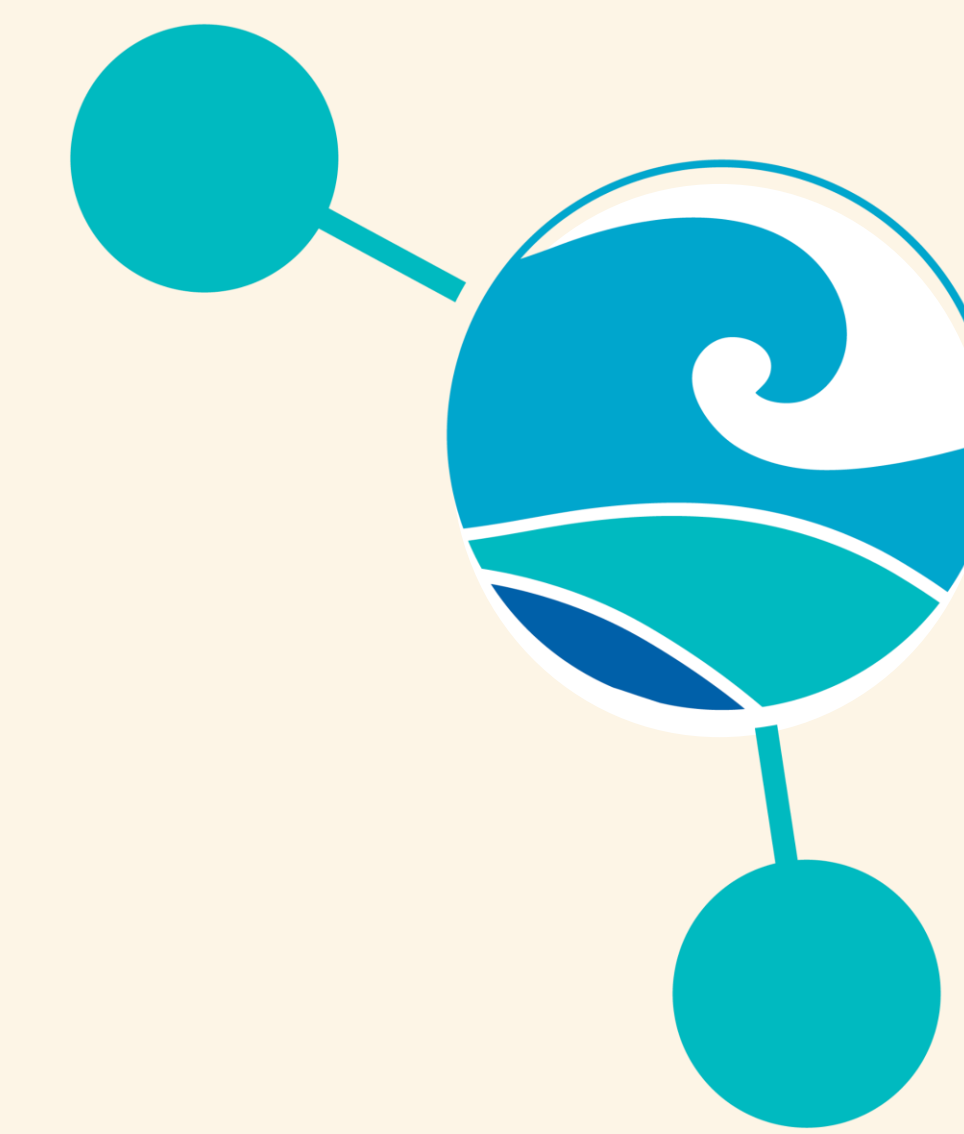


Modelling the inorganic complexation of the GEOTRACES core elements, with a focus on Fe(III) hydrolysis

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1. Trace elements in MarChemSpec

The MarChemSpec chemical speciation modelling software includes key GEOTRACES core elements: Mn(II), Fe(II), Co(II), Ni, Cu(II), Zn, Cd, Pb(II), Al and Fe(III). MarChemSpec uses Pitzer equations to calculate activity coefficients, which means that relatively weak cation – anion interactions are described by Pitzer parameters (interactions between free ions) rather than by complex formation. For the trace elements, this approach is used for many chloride and sulphate interactions. The resulting Pitzer parameters are based on a thermodynamic database that is much more extensive than the sets of stoichiometric equilibrium constants used in a traditional complexation description. The diagram below summarises the modelling approach and data quality for the interactions of these cations with the inorganic ions of seawater.

