

Chloride green rust as scavenger of technetium: Immobilization and spectroscopic studies

Natalia Mayordomo¹, André Rossberg^{1,2}, Diana M. Rodríguez¹, Dieter Schild³,
Andreas C. Scheinost^{1,2}, Vinzenz Brendler¹, and Katharina Müller¹.

¹Helmholtz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology, 01328 Dresden, Germany

²The Rossendorf Beamline, European Synchrotron Radiation Facility, 38034 Grenoble Cedex, France

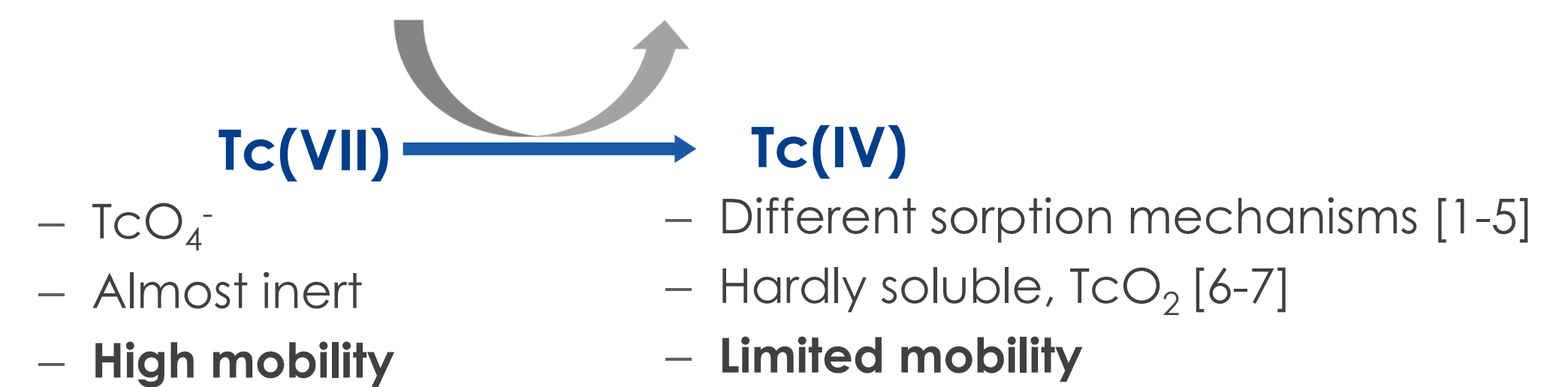
³Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, 76344 Eggenstein-Leopoldshafen, Germany

⁹⁹Tc as fission product in the environment of a repository for high level radioactive waste

- Long half-life ($\tau_{1/2} = 0.213$ Ma)
- Poorly retained by the natural and technical barriers in the repository

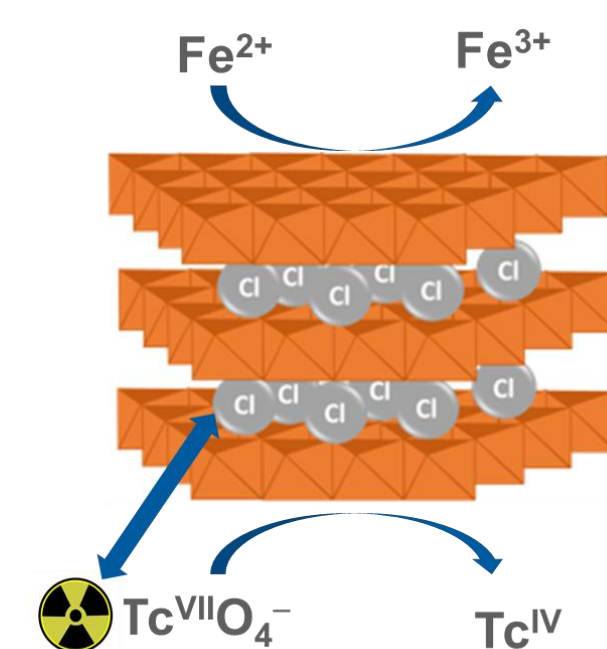
Improving knowledge about their **solubility** and **retention** can reduce conservatism and uncertainty in long-term safety assessment

Reductant in aqueous solutions or interfaces



Chloride green rust (GR-Cl)

- Corrosion product of iron \rightarrow near-field of repository
- Synthesized by coprecipitation of Fe^{II} and Fe^{III} at pH 9
- Specific surface area 55.8 m²/g
- Isoelectric point at pH 9.0



