



**HAL**  
open science

**On the formation and transformation of  
Fe(III)-containing chukanovite,  
 $\text{FeII}_{2-x}\text{FeIII}_x(\text{OH})_{2-x}\text{O}_x\text{CO}_3$**

J. Duboscq, M. Abdelmoula, C. Rémazeilles, M. Jeannin, R. Sabot, Ph Refait

► **To cite this version:**

J. Duboscq, M. Abdelmoula, C. Rémazeilles, M. Jeannin, R. Sabot, et al.. On the formation and transformation of Fe(III)-containing chukanovite,  $\text{FeII}_{2-x}\text{FeIII}_x(\text{OH})_{2-x}\text{O}_x\text{CO}_3$ . *Journal of Physics and Chemistry of Solids*, 2020, 138, pp.109310. 10.1016/j.jpms.2019.109310 . hal-02480974

**HAL Id: hal-02480974**

**<https://univ-rochelle.hal.science/hal-02480974>**

Submitted on 21 Dec 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

1 **On the formation and transformation of Fe(III)-containing chukanovite,**



3  
4 J. Duboscq<sup>1</sup>, M. Abdelmoula<sup>2</sup>, C. Rémazeilles<sup>1</sup>, M. Jeannin<sup>1</sup>, R. Sabot<sup>1</sup> and Ph. Refait<sup>1,\*</sup>

5 <sup>1</sup> *Laboratoire des Sciences de l'Ingénieur pour l'Environnement (LaSIE), UMR 7356 CNRS -*  
6 *Université de La Rochelle, Bât. Marie Curie, Av. Michel Crépeau,*  
7 *17042 La Rochelle cedex 01, France.*

8 <sup>2</sup> *Laboratoire de Chimie Physique et Microbiologie pour les Matériaux et l'Environnement*  
9 *(LCPME), UMR 7564 CNRS – Université de Lorraine, 405, rue de Vandoeuvre, 54600*  
10 *Villers-lès-Nancy, France*

11  
12 **Abstract.** Aqueous suspensions of Fe(II)-chukanovite were obtained by mixing FeSO<sub>4</sub> and  
13 (Na<sub>2</sub>CO<sub>3</sub> + NaOH) solutions and studied by X-ray diffraction, vibrational spectroscopy  
14 (Raman and infrared) and Mössbauer spectroscopy. After 1 week of ageing in suspension in  
15 anoxic conditions, the Fe(II)-chukanovite particles remained poorly crystallized. A partial  
16 oxidation by air led to the formation of Fe(III)-containing chukanovite, i.e. Fe<sup>II</sup><sub>2-x</sub>Fe<sup>III</sup><sub>x</sub>(OH)<sub>2-x</sub>  
17 O<sub>x</sub>CO<sub>3</sub>, with a Fe(III) proportion about 11-13%. The lattice parameters of the monoclinic  
18 structure varied with the Fe(III) content, in particular the *b* parameter decreased significantly  
19 with increasing oxidation time. Fe(III)-containing chukanovite proved metastable in anoxic  
20 conditions and transformed upon ageing at room temperature into a mixture of Fe(II)-  
21 chukanovite and magnetite Fe<sub>3</sub>O<sub>4</sub>. Finally, trying to form Fe(III)-containing chukanovite by  
22 co-precipitation from Fe(II) and Fe(III) dissolved species led to a mixture of Fe(II)-  
23 chukanovite, i.e. Fe<sup>II</sup><sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>, and sulfated green rust.

24 **Keywords:** Iron, Carbonate, X-ray diffraction, Mössbauer spectroscopy, Raman  
25 spectroscopy, Infrared spectroscopy.

26 \* Corresponding author: Tel: +33 5 46 45 82 27; fax: +33 5 46 45 82 41

27 E-mail: [prefait@univ-lr.fr](mailto:prefait@univ-lr.fr) (Ph. Refait).

## 1 **1. Introduction**

2 Chukanovite, the Fe(II) hydroxycarbonate with formula  $\text{Fe}_2(\text{OH})_2\text{CO}_3$ , was reported  
3 first as a corrosion product of steel and identified as a “basic ferrous carbonate” [1]. It was  
4 discovered thirty years later as a mineral on an iron meteorite found in Russia near the city of  
5 Dronino [2] and found a common corrosion product on ferrous archaeological artifacts [3-5].  
6 Following these discoveries, various studies were devoted to chukanovite dealing with its  
7 synthesis in laboratory conditions [6], the determination of its standard Gibbs free energy [7-  
8 9], the refinement of its crystal structure [2,10], or the understanding of its oxidation and  
9 transformation mechanisms [11,12]. Chukanovite was also observed as a corrosion product of  
10 steel in the specific conditions associated with the storage of high-level radioactive waste in  
11 deep geological disposals [10,13-16]. It might play a role on the behavior of the corrosion  
12 system, depending on the protective efficiency it can give to the corrosion product layer  
13 (CPL). In some cases, chukanovite was observed in the inner stratum of the CPL, in contact  
14 with the metal [3-5,16], or separated from the metal surface by a thin layer of conductive iron  
15 compounds such as magnetite or mackinawite [13,15,17]. If this inner stratum of chukanovite  
16 were conductive it could facilitate, in aerated conditions, the reduction of dissolved  $\text{O}_2$   
17 because  $\text{O}_2$  molecules from the surrounding environment could be reduced at the outer surface  
18 of the chukanovite stratum, thus only having to diffuse through the outer part of the CPL.  
19 Chukanovite proved also a major corrosion product of permeable reactive barrier (PRB) systems  
20 [8,18-20], an environmental technology utilizing granular zero-valent iron for treating  
21 contaminated ground water. It can then affect the long-term performance of these systems.

22 Chukanovite may also be present as a mineral in natural environments (soils or  
23 sediments). It was reported as a product of the transformation of unstable cation-excess  
24 magnetite biogenerated by iron reducing bacteria and considered as a possible overlooked  
25 mineral phase in anoxic sediments [21]. In hydromorphic soils, it could result from the

1 spontaneous transformation of carbonated green rust (i.e. the mineral fougèrite [22]) in anoxic  
2 conditions [23]. In sediments, it could crystallize from a nanocrystalline hydrated Fe-  
3 carbonate precursor [24].

4 Chukanovite may be deficient in cations, with a consequent partial substitution of OH<sup>-</sup>  
5 ions by H<sub>2</sub>O, thus leading to the formula Fe<sub>2-x</sub>(OH)<sub>2-x</sub>CO<sub>3</sub>.xH<sub>2</sub>O [2]. Chemical analysis of  
6 chukanovite as a corrosion product revealed that it could contain Fe(III) [1]. The composition  
7 Fe<sup>II</sup><sub>1.8</sub>Fe<sup>III</sup><sub>0.2</sub>(OH)<sub>2.2</sub>CO<sub>3</sub> was proposed but it could not be excluded that this composition  
8 actually corresponded to that of a mixture of Fe(II)-chukanovite (i.e. Fe<sup>II</sup><sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>) with an  
9 amorphous FeOOH phase [1]. More recently, the formation of such Fe(III)-containing  
10 chukanovite was also assumed, but not demonstrated, and it was proposed [11] that this  
11 partially oxidized chukanovite was an intermediate transient compound during the oxidation  
12 of chukanovite to Fe(III) oxyhydroxides. The general formula Fe<sup>II</sup><sub>2-x</sub>Fe<sup>III</sup><sub>x</sub>(OH)<sub>2-x</sub>O<sub>x</sub>CO<sub>3</sub> was  
13 forwarded [11] for Fe(III)-containing chukanovite, assuming that the oxidation of a Fe<sup>2+</sup>  
14 cation into a Fe<sup>3+</sup> cation was accompanied by the deprotonation of an OH<sup>-</sup> ion, i.e. the  
15 formation of an O<sup>2-</sup> ion. Using hydrogen peroxide as a strong oxidizing agent, the Fe(III)  
16 oxycarbonate Fe<sup>III</sup><sub>2</sub>O<sub>2</sub>CO<sub>3</sub> could be obtained from chukanovite, supporting the deprotonation  
17 model [11].

18 In magnetite (Fe<sub>3</sub>O<sub>4</sub>) at room temperature, the electrons associated with the Fe(II) and  
19 Fe(III) cations present in the octahedral sites of the inverse spinel structure are delocalized  
20 and migrate within the structure thus giving magnetite its well-known electrical conductivity.  
21 Similarly, it cannot be excluded that the presence of Fe(III) in chukanovite could give this  
22 compound some electrical conductive properties. In this case, Fe(III)-containing chukanovite  
23 could play a significant role in the corrosion product layers. It could act as cathode and  
24 promote galvanic effects and corrosion cells, as observed for magnetite [25-30]. In the  
25 environment, Fe(III)-containing chukanovite would then be characterized by an in situ redox

1 flexibility similar to that of fougèrite [31], allowing Fe(III) to be reduced and Fe(II) to be  
2 oxidized in-situ in the crystal structure of chukanovite.

3         Though some previous works mention its possible formation [1,11,12], not a single  
4 study has been devoted to Fe(III)-containing chukanovite. Actually, the conditions favoring  
5 its formation and the corresponding mechanisms are not known. Besides, its stability over  
6 time is yet to be established. Actually, it was shown that Fe(II)-chukanovite was metastable  
7 with respect to siderite [9], which implies that it could transform spontaneously to siderite.  
8 The objectives of the present study were then:

9         - to investigate different pathways for the formation of aqueous suspensions of Fe(III)-  
10 containing chukanovite,

11         - to characterize Fe(III)-containing chukanovite using complementary analytical tools,  
12 namely X-ray diffraction, Raman spectroscopy, Mössbauer spectroscopy and infrared  
13 spectroscopy,

14         - to follow the possible transformation over time of Fe(III)-containing chukanovite in  
15 anoxic conditions.

16

## 17 **2. Materials**

18         All the chemical products used for the preparation of the various precipitates had a  
19 98% min. purity.

20

### 21 *2.1. Synthesis of Fe(II)-chukanovite suspensions*

22         The procedure used here was derived from previous studies [6,9,11,12]. It consisted in  
23 mixing  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , NaOH, and  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  solutions with concentrations corresponding  
24 to the ratios  $[\text{FeSO}_4 \cdot 7\text{H}_2\text{O}]/[\text{NaOH}] = 1.0$  and  $[\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}]/[\text{NaOH}] = 0.5$ . These ratios  
25 correspond to the stoichiometry of the precipitation reaction of  $\text{Fe}_2(\text{OH})_2\text{CO}_3$ :



2 All the experiments were performed with a NaOH concentration equal to 0.2 mol L<sup>-1</sup>.  
3 The FeSO<sub>4</sub>·7H<sub>2</sub>O and Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O concentrations were then equal to 0.2 mol L<sup>-1</sup> and 0.1  
4 mol L<sup>-1</sup>, respectively. The volume of solution was 300 mL in each case, corresponding to a  
5 total of 0.06 mol of Fe(II). The proportion of dissolved Fe(II) species remaining in solution in  
6 equilibrium with the solid phase can be considered as negligible due to the low solubility of  
7 chukanovite in these experimental conditions [9].

