



UNIVERSIDAD
DE GRANADA



Universidad de Oviedo
Universidá d'Uviéu
University of Oviedo



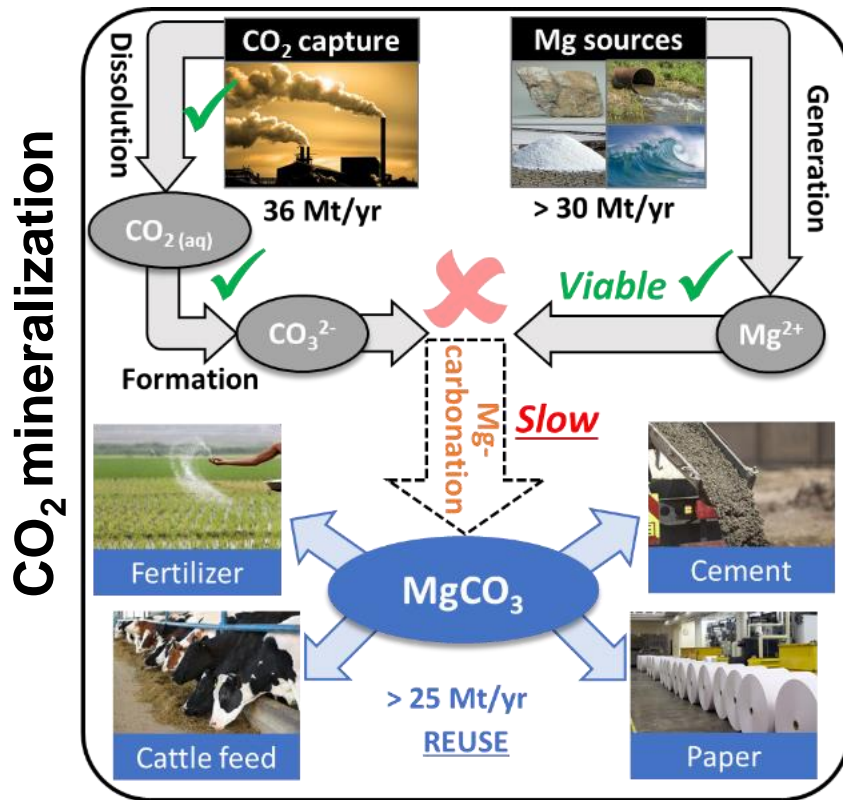
FUNdamental Studies of MINeral Carbonation with Application to CO₂ Utilisation



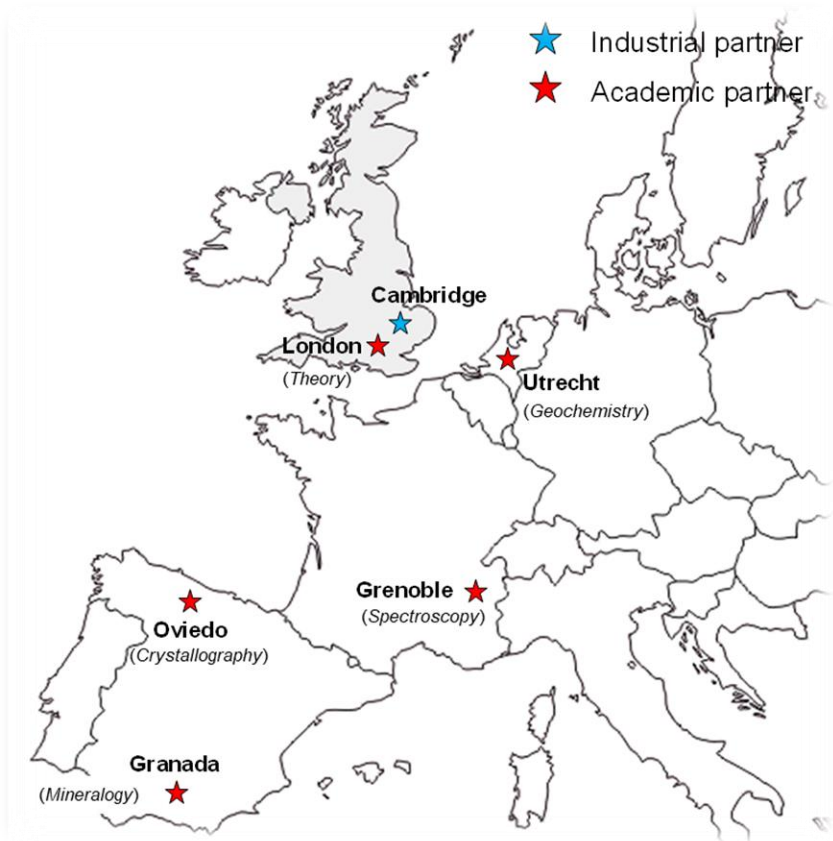
By Devis Di Tommaso, Queen Mary
17.11.2020, ACT Knowledge Sharing Workshop

