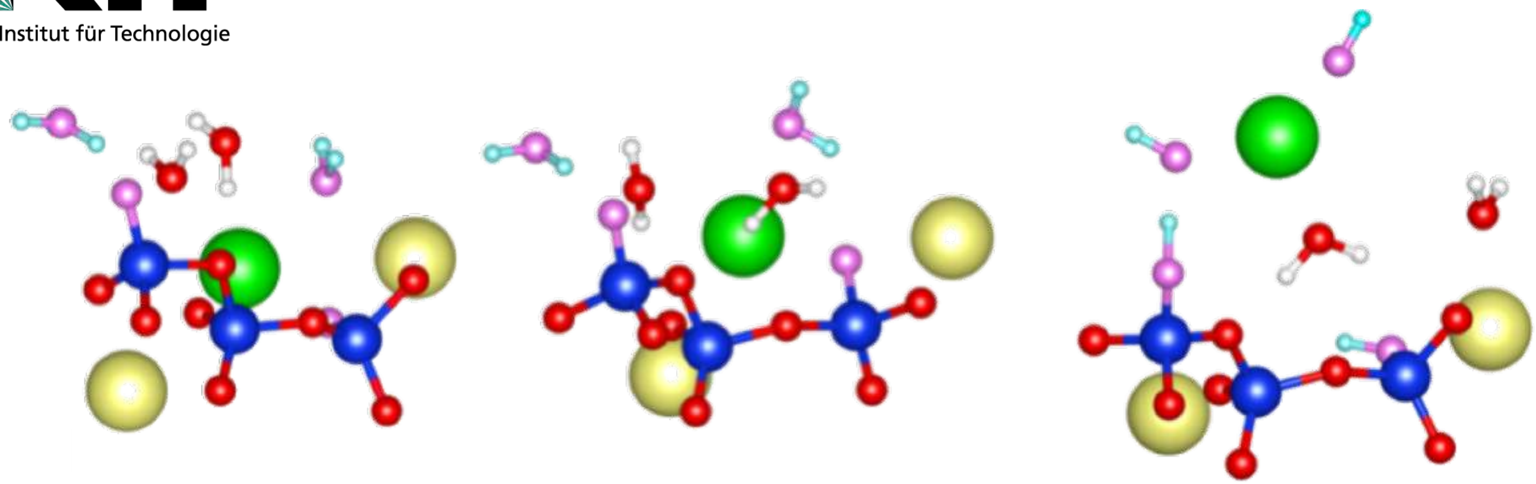


Dr. Peter Thissen

Molekulare Mechanismen der mechanischen und chemischen Korrosion auf zementgebundenen Werkstoffen

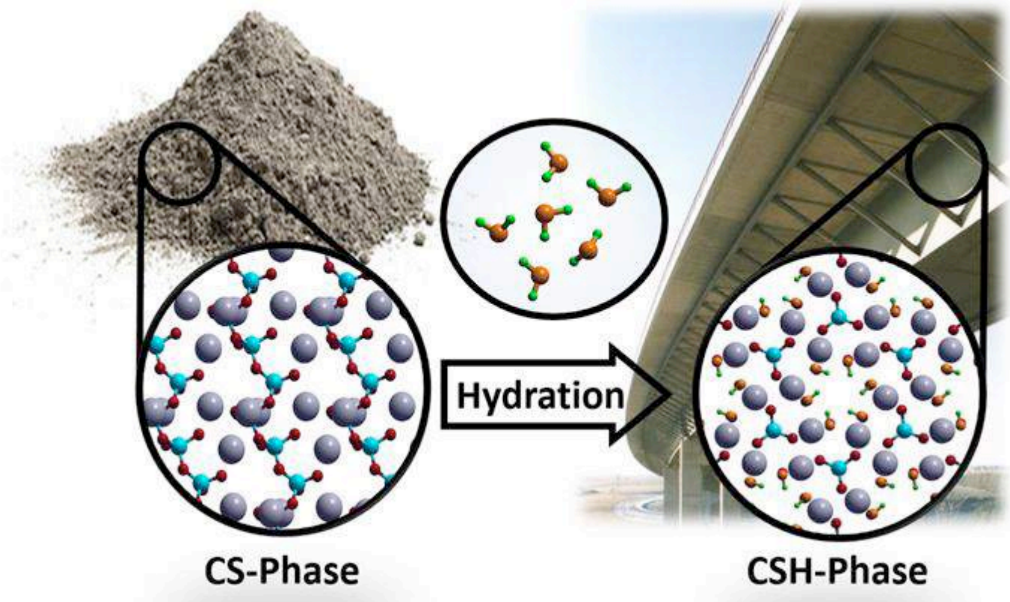
STRUCTURE

PART I: Chemical corrosion based on H_2O

PART II: Chemical corrosion based on $H_2O + CO_2$

PART III: Possible solutions for the future

PART I: Chemical corrosion based on H_2O



1. Concrete is the most important construction material used by mankind.

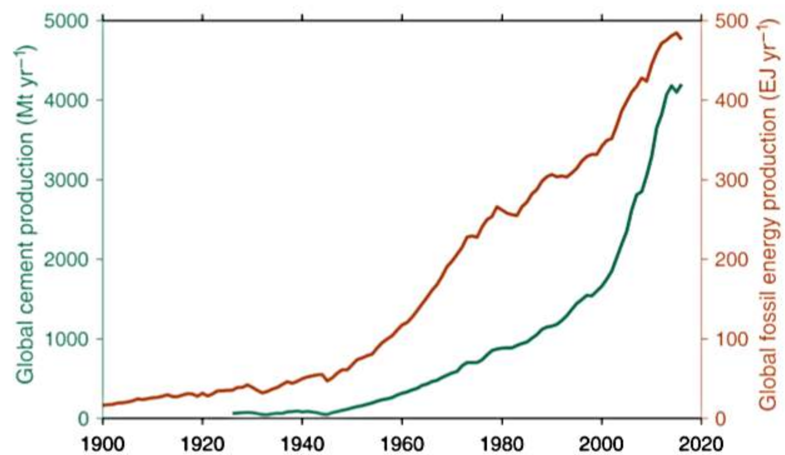


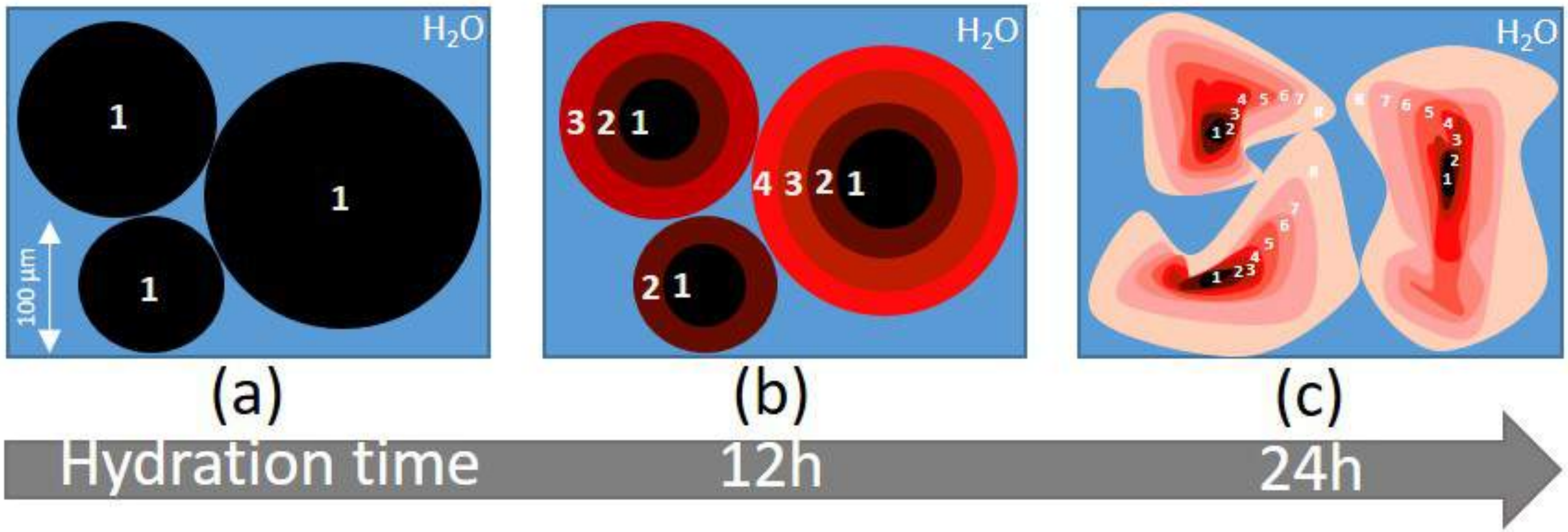
Figure 1. Global cement and fossil energy production to 2016 (USGS, 2014; Mohr et al., 2015).

