

Siderite Oxidation in the Presence of Organic Ligands

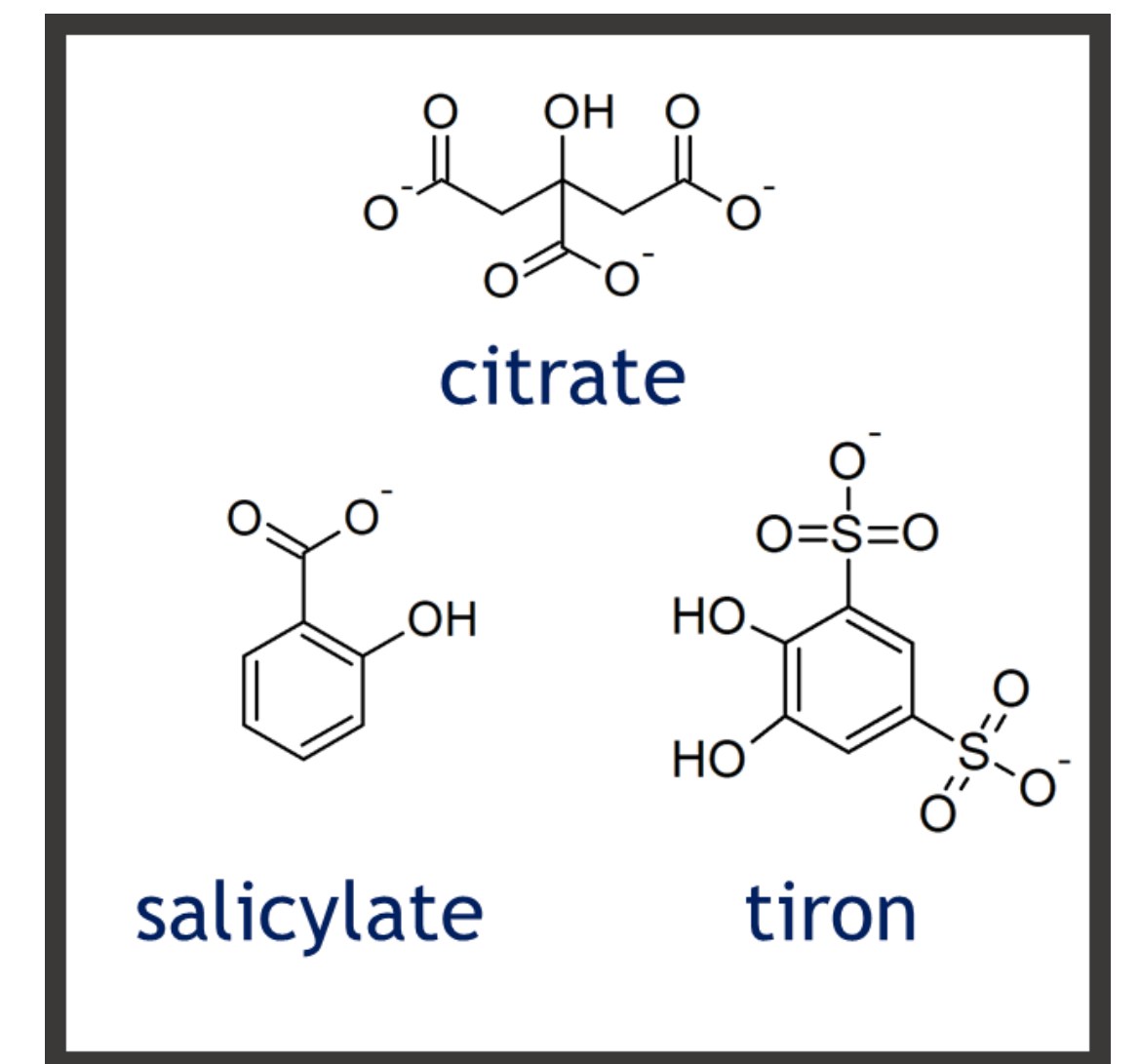
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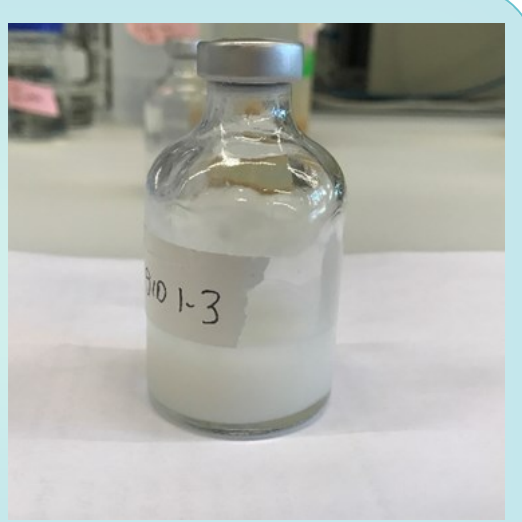
Background