FUNMIN

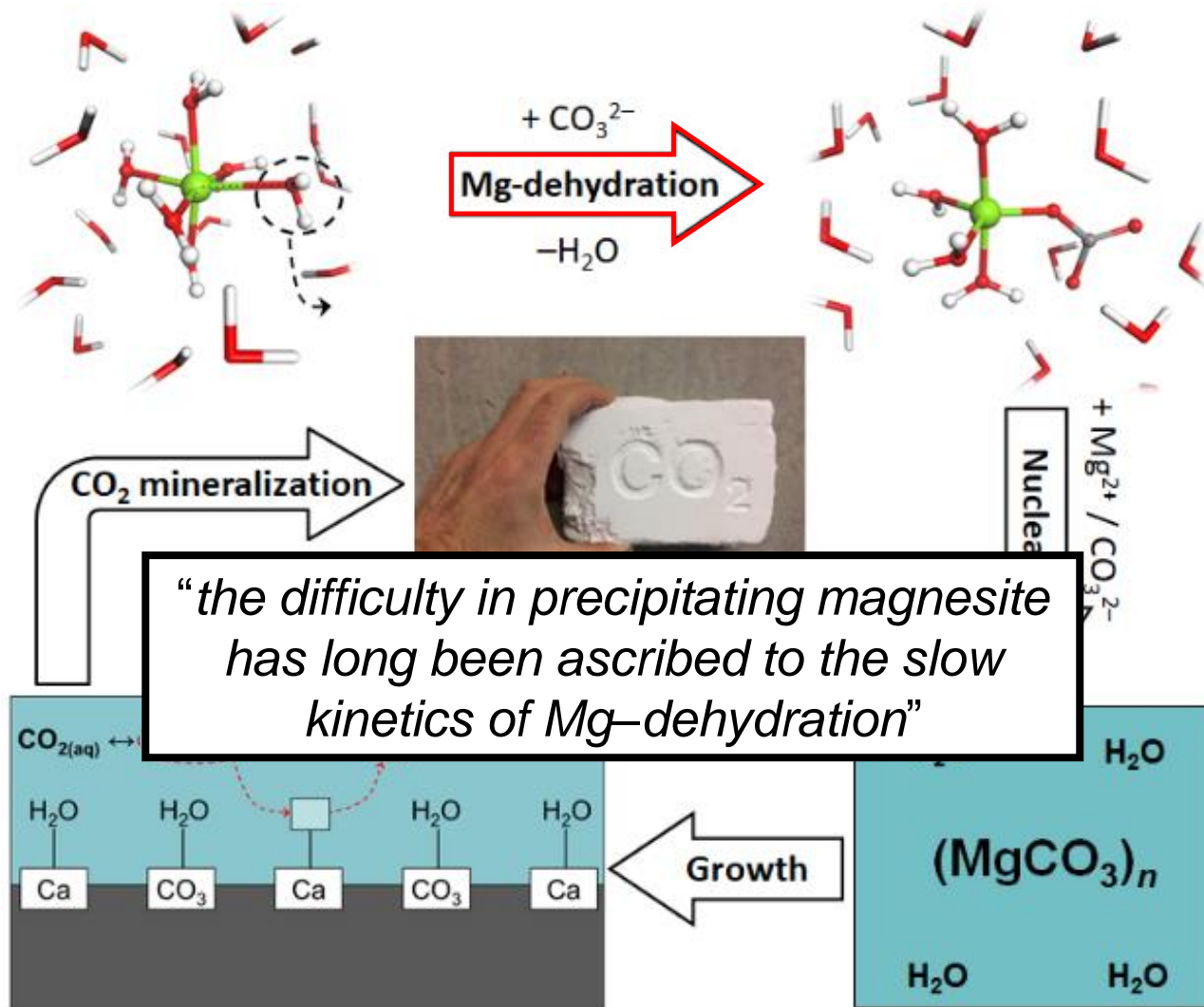
Complementary expertise in mineralization guiding Industrial technologists to mineralise CO₂



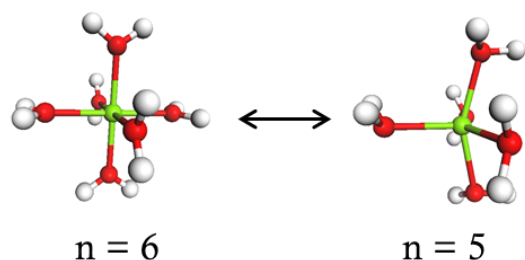
CO₂ into added value products



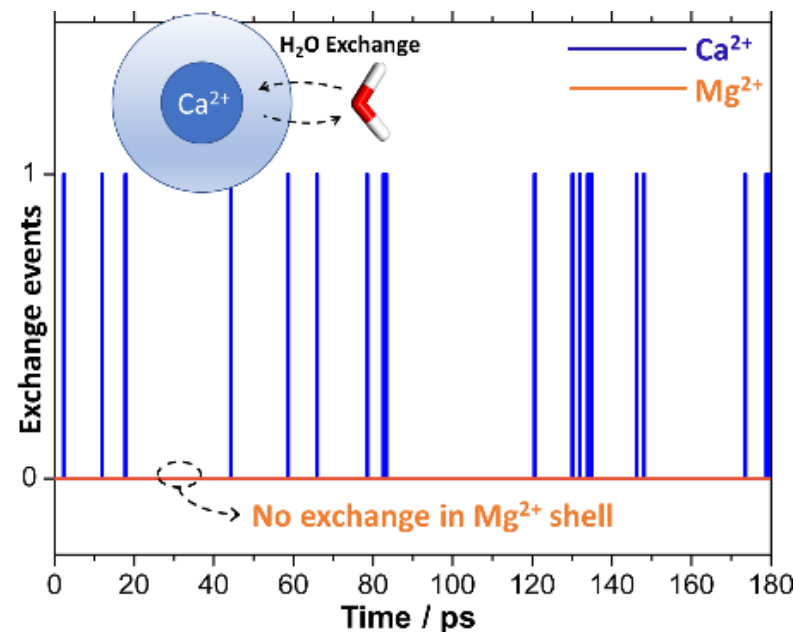
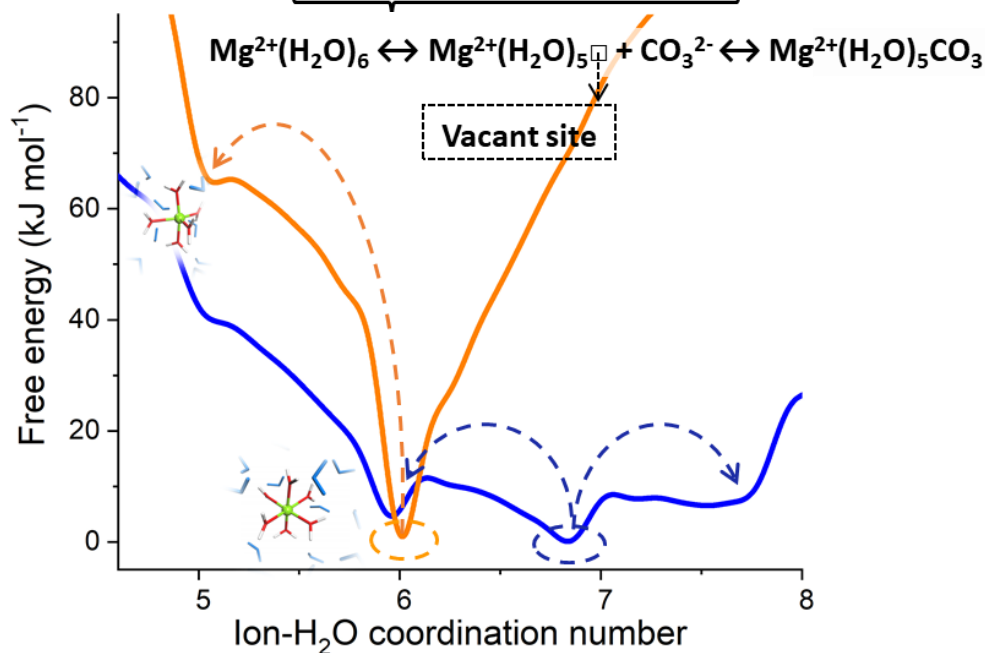
Mineral carbonation



