

Fe in GGBFS: new insights from laboratory experiments and synchrotron-based investigations

Mancini A.^{1,3}, Wieland E.¹, Lothenbach B.², Geng G.¹, Dähn R.¹, Wehrli B.³

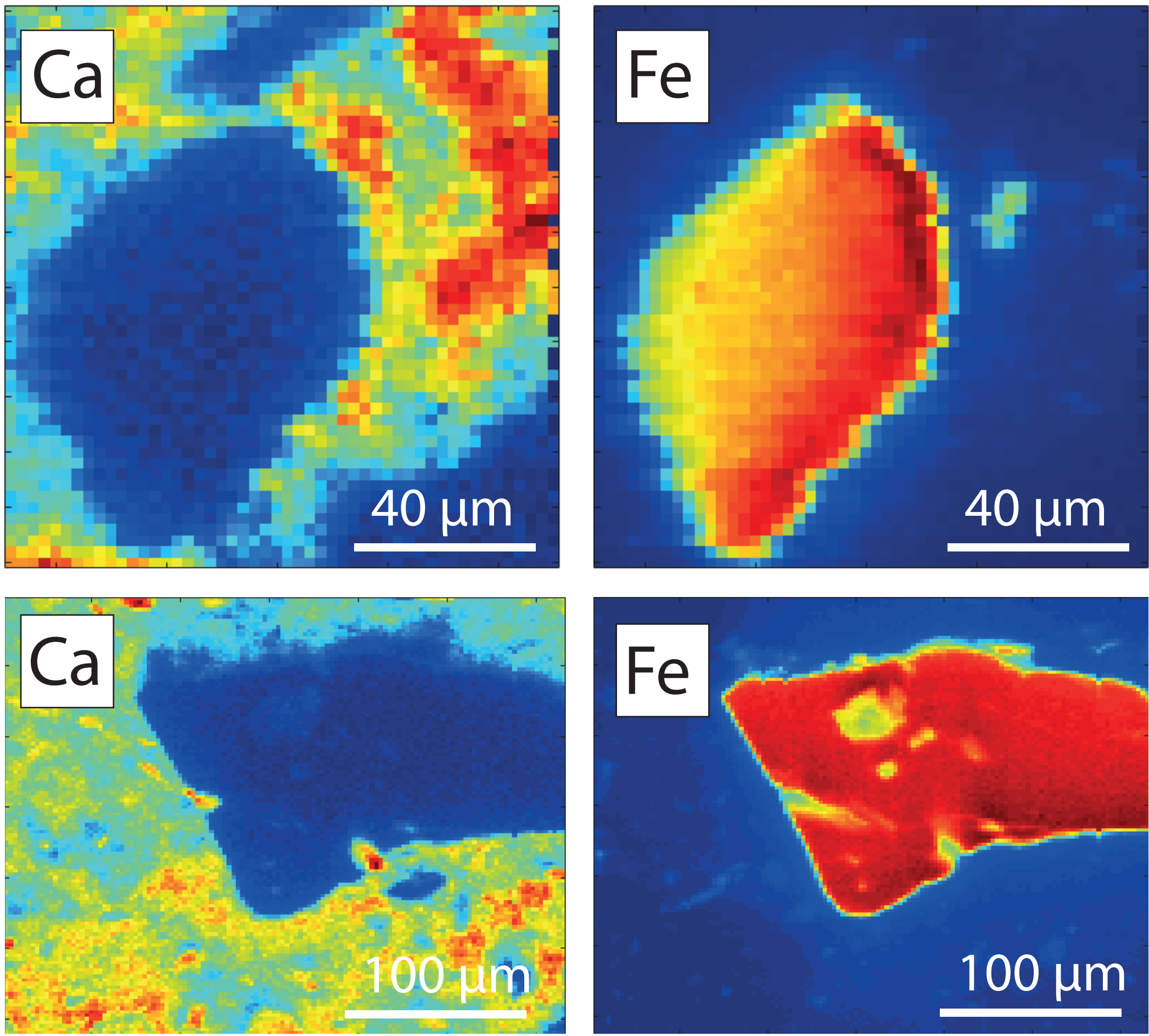
¹Paul Scherrer Institute, Laboratory for Waste Management, Villigen, Switzerland

