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## Siderite Oxidation in the Presence of Organic Ligands

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The biogeochemical cycle of iron is fundamentally important in natural systems and facilitates processes ranging from the carbon cycle to the immobilisation of potentially toxic elements. In the absence of oxygen, iron is the most abundant terminal electron acceptor for microbial respiration, which produces both Fe(II) and oxidised organic matter. Thus, in low-sulfur reducing environments it is likely that conditions favouring the precipitation of the ferrous carbonate mineral siderite are abundant. Previous research has suggested that the oxidation of siderite in the presence of arsenic produced a combination of goethite and siderite that had a sorption capacity for arsenic that was an order of magnitude higher than either siderite or synthetic goethite alone<sup>1</sup>. Furthermore, the oxidation of siderite may produce reactive oxygen species, such as hydroxyl radicals, that are capable of oxidising recalcitrant contaminants and may influence CO<sub>2</sub> release in soils<sup>2,3</sup>. However, despite the clear environmental importance, little is currently known about the oxidative transformation of siderite under environmentally relevant conditions.

Here, we used a series of batch experiments (2 g L<sup>-1</sup> mineral suspension, pH 7.5) to characterise siderite oxidation kinetics under oxic conditions, in the presence and absence of the organic ligands citrate, EDTA, tiron, and salicylate (10 mM). We selected these ligands to be representative of small organic acids that are likely ubiquitous in environments where siderite forms and to contain a range of interesting functional groups, namely carboxylates, catechols and thiols. Alongside batch experiments, we used a combination of Raman microspectroscopy and X-ray diffraction for mineral characterisation.

Our results show that synthetic siderite oxidises extremely quickly and undergoes a complete transformation to poorly crystalline goethite in less than 6 hours. However, in the presence of an organic ligand, up to 50 % of structural Fe(II) remains after 300 hours, which we propose is due to surface passivation of the mineral by the organic ligand. We found that the rate and products of oxidation are dependent on the ligand structure. For the carboxylate ligands citrate and EDTA we found that siderite remained the dominant phase whereas ferrihydrite and lepidocrocite/magnetite predominated in the presence of tiron and salicylate respectively.

Our findings are important for understanding iron dynamics in periodically reducing environments, as siderite may be more stable in the presence of oxygen than previously thought and therefore iron redox cycling may occur at a slower rate than would be otherwise accounted for in biogeochemical models.

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