Cr release from Cr-substituted goethite during the aqueous Fe(II)-induced recrystallization

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INTRODUCTION

- Iron (hydr)oxides rarely occur in a chemically pure form, and usually contain structural trace metal admixtures in soils, especially in polluted soils with metallic contaminants.
- The direct reaction between aqueous Fe(II) ($Fe(II)_{aq}$) and iron (hydr)oxides is the important reaction in the soil iron cycle.
- This reaction results in the structural incorporation of co-existing metals through the isomorphous replacement of these metals with the Fe(III) sites of the iron (hydr)oxides, as well as the occlusion of metals by the crystal units.
- Chromium (Cr) is a common metal contaminant and is of increasing concern due to its toxicity and health risks among humans.
- The influence of $Fe(II)_{aq}$-induced recrystallization of Cr-goethite on the behavior of Cr is not yet to be fully understood.
- In this study, we focused on investigating the structural recrystallization of Cr-substituted goethite (Cr-goethite) and quantifying the release of Cr(III) induced by $Fe(II)_{aq}$ under various reaction conditions.

RESULTS

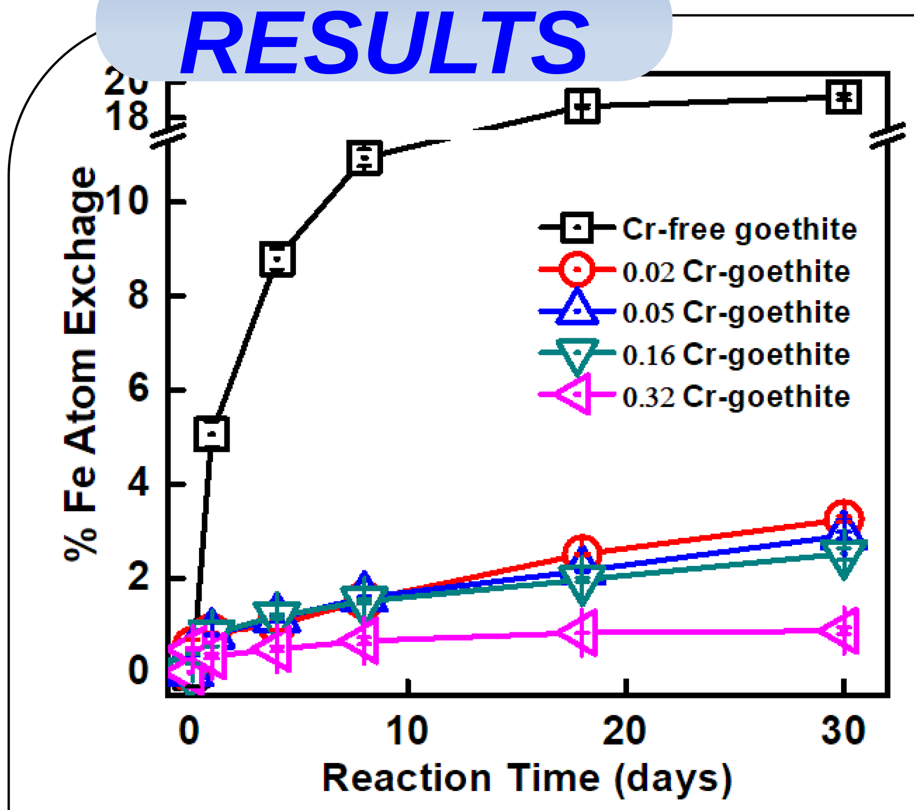

Fig 1. Percent exchange of Fe in goethite

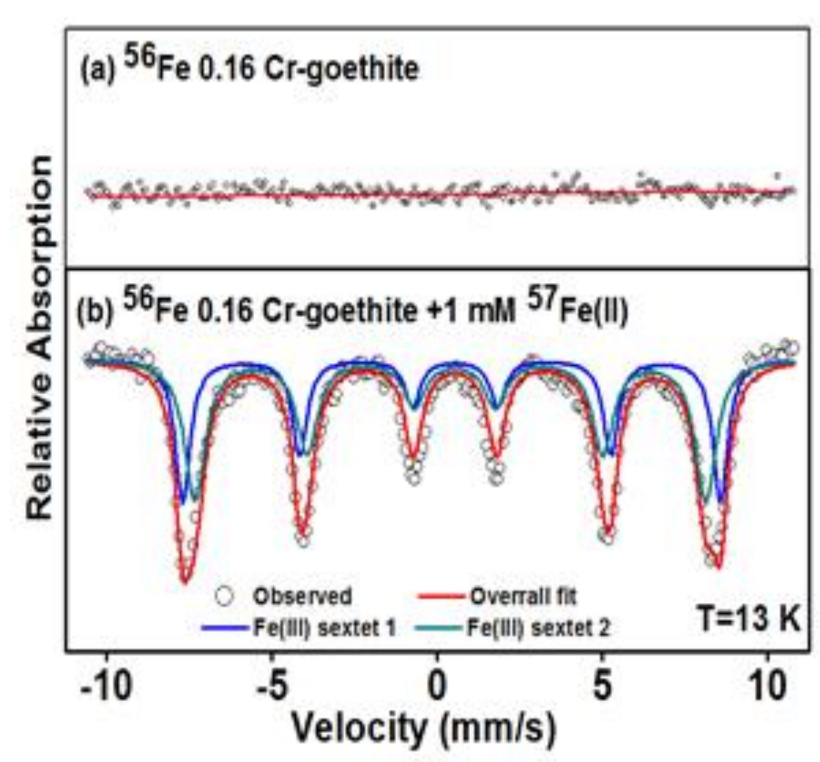

Fig 2. Mössbauer spectra

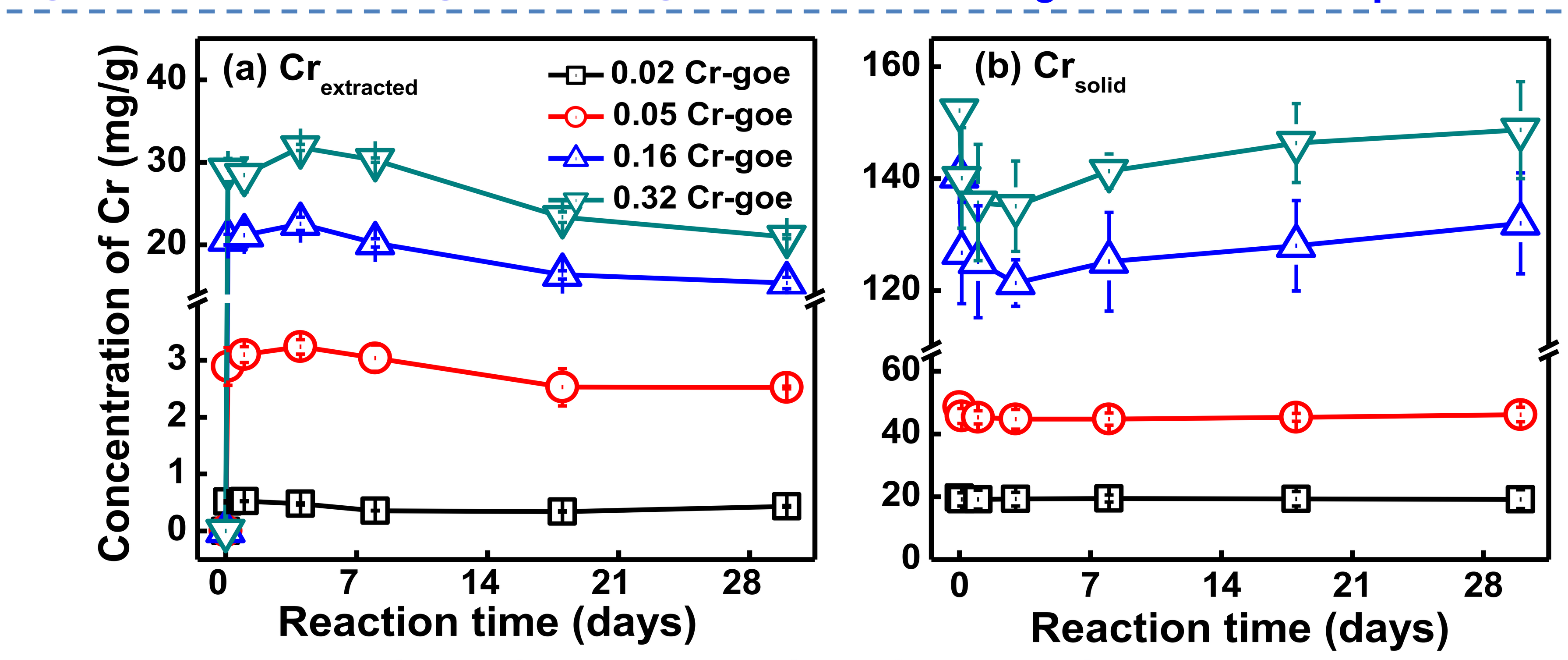

Fig 3. The concentration of Cr_{extr} and Cr_{solid}.

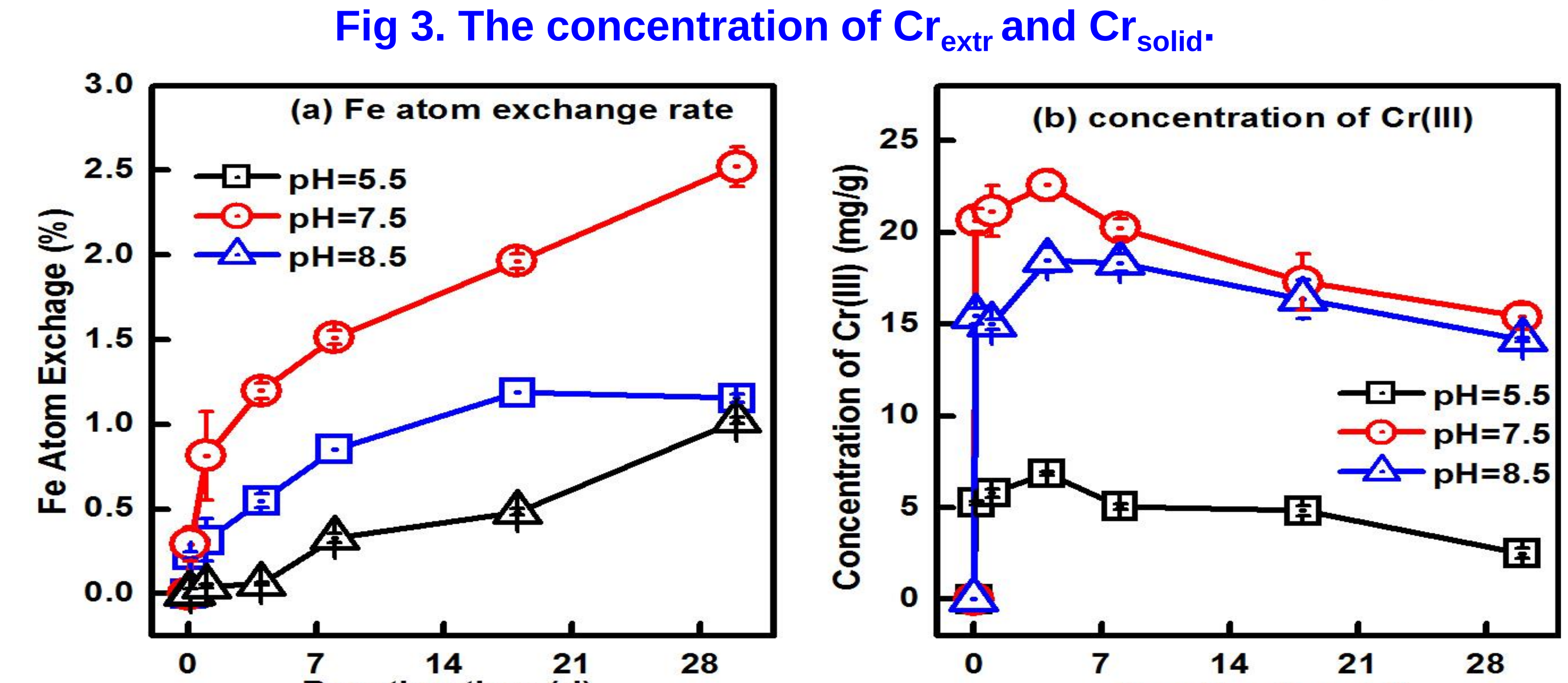

Fig 4. (a) Fe atom exchange percentage and (b) $Cr(III)_{extr}$ concentrations under various pH conditions

