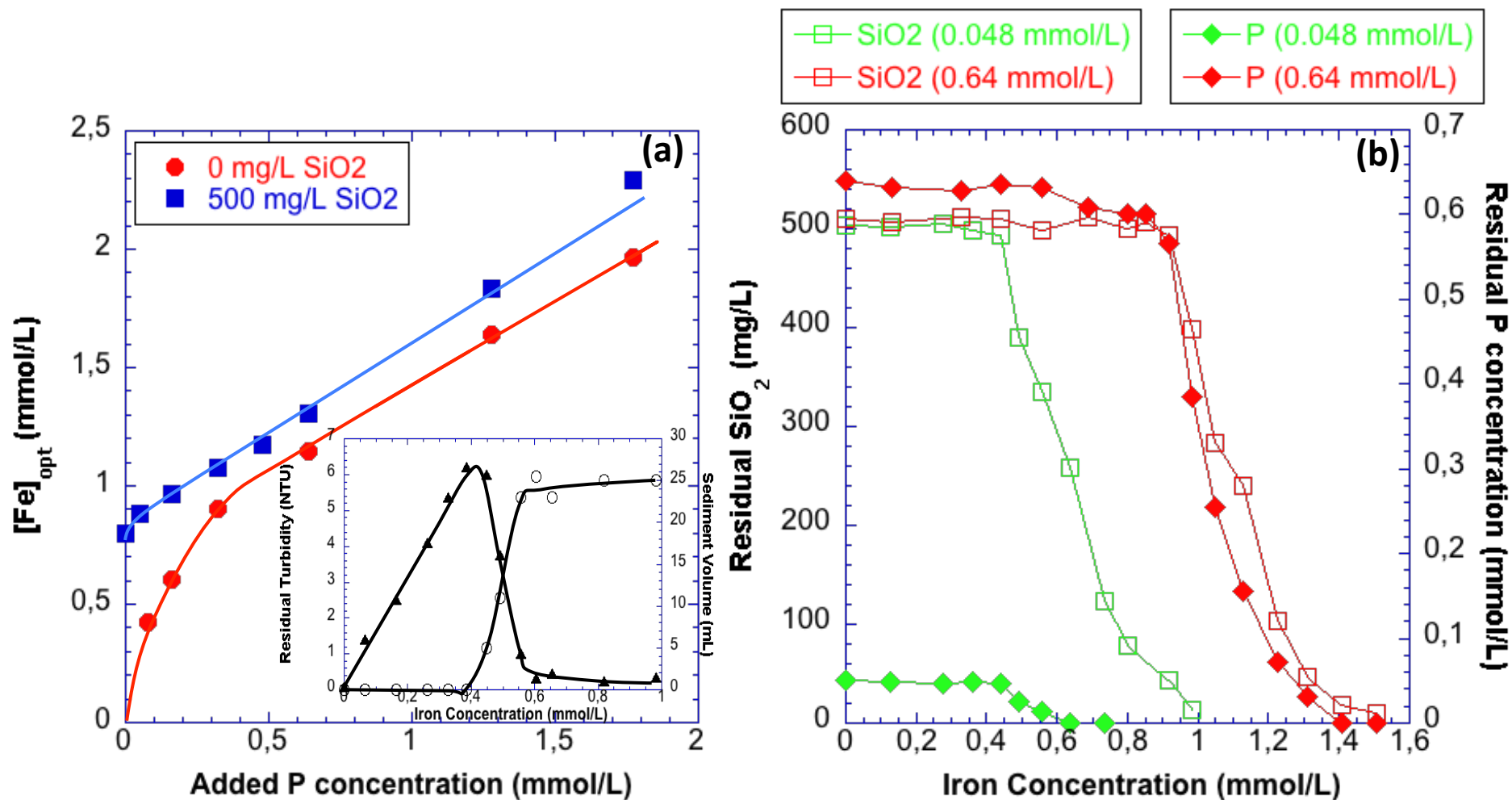
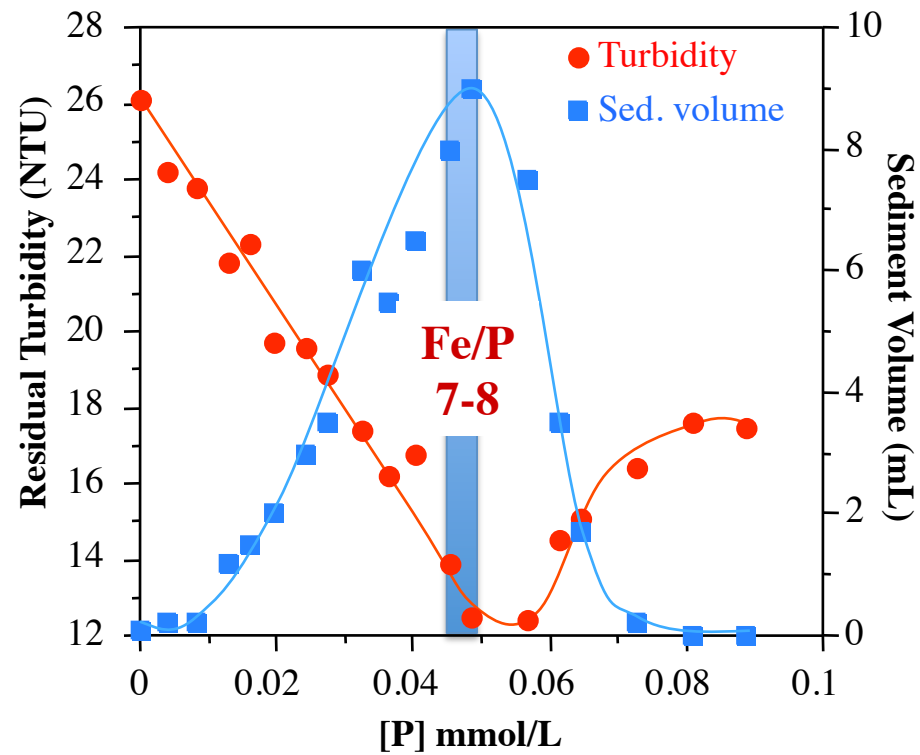


