Available online at www.sciencedirect.com

ScienceDirect

Chemosphere 70 (2008) 942–947

CHEMOSPHERE

www.elsevier.com/locate/chemosphere

Short Communication

# Abiotic reduction of antimony(V) by green rust ($Fe_4(II)Fe_2(III)(OH)_{12}SO_4 \cdot 3H_2O$)

Satoshi Mitsunobu [a,*], Yoshio Takahashi [a,b], Yoichi Sakai [c]

[a] Department of Earth and Planetary Systems Science, Graduate School of Science, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8526, Japan
[b] Laboratory for Multiple Isotope Research for Astro- and Geochemical Evolution (MIRAGE), Hiroshima University, Hiroshima 739-8526, Japan
[c] Department of Chemistry, Daido Institute of Technology, Nagoya 457-8530, Japan

Received 6 April 2007; received in revised form 6 July 2007; accepted 11 July 2007
Available online 29 August 2007

---

## Abstract

Green rust ($Fe_4(II)Fe_2(III)(OH)_{12}SO_4 \cdot 3H_2O$) is an intermediate phase in the formation of iron (oxyhydr)oxides such as goethite, lepidocrocite, and magnetite. It is widely considered that green rust occurs in many soil and sediment systems. Green rust has been shown to reduce sorbed Se(VI), Cr(VI), and U(VI). In addition, it is also reported that green rust does not reduce As(V) to As(III). In this study, we have investigated for the first time the interaction between Sb(V) and green rust using XAFS and HPLC–ICP–MS. Most of the added Sb(V) was adsorbed on green rust, and Sb(III), a reduced form, was observed in both solid and liquid phases. Thus, it was shown that green rust has high affinity for Sb(V), and that Sb(V) was reduced to more toxic Sb(III) by green rust despite the high stability of the Sb(V) species even under reducing condition as reported in previous studies. Therefore, green rust can be one of the most important reducing agents for Sb(V), which can influence the Sb mobility in suboxic environments where green rust is formed.

*Keywords:* Antimony; Green rust; XAFS; HPLC–ICP–MS

---

## 1. Introduction

Antimony (Sb) is a toxic element widely distributed in the lithosphere and mainly associated with arsenic (As) as sulfide or oxide. Antimony compounds are considered to be pollutants of high interest by the United States Environmental Protection Agency (1979) and the Council of the European Communities (1976). However, the geochemical behavior of Sb in soil and sediment is still largely unknown. Antimony belongs to the group 15 of the periodic table below As and can exist in four oxidation states ($-$III, 0, III, and V), though Sb(III) and Sb(V) are the most frequently encountered species in the environment (Filella et al., 2002). To a great extent, the behavior of Sb in the environment depends on its oxidation state. Moreover, the toxicity of inorganic Sb is assumed to be similar to that of As and also depends on the oxidation state; Sb(III) is more toxic than Sb(V) (Picard and Bosco, 2003). Although very few sorption studies of Sb on natural sorbents have been reported to date, the major host phase of Sb in natural soil and sediment is Fe oxyhydroxides (Chen et al., 2003; Scheinost et al., 2006; Mitsunobu et al., 2006). Mitsunobu et al. (2006) reported that Sb can exist as the oxidized form, Sb(V), over a wide redox range in soil, suggesting that Sb(V) is a stable form in the environment, while the oxidation state of As changes readily depending on the redox condition.

Green rusts are layered $Fe^{II}$–$Fe^{III}$ hydroxides that have a pyroaurite-type structure consisting of alternating positively charged hydroxide layers and hydrated anion layers. Isomorphic substitution of $Fe^{3+}$ for $Fe^{2+}$ in the trioctahedral sheets of $Fe(OH)_2$ confers a positive charge to the hydroxide layer that is balanced by hydrated anions in the interlayer (typically $Cl^-$, $SO_4^{2-}$, or $CO_3^{2-}$). Green rusts are formed by a number of abiotic and biotic processes

---

[*] Corresponding author. Tel.: +81 82 424 7460; fax: +81 82 424 0735.
*E-mail address:* mitsunobu@hiroshima-u.ac.jp (S. Mitsunobu).

0045-6535/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2007.07.021

under circumneutral to alkaline conditions in suboxic environments. They have been initially identified as products of both abiotic and microbially induced corrosion of iron and steel (Bigham and Tuovinen, 1985; Génin et al., 1998; Kumar et al., 1999; Refait et al., 1998).

Green rusts may be important for trace metal mobility in the environment because of their high reactive surface areas and their potential to reduce metal species such as Se(VI), Cr(VI), and U(VI) (Myneni et al., 1997; Loyaux-Lawniczak et al., 2000; O'Loughlin et al., 2003). Hansen et al. (1996) have also shown that sulphate green rust is capable of reducing nitrate to ammonium ions. On the other hand, it is also reported that sulphate green rust cannot reduce As(V) to As(III) (Randall et al., 2001) and that As(III) is partially oxidized to As(V) by carbonate green rust (Su and Puls, 2004). Thus, the reducing potential of green rust should greatly depend on its reactant. The reduction of Sb(V) to Sb(III) is important for the toxicology and environmental chemistry of Sb, since Sb(III) is more toxic than Sb(V) and Sb mobility depends on its oxidation state. However, the interactions between Sb(V) and any green rusts have not been studied previously.

