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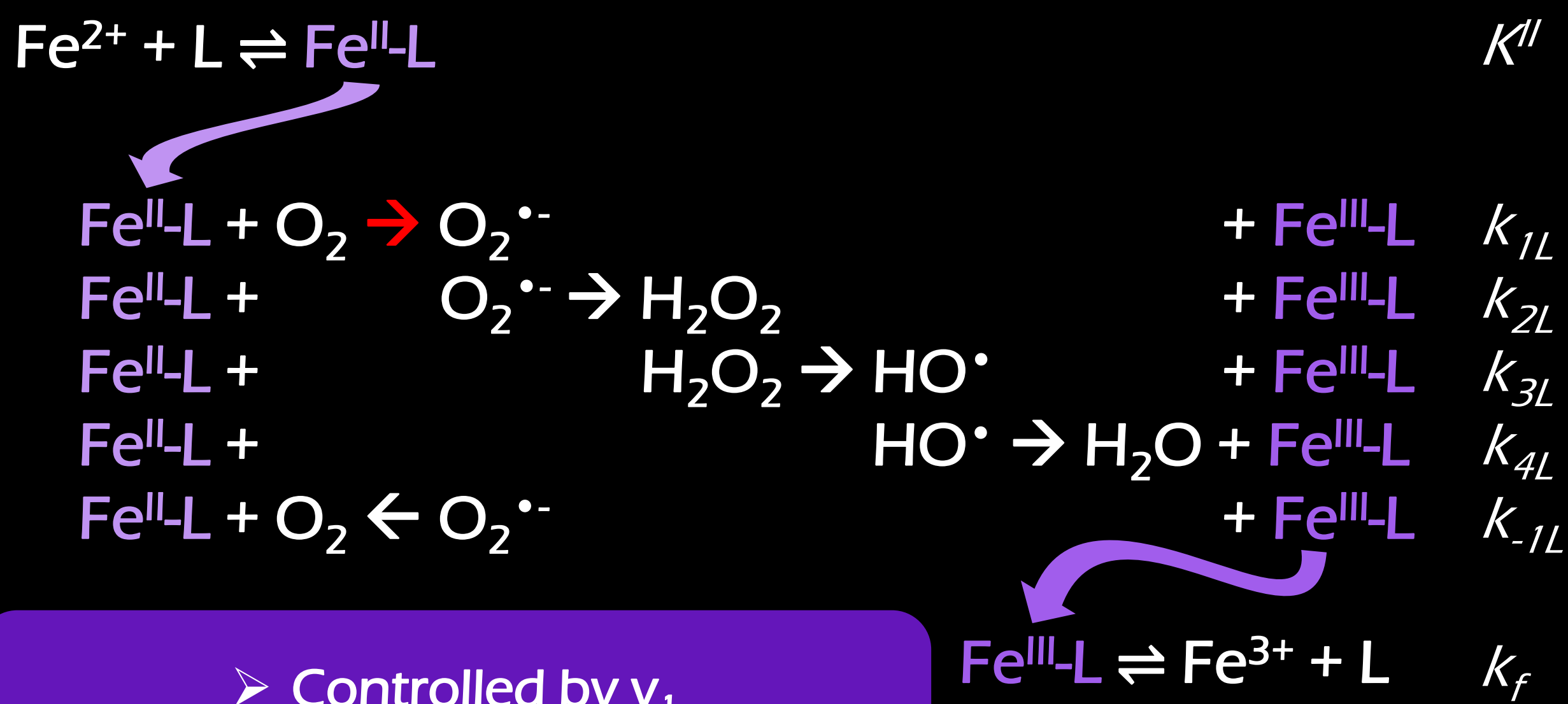
Unraveling the Role of Organic Ligands in Aphotic Iron Oxidation: Mechanisms, Kinetics, and Environmental Implications

Lucas Mousques-Soulas¹, Thierry Pigot^{1,2}, Mathilde Monperrus², Simon Negre², Aubin Thibault de Chanvalon¹

1 - Université de Pau et des Pays de l'Adour, E2S UPPA, CNRS, IPREM, Pau, France
2 - Université de Pau et des Pays de l'Adour, E2S UPPA, CNRS, IPREM, Anglet, France