**Figure 1.** Jar-test results for a 500 mg/L suspension of silica particles in the presence of various phosphate ligand additions. (a) Residual turbidity as a function of iron concentration. (b) Sediment volume as a function of iron concentration. The hyphenated lines indicate the 0.36 mmol/L iron coagulant concentration. The arrows show the optimum coagulant concentrations. The error bars are smaller than the size of the symbols.

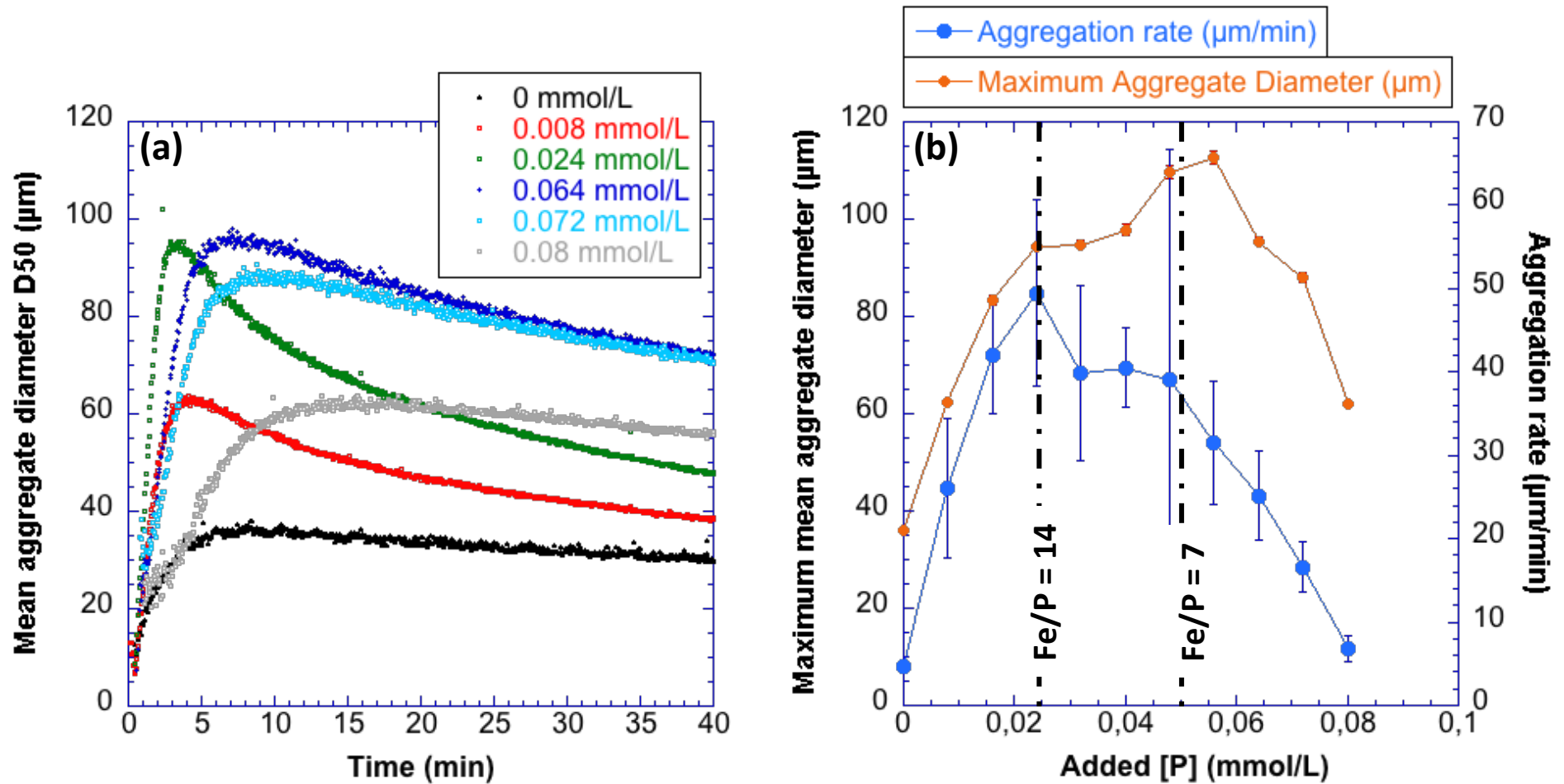


**Figure 2.** (a) Optimum iron coagulant dose as a function of phosphate addition, (•) without silica particles in suspension, (■) with a 500 mg/L silica suspension. The inset shows the jar-test results for a 0.32 mmol/L P concentration coagulated with the iron coagulant in the absence of silica nanoparticles. The other jar-test results are given in figure S1 of Supporting Information.

(b) Residual concentrations in phosphorus (◆) and SiO<sub>2</sub> (□) as a function of iron concentration for suspensions of 500 mg/L SiO<sub>2</sub> and initial phosphorus additions of 0.048 mmol/L and 0.64 mmol/L.

