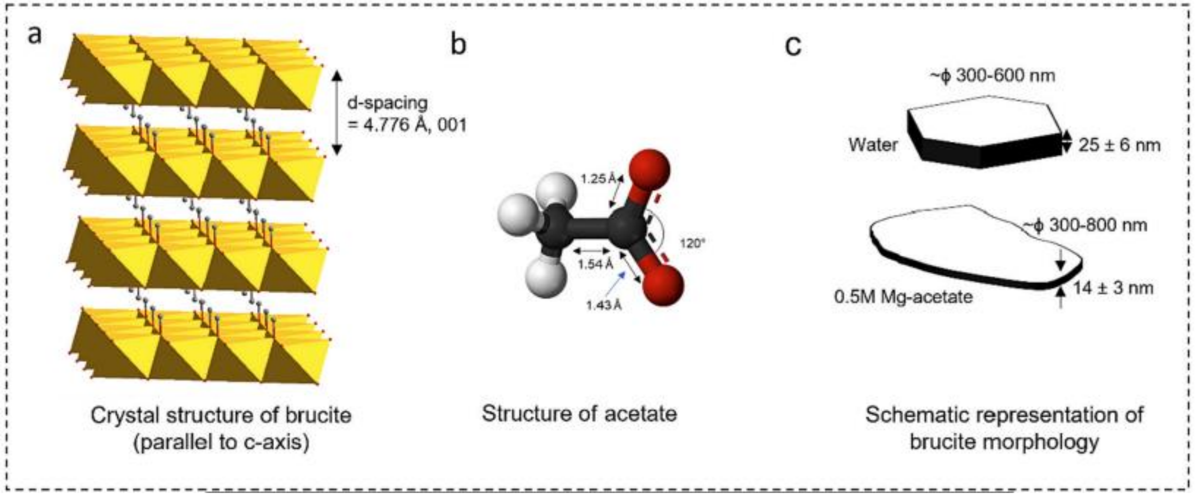
Mg-acetate increases the hydration kinetics and modifies the properties (morphology, crystallite size) of brucite formed

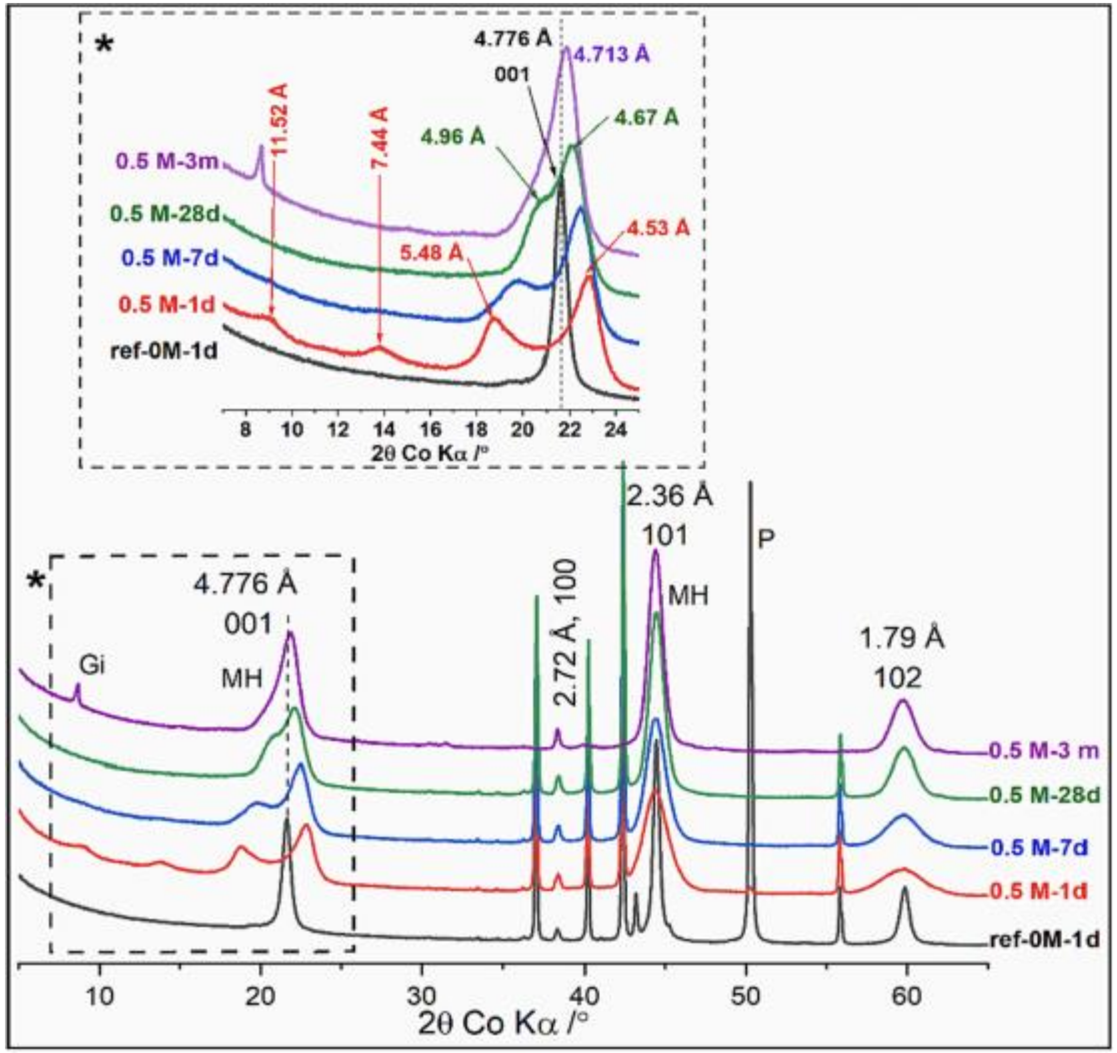
Mg-acetate influences the magnesium carbonate (hydrate) formed