In non-sulfidic, reducing environments, siderite (FeCO_3) is an important sink for solid-bound ferrous iron. The oxidation of siderite may be coupled to the reduction and enhanced sorption of a range of contaminants¹. However, little is currently known about siderite oxidation in natural environments. Fe-chelating organic ligands are likely to be present in high concentrations in geochemical conditions that also favour the formation of siderite and have a strong influence on iron redox processes.

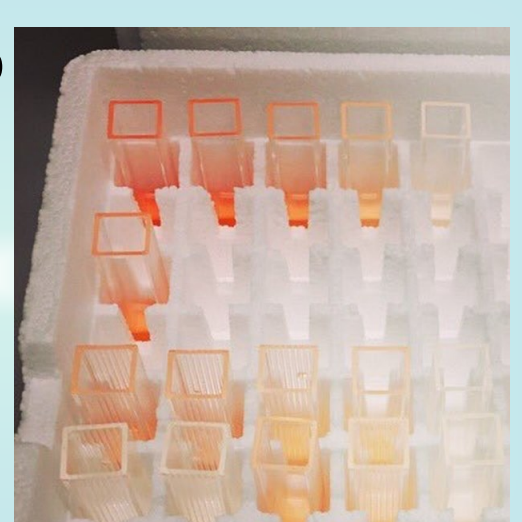
Our aim for this work is therefore to determine the influence of three representative organic ligands; citrate, salicylate, and tiron, on the kinetics and products of siderite oxidation.



1. Triplicate batch reactors prepared with 2 g/L synthetic siderite and 10 mM ligand of interest.



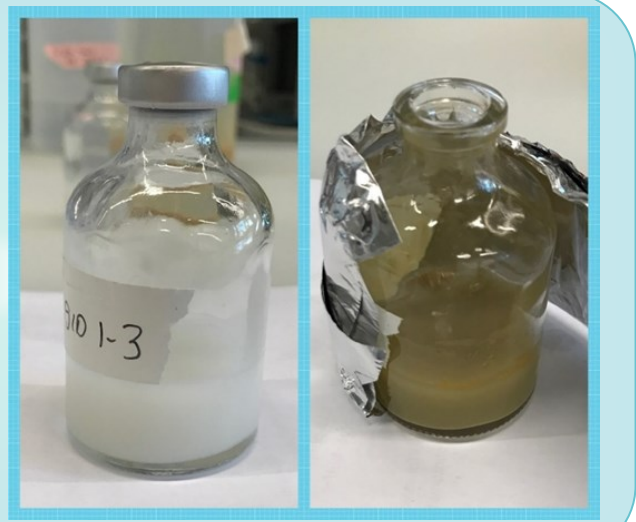
2. $\text{Fe(II)}/\text{Fe(tot)}$ ratio measured colourimetrically over time.