8 Because this work was focused on Fe(III)-containing chukanovite, the reference  
9 precipitate, used as the starting point for all the various parts of the study, was prepared with  
10 solutions that were not deaerated. Similarly, the mixing and stirring (30 seconds) of the  
11 solutions that led to the chukanovite precipitate was achieved without protection from air.  
12 Once obtained, the suspension was poured in a flask filled to the rim and the flask was  
13 hermetically sealed. The precipitate was finally aged for 1 week at room temperature (RT =  
14 21±2 °C) before analysis or partial oxidation. This reference precipitate, aged 1 week, is  
15 called CF0 and was assumed to be close to Fe(II)-chukanovite (this point is thoroughly  
16 discussed in section 4.1).

17 Samples of chukanovite CF0 were also aged in suspension at RT for up to 8 months.

18

## 19 *2.2. Oxidation of Fe(II)-chukanovite CF0 suspensions*

20 A progressive partial oxidation of Fe(II)-chukanovite CF0 precipitates was achieved  
21 by a magnetic stirring (600 rpm, rod 4-cm long and 8-mm diameter) of the suspensions in the  
22 open air. The 300 mL suspensions were aerated at the liquid-air interface in a 600 mL beaker  
23 of 9-cm diameter. According to previous study [11], Fe(III)-containing chukanovite should be  
24 obtained as an intermediate transient compound before the end products of the oxidation  
25 process, i.e. Fe(III) oxyhydroxides, appear. The Fe(III) content able to accumulate in the

1 chukanovite structure during this process was estimated at 11-14% [11]. This estimation was  
2 obtained via the determination of the oxidation time  $t_F$  required for the formation of FeOOH  
3 phases (i.e. oxidation of 100% Fe<sup>II</sup>) and the oxidation time  $t_I$  required for the formation of  
4 Fe(III)-containing chukanovite, assuming a constant oxidation rate.

5         Oxidation times of 15, 30 and 60 minutes were chosen according to previous work  
6 [11]. Before a time  $t_I \sim 55$  minutes, the oxidation of Fe(II) did not lead to the formation of any  
7 additional solid phase and it was forwarded that the oxidation of Fe(II) took place in situ  
8 inside the crystal structure of chukanovite [11]. After time  $t_I$ , the formation of FeOOH phases  
9 began, possibly because the crystal structure of chukanovite could host no more Fe(III). At  
10 the end of the oxidation period, one half of the precipitate was filtered for analysis. The other  
11 half was left in suspension, sheltered from air as described in the previous section for Fe(II)-  
12 chukanovite CF0, to be analyzed after ageing. Each experiment was performed at least three  
13 times with ageing durations up to 10 months.

14         The pH of the suspension was measured in each case before and after the oxidation  
15 period using a glass electrode.

16

### 17 *2.3. Co-precipitation of Fe(II) and Fe(III)*

18         With the aim of preparing Fe(III)-containing chukanovite by co-precipitation of  
19 dissolved Fe(II) and Fe(III) species with carbonate and hydroxide ions, another procedure was  
20 used. It consisted in mixing a FeSO<sub>4</sub>·7H<sub>2</sub>O + FeCl<sub>3</sub>·6H<sub>2</sub>O solution with a NaOH +  
21 Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O solution, with concentrations corresponding to the ratios  
22 [Fe(II)+Fe(III)]/[NaOH] = 1.0 and [Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O]/[NaOH] = 0.5 as for the formation of  
23 chukanovite (reaction 1). The considered amounts of Fe(III), expressed as [Fe<sup>III</sup>]/[Fe<sup>II</sup> + Fe<sup>III</sup>]  
24 concentration ratios (in %), were 2%, 5% and 10%. The maximal Fe(III) content of 10%

1 considered here is similar to that reported previously for Fe(III)-containing chukanovite  
2 [1,11].

3 All the samples were aged 1 week at RT using the procedure described in the previous  
4 section for Fe(II)-chukanovite CF0.

5

### 6 **3. Methods**

7 The precipitates were characterized by a combination of four techniques, namely X-  
8 ray diffraction (XRD), Transmission Mössbauer spectroscopy (TMS), Fourier-Transform  
9 Infrared (FTIR) spectroscopy and  $\mu$ -Raman spectroscopy. The first aim was to identify all the  
10 phases, crystalline or not, possibly present with chukanovite in the precipitates. TMS was  
11 more specifically used to demonstrate that chukanovite could indeed contain some Fe(III) and  
12 to quantify this Fe(III) content. XRD data were thoroughly analyzed to confirm, via a possible  
13 evolution of lattice parameters, the presence of a variable amount of Fe(III).

14

#### 15 *3.1. XRD analysis*

16 Since chukanovite is very sensitive to the oxidizing action of O<sub>2</sub>, a specific procedure  
17 was used. The precipitate was filtered while being sheltered from air during the process with a  
18 plastic membrane. A slightly wet paste was then obtained.

19 XRD analysis was performed at RT with an Inel EQUINOX 6000 diffractometer,  
20 using a curved detector (CPS 590), with the Co-K $\alpha$  radiation ( $\lambda = 0.17903$  nm). The curved  
21 detector is designed for the simultaneous detection of the diffracted photons on a  $2\theta$  range of  
22 90°. The calibration of the angular scale was made specifically for the present study using a  
23 standard sample of LaB<sub>6</sub>. Acquisition was made with a constant angle of incidence (5  
24 degrees) over 45 minutes. To prevent the oxidation of chukanovite during preparation and  
25 analysis, the slightly wet paste obtained after filtration was mixed with a few drops of

1 glycerol in a mortar. It was then crushed until a homogenous oily paste was obtained. With  
2 this procedure the various chukanovite particles are coated with glycerol and sheltered from  
3 the oxidizing action of O<sub>2</sub> [32,33].

4 To obtain a maximum of reliable information from the XRD data, Rietveld  
5 refinements [34] of the patterns were performed using the MAUD (Materials Analysis Using  
6 Diffraction) software [35]. With this software, the whole XRD patterns are fitted taking into  
7 account structural and microstructural parameters of the sample, and instrumental  
8 characteristics. Lattice parameters of chukanovite and phase composition of mixtures of  
9 magnetite and chukanovite were determined using this procedure. The reliability of the  
10 computer fitting is testified in each case by two factors, the weighted profile *R*-factor, *R*<sub>wp</sub>,  
11 and the goodness of fit,  $\chi^2$  [36].

12 In any case, the signal due to glycerol was subtracted from the experimental data using  
13 an XRD pattern of glycerol acquired in the same experimental conditions. Such a data  
14 processing may have an influence, affecting in particular the intensity of the diffraction peaks.  
15 However, the only objective of the study was to observe the evolution of lattice parameters  
16 and phase composition with oxidation/ageing time. Consequently, only a comparison between  
17 the data obtained for various oxidation/ageing times was made and each XRD pattern was  
18 treated with the same procedure. To check the validity of this methodology, two XRD  
19 patterns of the same sample were treated so that the dispersion of computed parameters for a  
20 given sample could be determined. The results proved sufficiently accurate (see tables 2 and  
21 4) to consider that the procedure used, if reproduced exactly the same way for each pattern,  
22 whether has no impact on the XRD data or has a systematic impact that influences similarly each  
23 XRD pattern.

24

25 *3.2. Mössbauer spectroscopy analysis*

1 TMS was performed at various temperatures, i.e. RT, 77 K and 8 K, with a constant  
2 acceleration Mössbauer spectrometer and 512 multichannel analyzer (Halder Electronic  
3 Gmbh), and a 50 mCi source of  $^{57}\text{Co}$  in Rh maintained at RT and mounted at the end of a  
4 Mössbauer velocity transducer. Data were obtained from appropriate amounts (10 mg of Fe  
5 per  $\text{cm}^2$ ) of solid samples to get optimal experimental conditions.

6 The samples were prepared under  $\text{N}_2$  atmosphere in an anoxic glove box (Jacomex)  
7 and quickly transferred under inert He atmosphere to the cold head cryostat manufactured by  
8 Advanced Research Systems, equipped with vibration isolation stand, developed in LCPME  
9 laboratory (CNRS and Lorraine University, France). The calibration of the velocity scale was  
10 carried out for the study using the Mössbauer absorption lines of a reference absorber, i.e.  $\alpha$ -  
11 iron, at RT. The Mössbauer spectrum of  $\alpha$ -iron is a sextet with well known hyperfine  
12 parameters, which provides a calibration based on 6 points, i.e. the position of each peak of  
13 the sextet.

14 The TMS spectra were analyzed using the Recoil software [37]. Two approaches were  
15 used for this analysis. For the spectra obtained near and above 35 K the Lorentzian-shape  
16 lines model was adequate. The experimental spectra were then fitted with doublets  
17 corresponding to paramagnetic sites with a quadrupole splitting. For the spectra obtained at  
18 very low temperature, due to the appearance of a magnetic ordering for the Fe(II)  
19 components, the full static Hamiltonian site analysis was required for solving the mixed  
20 hyperfine interactions.

21

### 22 *3.3. FTIR analysis*

23 FTIR measurements were performed with a Thermo-Nicolet iS50 spectrometer using  
24 an iTX ATR (attenuated total reflectance) accessory with a diamond crystal. The apparatus is  
25 equipped with a KBr beamsplitter and a DTGS detector and monitored by the Omnic

1 software. It is checked each 6 months using the bench diagnosis function of the software,  
2 based on the ATSM E 1421-99 (Standard practice for describing and measuring performance  
3 of FTIR spectrometer level zero and level one tests). Furthermore, the wavenumber scale is  
4 checked each three months using a standard polystyrene film.

5 For the present study, the sample holder was covered by a cell insulating it and  
6 allowing a nitrogen flow to pass through. A background spectrum was acquired each hour and  
7 used for all sample spectra acquired within this hour. The validity of the background spectrum  
8 was however checked before each acquisition using the previsualization function of the  
9 Omnic software. This previsualization was performed before the sample was set on the  
10 diamond crystal of the ATR device, i.e. the signal had to be equal to zero if the background  
11 spectrum was still valid. The background spectra were acquired under nitrogen flow like those  
12 of the samples.

13 The slightly wet paste obtained after filtration (see section 3.1) was rinsed with water  
14 and ethanol while being sheltered from air. It was then rapidly set on the diamond crystal of  
15 the ATR accessory. After a complete evaporation of the ethanol remaining in the sample,  
16 verified via the previsualization function, the spectrum was recorded with a resolution of 8  
17  $\text{cm}^{-1}$  which proved sufficient to distinguish all the characteristic vibration bands of  
18 chukanovite [6]. 128 scans were acquired for each spectrum.