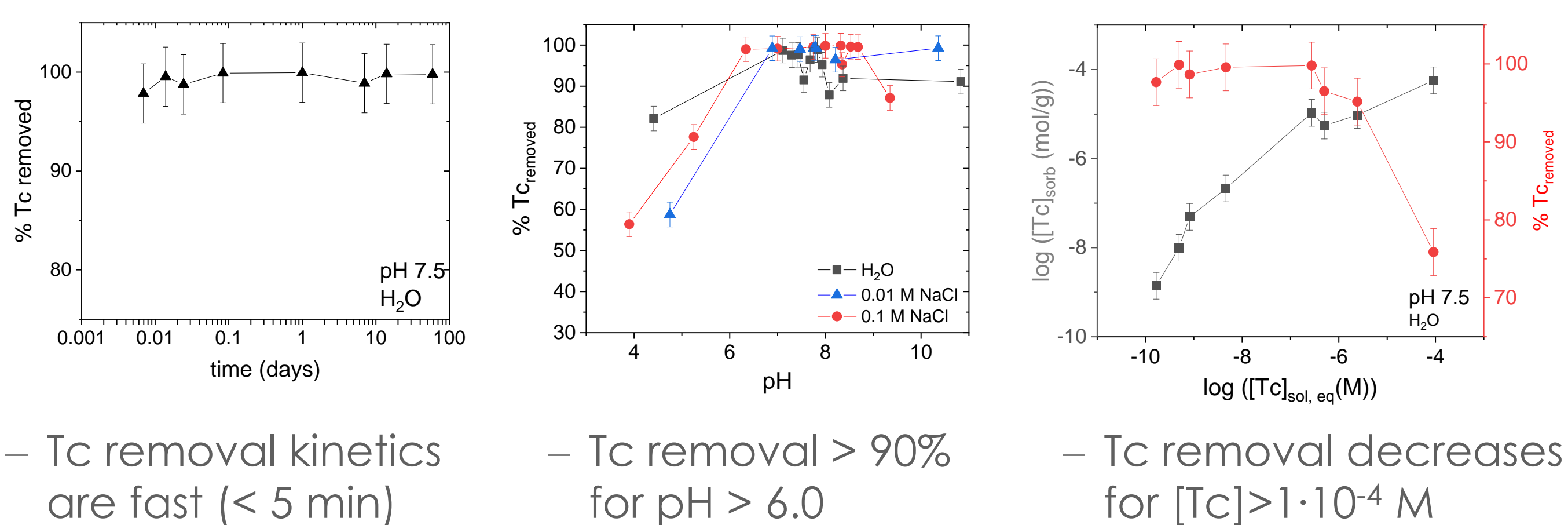
Tc sorption mechanisms on GR

- Tc^{VII} **anion exchange**
- Fe^{2+} in the structure \rightarrow **reductive immobilization**
- Sorption of reduced $Tc^{IV} \rightarrow$ **surface complexation, precipitation, incorporation**

