**Supplementary Material**

**Greigite formation in aqueous solutions: critical constraints into the role of iron and sulphur ratios, pH and Eh, and temperature using reaction pathway modelling.**

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Table S1. Comparison of databases used in PHREEQC modelling containing the reactions and thermodynamic properties for mackinawite, greigite, pyrite and pyrrhotite. Reactions are formatted as found in the databases. Data used for this study has been highlighted in bold and included for comparison.

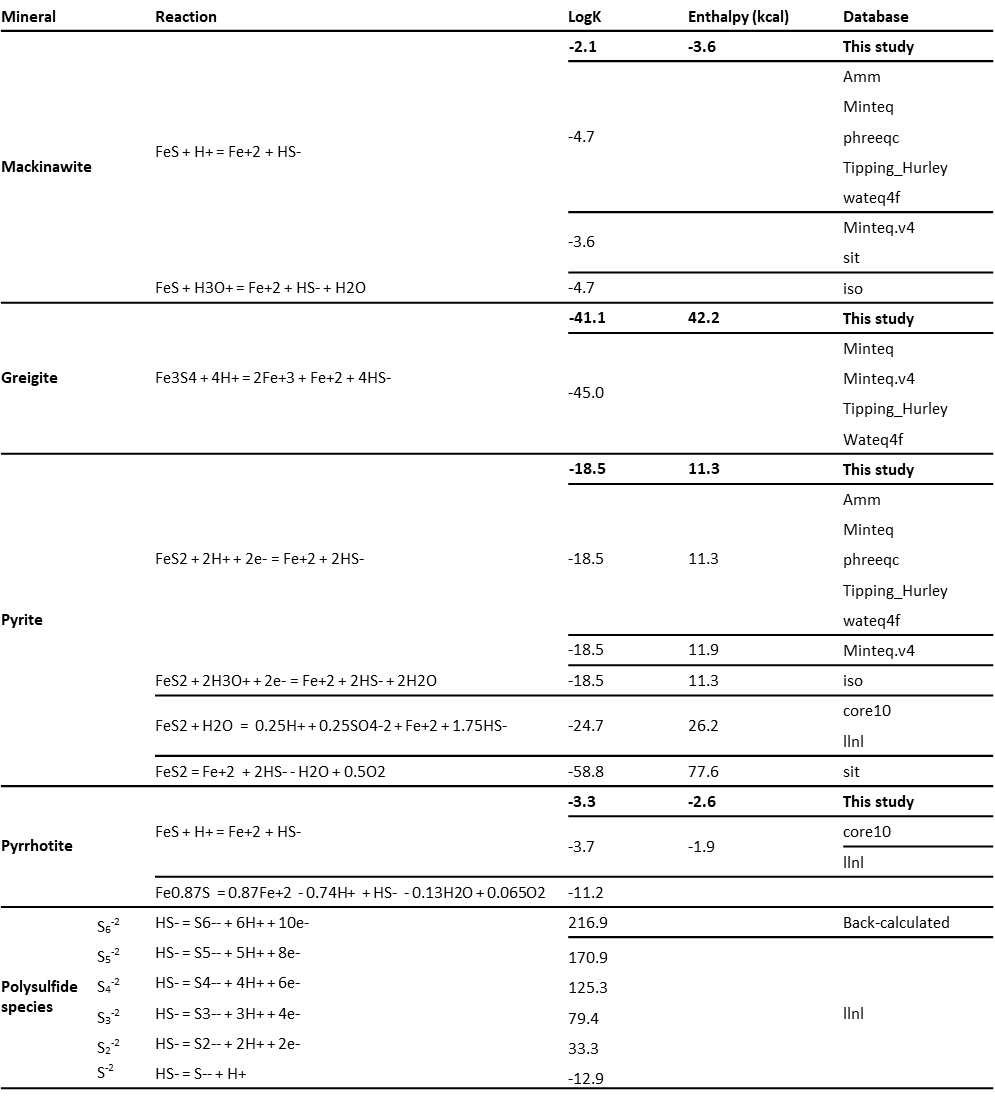
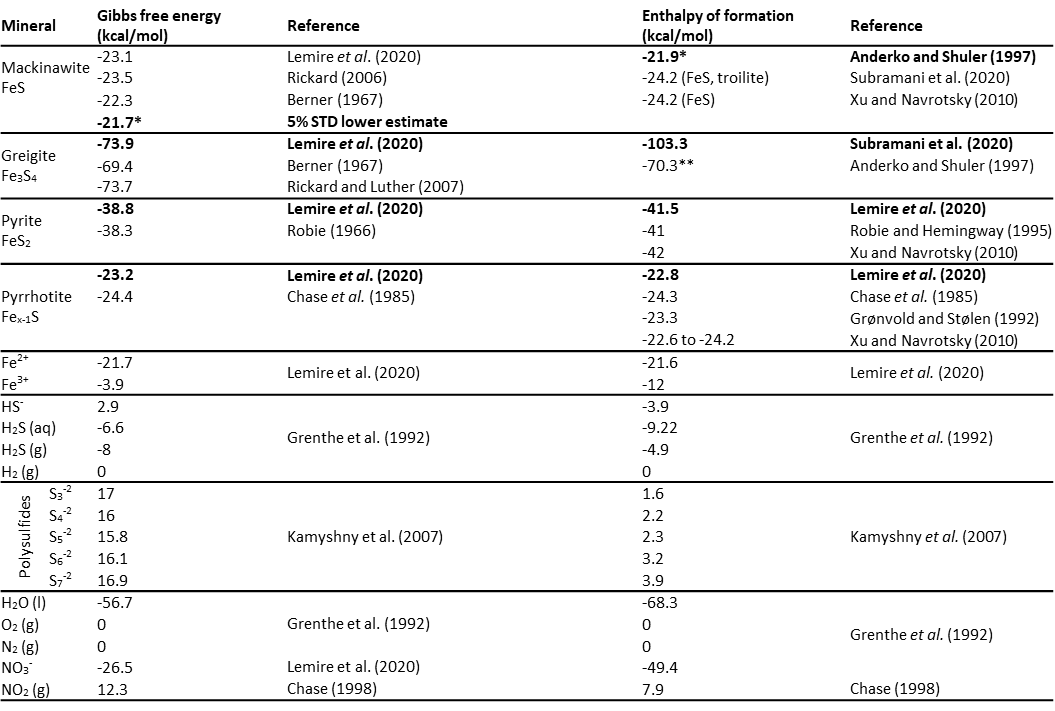


Table S2. Compilation of literature Gibbs free energy and enthalpy of formation values for the minerals and species of interest. Data taken from Grenthe *et al*. (1992) was also used in Lemire *et al*. (2020). The data used in this study to calculate logK and enthalpy values seen in Table S1 has been highlighted in bold. Enthalpy data for troilite has been included due to its similar chemical structure to mackinawite.



\*value calculated from two relative standard deviations of 5% using published values in the table. A 95% confidence interval of the mean (-23.0) calculated a margin of error of +/- 1.35.