2. Unfortunately, nearly 10% of the yearly CO_2 emissions are due to cement production.

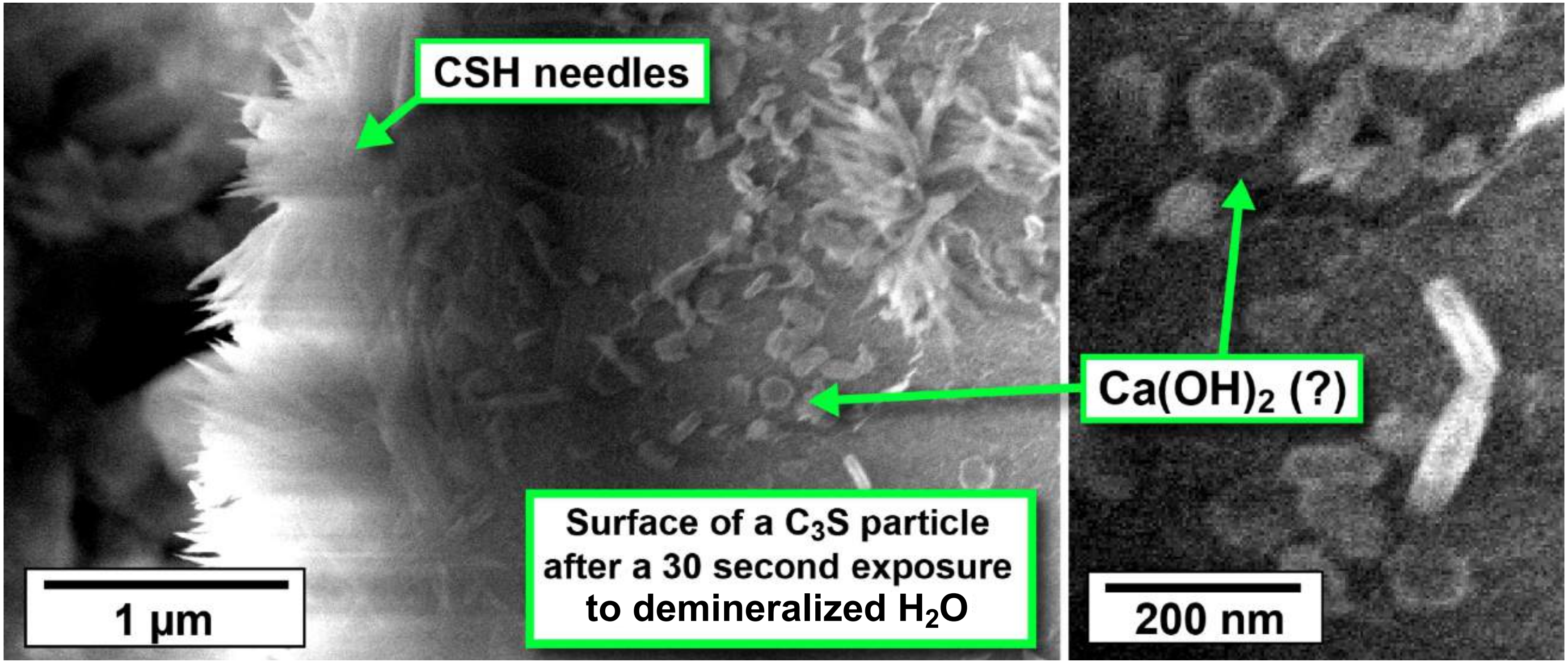
A simple model of hydration

1. Hydration of cement with water is defined by a series of chemical reactions which form the binding material.

2. The time of hydration is a major criterion to produce additional phases over time.



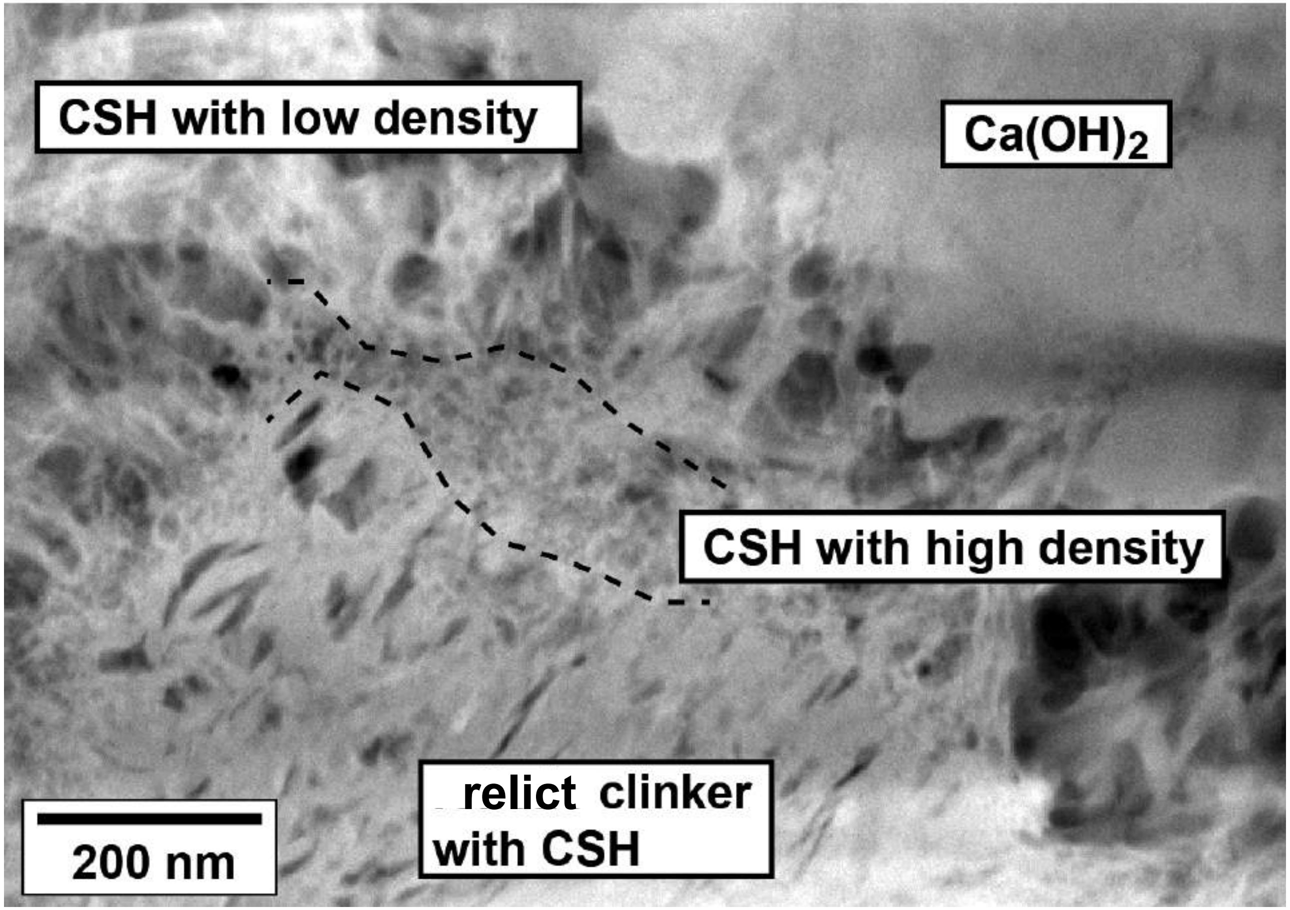
1. Hydration of cement with water is defined by a series of chemical reactions which form the binding material.



2. The time of hydration is a major criterion to produce additional phases over time.

Structure determines the properties

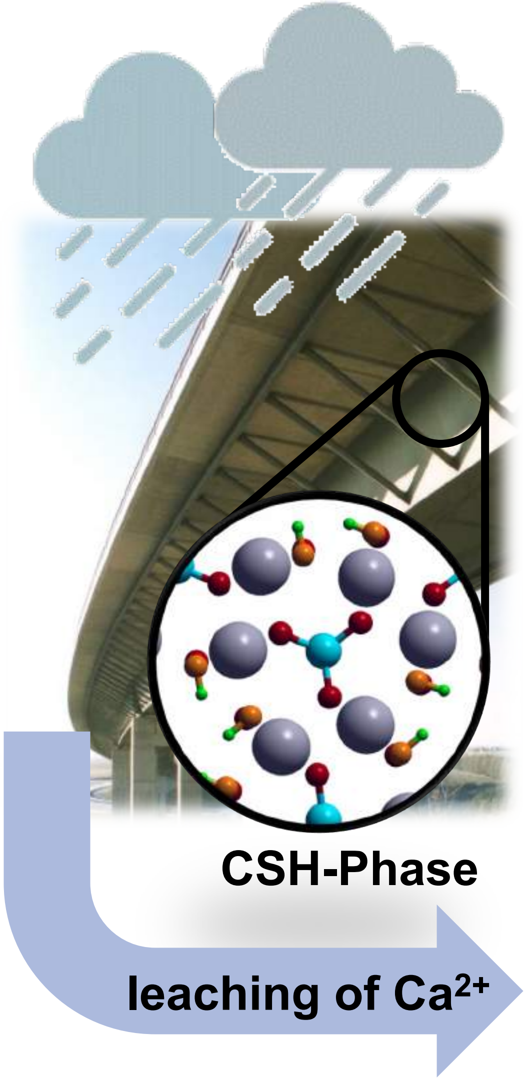
Reaction products of the hydration reaction of C_3S differing in structure and as well in composition



1. Concrete incorporates a complex structure of composite materials

2. The structure is highly porous, varying from nm to cm

Fundamental understanding of processes is needed to increase resilience of cement based materials



1. Metal-proton transfer is a chemical reaction of key importance, since on the one hand it triggers the hydration, but on the other hand also governs the corrosion of the material.

2. Detailed, spectroscopic investigations of model reactions on well-defined mineral substrates under UHV-conditions are largely lacking, thus prohibiting a validation of theoretical methods.

H_2O induces leaching of Ca at the CSH interface

- **Nanoscale $Ca(OH)_2$** is coexisting with the CSH gel in "interlayers"

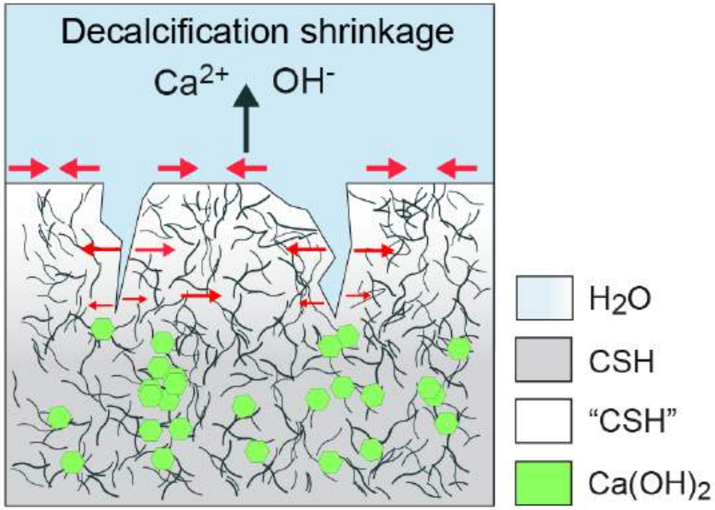
  Allen et al. *Nat. Mater. 2007, 6 (4), 311–316*

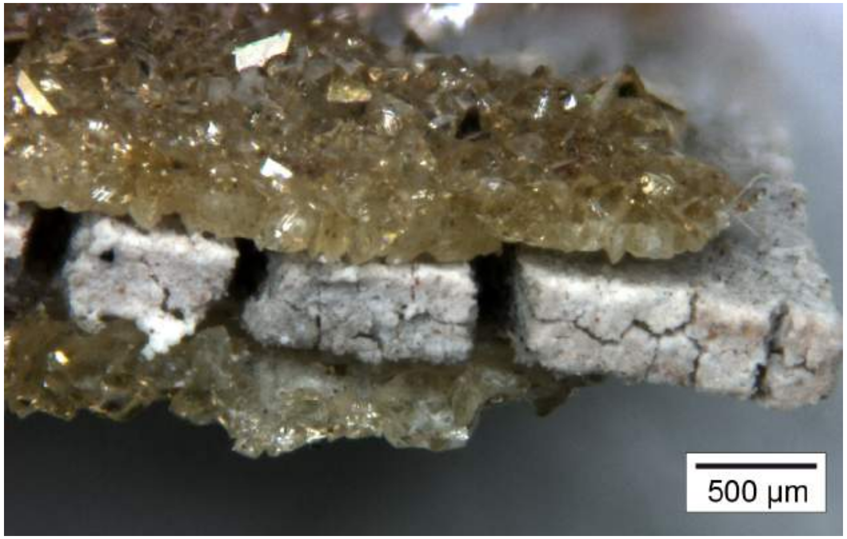
- The **leaching** of "nanoscale $Ca(OH)_2$" creates mechanical stress in the structure
- The resulting **decalcification shrinkage** is followed by crack formation

  Chen et al. *Cem. Concr. Res. 2006, 36 (5), 801–809*

  ➔ Detachment of crystalline covering layers
  ➔ Fracture system promotes further degradation

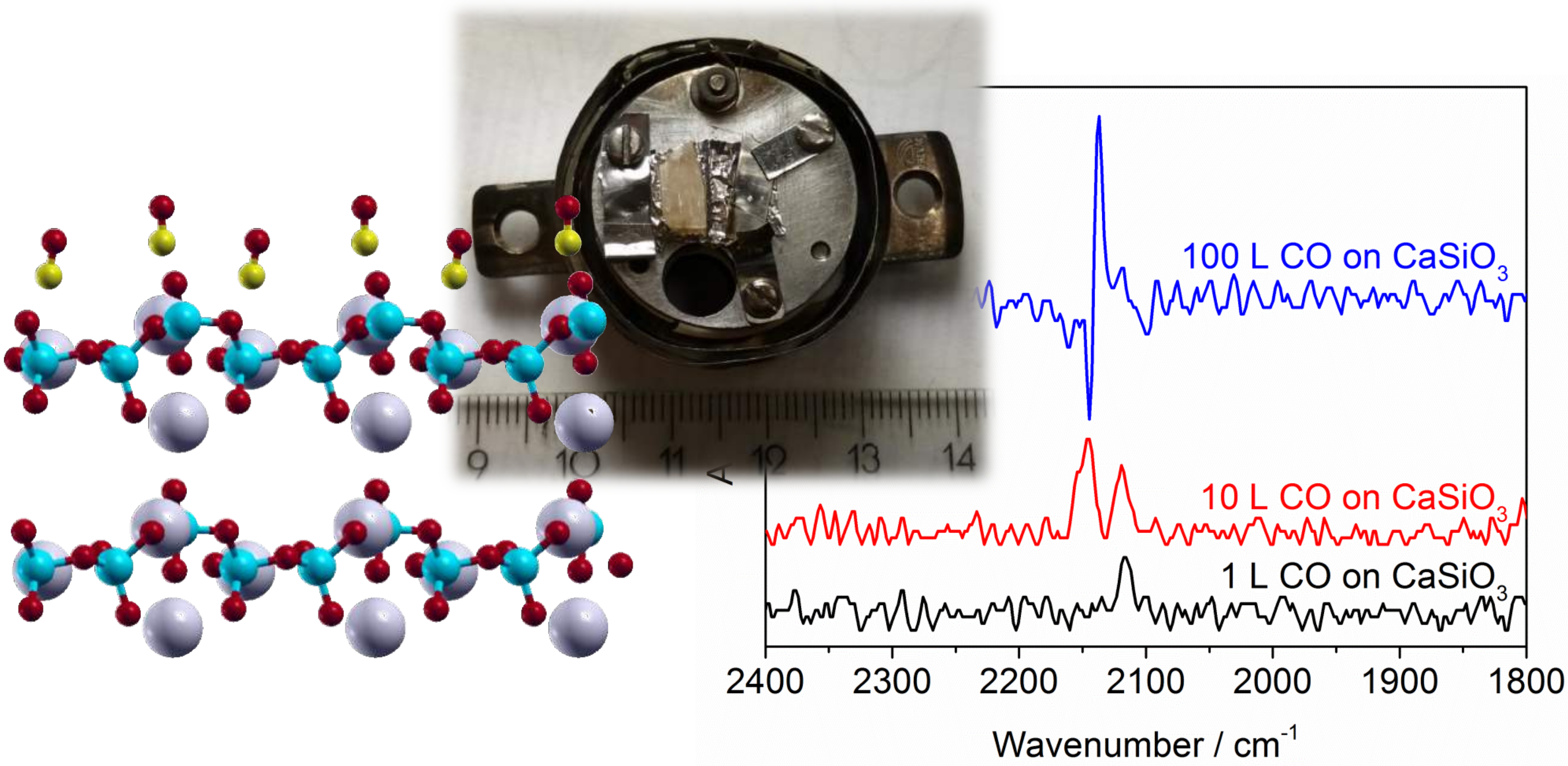
  Schwotzer et al. *Cem. Concr. Compos. 2016, 74, 236–243*



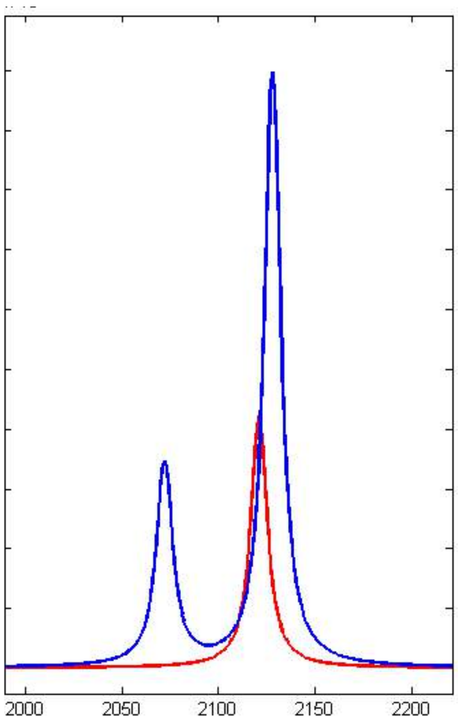


Cement paste with features of **decalcification shrinkage (e.g.** resulting from Ca-tartrate crystallization)

How to bridge the gap between atomistic theory and detailed spectroscopy?