The origin of slow Mg-dehydration



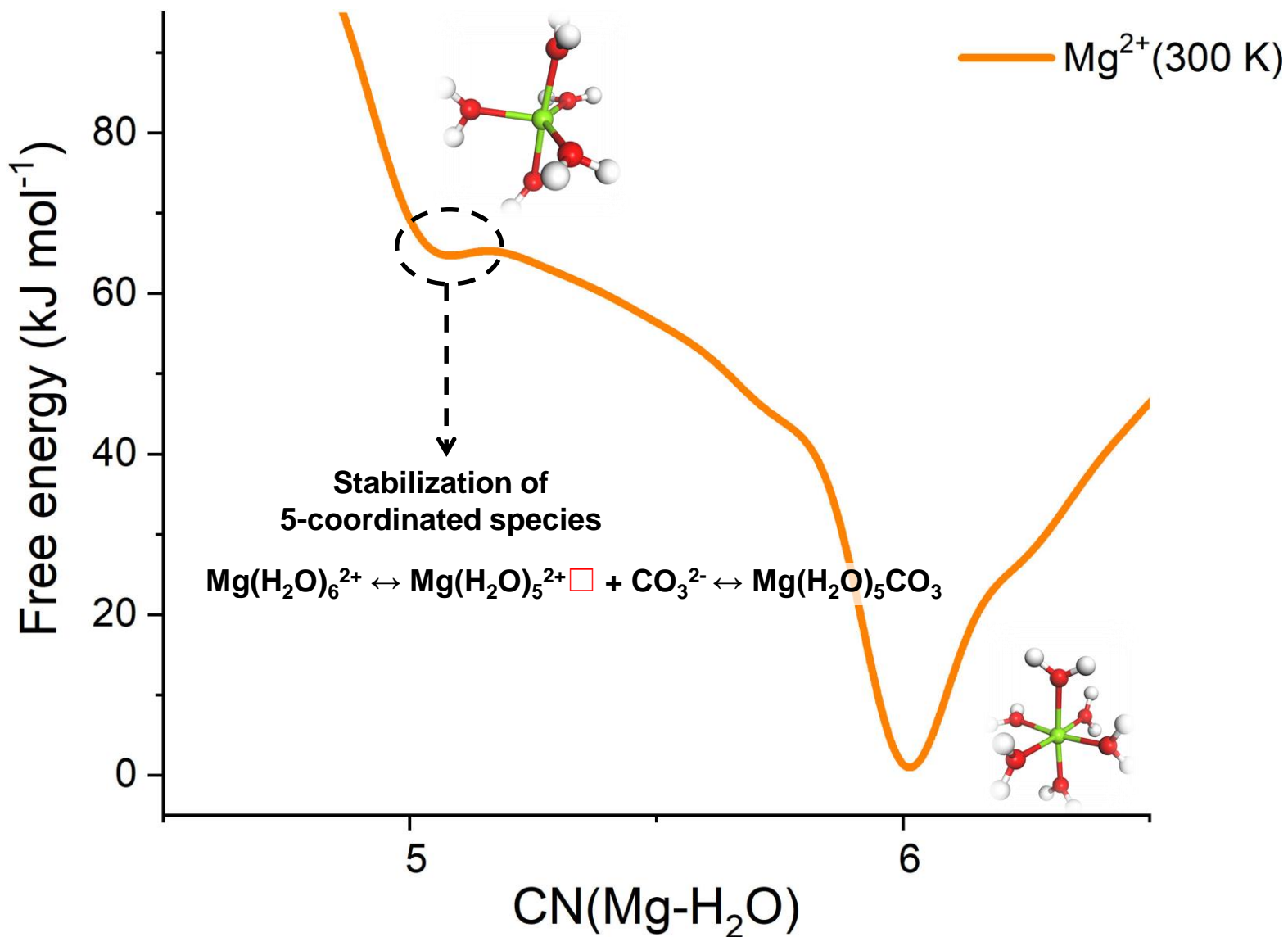
Precipitate rates of MgCO_3 is 6 orders of magnitude slower than CaCO_3 (300K)



Classical metadynamics (MetaD) simulations (1 μs)