The objective of this work is to thus understand the interactions (sorption and reduction) between Sb(V) and green rust phases, as well as to examine whether green rust can reduce the stable Sb(V). For this purpose, we employed X-ray absorption fine structure (XAFS) analysis to determine directly the oxidation state of Sb sorbed on green rust, while we also determined the Sb(III)/Sb(V) ratio in water phase by high performance liquid chromatography connected to ICP–MS (HPLC–ICP–MS). Based on these results, some implications for the influence of green rust upon Sb behavior in the environment are also given.

## 2. Materials and methods

### 2.1. Reaction of Sb(V) with green rust

The methods of Schwertmann and Fechter (1994) and Heasman et al. (2003) were followed to prepare sulphate green rust with the expected approximate bulk formula $Fe^{II}_2Fe^{III}(OH)_5(SO_4)$. The green rust samples were not exposed to light during preparation and analysis to prevent unwanted photoredox reactions. The sample was prepared in a 500 ml glass vessel in a water bath maintained at 25 ± 0.1 °C. The vessel containing a magnetic stirrer was capped by an airtight PVC lid with holes for pH electrode, a gas inlet/outlet port, and a sample port.

Initially, 370 ml of Milli-Q water was added to the vessel and purged with $N_2$ for 48 h to remove dissolved oxygen before the addition of 20.57 g of $FeSO_4 \cdot 7H_2O$. Once pH in the solution reached pH 7.0 by the addition of a $CO_2$-free 1.0 M NaOH solution, the $N_2$ flow was replaced with laboratory air supplied by a small pump via an open-ended glass tube. Since the oxidation/hydrolysis reaction liberates protons, a titrator (Metrohm 665 Dosimat) was used to constantly add a 1.0 M NaOH solution throughout the reaction and maintain pH at 7.0 ± 0.1.

Sampling was achieved with a 10 ml plastic pipette, and the suspension collected was transferred immediately to a 50 ml screw-top polypropylene centrifuge tube that was filled to the brim without any air trapped inside. Here, we define the reaction time of Fe(II) oxidation as $T_R$. The dark green suspension was first sampled after 30 min ($T_R = 0.5$ h). At $T_R = 0.83$ h (50 min), 10 ml of a 1500 mg/dm$^3$ Sb(V) stock solution prepared from $K[Sb(OH)_6]$ (Wako, Japan) was added. Subsequently, the suspension samples were taken at $T_R = 1.0$, 1.5, 2.0, and 2.5 h. After the final sampling at $T_R = 2.5$ h, all the samples were centrifuged and filtered through 0.22 μm membrane filters in a $N_2$ purged glove box. A loss of dissolved Sb during the filtration was below 1% in this study, suggesting that Sb sorption to filter did not influence for the determination of Sb abundance in water phase. Moreover, in the control sample (system without green rust), Sb recovery from the solution was approximately 100%. Thus, Sb sorption to the glass vessel used for reducing experiment is negligible. The filtrates were then stored in the dark at 4 °C until analysis. The Sb(III)/Sb(V) ratio in the filtrate was then measured by HPLC–ICP–MS on the sampling day. All of the collected green rust samples were packed into polyethylene bag for XAFS analysis under $N_2$ and frozen immediately in liquid $N_2$ to prevent oxidation during storage.

### 2.2. X-ray diffraction analysis

The mineralogy of collected samples was determined by X-ray diffractometer (XRD; MAC Sci., M18XHF) using Cu Kα radiation with monochromator before the detector. The XRD slides were prepared by drying a glycerol-based suspension of each sample onto small glass discs in the $N_2$ purged glovebox. The obtained viscous paste could protect the air-sensitive samples against oxidation during XRD analysis (Hansen and Poulsen, 1999). A comparison of the relative intensity of observed green rust and lepidocrocite diffraction peaks allowed a qualitative assessment of the rate of green rust oxidation.

### 2.3. Water analysis

Total Fe and Sb abundances in the filtrates were measured by graphite-furnace atomic absorption spectroscopy (Shimadzu AA6650) and ICP–MS (Thermoelectron, PQ-3), respectively. The precision of the measurement was better than 5% for both Fe and Sb. The Sb(III)/Sb(V) ratio in the solution was determined by HPLC–ICP–MS. The HPLC system consisted of a Pu-2089 (JASCO) HPLC pump, a Co-2065 Plus (JASCO) column oven, and a PRP-X100 anion-exchange column (Hamilton; 250 mm × 4.1 mm, 10 μm particle size). The experimental conditions were the same as those described by Krachler and Emons (2001). The mobile phase was a 20 mM EDTA (Wako,