\*\*enthalpy data from Anderko and Shuler (1997) was not produced from experimental work but was estimated from contributions by Latimer (1952).

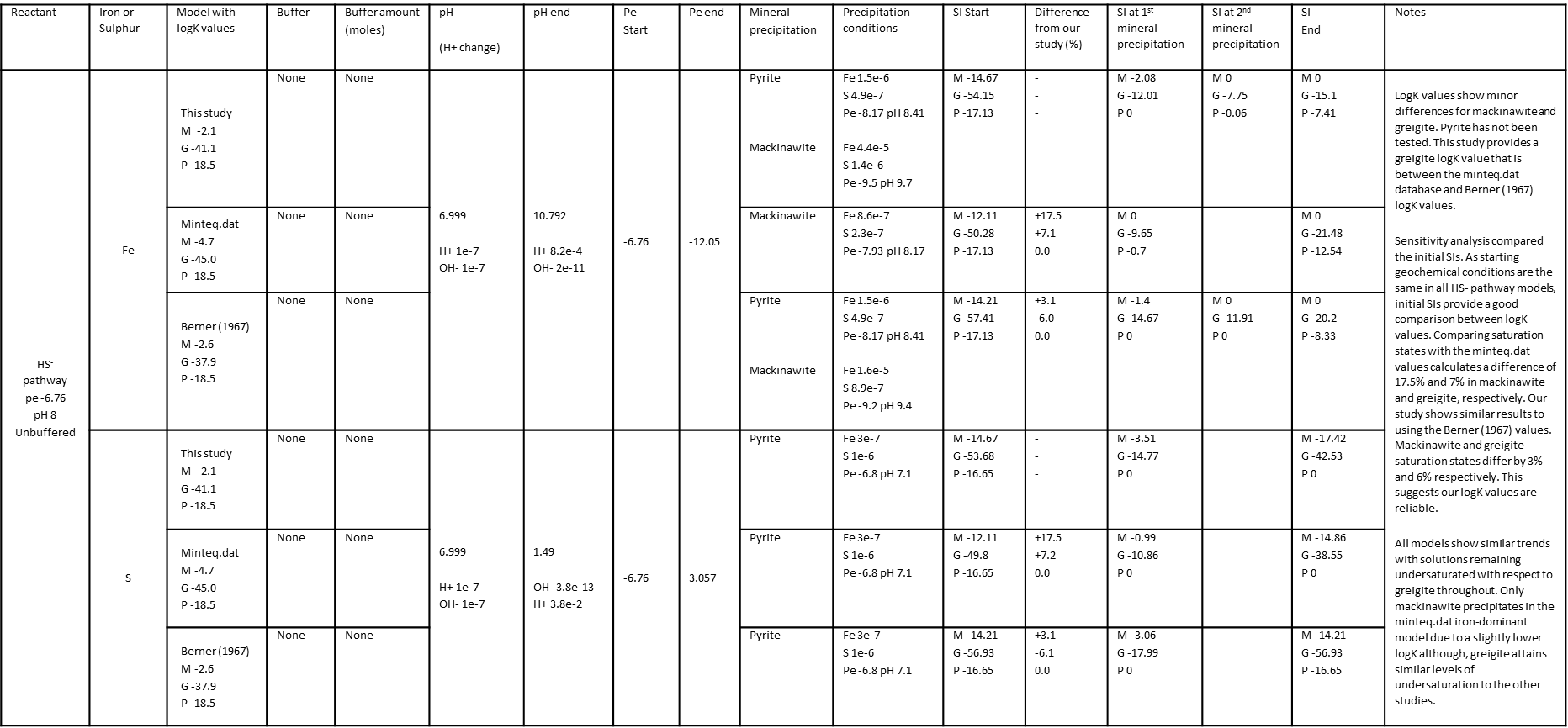


Table S3. Comparing the results using thermodynamic data from this study with the original data calculated by Berner (1967) and the minteq.dat database from PHREEQC. Greigite attains a similar SI and pyrite is close to or reaches saturation in all models.