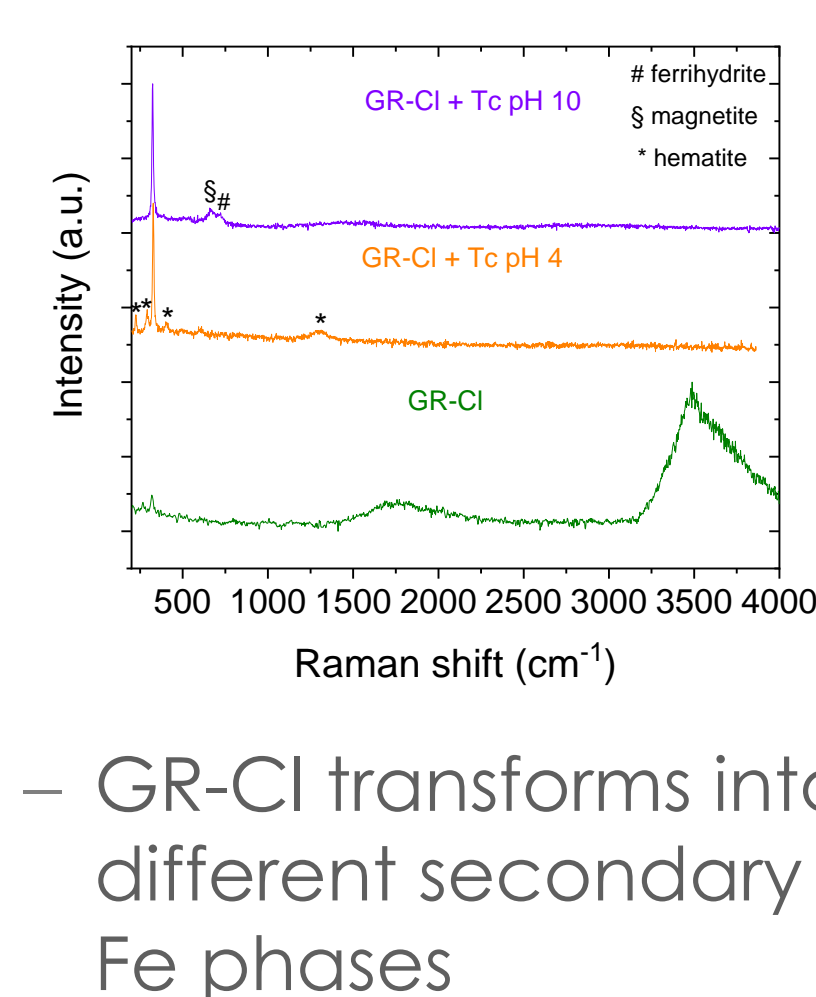
Improve knowledge of Tc immobilization by GR under a wider range of chemical conditions than [8]

Results

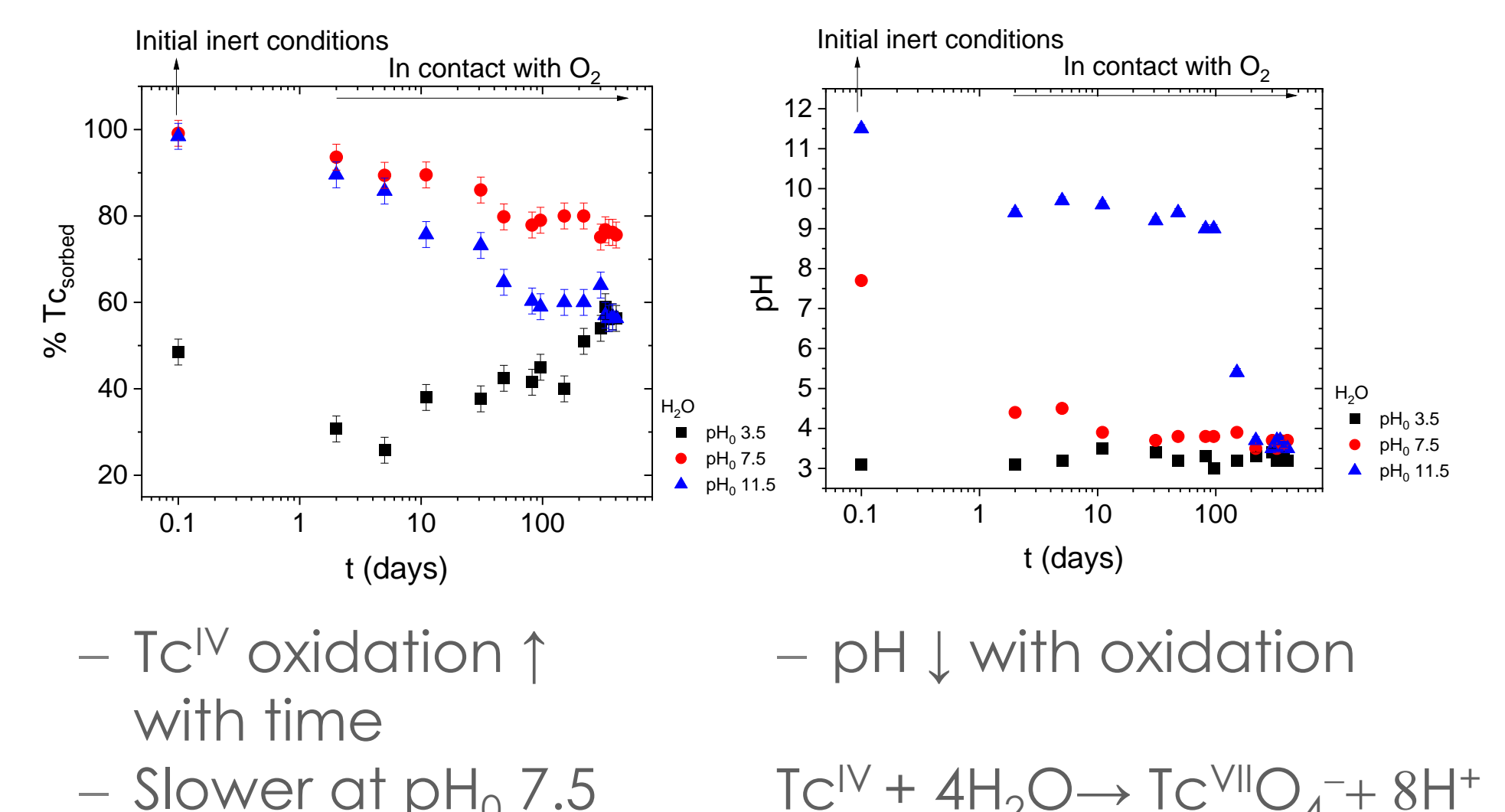
Contact experiments of Tc^{VII} with GR-Cl