3. HPLC: to monitor ligand sorption over time.



4. Solid phase analysis with XRD, Raman, EM, and Fe XAS.



Findings

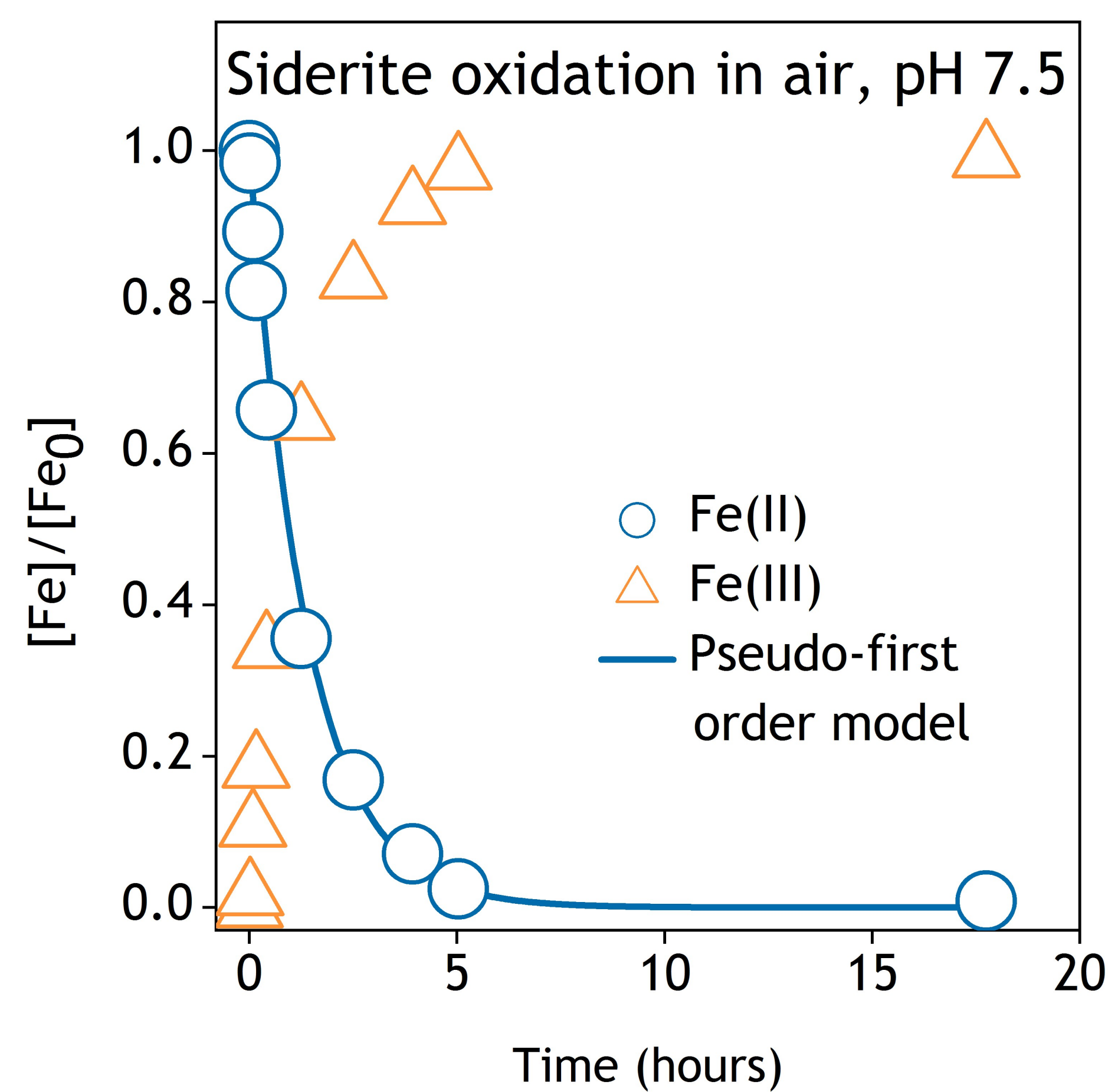


Fig 1. Siderite oxidation kinetics in air

Fig 1. In the absence of an organic phase, our synthetic siderite was rapidly oxidised in air and no Fe(II) was detectable in suspension after **5 hours**. The oxidation kinetics followed a pseudo-first order model.

Fig 2. The oxidation was **significantly slower** in the presence of the organic ligand phases, with up to **50% Fe(II)** remaining in suspension after **500 hours**.