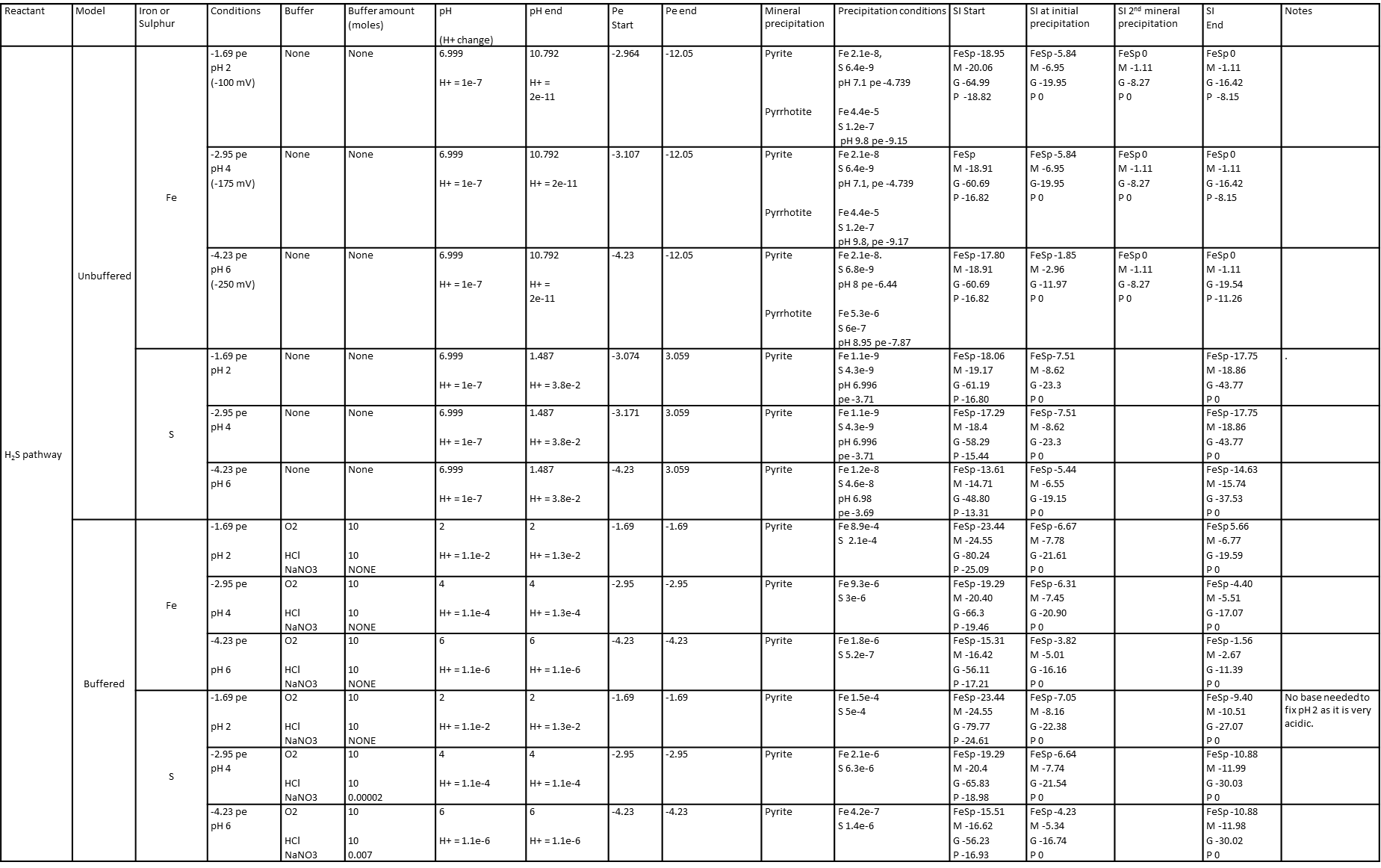


Table S4. Full experimental results for the H2S reaction pathway showing unbuffered and buffered solutions. Concentrations measured by molality (m).

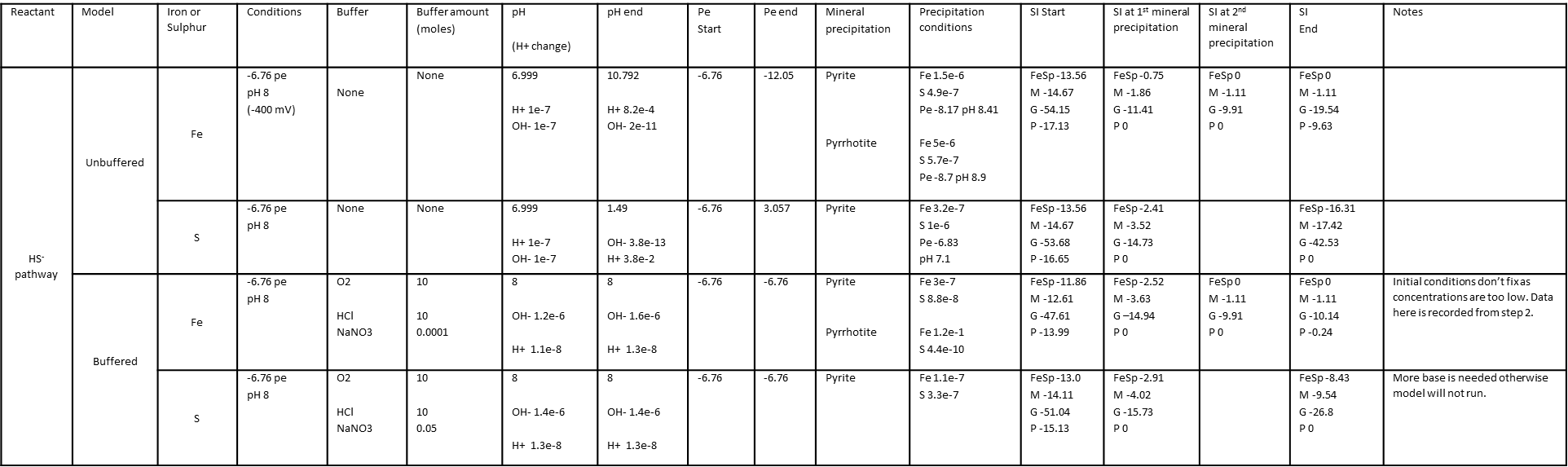


Table S5. Full experimental results for the HS- reaction pathway showing unbuffered and buffered solutions. Concentrations measured by molality (m).

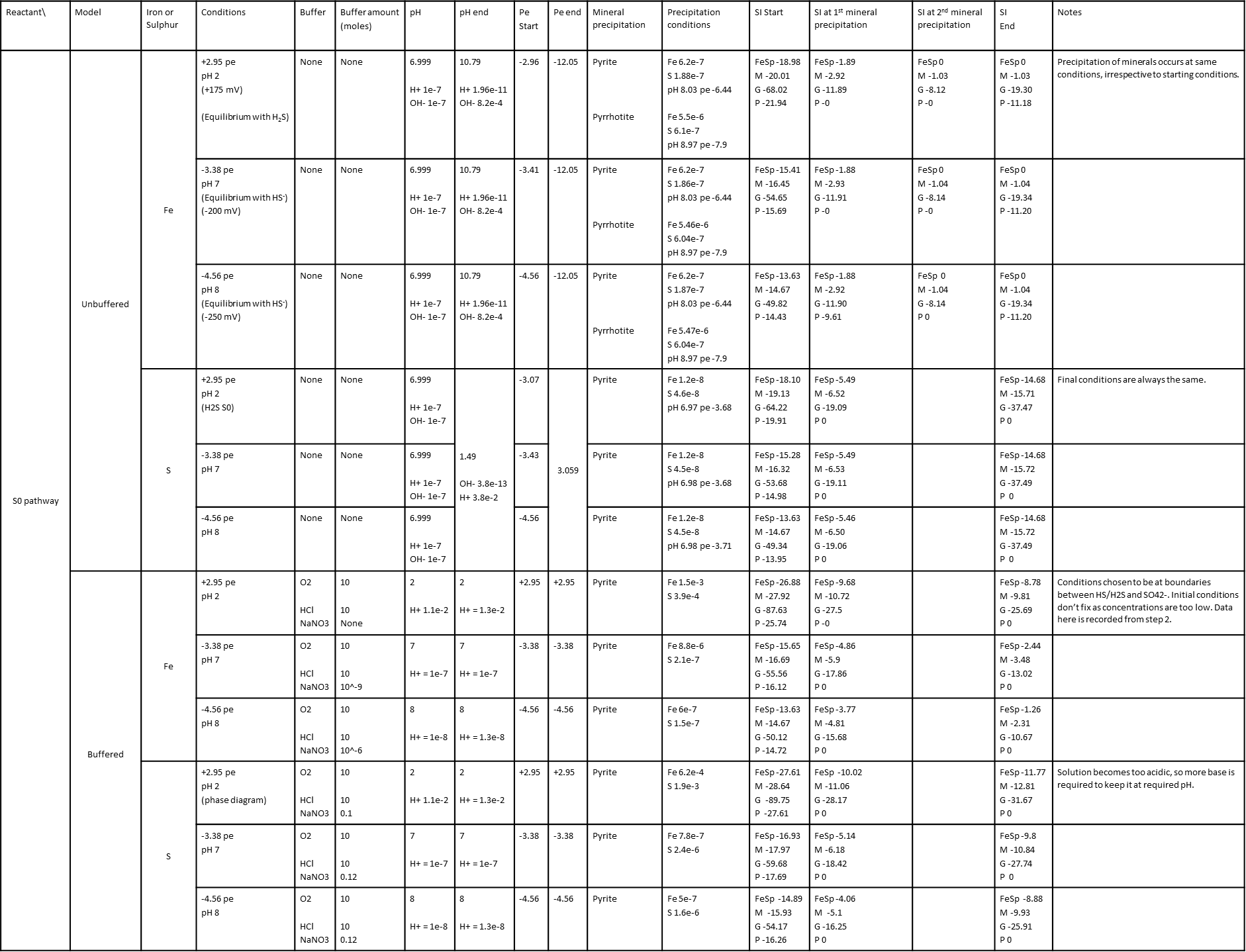


Table S6. Full experimental results for the S0 reaction pathway showing unbuffered and buffered solutions. Concentrations measured by molality (m).

