

Reductive immobilization of ⁹⁹Tc(VII) by pyrite and marcasite

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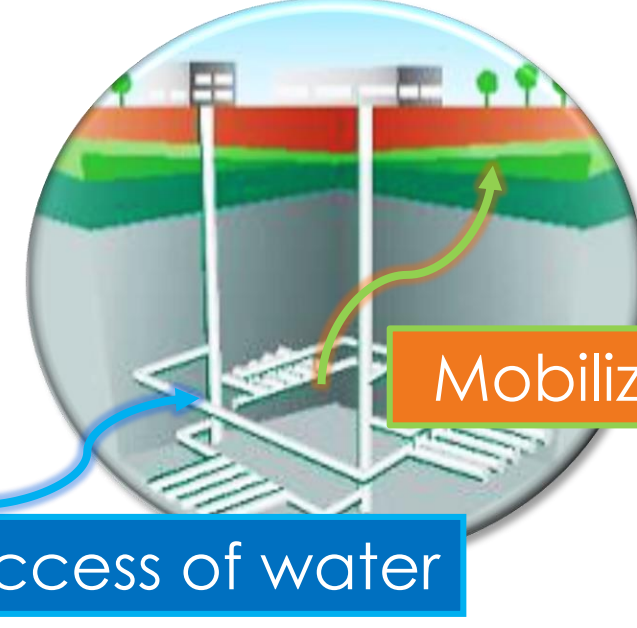
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Fission products (FPs) in the environment of a repository for high level radioactive waste

FPs main part of resulting additional dose in the biosphere:
¹³⁵Cs, ¹²⁹I, ⁹⁹Tc, ⁷⁹Se, ³⁶Cl, ¹⁴C
→ poorly retained by the natural and technical materials in the repository

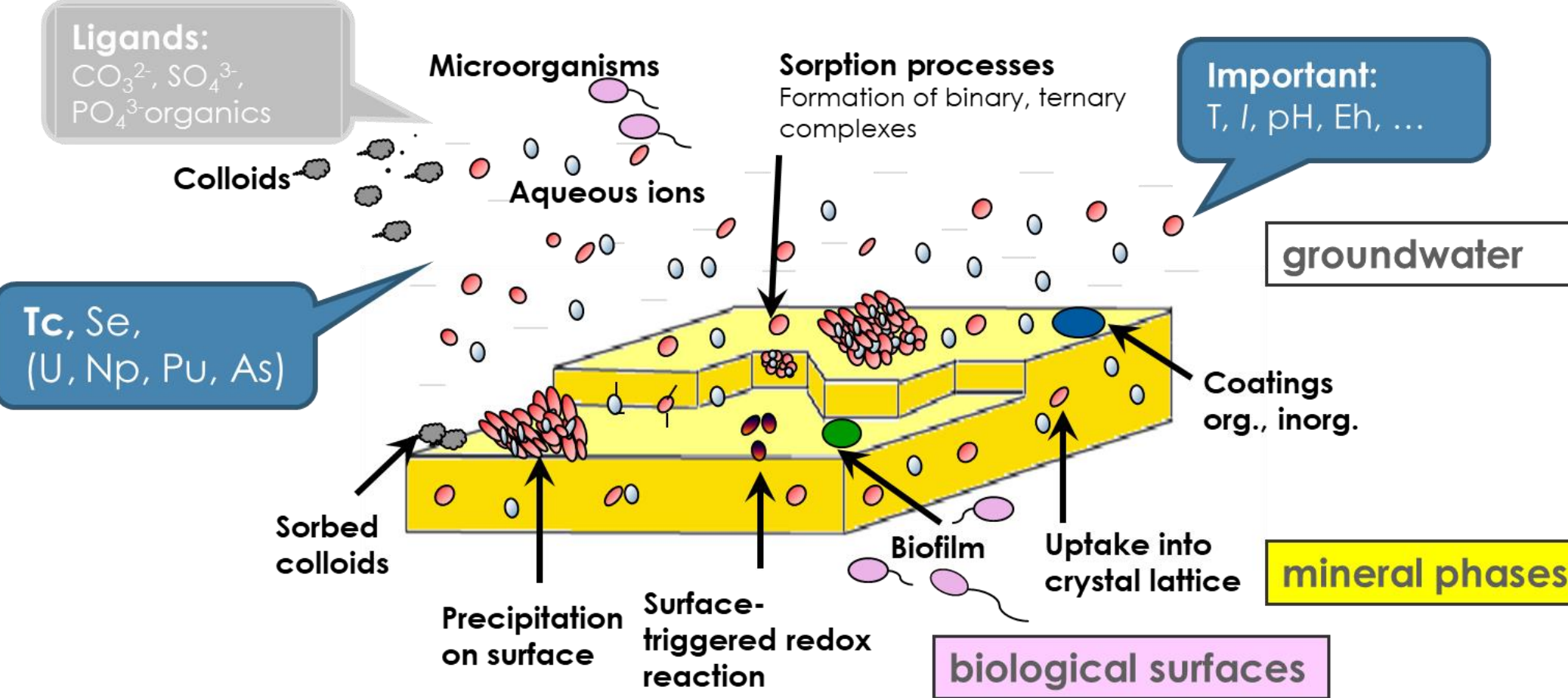


Improving the level of knowledge about their **solubility** and **retention** can, if taken into account in the long-term safety analysis, lead to a significant reduction in uncertainty.