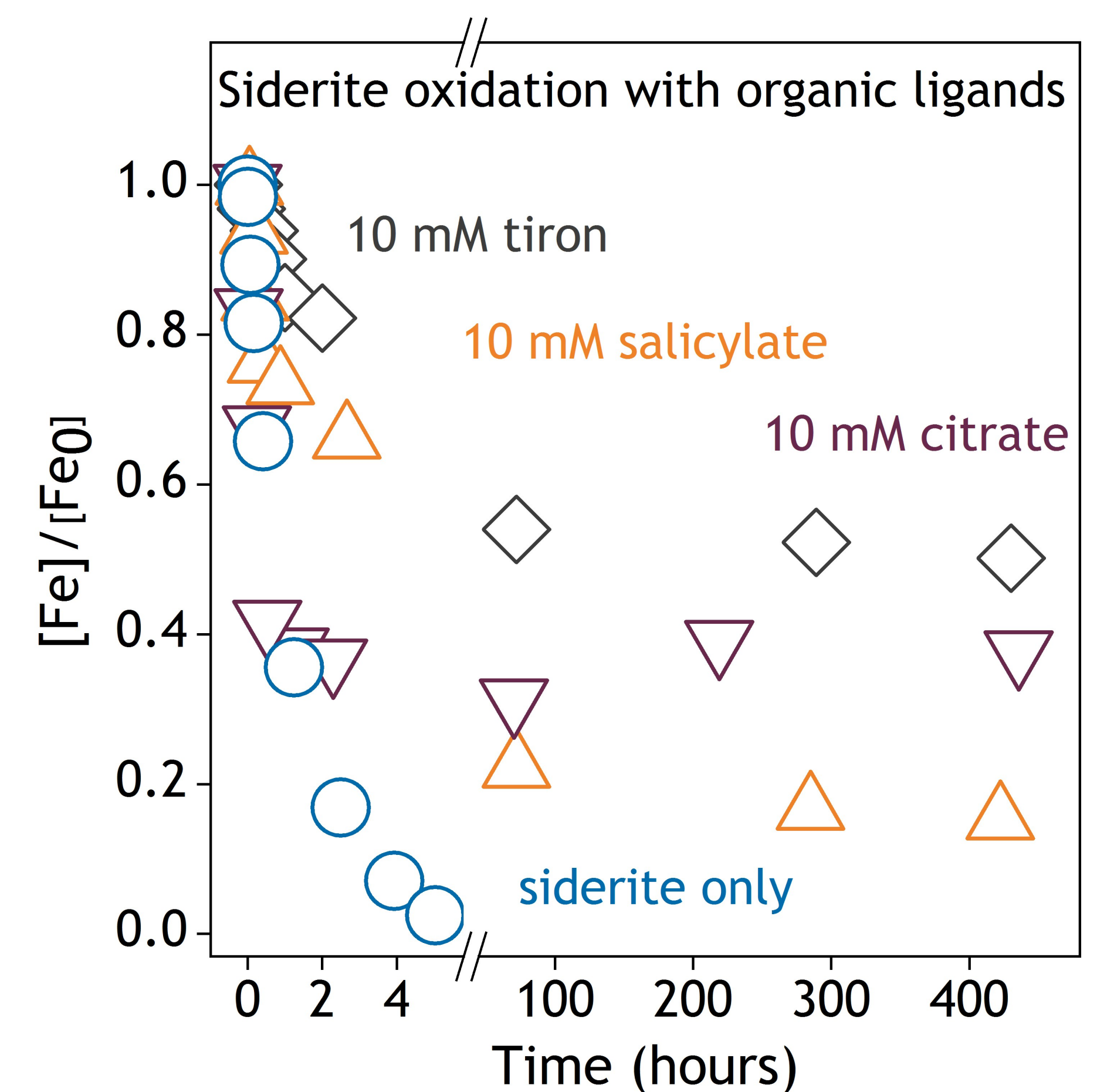


Fig 2. Siderite oxidation in the presence of organic ligands

Fig 3. The presence of an organic ligand affected the **oxidation products** we observed. In the absence of a ligand, siderite was transformed to a mixture of **ferrihydrite, goethite, and lepidocrocite**. After 24 hours in the presence of citrate, **siderite** was preserved as the majority phase with ferrihydrite. In the presence of tiron, the major product was **ferrihydrite** whereas in the presence of salicylate, more crystalline products were formed and **lepidocrocite** was the dominant phase.

Fig 4. We measured between 0.9 mM and 1.8 mM sorption of organic ligand to the mineral phase. We **hypothesise** that the ligand forms a **passivation layer** at the mineral surface, slowing the rate of oxidation. Siderite is preserved in the presence of citrate, which sorbs at time 0 (**black line** in Fig 4).