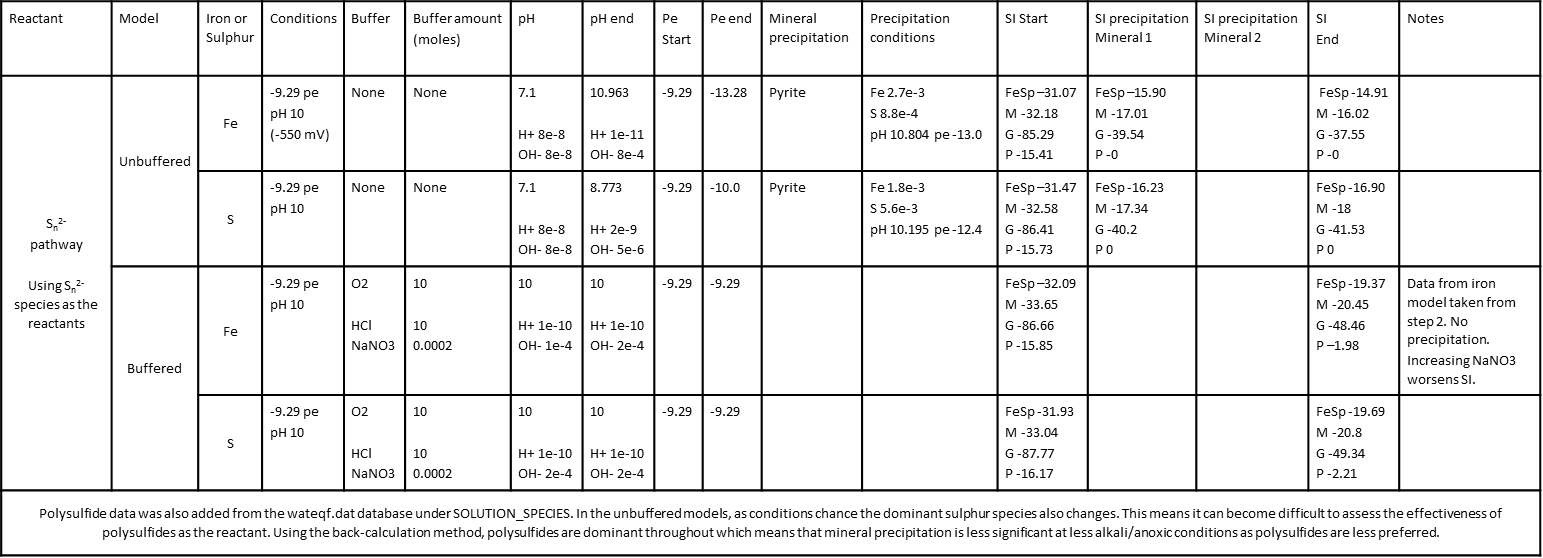
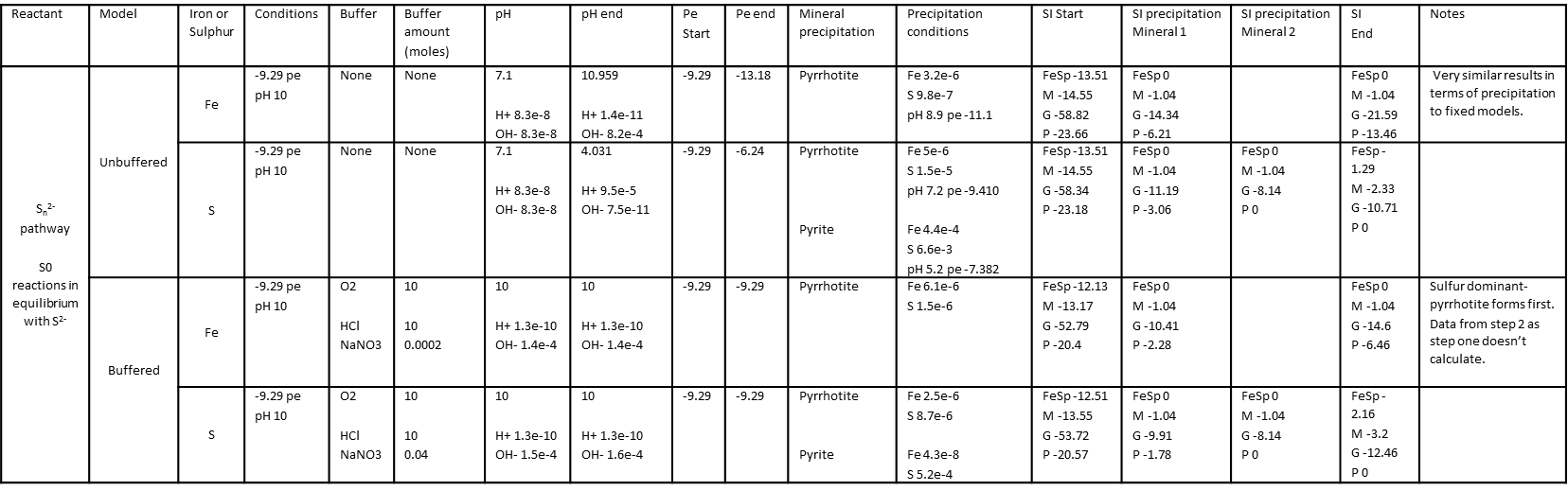


Table S8. Full experimental results for the polysulfide reaction pathway showing unbuffered and buffered solutions. Reactions use S0 which is in equilibrium with Sn2- and PHEREQC calculates the polysulfides species present under the specified conditions. Concentrations measured by molality (m).

Table S7. Full experimental results for the polysulfide reaction pathway showing unbuffered and buffered solutions. Reactions use individual polysulfide species. Concentrations measured by molality (m).