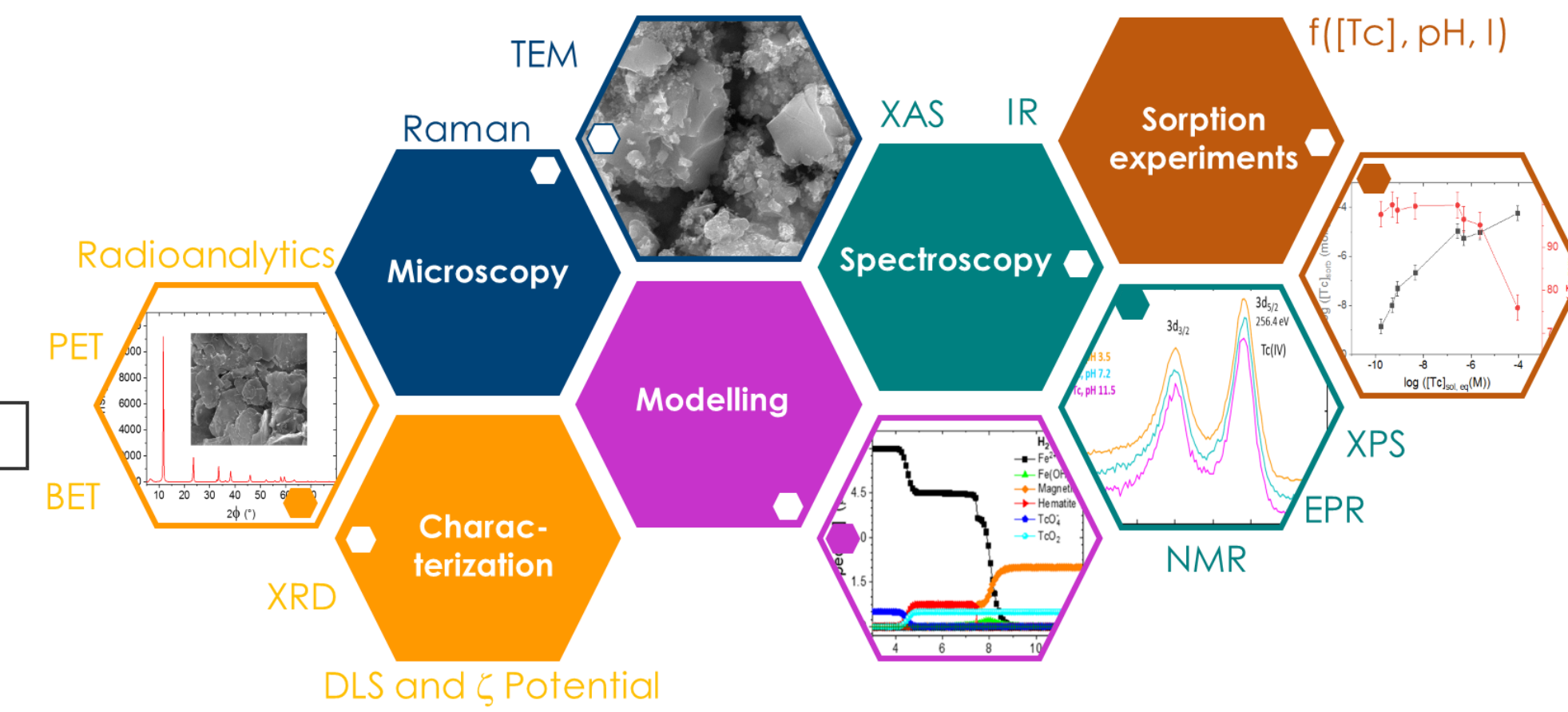
Mobility of contaminants at water-mineral interfaces

Environmental safety assessment

- To consider **all** processes comprehensively
- Thermodynamic databases need **species verification**