19

#### 20 *3.4. $\mu$ -Raman spectroscopy analysis*

21 Raman analysis was performed on a Jobin Yvon High Resolution Raman spectrometer  
22 (LabRAM HR Evolution) equipped with a confocal microscope, a Peltier-based cooled charge  
23 coupled device (CCD) detector and a solid-state diode pumped green laser (532 nm). The  
24 apparatus is calibrated at least each 3 months using a Si wafer and more precisely the Raman  
25 peak of Si located at  $520.5 \text{ cm}^{-1}$ .

1           The slightly wet paste obtained after filtration (see section 3.1) was crushed between a  
2 glass plate and a very thin glass platelet so that the Fe(II)-compounds were sheltered from air  
3 during the acquisition of the spectrum. The laser was then focused on the sample through the  
4 thin glass platelet. Its power was reduced between 25% and 1% of the maximum (i.e. between  
5 1.94 and 0.07 mW) because an excessive heating can induce the transformation of the  
6 analyzed Fe compounds into hematite  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. More precisely, the sample was first analyzed  
7 using the lower laser power, i.e. 1% of the maximum, to identify the main phases present in  
8 the sample. Then, to obtain high quality spectra that may reveal minor phases, several  
9 acquisitions were performed with increasing laser power, until a high signal to noise ratio was  
10 obtained. An excessive heating, i.e. an excessive laser power, is revealed by the presence of  
11 the well-known Raman peaks of hematite. In any case, the acquisition time did not exceed 2  
12 minutes.

13

#### 14 **4. Experimental results**

##### 15 *4.1. Characterization of Fe(II)-chukanovite CF0 after various times of ageing in suspension*

16           Figure 1 shows the corresponding XRD pattern and FTIR spectrum of reference  
17 Fe(II)-chukanovite CF0 aged for 1 week. The XRD pattern (fig. 1a) is made of rather broad  
18 diffraction peaks, indicating a poor crystallinity. Moreover, these peaks are found on a broad  
19 hump, extending from  $2\theta \sim 25^\circ$  to  $2\theta \sim 35^\circ$ , due to the presence of glycerol. Nevertheless, all  
20 visible diffraction peaks could be attributed to chukanovite (ICDD-JCPDS file 01-076-6357  
21 corresponding to [2]), except for the one denoted by a star. Consequently, XRD analysis  
22 shows that chukanovite is the only detected crystalline phase. However, the presence of  
23 amorphous/nano-crystalline matter or minor phases cannot be discarded.

24           The full width at half maximum is the smallest for the 020 (and 12-1/021) peak, which  
25 indicates that chukanovite particles grew preferentially along the *b* axis of the monoclinic

1 crystal structure. This is consistent with the previous descriptions of chukanovite crystals,  
2 reported as acicular or fibrous [2] and acicular to platy [8].

3 Chukanovite is also the only solid phase detected by FTIR spectroscopy (fig. 1b). The  
4 signal observed between 1800 and 2300  $\text{cm}^{-1}$  is due to the ATR device and does not  
5 correspond to a vibration band. The two broad peaks observed here are only artifacts located  
6 in the wavenumber regions where the diamond of the ATR device strongly absorbs the IR  
7 incident beam. All the other peaks are those reported previously for chukanovite [2,6,10,11]  
8 and interpreted as follows [6]: the bands at 3484 and 3322  $\text{cm}^{-1}$  are attributed to OH  
9 stretching, those at 1540 and 1355  $\text{cm}^{-1}$  to the  $\nu_3$  antisymmetric  $\text{CO}_3^{2-}$  stretching. The weaker  
10 band at 1100  $\text{cm}^{-1}$  is attributed to  $\nu_1$  symmetric  $\text{CO}_3^{2-}$  stretching while those at 1054 and 955  
11  $\text{cm}^{-1}$  are due to  $\delta$  OH deformation modes. The band at 837  $\text{cm}^{-1}$  can be attributed whether to  
12  $\nu_2$   $\text{CO}_3^{2-}$  bending or  $\delta$  OH deformation modes. Finally, the three last bands at 782, 695 and  
13 654  $\text{cm}^{-1}$  corresponds to  $\nu_4$   $\text{CO}_3^{2-}$  bending modes. Because FTIR spectroscopy can detect  
14 crystalline phases and non-crystalline phases as well, this result shows that chukanovite is the  
15 only solid phase present in the precipitate.

16 The evolution over time of Fe(II)-chukanovite CF0 was also studied. Figure 2 shows  
17 the XRD pattern of a sample aged 8 months at RT. It is very similar to the previous one (fig.  
18 1a) but some diffraction peaks of chukanovite are better defined (i.e. 001, 330, 250/511, 431  
19 and 44-1) which indicates a slightly improved crystallinity. For instance, the FWHM of the  
20 peaks 210 and 020 decreased from 2.09° (201) and 0.85° (020) for unaged CF0 to 1.73° (210)  
21 and 0.45° (020) for aged CF0. The relative intensity of the non-interpreted diffraction line (\*)  
22 is smaller, which indicates that its presence may be associated with the poor crystallinity, i.e.  
23 imperfect ordering, of the obtained chukanovite particles, or to the presence of a minor phase  
24 now disappeared. Fe(II)-chukanovite may be metastable with respect to siderite [9] but, in the

1 considered experimental conditions and after 8 months, it remained the only solid phase  
2 present.

3 Other analytical methods confirmed this result. As an example, TMS spectra of 2  
4 months old chukanovite CF0, collected at 77 K and 8 K, are displayed in figure 3. At 77 K,  
5 the precipitate is in paramagnetic state and its spectrum only made of quadrupole doublets.  
6 The spectrum could be adequately fitted with two doublets characterized by the same center  
7 shift (CS) typical of ferrous state in high spin configuration, indicated by its value of 1.23 mm  
8 s<sup>-1</sup> and two slightly different values for quadrupole splitting  $\Delta$ , i.e. 2.09 and 2.56 mm s<sup>-1</sup> (table  
9 1). These two values are ascribable to the presence of two Fe(II) octahedral sites Fe1 and Fe2  
10 [2,10]. The octahedral environment of Fe1 is made up of four oxygen atoms belonging to  
11 carbonate ions and two OH<sup>-</sup> ions, whereas four OH<sup>-</sup> ions and two oxygen atoms from CO<sub>3</sub><sup>2-</sup>  
12 ions surround Fe2. The Fe1 octahedron is more distorted than the Fe2 octahedron [2]. In  
13 Mossbauer spectroscopy, the quadrupole splitting  $\Delta$  arises from the second hyperfine  
14 interaction that is the interaction between quadrupole moment  $Q$  (due to non-spherical charge  
15 distribution of the nucleus) and electric field gradient (EFG). The EFG, caused by the spatial  
16 distribution of the electrons around the nucleus, has a strong relation to site symmetry and  
17 local structure. For chukanovite, the quadrupole doublet with the highest quadrupole splitting  
18  $\Delta$  must then correspond to the most distorted Fe1 octahedral site. The doublet with smaller  
19 quadrupole splitting  $\Delta$  then corresponds to Fe2. The two doublets are found in similar  
20 proportion, in agreement with the crystal structure of chukanovite, where Fe(II) cations are  
21 present in equal proportions in the two octahedral sites [2,10].

22 The shape of the 8 K spectrum is more complex and completely different from that of  
23 the 77 K spectrum. It indicates that all the Fe(II) sites are magnetically ordered and are  
24 represented by octets (table 1). Modelling with the software package Recoil [37] of such a  
25 spectrum is complex because for Fe(II) compounds electric quadrupole and magnetic

1 hyperfine interactions are generally of the same order of magnitude and it is not possible to  
2 analyze the spectrum with six line patterns (sextets) as it is usually done for Fe(III)  
3 compounds [38,39]. Each octet comprises eight lines that have to be fully computed by  
4 solving the eigenvalues of the Hamiltonian. Due to the considerable line broadening revealed  
5 by the experimental spectrum, we have improved the fitting of the low temperature spectrum  
6 by adding a paramagnetic component as a quadrupole doublet typical of Fe(III) but of very  
7 low intensity. However, this may be an artifact due to the complexity of the spectrum.

8 In conclusion, the precipitate CF0 proved to be composed of chukanovite as a major  
9 phase hosting a very low proportion of Fe(III) (if any), and did not transform over time in  
10 anoxic conditions, i.e. remained unchanged after 8 months of ageing in suspension at RT  
11 except for a slight increase of crystallinity. In the following, CF0 is then considered as the  
12 reference Fe(II)-chukanovite.

13

#### 14 *4.2. Synthesis and characterization of Fe(III)-containing chukanovite*

15 Precipitates CF0 were aged for 1 week and subsequently exposed to air in a beaker, as  
16 described in section 2.3, for 15, 30 or 60 minutes. The pH of the initial CF0 suspensions was  
17 measured at  $9.6 \pm 0.2$ . The oxidation process was accompanied by a decrease of pH, as already  
18 observed [11]. After the 15-minute oxidation period, the pH was measured at  $9.5 \pm 0.2$ , i.e.  
19 was similar to the initial pH. After the 30-minute oxidation period, an important discrepancy  
20 was observed from one experiment to another, leading to an average value of  $9.0 \pm 0.4$ . After  
21 the 60-minute oxidation period, the pH was significantly lower, at  $7.8 \pm 0.2$ . According to  
22 previous study [11], this rapid decrease of pH, occurring between 30 and 60 minutes of  
23 oxidation, is associated with the beginning of the formation of FeOOH phases.

24 Figure 4 displays the corresponding XRD patterns. After 15 minutes of exposure to  
25 air, only the diffraction lines of chukanovite are seen, in agreement with previous work [11].

1 Because an exposure to air of 15 minutes necessarily implies that part of the Fe(II) cations are  
2 oxidized to Fe(III), the absence of any other compound suggests that the oxidation process  
3 only involved an in-situ oxidation of Fe(II) cations inside the chukanovite structure. Note that  
4 the oxidation process leads to visible effects: the color of the suspension turned to a slightly  
5 darker shade of grey after the 15 minutes exposure to air.

6 After 30 minutes of exposure to air, the main diffraction lines of goethite ( $\alpha$ -FeOOH),  
7 one of the end products of the oxidation of chukanovite [11,12], were observed in some  
8 samples (G<sub>111</sub> and G<sub>110</sub>, corresponding respectively to  $I_{110} = 100$ ,  $d_{110} = 4.14 \text{ \AA}$  and  $I_{111} = 50$ ,  
9  $d_{111} = 2.45 \text{ \AA}$  according to ICDD-JCDS file No 00-29-0713). In other samples, they were not  
10 observed (data not shown) and it is then questionable whether the small amount of goethite,  
11 when detected, resulted from the 30-minute oxidation of the aqueous suspension or has  
12 formed during the preparation (filtration...) and analysis of the sample.