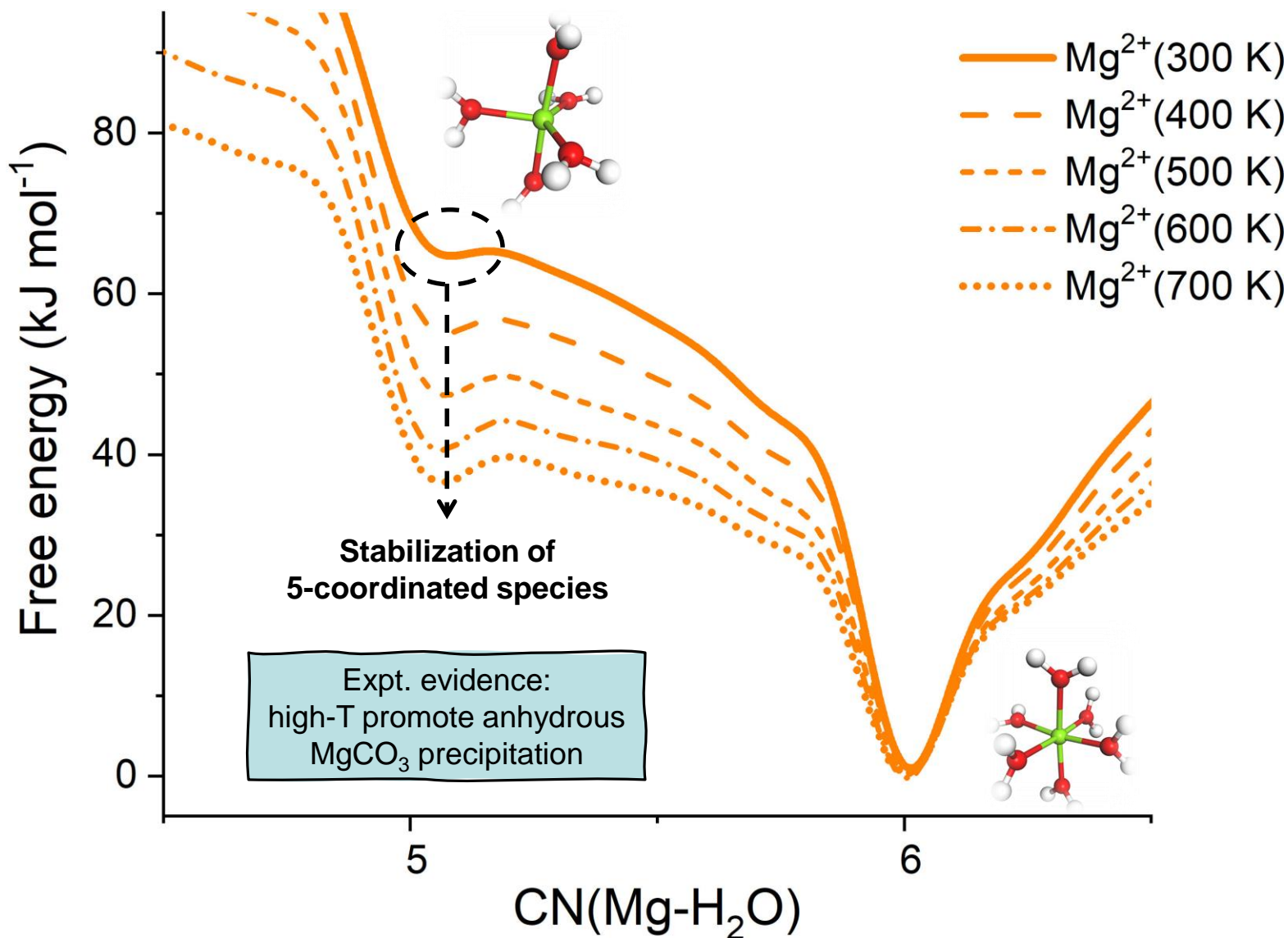
Ab initio MD simulations (500 ps)

How can Mg-dehydration be promoted?





How can Mg-dehydration be promoted?



Research hypothesis

Natural solutions are far from pure water, are rich in ions, making **solution environments highly influential on molecular processes controlling magnesite crystallization: Mg-dehydration, nucleation & growth**



Research papers

Ion-specific effects on the kinetics of mineral dissolution

Encarnación Ruiz-Agudo ^{a,*}, Maja Urosevic ^b, Christine V. Putnis ^a, Carlos Rodríguez-Navarro ^b, Carolina Cardell ^b, Andrew Putnis ^a

^a Institut für Mineralogie, Universität Münster, Corrensstrasse 24, 48149, Münster, Germany

^b Department of Mineralogy and Petrology, University of Granada, Campus Fuentenueva s/n, 18071, Granada, Spain

Specific effects of background electrolytes on mineral growth and dissolution can be interpreted on the basis of the ability of ions to modify solute hydration, in a similar way to the systematic effects of inorganic ions on precipitation, structure and function of organic macromolecules (i.e., the Hofmeister effect). Here, the

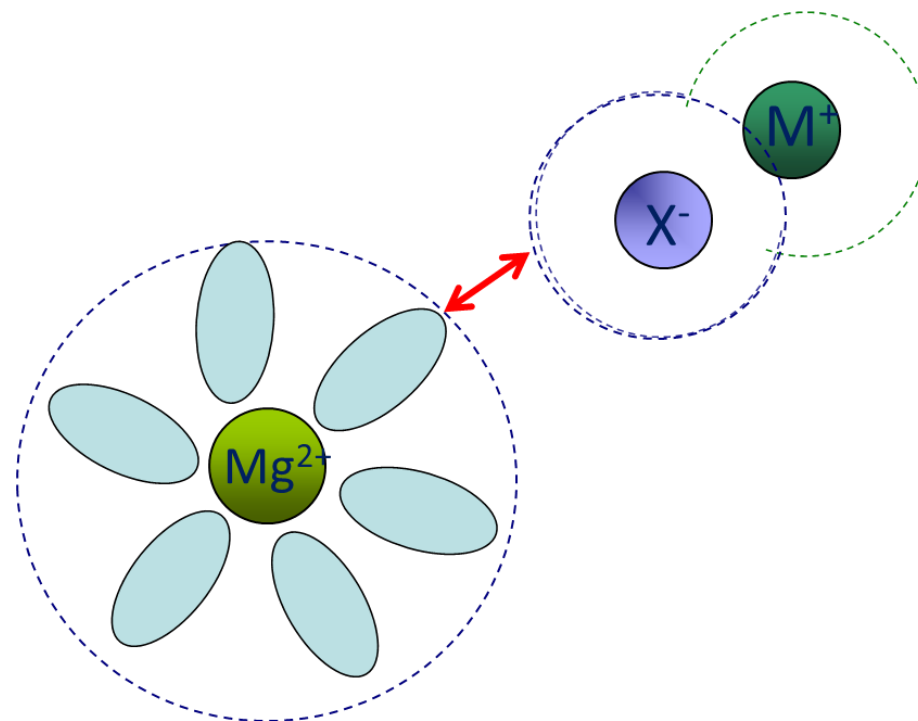
Accepted 3 January 2011
Available online 7 January 2011