²Empa, Laboratory for Concrete & Construction Chemistry, Dübendorf, Switzerland

³ETH Zurich, Institute of Biogeochemistry and Pollutant Dynamics, Zurich, Switzerland

Slag blended cements

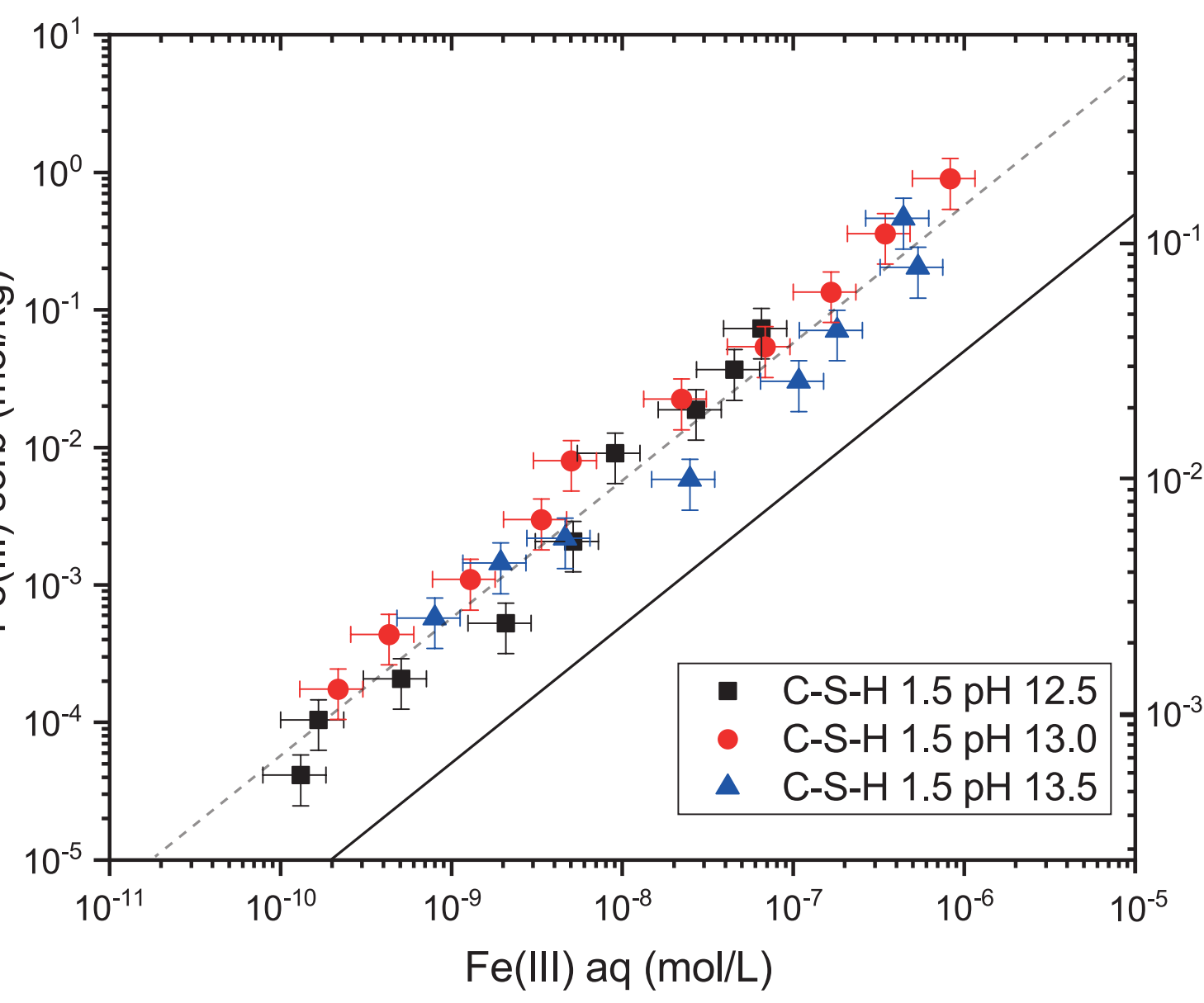
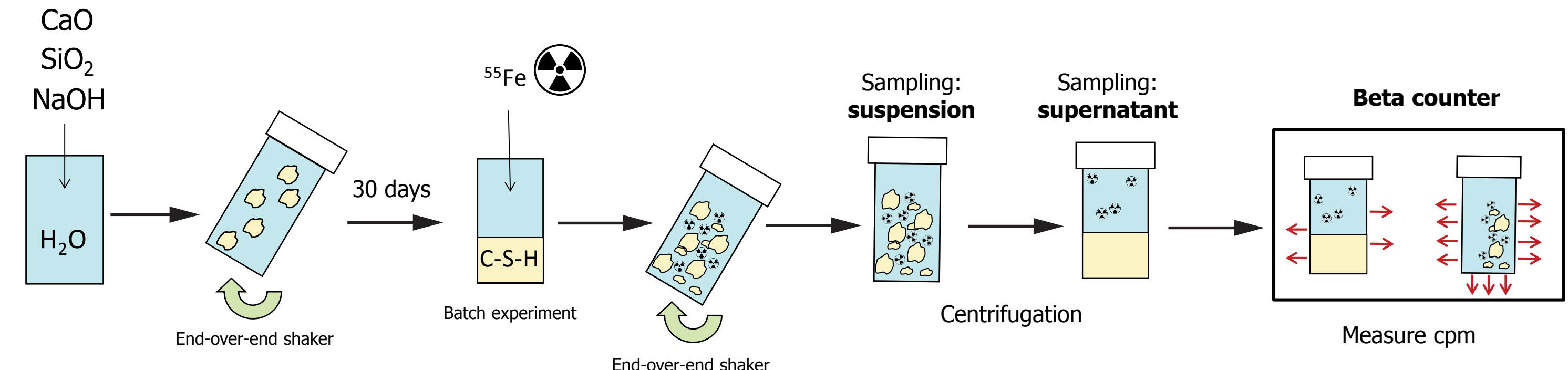
To reduce CO₂ emission, **cement is blended with inorganic** supplementary cementitious materials (fly ash, pozzolans, blast furnace slag,...), which partially replace the clinker phases. **Blast furnace slags** are a by-product of the iron- and steel-making industry and can contain a substantial amount of Fe(0) (ca. 4%), which is present as micron-sized particles^[1].



