



## Effects of phosphate and silicate on the transformation of hydroxycarbonate green rust to ferric oxyhydroxides

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Received 11 February 2015; accepted in revised form 25 August 2015; available online 6 September 2015

### Abstract

Hydroxycarbonate green rust (GR1(CO<sub>3</sub><sup>2-</sup>)) was prepared by oxidation of aerated aqueous suspensions of Fe(II) hydroxide, and the presence of light promoted the transformation of GR1(CO<sub>3</sub><sup>2-</sup>) by dissolved O<sub>2</sub> at pH 7.8 and 25 °C. Further transformation of GR1(CO<sub>3</sub><sup>2-</sup>) in the light was conducted in the presence of orthophosphate (P) or silicate (Si) anions, followed by solution analysis and solid product characterization using X-ray diffraction (XRD), transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FTIR). Results show that both P and Si anions significantly affect the transformation of GR1(CO<sub>3</sub><sup>2-</sup>) through adsorption on the intermediate products. The time required for complete GR1(CO<sub>3</sub><sup>2-</sup>) transformation and the phases, crystallinity and morphology of the transformation products all depend on the Fe/anion molar ratio. When compared to the control, the transformation can be promoted by low Si concentrations but retarded by P. With decreasing Fe/P ratio, the products change from acicular goethite (absence of P) to tabular lepidocrocite (Fe/P: 120–48) and to mixed phases of platelets of ferric GR1(CO<sub>3</sub><sup>2-</sup>) (EX-GR1) and minor ferrihydrite (Fe/P: 24–3). In terms of Si, the products are goethites when the Fe/Si ratio of 48–12, and with increasing ratio, the goethite crystallinity and particle size decrease and the morphology changes from acicular (absence of Si) to plate-like or isodimensional particles. The goethite morphology at low Fe/Si ratios is comparable to natural goethite samples commonly found in soils. At Fe/Si = 3, the products are EX-GR1 platelets with minor ferrihydrite coexisting. The likely pathway of the oxidative GR1(CO<sub>3</sub><sup>2-</sup>) transformation in the control system and in the presence of low concentrations of Si (Fe/Si ≥ 12) is GR1(CO<sub>3</sub><sup>2-</sup>) → amorphous γ-FeOOH-like phase → α-FeOOH via a dissolution–oxidation–precipitation mechanism. In addition, Fe(II) released during dissolution of GR1(CO<sub>3</sub><sup>2-</sup>) is adsorbed on the products and the transformation of the γ-FeOOH-like phase to goethite is catalyzed by the adsorbed Fe(II). For the P system, the released Fe(II) forms ternary surface complexes with P on the mineral surfaces without any catalytic role, leading to the formation of lepidocrocite at low P concentrations. Clearly, the oxidative transformation of green rust to various crystalline iron oxyhydroxides depends on the type and concentration (Fe/anion molar ratio) of co-existing anions. This study also suggests that the natural goethite formed by Fe(II) oxidation in the form of plate-like or isodimensional particles is most likely related to the ubiquitous presence of silicates in soil environments.

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## 1. INTRODUCTION

Green rusts (GRs) commonly occur in the environment and affect redox processes in suboxic environments, such as paddy soils, ground-water, sediments and iron corrosion products (Cornell and Schwertmann, 2003). The blue-greenish color of GR characterizes the moderately reduced grey and waterlogged soils, which turn into ochre due to Fe(II) oxidation upon the exposure of the soils to the atmosphere (Trolard, 2006; Trolard and Bourrié, 2006; Antony et al., 2008). The structure of GRs belongs to the class of layered double hydroxides (LDH) consisting of stacking brucite-like layers of  $[\text{Fe}_{(1-x)}^{\text{II}}\text{Fe}_x^{\text{III}}(\text{OH})_2]^{x+}$  ( $x = [\text{Fe}^{\text{III}}]/[\text{Fe}_{\text{total}}]$ ) with a positive charge compensated by hydrated interlayer anions (Refait et al., 2003). The structures and the chemical formula of GRs depend on the type of the interlayer anion  $A^{n-}$  ( $A^{n-} = \text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{OH}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{SeO}_4^{2-}$ ...) (Bernal et al., 1959; Refait et al., 2000). Here we concentrate on hydroxycarbonate green rust, briefly indicated as  $\text{GR1}(\text{CO}_3^{2-})$ .

$\text{GR1}(\text{CO}_3^{2-})$  has a trigonal structure similar to that of pyroaurite with a stacking sequence AcBiBaCjCbAkA... , where A, B, and C represent  $\text{OH}^-$  planes, a, b, and c are Fe(II)–Fe(III) cation layers and i, j, and k stand for the intercalated layers (Allmann, 1968). The composition of  $\text{GR1}(\text{CO}_3^{2-})$  formed by air oxidation is similar to that of hydroxycarbonate  $[\text{Fe}_4^{\text{II}}\text{Fe}_2^{\text{III}}(\text{OH})_{12}]^{2+} \cdot [\text{CO}_3 \cdot 3\text{H}_2\text{O}]^{2-}$  with  $x = [\text{Fe}^{\text{III}}]/[\text{Fe}_{\text{total}}] = 1/3$  (Génin and Ruby, 2008), while  $\text{GR1}(\text{CO}_3^{2-})$  prepared by coprecipitation of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions has  $x$  of  $1/4$ – $1/3$  as shown by Mössbauer spectroscopy (Génin et al., 2005).