Model surface Wollastonite ($CaSiO_3$)



Wavenumber (cm^{-1})

- Low coverage
- High coverage

Davydov-splitting

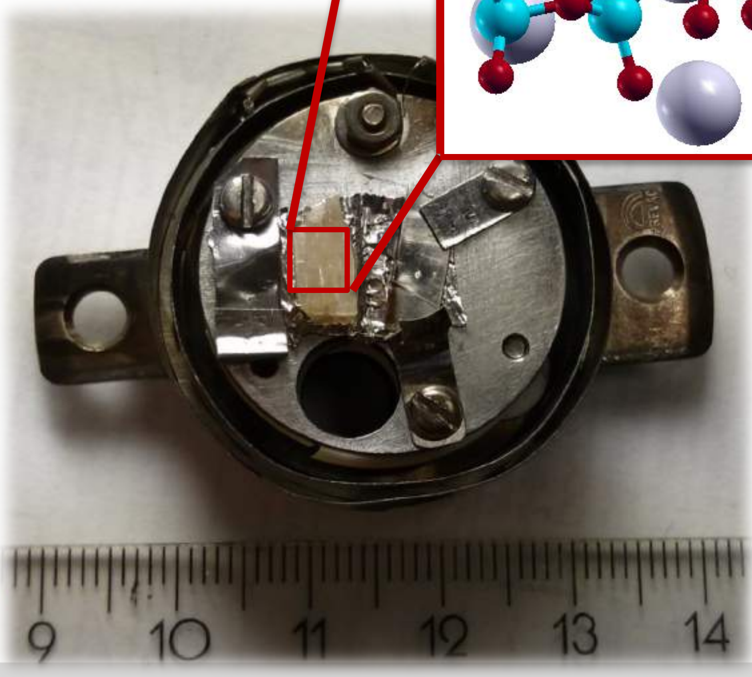
C-O distance:
1.14 Å

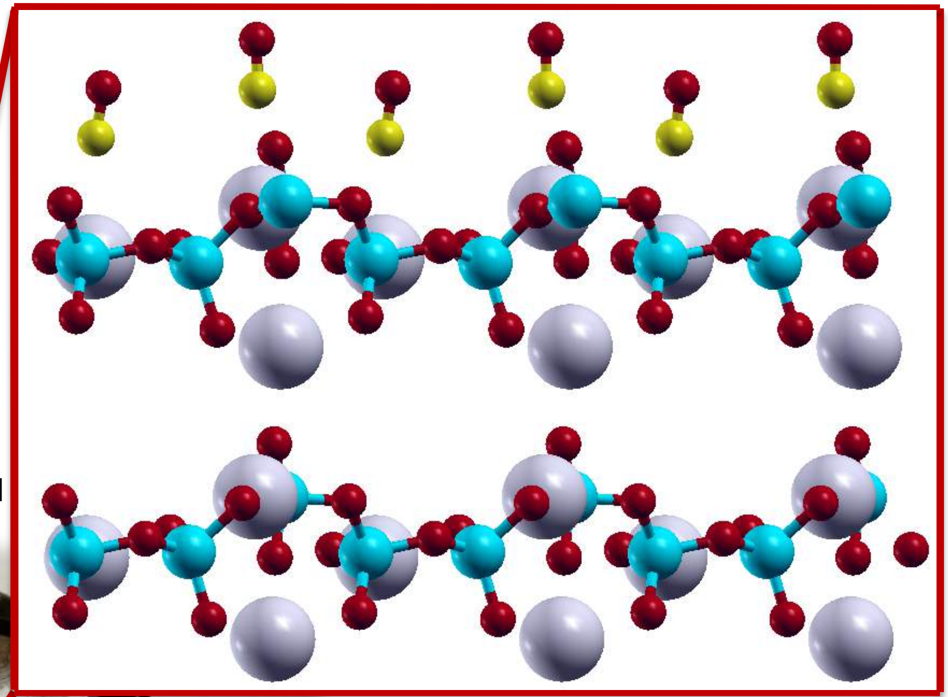
C-Ca distance:
2.71 Å

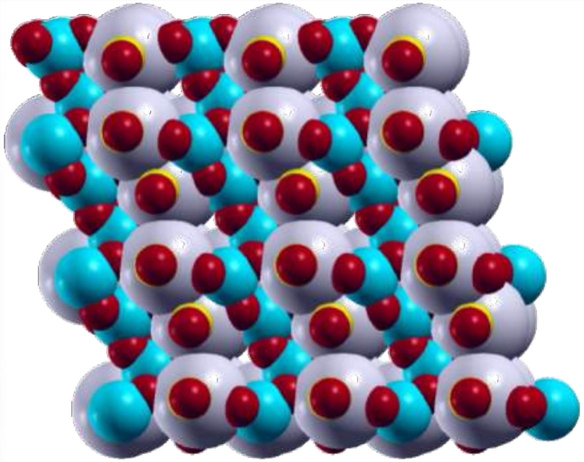
Ca-C-O angle:
165 degrees

E_{Ads} ~ 0.3 eV

$\nu(C\equiv O)$ ~ 2121 cm^{-1}

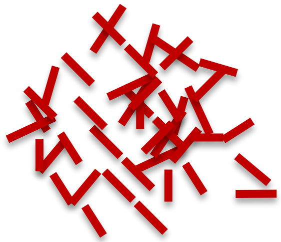




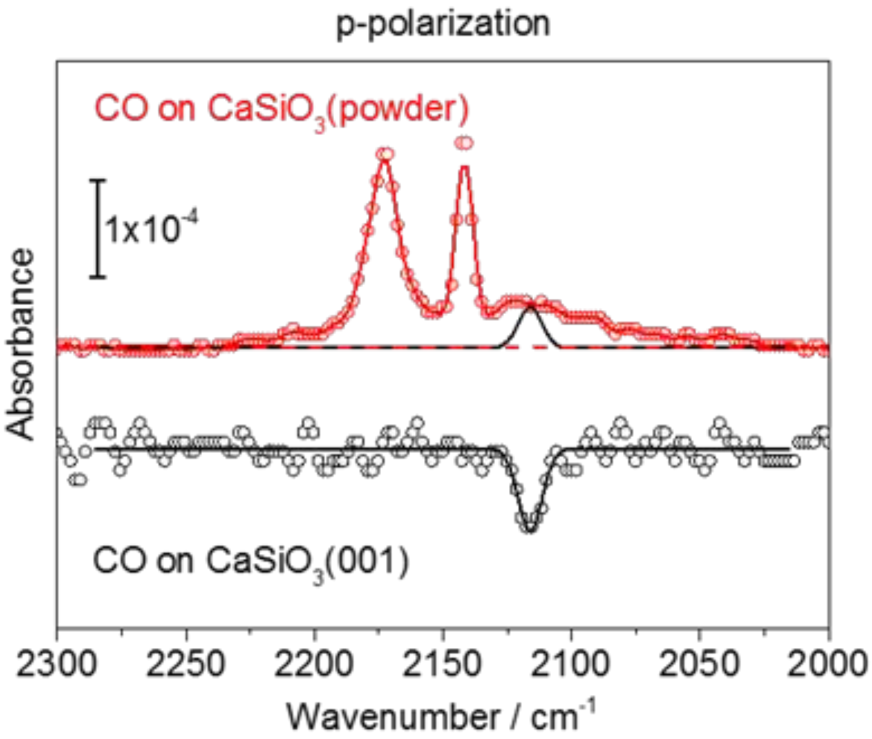


Infrared reflection absorption spectra (IRRAS)

(1) Wollastonite powder (red line)

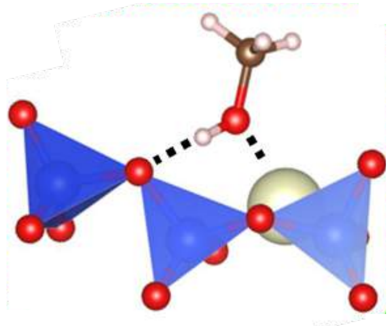


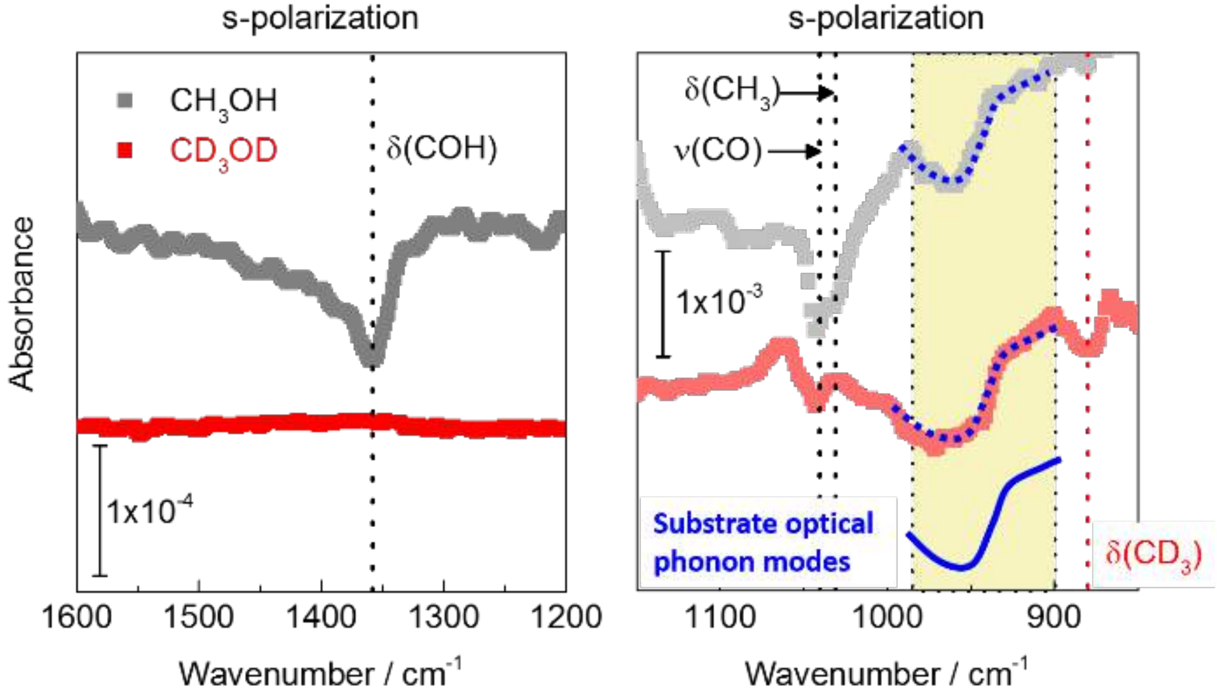
(2) Wollastonite(001) surface (black line)



Samples were exposed to 1 Langmuir carbon monoxide at 80 K. Spectra are referenced to clean Wollastonite.

Methanol as sensor molecule on the wollastonite surface



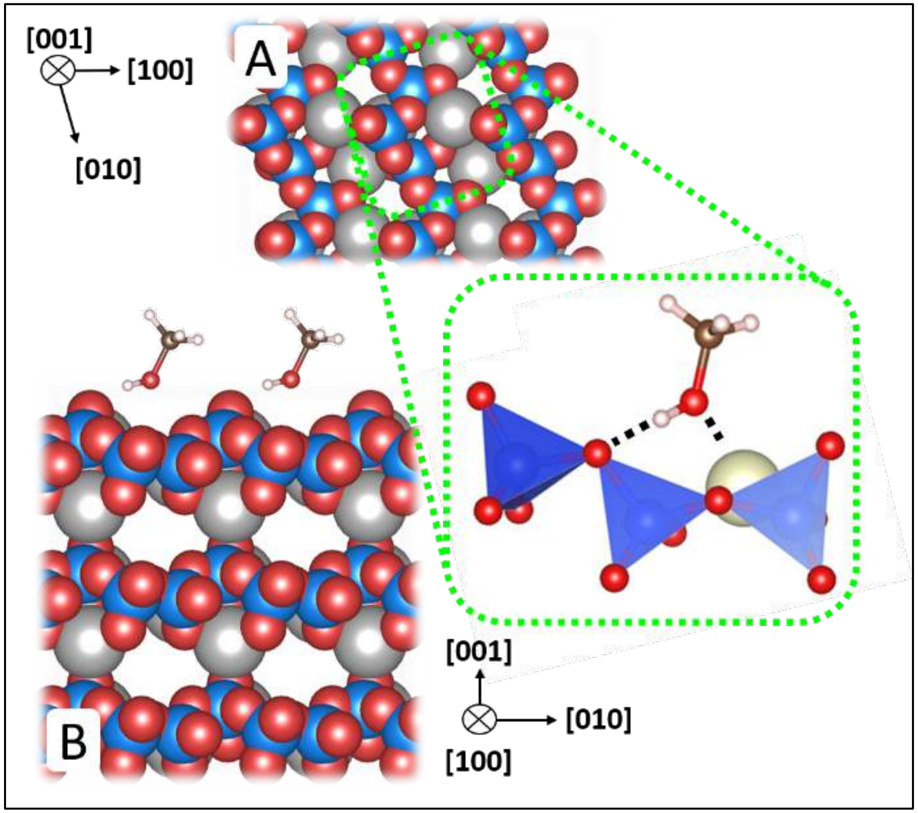


(1) 1 mL CH_3OH on Wollastonite adsorbed at 100 K (black line)

(2) 1 mL CD_3OD on Wollastonite adsorbed at 100 K (red line)

In frequency regimes where substrate phonons are absent adsorbate vibrations can be identified.
Isotopologues are required to distinguish adsorbate vibrations from features resulting from adsorption-induced shifts of substrate phonons.