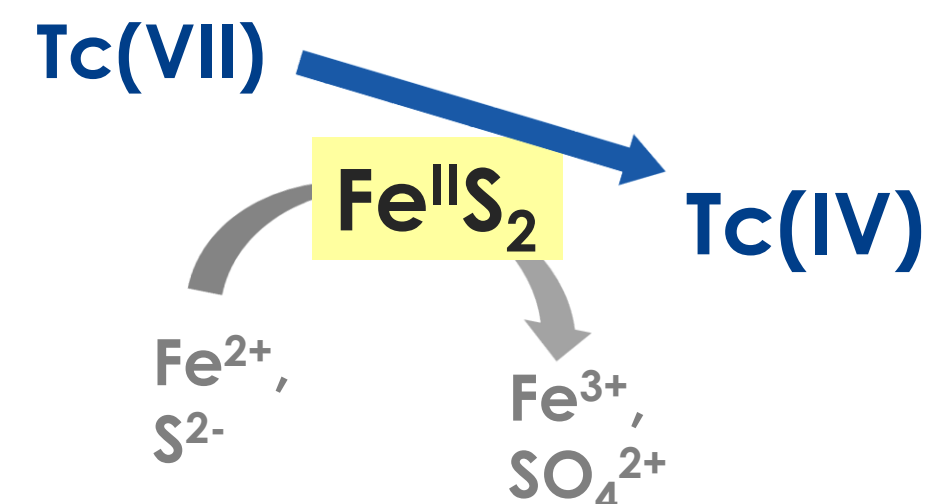


Tool box for comprehensive molecular understanding



Hypothesis

- Tc^{VII}O₄⁻
- Almost inert
- **High mobility**

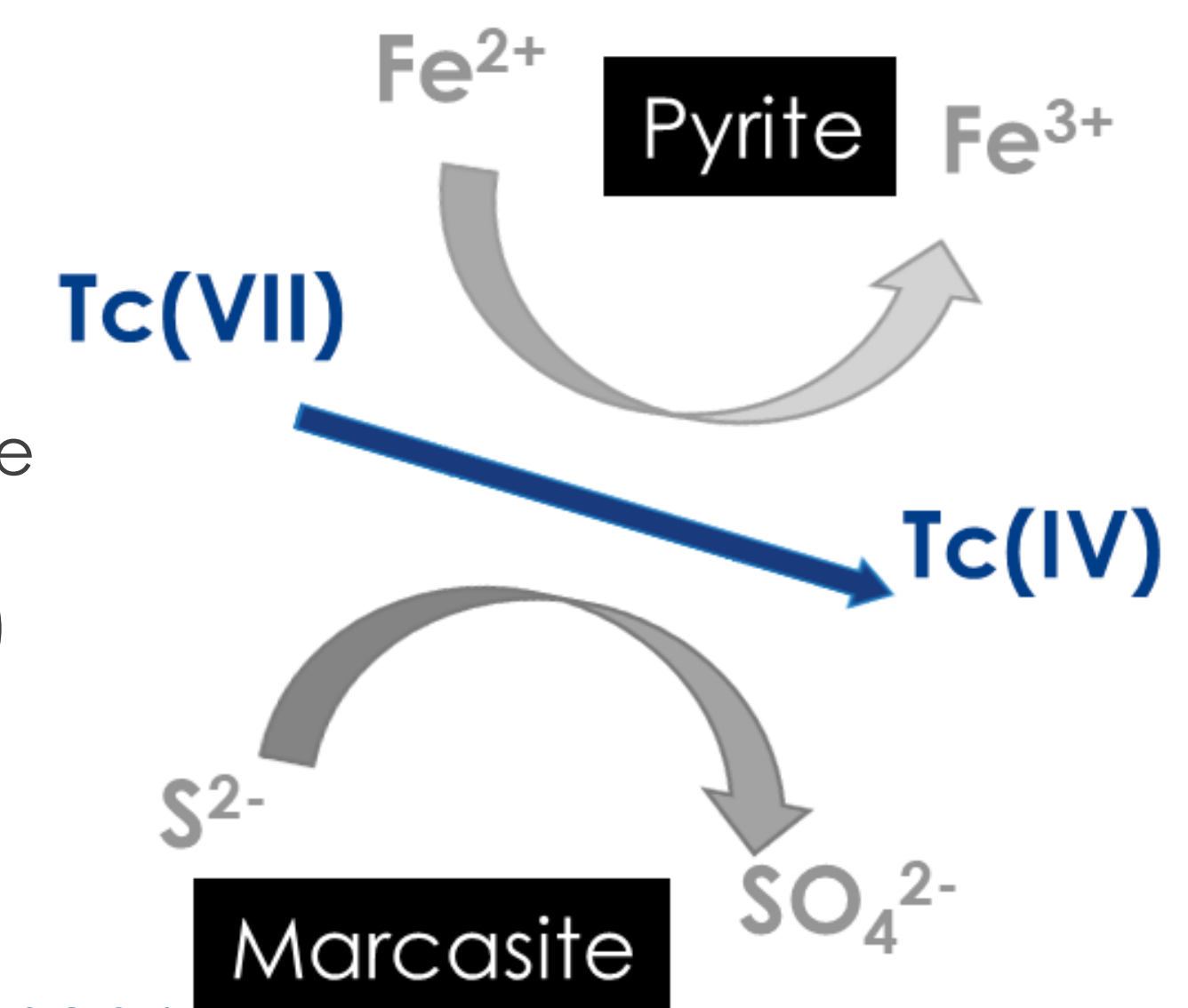


- Hardly soluble, TcO₂
- Precipitated, sorbed or incorporated 1,2,3,4
- **Reduced mobility**

- Fe(II) sulphur minerals are ubiquitous minerals and very redox sensitive
- Mackinawite (FeS) showed excellent Tc immobilization capabilities 5,6
- Due to the repository conditions, FeS₂ will be formed as pyrite and marcasite

Conclusions & Outlook

- Tc removal by FeS₂ minerals is driven by the reduction from Tc(VII) to Tc(IV)
- Pyrite shows a higher affinity for Tc than the mixture, suggesting that marcasite inhibits the Tc uptake
- Different redox functionalities (Fe²⁺ and S²⁻) are responsible
- pH dependent retention mechanisms on both FeS₂