https://doi.org/10.1016/j.cemconres.2023.107357

Research Council of Finland

Latest research





Ilango et al. 24,

Latest research

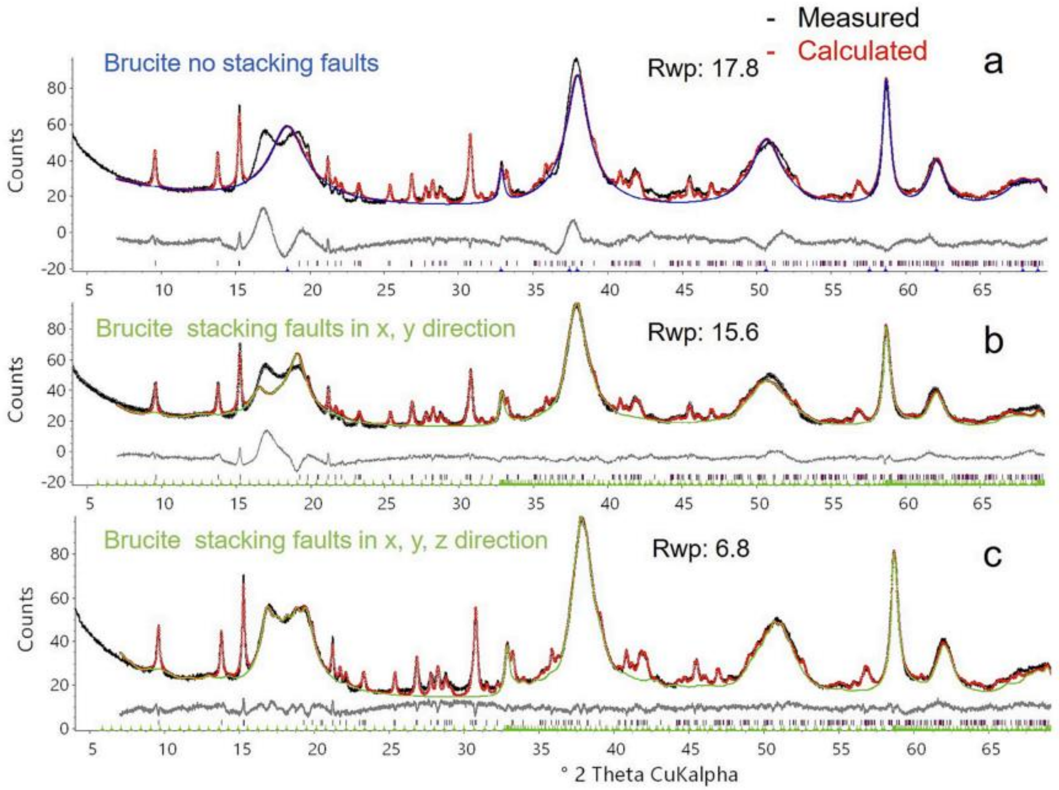


Fig. 6. Rietveld refinements of the XRD pattern of sample MgO/hydromagnesite 70/30 cured at 20 °C a) without stacking faults, b) considering stacking faults in x and y direction, and c) considering stacking faults in x, y and z direction. Rwp = weighted profile R-factor. All reflections, which are not assigned to the HCB phase (hydrous carbonate-containing brucite with stacking faults), can be assigned to the phase hydromagnesite.