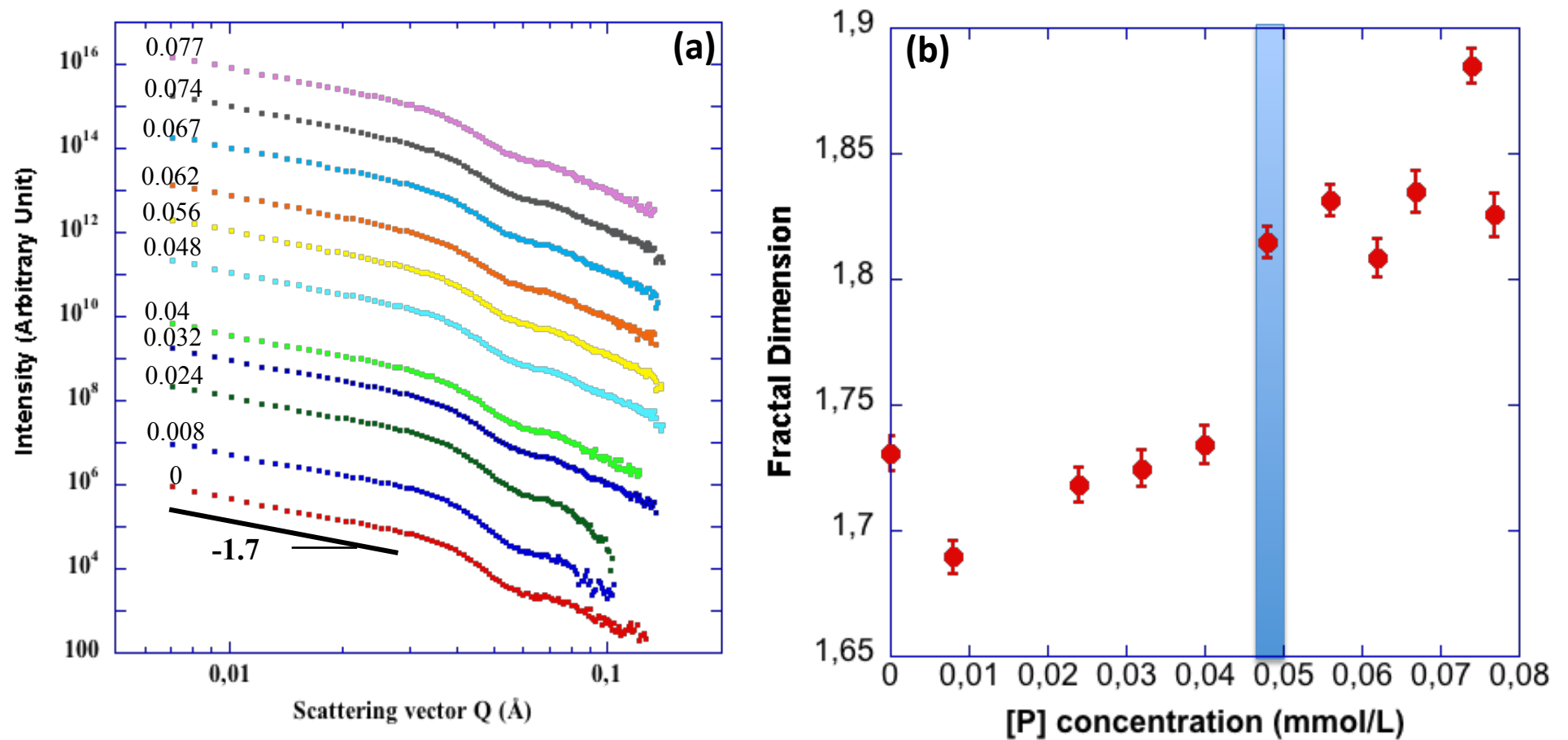


**Figure 3.** Evolution of Residual turbidity (●) and sediment volume (■) as a function of phosphate addition For an iron coagulant concentration of 0.36 mmol/L. The thick bar in blue indicates the [7-8] range in Fe/P.



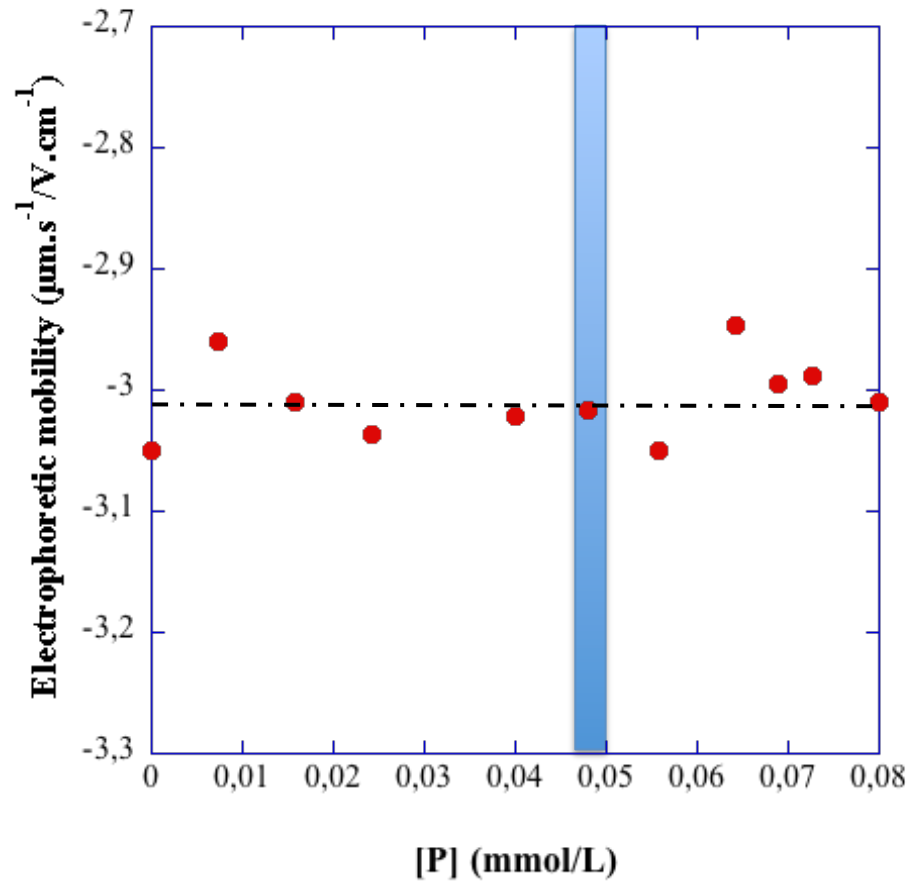
**Figure 4:** (a) Temporal evolution of mean aggregate diameter (D50) for various added P concentrations and an iron coagulant concentration of 0.36 mmol/L.

(b) Evolution of aggregation rate (●) and maximum aggregate size (●) as a function of phosphate concentration for an iron coagulant concentration of 0.36 mmol/L. The confidence intervals for the aggregation rate were obtained using a Student t-test with a significance level of 5%. The standard deviation for the maximum mean aggregate diameter was calculated from the variation of diameter in the vicinity of the maximum of the  $D_{50}$  vs time curve.