With time, these iron particles (Fe(0)) will undergo oxidation (corrosion), which can be accelerated under particular environmental conditions. However, the **rate** of corrosion, the generated **corrosion products**, and the **interactions with cement phases** are **poorly known**. These information are crucial to predict the long-term behaviour, hence the durability, of slag cements.

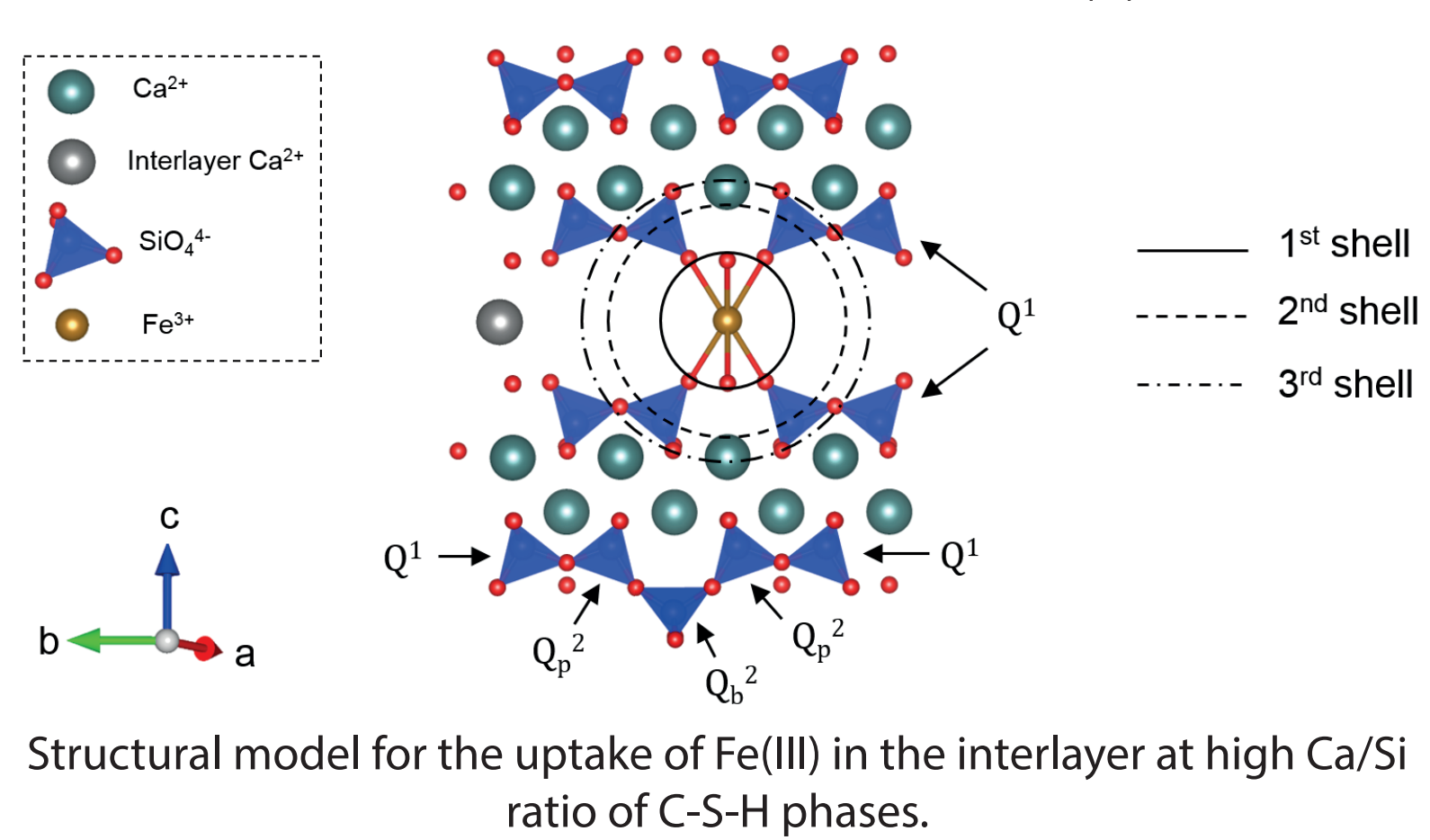
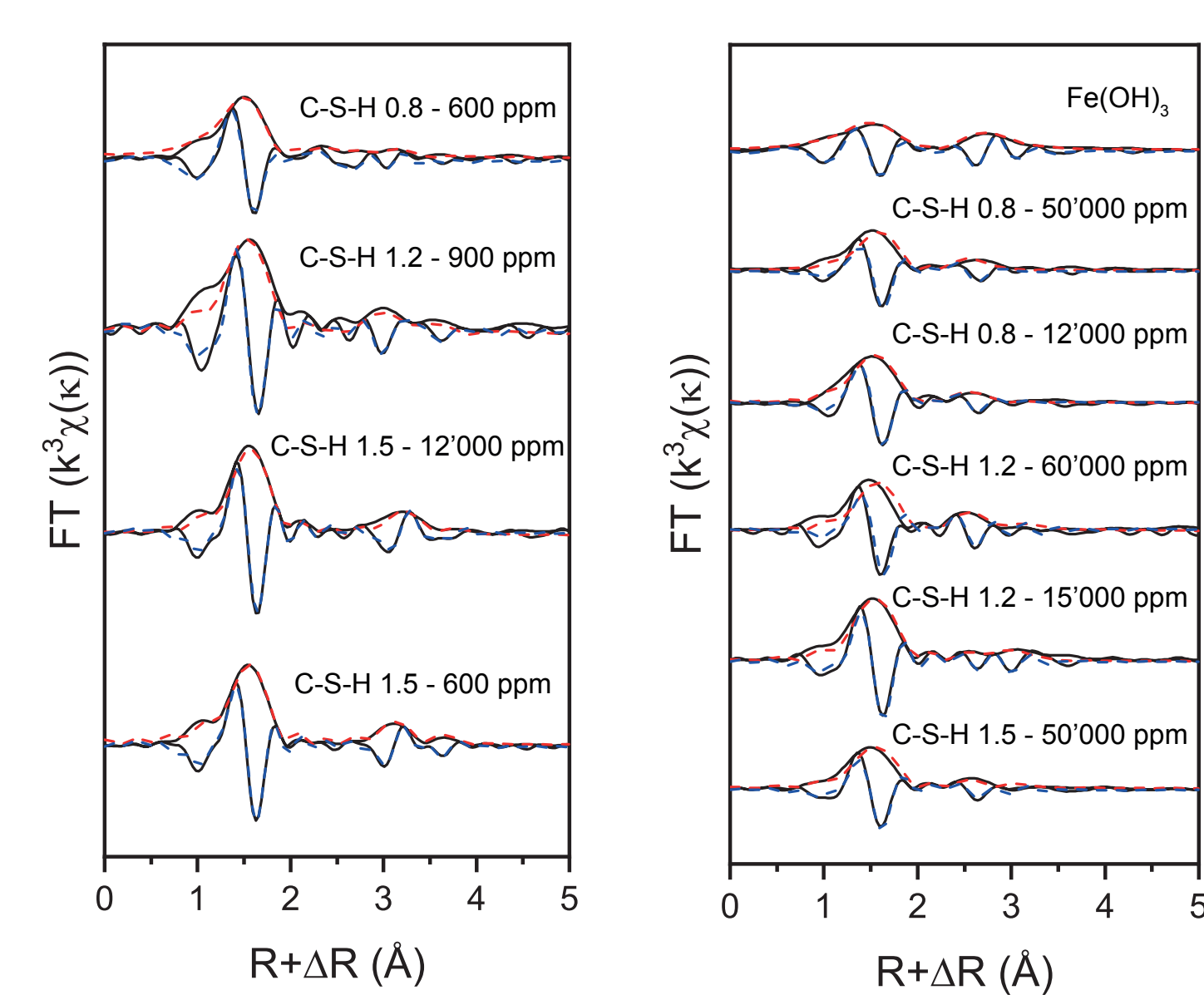
Wet chemistry experiments - Fe uptake by C-S-H