13 After 60 minutes of exposure to air, the two main diffraction lines of goethite were  
14 clearly seen in any case. This means that at 60 minutes of exposure to air the second oxidation  
15 stage of chukanovite, i.e. the formation of FeOOH phases, has already begun.

16 Figure 4 clearly shows a shift of the main diffraction line of chukanovite with  
17 increasing oxidation time. This suggests that the increasing Fe(III) content induces changes of  
18 the lattice parameters of the chukanovite structure. Table 2 gathers the lattice parameters  
19 determined for chukanovite after 1 week of ageing with and without subsequent oxidation. As  
20 explained in section 3.1, only the influence of the oxidation time is to be discussed. It can then  
21 be observed that the lattice parameter  $c$  appears rather constant, only varying between  $3.190 \text{ \AA}$   
22 for 15 minutes of oxidation and  $3.205 \text{ \AA}$  for 60 minutes of oxidation. However, clear trends  
23 are observed for the other lattice parameters. In particular, lattice parameter  $b$  decreases  
24 significantly, from  $9.37 \text{ \AA}$  to  $9.16 \text{ \AA}$ , with increasing oxidation time. The angle  $\beta$  decreases  
25 from  $97.04^\circ$  to  $95.1^\circ$  while the lattice parameter  $a$  increases with increasing oxidation time.

1 These variations of the lattice parameters, linked to the oxidation time, can be attributed to the  
2 increasing Fe(III) content of chukanovite. Actually, the ionic radius of  $\text{Fe}^{3+}$  is smaller than  
3 that of  $\text{Fe}^{2+}$ , with 0.645 Å instead of 0.78 Å [40]. The decrease of the lattice parameter  $b$  may  
4 then be due to the decrease of the average ionic radius of the Fe cations as the proportion of  
5 Fe(III) increases. The increase of the lattice parameter  $a$ , associated with the decrease of the  
6 angle  $\beta$ , however reveals a strongly anisotropic behavior of the cell parameters as a result of  
7 the substitution of Fe(II) to Fe(III) and the corresponding substitution of 1  $\text{OH}^-$  to 1  $\text{O}^{2-}$  ion in  
8 the surrounding octahedron of oxygen atoms. This anisotropic behavior of cell parameters  
9 must be linked to structural features of chukanovite. A similar example was reported for  
10 cobaltoan malachites [41].

11 The oxidized precipitates were also analyzed by other methods. Figure 5 displays as an  
12 example the FTIR spectrum of a precipitate oxidized 30 minutes by air. This spectrum is  
13 typical of chukanovite. Goethite, as well as any other  $\text{FeOOH}$  compound, was not detected.  
14 FTIR analysis confirms that the 30 minutes of oxidation have mainly led to an in situ  
15 oxidation of Fe(II) cations inside the crystal structure of chukanovite. This duration can then  
16 be considered as the maximum oxidation time that, in our experimental conditions, can lead to  
17 a single phase system, i.e. a precipitate only composed of Fe(III)-containing chukanovite. For  
18 60 minutes of oxidation, a two-phase system, i.e. Fe(III)-containing chukanovite + goethite,  
19 was obtained in any case.

20 Mossbauer analysis was then focused on samples oxidized 30 minutes. The analysis  
21 was performed at RT and 77 K and the obtained spectra are displayed in figure 6. Both  
22 spectra are mainly composed of two Fe(II) quadrupole doublets characterized by large CS and  
23 quadrupole splitting values (table 3) and one Fe(III) doublet, characterized by smaller CS and  
24  $\Delta$  values. The parameters obtained at 77 K for the Fe(II) doublets are similar to those obtained  
25 for sample CF0 at the same temperature (see table 2) and can then be assigned to chukanovite.

1 They are found at both temperatures in a ratio Fe1:Fe2 = 1 in agreement with the crystal  
2 structure of chukanovite (see also section 4.1). The Fe(III) doublet, present at both  
3 temperatures, cannot be attributed to goethite. Actually, goethite is magnetically ordered at  
4 RT and should give rise to a sextet characterized by a small CS of 0.53 mm/s, a quadrupole  
5 splitting  $\Delta$  close to zero and a hyperfine field of 360 kOe [42,43]. However, microcrystalline  
6 goethite is often characterized by a superparamagnetic behavior at RT, i.e. may give rise to a  
7 paramagnetic doublet, due to small particle size [44]. It however tends to order magnetically  
8 when the temperature is lowered and give rise to a magnetically split sextet at 77 K [43,45].  
9 This sextet is not observed here, i.e. TMS shows that goethite was not present in this sample.

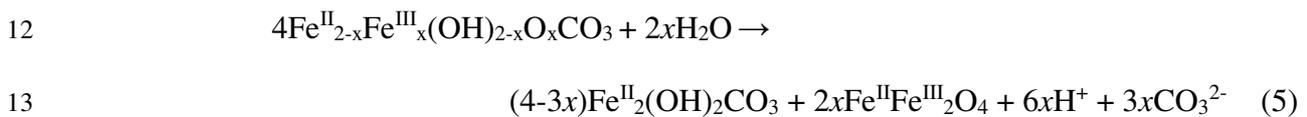
10 The observed Fe(III) doublet can then be attributed to the Fe(III) cations present in the  
11 crystal structure of chukanovite. Its quadrupole splitting is high (for Fe<sup>III</sup> state), indicating a  
12 strongly distorted environment. The obtained values of 0.87 mm/s (RT) and 0.74 mm/s (77 K)  
13 are for instance significantly higher than those of Fe(III) in GR compounds, e.g. 0.45 mm/s at  
14 77 for GR(SO<sub>4</sub><sup>2-</sup>) [46] or in lepidocrocite  $\gamma$ -FeOOH, i.e. 0.55 mm/s at 77 K [47]. High  
15 quadrupole splitting values are found for ferrihydrite (0.7 – 0.85 mm/s [48]), a poorly  
16 crystalized and poorly ordered Fe(III) oxyhydroxide where the sites are also highly distorted.  
17 It must also be noted that the Fe1:Fe2 ratio remains equal to 1 in Fe(III)-containing  
18 chukanovite, which implies that the Fe(III) cations are equally distributed in both octahedral  
19 sites. The unique Fe(III) doublet used for the interpretation of the spectra then corresponds to  
20 both Fe(III)1 and Fe(III)2 sites.

21 The proportion of Fe(III) present in the crystal structure of chukanovite after 30 min.  
22 of oxidation is then estimated at 11-13% by TMS (table 3). A similar Fe(III) content was  
23 previously reported [1,11].

24

25 *4.3. Evolution of Fe(III)-containing chukanovite suspensions under anoxic conditions*

1           The precipitates obtained after 15, 30 and 60 minutes of oxidation by air were aged 10  
2 months in anoxic conditions. The results of the XRD analysis of the precipitates after ageing  
3 are summarized in figures 7-9. The precipitate oxidized 15 minutes by air was initially only  
4 composed of Fe(III)-containing chukanovite (fig. 4). After ageing (fig. 7a), the diffraction  
5 lines of magnetite Fe<sub>3</sub>O<sub>4</sub> are clearly seen. In section 4.1, it was observed that the ageing of  
6 Fe(II)-chukanovite CF0 precipitates only induced a slight increase of crystallinity. The  
7 formation of magnetite during the ageing of the precipitate must then be attributed to the  
8 transformation of Fe(III)-containing chukanovite. Because only magnetite and chukanovite  
9 are present, this transformation more likely leads to magnetite and Fe(II)-chukanovite, i.e. the  
10 Fe(III) cations are expelled from the chukanovite structure to form magnetite. The reaction  
11 can be written as follows:



14           Because the crystal structure of magnetite differs strongly from that of chukanovite,  
15 reaction (5) is not likely to take place through a solid-state transformation and a dissolution-  
16 reprecipitation process can be reasonably proposed.

17           The ageing of the precipitate oxidized 30 minutes also led to the formation of  
18 magnetite. A detailed view of the 32°-46° angular region of its XRD pattern is compared in  
19 fig. 7b with that of the precipitate oxidized 15 minutes. It can clearly be seen that the intensity  
20 of the M220 and M311 diffraction lines of magnetite increase with the oxidation time. This  
21 confirms that the amount of magnetite due to ageing is associated with the Fe(III) amount  
22 initially present in chukanovite, i.e. that magnetite comes from the transformation of Fe(III)-  
23 containing chukanovite.

24           The Rietveld refinements of the XRD patterns confirmed this analysis. The results are  
25 listed in table 4 and two computed patterns (oxidation times of 15 min. and 60 min.) are

1 compared to experimental data in figure 8 to illustrate the accuracy of the fitting. The  
2 proportion of magnetite is found to increase with the oxidation time, from 2 % for 15 min.  
3 oxidation to 5 % for 30 min oxidation and finally 12 % for 60 min. oxidation. The amount of  
4 goethite present after 60 min. oxidation is about 9%. If we assume that magnetite comes from  
5 the transformation of Fe(III)-containing chukanovite, then the Fe(III)-containing chukanovite  
6 present in the sample oxidized 60 minutes would have contained more Fe(III) than the Fe(III)-  
7 containing chukanovite present in the sample oxidized 30 minutes. This is consistent with the  
8 evolution of the lattice parameters with the oxidation time (see table 2) that still vary from 30  
9 to 60 minutes of oxidation.

10 The lattice parameters  $a$  and  $b$  of chukanovite after the 10 month ageing period (table  
11 4) still depend on the oxidation time but their variations are less significant. This confirms  
12 that the formation of magnetite, i.e. reaction (5), has indeed led to a significant decrease of the  
13 Fe(III) content of chukanovite. Parameter  $b$ , which varied from 9.31 Å (15 min. oxidation) to  
14 9.16 Å (60 min. oxidation) before ageing, varies from 9.34 Å (15 min. oxidation) to 9.30 Å  
15 (60 min. oxidation) after ageing. In each case, parameter  $b$  has increased and parameter  $a$  has  
16 decreased after ageing. The  $\beta$  angle is even constant at  $98(\pm 0.1)^\circ$ . It was observed (table 2),  
17 that the increase of the oxidation time, i.e. the Fe(III) content, led to a decrease of  $b$ , an  
18 increase of  $a$  and a decrease of  $\beta$ . The evolution of the lattice parameters during ageing is  
19 indeed consistent with a decrease of the Fe(III) content.

20 The transformation of Fe(III) chukanovite was also followed over time. In figure 9, the  
21 XRD patterns of precipitates oxidized for 15 minutes by air and subsequently aged 15  
22 minutes, 7 days and 10 months are compared. The 7 main diffraction lines of magnetite are  
23 seen for the sample aged 10 months. None of the magnetite diffraction lines is seen after 15  
24 minutes of ageing while only the main one, M311, is detected after 7 days of ageing. This  
25 shows that the transformation of Fe(III)-chukanovite is only partial, in our experimental

1 conditions, after 1 week. The transformation rate of Fe(III)-containing chukanovite is  
2 sufficiently low so that this compound can persist at that time scale.