	Cl ⁻	SO ₄ ²⁻	OH ⁻	CO ₃ ²⁻	F ⁻
Mn ²⁺	γ(T)	γ(T)	K(T)	K(T)	
Fe ²⁺	γ(T)	γ(T)	K(T)	K(T)	
Co ²⁺	γ(T)	γ(T)	K(T)	K(T)	
Ni ²⁺	γ(T)	γ(T)	K(T)	K(T)	
Cu ²⁺	γ(T)	γ(T)	K(T)	K(T)	
Zn ²⁺	γ(T)	γ(T)	K(T)	K(T)	
Cd ²⁺	γ(T)	γ(T)	K(T)	K(T)	
Pb ²⁺	K(T)	γ(25)	K(T)	K(T)	
Al ³⁺	γ(25)	γ(25)	K(T)		K(25)
Fe ³⁺	γ(T)	γ(25)	K(T)		K(25)

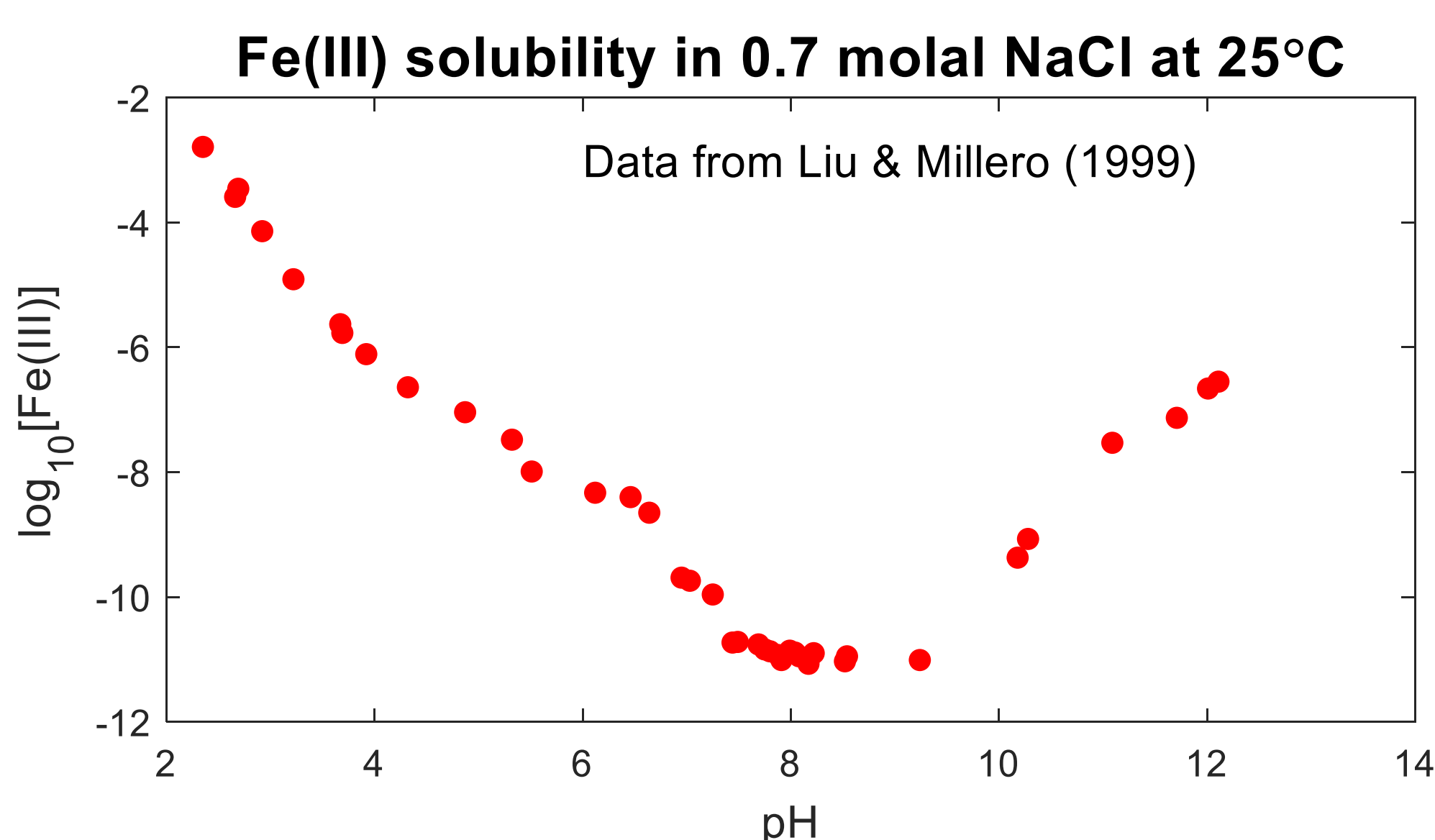
Parameterisation of trace metal interactions:

- γ – Pitzer parameters (ion interaction)
- K – stability constant(s) (complex formation)
- (25) – data available only at 25°C
- (T) – data available over a temperature range
- The temperature dependences of many of the hydrolysis constants are derived from fitting functions for ΔH and ΔC_p
- The temperature dependence of all the carbonate constants is derived from an estimate of ΔH for CuCO_3^0 . The constants for Co and Ni carbonates have been estimated using a linear free energy relationship since no measurements have been identified.

There appears to be an unfortunate general rule that the more important the interaction in seawater, the harder it is to study, with the result that many key thermodynamic data are very limited. Carbonate complexation of the divalent cations, and most particularly the hydrolysis of Fe(III), are interactions that are both important and poorly characterised. Fe(III) hydrolysis is particularly important for the calculation of the ratio α between total inorganic Fe(III) and the ion Fe^{3+} , which is an essential parameter in analysis of CLE-CSV titrations involving Fe(III), and also controls Fe(III) solubility. We present here a new Pitzer model for Fe(III) hydrolysis based to a large extent on solubility measurements in NaCl.

2. Fe(III) hydrolysis in NaCl

Liu and Millero (Geochim.Cosmochim Acta, 63, 3487-3497, 1999) have measured Fe(III) solubility in NaCl at several temperatures and ionic strengths. Below we show the solubility – pH relationship at 0.7 molal NaCl and 25°C.