Molecular adsorption of methanol on the Wollastonite (001) surface.



The splitting of the CH_3 umbrella mode amounts to 21 cm^{-1} for the (001) substrate.

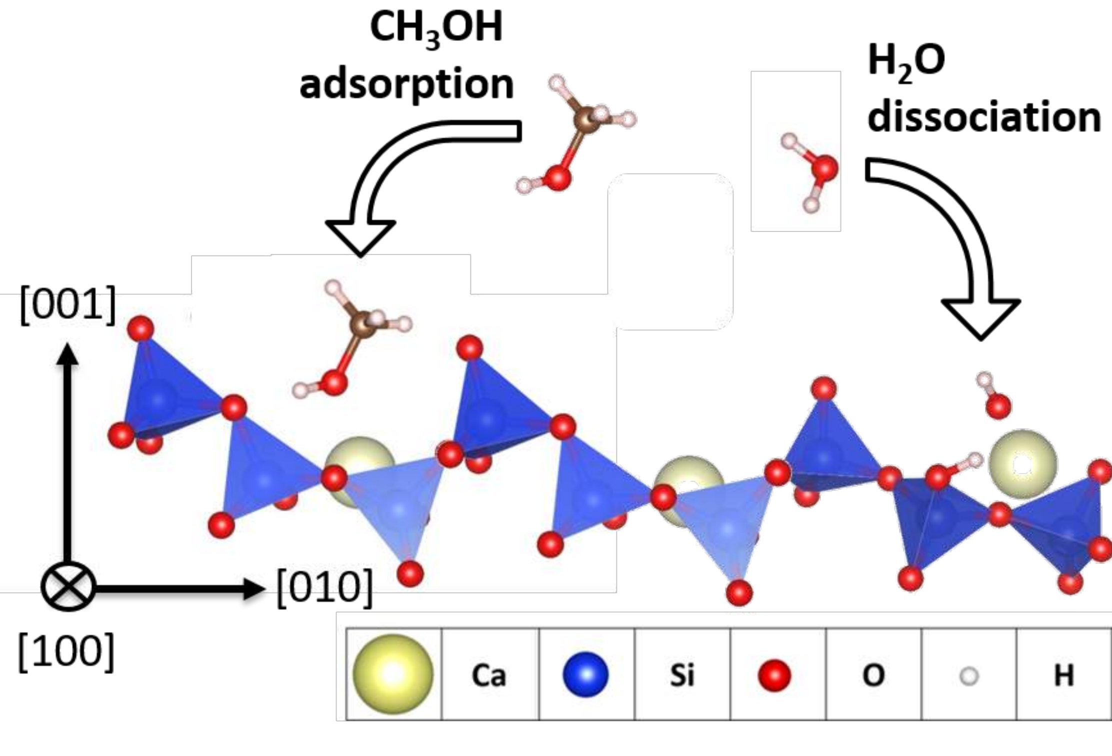
The experimental splitting observed for the (001) surface amounts to 20 cm^{-1}.

In our DFT calculations, we find an adsorption energy of 1.2 eV for one methanol monomer on the Wollastonite (001) surface; a hypothetical dissociated species is found to be less favorable in energy by 0.5 eV.

Summary I: Metal-Proton Exchange Reaction

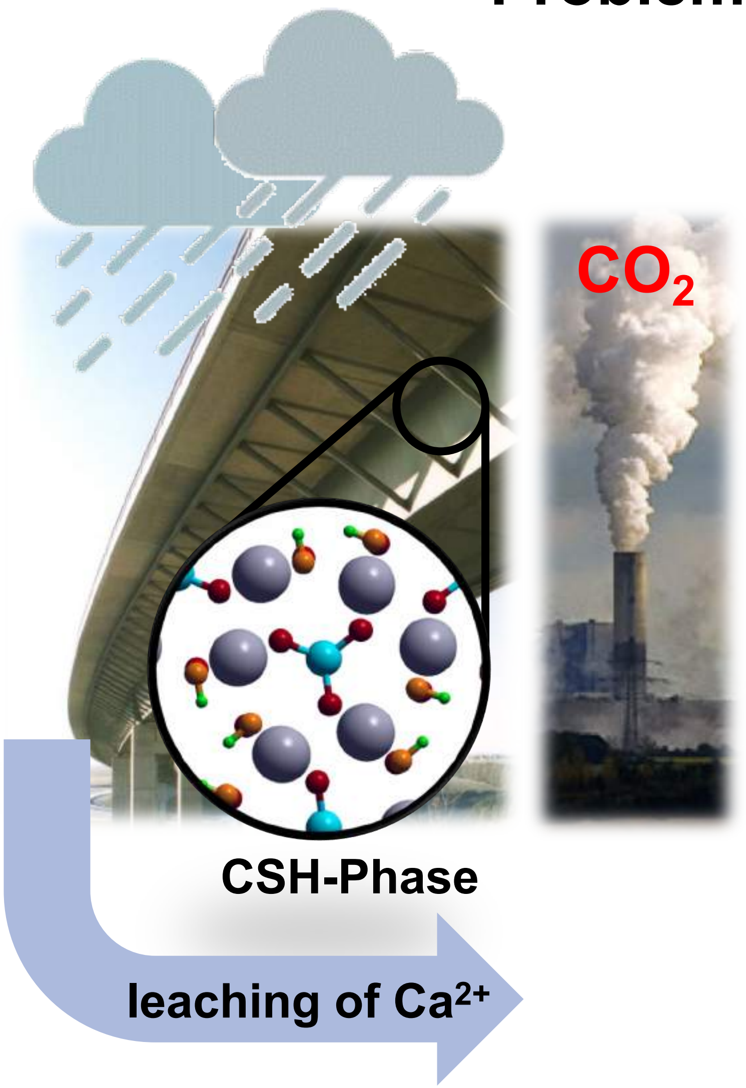
Our results obtained for methanol suggest that the leaching of Ca is strongly inhibited when replacing water by methanol, thus strongly reducing water-induced corrosion of the concrete.

The results for methanol provide the basis for developing new corrosion-protection strategies.



P. Thissen, C. Natzeck, N. Giraudo, P. Weidler, C. Wöll, Chem. Eur. J. ***2018****, 24, 8603.*

Problems

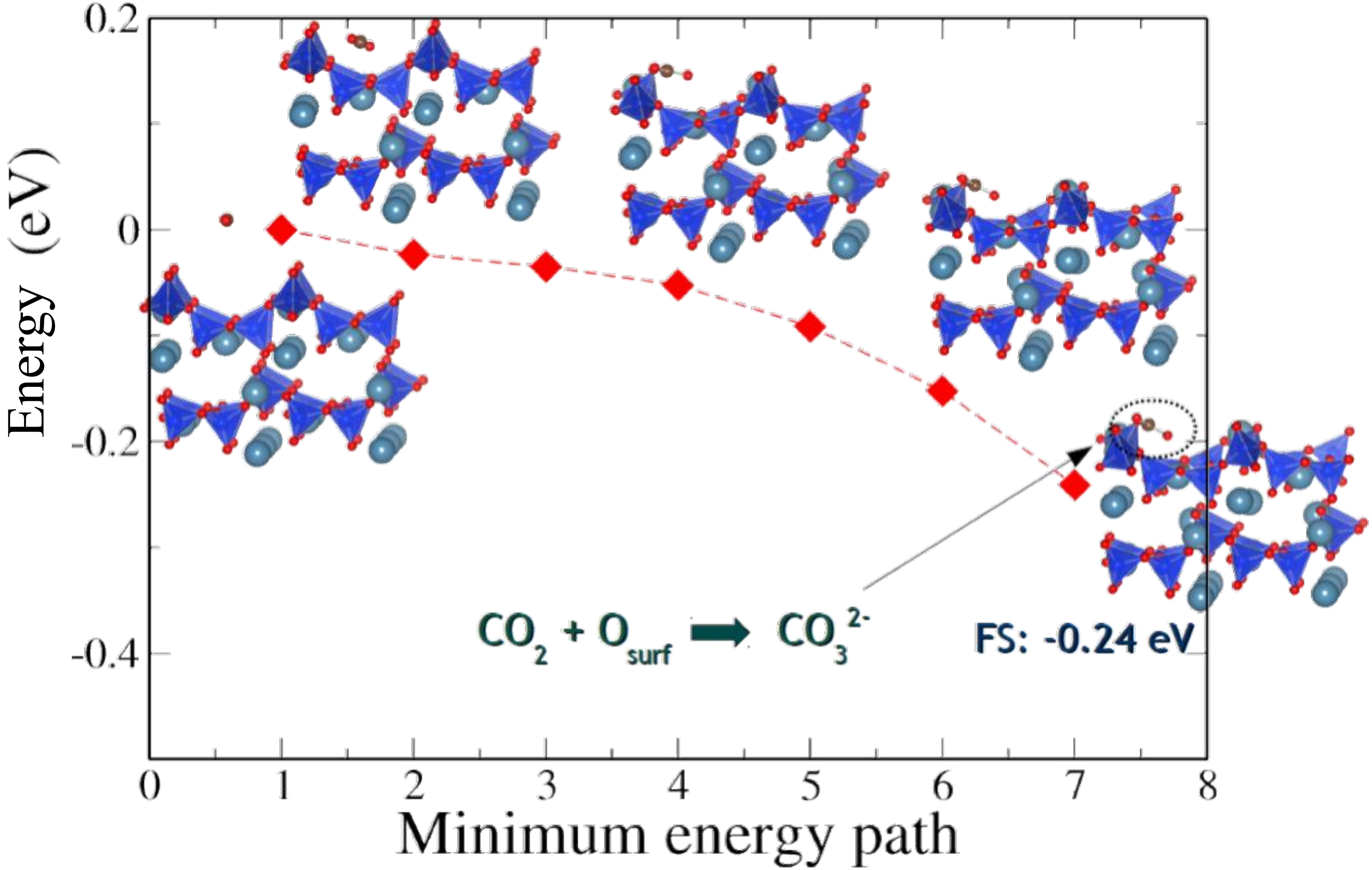


1. Metal-proton transfer is a chemical reaction of key importance, since on the one hand it triggers the hydration, but on the other hand also governs the corrosion of the material.

2. Detailed, spectroscopic investigations of model reactions on well-defined mineral substrates under UHV-conditions are largely lacking, thus prohibiting a validation of theoretical methods.

