The oxidation of carbonate green rust into ferric phases: solid-state reaction or transformation via solution

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Abstract—The oxidation of carbonate green rust, GR(CO3
2
−), in NaHCO3 solutions at T = 25°C has been investigated through electrochemical techniques, FTIR, XRD, TEM and SEM. The used GR(CO3
2
−) samples were made of either suspended solid in solution or a thin electrochemically formed layer on the surface of an iron disc. Depending on experimental conditions, oxidation occurs, with or without major modifications of the GR(CO3
2
−) structure, suggesting the existence of two pathways: solid-state oxidation (SSO) leading to a ferric oxyhydroxycarbonate as the end product, and a dissolution-oxidation-precipitation (DOP) mechanism leading to ferric oxyhydroxides such as lepidocrocite, goethite, or ferrihydrite. A formula was proposed for this ferric oxyhydroxycarbonate, Fe6
ii
,III
ii
O
2+x
(2x)(OH)12−2x(H2O)x(CO3)x, assuming that the solid-state oxidation reaction is associated to a deprotonation of the water molecules within the interlayers, or of the hydroxyl groups in the Fe(OH) octahedra layers. The DOP mechanism involves transformation via solution with the occurrence of soluble ferrous-ferric intermediate species. A discussion about factors influencing the oxidation of carbonate green rust is provided hereafter. The ferric oxyhydroxycarbonate can be reduced back to GR(CO3
2
−) by a reverse solid-state reduction reaction. The potentiality for a solid-state redox cycling of iron to occur may be considered. The stability of the ferric oxyhydroxycarbonate towards thermodynamically stable ferric phases, such as goethite and hematite, was also studied. Copyright © 2004 Elsevier Ltd

1. INTRODUCTION

Green rains (GRs) are layered Fe(II)-Fe(III) hydroxi-salts that are suspected to occur as minerals in soils alternating redox conditions (Ponnamperuma, 1972; Lindsay, 1979; Taylor, 1980; Trolard et al., 1997). The bluish-green colour of such soils, which turns ochre once exposed to air, would be due to the presence of these mixed-valence compounds. This natural occurrence was postulated on the basis of Mössbauer spectroscopy analysis. Green rains have also been identified in aerobic/anoxic redox environments (Butler and Beynon, 1967; Stampfl, 1969; McGill et al., 1976; Génin et al., 1993; Abdelmoula et al., 1996; Bonin et al., 2000; Savoye et al., 2001).

Green rains belong to the general class of layered double hydroxide (LDH) characterised by a crystalline structure consisting in the stacking of brucite-like layers carrying positive charges and interlayers constituted by anions and water molecules. The structure and the chemical formula of GRs depend upon the specific anions A
n−
 that they incorporate (A
n− = Cl−, SO4
2−, CO3
2−...) (Bernal et al., 1959; Génin et al., 1998). Carbonate green rust, GR(CO3
2
−), has a trigonal structure looking like that of pyroaurite with a stacking sequence A
Cl−B
BaC
CjCkA,..., where A, B, and C represent OH− planes, a,b, and c Fe(II)-Fe(III) cations layers and i,j, and k intercalated layers (Allmann, 1968). The Fe(II)/Fe(III) ratio usually found for carbonate green rust is 1. (Hansen, 1989) and the chemical formula, [Fe4
ii
FeII
i
(OH)jCk
2+x(H2O)x(CO3)x, should be proposed by analogy with pyroaurite. Previous studies have shown that incorporation of HCO3
− into the lattice of GR(CO3
2
−) is very improbable, on the basis of FTIR analysis and site availability in interlayers (Benali et al., 2001; Legrand et al., 2001a).

Synthetic GRs have been prepared in the laboratory, using various chemical procedures, from solutions containing ferrous species and chloride ions (Feitknecht and Keller, 1950; Detournay et al., 1976; Refait and Génin, 1993; Schwertmann and Fechter, 1994), ferrous species and sulphate ions (Detournay et al., 1975; Olowe and Génin, 1991; Génin et al., 1996), and ferrous species and carbonate ions (Taylor, 1980; Hansen, 1989; Drissi et al., 1995). Carbonate green rust films have also been obtained from the electrochemical oxidation of iron discs (Legrand et al., 2000).

Recent studies have reported the formation of green rains from the bioreduction of ferric oxyhydroxides by dissimilatory-iron-reducing bacteria (DIRB) (Fredrickson et al., 1998; Ona-Ngouema et al., 2002). Such bacteria can use the ferric oxyhydroxide as an electron acceptor for the oxidation of organic matter. Ona-Ngouema et al. (2002) have shown that large hexagonal crystals of carbonate green rust could be obtained, and they stated that this process may occur in soil solutions and aquifers.

The chemistry and mobility of iron is strongly related to the redox conditions. In environments alternating oxidising and reducing conditions, the cycling of iron will induce oxidation of green rust by dissolved oxygen into ferric products. This oxidation process also occurs when GR interacts with oxidising species such as NO3 (Hansen and Bender Koch, 1998), CrO4
2− (Loyaux-Lawniczak et al., 2000; Williams and Scherer, 2001), CCl4 (Erbs et al., 1999), SeO2
2− (Refait et al., 2000), both in natural aquifers and iron permeable reactive barriers (PRBs). Several studies were dedicated to the characterisation of the products resulting from the oxidation of carbonate green rust. However, the reaction pathways have not been fully under-
stood. Drissi et al. (1995) suggested that the oxidation of GR(CO$_3$]$^-$) in HCO$_3$$^-$/CO$_3$$^-$$^2$ solutions leads first to a so-called “amorphous active FeOOH” phase distinct from α or γ-FeOOH. In a recent study, Benali et al. (2001) asserted that this intermediate phase is ferrihydrite, and proposed the following sequence for the oxidation: GR(CO$_3$]$^-$) oxidizes into ferrihydrite, and then, ferrihydrite transforms into goethite, α-FeOOH, via a dissolution-precipitation mechanism. Taylor (1980), Hansen (1989) and Abdelmoula et al. (1996) studied the oxidation by air of dry samples of carbonate green rust. The formation of feroxyhite, δ-FeOOH, or ferrihydrite was claimed, based on the presence of a line at 0.254 nm in the diffraction pattern. And last, a study by Markov et al. (1990) in which an iron(III) hydroxide carbonate was obtained from the decomposition of siderite in wet air, can also be mentioned.