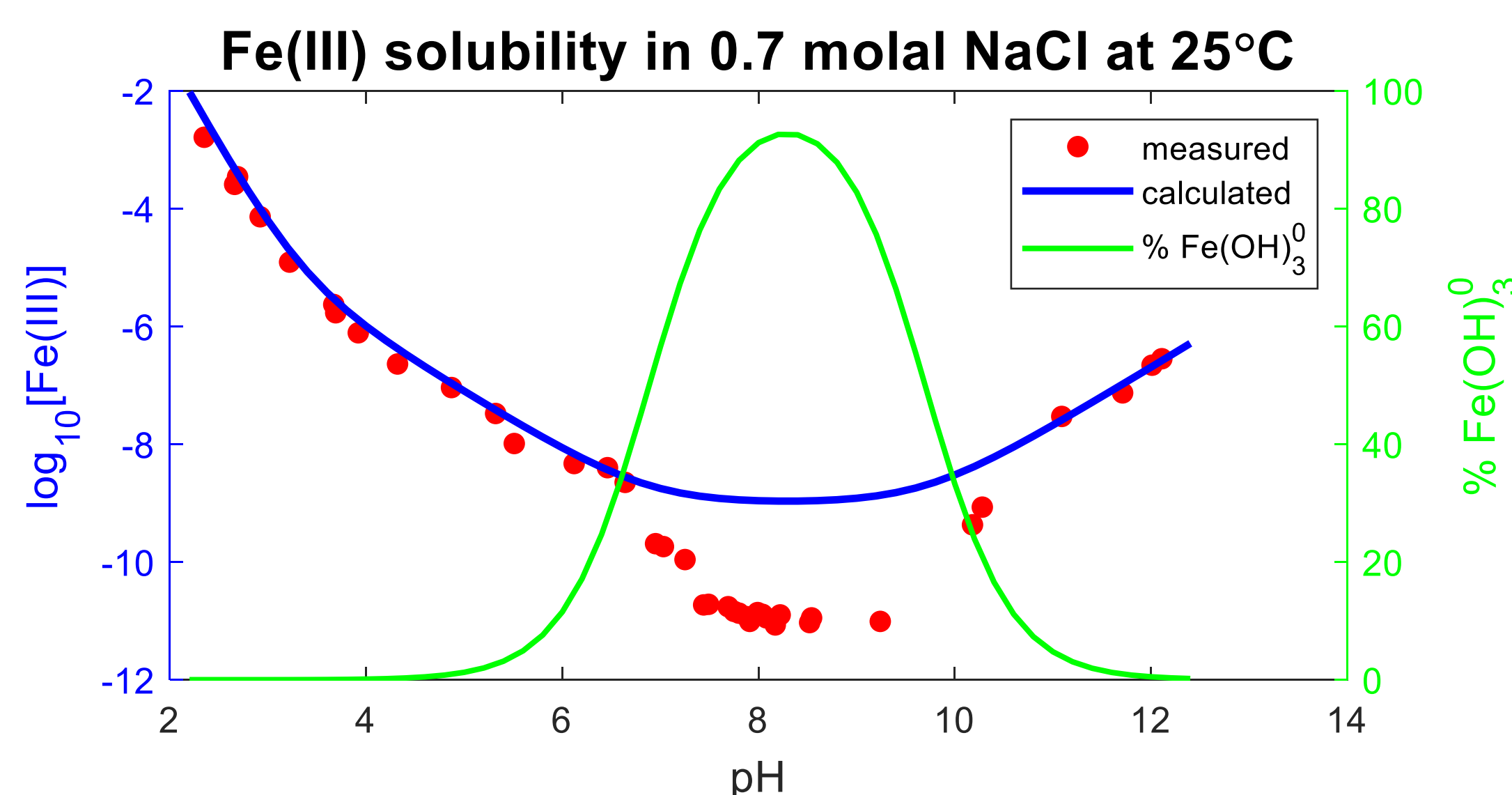
The solubility curve is unusual, with a sharp change between pH 6 and 7 that is found under all the conditions studied. Our general approach has been to estimate the thermodynamic stability constants for the four Fe(III) hydrolysis products from solubilities in the relevant pH range as summarised below.

Parameters	Data source
Equilibrium constants	
K_1 (FeOH ²⁺ formation)	Byrne et al. 2005
K_2 (Fe(OH) ₂ ⁺ formation)	Solubility in 0.7m NaCl at 25°C, pH 5 – 6.5
K_3 (Fe(OH) ₃ ⁰ formation)	Assigned free energy value
K_4 (Fe(OH) ₄ ⁻ formation)	Solubility in 0.7m NaCl at 25°C, pH > 10.5
Temperature dependence	Byrne et al. 2005 (K_1) Baes & Mesmer 1981 ($K_2 - K_4$)
Pitzer parameters	
FeOH ²⁺ – Cl ⁻	Byrne et al. 2005
Fe(OH) ₂ ⁺ – Cl ⁻	Assumed equal to K ⁺ – Cl ⁻
Fe(OH) ₃ ⁰ – Na ⁺	Assumed equal to B(OH) ₃ ⁰ – Na ⁺
Fe(OH) ₄ ⁻ – Na ⁺	Assumed equal to B(OH) ₄ ⁻ – Na ⁺

References: Baes, C.F. and Mesmer, R.E., 1981. American Journal of Science, 281: 935-962
Byrne, R.H. et al., 2005. Marine Chemistry, 97: 34-48