$\text{GR1}(\text{CO}_3^{2-})$  is a metastable product that readily transforms into more stable iron (oxyhydr)oxides, such as goethite, lepidocrocite, ferrihydrite, hematite, magnetite, as well as ferric GRs (EX-GR1), through oxidation by  $\text{O}_2$  or other oxidants (O'Loughlin et al., 2003; Legrand et al., 2004a). The  $\text{GR1}(\text{CO}_3^{2-})$  transformation and the crystallinity and crystallite size of the transformation products are affected by the Fe(II) oxidation rate, which depends on pH, temperature, and dissolved  $\text{O}_2$  (DO) concentration (Wang et al., 2013b). With increasing Fe(II) oxidation rate, the products follow the sequence of magnetite, goethite, and lepidocrocite, while the crystallite size and the crystallinity of the products decrease (Wang et al., 2013b). Furthermore, the Fe(III)/Fe(II) system is sensitive during photochemical cycling (Voelker et al., 1997; Page et al., 2013), and thus light is also a factor that may affect the  $\text{GR1}(\text{CO}_3^{2-})$  transformation and that deserves attention.

The presence of co-existing anions, such as phosphate (P) and silicate (Si), have a strong impact on the products formed (Benali et al., 2001; Legrand et al., 2004b; Ruby et al., 2006; Kwon et al., 2007; Refait et al., 2007). According to Benali et al. (2001),  $\text{GR1}(\text{CO}_3^{2-})$  transforms into goethite in the absence of P, but into ferrihydrite with the Fe/P molar ratio = 3. However, Legrand et al. (2004b) suggested that the product was EX-GR1, a GR-like layered structure that contains only Fe(III), with P adsorbed on the surface of EX-GR1. In contrast, Refait et al. (2007) reported that nano-phase lepidocrocite was the main final product at Fe/P = 120, while EX-GR1 was the only final

product at Fe/P = 6. These reports suggest that the final transformation products of  $\text{GR1}(\text{CO}_3^{2-})$  in the presence of P depend on the Fe/P ratio. Additionally, the effect of P on  $\text{GR1}(\text{Cl}^-)$  transformation has also been investigated, and the results indicate that it delays the transformation of  $\text{GR1}(\text{Cl}^-)$  and reduces the particle size of final lepidocrocite particles (Sahoo et al., 2011).

In crustal material, silicate is abundant and its aqueous anions (Si) are ubiquitous in soils (Seyfferth et al., 2013), so the effect of Si on the transformation of GRs has attracted attention as well. Ruby et al. (2006) and Kwon et al. (2007) have reported in some detail the effects of Si on the stability and oxidation of  $\text{GR2}(\text{SO}_4^{2-})$ , but the transformation of  $\text{GR1}(\text{CO}_3^{2-})$  in the presence of Si has only been briefly explored (Legrand et al., 2004b). Considering the ubiquitous presence of Si, a further systematic examination of the effects of Si on the transformation of  $\text{GR1}(\text{CO}_3^{2-})$  is essential and a comparison of the effects between Si and P anion will reveal the differences between their roles.

Consequently, although the inhibitory effects of phosphate or silicate on the oxidation of green rust have been reported (Benali et al., 2001; Legrand et al., 2004b; Kwon et al., 2007; Refait et al., 2007), our understanding is still limited about the concentration effects of P or Si, differences in mineral transformation processes between P and Si, and the underlying mechanisms. To this end, the transformation of  $\text{GR1}(\text{CO}_3^{2-})$  in the presence of different silicate or phosphate concentrations has been comparatively explored in terms of reaction processes controlling the formation of different ferric phases and the operating mechanisms. In addition, the effects of light on the  $\text{GR1}(\text{CO}_3^{2-})$  transformation without inhibitors were also examined. To reach these aims, we synthesized  $\text{GR1}(\text{CO}_3^{2-})$  and monitored its transformation in the presence of various concentrations of P or Si at a constant pH and temperature through electrochemical measurements. The phases of the intermediate products of  $\text{GR1}(\text{CO}_3^{2-})$  oxidation were characterized by the instant fast-scanning X-ray diffraction (XRD) on sampled wet solid pastes. The final dried products were investigated by slow-scanning XRD, Fourier transform infrared (FTIR) spectroscopy, and transmission electron microscopy (TEM). The anion concentrations in the solution were also measured. Based on the mineral phases identified and the corresponding variations of Eh and anion concentrations, the effects of silicate and phosphate on the mechanisms and transformation products of  $\text{GR1}(\text{CO}_3^{2-})$  were compared and discussed. Furthermore, a mechanism of formation of goethite with different morphologies was also proposed.

## 2. MATERIALS AND METHODS

### 2.1. Formation of $\text{GR1}(\text{CO}_3^{2-})$

$\text{GR1}(\text{CO}_3^{2-})$  was synthesized by following Benali et al. (2001), using the procedure and reaction cell as described in our previous study (Wang et al., 2013b). A schematic representation of the reaction cell is depicted in Fig. EA-1.

Briefly, the synthesis was started by adding 95 mL 0.18 M  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  to 95 mL solution containing 0.3 M

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