3 Other analytical tools led to consistent results. As an example, two Raman spectra are  
4 shown in figure 10. They are both representative of the numerous spectra acquired during the  
5 analysis of these samples. Raman analysis is performed locally on a 5-6  $\mu\text{m}$  diameter region  
6 of the considered precipitate. It is a local analysis but it appeared that the precipitates,  
7 composed of much smaller particles, were rather homogeneous at that scale. In the case of a  
8 multiphase system, each Raman spectrum proved composed of the spectral components of  
9 each phase, with only the respective intensity of the vibration bands associated with the  
10 different phases varying from one spot to another. The first spectrum (fig. 10a) is that of  
11 reference Fe(II)-chukanovite CF0 after two weeks of ageing. The only solid phase identified  
12 is indeed chukanovite, characterized here by its main Raman band at  $1071\text{ cm}^{-1}$  [3-6]. The  
13 other sharp peak at  $981\text{ cm}^{-1}$  is attributed to sulfate ions. These ions are whether present in  
14 solution (wet precipitates were analyzed) or adsorbed on chukanovite particles. The broad  
15 humps at  $\sim 450\text{ cm}^{-1}$  and  $\sim 950\text{ cm}^{-1}$  are due to the thin glass platelet that shelters the  
16 precipitate from air.

17 The second spectrum (fig. 10b) is that of the precipitate oxidized 60 minutes by air and  
18 subsequently aged 1 month in anoxic conditions. Magnetite is identified by its main Raman  
19 band at  $673\text{ cm}^{-1}$  [49,50], indicating that the transformation of Fe(III)-containing chukanovite  
20 has already led to detectable effects. Goethite is identified by two intense bands at  $302\text{ cm}^{-1}$   
21 and  $387\text{ cm}^{-1}$  and three smaller ones at  $243\text{ cm}^{-1}$  and  $485\text{ cm}^{-1}$  [49,50]. This phase was already  
22 present after the 60-minute oxidation period (fig. 4).

23

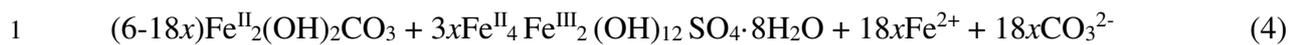
24 *4.4. Characterization of the precipitates obtained from Fe(II) and Fe(III) salts*

1           The results can be summarized by the description of the XRD analysis. Because of the  
2 poor crystallinity of chukanovite, a well crystallized phase present with chukanovite is easily  
3 detected on the XRD patterns, as illustrated by figure 11. The whole XRD pattern of the  
4 precipitate obtained with 5% Fe(III) is presented in figure 11a. The characteristic (broad)  
5 diffraction peaks of chukanovite are accompanied by thin and sharp lines of the sulfated green  
6 rust  $\text{GR}(\text{SO}_4^{2-})$  [51], i.e. the Fe(II-III) double layered hydroxysulfate with chemical formula  
7  $\text{Fe}^{\text{II}}_4\text{Fe}^{\text{III}}_2(\text{OH})_{12}\text{SO}_4 \cdot 8\text{H}_2\text{O}$  [51].

8           In figure 11b, a detailed view of the  $5^\circ$ - $35^\circ$  angular region, where the 3 main  
9 diffraction peaks of  $\text{GR}(\text{SO}_4^{2-})$  are located, is presented for the precipitates obtained with 2%,  
10 5% and 10% of Fe(III). In any case, the  $\text{GR}_{\text{hkl}}$  lines are clearly observed, even with only 2%  
11 of Fe(III). The intensity of those lines increases with the proportion of Fe(III). More precisely,  
12 the intensity of the  $\text{GR}_{001}$  peak, determined via a fitting of the experimental curves with a  
13 Gauss function, was found to increase from 800 to 2200 and 4100 (arbitrary unit) with Fe(III)  
14 content increasing from 2% to 5% and 10%. This shows that the amount of  $\text{GR}(\text{SO}_4^{2-})$  is  
15 roughly proportional to the quantity of Fe(III) available in the system (i.e.  $800 \times 2.5 = 2000$   
16 and  $800 \times 5 = 4000$ ).

17           In conclusion, the presence of Fe(III) in solution has mainly induced, in the considered  
18 experimental conditions, the formation of  $\text{GR}(\text{SO}_4^{2-})$ . The Fe(II-III) hydroxysulfate was  
19 obtained as a consequence of the high sulfate concentration of the medium. Chloride ions  
20 were also present but  $\text{GR}(\text{Cl}^-)$  did not form, in agreement with previous work [33], because  
21 the layered structure of GRs has a greater affinity for sulfate ions, and more generally for  
22 divalent anions that give the structure a greater stability [52,53]. In the presence of Fe(III) and  
23 sulfate species, the precipitation reaction leading to a mixture of chukanovite and  $\text{GR}(\text{SO}_4^{2-})$   
24 can be written as follows:





2 As such, the proportion of Fe(III), that is  $[\text{Fe}^{3+}]/([\text{Fe}^{2+}]+[\text{Fe}^{3+}])$ , is equal to  $6x/(12-$   
3  $6x+6x)$ , that is  $x/2$ . The Fe(III) proportions considered here, i.e. 2%, 5% and 10%, then  
4 correspond to  $x = 0.04, 0.1$  and  $0.2$ . The amount of  $\text{GR}(\text{SO}_4^{2-})$  formed is  $3x$ , i.e. is  
5 proportional to the amount of Fe(III).

6 According to reaction (4),  $\text{OH}^-$  ions are lacking so that part of the  $\text{Fe}^{2+}$  cations should  
7 be left in solution with a corresponding amount of carbonate ions. These species could lead to  
8 siderite  $\text{FeCO}_3$  that was however not detected. Similar results, i.e. absence of siderite while  
9  $\text{Fe}^{2+}$  and  $\text{CO}_3^{2-}$  ions are left in excess in solution together with chukanovite, were already  
10 reported [6,9]. The  $\text{CO}_3^{2-}$  ions left in excess in solution can react with water molecules to  
11 produce  $\text{HCO}_3^-$  and  $\text{OH}^-$  ions, thus leading to alkaline conditions that were assumed to inhibit  
12 the formation of siderite [6,9].

13 One can finally notice that even for 10% Fe(III), chukanovite is still the major phase;  
14 it would represent (using  $x = 0.2$  in equation 4) 4.8 moles of Fe for 3.6 moles of Fe in  
15  $\text{GR}(\text{SO}_4^{2-})$ .

16

## 17 **5. Discussion**

18 Fe(III)-containing chukanovite could only be obtained by oxidation of Fe(II)-  
19 chukanovite precipitates. It was mixed with  $\alpha\text{-FeOOH}$  for an oxidation time of 60 minutes but  
20 was the only solid phase for oxidation times up to 30 minutes, with a maximum Fe(III)  
21 content of 11-13%. When Fe(II) and Fe(III) salts were used, the obtained precipitate consisted  
22 of a mixture of Fe(II)-chukanovite and  $\text{GR}(\text{SO}_4^{2-})$ . In this case, the Fe(III) cations marginally  
23 participated to the building up of the chukanovite structure. These results show that  $\text{Fe}^{3+}$   
24 cations can be present in this structure only if they result from the in-situ oxidation of  $\text{Fe}^{2+}$   
25 cations already present in the crystal structure.

1 Fe(III)-containing chukanovite transformed in anoxic conditions into a mixture of  
2 Fe(II)-chukanovite and magnetite, which shows that the two-phase system  $\text{Fe}^{\text{II}}_2(\text{OH})_2\text{CO}_3 +$   
3  $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}_2\text{O}_4$  is more stable than the one-phase system  $\text{Fe}^{\text{II}}_{2-x}\text{Fe}^{\text{III}}_x(\text{OH})_{2-x}\text{O}_x\text{CO}_3$  in the  
4 considered experimental conditions. In section 4.4, it was observed that the co-precipitation of  
5 Fe(II) and Fe(III) also led to a two-phase system, in this case  $\text{Fe}^{\text{II}}_2(\text{OH})_2\text{CO}_3 + \text{GR}(\text{SO}_4^{2-})$ .  
6 According to available thermodynamic data and previous experimental results [54],  $\text{GR}(\text{SO}_4^{2-})$   
7 is metastable with respect to magnetite. The most stable system is then more likely the two-  
8 phase system  $\text{Fe}^{\text{II}}_2(\text{OH})_2\text{CO}_3 + \text{Fe}^{\text{II}}\text{Fe}^{\text{III}}_2\text{O}_4$ , the other two-phase system  $\text{Fe}^{\text{II}}_2(\text{OH})_2\text{CO}_3 +$   
9  $\text{GR}(\text{SO}_4^{2-})$  being obtained as a result of the co-precipitation process due to the fast kinetic it  
10 implies.

11 In contrast, Fe(II)-chukanovite did not transform after 8 months in anoxic conditions,  
12 though it is metastable with respect to siderite [9]. This is consistent with its common  
13 identification as a corrosion product on ferrous archaeological artifacts [3-6]. In such ancient  
14 systems, chukanovite is in most cases associated with siderite. This suggests that the  
15 transformation of Fe(II)-chukanovite to siderite could be very slow and lead to significant  
16 effects only at very long term, i.e. not after a few months. Magnetite was not observed either.  
17 This result suggests that in anoxic conditions, Fe(II)-chukanovite cannot be oxidized into  
18 Fe(III)-containing chukanovite. The presence of  $\text{Fe}^{3+}$  cations inside the crystal structure of  
19 chukanovite requires an oxidizer stronger than  $\text{H}_2\text{O}$ , e.g. dissolved  $\text{O}_2$  as illustrated by our  
20 results. In actual corrosion systems (nuclear waste, storage, buried archaeological artefacts,  
21 permeable reactive barriers...) the formation of Fe(III)-containing chukanovite could then only  
22 result from isolated and/or moderate  $\text{O}_2$  ingress.

23 Therefore, according to these results, Fe(III)-containing chukanovite may only persist  
24 for days or maybe weeks. Consequently, whatever its possible electrical conductivity, it does  
25 not seem able to play an important role in long-term corrosion processes such as those studied

1 in the frame of nuclear waste management in deep geological disposals. Actually, a recent  
2 study of the electrical properties of rust layers containing chukanovite revealed that this  
3 compound behave as an insulator [55].

4 Fe(III)-containing chukanovite may however be involved as a transient phase in redox  
5 processes occurring at a smaller time scale (e.g. a few days). It is also possible that in some  
6 cases, the transformation of Fe(III)-containing chukanovite could be inhibited, e.g. via the  
7 adsorption of strongly bound molecules/ions on Fe(III)-containing chukanovite particles,  
8 which may prevent the dissolution-precipitation process leading to the two phase system  
9  $\text{Fe}^{\text{II}}_2(\text{OH})_2\text{CO}_3 + \text{Fe}^{\text{II}}\text{Fe}^{\text{III}}_2\text{O}_4$ .