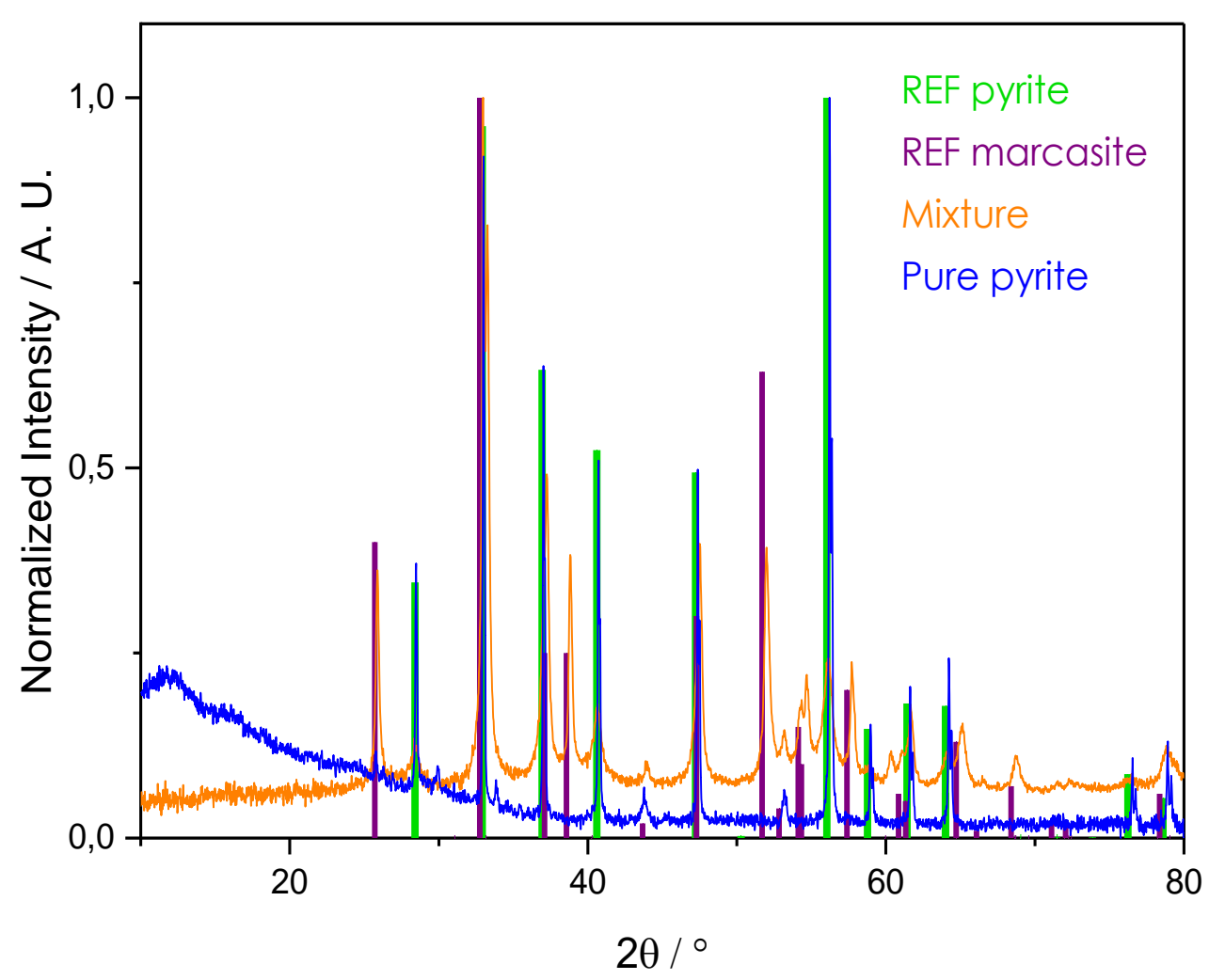


Surface-mediated reduction of Tc(VII) to Tc(IV) followed by retention reactions on mineral surfaces

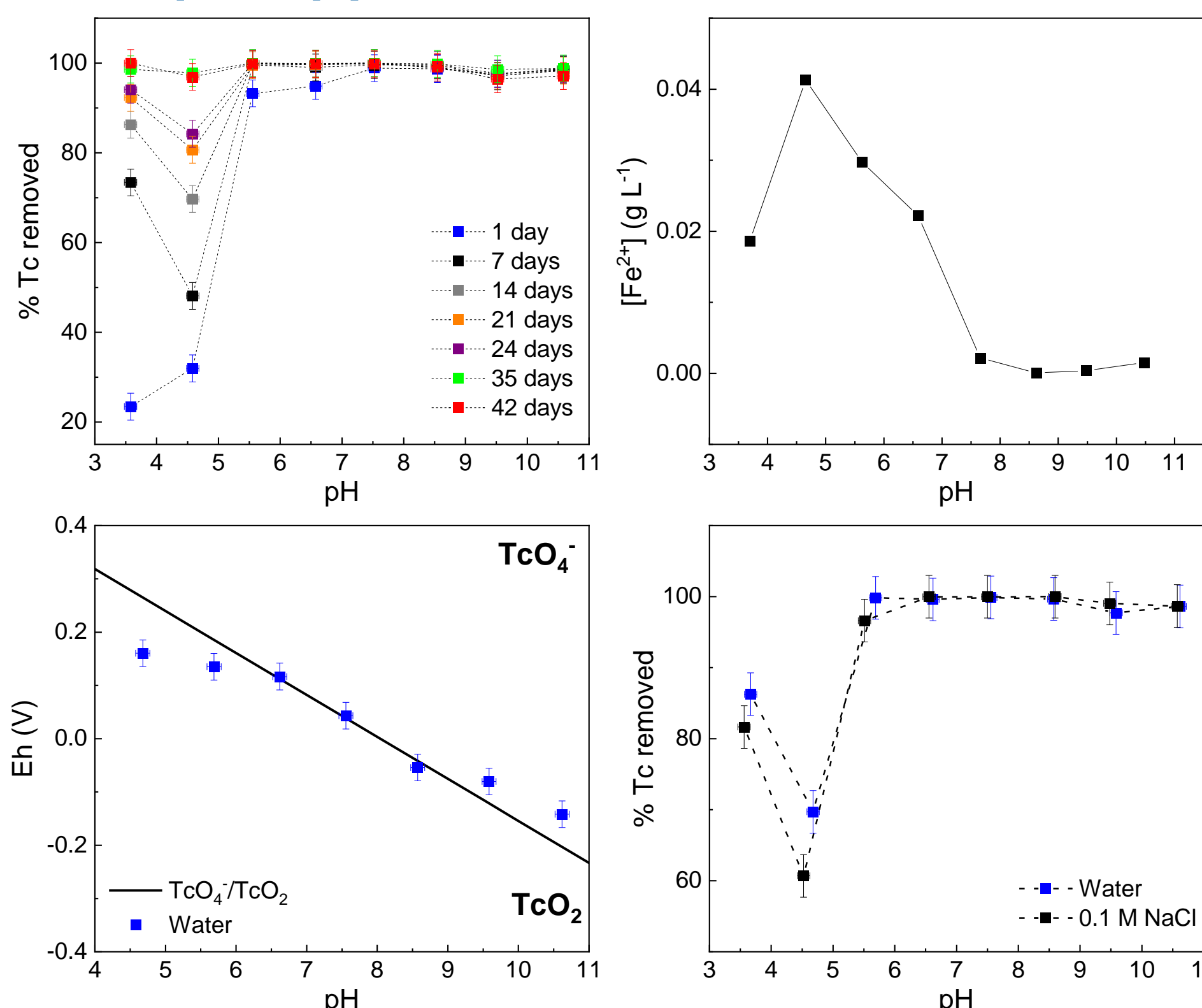
Reduced Tc mobility is expected in the near- and far-field of nuclear waste repositories where FeS₂ is abundant