Two opposed models of iron oxidation

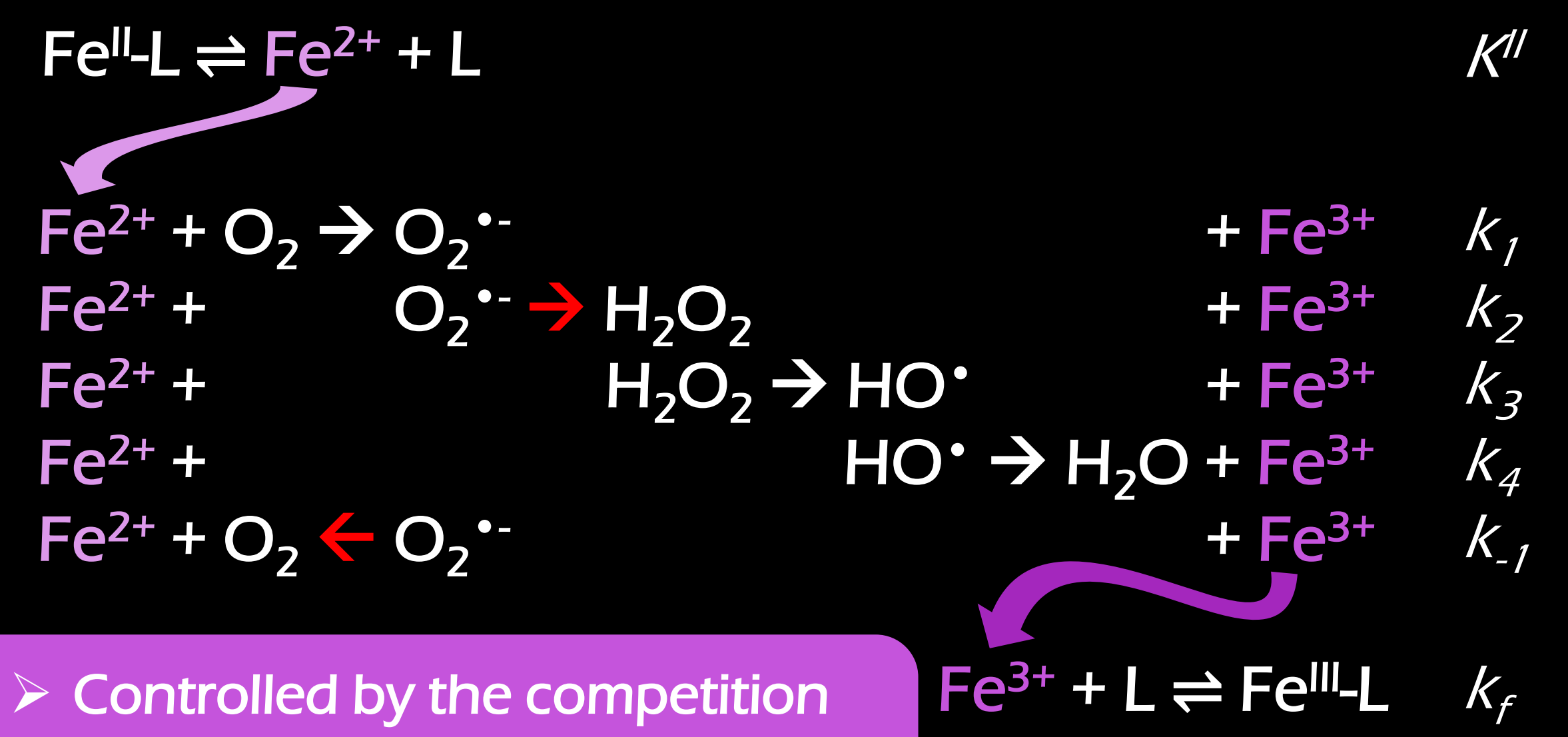
v_1 controlled model



- Controlled by v_1
- Direct oxidation of the complexes

Ref: every publication

v_2 controlled model



- Controlled by the competition between v_2 and v_1
- Oxidation of inorganic Fe^{2+} only