Sorption experiments were carried out using ⁵⁵Fe as the radiotracer in order to determine the Fe(III) uptake by C-S-H phases.



²⁹Si NMR and EXAFS measurements on C-S-H loaded with different Fe(III) concentrations provided evidences that **Fe(III) substitutes interlayer Ca(II)** at high Ca/Si ratio of C-S-H. On the other hand, at low Ca/Si ratio Fe(III) does not substitute in the interlayer (structural incorporation or formation of a secondary phase). At higher concentrations, Fe(III) precipitates as Fe(OH)₃.

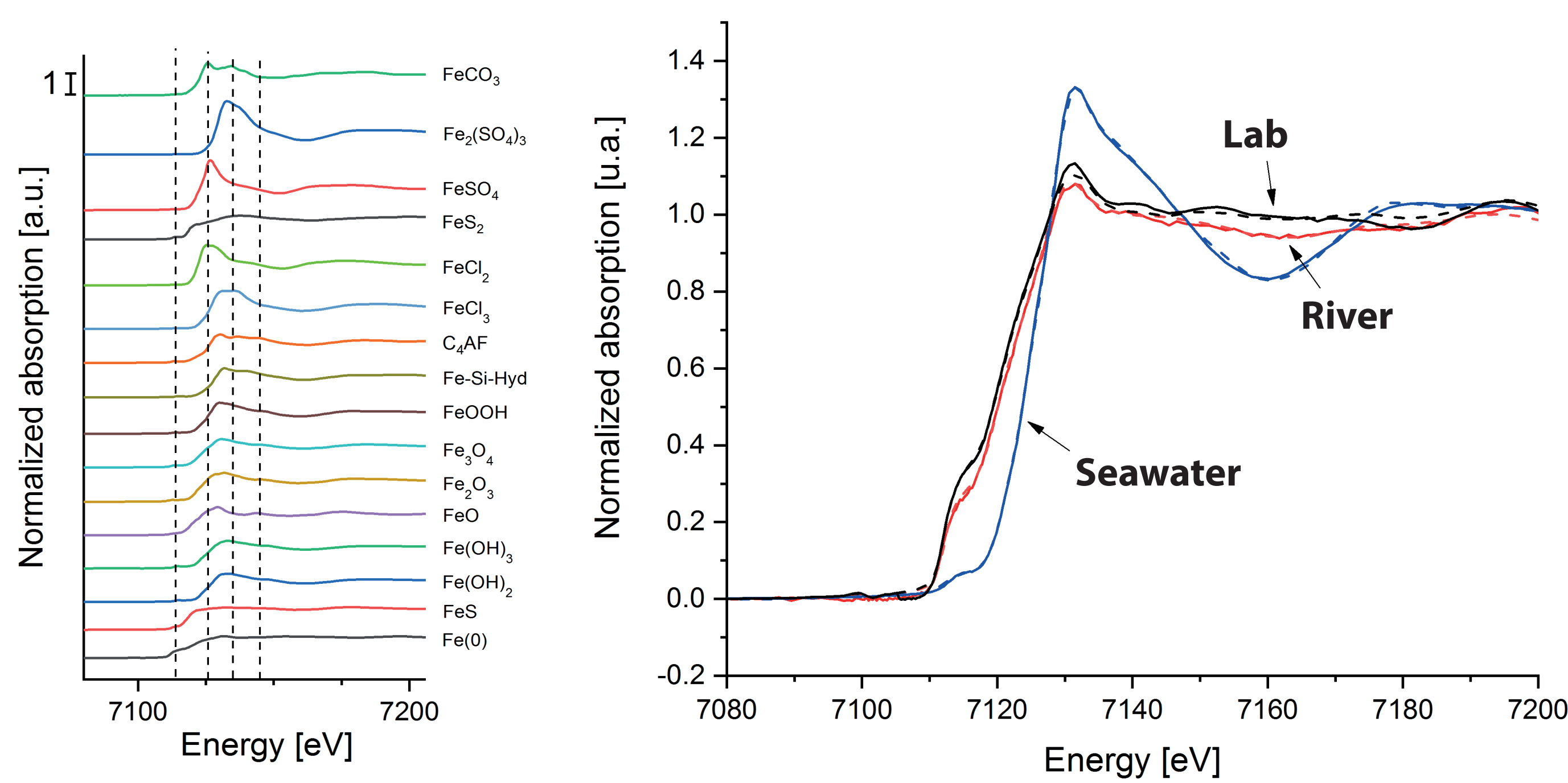
Sorption experiments show a continuous uptake of Fe(III) by C-S-H with increasing Fe(III) concentration. The uptake is not pH dependent.