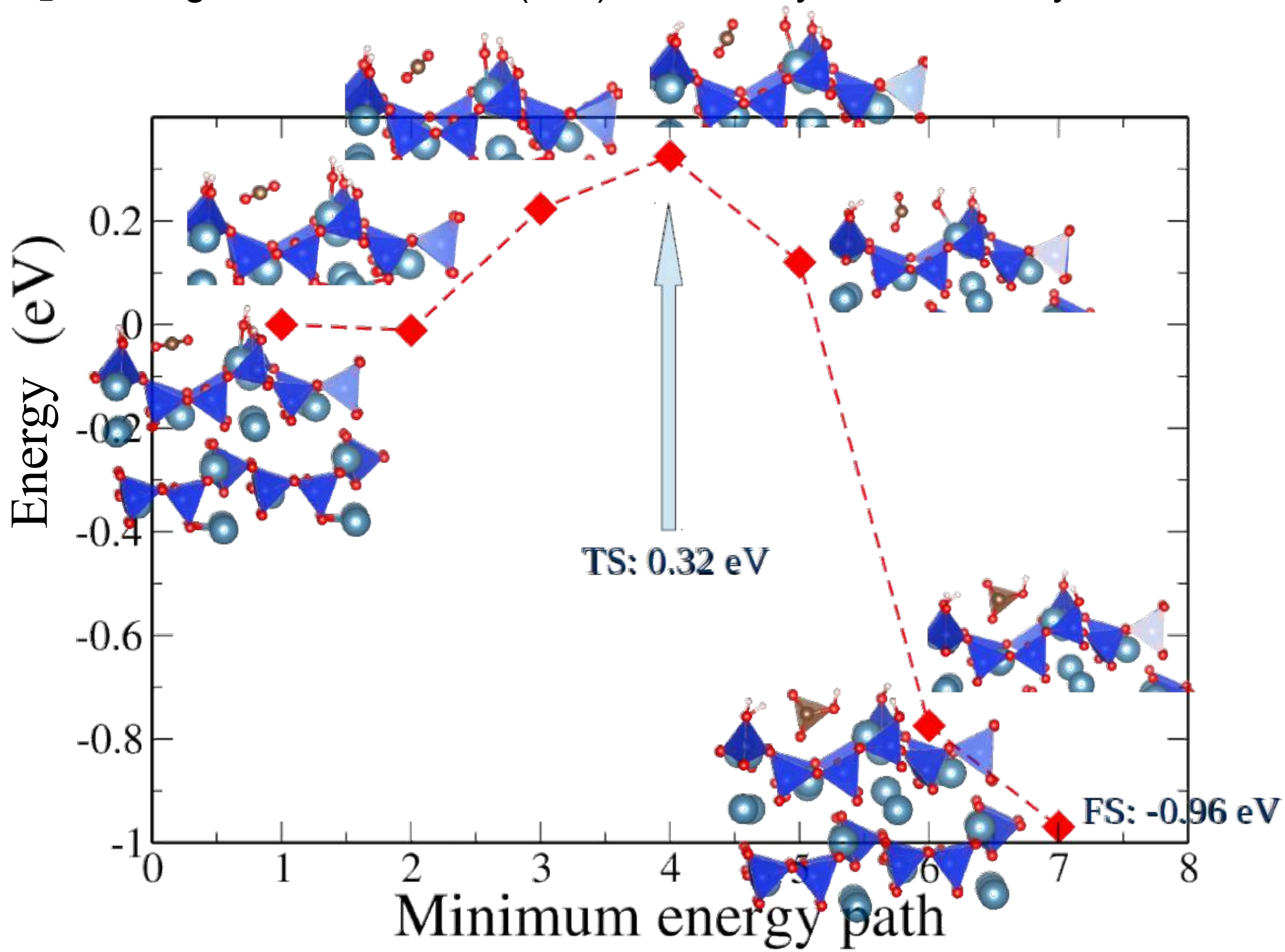
3. Carbonation becomes an increasing problem due to the climate change.

Minimum energy path of CO_2 reacting with water-free Wollastonite(001).

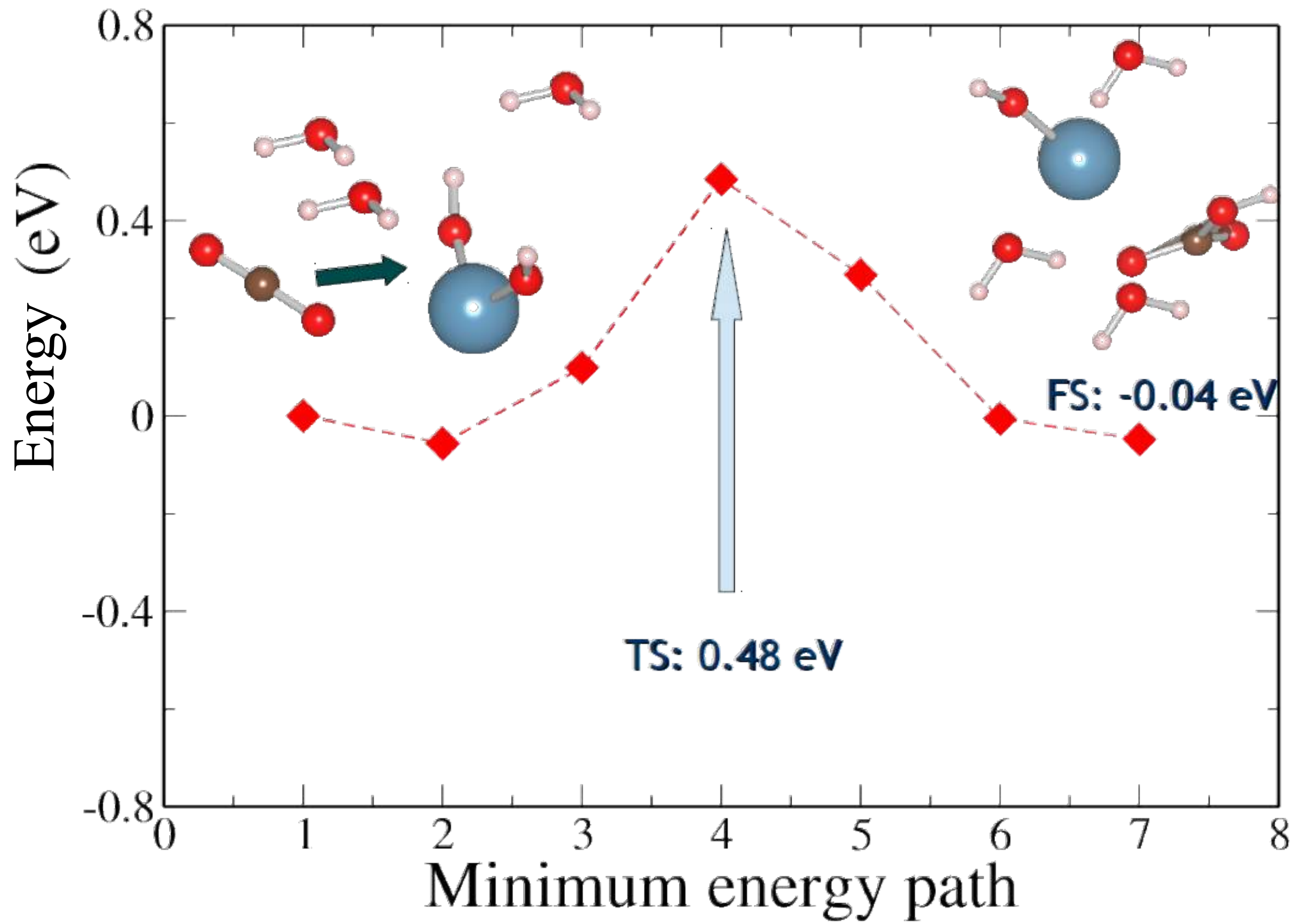


CO_2 reacts with dangling oxygen to silicate-carbonate

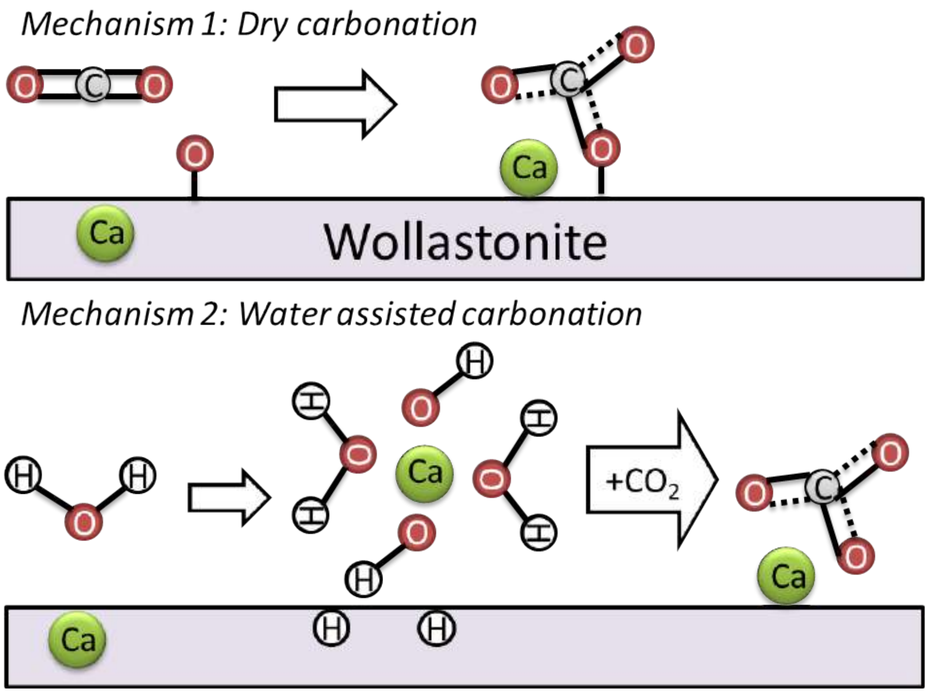
CO_2 reacting with Wollastonite(001) covered by a full monolayer of water.

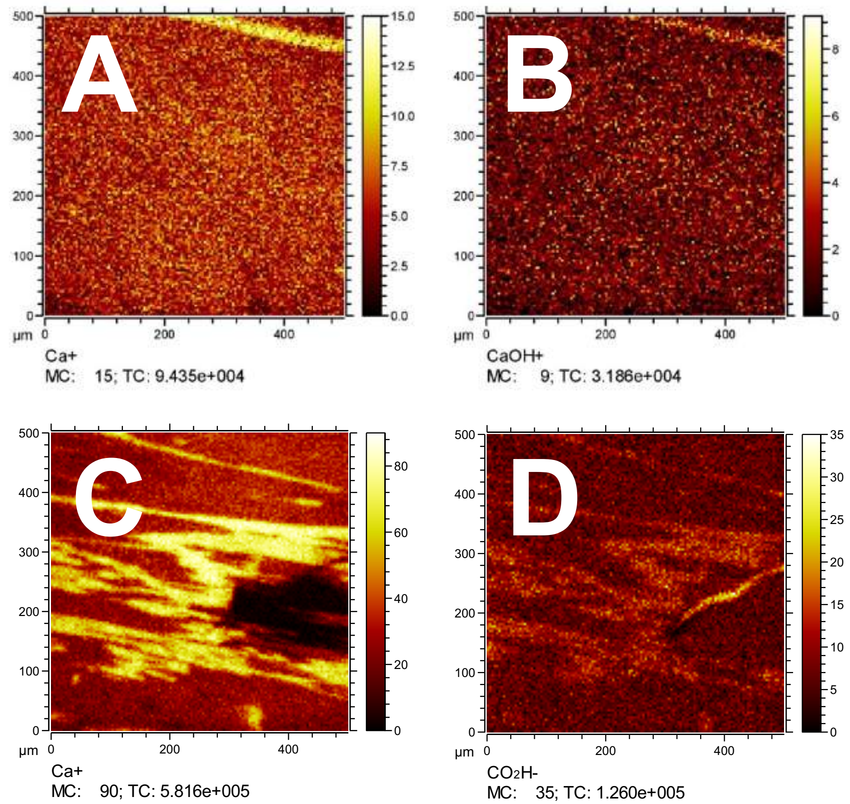


Cluster model of the minimum energy path of CO_2 reacting with Wollastonite(001) covered by more than one monolayer of water.



The exposure of $CaSiO_3$ to CO_2 results in a very fast carbonate production.
CO_2 reacts with the surface oxygen and forms CO_3 complexes.
After a carbonate monolayer has been formed, the reaction comes to a standstill.

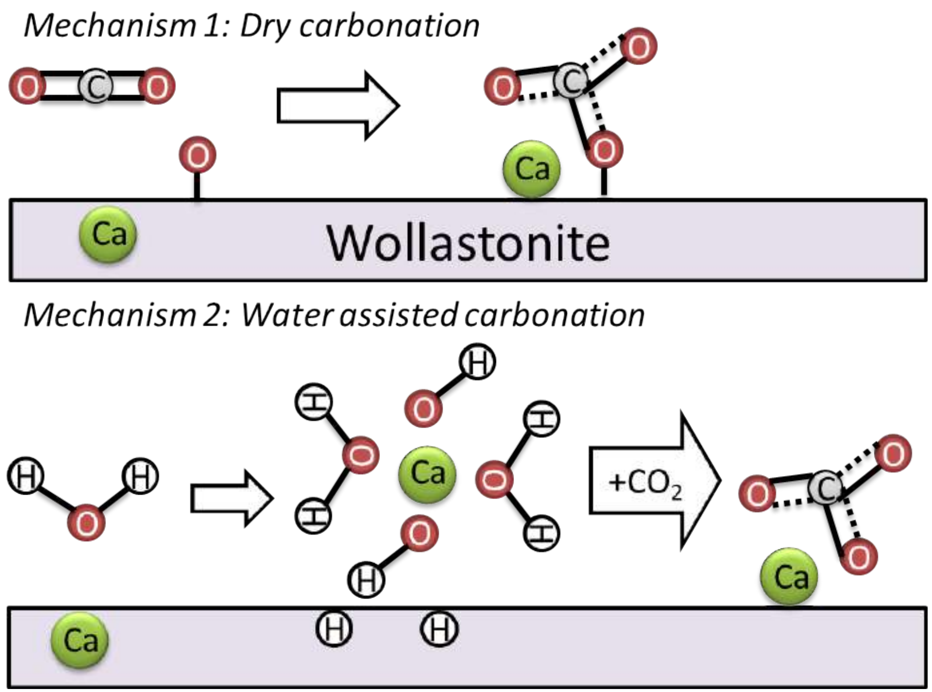




Due to the metal−proton exchange reaction, the Ca^{2+} has been removed partially from the surface and is available for the carbonate reaction in the solution.