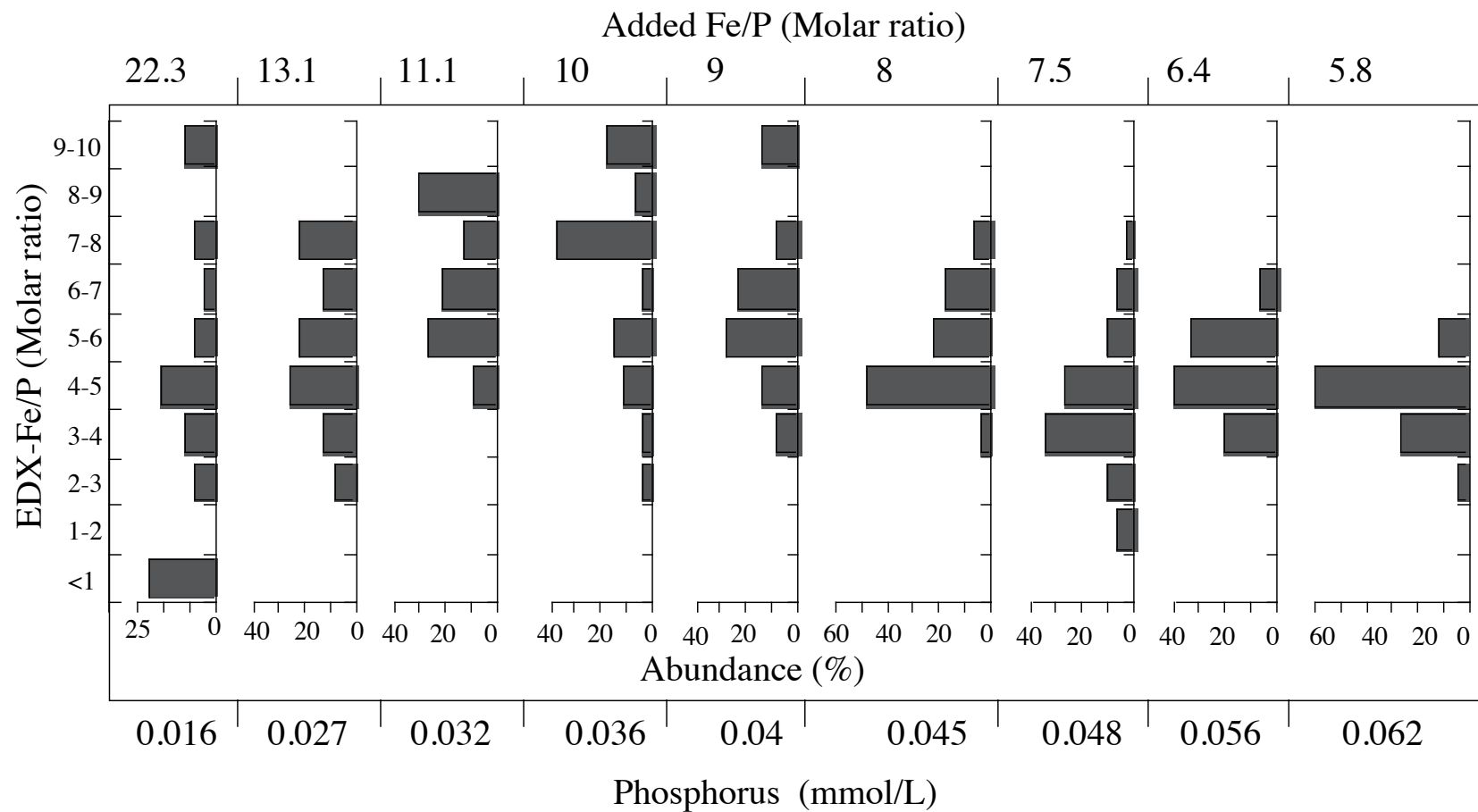


**Figure 5:** (a) Log-Log plot of scattering intensity versus scattering vector for sediments obtained with an iron coagulant concentration of 0.36 mmol/L and various phosphate concentrations (mmol/L) indicated on the left of the SAXS curve.