The aim of the present work is to provide a better description of the oxidation process of carbonate green rust and the resulting ferric products. The transformation of carbonate green rust under various oxidising conditions was studied through electrochemical measurements, X-ray diffraction, FTIR spectroscopy, TEM, and SEM.

2. EXPERIMENTAL METHODS

2.1. Synthesis and Oxidation of GR(CO$_3$]$^-$) Suspension

50 mL of 0.4 or 0.04 mol/L NaHCO$_3$ solution (prepared with NaHCO$_3$ as received from Fluka, purity $>$99.5%, and 18 MΩ cm nano-pure water) were introduced in a glass cell (−50 mm diam.) with five holes on the top. Three of the holes were used for the electrodes: platinum electrode, saturated calomel electrode (0.25 V$_\text{SCE}$) and combined pH electrode (WTW sentix 41). Another hole was used for the argon inlet and outlet. The fifth hole 15 mm diameter), located in the middle position, was closed by a rubber cap during the deaeration of the solution; for the aeration of the solution, the argon flow was stopped and the rubber cap was removed to allow the air oxygen to get in contact with the solution at the air/liquid interface. The solution was magnetically stirred (300 rpm) and thermostated at 25°C during the chemical procedure. The solution/air interface was $\sim 20$ cm$^2$ in area. Before Fe(II) addition, the NaHCO$_3$ solution was deaerated with argon, (argon U, Air liquide, $\sim 20$ mL min$^{-1}$) whose residual oxygen content was eliminated by bubbling in a Fe(OH)$_2$ suspension present in the liner before injection into the cell. Then 0.5 mL (giving an initial Fe(II) concentration of 10$^{-2}$ M) of a 1 mol/L FeCl$_2$ solution was injected into the solution using a syringe through the rubber cap. To get an appropriate initial pH value, 10 mol/L (or 1 mol/L) NaOH solution was dropped into the preparation. FeCl$_2$ solution was prepared by dissolving the appropriate amount of FeCl$_3$, 4H$_2$O from Aldrich (purity 99%) in deaerated 18 MΩ cm nano-pure water. The oxidation reaction was monitored by recording both redox potential (E$_\text{HCl}$) and the current density, recorded by inserting a Ag/AgCl-coated silver wire immersed in a compartment with a fine porosity glass frit and filled with 0.1 mol/L NaCl was used as a reference electrode (0.28 V$_\text{SCE}$). The iron disk was polished on abrasive foils from grade 500 to grade 4000 and rinsed with 18 MΩ cm nano-pure water before use. The iron disk was then placed at the bottom of the cell. The surface in contact with the electrolyte was measured as 0.785 cm$^2$. Electrolyte solutions were deaerated with argon for 15 min before electrolysis, and the argon bubbling was maintained during the whole electrochemical measurements.

Electrochemical preparation and investigations were performed using a potentiostat PAR 273 A controlled by an IBM computer and the PAR Model 270 software package. The electrochemical synthesis of GR(CO$_3$]$^-$) layer was done by applying an anodic potential (−0.45 V$_\text{SCE}$) to the iron disk in 0.4 mol/L NaHCO$_3$ solution at pH $\sim$ 9.6. The electrolysis was stopped as the current density became lower than 10 µA cm$^{-2}$, indicating that the current density at the electrode surface was fully covered by the GR(CO$_3$]$^-$) particles. The Coulombic charge required for this purpose was $\sim$ 150 mC cm$^{-2}$. More details about the electrochemical synthesis and FTIR analysis of GR(CO$_3$]$^-$ layers can be found in Legrand et al. (2001a and 2001b).

2.3. Characterisation of Solid Products

XRD measurements were carried out by using a Philips PW1830 diffractometer with a Co K$_\alpha$ radiation (1.7902 Å). The samples were scanned from 5° to 90° 2θ. FTIR data were recorded on a Bruker IFS 28 Fourier Transform Infrared spectrometer. Powder samples were pressed to pellets with KBr and analysed by direct transmission mode. Electrochemically formed layers on the surface of the iron disk were directly analysed using a reflection transmission tool (Grazeby-Specac). 20 scans were done for the spectrum acquisition and the acquisition time was $\sim$ 30 s. TEM measurements were performed with a JEOL 2000FX operating at 200 kV. A double-tilt ±30° specimen holder was used, and observations were directly achieved on powders deposited on copper grids. SEM measurements were performed with a Philips XL30 microscope.