Ref: my future publication

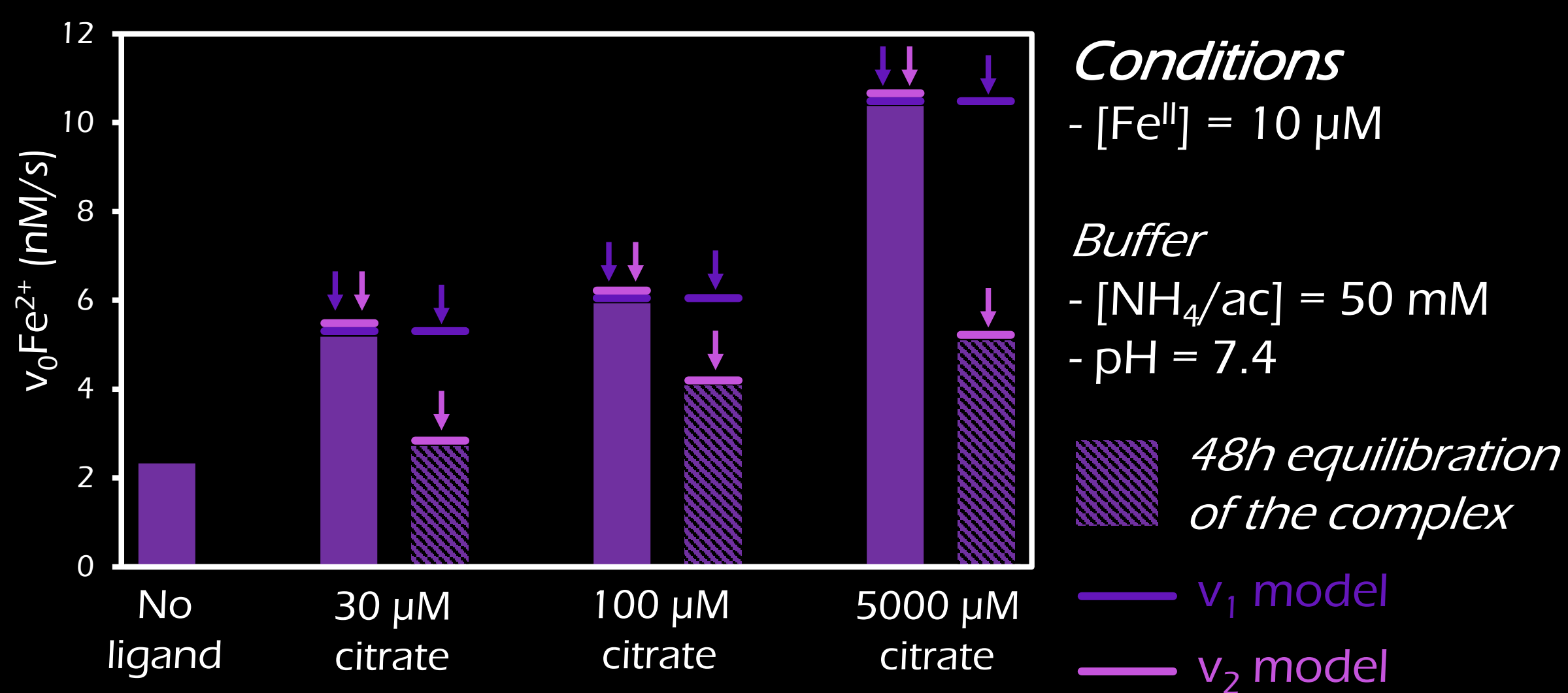
Exact expression $v_{app} = 4k_{1L}[\text{O}_2][\text{Fe}^{\text{II}}\text{L}] \rightarrow$ Limiting step

As a function of L_T and Fe_T $v_{app} = 4[\text{O}_2]k_{1L}[L]_T K^{\text{II}} \frac{[\text{Fe}]_T}{1 + K^{\text{II}}[L]_T}$

Exact expression $v_{app} = 4k_1[\text{O}_2][\text{Fe}^{2+}] \frac{k_2}{k_2 + k_{-1} \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}}$

