



# Chemical, structural and hyperfine characterization of goethites with simultaneous incorporation of manganese, cobalt and aluminum ions



M. Alvarez<sup>a</sup>, A.E. Tufo<sup>b,\*</sup>, C. Zenobi<sup>a</sup>, C.P. Ramos<sup>c</sup>, E.E. Sileo<sup>b</sup>

<sup>a</sup> INQUISUR, Departamento de Química, Universidad Nacional del Sur, Avenida Alem 1253, B8000CPB, Bahía Blanca, Argentina

<sup>b</sup> INQUIMAE, Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pabellón II, Ciudad Universitaria, C1428EHA, Buenos Aires, Argentina

<sup>c</sup> Gerencia Investigación y Aplicaciones, Centro Atómico Constituyentes – Comisión Nacional de Energía Atómica, Av. Gral. Paz 1499, San Martín (1650), Buenos Aires, Argentina

## ARTICLE INFO

### Article history:

Received 14 January 2015

Received in revised form 18 August 2015

Accepted 19 August 2015

Available online 28 August 2015

### Keywords:

Al-, Co-, Mn-goethites

Multi-substitution

Co-ferrite

Hyperfine properties

Rietveld refinement

## ABSTRACT

To elucidate the influence of bi-substitution on the structural and hyperfine properties of goethites, two series of (Al,Co)- and (Mn,Co)-substituted goethites were synthesized in alkaline media by aging several ferrihydrites with different Al/Co and Mn/Co ratios. The samples were fully characterized by chemical analyses, X-ray diffraction (XRD) and Mössbauer spectroscopy; scanning electron microscopy (SEM), zeta potential and BET surface area measurements were also performed. All the solids presented only an  $\alpha$ -FeOOH-like structure, with the exception of two preparations with high Co concentrations that developed two phases, goethite and small amounts of the Co-ferrite ( $\text{CoFe}_2\text{O}_4$ ). The cell parameters in the Co-substituted goethites were markedly smaller than that of the pure sample indicating a oxidation of Co(II) to Co(III) before the incorporation step. In the Co + Mn series the metal substitution followed the trend Co ~ Mn, and in the Co + Al series the trend was Al > Co, and in both cases the incorporation of Co decreased the crystallite size of the samples. The metal-for-Fe incorporation changed the specific surface areas and the morphology of the acicular formed particles. Cobalt containing samples had the highest SSA, while Mn-containing samples had the lowest SSA. The IEP values of the bi-substituted samples were similar to that of pure  $\alpha$ -FeOOH, but mono-substitution by Mn and Al diminished the isoelectric points. The low IEP values detected in Mn-goethite (5.8) and Al-goethite (5.2) could be respectively ascribed to an inhomogeneous distribution of Mn(III), and to the different basicity properties of the surface Fe–OH and Al–OH groups. The hyperfine magnetic field  $B_{\text{hf}}$  increased quasi linearly with the incorporation of Co in both series. In the Co–Mn series the effect was attributed to variations in particle size distribution, in contrast the marked increase observed in the Co–Al series can be attributed to the decrease in the content of diamagnetic ion Al(III). The results indicate that simultaneous substitutions produce substantial changes in the structural, surface and hyperfine properties of goethites. As the characteristics of the dissolution and adsorption processes of the goethites greatly depend on particle size, BET areas and surface charge of the solids, the reported results will allow us to predict changes in the chemical reactivity and adsorption of the multi-substituted goethites. Also the data on hyperfine properties will help to elucidate the probable substitution in natural samples. The fact that Co-incorporation in bi-substituted samples greatly decreased the particle size increasing the specific surface area is an important parameter for technological applications in adsorption removal processes.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Goethite ( $\alpha$ -FeOOH) is naturally present in various soils, marine sediments and ore deposits. Commonly, natural goethite is not pure, and is associated with a number of cations that are iso- or heterovalent to Fe(III). In fact, in natural environments and in many industrial processes, the oxy-hydroxide forms in the presence of multiple metal cations. Mine effluents contain metals such as Cr, Ni, Zn, Cd, Pb that can be incorporated into  $\alpha$ -FeOOH; the same occurs in soils, which may be contaminated with a number of heavy metals from industrial

effluents, fertilizers, etc. (Vega et al., 2004). Thus the coprecipitation of metals with Fe could lead to the simultaneous incorporation of multiple metals into the goethite structure under natural conditions.