Solid products, resulting from chemical synthesis, were separated from the solutions by collecting on 0.22 µm Millipore filters under argon atmosphere. They were rinsed with deaerated nano-pure water. The filters were then quickly removed from the filtration tool and introduced into a closed glass tube equipped with argon inlet and outlet for drying. The solid products were maintained under argon flow for $\sim$ 1 h before analysis. In the case of the intermediate product (carbonate green rust), the preparation of the KBr pellets for FTIR measurements was done under argon atmosphere to avoid oxidation by air. For XRD measurements, the intermediate product was protected from air oxidation by mixing glycerol, once filtered (Hansen, 1989). Oxidation products electrochemically formed at the surface of an iron disk were washed with deaerated 18 MΩ cm nano-pure water, dried under argon flow, and quickly introduced into the chamber for FTIR or SEM analysis. The contact with air was less than 1 min.

The following procedure was used to determine the Fe(II) content in solid suspensions at a given time. After Fe(II) addition, the NaHCO$_3$ solution was deaerated with argon purge to stop the oxidation, the solution was acidified with concentrated H$_2$SO$_4$ down to a pH of $\sim$ 0.5 to induce the dissolution of the solid phases. Titration of Fe$^{2+}$ ions was done with a 0.01 mol/L KMnO$_4$ solution.

The total iron content was assessed by two methods. The first one consists in a complexometric titration of Fe(III) by ethylene diamine tetraacetic acid (EDTA from Prolabo, normapur). 50 mg of dried solids (50 mg) are dissolved in hot 1 mol/L HCl (−5−7 mL). After complete dissolution, 18 MΩ cm nano-pure water is added until a volume of 50 mL is reached. The solution is then thermostated at 45°C, and 3 drops of sulfosalicylic acid indicator are added. The equivalent volume of EDTA (0.05 mol/L) is measured when the colour changes from dark purple to light yellow. In the case of GR(CO$_3$]$^-$), 2 mol% of H$_2$O$_2$ are added to the solution before titration, to oxidise Fe$^{2+}$ ions into Fe$^{3+}$ ions. The second method consists in gravimetric analysis (i.e., transformation of the product into hematite, α-Fe$_2$O$_3$). The dried product is first weighted (m$_0$) and then heated to 300°C for 40 h. After this treatment, the product is fully transformed into hematite, whose mass can be determined (m$_f$). The mass of iron, m$_{\text{Fe}}$, is equal to 0.699m$_f$. Finally, the total Fe content in the solid product is determined by the m$_{\text{Fe}}$/m$_0$ ratio. It has to be noted that the complete transformation into hematite is controlled by FTIR.

The CO$_2$ content in the solid samples was determined by acid-base titration. A weighted amount of dried solid sample (in the 52−57 mg range) was introduced into an inner glass tube (−10 mL) located in an outer glass tube (−50 mL) filled in with 5 mL of 0.1 mol/L NaOH solution; the latter solution was prepared from 30% NaOH solution (RP
Prolabo) containing less than 1% of Na₂CO₃ impurity. Both tubes were equipped with a magnetic bar. The inner tube was maintained open while the outer one was closed by a gas-proof rubber stopper. Then, 7 mL of 1 mol/L HCl solution were injected into the inner tube through the stopper by using a syringe. The tubes were settled on a magnetic stirrer (300 rpm) for 5 h. The suspended solid completely dissolved within 3 h. CO₂ resulted from the dissolution and was absorbed in NaOH solution. CO₂ was then determined by acid/base titration of the carbonated NaOH solution. Note that the blank titration was carried out and the CO₂ content of the 0.1 mol/L NaOH solution was subtracted from the experimental values.

3. RESULTS

3.1. Synthesis and Oxidation of GR(CO₃²⁻/H₁₁₅₄₆) Suspension In 0.4 mol/L NaHCO₃ Solution

3.1.1. E-t and pH-t transients

Figure 1 reports the potential values recorded with a platinum electrode as a function of time during the aerial oxidation of a Fe(II) suspension in 0.4 mol/L NaHCO₃ solution with an initial pH = 9.6, T = 25°C; stirring 300 rpm.

![Figure 1](image)

They are consistent with those reported in the literature for carbonate green rust GR(CO₃²⁻) (McGill et al., 1976; Taylor, 1980; Hansen, 1989; Drissi et al., 1995; Legrand et al., 2001a). As GR(CO₃²⁻) belongs to the R₃m group, c parameter indicates a 0.738 nm interplanar distance between Fe⁵⁺-Fe³⁺ layers. XRD pattern of the ferric product, sampled at point C (Fig. 2c), displays a main line, corresponding to an interplanar distance of 0.734 nm. Some minor lines at 0.367 nm (0.734/2), 0.253 nm, and 0.226 nm are also observed. Such a diagram has already been reported in the literature for GR(CO₃²⁻) powders oxidised by air in dry conditions (Taylor, 1980; Hansen, 1989; Abdelmoula et al., 1996). The 0.734 nm interplanar distance value may indicate that some relics of the lamellar structure of the parent GR(CO₃²⁻) remain in the Fe(III) product structure obtained at point C. Since the ionic radii of Fe⁵⁺ and Fe³⁺ are 0.078 and 0.0645 nm, respectively, the difference between 0.734 nm and 0.758 nm could be related to a contraction in the...

![Figure 2](image)
solid lattice induced by the Fe$^{2+}$-to-Fe$^{3+}$ transformation (Abdelmoula et al., 1996). Moreover, the small variation of the interplanar distance might be consistent with the presence of CO$_3^{2-}$ anions in the interlayers of the Fe(III) product. The ferric product sampled at point C will thereafter be referred as exGR-Fe(III).