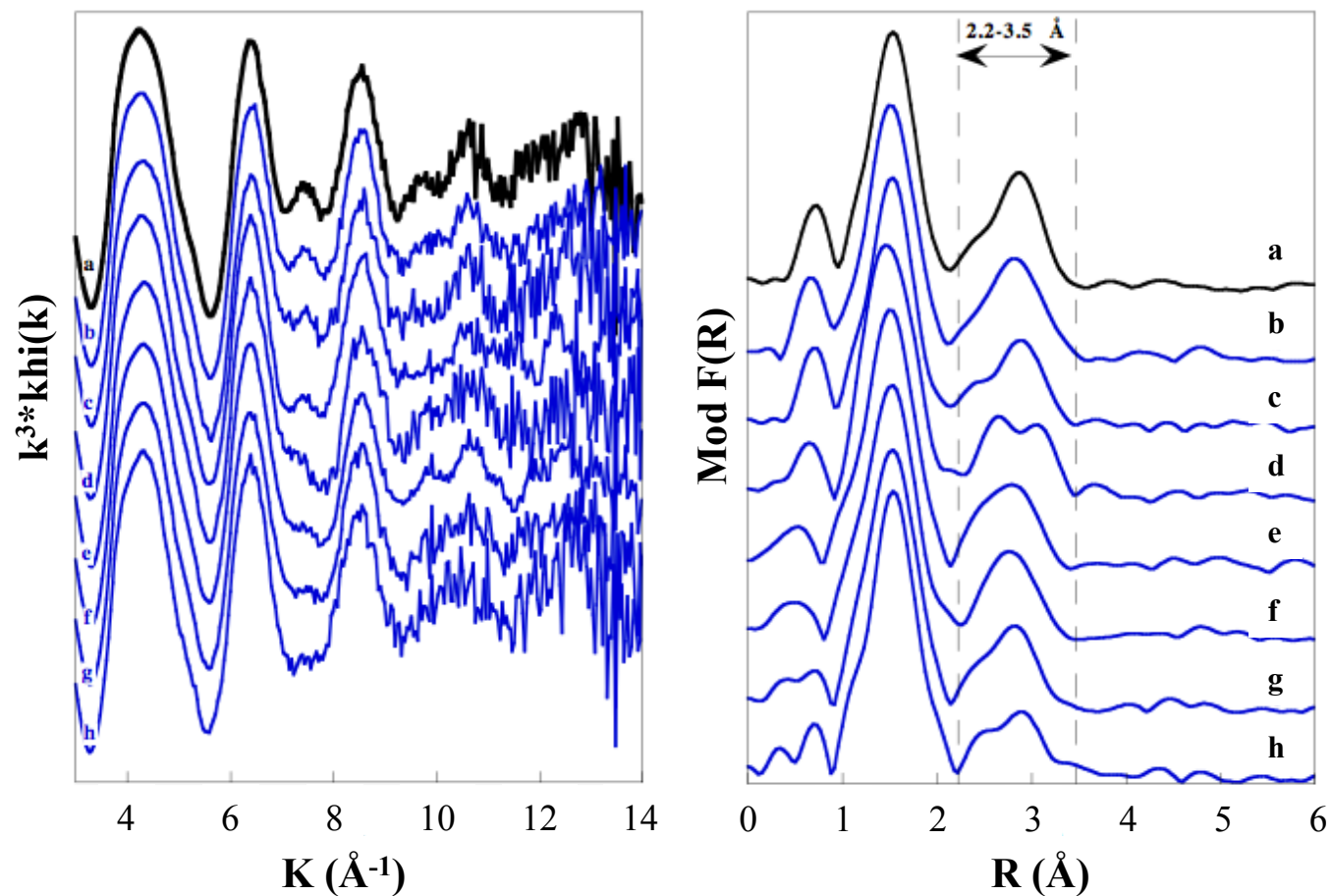
(b) Evolution of the fractal dimension (inferred from the slope of the linear portion of the SAXS curves in (a)) as a function of phosphate concentration. The thick bar in blue indicates the [7-8] range in Fe/P. The confidence intervals for the slope of the regression line giving the fractal dimension were calculated using a Student t-test with a significance level of 5%.



**Figure 6:** Evolution of the aggregate electrophoretic mobility as a function of phosphate addition for an iron coagulant concentration of 0.36 mmol/L. The thick bar in blue indicates the [7-8] range in Fe/P.