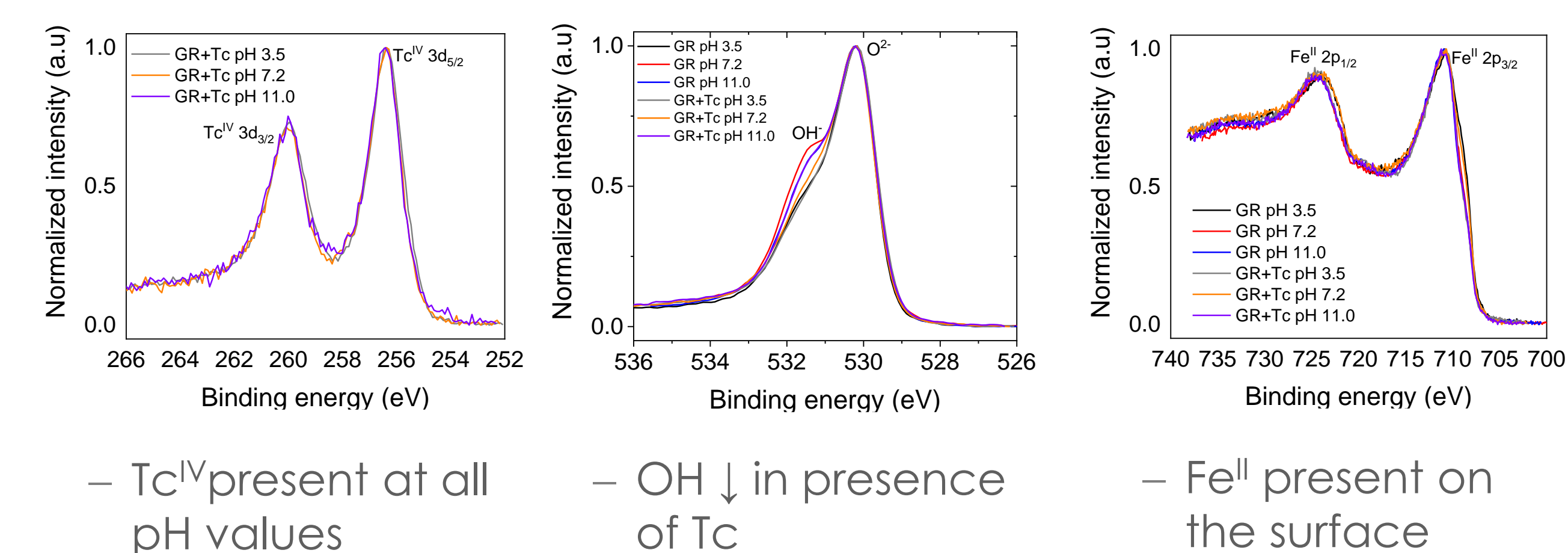
Raman



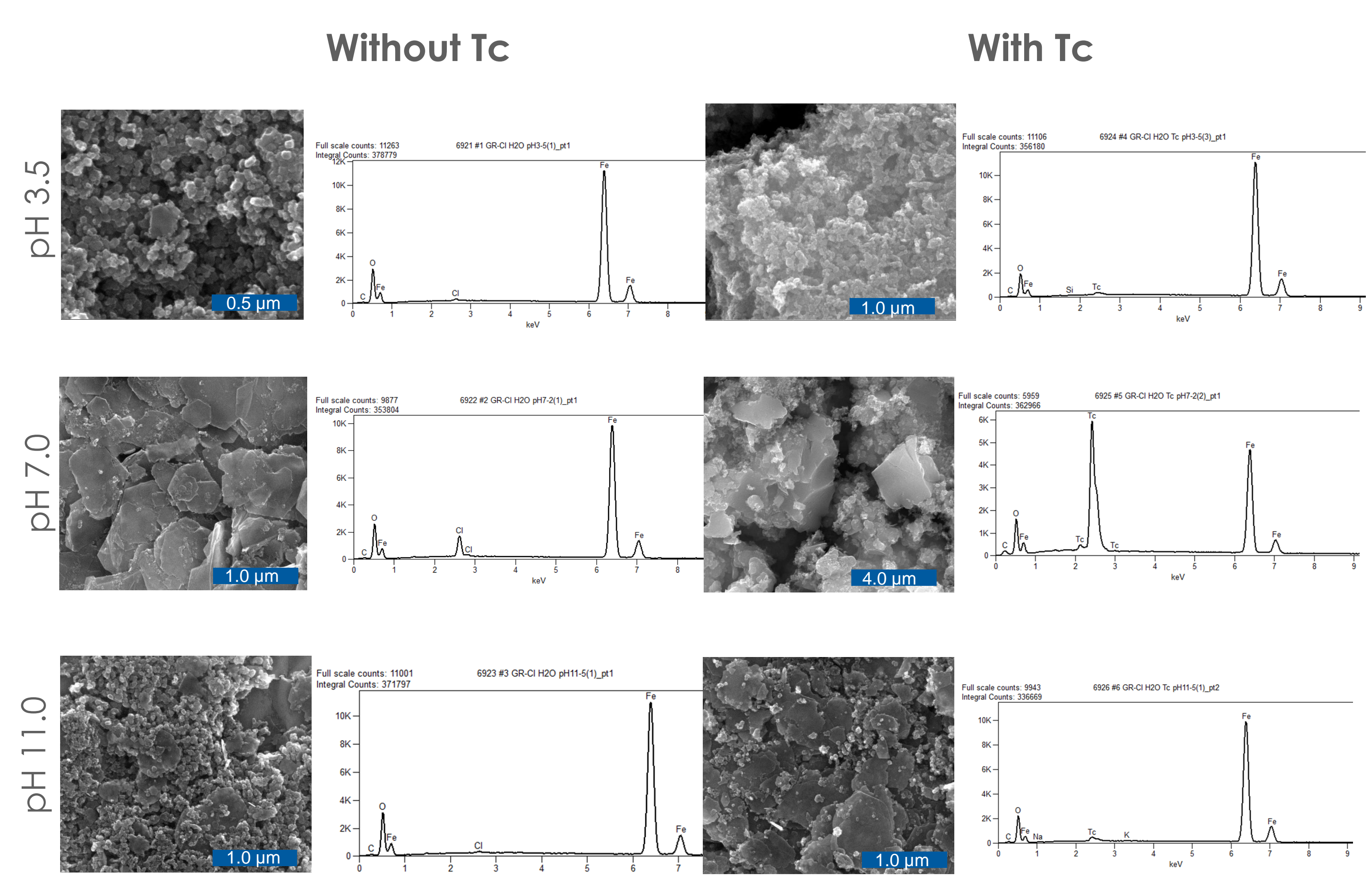
Tc^{IV} re-oxidation experiments



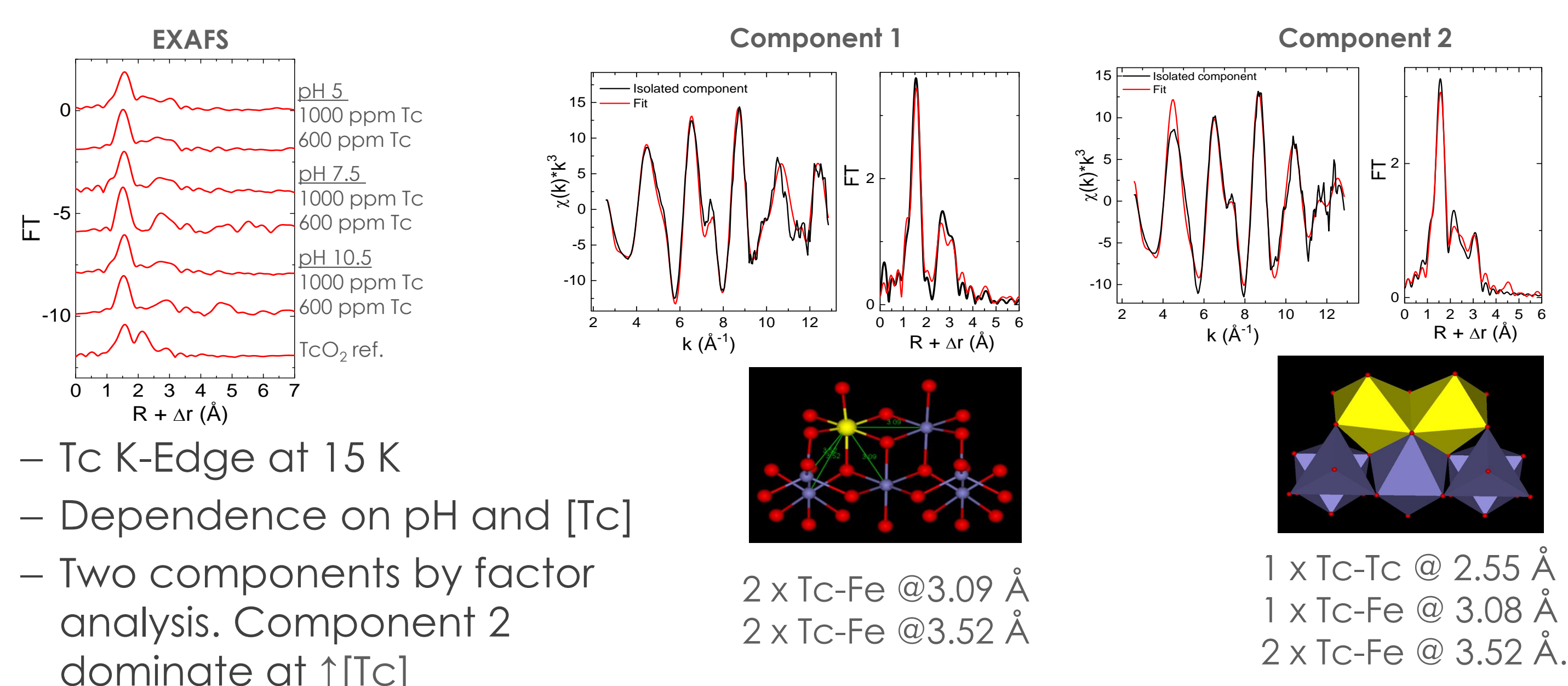
X-ray photoelectron spectroscopy



Scanning electron microscopy



X-ray absorption spectroscopy



Conclusions

- GR-Cl removes Tc by reductive immobilization
- Tc immobilization is quantitative despite of GR-Cl transformation into other Fe-mineral phases with pH and Tc presence
- Tc interaction with the solid occurs through two different mechanisms, including Tc^{IV} monomer and Tc^{IV} dimer surface complexation