Although single metal-for-Fe substitution has been extensively studied, a few studies have investigated multiple metal substitutions in goethite (Cornell, 1991; Manceau et al., 2000; Alvarez et al., 2007; Kaur et al., 2009a,b; Singh et al., 2010). While Manceau et al. (2000), observed simultaneous incorporation of Cr, Mn, Co, Ni, Cu and Zn in natural goethite, the other authors studied the simultaneous inclusion of cations in the structure of the synthetic goethite. Cornell (1991) reported a maximum incorporation of 8 mol% for Ni, Co and Mn, and Kaur et al. (2009a) reported a maximum value of 10.5 mol% for Cr, Zn, Cd and Pb, into the structure of the oxyhydroxide. The authors also

\* Corresponding author.

reported differences in the maximum level of substitution between single-metal systems and multi-substitution that indicated both synergistic and antagonistic incorporation effects. For instance, in single-metal substitution the sequence for maximum incorporation was  $Zn \sim Cr > Cd > Pb$ , and in multiple metal systems the sequence changed to  $Cr \geq Cd > Zn > Pb$ . Regarding the incorporation of aluminum and manganese in goethite, previous research in the authors' laboratory has shown the dominance of Mn over Al in the simultaneous incorporation of both ions in the solid structure (Alvarez et al., 2007).

The substitution of Fe by foreign ions affects the physicochemical properties of the oxy-hydroxide. In particular, cation substitution produces changes around the Fe nucleus that modify the Mössbauer spectrum. For instance, the spectrum of pure well crystallized goethite at room temperature consists of a single sextet with narrow lines, intensity ratios 3:2:1:1:2:3 and a hyperfine magnetic field ( $B_{hf}$ ) of about 38 T (Cornell and Schwertmann, 2000); however, isomorphous substitutions change the spectrum of  $\alpha$ -FeOOH inducing a decrease in the average  $B_{hf}$ . The amount of this decrease varies for different incorporated cations (Schwertmann and Taylor, 1989; dos Santos et al., 2001; Krehula and Musić, 2008, 2009; Guimarães et al., 2009), and also depends on the synthesis route of the solid as it modifies the particle and crystallite size of the formed particles. It is well known that changes in crystallinity and particle size generate variations in the hyperfine properties of goethite (Murad and Bowen, 1987; Vandenberghe, 1991; De Grave et al., 2002; Krehula et al., 2005; Krehula and Musić, 2006), inducing the broadening of the resonant lines and modifying the ideal intensity ratios. For example, in the case of very fine particles (<20 nm), the spectrum of goethite collapses to a doublet (Murad and Johnston, 1987), meanwhile increasing particle size and higher crystallinity cause an increase in  $B_{hf}$ . Therefore,  $B_{hf}$  is particularly sensitive to: particle size distribution, crystallinity and cation substitution that are known to be influenced by Me-for-Fe substitution.

Because the knowledge of the mechanisms by which trace metals associate with goethite in multi-element systems is essential to assess the role played by goethite in the bioavailability of certain ions under natural conditions, in this work we have studied the synthesis of goethite formed from ferrihydrite in the simultaneous presence of three foreign metal cations that are associated with iron oxides in soils and sediments: Al, Co and Mn. Even though the individual effect of each cation on the final products of the crystallization of ferrihydrite have already been fully investigated (Sileo et al., 2001; González et al., 2002; Alvarez et al., 2005, 2008 and references therein), as well as the variations induced by their individual incorporation in the Mössbauer spectrum of goethite (Murad and Bowen, 1987; De Grave et al., 2002; Krehula and Musić, 2006, 2008), the effect of the simultaneous presence of the Co + Mn or Co + Al cations during the formation of goethite, is unknown. For this reason in this study we explore the influence of the simultaneous presence of these cations during the transformation of ferrihydrite to goethite, establishing the maximum uptake of each cation in the presence of the other, and also determining the morphological, structural, surface charge changes, and hyperfine properties in the multi-substituted final goethites. In particular we have used a method sensitive to long-range atomic order (Rietveld refinement) to determine the changes in structure and crystallite size of the oxide, and a method sensitive to short-range atomic order ( $^{57}\text{Fe}$  Mössbauer spectroscopy) to detect changes in the goethites due to the cations incorporation.

These findings will allow us to fully characterize the substituted goethites and to elucidate the role played by bi-substituted goethites in metal cation sequestration in natural environments, establishing if there are antagonistic or synergistic effects on the sequestration process, while data on hyperfine properties will help in the analyses of natural metal-substituted samples. Additionally, the measurements of the morphology, BET surface areas and surface charge characteristics of the solids will allow us to predict changes in the adsorption and dissolution properties of multi-substituted goethites.

## 2. Experimental

### 2.1. Samples preparation

Two series of metal (Me) substituted goethites (Mn,Co-goethites and Co,Al-goethites) were synthesized, keeping a maximum substituting ion concentration ( $\chi_{\text{Me}}$ ) at 12 mol mol<sup>-1</sup>% ( $\chi_{\text{Me}} = [\text{Me}] \times 100 / ([\text{Me}] + [\text{Fe}])$ ). Higher Me concentrations were not used to avoid the formation of additional phases (Alvarez et al., 2007). A sample of pure and a tri-substituted goethite were also prepared.