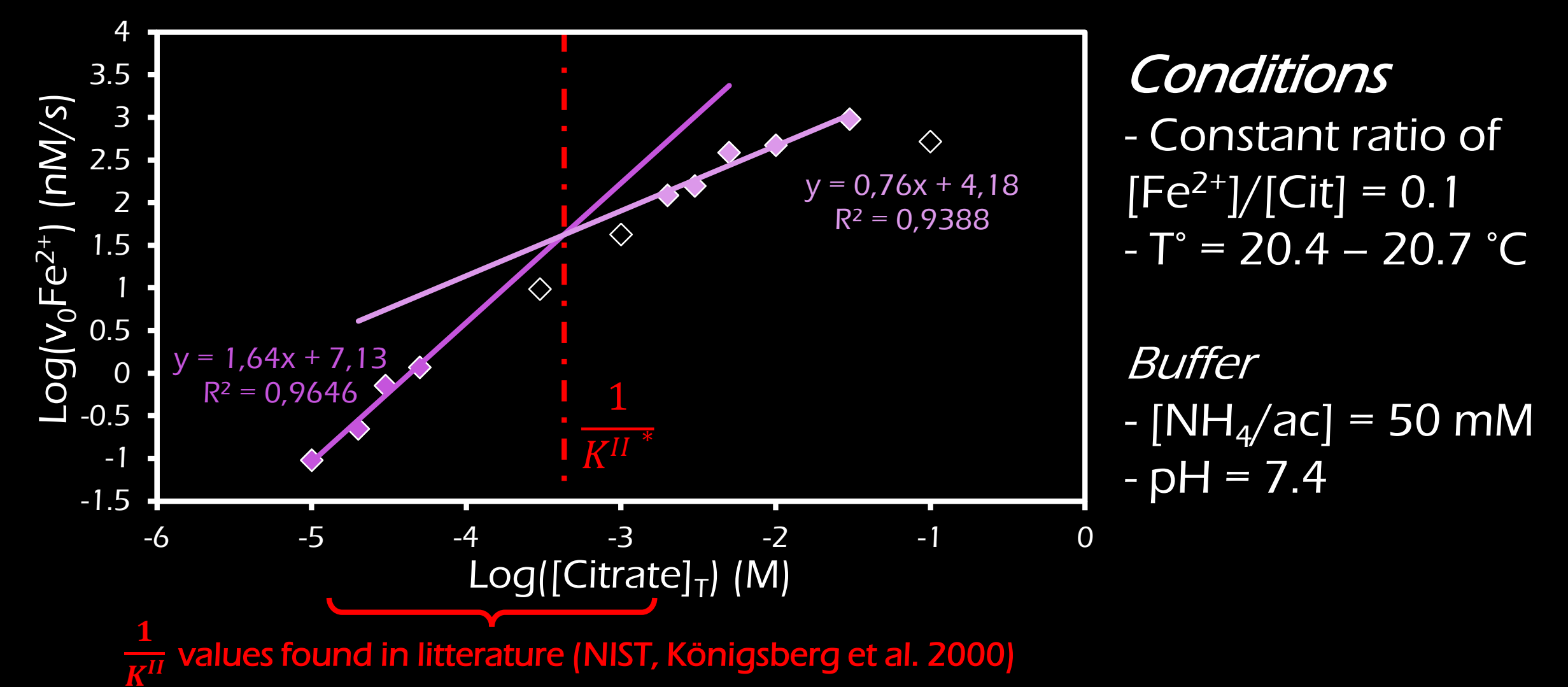
As a function of L_T and Fe_T $v_{app} = 2 \sqrt{\frac{k_2}{k_{-1}}} k_1 [\text{O}_2] k_f [L]_T \frac{[\text{Fe}]_T}{1 + K^{\text{II}}[L]_T}$