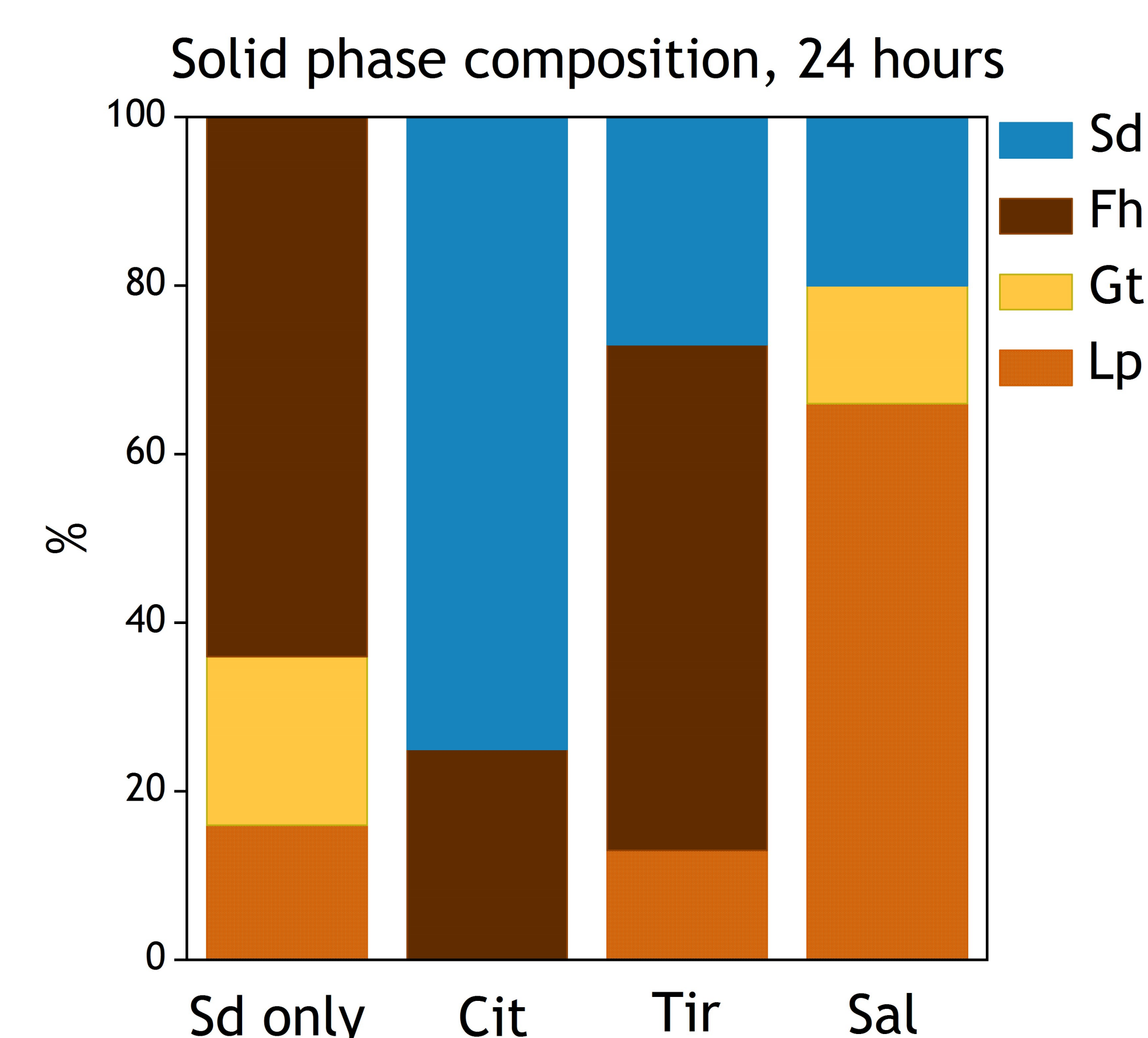


Fig 3. The solid phase composition after 24 hours in air, as determined using Fe k-edge EXAFS.