Characterization of Fe(II) sulfides

Pure pyrite: BET = 2.0 m² g⁻¹, pH_{IEP} = 7.9
Mixture 60:40 marcasite-pyrite: BET = 5.3 m² g⁻¹, pH_{IEP} = 7.4

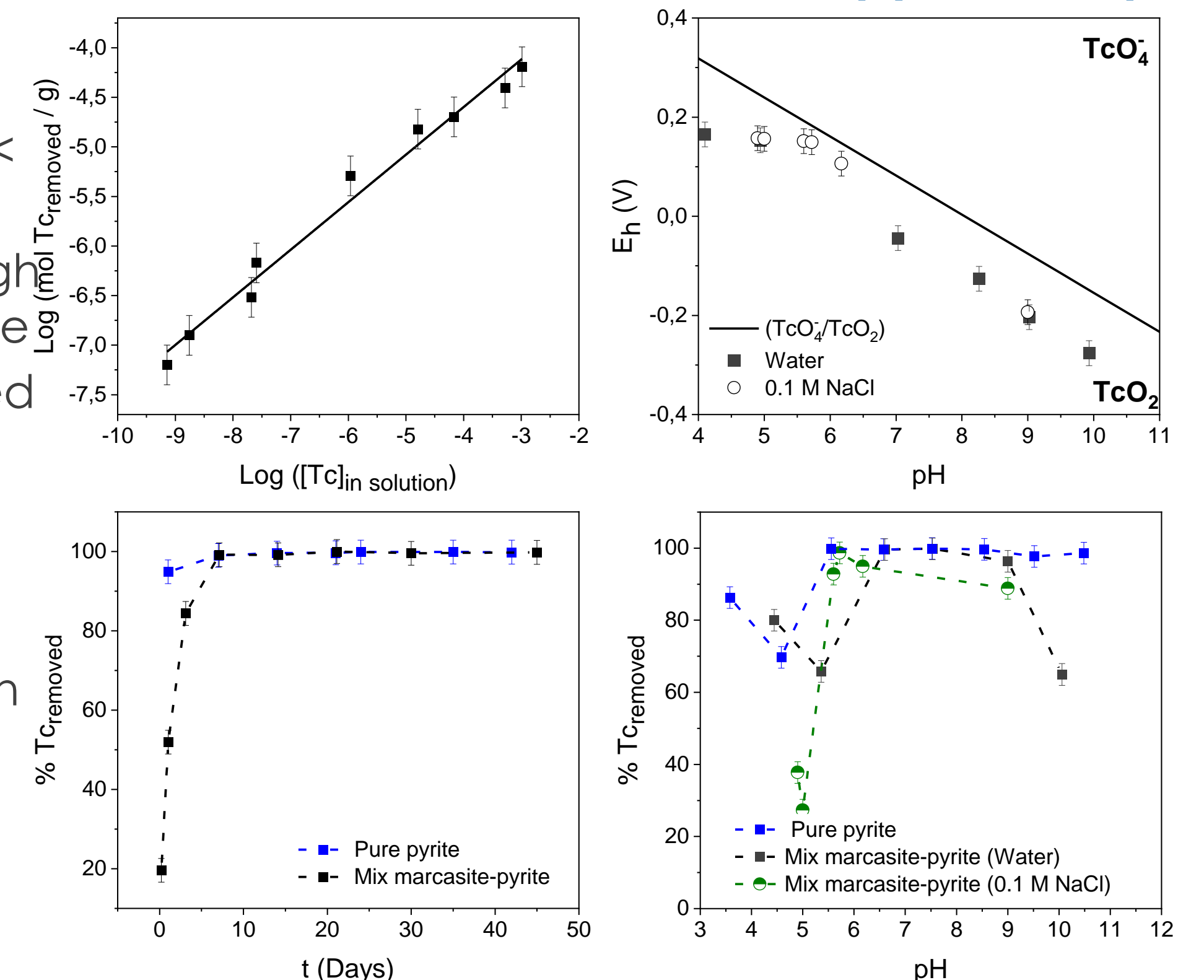


Batch retention experiments of Tc(VII) on pure pyrite 7 ...