Editor: J. Fein

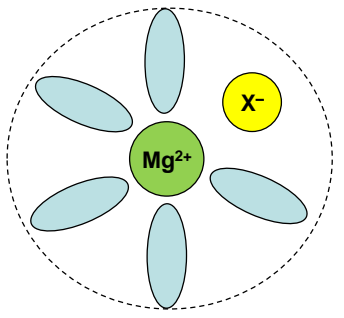
Keywords:
Dolomite dissolution
In situ AFM
Background electrolytes

effect of a range of background electrolytes (sodium and chloride salts) on dolomite ($\text{Ca}_2\text{Mg}_2\text{CO}_3$) reactivity was investigated as a model system by measuring dissolution rates using in-situ Atomic Force Microscopy. The systematic trends found for the different ions are interpreted in terms of characteristic parameters of background ions such as effective hydrated radii. Entropic effects associated with the ordering of solvent molecules induced by constituting cations from the crystal ultimately dictate how electrolytes affect dissolution rates. In dilute electrolyte solutions, ion-ion interactions dominate and the stabilisation of the solvation shell of ions constituting the crystal, by counter-ions present in solution enhances the unfavourable entropic effect on dolomite dissolution. The tendency for electrolytes to form ion pairs in solution reduces such an effect, thus leading to an inverse correlation between dissolution rates and background ion separation in solution. On the other hand, in concentrated saline solutions the interaction between background ions and water molecules determines the hydration of a constituent ion immersed in an electrolyte solution. In this case, dissolution rates correlate with the mobility of background ions and, therefore, with their effective hydration radii. The observed effects of background ions on growth and dissolution could be applicable for other inorganic systems where the Hofmeister effect has been reported.

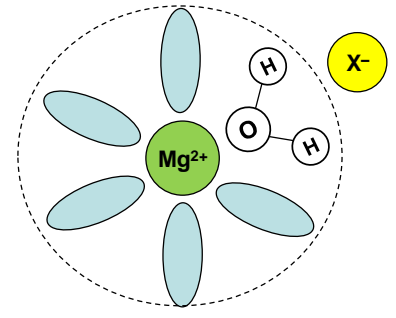
© 2011 Elsevier B.V. All rights reserved.



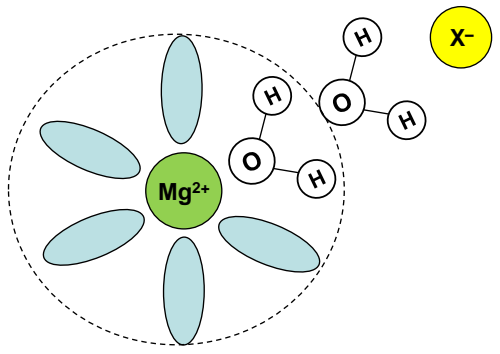
Mg²⁺ interaction with solution additives



CIP

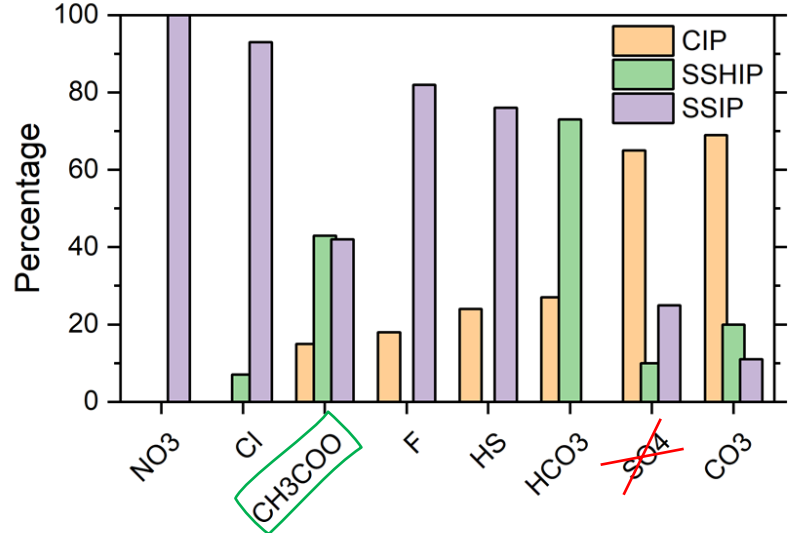
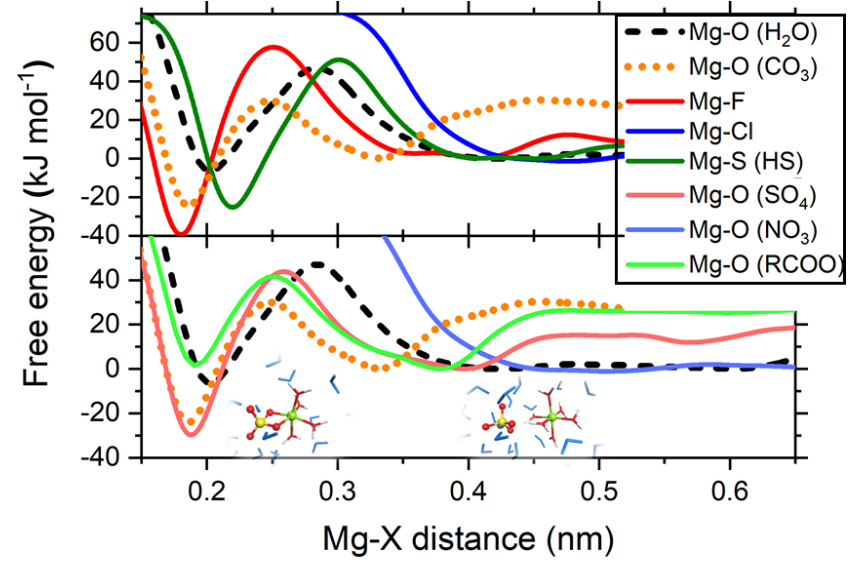