Ligand vs Complexation



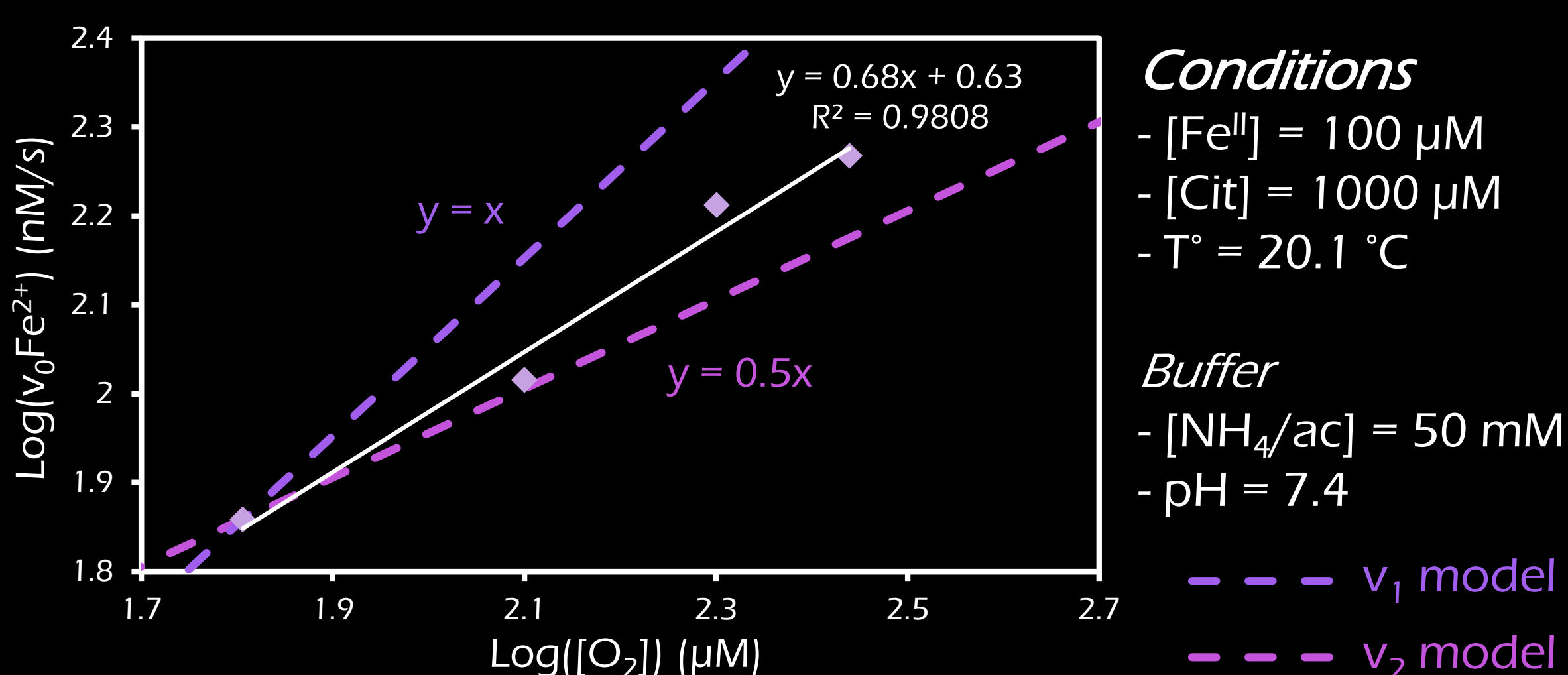
- The presence of the ligand itself accelerates more the oxidation reaction than the complexation of iron in accordance to the v_2 controlled model