The FTIR spectrum of the initial ferrous suspension (Fig. 3a) exhibits bands at 1530, 1355, 1075, 955, 780, 760 cm$^{-1}$, that have already been reported for ferrous hydroxide-carbonate, Fe$_2$(OH)$_2$CO$_3$ (Erdös and Altorfer, 1976). The broadness of the IR bands is consistent with the amorphous nature of the solid product, as pointed out by XRD. The FTIR spectrum of the initial ferrous suspension (Fig. 3a) exhibits only the GR(CO$_3^{2-}$) bands: i.e., H$_2$O and -OH stretching modes at 3500, 3410, 3310 cm$^{-1}$, and 3170 cm$^{-1}$; H$_2$O bending vibration (b) at 1630 cm$^{-1}$; CO$_3^{2-}$ stretching modes at 1350 ($v_3$); and lattice Fe-OH modes at 845, 770, 510, and 480 cm$^{-1}$ (Taylor, 1980; Legrand et al., 2001b, Peulon et al., 2003). The lack of the 1070 and 955 cm$^{-1}$ bands in spectrum (b) is consistent with the complete removal of the initial ferrous suspension. The FTIR spectrum of the exGR-Fe(III) product is given in Figure 3c. The 470 and 655 cm$^{-1}$ bands are assigned to stretching Fe-O modes in octahedral Fe-O(OH) coordination (Markov et al., 1990). The broad band between 2300 and 3600 cm$^{-1}$, attributed to OH stretching vibrations in water molecules and hydroxyl groups, is the sum of three contributions located at 3465, 3290, and 3020 cm$^{-1}$. The absorption at 1635 cm$^{-1}$ is assigned to the bending vibration of water. The presence of CO$_3^{2-}$ ions is revealed by the two strong absorption bands at 1360 ($v_3$) and 690 cm$^{-1}$ ($v_3$) and two much weaker ones at 1070 ($v_1$) and 850 cm$^{-1}$($v_2$). The symmetry of CO$_3^{2-}$ deviates from D$_{3h}$ as seen from the splitting of the $v_3$ mode (1360 and 1480 cm$^{-1}$) and from the observation of the normally IR-fornbidden $v_1$ absorption. To prove that CO$_3^{2-}$ anions are inside the lattice rather than adsorbed species, an exGR-Fe(III) sample was synthesized according to the same procedure as given in Figure 1, except that 10$^{-2}$ M Na$_3$HPO$_4$ was added at point B. The final product is also exGR-Fe(III), as revealed by XRD (pattern not shown) and FTIR analysis (Fig. 3d). The adsorption of phosphate species is indicated by the antisymmetric $v_3$ PO$_4$ stretching (1000 and 1105 cm$^{-1}$) and $v_4$ PO$_4$ deformation (620 and 640 cm$^{-1}$) modes, which split due to the monodentate or bidentate coordination to the o xo or hydroxo-groups. The carbonate bands are not affected by the presence of adsorbed phosphate species.

The transmission electron microscopy image of exGR-Fe(III) is given in Figure 4. It shows a hexagonal platelets morphology identical to that commonly reported in the literature for green rust (McGill et al., 1976; Legrand et al., 2001a; Gehin et al., 2002; Peulon et al., 2003), suggesting a solid-state oxidation of carbonate green rust into exGR-Fe(III). The electron diffraction studies exploring the reciprocal lattice did not allow us to identify the structure of this phase due to the very anisotropic morphology of these platelets. This anisotropy limits the variety of crystallographic planes which can be studied, and it is not possible to measure the c parameter that is perpendicular to the observation plane.

Table 1 reports the results of chemical analysis of GR(CO$_3^{2-}$) and exGR-Fe(III) samples and the data computed for some ferric oxihydroxides that should be expected according to the literature (see Introduction). The total Fe and CO$_2$ contents of GR-CO$_3^{2-}$ and exGR-Fe(III) compare quite well. The theoretical values calculated for ferrihydrite and feroxyhite do not match at all with the experimental data obtained for exGR-Fe(III).
3.2. Synthesis and Oxidation of GR(CO$_3^{2-}$/H$_{11}O_{15}$) Suspension In 0.04 mol/L NaHCO$_3$ Solution

3.2.1. E-t and pH-t transients

Experiments were done in solutions with lower NaHCO$_3$ concentration to address compositions more closely simulating groundwater or aquifers. Figure 5a reports the E-t and pH-t curves recorded during the oxidation of an Fe(II) suspension in 0.04 mol/L NaHCO$_3$ solution at initial pH $\approx$ 8.6. The step A-B corresponds to the oxidation of the initial Fe(II) suspension into GR(CO$_3^{2-}$/H$_{11}O_{15}$), as revealed by the dark green colour of the suspension at point B, and FTIR analysis. The average oxidation rate, 5.6 $\mu$moles Fe II min $^{-1}$, is very close to that determined in Figure 1. A pH decrease from 8.6 to 7.5 is observed during this step. The oxidation of GR(CO$_3^{2-}$/H$_{11}O_{15}$) into ferric product takes place from B to C. The shape of the E-t transient from B to C strongly differs from what has been recorded during the oxidation experiment reported in Figure 1. Moreover, the average oxidation rate, 5.8 $\mu$moles Fe II min $^{-1}$, is 2 to 3 times larger than that of Figure 1. The FTIR analysis of the solid product obtained at point C (Fig. 5b) shows the characteristic bands of lepidocrocite, $\gamma$-FeOOH, at 745, 1020, 1155, 2800 and 3150 cm$^{-1}$ (Schwertmann and Cornell, 1991; Weckler and Lütz, 1998), suggesting that another oxidation mechanism occurs. A small quantity of goethite is also detected (see shoulders at $\approx$900 and 800 cm$^{-1}$). Moreover, the formation of ferrihydrite cannot reasonably be excluded.