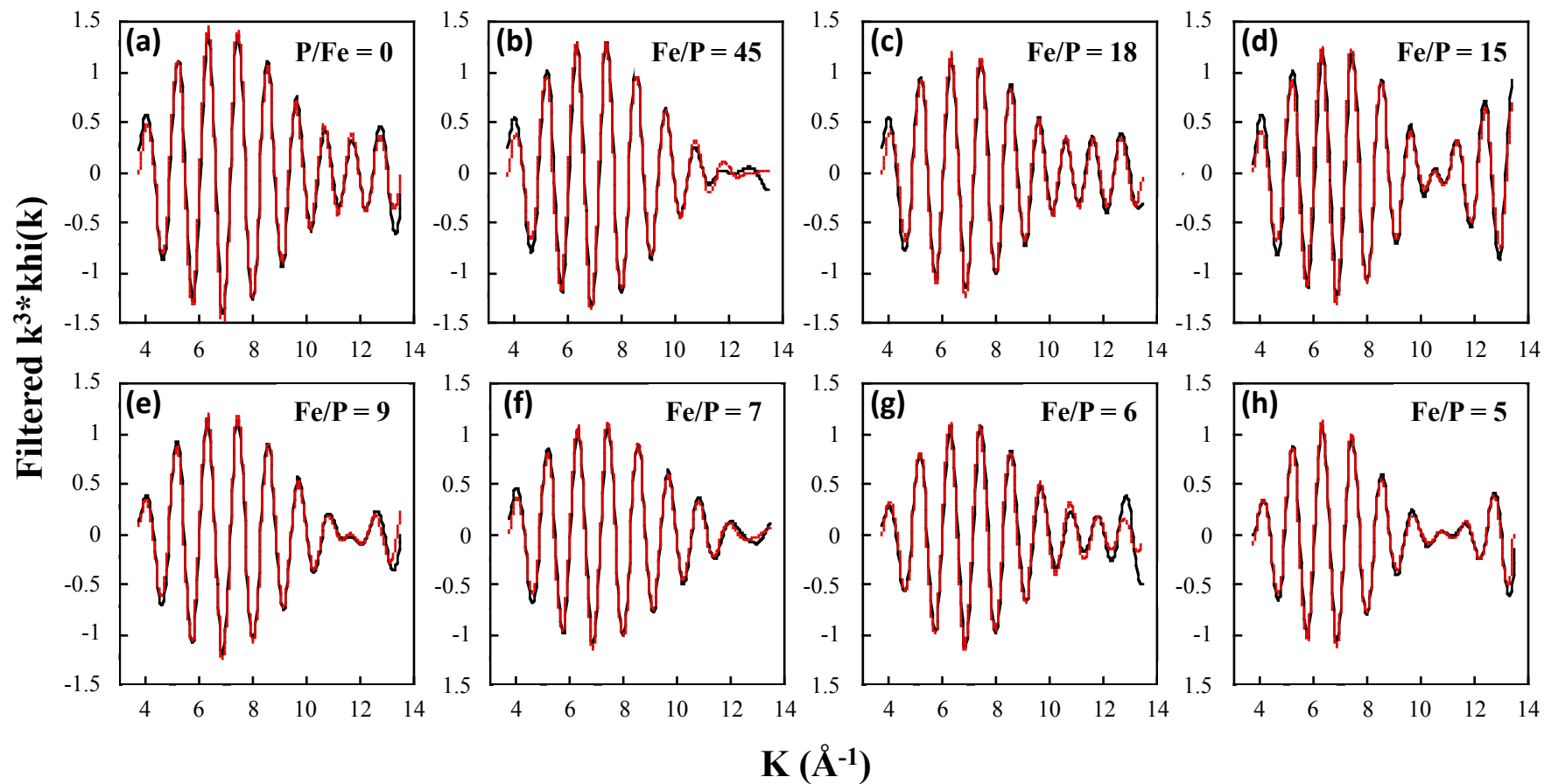


**Figure 7.** Frequency histograms of Fe/P elemental ratio obtained from TEM-EDXS microanalysis on freeze-dried sediments as a function of phosphate concentration for an iron coagulant concentration of 0.36 mmol/L.