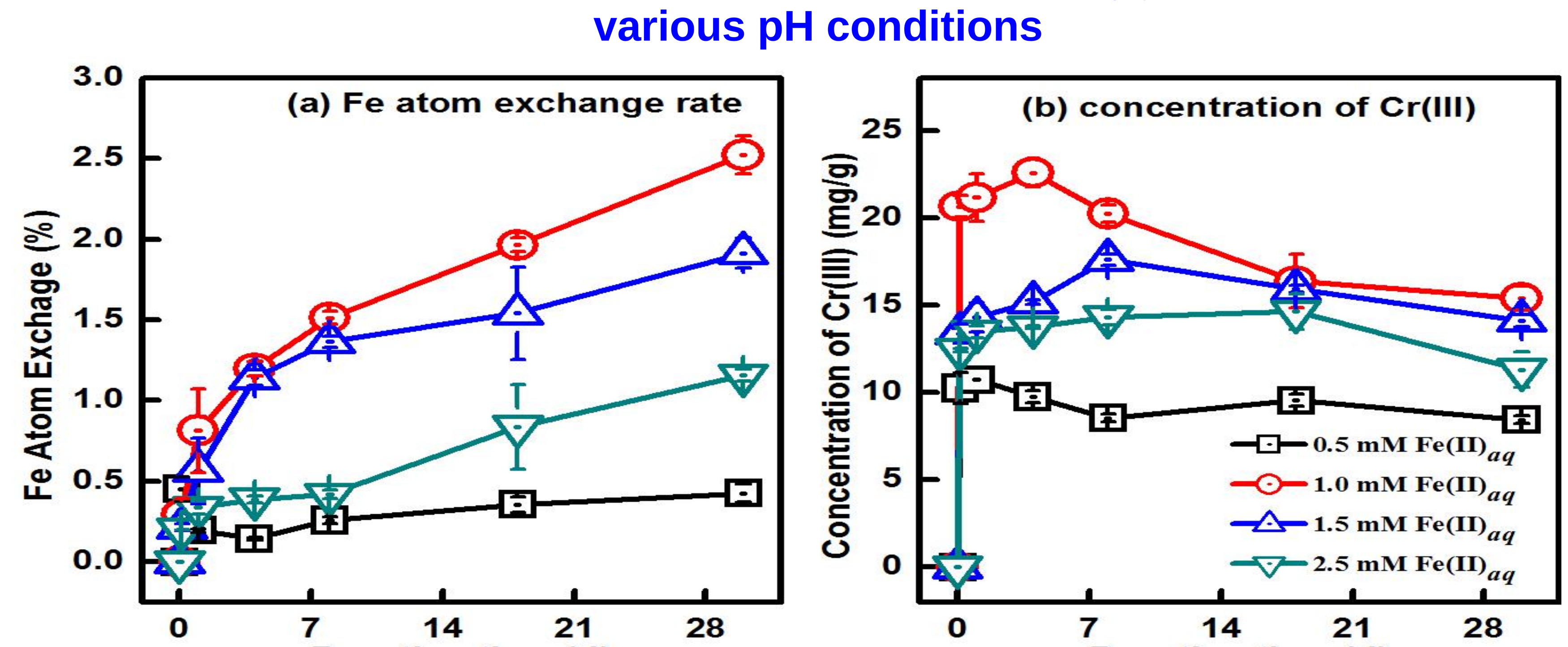

Fig 5. (a) Fe atom exchange percentage and (b) $Cr(III)_{extr}$ concentrations under various concentrations of initial $Fe(II)_{aq}$ conditions

METHODS

Set up: anoxic shaking of 2 g/L goethite / Cr-goethite suspension on an end-overend rotator.