10 The transformation of Fe(III)-chukanovite in anoxic conditions however leads to  
11 magnetite that is a well-known electronic conductor. More precisely, it may lead to the  
12 formation of numerous small magnetite particles scattered in a matrix of Fe(II)-chukanovite.  
13 Such magnetite “islets”, already observed inside the corrosion product layer covering  
14 archaeological artefacts [55-57], may favor the decoupling of anodic and cathodic reactions  
15 and contribute actively to the corrosion process. This decoupling was observed in some cases  
16 and the presence of a network of nanometric magnetite particles connecting the metal to the  
17 outer part of the corrosion product layer was forwarded [57].

18

## 19 **6. Conclusions**

20 - Fe(III)-containing chukanovite could not be prepared by precipitation from Fe(II)  
21 and Fe(III) dissolved species. The Fe(III) species were mainly incorporated into a green rust  
22 compound, i.e.  $\text{GR}(\text{SO}_4^{2-})$  in the considered experimental conditions, and Fe(II)-chukanovite  
23 precipitated from the excess Fe(II) species.

24 - Fe(III)-containing chukanovite could only be obtained via the oxidation (by  
25 dissolved  $\text{O}_2$ ) of Fe(II) cations already present in the crystal structure. The amount of Fe(III)

1 present in chukanovite after 30 minutes of oxidation could be estimated by TMS analysis at  
2 11-13%. Subsequent oxidation led to the formation of an additional Fe(III)-bearing phase, i.e.  
3 goethite.

4 - The increasing oxidation time of chukanovite led to significant variations of the  
5 lattice parameters, in particular to a contraction in the *b* direction, due to the increasing Fe(III)  
6 content.

7 - Fe(III)-containing chukanovite proved metastable in the considered experimental  
8 anoxic conditions. It tends to transform during ageing into a mixture of magnetite and Fe(II)-  
9 chukanovite. This shows that Fe(III)-containing chukanovite, whatever its electrical  
10 conductivity, is not likely to play an important role in corrosion systems at long term. It may  
11 however have an indirect influence through its transformation, that can favor the formation of  
12 magnetite particles scattered in the corrosion product layer.

13

14 **Acknowledgements:** This work is part of the PhD thesis of Julien DUBOSCQ financially  
15 supported by the “Communauté d’Agglomération de La Rochelle” (CDA La Rochelle) and  
16 part of the CPER/FEDER project “DYPOMAR”.

17

## 18 **References**

19 [1] E. Erdös E., H. Altorfer, Ein dem Malachit ähnliches basisches Eisenkarbonat als  
20 Korrosionsprodukt von Stahl, Werkstoffe und Korrosion 27 (1976) 304-312.

21 [2] I.V. Pekov, N. Perchiazzi, S. Merlino, V.N. Kalachev, M. Merlini, A.E. Zadov,  
22 Chukanovite, Fe<sub>2</sub>(CO<sub>3</sub>)(OH)<sub>2</sub>, A new mineral from the weathered iron meteorite Dronino,  
23 Eur. J. Mineral. 19 (2007) 891-898.

- 1 [3] M. Saheb, D. Neff, P. Dillmann, H. Matthiesen, E. Foy, Long-term corrosion behaviour of  
2 low-carbon steel in anoxic environment: Characterisation of archaeological artefacts, *J.*  
3 *Nuclear Mat.* 379 (2008) 118-123.
- 4 [4] M. Saheb, D. Neff, P. Dillmann, H. Matthiesen, E. Foy, L. Bellot-Gurlet, Multisecular  
5 corrosion behaviour of low carbon steel in anoxic soils: Characterisation of corrosion system  
6 on archaeological artefacts, *Materials and Corrosion* 60 (2009) 99-105.
- 7 [5] M. Saheb, D. Neff, L. Bellot-Gurlet, P. Dillmann, Raman study of deuterated iron  
8 hydroxycarbonate to assess long-term corrosion mechanisms in anoxic soils, *J. Raman*  
9 *Spectroscopy* 42 (2011) 1100-1108.
- 10 [6] C. Rémazeilles, Ph. Refait, Fe(II) hydroxycarbonate  $\text{Fe}_2(\text{OH})_2\text{CO}_3$  (Chukanovite) as iron  
11 corrosion product: Synthesis and study by Fourier Transform Infrared Spectroscopy,  
12 *Polyhedron* 28 (2009) 749–756.
- 13 [7] T. Nishimura, J. Dong, Corrosion behavior of carbon steel for overpack in groundwater  
14 containing bicarbonate ions, *J. Power and Energy Systems* 3 (2009) 23-30.
- 15 [8] T. R. Lee, R. T. Wilkin, Iron hydroxy carbonate formation in zerovalent iron permeable  
16 reactive barriers: Characterization and evaluation of phase stability, *Journal of Contaminant*  
17 *Hydrology* 116 (2010) 47–57.
- 18 [9] I. Azoulay, C. Rémazeilles, Ph. Refait, Determination of standard Gibbs free energy of  
19 formation of chukanovite and Pourbaix diagrams of iron in carbonated media, *Corros. Sci.* 58  
20 (2012) 229-236.
- 21 [10] I. Pignatelli, E. Mugnaioli, R. Mosser-Ruck, O. Barres, U. Kolb, N. Michau, A multi-  
22 technique, micrometer- to atomic-scale description of a synthetic analogue of chukanovite,  
23  $\text{Fe}_2(\text{CO}_3)(\text{OH})_2$ , *Eur. J. Mineral.* 26 (2014) 221-229.
- 24 [11] I. Azoulay, C. Rémazeilles, Ph. Refait, Corrosion of steel in carbonated media: the  
25 oxidation processes of chukanovite ( $\text{Fe}_2(\text{OH})_2\text{CO}_3$ ), *Corros. Sci.* 85 (2014) 101-108.

- 1 [12] I. Azoulay, C. Rémazeilles, Ph. Refait, Oxidation of chukanovite ( $\text{Fe}_2(\text{OH})_2\text{CO}_3$ ):  
2 Influence of the concentration ratios of reactants, *Corros. Sci.* 98 (2015) 634-642.
- 3 [13] M. Schlegel, C. Bataillon, C. Blanc, D. Pret, E. Foy, Anodic Activation of Iron Corrosion  
4 in Clay Media under Water-Saturated Conditions at 90 °C: Characterization of the Corrosion  
5 Interface, *Environ. Sci. Technol.* 44 (2010) 1503–1508.
- 6 [14] A. Romaine, R. Sabot, M. Jeannin, S. Necib, Ph. Refait, Electrochemical synthesis and  
7 characterization of corrosion products on carbon steel under argillite layers in carbonated  
8 media at 80°C, *Electrochim. Acta* 114 (2013) 152-158.
- 9 [15] M.L. Schlegel, C. Bataillon, F. Brucker, C. Blanc, D. Prêt, E. Foy, M. Chorro, Corrosion  
10 of metal iron in contact with anoxic clay at 90°C: Characterization of the corrosion products  
11 after two years of interaction, *Appl. Geochem.* 51 (2014) 1-14.
- 12 [16] A. Romaine, M. Jeannin, R. Sabot, S. Necib, Ph. Refait, Corrosion processes of carbon  
13 steel in argillite: Galvanic effects associated with the heterogeneity of the corrosion product  
14 layer, *Electrochim. Acta* 182 (2015) 1019-1028.
- 15 [17] Y. Leon, M. Saheb, E. Drouet, D. Neff, E. Foy, E. Leroy, J.J. Dynes, P. Dillmann,  
16 Interfacial layer on archaeological mild steel corroded in carbonated anoxic environments  
17 studied with coupled micro and nano probes, *Corros. Sci.* 88 (2014) 23-35.
- 18 [18] R.T. Wilkin, R.W. Puls, Capstone Report on the Application, Monitoring and  
19 Performance of Permeable Reactive Barriers for Ground Water Remediation. Performance  
20 Evaluations at Two Sites. EPA/600/R-03/045a. Office of Research and Development,  
21 Cincinnati, OH. 140 pp (2003).
- 22 [19] T. Kohn, K. Livi, A.L. Roberts, P. Vikesland, Longevity of granular iron in groundwater  
23 treatment processes: Corrosion product development, *Environ. Sci. Technol.* 39 (2005) 2867-  
24 2879.

- 1 [20] S.-W Jeen, J.L. Jambor, D.W. Blowes, R.W., Gillham, Precipitates on granular iron in  
2 solutions containing calcium carbonate with trichloroethene and hexavalent chromium.  
3 Environ. Sci. Technol. 41 (2007) 1989–1994.
- 4 [21] R.K. Kukkadapu, J.M. Zachara, J.K. Fredrickson, D.W. Kennedy, A.C. Dohnalkova,  
5 D.E. Mccready, Ferrous hydroxy carbonate is a stable transformation product of biogenetic  
6 magnetite, Amer. Min. 90 (2005) 151-515.
- 7 [22] Ph. Refait, M. Abdelmoula, F. Trolard, J.M. Génin, J.J. Ehrhardt, G. Bourrié, Mössbauer  
8 and XAS study of a green rust mineral ; the partial substitution of Fe<sup>2+</sup> by Mg<sup>2+</sup>, Amer. Min.  
9 86 (2001) 731-739.
- 10 [23] Ph. Refait, M. Reffass, J. Landoulsi, R. Sabot, M. Jeannin, Role of nitrite species during  
11 the formation and transformation of the Fe(II-III) hydroxycarbonate Green Rust, Colloids  
12 Surf. A: Physicochem. Eng. Aspects 459 (2014) 225-232.
- 13 [24] K. Dideriksen, C. Frandsen, N. Bovet, A.F. Wallace, O. Sel, T. Arbour, A. Navrotsky,  
14 J.J. De Yoreo, J.F. Banfield, Formation and transformation of a short range ordered iron  
15 carbonate precursor, Geochim. Cosmochim. Acta 164 (2015) 94-109.
- 16 [25] J. Han, S. Nešić, B.N. Brown, Galvanic model for localized CO<sub>2</sub> corrosion, NACE  
17 Corrosion/08 Conference, paper n°2687 (2008).
- 18 [26] J. Han, D. Young, S. Nešić, Characterization of the passive film on mild steel in CO<sub>2</sub>  
19 environments, NACE Corrosion/08 Conference, paper n°2511 (2008).
- 20 [27] S.M. Wilhem, Galvanic corrosion caused by corrosion products, in Galvanic Corrosion,  
21 ASTM STP 978, Harvey P. Hack, Ed. American Society for Testing and Materials,  
22 Philadelphia, (1988) 23-34.
- 23 [28] A.M. Al-Mayouf, N.A. Al-Mobarak, A.A. Al-Swayih, Dissolution of magnetite coupled  
24 with iron of various surface areas, Corrosion 63 (2007) 916.