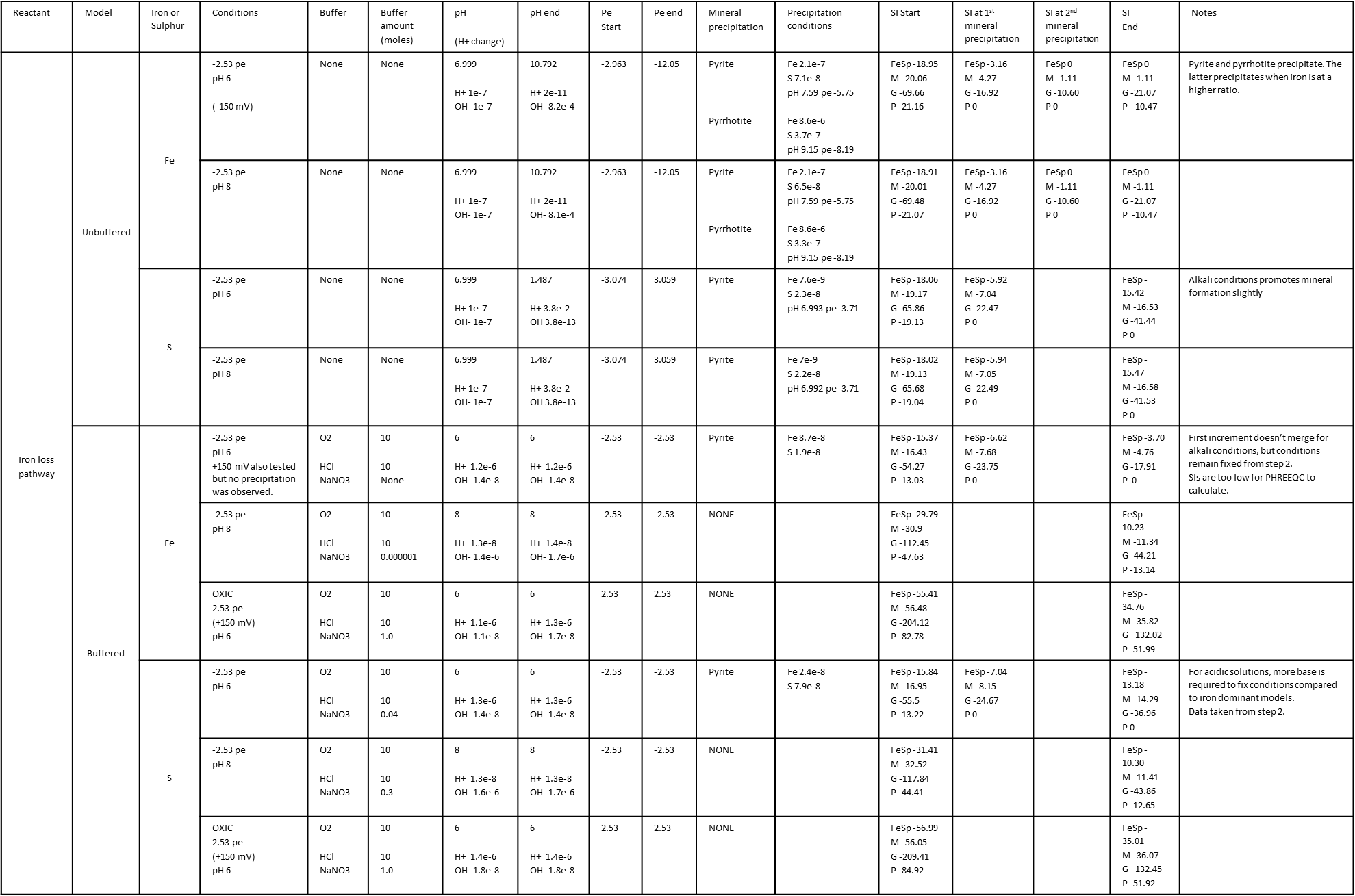


Table S9. Full experimental results for the iron loss reaction pathway showing unbuffered and buffered solutions. Concentrations measured by molality (m).

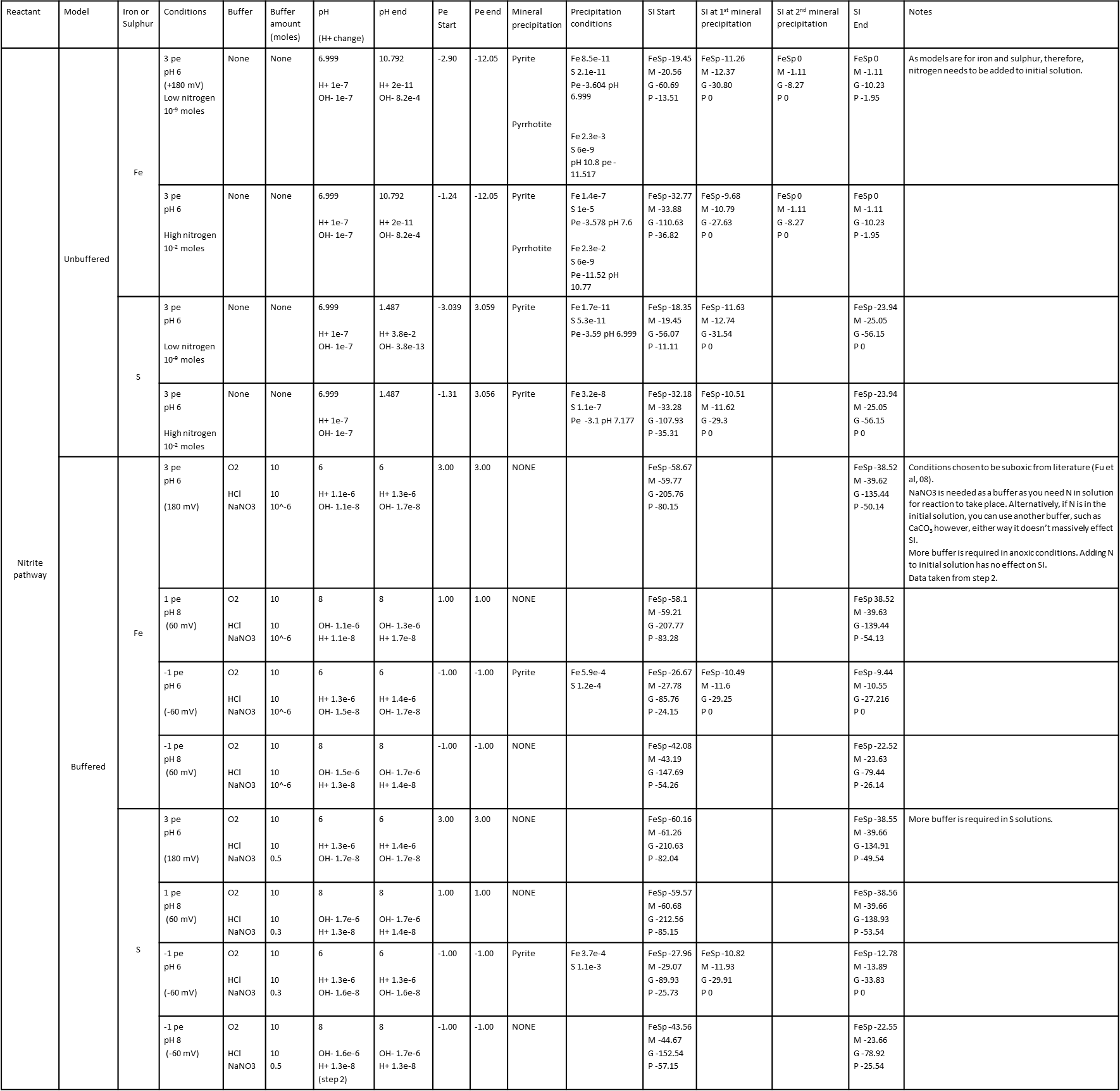


Table S10. Full experimental results for the nitrite pathway showing unbuffered and buffered solutions. Initial solutions have low (10-9 m) and high (10-2 m) nitrogen concentrations. Concentrations measured by molality (m).