SSHIP

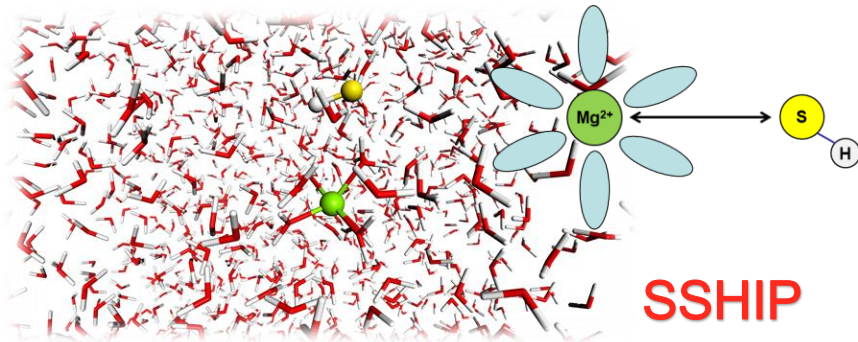


SSIP

Rule #1
To not inhibit MgCO₃ nucleation an additive should form **stable SSHIP** with Mg²⁺ or **CIP** less stable than Mg²⁺...CO₃²⁻

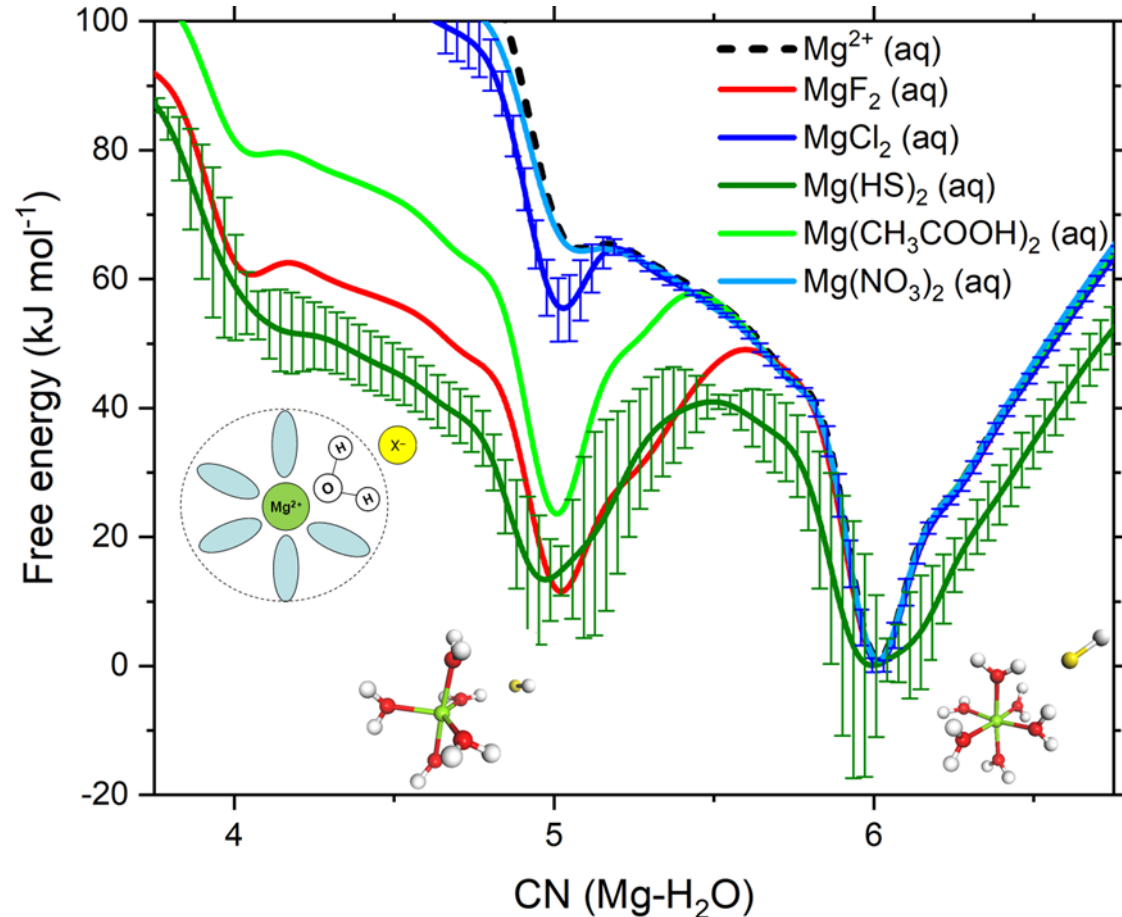
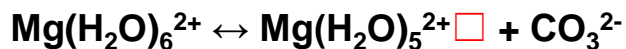