- 1 [29] A.M. Al-Mayouf, Dissolution of magnetite coupled galvanically with iron in  
2 environmentally friendly chelant solutions, *Corrosion Science* 48 (2006) 898-912.
- 3 [30] M. Robineau, A. Romaine, R. Sabot, M. Jeannin, V. Deydier, S. Necib, Ph. Refait,  
4 Galvanic corrosion of carbon steel in anoxic conditions at 80°C associated with a  
5 heterogeneous magnetite (Fe<sub>3</sub>O<sub>4</sub>) / mackinawite (FeS) layer, *Electrochim. Acta* 255 (2017)  
6 274-285.
- 7 [31] C. Ruby, C. Upadhyay, A. Géhin, G. Ona-Nguema, J.-M.R. Génin, In situ redox  
8 flexibility of Fe<sup>II-III</sup> oxyhydroxycarbonate green rust and fougérite, *Environ. Sci. Technol.* 40  
9 (2006) 4696-4702.
- 10 [32] H.C.B. Hansen, Composition, stabilisation, and light absorption of Fe(II)-Fe(III)  
11 hydroxycarbonate (green rust), *Clay Miner.* 24 (1989) 663-669.
- 12 [33] Ph. Refait, R. Sabot, M. Jeannin, Role of Al(III) and Cr(III) on the formation and  
13 oxidation of the Fe(II-III) hydroxysulfate Green Rust, *Colloids Surf. A: Physicochem. Eng.*  
14 *Aspects* 531 (2017) 203-212.
- 15 [34] H. M. Rietveld, A profile refinement method for nuclear and magnetic structures, *J.*  
16 *Appl. Crystallogr.* 2 (1969) 65-71.
- 17 [35] L. Lutterotti, Maud: a Rietveld analysis program designed for the internet and experiment  
18 integration, *Acta Cryst. A* 56 (2000) s54.
- 19 [36] R.A. Young, "Introduction to the Rietveld method," *The Rietveld Method*, edited by R.A.  
20 Young, Oxford University Press, Oxford, 1993, pp. 1-38.
- 21 [37] K. Lagarec, D. G. Rancourt, *Mössbauer analysis software Recoil*; University of Ottawa.
- 22 [38] B. Rusch, J.M. R. Génin, C. Ruby, M. Abdelmoula, P. Bonville, Ferrimagnetic properties  
23 in Fe<sup>II-III</sup> (oxy)hydroxycarbonate green rusts, *Solid State Sci.* 10 (2008) 40-49.

- 1 [39] B. Maitte, F.P.A. Jorand, D. Gregic, M. Abdelmoula, C. Carteret, Remineralization of  
2 ferrous carbonate from bioreduction of natural goethite in the Lorraine iron ore (Minette) by  
3 *Shewanella putrefaciens*, Chem. Geol. 412 (2015) 48-58.
- 4 [40] R. D. Shannon, Revised effective ionic radii and systematic studies of interatomic  
5 distances in halides and chalcogenides, Acta cryst. A32 (1976) 751-767.
- 6 [41] N. Perchiazzi, R. Dragone, N. Demitri, P. Vignola, C. Biagioni, Incorporation of Co in  
7 the rosasite–malachite carbonate group of minerals: crystal structure studies of kolwezite and  
8 synthetic cobaltoan malachites, Eur. J. Mineral. 30 (2018) 609–620.
- 9 [42] M.J. Rossiter, A.E.M. Hodgson, A Mössbauer study of ferric oxy-hydroxide, J. Inorg.  
10 Nucl. Chem. 27 (1965) 63-71.
- 11 [43] E. Murad, The characterization of goethite by Mössbauer spectroscopy, Amer. Min. 67  
12 (1982) 1007-1011.
- 13 [44] M.B. Madsen, S. Morup, Asymmetric doublet in Mössbauer spectra of  
14 superparamagnetic goethite, Hyperfine Interactions 42 (1988) 1059-1062.
- 15 [45] C.J.W. Koch, M.B. Madsen, S. Morup, Decoupling of magnetically interacting  
16 crystallites of goethite, Hyperfine Interactions 28 (1986) 549-552.
- 17 [46] J.-M.R. Génin, A.A. Olowe, Ph. Refait, L. Simon, On the stoichiometry and Pourbaix  
18 diagram of Fe(II)-Fe(III) hydroxy-sulphate or sulphate-containing green rust 2; an  
19 electrochemical and Mössbauer spectroscopy study, Corros. Sci. 38 (1996) 1751-1762.
- 20 [47] C.E. Johnson, Antiferromagnetism of  $\gamma$ -FeOOH: a Mössbauer effect study, J. Phys. C 2  
21 (1969) 1996-2002.
- 22 [48] E. Murad, The Mössbauer spectrum of well-crystallized ferrihydrite, J. Magn. Magn.  
23 Mater. 74 (1988) 153-157.
- 24 [49] D.L.A. De Faria, S.V. Silva, M.T.D. Oliveira, Raman micro spectroscopy study of some  
25 iron oxides and oxyhydroxides, J. Raman Spectroscopy 28 (1997) 873-878.

- 1 [50] D. Neff, P. Dillmann, L. Bellot-Gurlet, G. Beranger, Corrosion of iron archaeological  
2 artefacts in soil: characterisation of the corrosion system, *Corros. Sci.* 47 (2005) 515-535.
- 3 [51] L. Simon, M. François, Ph. Refait, G. Renaudin, M. Lelaurain, J.M. Génin, Structure of  
4 the Fe(II-III) layered double hydroxysulphate green rust two from Rietveld analysis, *Solid*  
5 *State Sci.* 5 (2003) 327-334.
- 6 [52] S. Miyata, Anion-exchange properties of hydrotalcite-like compounds, *Clays Clay*  
7 *Miner.* 31 (1983) 305-311.
- 8 [53] Ph. Refait, S.H. Drissi, J. Pytkiewicz, J.-M. Génin, The anionic species competition in  
9 iron aqueous corrosion: role of various green rust compounds, *Corros. Sci.* 39 (1997) 1699-  
10 1710.
- 11 [54] Ph. Refait, A. Géhin, M. Abdelmoula, J.M. Génin, Coprecipitation thermodynamics of  
12 iron(II-III) hydroxysulphate green rust from Fe(II) and Fe(III) salts, *Corros. Sci.* 45 (2003)  
13 656-676.
- 14 [55] F. Mercier-Bion, Jiaying Lia, H. Lotz, L. Tortech, D. Neff , Ph Dillmann, Electrical  
15 properties of iron corrosion layers formed in anoxic environments at the nanometer scale,  
16 *Corros. Sci.* 137 (2018) 90-110.
- 17 [56] M. Saheb, D. Neff, E. Foy, J. Demory, P. Dillmann, Characterisation of the corrosion  
18 layers formed on ferrous archaeological artefacts buried in anoxic media, *Corros. Eng. Sci.*  
19 *Technol.* 45 (2010) 381–387.
- 20 [57] M. Saheb, D. Neff, C. Bataillon, E. Foy, Ph. Dillmann, Copper tracing to determine the  
21 micrometric electronic properties of a thick ferrous corrosion layer formed in an anoxic  
22 medium, *Corros. Sci.* 53 (2011) 2201-2207.

23

## Figure captions

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25

Figure 1: Analysis of reference Fe(II)-chukanovite CF0 after one week of ageing at RT: XRD pattern (a) and FTIR spectrum (b). The main diffraction peaks of chukanovite are indexed with the corresponding Miller index. On the IRTF spectrum, the vibration bands of chukanovite are denoted by their position in  $\text{cm}^{-1}$ .

Figure 2: XRD pattern of reference Fe(II)-chukanovite CF0 after 8 months of ageing at RT. The main diffraction peaks of chukanovite are denoted by the corresponding Miller index.

Figure 3: TMS spectra of reference Fe(II)-chukanovite CF0 after 2 months of ageing at RT: Measurements run at 77 K and 8 K. The experimental and computed curves are shown together with the various spectral components.

Figure 4: XRD patterns of CF0 precipitates after 15, 30 and 60 minutes of oxidation by air. The main diffraction peaks of chukanovite are denoted by the corresponding Miller index. Ghkl lines are those of goethite.

Figure 5: FTIR spectrum of CF0 precipitate after 30 minutes of oxidation; the vibration bands of chukanovite are denoted by their location in  $\text{cm}^{-1}$ .

Figure 6: TMS spectra run at RT and 77 K of CF0 precipitate after 30 minutes of oxidation by air. The experimental and computed curves are shown together with the various spectral components.

1 Figure 7: XRD patterns of CF0 precipitates after 15 minutes and 30 minutes of oxidation by  
2 air followed by 8 months of ageing at RT: Whole pattern of the precipitate oxidized 15  
3 minutes (a) and detailed view of the 32°-46° angular region of the patterns of the precipitates  
4 oxidized 15 and 30 minutes. The main diffraction peaks of chukanovite are denoted by the  
5 corresponding Miller index. Mhkl and Ghkl lines are those of magnetite and goethite  
6 respectively.

7

8 Figure 8: Rietveld analysis of the XRD data obtained for CF0 precipitate after (a) 15 minutes  
9 or (b) 60 minutes of oxidation by air followed by 10 months of ageing. Experimental pattern  
10 (black dots), computed pattern (light grey line), error curve (black dotted line) and  
11 contributions of chukanovite (grey dash line), and magnetite (black line).

12

13 Figure 9: XRD pattern of CF0 precipitate after 15 minutes of oxidation by air followed by 15  
14 minutes, 7 days or 10 months of ageing at RT. Mhkl lines are those of magnetite whereas the  
15 other, unindexed, diffraction peaks are those of chukanovite.

16

17 Figure 10: Raman spectra of CF0 precipitate after 2 weeks of ageing at RT (a) and CF0  
18 precipitate after 60 minutes of oxidation by air followed by 1 month of ageing at RT (b). A  
19 letter and their position in  $\text{cm}^{-1}$  denote the vibration bands. Ck = chukanovite, G = goethite  
20 and M = magnetite.

21

22 Figure 11: XRD patterns of the precipitates obtained by coprecipitation of Fe(II) and Fe(III)  
23 salts. Whole pattern of the precipitate obtained with 5% Fe(III) (a) and detailed view of the  
24 5°-35° angular region of the patterns of the precipitate obtained with 2%, 5% and 10% Fe(III).

- 1 The main diffraction peaks of chukanovite are denoted by the corresponding Miller index.
- 2 GRhkl lines are those of sulfated green rust.
- 3

TABLES

Table 1. Hyperfine parameters obtained for Fe(II)-chukanovite CF0 at 77 K and 8 K. The error was determined by analyzing three samples. It was estimated at  $\pm 0.02$  mm/s for CS and  $\Delta$  in any case.