- **The presence of GR-Cl in the near-field of the nuclear waste repository ensures the retardation of Tc**

References and acknowledgments

- [1] Rodríguez, D. M. *et al. Env. Sci. Technol.* 54, 2678–2687 (2020).
- [2] Rodríguez, D. M. *et al. Chemosphere* 281, 130904 (2021).
- [3] Mayordomo, N. *et al. J. Hazard. Mater.* 388, 122066 (2020).
- [4] Mayordomo, N. *et al. Chem. Eng. J.* 408, 127265 (2021).
- [5] Yalçınbaş, E. *et al. Dalton Trans.* 45, 17874–17885 (2016).
- [6] I. Baumann, A. *et al. App. Geochemistry* 98, 321–330 (2018).
- [7] Duckworth S. B. *et al. Radiochim. Acta* 109(9), 681 (2021)
- [8] I. Pepper, S. *et al. J. Colloid Interface Sci.* 2003, 268, 408–412.
- [9] TecRad webpage <https://www.hzdr.de/db/Cms?pNid=1375>.



Young investigator group [9]



VESPA II project <https://vespa2.grs.de>

Funding acknowledged from
Federal Ministry of Education and Research
02NUK072

Funding acknowledged from
Federal Ministry for the Environment, Nature Conservation and Nuclear Safety
02E11607B