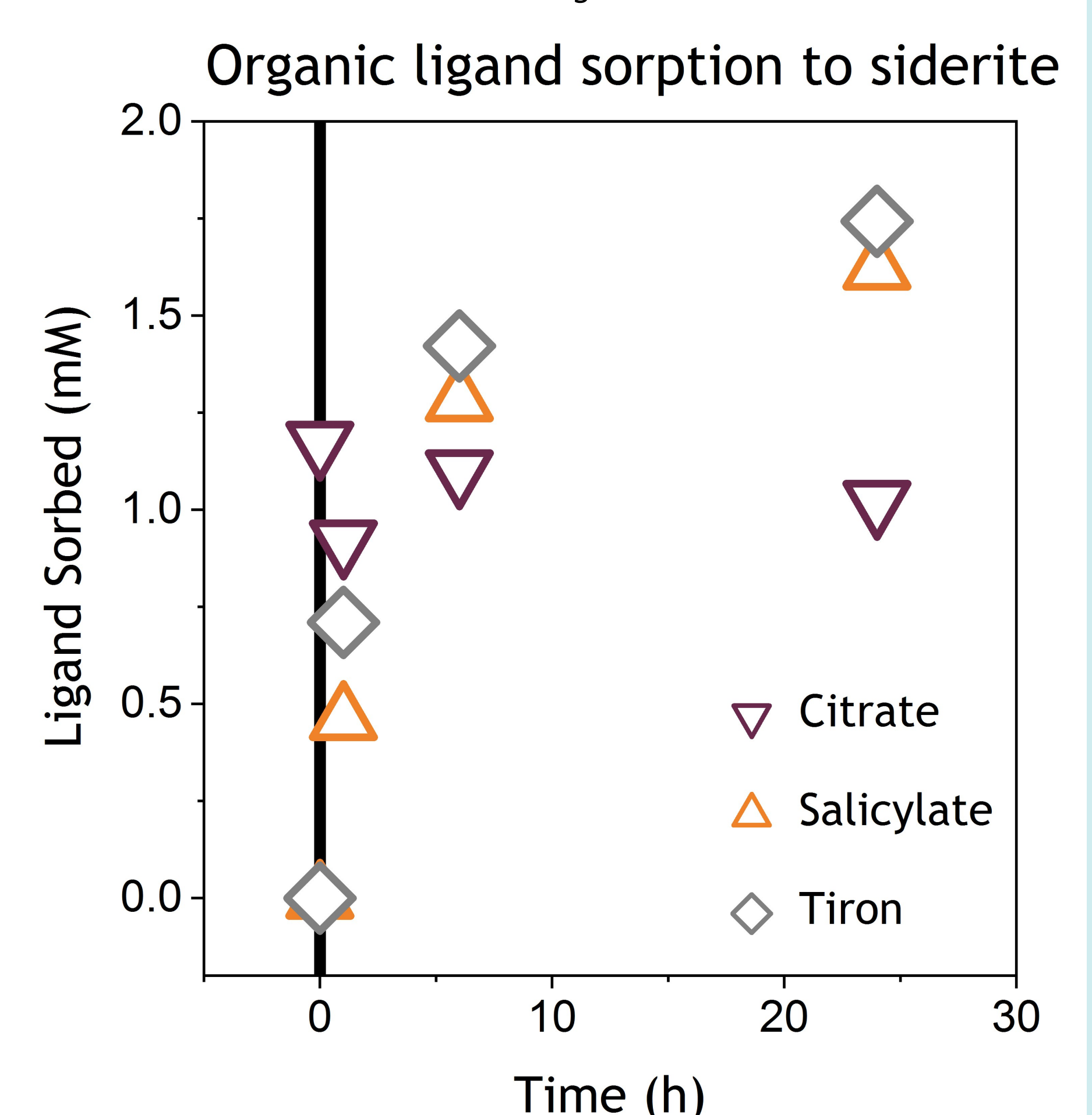


Fig 4. Organic ligand sorption to the solid phase. The black line denotes time zero, where sorption was measured after 24 hours of equilibration before contact with air.

Summary and Ongoing Work

We have shown that the presence of organic ligands stabilises siderite against oxidation in air, with up to 50 % Fe(II) remaining in the mineral structure for up to 500 hours. The presence of organic ligands also affects the oxidation products, and the products vary depending on the structure of the ligand present. We are working to prove our hypothesis that the ligands cause a passivation layer that stabilises the siderite with electron microscopy to gain a deeper understanding of how ligand structure affects siderite oxidation. Our findings are of importance for understanding iron dynamics in periodically reducing environments.

References: 1. Guo, H.; Ren, Y.; Liu, Q.; Zhao, K.; Li, Y. Enhancement of Arsenic Adsorption during Mineral Transformation from Siderite to Goethite: Mechanism and Application. *Environ. Sci. Technol.* **2013**, *47* (2), 1009–1016. 2. Tong, M.; Yuan, S.; Ma, S.; Jin, M.; Liu, D.; Cheng, D.; Liu, X.; Gan, Y.; Wang, Y. Production of Abundant Hydroxyl Radicals from Oxygenation of Subsurface Sediments. *Environ. Sci. Technol.* **2015**, *50* (1), 214–221.

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This research is part of a project that has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme ((788009-IRMIDYN-ERC-2017-ADG)).