Ligand concentration



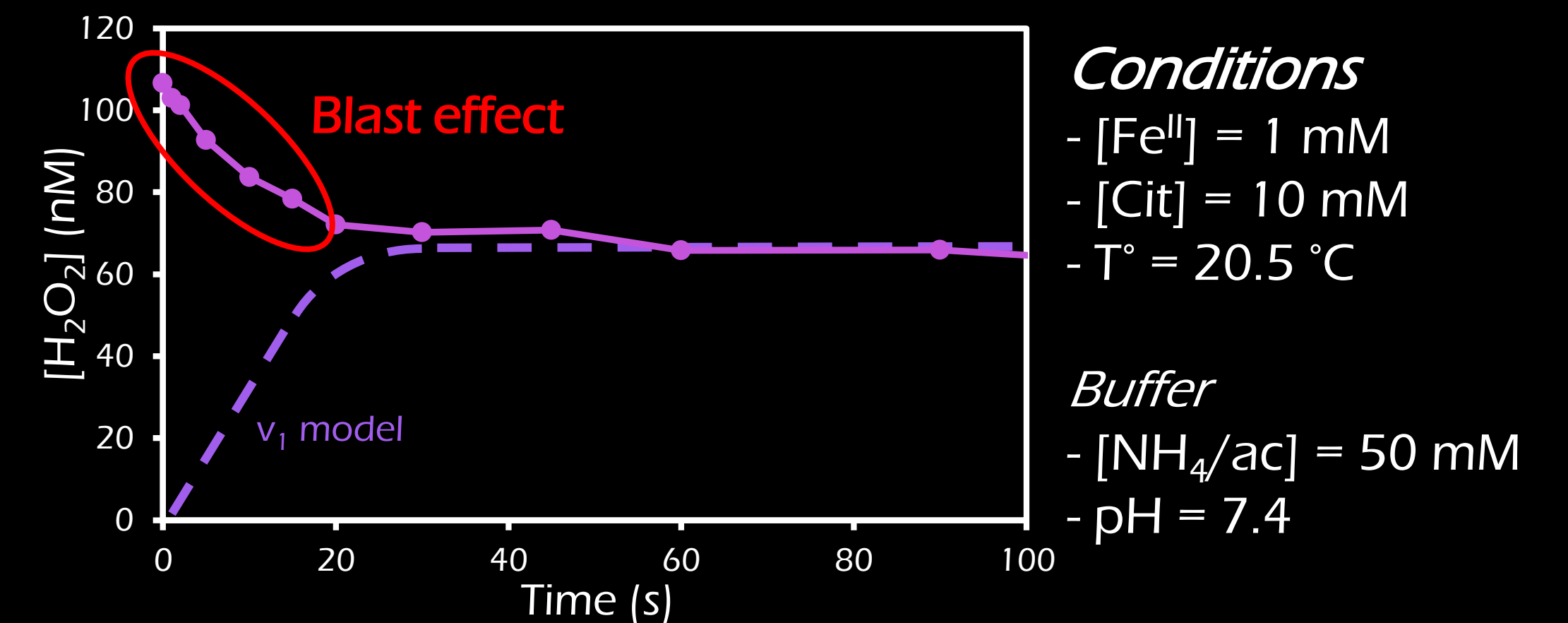
- The order of reaction with Fe_T and L_T corresponds to the v_2 controlled model with an order of 1.5 when $K^{\text{II}}[L]_T \ll 1$ and 0.5 when $K^{\text{II}}[L]_T \gg 1$

$[\text{O}_2]$ dependency



- The first order with dioxygen is not immediately evident. However, enhanced measurements are planned in the near future

H_2O_2 concentration during oxidation



- The v_1 controlled model can't explain the high concentration of H_2O_2 in the first seconds and then its decrease until the steady state.
- On the contrary, with the v_2 controlled model, the v_{app} calculation can explain this observation

Take-home message

The experimental results clearly support the v_2 controlled model, where the inorganic form of Fe^{2+} reacts, in contrast to the v_1 controlled model, where the first reactional step involves the iron-ligand complexes. This v_1 controlled model supported by most publications until now, fails to explain observed phenomena like differences in oxidation rates with equilibrated complexes, orders of reaction of 1.5 and 0.5 in regard of Fe_T and L_T and the newly discovered "Blast effect" in H_2O_2 concentration.

Meanwhile, all of these results can be explained by the v_2 controlled model

This discovery has very large implications, embracing the full scale of iron geochemistry, in particular, 1 - We demonstrated that the complexation of iron is likely to accelerate the oxidation rather than stabilizing Fe^{II} which can be critical at redox interfaces such as sediment/water column or oxygen minimum zone boundaries. 2 - The demonstration of a blast effect paves a new way to describe the oxidative stress in bacterial community or contaminant degradation by Fenton processes