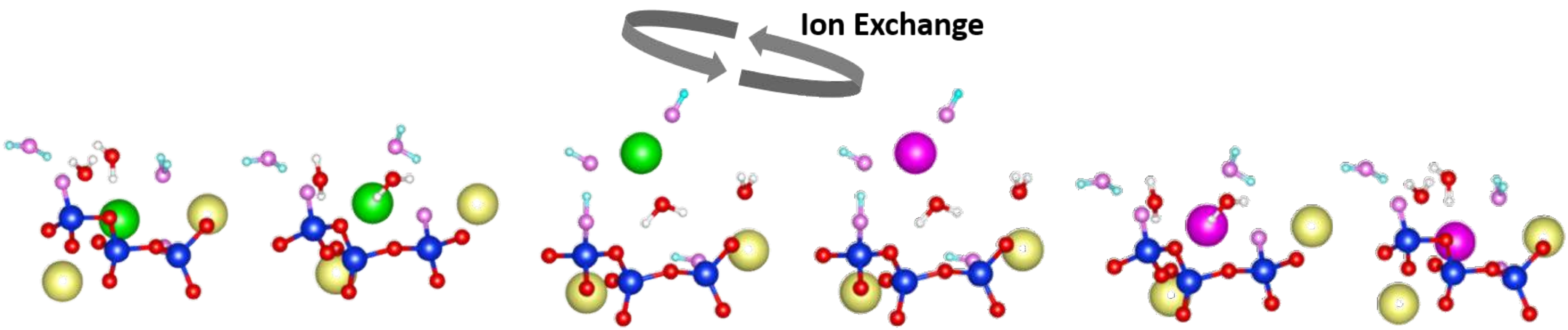
Summary II: Carbonation

CSH are considered promising compounds for CO_2 storage, using the so-called supercritical CO_2 conditions. However, the use of hydrated cement for CO_2 storage remains controversial, because the impact of such process on the mechanical properties of concrete is still unknown.



R. Longo, P. Thissen, Carbonation of Wollastonite(001) Competing Hydration: Microscopic Insights from Ion Spectroscopy and Density Functional Theory, ACS Appl. Mater. Interfaces, 2015, 7 (8), pp 4706–4712.

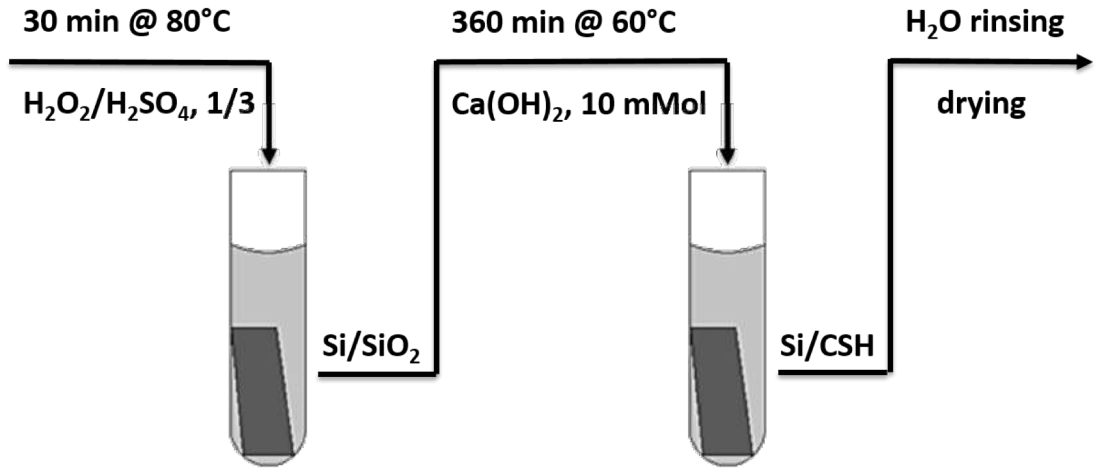
Is it possible to tailor the properties of CSH phases after hydration?



Metal-Ion Exchange Reaction

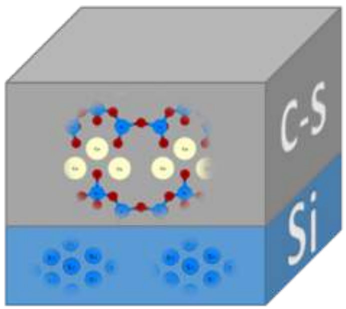
Hydrophobic Properties of Calcium-Silicate Hydrates Doped with Rare-Earth Elements, ACS Sustainable Chem. Eng., 2018, 6 (11), pp 14669–14678

Ultra-thin C-S-H phases grown on silicon

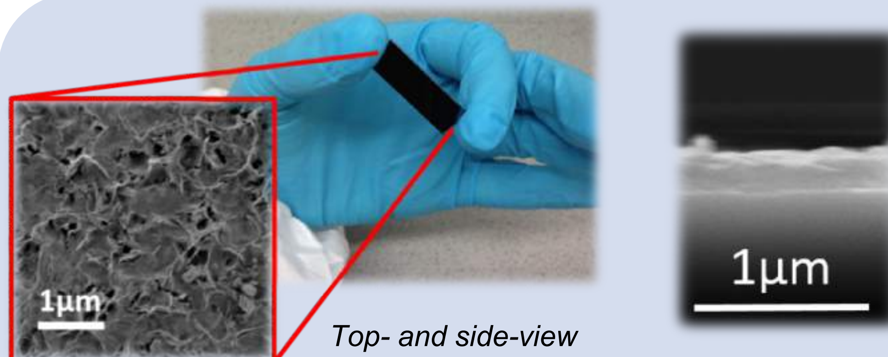


1. Work on Wollastonite was limited due to impurities of nature stone and availibility of the material

Wollastonite(001)



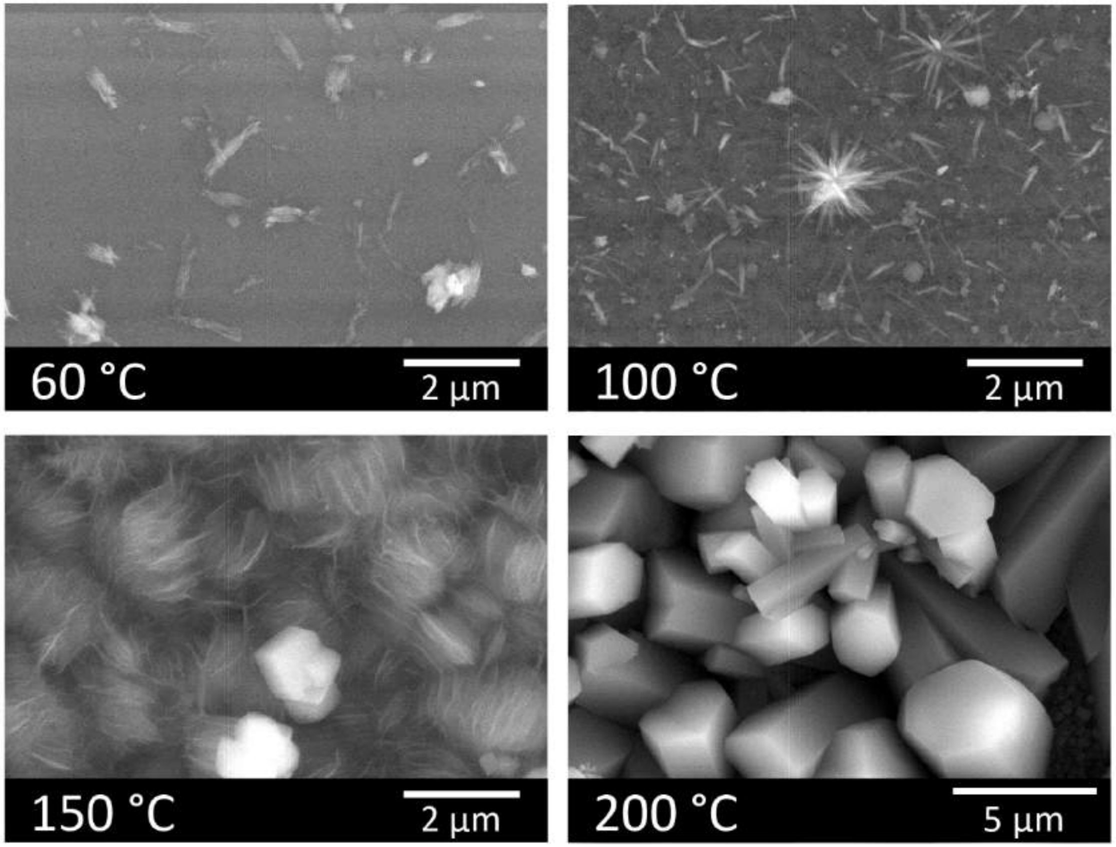
2. Synthesis of a new model of C-S-H and C-S phases was designed: Ultra-thin phases grown on silicon wafer



Top- and side-view of C-S-H phases synthesized on a silicon wafer.

Toward a microscopic understanding of the calcium–silicate–hydrates/water interface, Applied Surface Science, 290, 30, 2014, 207-214

First step: growth of CSH phases on silicon wafer

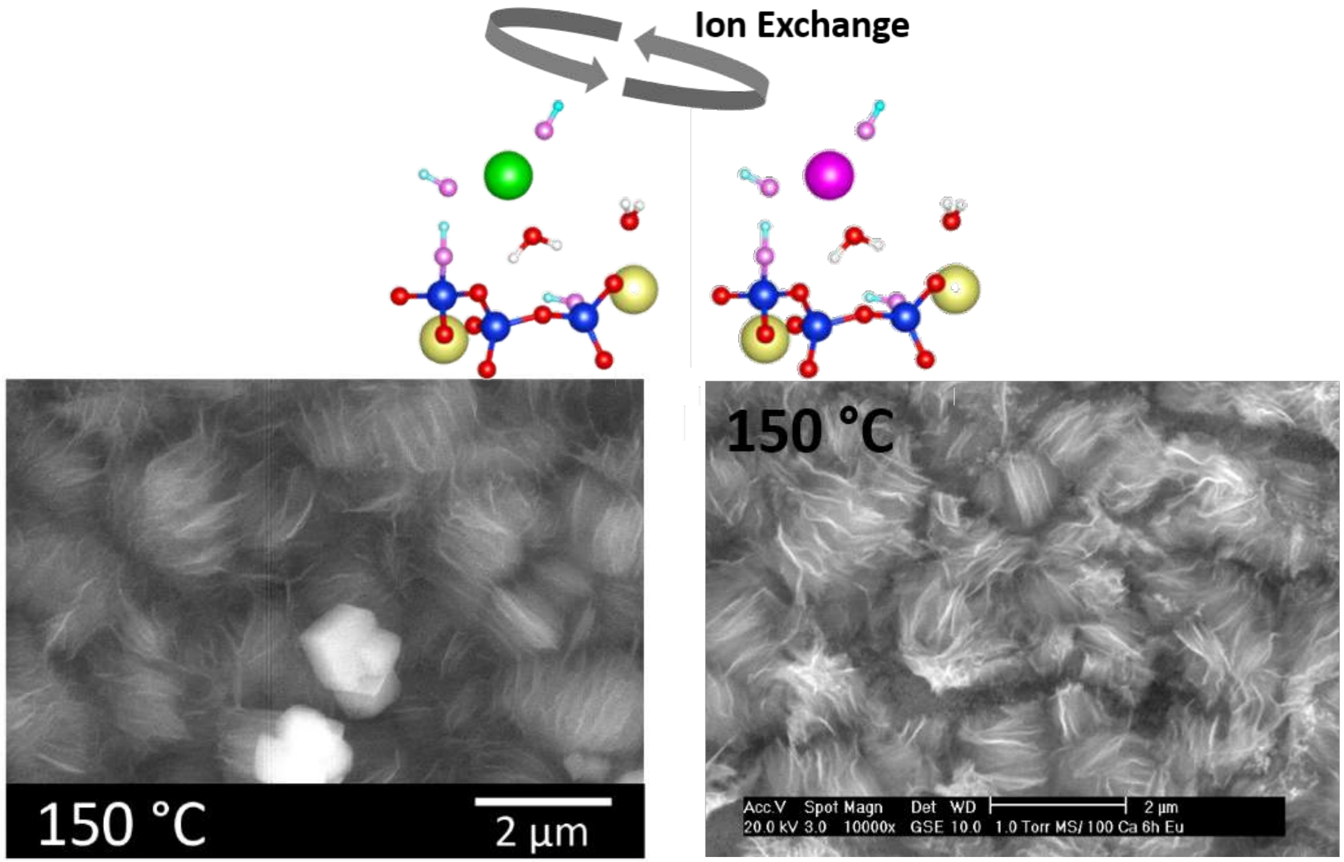


Typical properties of CSH phases:

(1) Reaction depends on time, temperature, concentration
(2) At 200 °C, the solution was oversaturated and $Ca(OH)_2$ precipitated
(3) Below 200 °C, a typical ‚hairy‘ structure of CSH has grown on the silicon wafer

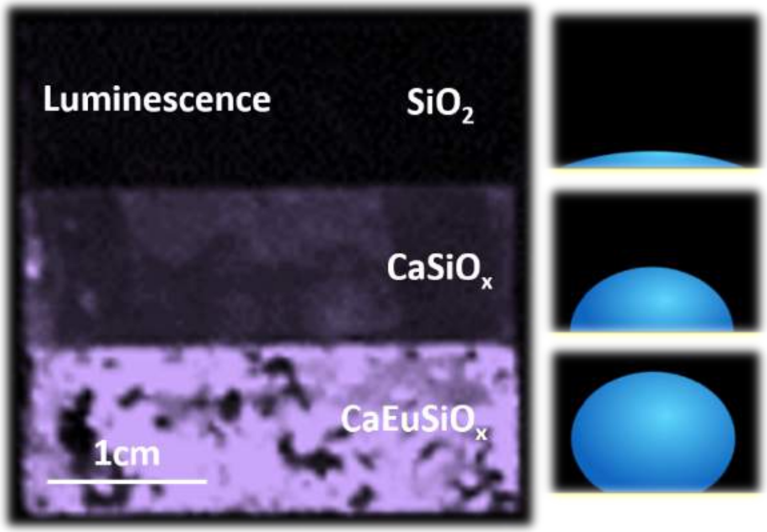
Environmental Scanning Electron Microscope images of ultrathin calcium silicate hydrate phases, grown on silicon wafers at different temperatures.