3.2.2. Influence of pH on GR(CO$_3^{2-}$/H$_{11}O_{15}$) oxidation

Some experiments similar to the one described in Figure 5a were carried out at different starting pH values, and consequently at different pH values during the step from B to C. The ferric products formed at point C were identified by means of FTIR and XRD measurements. Figure 6 indicates the ferric products that were obtained as a function of the pH range recorded during the B-to-C step. For pHs lower than 8, the formation of lepidocrocite is favoured. For pHs greater than 8.9, only exGR-Fe(III) is formed. For pHs between 8 and 8.9, a mixture of both lepidocrocite and exGR-Fe(III) is obtained.

3.2.3. Influence of the rate of GR(CO$_3^{2-}$/H$_{11}O_{15}$) oxidation

Figure 7a reports the same experiment as Figure 5a, except that the stirring rate was increased from 300 to 700 rpm at point B. The increase of the stirring rate induces an increase of the oxygen supply, and then a decrease of the time duration of the oxidation experiment reported in Figure 1 (point B or C). An average value and the corresponding standard deviation were then calculated.

### Table 1. Chemical analysis data of products sampled at point B, GR(CO$_3^{2-}$/H$_{11}O_{15}$), and at point C, exGR-Fe(III). Comparisons of experimental data of exGR-Fe(III) with theoretical data of ferrihydrite and goethite.

<table>
<thead>
<tr>
<th></th>
<th>Total Iron Content (% wt)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Fe(II)$^a$ (%)</td>
</tr>
<tr>
<td>GR(CO$<em>3^{2-}$/H$</em>{11}O_{15}$) samples taken at point B</td>
<td>66 ± 2 (4)</td>
</tr>
<tr>
<td>Carbonate green rust$^b$</td>
<td>67</td>
</tr>
<tr>
<td>ExGR-Fe(III) samples taken at point C</td>
<td>0 (1)</td>
</tr>
<tr>
<td>Ferrhydrite$^c$</td>
<td>0</td>
</tr>
<tr>
<td>Ferroxyhyte$^d$</td>
<td>0</td>
</tr>
</tbody>
</table>

In brackets, we give the number of samples that were analyzed. Each value was obtained from one solid sample synthesized according to the procedure given in Figure 1 (point B or C). An average value and the corresponding standard deviation were then calculated.

$^a$ KMnO$_4$ titration; Fe(II)% = nFe(II)/n(total iron).

$^b$ Theoretical values calculated by assuming the formula [Fe$_4$Fe$_{12}$OH$_{12}$] $\cdot$ [CO$_3$, $\cdot$H$_2$O] given by Drissi et al. (1995).

$^c$ Theoretical values calculated by assuming the formula Fe$_{6.4}$HO$_{8.4}$H$_2$O given by Towe and Bradley (1967).

$^d$ Theoretical values calculated by assuming the formula $\delta$-FeOOH given by Chukhrov et al. (1977).

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**Fig. 5.** (a) E-t and pH-t curves recorded during the oxidation by air of 10$^{-2}$ M Fe(II) suspension in 0.04 mol/L NaHCO$_3$ solution, starting pH $\approx$ 8.6, $T$ = 25°C, stirring 300 rpm; (b) FTIR spectrum of the ferric product obtained at point C, L = lepidocrocite; G = goethite.
B-to-C step (26 min. in Fig. 7a against 57 min. in Fig. 5a). ExGR-Fe(III) is predominantly formed at the completion of oxidation (Fig. 7c); only a very small amount of lepidocrocite can be detected.

Another set of experiments in which H₂O₂ was used as a soluble, strongly oxidizing species, was done in 0.04 mol/L NaHCO₃ solutions with starting pHs in the 7 to 10 range. At point B, the cell was closed, placed under argon bubbling, and 0.25 mL of 1 mol/L H₂O₂ (i.e., 5 × 10⁻³ M) was added to GR(CO₃²⁻/H₂O) suspension. Figure 7b gives typical E-t and pH-t transients. A sharp increase of potential in less than 1 min, along with a colour change from dark green to light brown is observed, indicating the oxidation completion. The ferric product is exGR-Fe(III), whatever the starting pH (FTIR spectrum not shown). Finally, in an experiment where a dried GR(CO₃²⁻/H₂O) powder was left in contact with air, the final ferric product was also exGR-Fe(III).

3.3. Acid Titration of GR(CO₃²⁻) Suspension

Figure 9 reports the results of acid titration of 0.04 mol/L NaHCO₃ solutions (50 mL) with (curve (a)) or without (curve (b)) 1.67 mM GR(CO₃²⁻) suspension. Curve (a) was obtained as follows: 1 mol/L NaOH was added to a 0.04 mol/L NaHCO₃ solution until pH reached 11.3. Then, 10⁻² M FeCl₂ was added and the pH decreased down to 10.4. The conversion of the starting ferrous suspension (10 mM) into GR(CO₃²⁻) suspension (1.67 mM = 10/6) was done by air oxidation (step A to B). At point B, the pH was 10.2. The cell was closed and placed under Ar bubbling and then, the acid titration of the solution + GR(CO₃²⁻) suspension was performed. The blank curve (b) was obtained from the acid titration of a 0.04 mol/L NaHCO₃ + NaOH solution with initial pH of 10.2. At first, both curves exhibit the neutralization of CO₃²⁻ species in the 10 - 9 pH range. A pH pseudoplateau at ~8.4, that should be attributed to