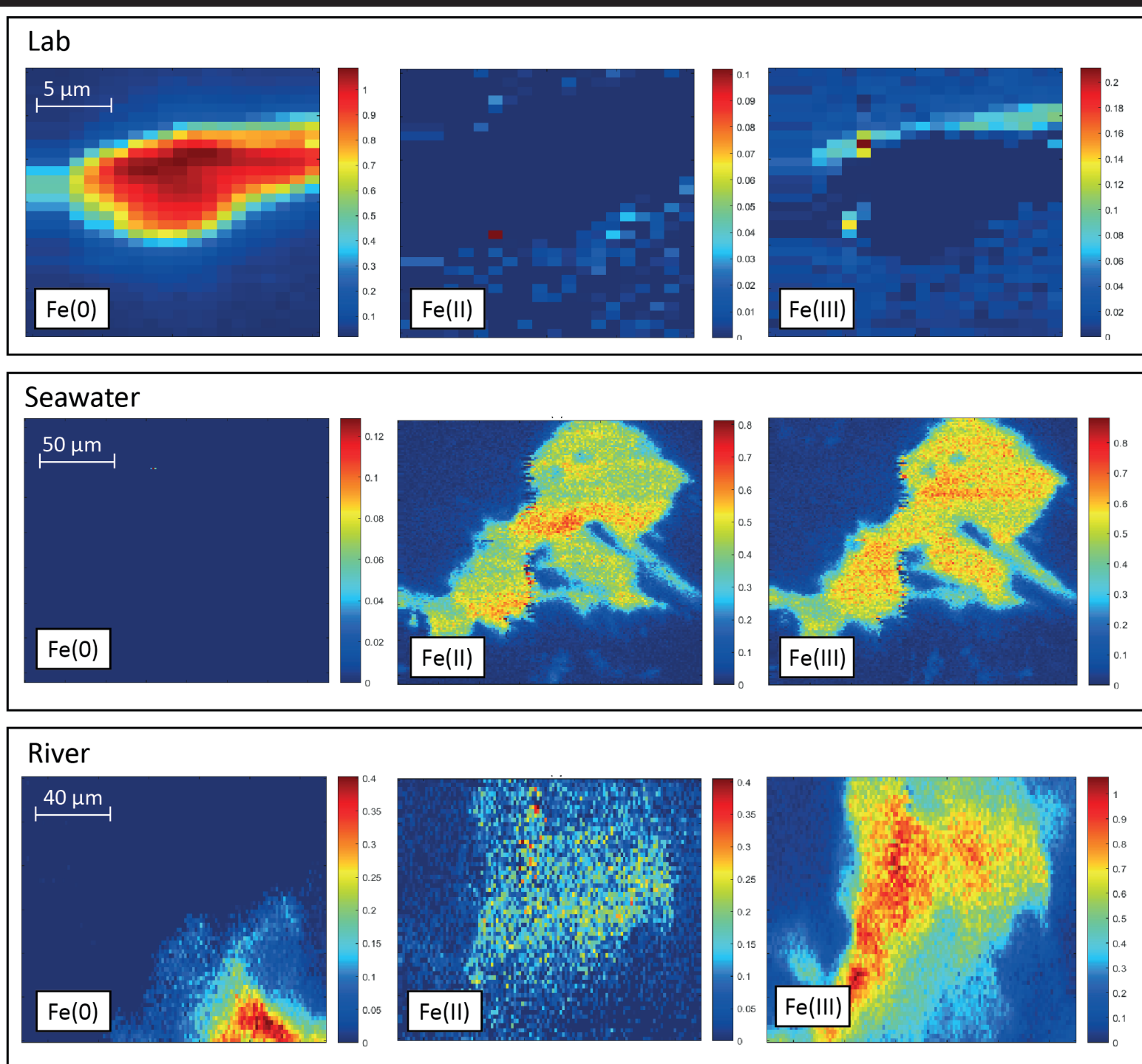
Corrosion in cement

Three different slag-containing cement samples (CEM III/B) exposed to different environmental conditions and different times were analyzed:

1. **Lab**: exposed to laboratory conditions for 6 yr
2. **Seawater**: bridge exposed to marine conditions (Denmark) for 34 yr
3. **River**: bridge exposed to fresh water (Germany) for 7 years



	Fe(0)	FeO	FeS	Fe ₂ O ₃	F ₃ O ₄	FeOOH	FeCl ₃	Fe-Si-Hyd	R-Factor
Lab	0.63(2)	-	0.10(2)	-	0.11(2)	-	-	-	0.0002
Seawater	-	0.15(1)	-	0.27(3)	-	-	0.10(1)	0.48(1)	0.0026
River	0.82(1)	-	0.06(1)	-	-	0.12(2)	-	-	0.0014



	Nr.	Fe(0)	FeO	FeS	Fe ₂ O ₃	F ₃ O ₄	FeOOH	FeCl ₂	Fe-Si-Hyd	Fe(OH) ₂	R-Factor
Lab	2	0.85(2)	-	-	-	0.15(3)	-	-	-	-	0.0012
Lab	3	0.90(1)	-	0.10(1)	-	-	-	-	-	-	0.0010
Seawater	5	-	0.61(3)	-	-	-	0.11(2)	0.28(2)	-	-	0.0025
Seawater	8	-	-	-	0.28(2)	-	-	0.30(1)	0.42(2)	-	0.0034
River	10	1	-	-	-	-	-	-	-	-	0.0012
River	11	-	-	-	-	-	0.39(2)	-	0.14(2)	0.47(4)	0.0005

- Lab and River samples have very similar XAS spectra --> Fe(0) rich
- Seawater sample has no Fe(0) --> strong corrosion
- Corrosion can be accelerated by chloride (detected in XAS and XRD)
- Results confirmed by different analytical techniques

Conclusions

- Fe(III) is strongly sorbed by C-S-H phases; only at high Fe(III) concentrations Fe(OH)₃ precipitate
- At high Ca/Si ratio, Fe(III) substitute Ca(II) in the interlayer, while at low Ca/Si ratio it is structurally incorporated into C-S-H (not in the interlayer) or it precipitates as a secondary phase
- Fe(0) corrosion is strongly influenced by environmental conditions and it is accelerated in presence of chloride

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Literature:
¹ Bernal et al., 2014 Mater. Chem. and Phys. 146: 1-5