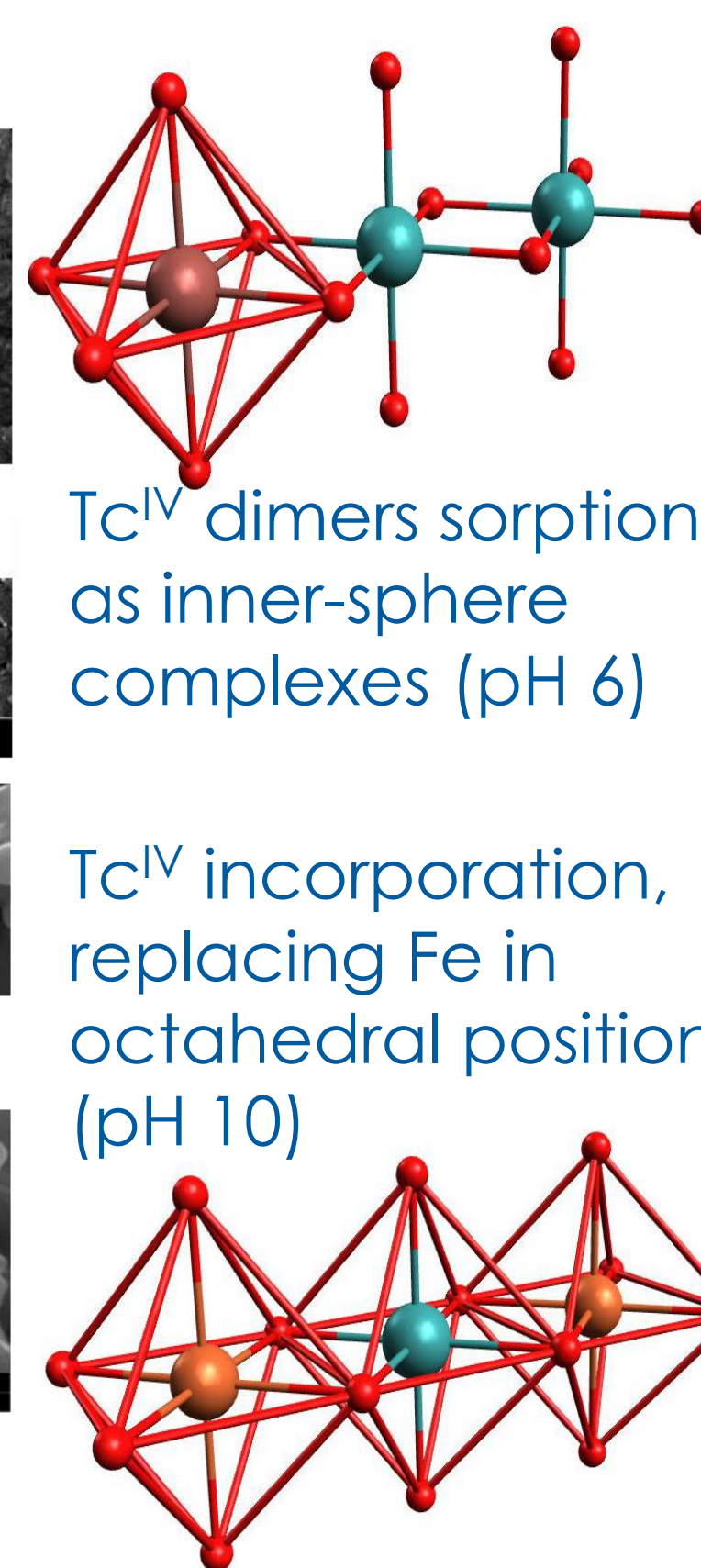
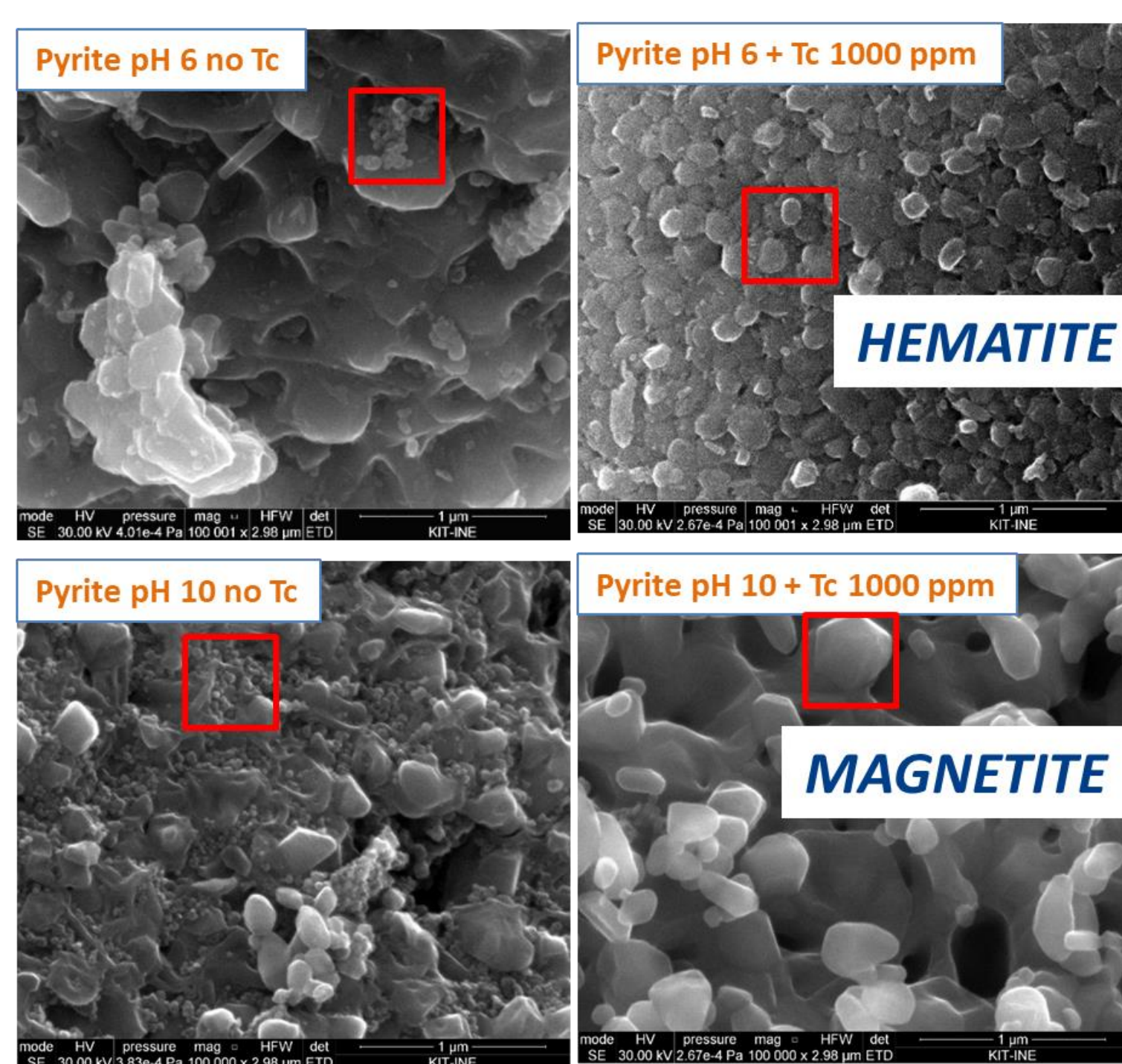