3.2.4. Influence of blocking adsorbed species on the oxidation of GR(CO₃²⁻)

Figure 8 reports the same experiment as in Figure 5a, except that 10⁻² M Na₂HPO₄ was added at point B. The addition of HPO₄²⁻ ions affects the shape of the B-to-C step, as compared to Figure 5a—a sharp increase of E followed by a potential plateau near 0.2 V is obtained. This shape is similar to that of Figure 1. Analysis of the ferric product formed at point C was carried out by FTIR. The spectrum (not shown) indicates that it is exGR-Fe(III) with phosphate species adsorbed at the surface (a spectrum resembling the one of Fig. 3d is obtained). Some similar experiments performed at different pH values in the 7 to 10 range also gave the same final ferric product. On the other hand, the formation of lepidocrocite became inhibited. ExGR-Fe(III) with silicate species adsorbed at the surface was obtained in solutions where Na₂SiO₃ was added instead of Na₂HPO₄. Note that the substitution of carbonate ions for phosphate or silicate ions inside GR(CO₃²⁻) interlayers is not considered (Benali et al., 2001).
the acid-induced dissolution of GR(CO$_3^{2-}$) suspension, is observed in curve (a). The volume of acid can be estimated to 4 mL, corresponding to an addition of 4.8 mol H$^+$ with respect to one mole GR(CO$_3^{2-}$). Note that the pH values recorded during the pseudoplateau are not strictly equilibrium values, mainly due to the too large rate of HCl addition, 0.05 mL min$^{-1}$.

3.4. Solid-State Redox Cycling of GR(CO$_3^{2-}$/exGR-Fe(III) System

GR(CO$_3^{2-}$) thin layers were electrochemically synthesized at the surface of an iron disk as described in part 2.2. Figure 10a shows the morphology of a layer after its oxidation by dissolved oxygen in an aerated 0.01 mol/L NaHCO$_3$ + 0.001 mol/L Na$_2$HPO$_4$ solution at pH = 8.5. ExGR-Fe(III) is formed (see FTIR spectrum (c1) in Fig. 10c); no change of the layer morphology is observed, as compared to the starting GR(CO$_3^{2-}$) particles. The hexagonal particles obtained from electrochemical synthesis have significantly larger sizes than those obtained from a suspension (compare Figs. 4 and 10a).

Figure 10b reports the E-t transient obtained during the galvanostatic reduction of an exGR-Fe(III) layer in simulated groundwater. A plateau is observed, indicating the occurrence of the exGR-Fe(III) reduction process. The potential values recorded on the plateau are close to -0.4 V. The completion of exGR-Fe(III) reduction is revealed by the sharp decrease of the potential (time ~ 4500 s), down to a range corresponding to the electrolyte reduction. The FTIR analysis of the layer, performed after the galvanostatic reduction (Fig. 10c, spectrum (c2), shows the disappearance of the GR(CO$_3^{2-}$) signals (c1), corresponding to the formation of Fe(III) oxide phases.
exGR-Fe(III) is very slow since only traces of goethite, which inhibit the dissolution step needed for the formation of complete conversion into goethite or into a hematite (suspensions are stored in a PTFE vessel (no silicate ions), the following schematic formula may be proposed \[(\text{Fe}^{\text{II}})_{2} (\text{Fe}^{\text{III}})_{1}\]. Misawa et al. (1973 and 1974). According to these authors, the species, whose occurrence has previously been claimed by lead to the production of soluble ferrous-ferric intermediate along the A-to-B oxidation step. The oxidation of the soluble FeII species supplied by the amorphous Fe(II) suspension might be compensated by some anionic species during the solid-state oxidation of GR(CO3\(^{2-}\)) can be ruled out since the number of remaining carbonate ions inside the exGR-Fe(III) crystal lattice is fully demonstrated in this study. Replacing O and H contents by O\(^{-}\), OH\(^{-}\), and H\(_2\)O, the following formula can be proposed, \[\text{Fe}^{\text{III}}_{x}\text{O}_{(12.11+x/2)}(\text{OH})_{(12.30-2x)}(\text{H}_2\text{O})_x(\text{CO}_2)_{0.74}\]. Hence, ExGR-Fe(III) is a ferric oxyhydroxycarbonate. Finally, the assumption that the solid-state oxidation of GR(CO3\(^{2-}\)) gives ferrihydrite or feroxyhyte (Taylor, 1980; Hansen, 1989; Abdelmoula et al., 1996) must be revisited.

### 4.2. Solid-State Oxidation of GR(CO3\(^{2-}\)), a ferric oxyhydroxycarbonate

The exGR-Fe(III) product resulting from the solid-state oxidation of GR(CO3\(^{2-}\)) exhibits a light brown colour and a hexagonal platelets morphology. Table 1 indicates that its composition is very close to that of GR(CO3\(^{2-}\)). From the results of Table 1 and the charge balance (see Appendix for details), the chemical composition of exGR-Fe(III) can be proposed, \((\text{Fe}^{\text{III}})_{6}(\text{O})_{14.41}(\text{H})_{12.30}(\text{CO}_3)_{0.74}\). The presence of remaining carbonate ions inside the exGR-Fe(III) crystal lattice is fully demonstrated in this study. Replacing O and H contents by O\(^{-}\), OH\(^{-}\), and H\(_2\)O, the following formula can be proposed, \[\text{Fe}^{\text{III}}_{x}\text{O}_{(12.11+x/2)}(\text{OH})_{(12.30-2x)}(\text{H}_2\text{O})_x(\text{CO}_2)_{0.74}\]. Hence, ExGR-Fe(III) is a ferric oxyhydroxycarbonate. Finally, the assumption that the solid-state oxidation of GR(CO3\(^{2-}\)) gives ferrihydrite or feroxyhyte (Taylor, 1980; Hansen, 1989; Abdelmoula et al., 1996) must be revisited.