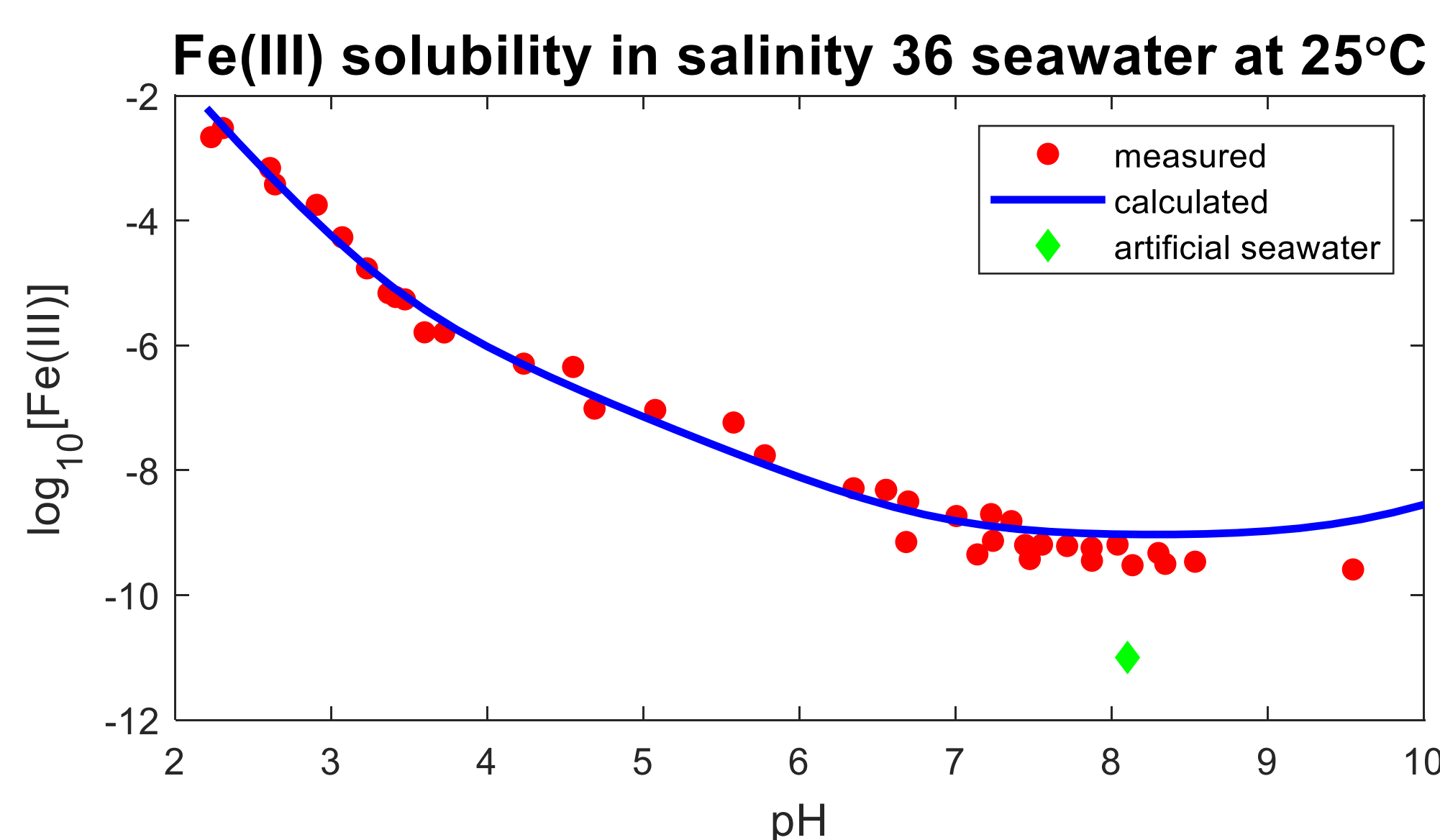
3. The neutral complex Fe(OH)₃⁰ behaves differently

The discontinuity in the solubility curve between pH 6 and 7 cannot be reproduced in a speciation model without resorting to highly unusual activity coefficients. In addition, a value for K_3 estimated from the lowest solubilities does not fit the expected sequence of free energies for successive proton loss from the hydrated Fe^{3+} ion. Our interpretation of this discontinuity is that the neutral complex Fe(OH)_3^0 has a lower solubility than the other hydrolysis products due to coagulation (salting out). In support of this interpretation, we note that (i) the pH range with lower solubilities is closely associated with the occurrence of Fe(OH)_3^0 (see plot below), and that this salting out effect is weaker at lower ionic strengths.