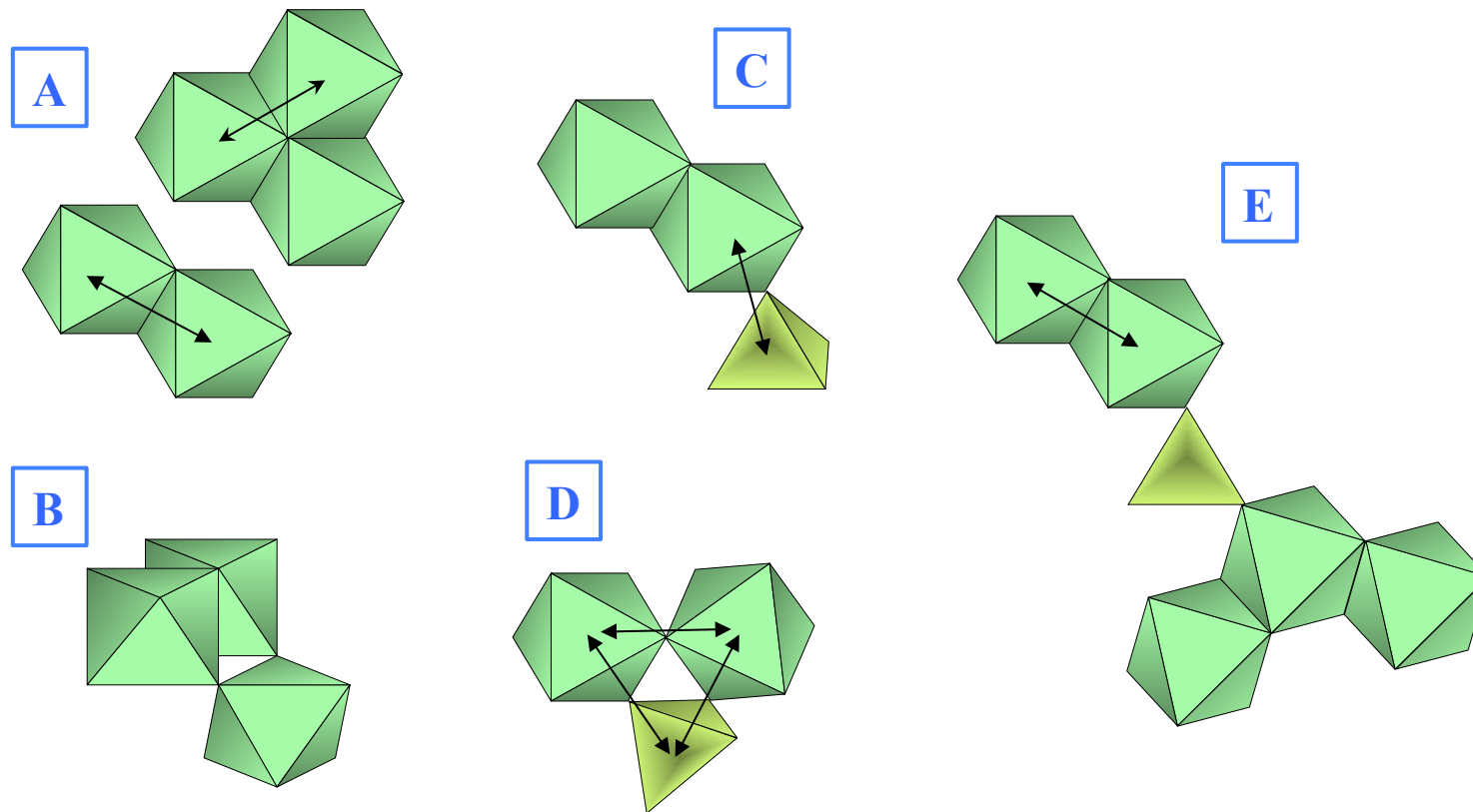


**Figure 8.** EXAFS oscillations ( $k^3 \cdot \chi(k)$ ) and Fourier Transform curves calculated in the  $[3.7-13] \text{\AA}^{-1}$  range with a Kaiser window,  $t=3$ ; a: P/Fe=0; b: Fe/P=45 (0.008mmol/L in P); c: Fe/P=18 (0.02mmol/L in P); d: Fe/P=15 (0.024mmol/L in P); e: Fe/P=9 (0.04mmol/L in P); f: Fe/P=7.5 (0.048mmol/L in P); g: Fe/P=6 (0.06mmol/L in P); h: Fe/P=5 (0.072mmol/L in P).





**Figure 9.** Experimental and theoretical (dashed line) back filtered  $k^3 \cdot k_{hi}(k)$  curves corresponding to 2<sup>nd</sup> coordination shell [2.2-3.5]Å. (a) P/Fe=0; (b) Fe/P=45 (0.008mmol/L P); (c) Fe/P=18 (0.02mmol/L P); (d) Fe/P=15 (0.024mmol/L P); (e) Fe/P=9 (0.04mmol/L P); (f) Fe/P=7.5 (0.048mmol/L P); (g) Fe/P=6 (0.06mmol/LP); (h) Fe/P=5 (0.072mmol/L P).



**Figure 10.** Possible local structures of Fe-P coagulant species: (A) Edge-sharing dimer or trimer, distance [Fe-Fe]  $\sim$  3.0-3.2 Å. (B) double corner-sharing trimer, distance [Fe-Fe]  $\sim$  3.45-3.55 Å. (C) Single corner sharing with a SiO<sub>4</sub> or PO<sub>4</sub> tetrahedron, distance [Fe-P]  $\sim$  3.0-3.3 Å. (D) Single corner sharing Fe complex, distance [Fe-Fe]  $\sim$  3.4-3.6 Å. (E) Fe-P oligomeric species.