#### 4.2.2. Deprotonation as a way for keeping electrical neutrality

The solid-state oxidation (SSO) of GR(CO3\(^{2-}\)) involves the transformation of Fe\(^{2+}\) ions into Fe\(^{3+}\) ions inside the crystal lattice. The formula of GR(CO3\(^{2-}\)) can be written as follows: \[\text{Fe}^{\text{II}}_{y}\text{Fe}^{\text{III}}_{y}(\text{OH})_{12}(\text{CO}_3)_{0.74}\text{H}_2\text{O}.\] This last formula and the corresponding molar mass 635.1 g mol\(^{-1}\) can be admitted for our GR(CO3\(^{2-}\)). The solid-state oxidation implies charge compensation to satisfy the electrical neutrality of the whole structure. The compensation by some anionic species during GR(CO3\(^{2-}\)) oxidation can be ruled out since the number of interlayer sites required for this purpose would be greater than the available sites (Legrand et al., 2003). The loss of protons to accommodate the charge compensation is more consistent with the results of Table 1. The solid-state oxidation (SSO) of GR(CO3\(^{2-}\)) can be written as:

\[
\text{[Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{OH})_{12}(\text{CO}_3)_{0.74}\text{H}_2\text{O}] + 4\text{H}^+ + 4e^- \rightarrow \text{Fe}^{\text{III}}_{x}\text{O}_{(12.11+x/2)}(\text{OH})_{(12.30-2x)}(\text{H}_2\text{O})_x(\text{CO}_2)_{0.74}\]
\]

The value of x depends on whether or not the deprotonation of interlayer water molecules to give OH\(^{-}\) ions is considered. Eqn. 3 shows that exGR-Fe(III) is obtained from the release of 4 protons and 4 electrons by GR(CO3\(^{2-}\)). Combining Eqn. 3 with the reduction reaction of O\(_2\) or H\(_2\)O\(_2\), reactions (4) and (5) can be established:
the following schematic reaction,

$$\text{Fe}^{II}_4\text{Fe}^{II}_2(\text{OH})_{12}[(\text{CO}_3)^2, 2\text{H}_2\text{O}] + \text{O}_2 \rightarrow \text{Fe}^{III}_6\text{O}_{2+4}\text{O}_2(\text{OH})_{12-24}$$

$$\times (\text{H}_2\text{O})_2(\text{CO}_3) + 2\text{H}_2\text{O} \quad (4)$$

$$\text{Fe}^{II}_4\text{Fe}^{II}_2(\text{OH})_{12}[(\text{CO}_3)^2, 2\text{H}_2\text{O}] + 2\text{H}_2\text{O}_1 \rightarrow \text{Fe}^{III}_6\text{O}_{2+4}\text{O}_2(\text{OH})$$

$$\times (\text{OH})_{12-24}(\text{H}_2\text{O})_2(\text{CO}_3) + 4\text{H}_2\text{O} . \quad (5)$$

4.3. Stability of the Ferric Oxyhydroxycarbonate, exGR-Fe(III)

At ambient temperature and below, exGR-Fe(III) remains stable even after long periods of aging, either as a dry powder or as particles in solution. The conversion into thermodynamically stable ferric phases, goethite or hematite, occurs only in moderately heated solutions stored in glass-free containers. The formation of the latter compounds requires the occurrence of a dissolution-precipitation (D-P) mechanism (Jambor and Dutrizac, 1998). In presence of silicate or phosphate species, the dissolution step is inhibited due to the adsorption of these species onto the exGR-Fe(III) surface (Sigg and Stumm, 1981; Cornell et al., 1987), and the latter compound transformation is prevented.

4.4. Oxidation of GR(CO$_3$$^2$$^-$) Via Solution

At point B, the solution contains GR(CO$_3$$^2$$^-$) suspension and soluble [(Fe$^{III}$)$_2$(Fe$^{II}$)$_1$] species (Misawa et al., 1973; Misawa et al., 1974) in equilibrium with the solid phase, as illustrated by the following schematic reaction,

$$\text{Fe}^{II}_4\text{Fe}^{II}_2(\text{OH})_{12}[(\text{CO}_3)^2, 2\text{H}_2\text{O}] \overset{\text{dissolution}}{\rightleftharpoons} 2[(\text{Fe}^{II})_2(\text{Fe}^{III})_1] . \quad (6)$$

Figure 9 showed that the dissolution of GR(CO$_3$$^2$$^-$) is promoted by acid addition and that the pH range where it occurs, $\sim 8.4$, is less alkaline than the one relative to the neutralisation of CO$_3$$^2$$^-$ species according to

$$\text{CO}_3^2^- + \text{H}^+ \rightarrow \text{HCO}_3^- . \quad (7)$$

On the other hand, protons will preferentially react with CO$_3$$^2$$^-$ (if available) rather than with GR(CO$_3$$^2$$^-$).