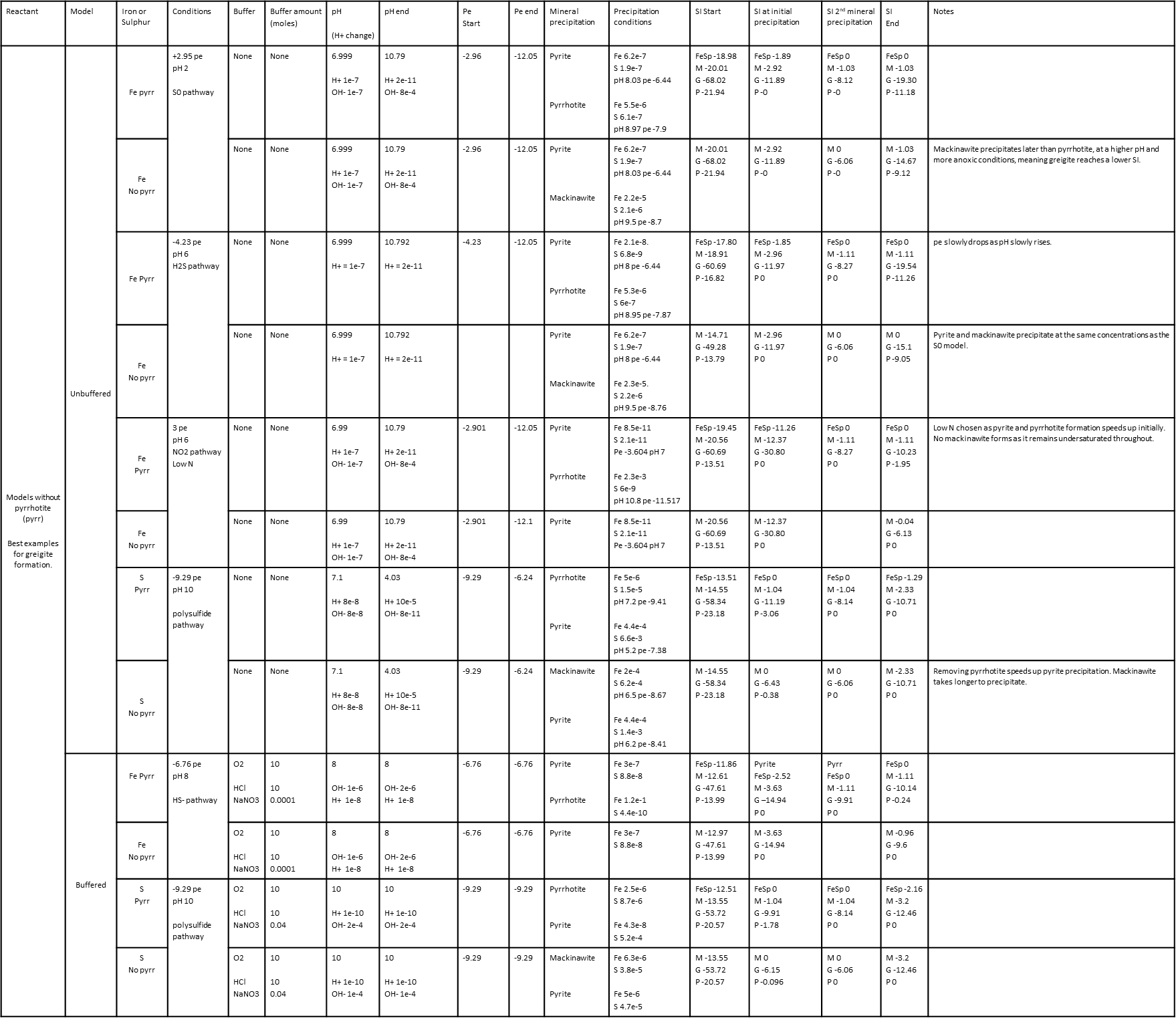


Table S11. Full experimental results showing comparisons between models with and without pyrrhotite. Models chosen produced greigite SIs that were closest to saturation with all minerals being at equilibrium. Concentrations measured by molality (m).