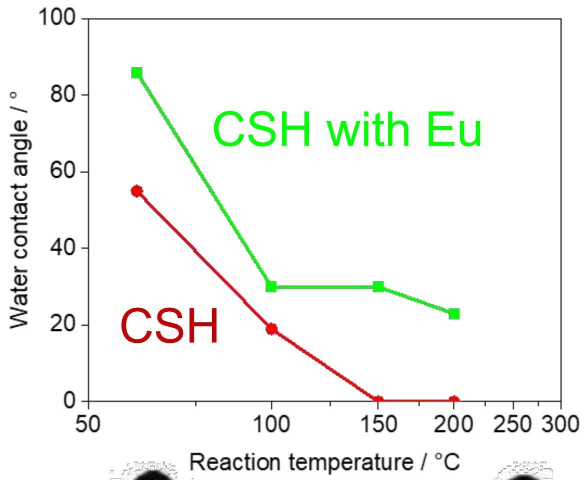
Second step: Exchange of Ca vs Eu



Environmental Scanning Electron Microscope images of ultrathin calcium silicate hydrate phases, immersed in an aqueous solution of $Eu_2(SO_4)_3$ (c = 1 mmol·L^{-1}) for 24 h at room temperature.

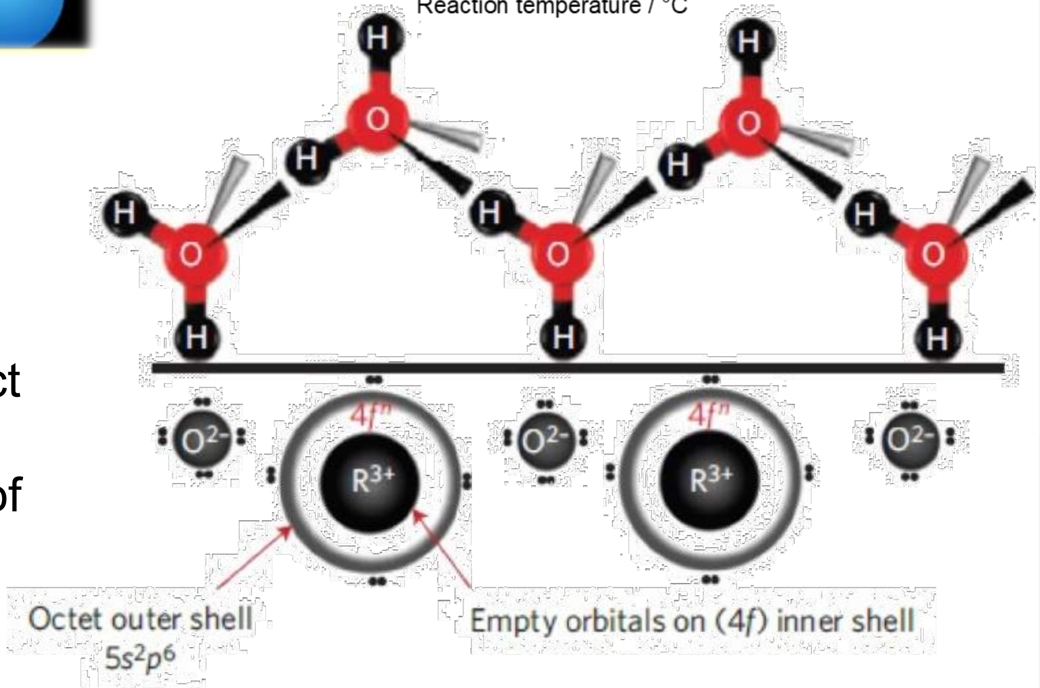
Property-relevant changes due to the exchange



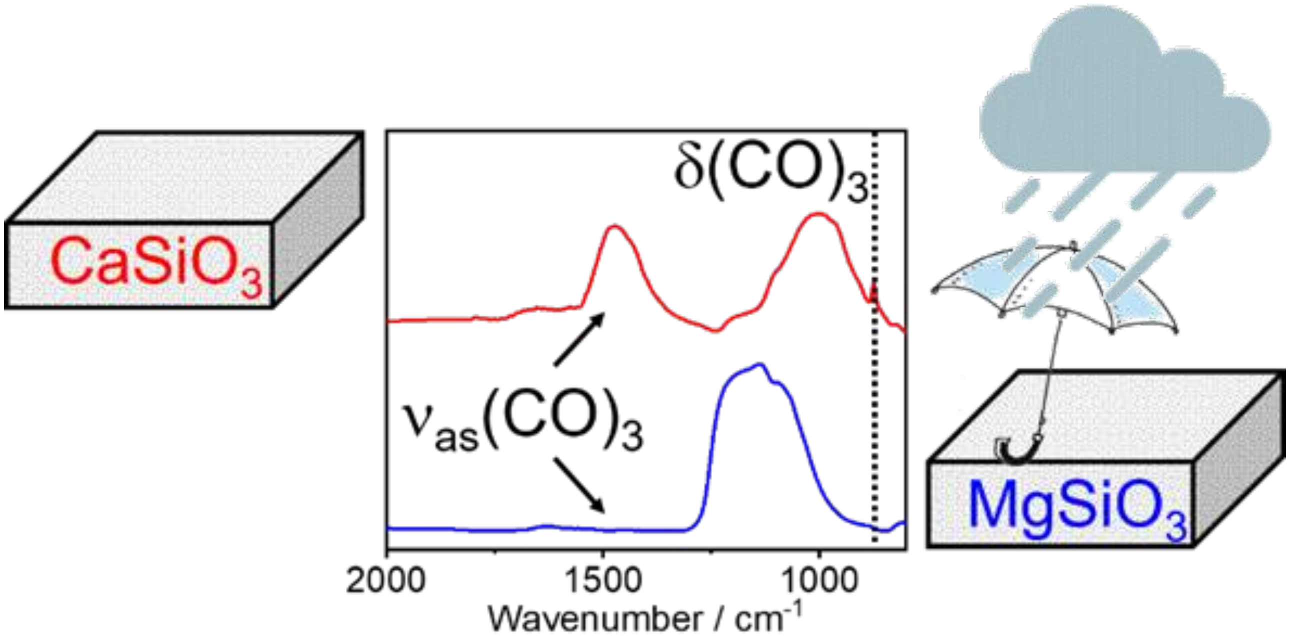


The inorganic coating technique.

Passivation techniques will be investigated with a hydrophobic effect on the surfaces in order to repel water, responsible for the corrosion of these materials.



Summary III: Metal-Ion Exchange Reaction



(1) The Metal-Ion Exchange Reaction, has been successfully performed for Eu, Sr and Mg vs Ca on cement.

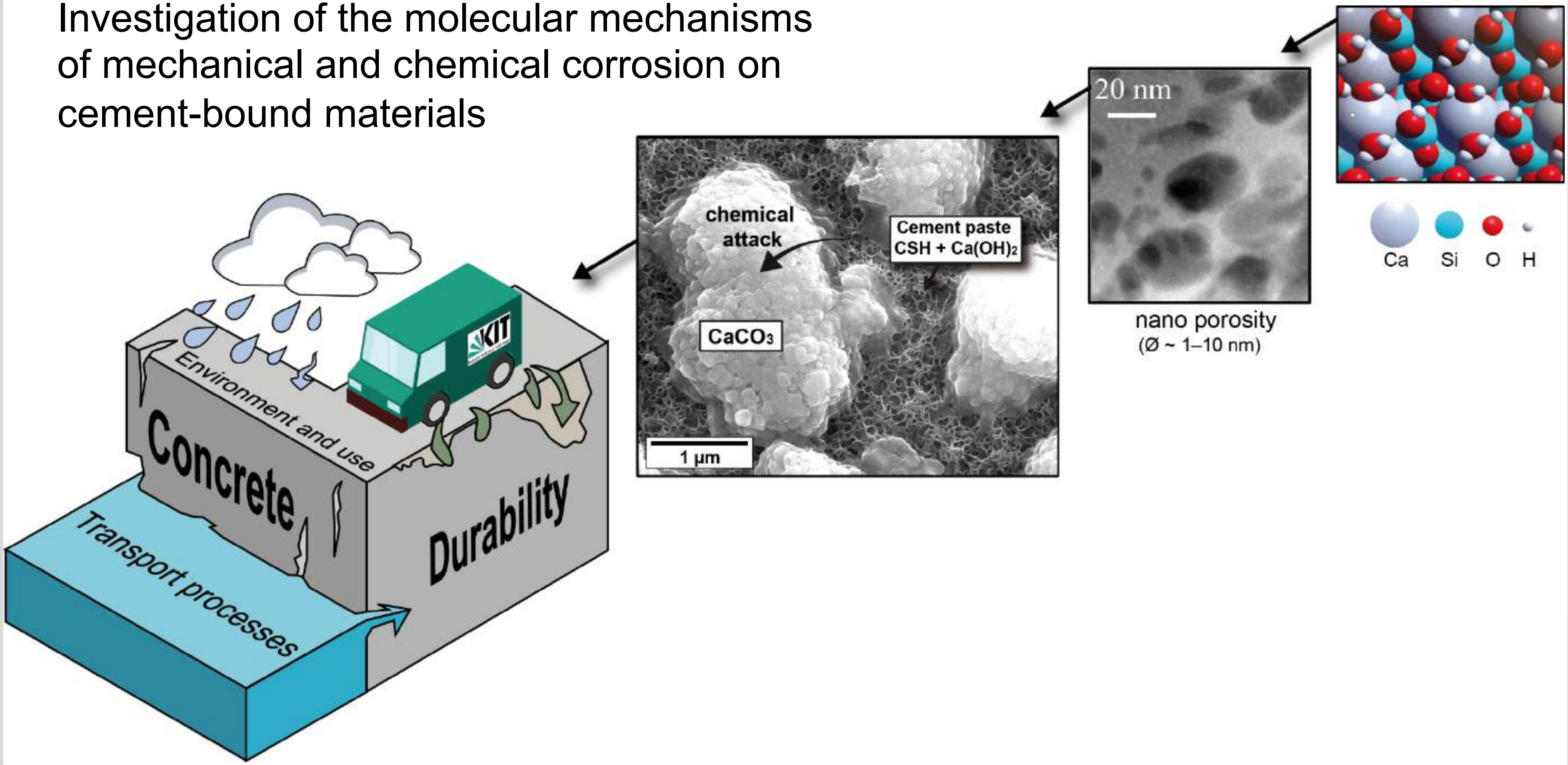
(2) Ca was exchanged by rare-earth elements for water repel

(3) Ca was exchanged by Mg for passivation against carbonation

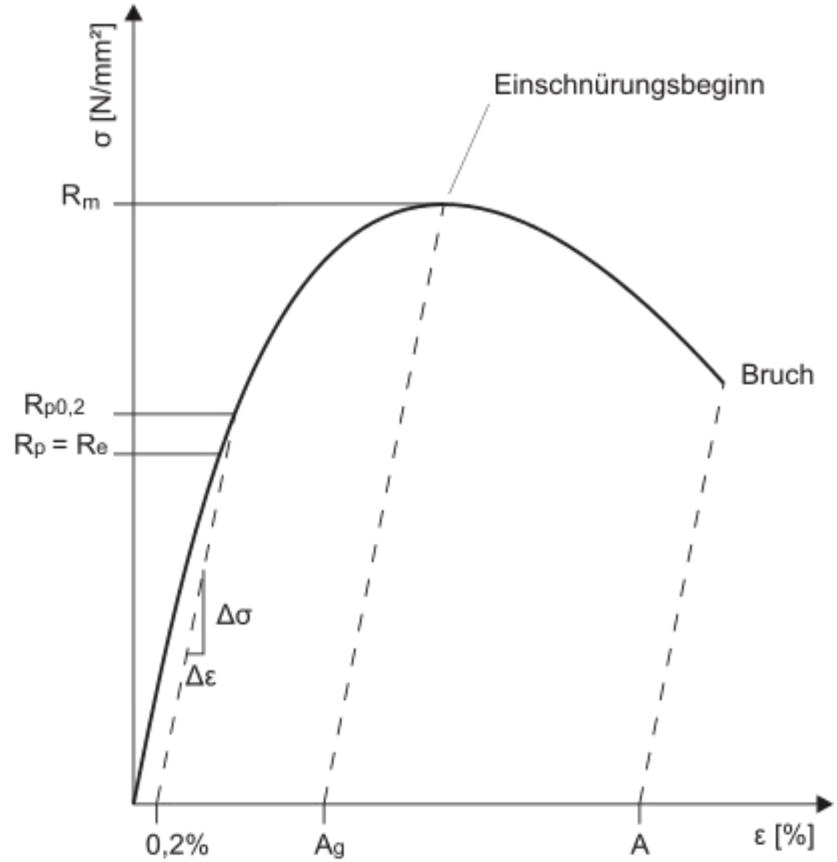
Outlook

What are the challenges in the near future?