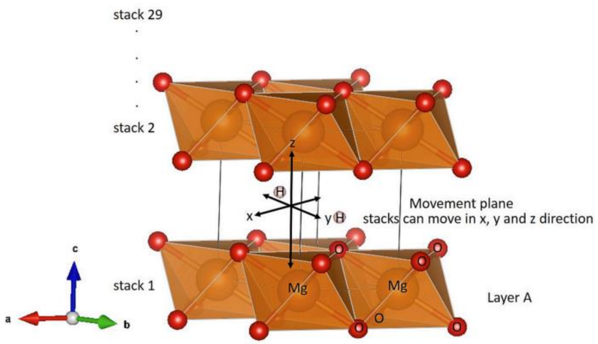


Fig. 2. Visualization of stacking layers in the brucite structure as well as movement plane and moving directions for stacking faults between repeating layer A (Visualization done using VESTA 3 [20]).

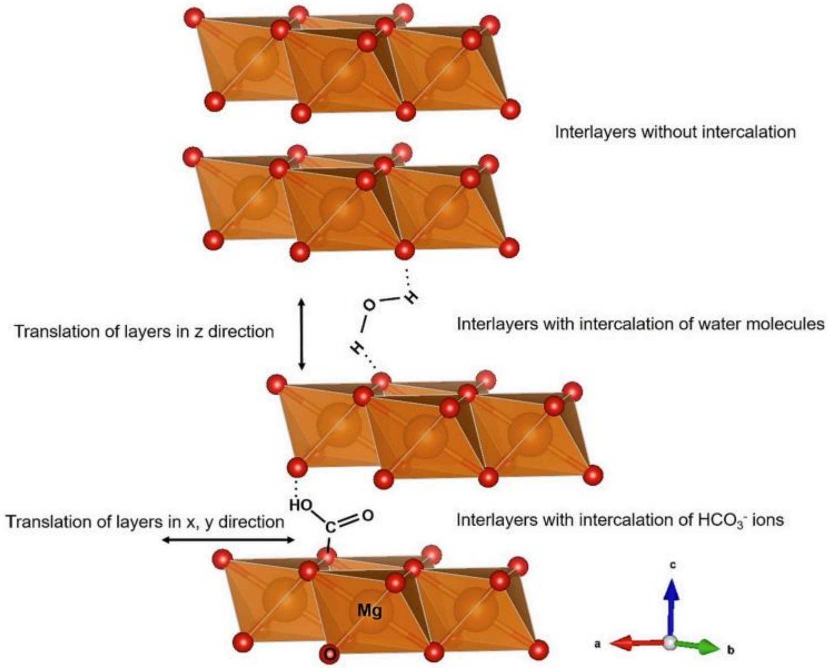


Fig. 8. Visualization of the possible brucite-like structure using VESTA 3 [20]. The possible intercalation options are shown in the figure. The sequence of the interlayers is shown as an example. The sequence in the real structure is probably an arbitrary combination of the possible interlayers.