Mg-dehydration in the presence of additives



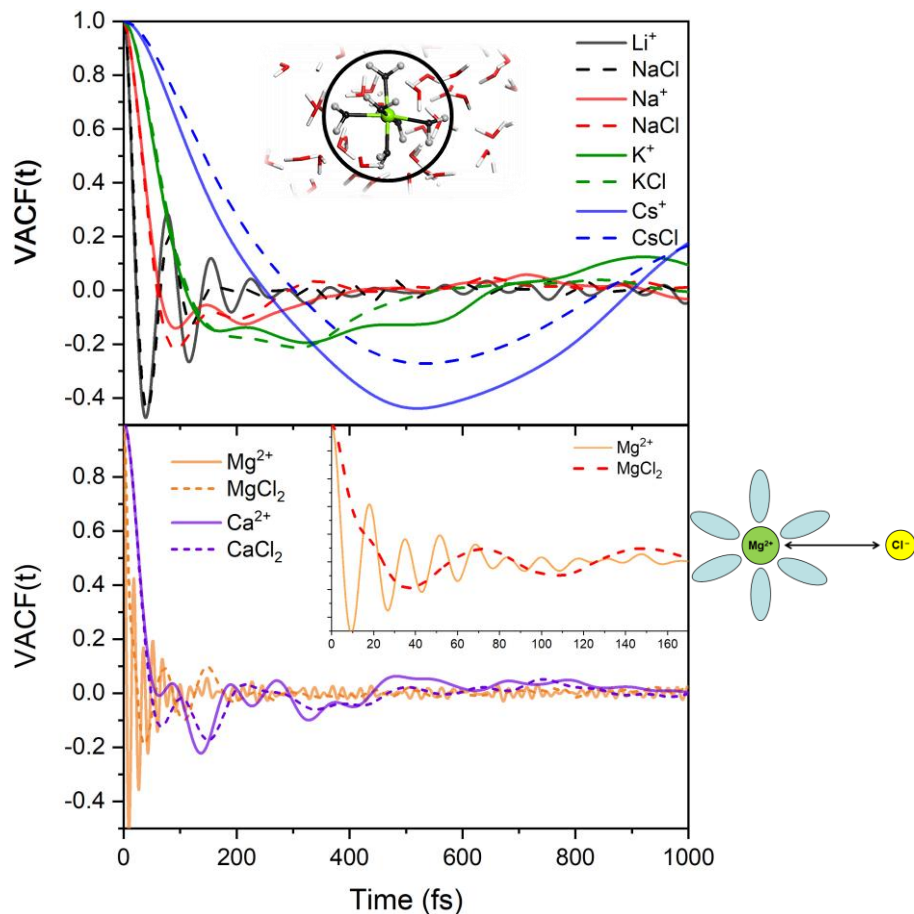
Rule #2

To promote Mg-dehydration (creation of vacant coordination site) an additive should stabilise 5-coordinate $\text{Mg}(\text{H}_2\text{O})_5$

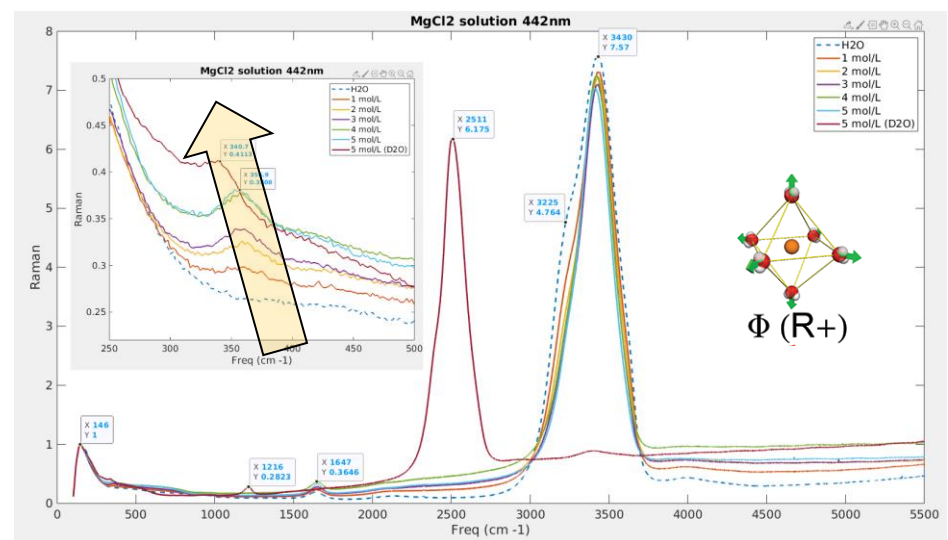


Weakening of the Mg²⁺ “hydration cage”

$$VACF(t) = \frac{1}{N_o} \sum_{j=1}^{N_o} \mathbf{v}_i(t_j) \cdot \mathbf{v}_i(t_j + t)$$



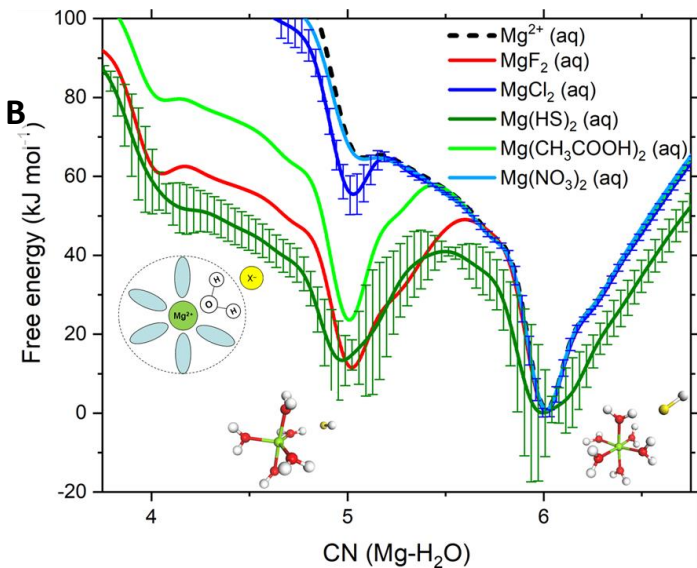
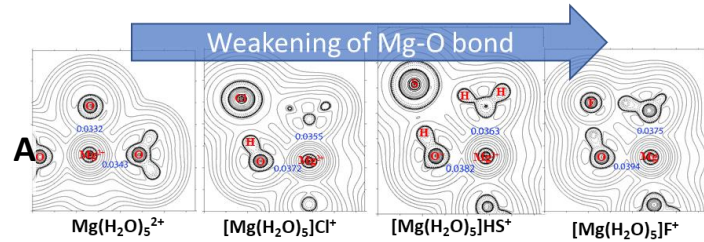
Rule #3
 To make the hydration shell more labile, an additive should **weaken the hydration “cage”** around the Mg²⁺ shell



VACF of cations electrolyte solutions, *ab initio* MD

Raman spectra of MgCl₂(aq). Peaks at 350 cm⁻¹ related to ν₁ MgO₆ symmetric stretching mode

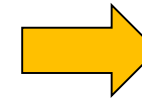
From atomistic description to practical application



Molecular-level information from atomistic simulations and spectroscopic measurements

Molecular-level criteria for solution additives:

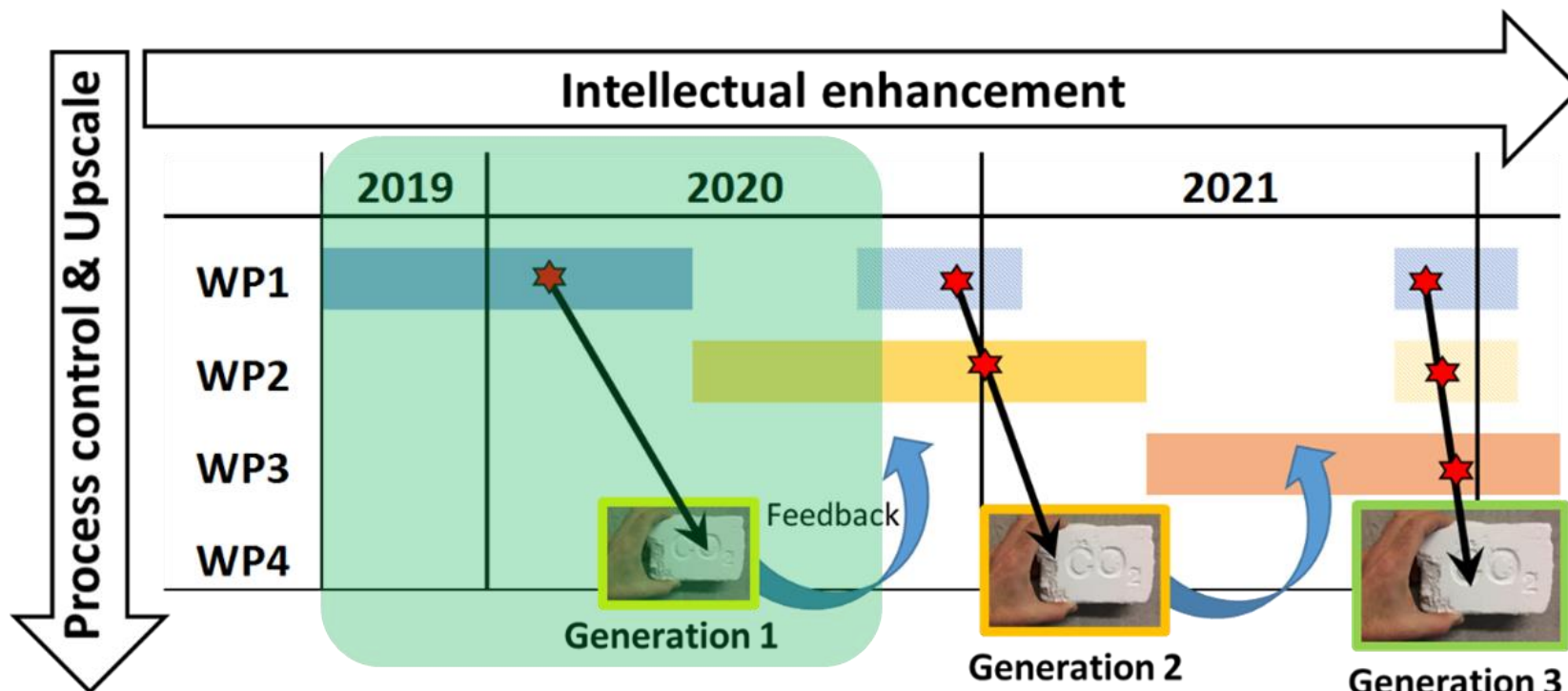
1. Form stable SSHIP with Mg^{2+} or CIP less stable than $Mg^{2+} \dots CO_3^{2-}$
2. Stabilise undercoordinated hydrated Mg^{2+} states
3. Weaken the "cage" hydrated Mg^{2+}



Formula	Additive	Abbreviation
Cl ⁻	Chloride	CL
F ⁻	Fluoride	F
I ⁻	Iodide	I
NO ₃ ⁻	Nitrate	NIT
HCO ₃ ⁻	Bicarbonate	HCO3
CO ₃ ²⁻	Carbonate	CO3
SO ₄ ²⁻	Sulphate	SO4
HS ⁻	Bisulfide	HS
HCOO ⁻	Formate	HCOO
CH ₃ COO ⁻	Acetate	CH3COO
PO ₄ ³⁻	Phosphate	PO4
HPO ₄ ²⁻	Hydrogen Phosphate	HPO4
H ₂ PO ₄ ⁻	Dihydrogen Phosphate	H2PO4
SiO ₃ ²⁻	Metasilicate	SiO3
C ₂ H ₆ NSO ₃ ⁻	Taurate	TAU
C ₂ O ₄ ²⁻	Oxalate	C2O4
C ₇ H ₅ O ₃ ⁻	Salicylate	SAL
C ₆ H ₅ O ₃ ³⁻	Citrate	CIT
C ₂ H ₆ NSO ₃ ⁻	Taurate	TAU
C ₄ H ₆ NO ₄ ²⁻	Aspartate	ASP
C ₄ H ₄ O ₆ ²⁻	Tartrate	TAR
C ₄ H ₄ O ₅ ²⁻	Malate	MAL
C ₆ H ₄ ONH ₂ ⁻	Amino phenolate	PHENAM
C ₂ H ₄ NO ₂ ⁻	Glycinate	GLY
C ₅ H ₈ NO ₄ ⁻	Glutamate	GLU
C ₄ H ₆ NO ₄ ²⁻	Aspartate	ASP
C ₆ H ₅ O ⁻	Phenolate	PHEN
C ₃ H ₇ O ²⁻	Isopropyl alcohol ionic	IPA
C ₈ O ₅ H ₁₆ ²⁻	Polyethylene glycol	PEG
SiF ₆ ²⁻	Hexafluoro Silicate	SIF6

Database of solution additives

Project status



✓ WP1 Mg-dehydration

✓ WP2 Nucleation: ongoing experiments at Grenoble (Raman) and Granada (AFM, TEM, titration)

✓ WP3 Growth

✓ WP4 Upscaling: design of flow cell for in-situ mineralisation neutron experiments; first experiment with prototype at ISIS Neutron Source (UK) in early 2021

Acknowledgements

@FUNMIN_CO2



QMUL

Prof Greg Chass
Dr Dimitrios Toroz
Dr Fu Song

CCC

Mr Michael Evans
Dr Tony Cox
Dr Rob Copcutt

Granada

Prof Encarni Agudo

Grenoble

Prof German Montes

Oviedo

Prof Pedro Alvarez

Utrecht

Prof Mariette Wolthers



This project, FUNMIN, is funded through the ACT programme (Project No 294766). Financial contributions made from BEIS together with extra funding from NERC and EPSRC research councils (UK), ADEME (FR), MINECO-AEI (ES)



Impact Acceleration Account