Investigation of the molecular mechanisms of mechanical and chemical corrosion on cement-bound materials

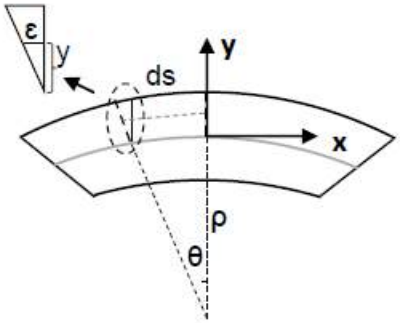


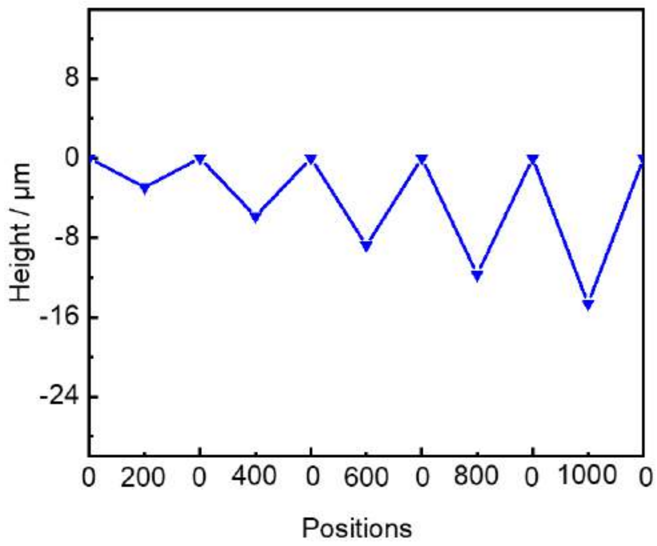
Die Universalprüfmaschine

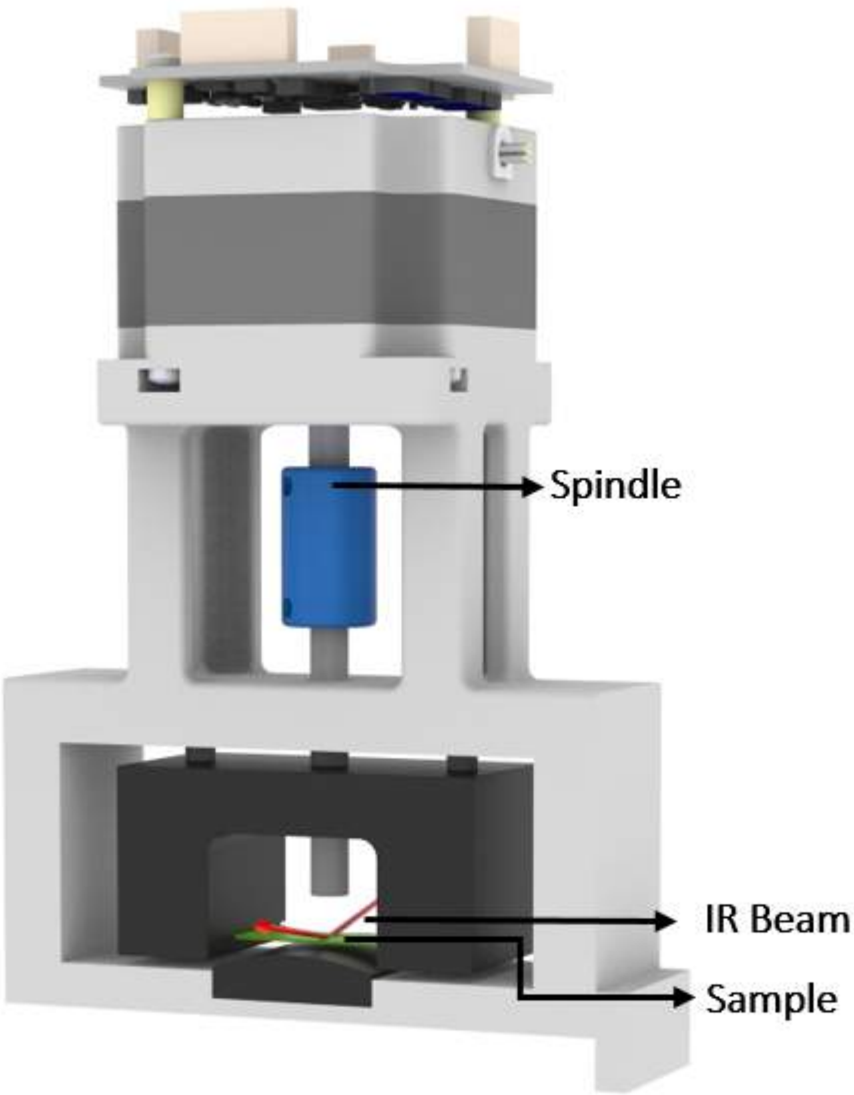


- Zugprüfmaschinen sind spezielle Prüfmaschinen,
- Fahren eindimensionale Bewegungsabläufe
- Stellen idR Spannungs-Dehnungs-Diagramm dar.

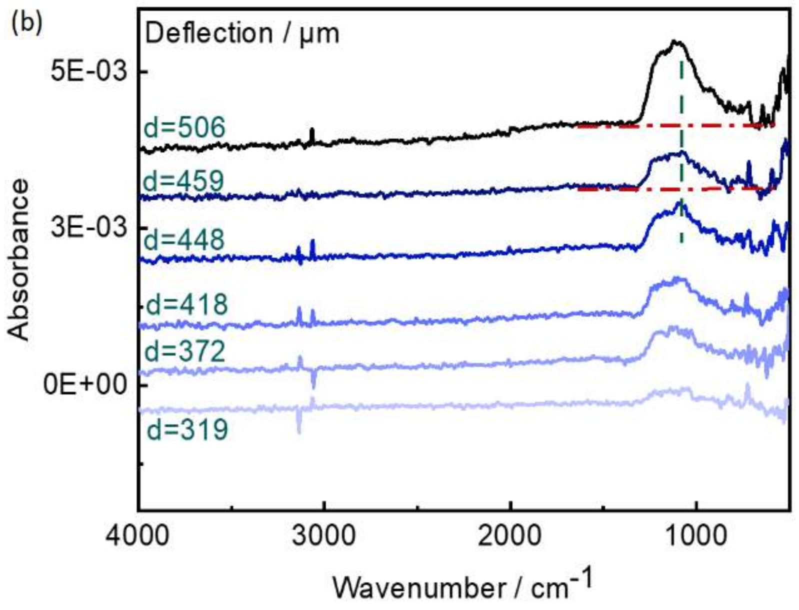
New experimental approach

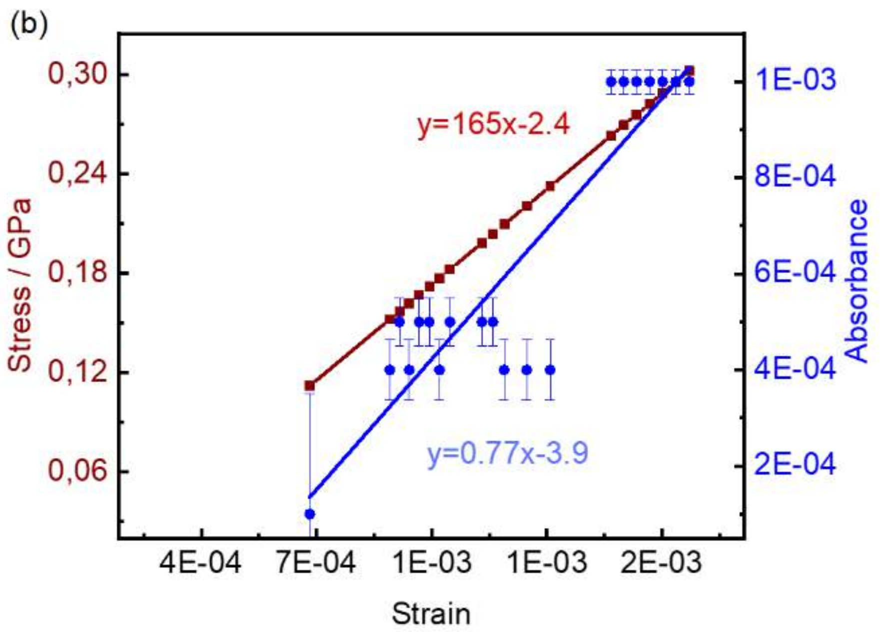


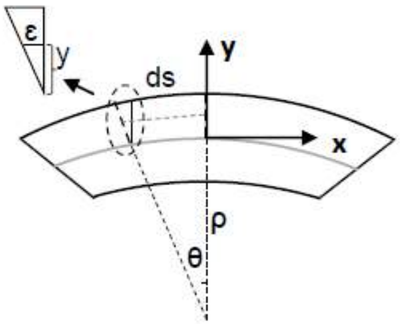


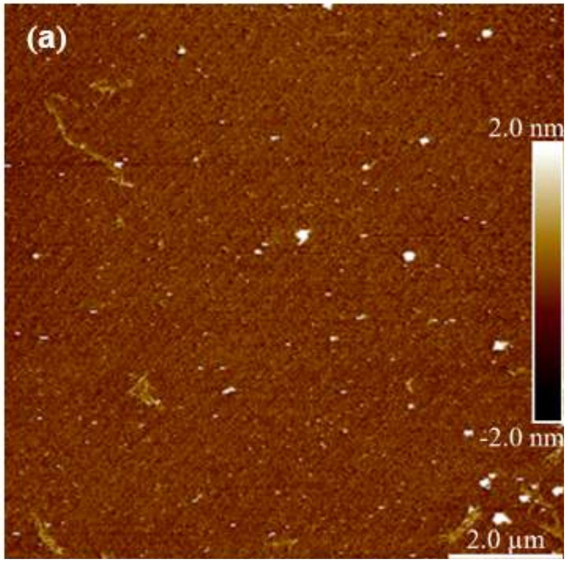


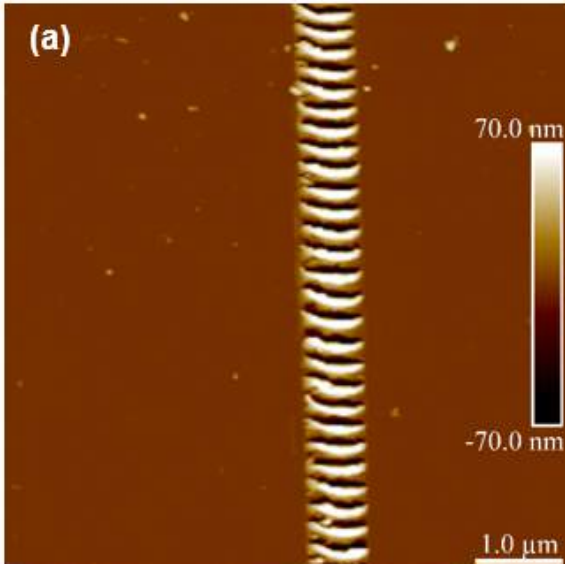
Monitoring of mechanical stress by IR-spectroscopy





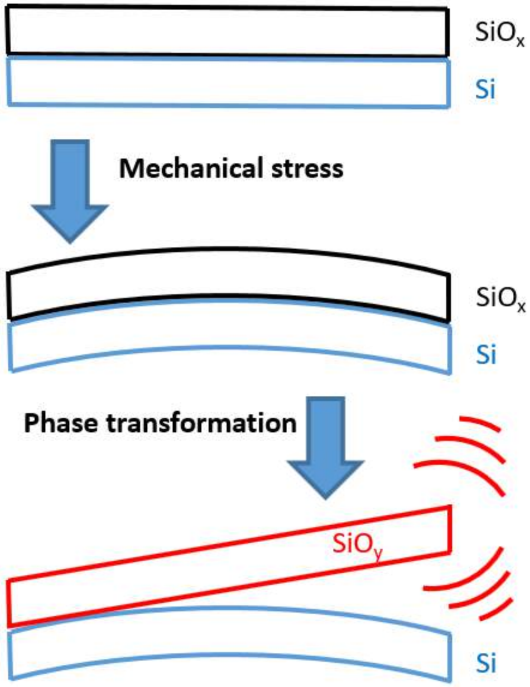






Atomic Force Microscopy

- before and after bending



- so far gives the idea of a stress-induced phase transformation

Thank you for you attention.

I would like to thank Prof. Dr. Wöll from KIT.

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Dr. Roberto Longo from University of Texas at Dallas.

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Prof. Dr. Wolf-Gero Schmidt and Prof. Dr. Guido Grundmeier from University of Paderborn.