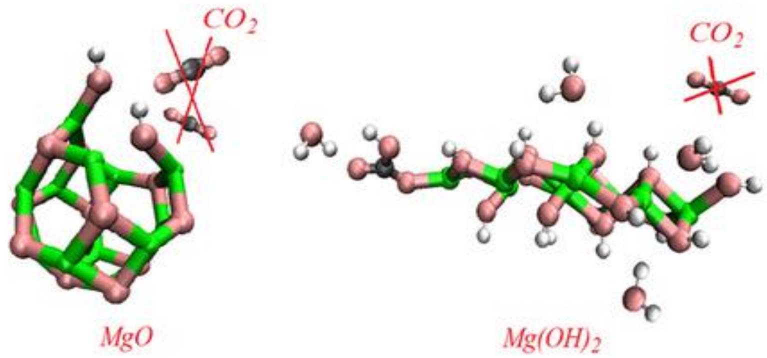
Ongoing – DFT modeling of the modified mineral structure

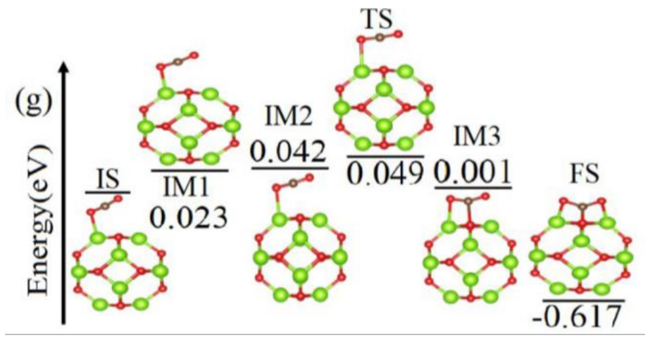
THE JOURNAL OF PHYSICAL CHEMISTRY C
A JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
pubs.acs.org/JPCC Article

Exploring Mechanisms of Hydration and Carbonation of MgO and $Mg(OH)_2$ in Reactive Magnesium Oxide-Based Cements

Mina Ghane Gardeh, Andrey A. Kistanov,* Hoang Nguyen, Hegoi Manzano, Wei Cao, and Paivo Kinnunen

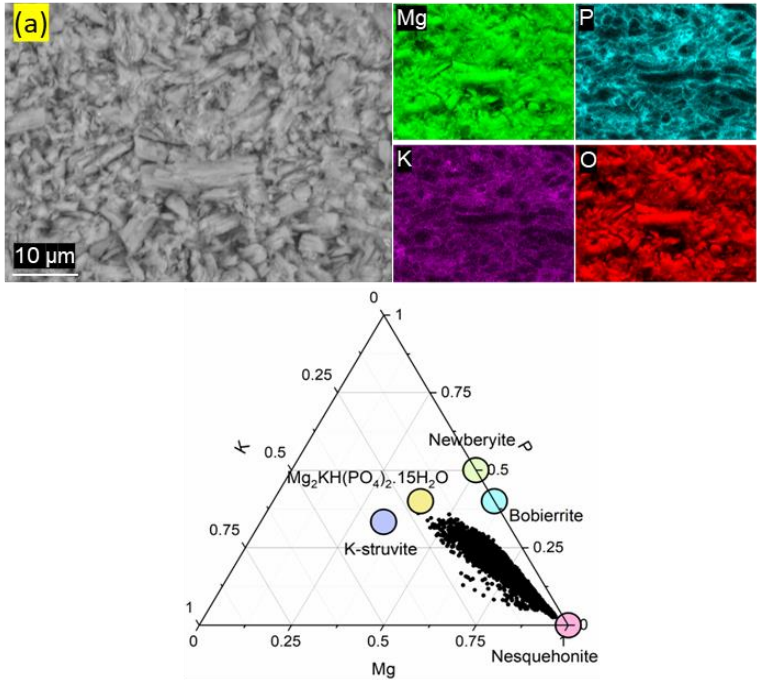
Cite This: J. Phys. Chem. C 2022, 126, 6196–6206 Read Online