4. Solubility in seawater follows a different pattern

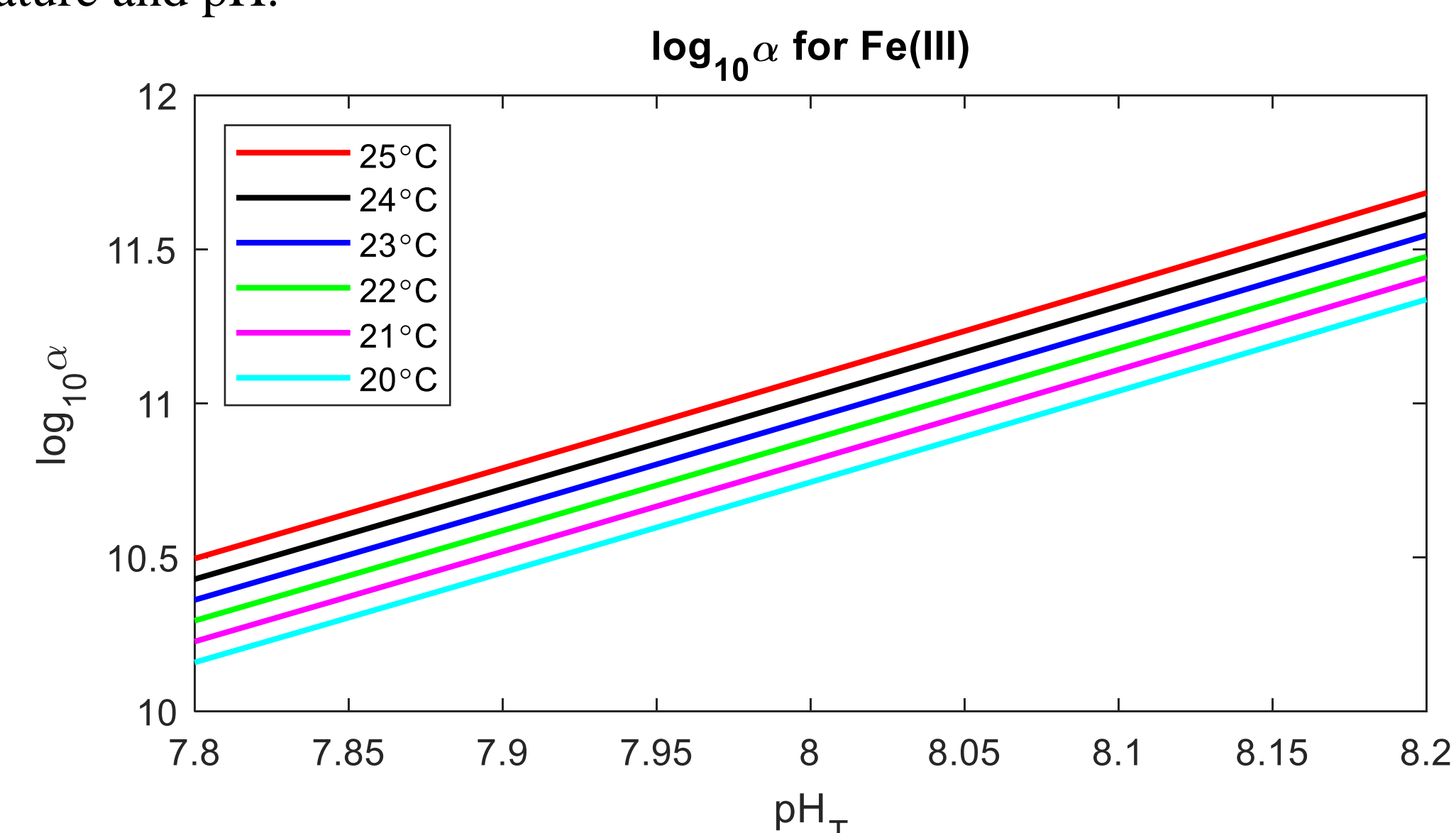
Liu and Millero (Mar.Chem., 77, 43-54, 2002) have measured Fe(III) solubility in natural seawater and in artificial seawater. At pH close to 8 there is a large difference between the solubilities in natural and artificial seawater, where the solubility in artificial seawater is close to that in NaCl. This is consistent with ultrafiltration studies that have shown that filterable Fe(III) in this pH region exists almost entirely in large (> 100 kDa) fractions in UV-irradiated seawater, but in the presence of natural organic matter can be found down to the smallest size fractions (5 kDa / 20μm), indicating organic iron binding that increases solubility.