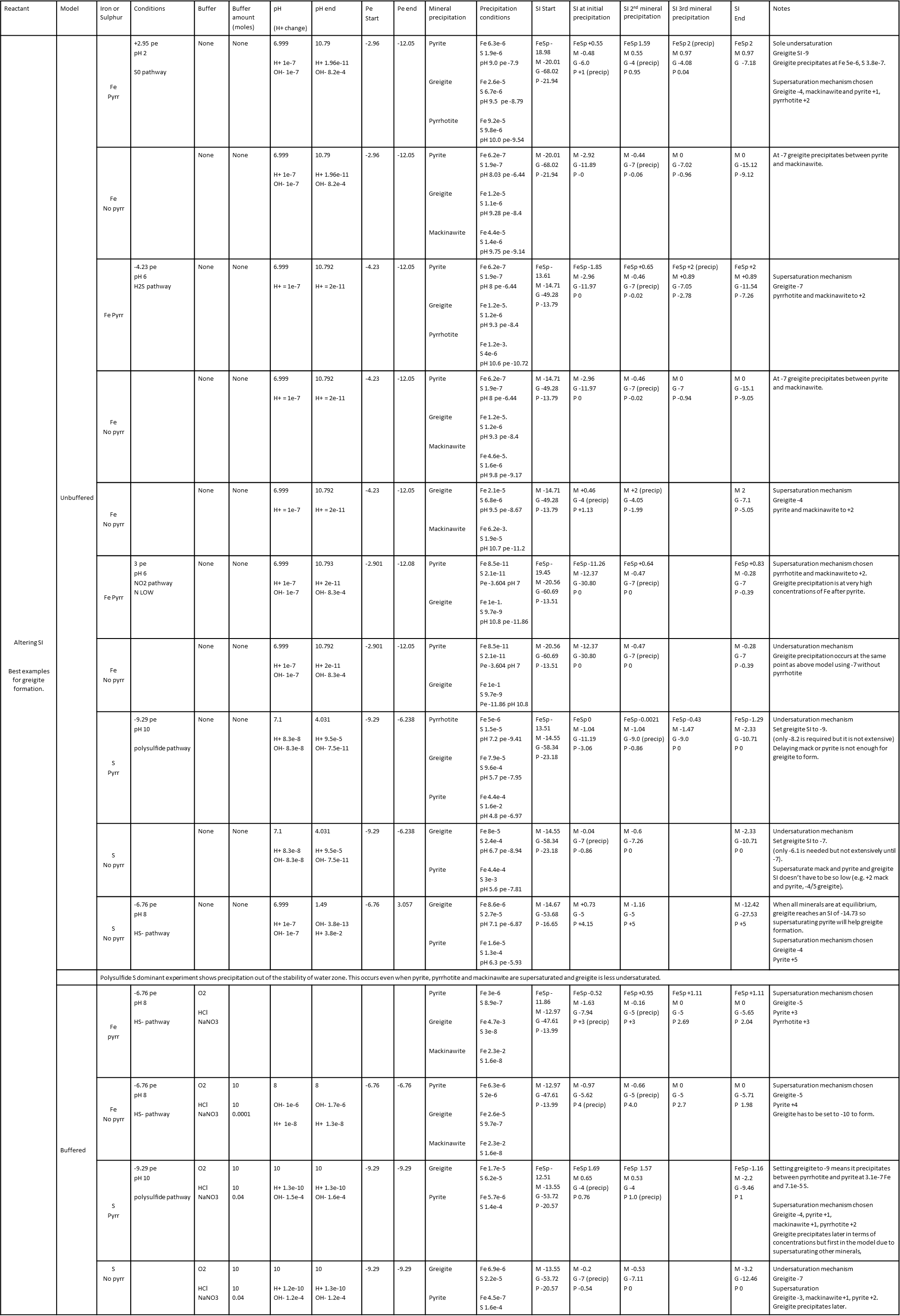


Table S12. Full experimental results for greigite forming models by the alteration of SIs. Models chosen produced greigite SIs that were closest to saturation with all minerals being at equilibrium. Concentrations measured by molality (m).

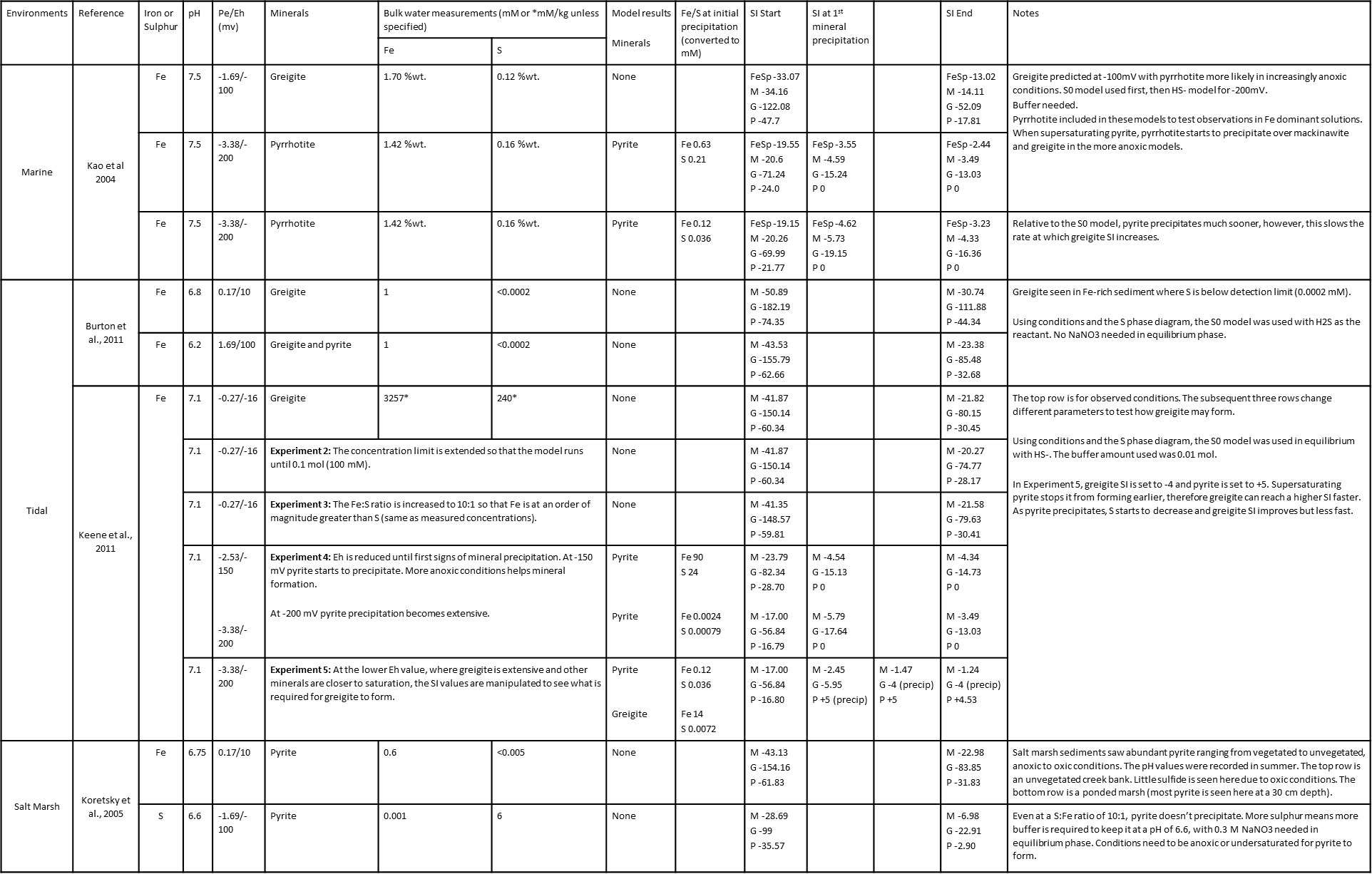


Table S13. Summary table of experiments when tested against literature observations. Using geochemical data from the literature, experiments were conducted then altered to promote the precipitation of iron sulphides. Concentrations measured by molality (m).