Energy barrier for the carbonation process

Stabilize Mg-carbonates and produce durable cements



(b)

- Academy research fellow Hoang Nguyen
- Project DCM

https://www.oulu.fi/en/projects/durable-mg-based-cement-toward-carbon-negative-concrete-dcm

E.g., phosphate can protect nesquehonite from its conversion and CO2 loss

Research Council of Finland

Research directions

- Novel MgO-based cements
- Applications of Mg-carbonates in Portland cements
- Novel synthesis of MgCO3 with low temperature and pressure
- Synthetic marble for carbon storage
  - CarbStone project: https://www.oulu.fi/en/projects/carbstone-synthetic-marble-for-carbon-storage-and-utilization
- Glass-based cements and SCMs
  - https://doi.org/10.1016/j.cemconres.2022.106859
  - https://doi.org/10.1016/j.jnoncrysol.2023.122204
  - https://doi.org/10.3389/fchem.2021.715052

RILEM Technical Committee of >60 researchers on MgO-based cement

MBC : Magnesia-based binders in concrete

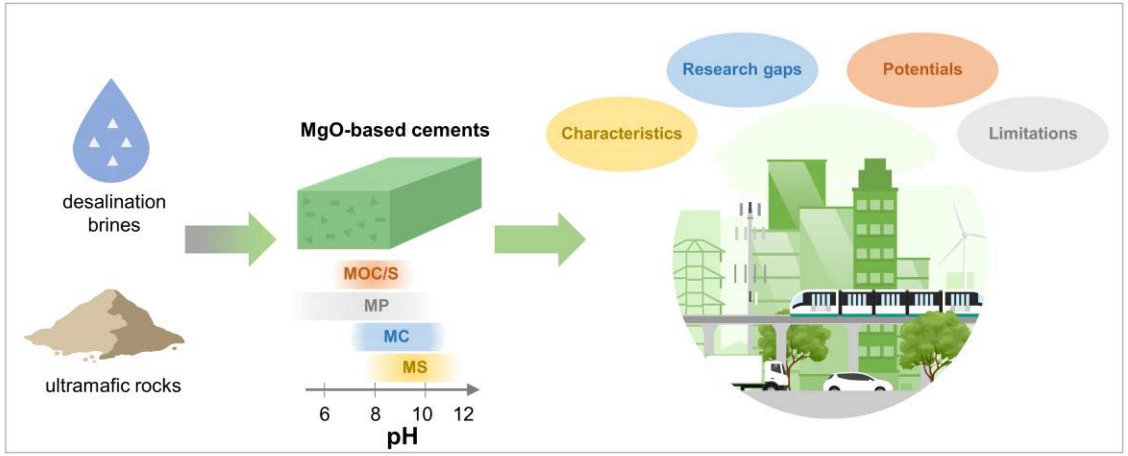
Presentation | Events | Members | Documents

Technical Committee MBC

General Information

Chair: Ass. Prof. Paivo KINNUNEN
Deputy Chair: Dr Ellina BERNARD
Activity starting in: 2022
Cluster A

https://doi.org/10.21809/rilemtechlett.2023.177



Ongoing collaborations on Mg-based cements

NTNU Norwegian University of Science and Technology

Tampere University Tampere University of Applied Sciences

Åbo Akademi

SAINT-GOBAIN

FINNSEMENTTI A CRH COMPANY

CRH

CHALMERS

DTU

MANCHESTER 1824 The University of Manchester

University of Sheffield

Brineworks

Universität Konstanz

ETH zürich

Empa Materials Science and Technology

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ZAG

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NordCem: Community of cement researchers in the Nordics

Current members:

University of Oulu,

NTNU,

Chalmers University,

Aarhus University,

DTU,

RISE

NORDCEM

Online meeting twice a year (next May 3rd)

We welcome researchers from Universities and research institutes

For more information, please contact Dr. Hoang Nguyen (hoang.nguyen@oulu.fi)

Thank you