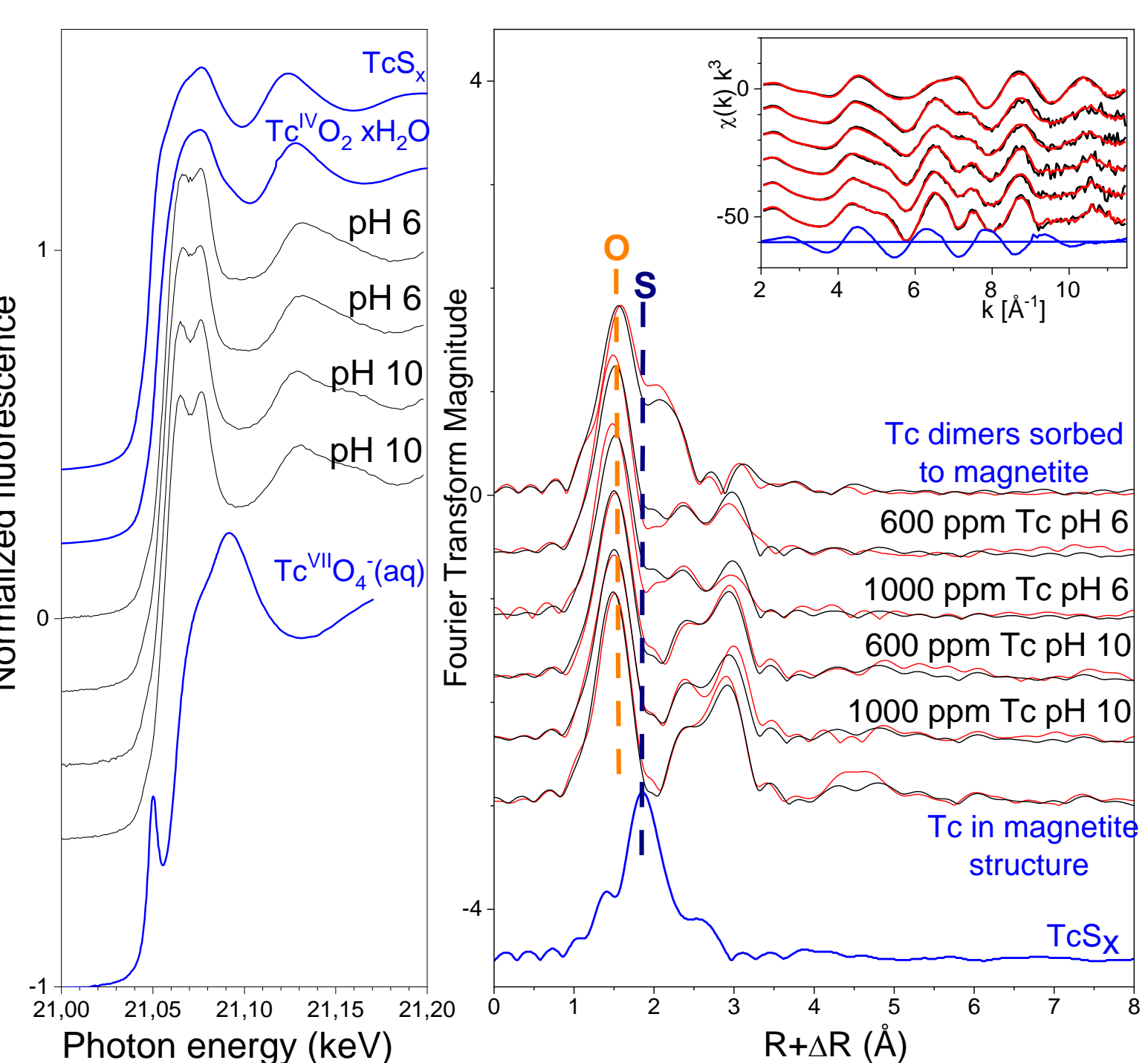