Treatments:

Microcosm I: 1 mM Fe(II) + Cr-goethite(0,0.02,0.05,0.16,0.32) at pH 7.5

Microcosm II: 0.16 Cr-goethite + Fe(II)(0,0.25,0.5,1,2.5 mM) at pH 7.5

Microcosm III: 0.16 Cr-goethite +1 mM Fe(II) at pH 6.5 / 7.5 / 8.5)

Conditions: 25 mM buffer at 25℃

Methodology: UV−vis spectrophotometer, ICP-MS, XRD, SEM

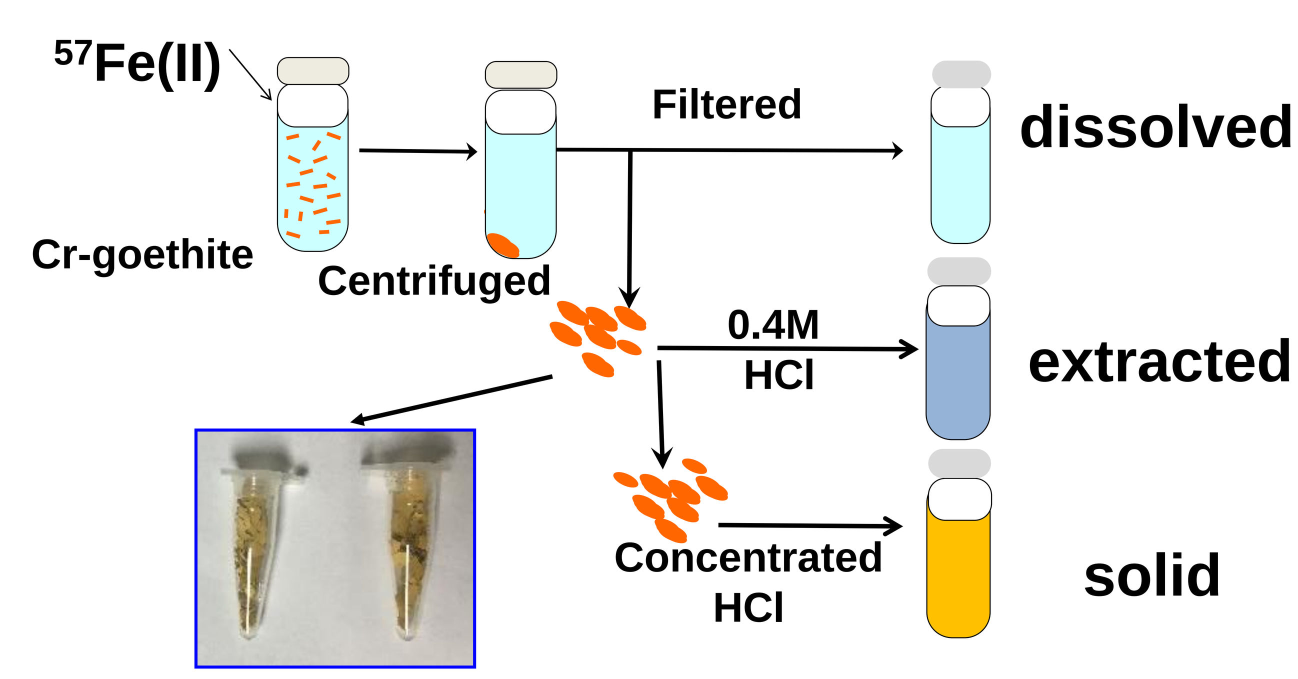

Fig. Experimental procedure

CONCLUSIONS

- Cr substitution inhibited Fe atom exchange during $Fe(II)_{aq}$-induced recrystallization of Cr-goethites.
- The Fe atom exchange between the $Fe(II)_{aq}$ and $Fe(III)_{oxide}$ resulted in the release of Cr(III), and Cr(III) was reincorporated into the goethites during the recrystallization process at a later reaction stage.
- The pH value and initial $Fe(II)_{aq}$ concentration affect the Cr(III) release, more Cr(III) were released during the recrystallization induced by $Fe(II)_{aq}$ at pH 7.5 and 1 mM Fe(II).
- More Cr(III) was released from Cr-goethite in the treatment involving higher Fe atom exchange rates, suggesting that the Fe atom exchange played an important role in the release of Cr(III).
- Cr(III) release was caused primarily due to Cr-related bond rupture and the dissociation of Cr-goethites.

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