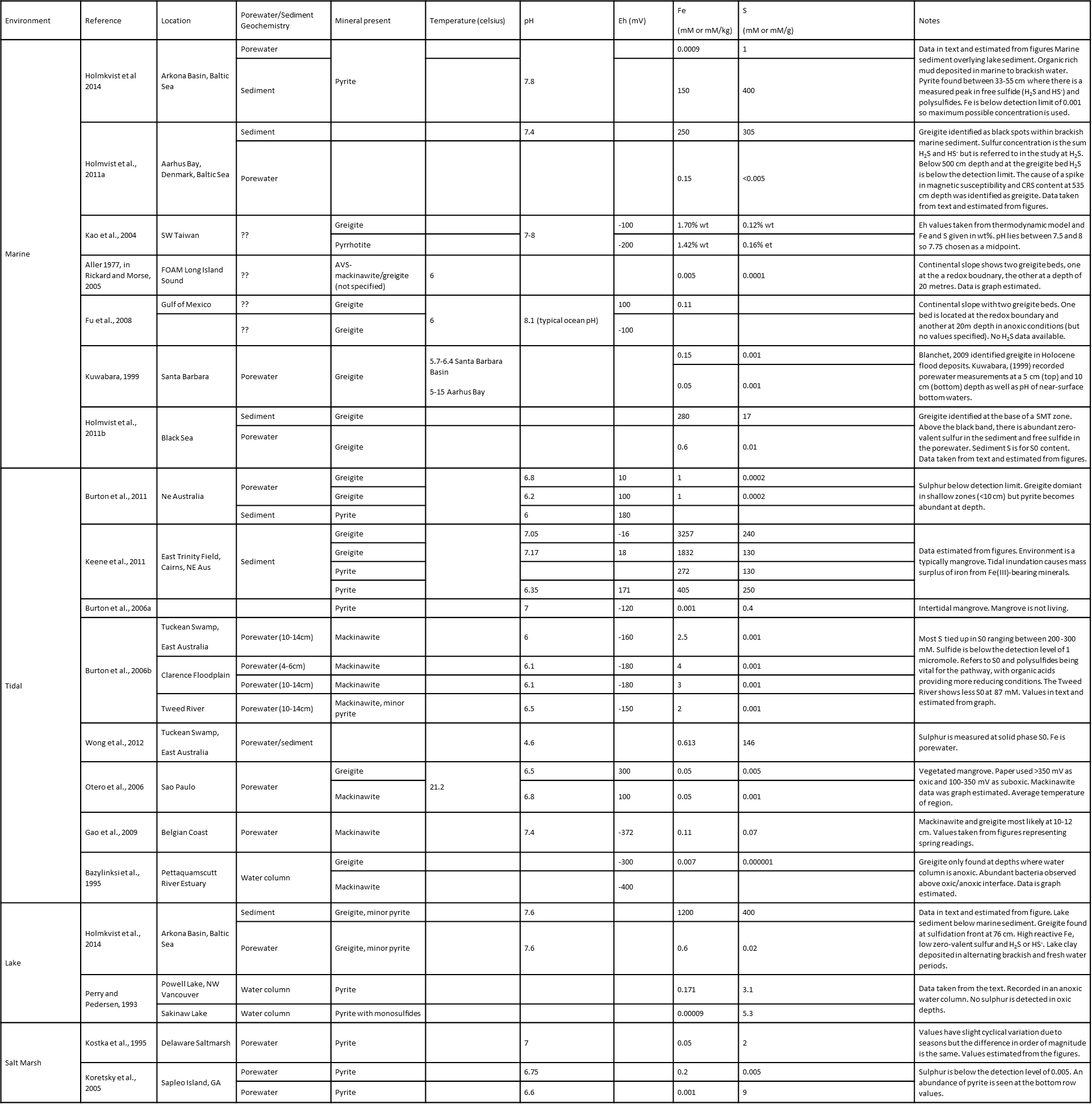


Table S14. Summary tables of geochemical data for iron sulphide-hosted natural sediments, taken from the literature. Values were estimated from the figures, taken from raw data or the text. Key observations have also been noted. Concentrations measured by molality (m).

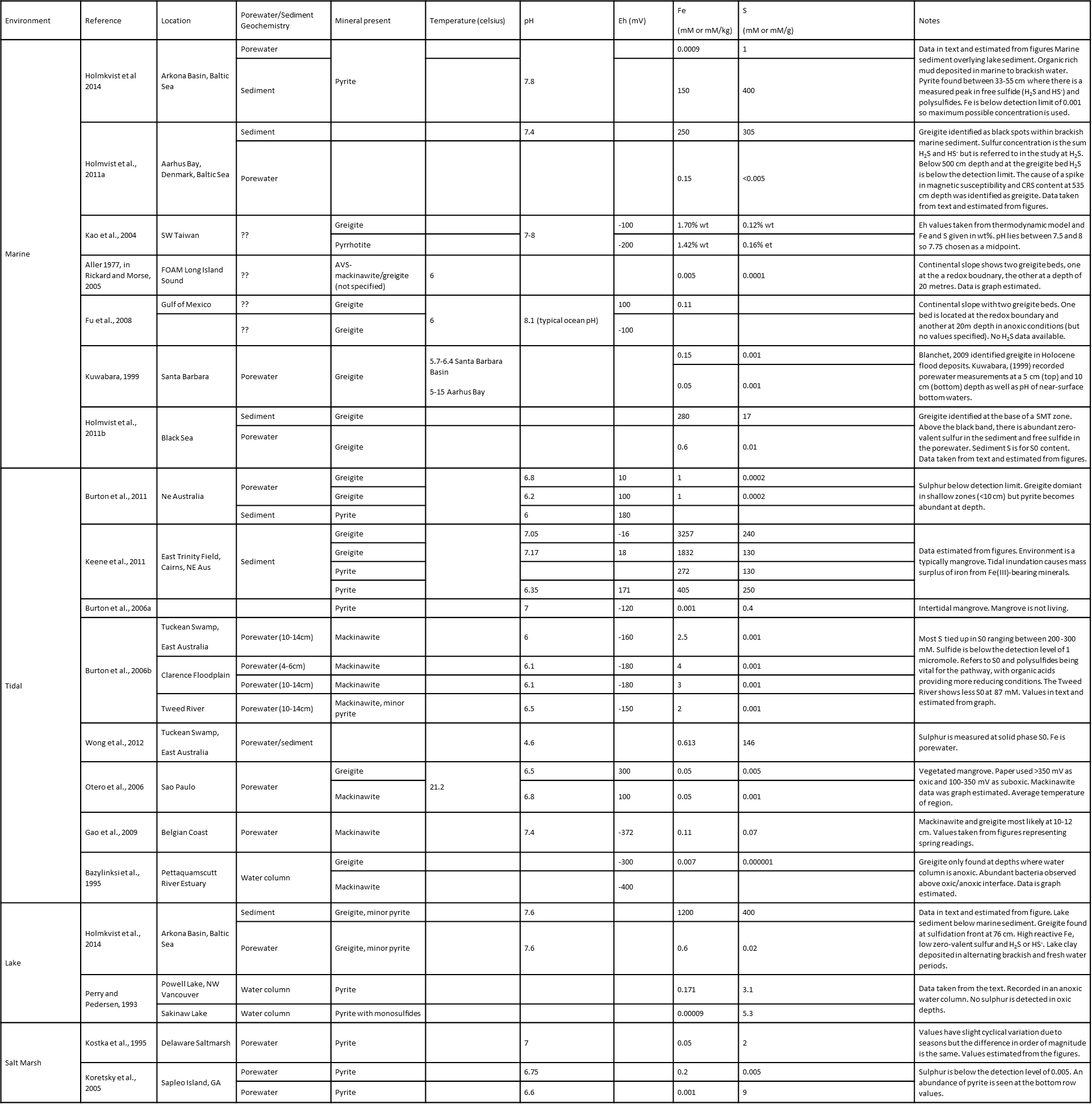


Table S14 continued.