... and on a mixed marcasite-pyrite sample 8

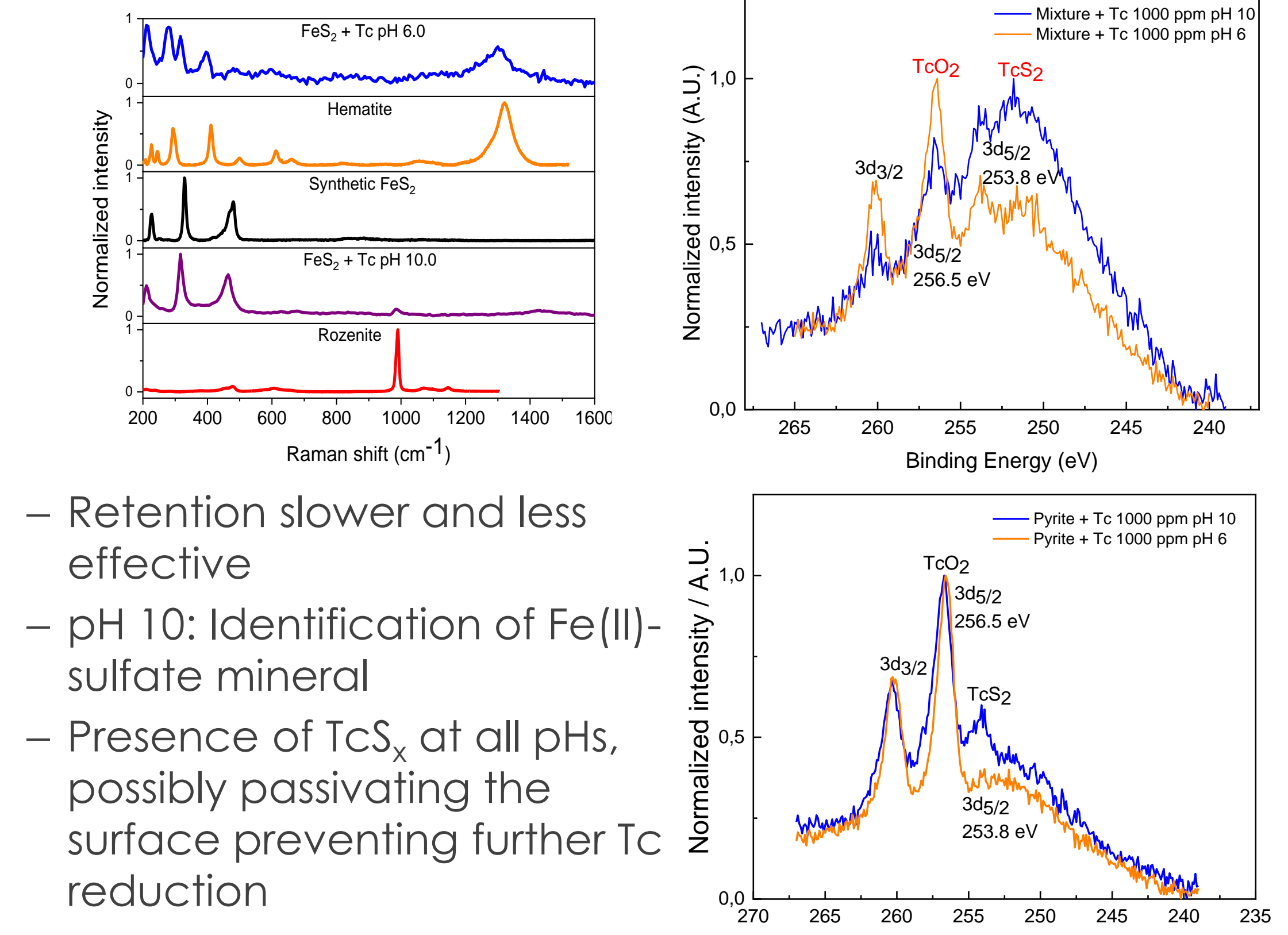
- FeS₂ removes Tc quantitatively at 6 < pH ≤ 9
- Less retention at high pH for mixed sample
- Kinetically controlled processes
- Eh confirms reduction of Tc(VII) to Tc(IV)
- No dependence on ionic strength



pH dependent retention mechanisms on pure pyrite 7



The impact of marcasite 8



Indication of the role of S²⁻ as reductant in marcasite

- Solely identification of Tc(IV)
- Tc is prevalently coordinated to oxygen
- pH dependent identification of secondary mineral phases



¹ Peretyazhko et al. (2008) GCA; ² Mayordomo et al. (2020) J. Hazard. Mater.; ³ Mayordomo et al. (2021) Chem. Eng. J.; ⁴ Schmeide et al. (2021) STOTEN; ⁵ Yalçintaş et al. (2016) Dalton Trans.; ⁶ Livens, et al. (2004) J. Environ. Radioact.; ⁷ Rodriguez et al. (2020) Environ. Sci. Technol.; ⁸ Rodriguez et al. (2021) Chemosphere