**Series<sub>I</sub>: Co,Mn-goethites.** Samples of Mn-, Co- and mixed Mn,Co-goethites were prepared by a modification of the synthesis proposed by Sileo et al. (2001). Ferrihydrite was precipitated by adding a 2 M NaOH solution to a mixed solution containing  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{Mn}(\text{NO}_3)_2$  and  $\text{Co}(\text{NO}_3)_2$ , until the ratio  $\text{Me}/\text{OH}^-$  was 0.076. For all samples the initial  $[\text{Fe}] + [\text{Mn}] + [\text{Co}]$  concentration was 0.53 M. After precipitation, the solids were immediately washed twice with bidistilled water, centrifuged and aged for 15 days at 60 °C in Teflon bottles containing 0.3 M NaOH. Mixed samples were synthesized with different nominal  $[\text{Co}]:[\text{Mn}]$  ratio (9:3, 6:6 and 3:9 mol mol<sup>-1</sup>), and the solids were named  $\text{S}_I\text{-Co}_9\text{Mn}_3$ ,  $\text{S}_I\text{-Co}_6\text{Mn}_6$  and  $\text{S}_I\text{-Co}_3\text{Mn}_9$ , respectively. Singly substituted Co-goethite and Mn-goethite (samples named  $\text{S}_I\text{-Co}_{12}\text{Mn}_0$  and  $\text{S}_I\text{-Co}_0\text{Mn}_{12}$ , respectively) were similarly produced by using Fe + Co or Fe + Mn nitrate solutions.

**Series<sub>II</sub>: Co,Al-goethites.** The samples were prepared following the procedure undertaken by Alvarez et al. (2007). Al-goethite was prepared by mixing two solutions (A and B), where solution A was 25.0 mL of 1 M  $\text{Fe}(\text{NO}_3)_3$ , and solution B was 62.5 mL of 0.5 M  $\text{Al}(\text{NO}_3)_3 + 37.5$  mL of 5 M KOH (ratio  $\text{OH}^-/\text{Al} = 6$ ). Three samples of Co,Al-goethites with different Co:Al ratio (9:3, 6:6 and 3:9 mol mol<sup>-1</sup>) were obtained by mixing adequate volumes of solutions A and B with 0.5 M  $\text{Co}(\text{NO}_3)_2$ , followed by 5 M KOH. The formed suspensions were also aged for 15 days at 60 °C in Teflon bottles, and bi-distilled water was added to reach a final KOH concentration of 0.3 M. Al-goethite (sample named  $\text{S}_{II}\text{-Co}_0\text{Al}_{12}$ ) was obtained similarly using A and B solutions. The solids were named  $\text{S}_{II}\text{-Co}_9\text{Al}_3$ ,  $\text{S}_{II}\text{-Co}_6\text{Al}_6$ , and  $\text{S}_{II}\text{-Co}_3\text{Al}_9$ . Following the same methodology used to synthesize the solids in Series<sub>II</sub>, an additional tri-substituted sample containing Co + Al + Mn was prepared using a 4:4:4 ( $[\text{Co}]:[\text{Al}]:[\text{Mn}]$ ) ratio (sample  $\text{Co}_4\text{Al}_4\text{Mn}_4$ ).

In all cases the bottles were opened daily, recapped and shaken by hand end-over-end for 5 s. After aging, the materials were washed with bidistilled water until the conductivity of the filtered solution was similar to that of bidistilled water (18 M $\Omega$ ). The remaining solids were dried at 40 °C and gently crushed in an agate mortar and subsequently treated with 0.4 M HCl at room temperature for 30 min to remove any non-incorporated metal cations or poorly crystalline material from the surface. The metal contents of the samples were determined on these final solids.

### 2.2. Chemical analysis

The amount of Co, Mn, Al and Fe was measured by atomic absorption spectrometry using a GBC, Model B-932 equipment. The HCl-extracted samples (30 mg) were dissolved at 80 °C in 6 M HCl (Series<sub>I</sub>) and 12 M HCl (Series<sub>II</sub>).

### 2.3. X-ray diffraction (XRD) and Rietveld analysis

X-ray diffraction patterns were obtained with a Cu target tube and diffracted beam with a graphite monochromator (Siemens D5000). XRD patterns were measured in the 17.5–130° 2 $\theta$  range, in 0.025° steps and using 8 s per step counting time. The data were analyzed using the GSAS software package (Larson and Von Dreele, 1996) with EXPGUI interface (Toby, 2002). The mean coherence path dimensions (MCP) or crystallite sizes, were determined in the parallel ( $P_{\text{paral}}$ ) and perpendicular ( $P_{\text{perp}}$ ) directions to the anisotropic broadening (110)

Download English Version:

<https://daneshyari.com/en/article/4698447>

Download Persian Version:

<https://daneshyari.com/article/4698447>

[Daneshyari.com](https://daneshyari.com)