5. Alpha values for CLE-CSV titrations

Hudson et al. (Mar.Chem., 38, 209-235, 1992) derived a value of $\log_{10}\alpha = 10$ for Fe(III) at pH 8.0 and 20°C. In order to obtain agreement with measurements of competition from EDTA they arbitrarily omitted the neutral complex Fe(OH)_3^0 . Comparison with the new Pitzer model suggests that this drastic omission was a result of estimated stoichiometric hydrolysis constants that were all far too strong.

Calculations with the new model show the following dependence of $\log_{10}\alpha$ on temperature and pH.



6. Conclusions and forward look

We have used measurements of Fe(III) solubility in NaCl to develop a self-consistent Pitzer model for Fe(III) hydrolysis in seawater. However, the data available for developing and testing the model are very limited. More work is needed, in particular to (i) test and quantify the conclusion that the neutral complex Fe(OH)_3^0 coagulates in organic-free media resulting in a reduced solubility where this complex dominates; and (ii) derive Pitzer parameters specific to the hydrolysis products rather than relying on analogues. Nevertheless, the model developed here provides improved estimates of $\log_{10}\alpha$ in seawater for a range of different conditions.

Our model of Fe(III) hydrolysis shows that $\log_{10}\alpha$ is dependent on both pH and temperature rather than having a constant value of 10 that is frequently used in CLE-CSV titrations.

The MarChemSpec model

The model calculates equilibrium acid-base, carbonate system, and trace metal speciation of natural waters of arbitrary composition including seawater. It is particularly suited to calculating the effects of *changes* of water composition from normal seawater stoichiometry. The model uses a state-of-the-art Pitzer treatment of activity coefficients, together with thermodynamic equilibrium constants.

Inputs: T , and S or individual species compositions of any of the solutes of reference seawater (Na^+ , Mg^{2+} , Ca^{2+} , K^+ , Sr^{2+} , Cl^- , SO_4^{2-} , Br^- , F^- ; acid-base carbonate and borate species and HF), and the trace metals Al, Cd, Co, Cu(II), Fe(II), Fe(III), Mn, Ni, Pb or Zn.

Outputs: Speciation of the input solution, together with values of the seawater state parameters (pH (total, free, and seawater scales), alkalinity, DIC, $\{p_f\}\text{CO}_2$, and carbonate, sulphate, borate, and fluoride equilibrium constants, and all activity coefficients.

Types of calculation:

1. The equilibrium speciation and properties of the input solution.
2. **NEW FEATURES** in version 1.10: Equilibration of the input solution to fixed (user supplied) values of any single value, or pair, of: pH (total or free), DIC, total alkalinity, $p\text{CO}_2$ or $f\text{CO}_2$.

Available codes:

1. Stand-alone executables (Windows, Linux, macOS)
2. Python function (Windows, Linux)
3. Matlab function (Windows, Linux)
- (4. R – we have a draft, would you like to help?)

Note: We have a parallel project to model the pH of Tris buffer solutions, for applications in the calibration of in-situ and other pH sensors. Please ask, if interested.

MarChemSpec resources

- Latest news, and links to downloads: marchemspec.org
- Recordings of presentations and tutorials: search for “**youtube marchemspec**”
- Zenodo archive of downloads for all model versions: zenodo.org/records/8373046
- Description of the model for seawater: there are three papers published in *Marine Chemistry* in 2022 and 2023, and a draft document on trace metal complexation. These are listed at marchemspec.org, and the Zenodo archive.

Acknowledgments

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