The introduction of oxygen into the cell at point B induces the oxidation of [(Fe$^{III}$)$_2$(Fe$^{II}$)$_1$] species according to the schematic reaction

$$2[(\text{Fe}^{III})_2(\text{Fe}^{II})_1] + \text{O}_2 \rightarrow 6 \text{FeOOH} + y \text{H}^+ . \quad (8)$$

The production of protons associated to the oxidation of Fe$^{II}$-containing species into FeOOH is well established (Schwertmann and Cornell, 1991). In 0.04 mol/L NaHCO$_3$ solution with very slightly alkaline pH, CO$_3$$^2$$^-$ concentration in solution is very low and reaction (7) is negligible. Then, the protons produced in Eqn. 8 can promote reaction (6) in the dissolution sense, leading to the release of fresh [(Fe$^{III}$)$_2$(Fe$^{II}$)$_1$] species in solution. A self-sustained mechanism is observed where GR(CO$_3$$^2$$^-$) and dissolved oxygen are the reagents, FeOOH the end product, and [(Fe$^{III}$)$_2$(Fe$^{II}$)$_1$] the intermediate species. The whole transformation is a dissolution-oxidation-precipitation (DOP) mechanism. The nature of the ferric oxyhydroxide

should depend on the experimental conditions; lepidocrocite predominantly formed in the present study, goethite was obtained in synthesis from Drissi et al. (1995), Schwertmann and Cornell (1991), ferrhydrsite may be present along with lepidocrocite and goethite. The DOP mechanism may be extended to sulphate and chloride green rusts as the occurrence of ferrous-ferric species (green complexes) has also been reported in neutral and mildly alkaline solutions containing sulphate or chloride ions (Misawa et al., 1973; Misawa et al., 1974).

4.5. Formation and Transformation Pathways of GR(CO$_3$$^2$$^-$)

Results of the present study allow the establishment of a schematic representation for formation and transformation pathways of GR(CO$_3$$^2$$^-$) (Fig. 11). The formation of GR(CO$_3$$^2$$^-$) from amorphous Fe(II) suspension involves three steps, as proposed in section 4.1: dissolution of amorphous Fe(II) suspension, oxidation of soluble ferrous species into soluble ferrous-ferric species, and precipitation to GR(CO$_3$$^2$$^-$). The oxidation of GR(CO$_3$$^2$$^-$) can proceed by solid-state reaction (SSO) or by reaction via solution (DOP). The SSO mechanism is promoted at the expenses of the DOP mechanism (i) by increasing the [CO$_3$$^2$$^-$]/[GR(CO$_3$$^2$$^-$)] ratio, (ii) by increasing the oxidation rate, and (iii) in the presence of adsorbed blocking species such as phosphate or silicate. Condition (i) is monitored by adjusting the total concentration of carbonate species, the pH, and the concentration of iron species. Condition (ii) is related to the flow of oxygen (solution stirring) or soluble oxidising species (addition rate). Condition (iii) may be fulfilled for many soil or corrosion environments since phosphate and silicate ions are widespread species. The GR(CO$_3$$^2$$^-$) oxidation mechanism (see Introduction) proposed by Benali et al. (2001) is not consistent with the results of the present paper. In
our mind, their mechanism is quite doubtful since it is well known that the ferrihydrite-to-goethite transformation is a very slow reaction at ambient temperature (Schwertmann and Cornell, 1991; Jambor and Dutrizac, 1998). As a matter of fact, the ferric product they synthesized might be exGR-Fe(III) rather than ferrihydrite. The solid-state reduction of exGR-Fe(III) back to GR(CO$_3$)$^{2-}$ was demonstrated in our present study. This reduction process should occur with a negligible release of soluble iron species in solution, as for the oxidation process. If it occurs in natural environments, the solid-state redox cycling of GR(CO$_3$)$^{2-}$ may affect the remobilization of iron. To state, the reaction pathways described in the present study should be considered in all environments where GR(CO$_3$)$^{2-}$ occurs.

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REFERENCES


APPENDIX

Chemical Composition of Carbonate Green Rust GR(CO$_3^{2-}$)

Fe$^{II}$ content 66%; average total iron content (Fe$^{II}$ + Fe$^{III}$) 52.1% wt; CO$_3$ content 7.91% wt.

Calculations for 100 g:

\[
\begin{align*}
n(\text{Fe}^{II}) &= 0.616 \text{ mole} \\
n(\text{Fe}^{III}) &= 0.317 \text{ mole} \\
n(\text{CO}_3) &= 0.132 \text{ mole}
\end{align*}
\]

Charge balance and mass balance

\[
n(\text{OH}) = 2 n(\text{Fe}^{II}) + 3 n(\text{Fe}^{III}) - 2 n(\text{CO}_3) = 1.919 \text{ moles}
n(\text{H}_2\text{O}) = [100 - 55.85 n(\text{Fe}^{III}) - 55.85 n(\text{Fe}^{II}) - 60 n(\text{CO}_3) - 17 n(\text{OH})]/18 = 0.408 \text{ mole}
\]

The chemical composition is then determined for 6 Fe atoms.

Chemical Composition of Ferric Oxyhydroxycarbonate ExGR-Fe(III)

Fe$^{III}$ content 0%; average total iron content (Fe$^{III}$) 51.8% wt; CO$_3$ content 6.82% wt.

Calculations for 100 g:

\[
\begin{align*}
n(\text{Fe}^{III}) &= 0.927 \text{ mole} \\
n(\text{CO}_3) &= 0.114 \text{ mole}
\end{align*}
\]

Charge balance and mass balance

\[
3 n(\text{Fe}^{III}) - 2 n(\text{CO}_3) - 2 n(\text{O}) + n(\text{H}) = 0
\]

\[
55.85 n(\text{Fe}^{III}) + 60 n(\text{CO}_3) + 16 n(\text{O}) + 1 n(\text{H}) = 100
\]

\[
n(\text{O}) = 2.227 \text{ mole}; n(\text{H}) = 1.900
\]

The chemical composition is then determined for 6 Fe atoms.