Sites	CS (mms <sup>-1</sup> )	$\Delta$ or $\epsilon$ (mms <sup>-1</sup> )	H (kOe)	Relative abundance (%)
77 K				
Fe1	1.23	2.56	-	52 $\pm$ 4
Fe2	1.25	2.09	-	48 $\pm$ 4
8 K				
Fe1	0.99	4.8	105	51 $\pm$ 4
Fe2	1.31	3.8	240	46 $\pm$ 4

Table 2. Lattice parameters of CF0 chukanovite precipitates with and without oxidation in air. The error was estimated via the analysis of two XRD patterns of each sample. The values given for  $\chi^2$  and  $R_{wp}$  are those of the best fit.

Sample	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\beta$ (degree)	$\chi^2$	$R_{wp}$ (%)
CF0	12.35 $\pm$ 0.02	9.37 $\pm$ 0.01	3.200 $\pm$ 0.005	97.04 $\pm$ 0.08	1.09	1.85
CF0 + 15' ox.	12.42 $\pm$ 0.02	9.31 $\pm$ 0.02	3.190 $\pm$ 0.005	96.5 $\pm$ 0.5	1.08	1.64
CF0 + 30' ox.	12.47 $\pm$ 0.02	9.28 $\pm$ 0.02	3.200 $\pm$ 0.005	96.0 $\pm$ 0.1	1.25	1.96
CF0 + 60' ox.	12.56 $\pm$ 0.03	9.16 $\pm$ 0.03	3.205 $\pm$ 0.005	95.1 $\pm$ 0.1	1.10	1.75

1  
2  
3  
4  
5

Table 3. Hyperfine parameters (RT) obtained for chukanovite CF0 oxidized 30 minutes. The error was determined by analyzing three samples. It was estimated at  $\pm 0.02$  mm/s for CS and  $\Delta$  in any case.

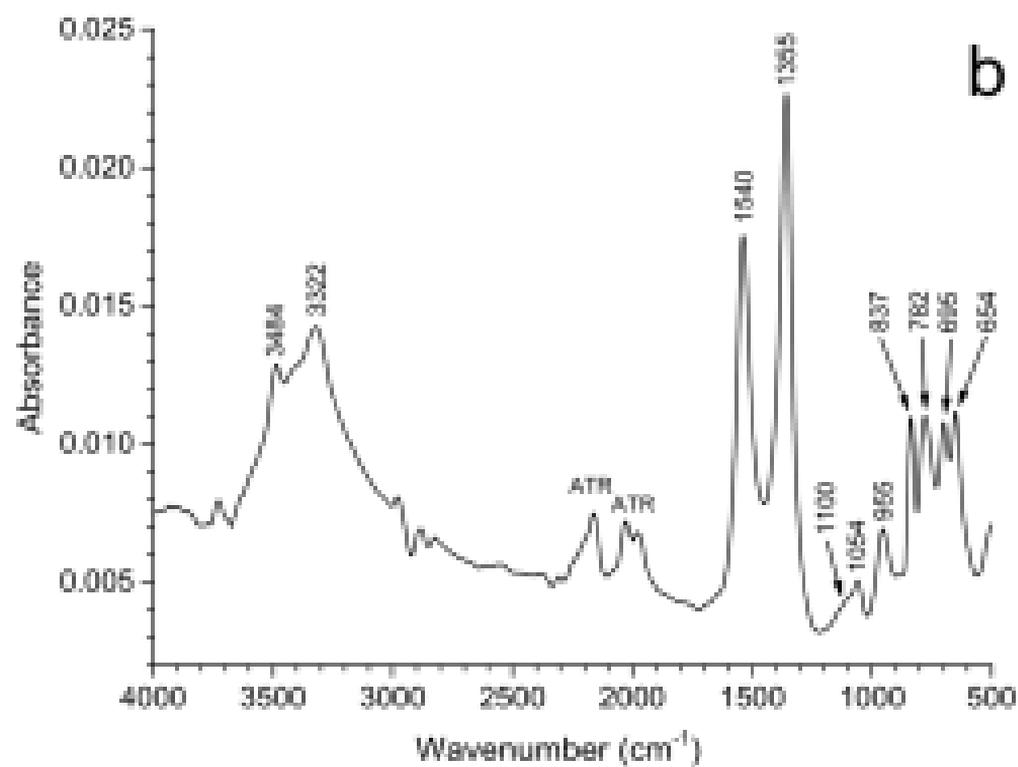
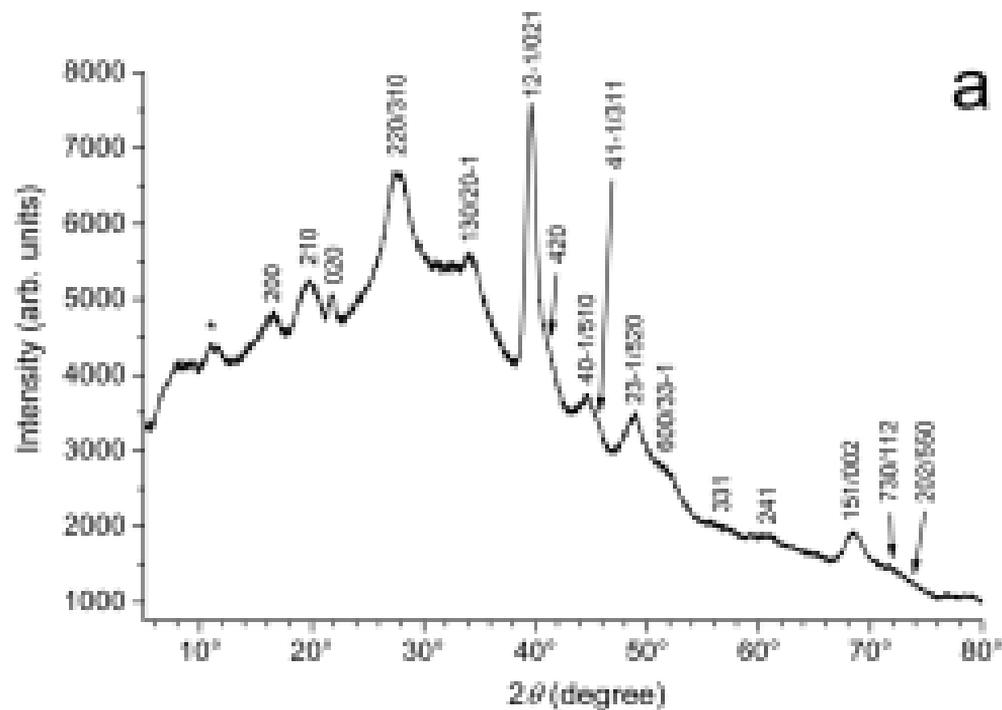
Sites	CS (mms <sup>-1</sup> )	$\Delta$ (mms <sup>-1</sup> )	Relative abundance (%)
RT			
Fe1	1.16	2.58	47( $\pm 5$ )
Fe2	1.13	1.99	42( $\pm 4$ )
Doublet Fe(III)	0.32	0.87	11( $\pm 1$ )
77 K			
Fe1	1.25	2.58	45( $\pm 4$ )
Fe2	1.25	2.06	42( $\pm 4$ )
Doublet Fe(III)	0.73	0.74	13( $\pm 1$ )

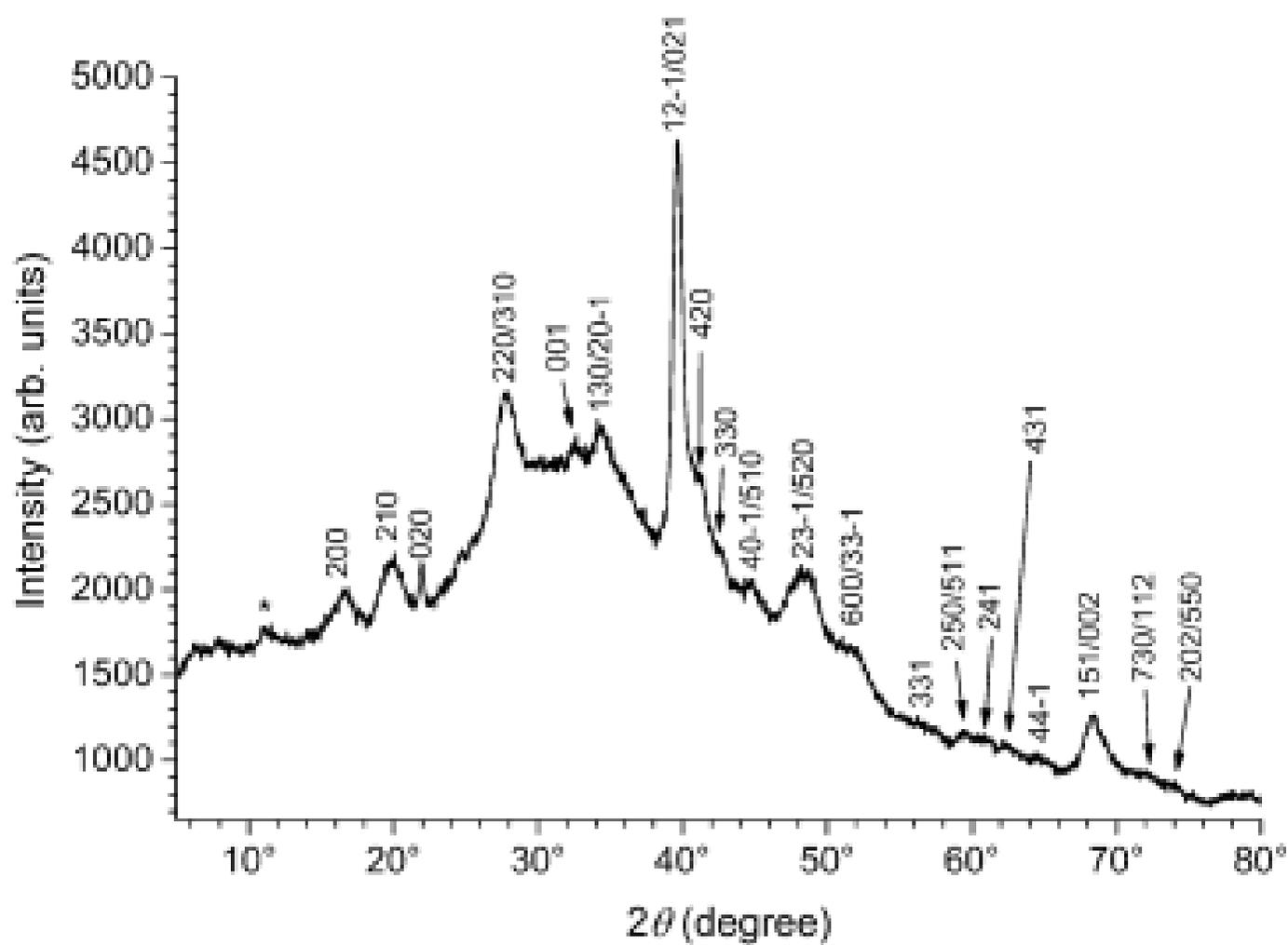
6  
7  
8  
9  
10  
11

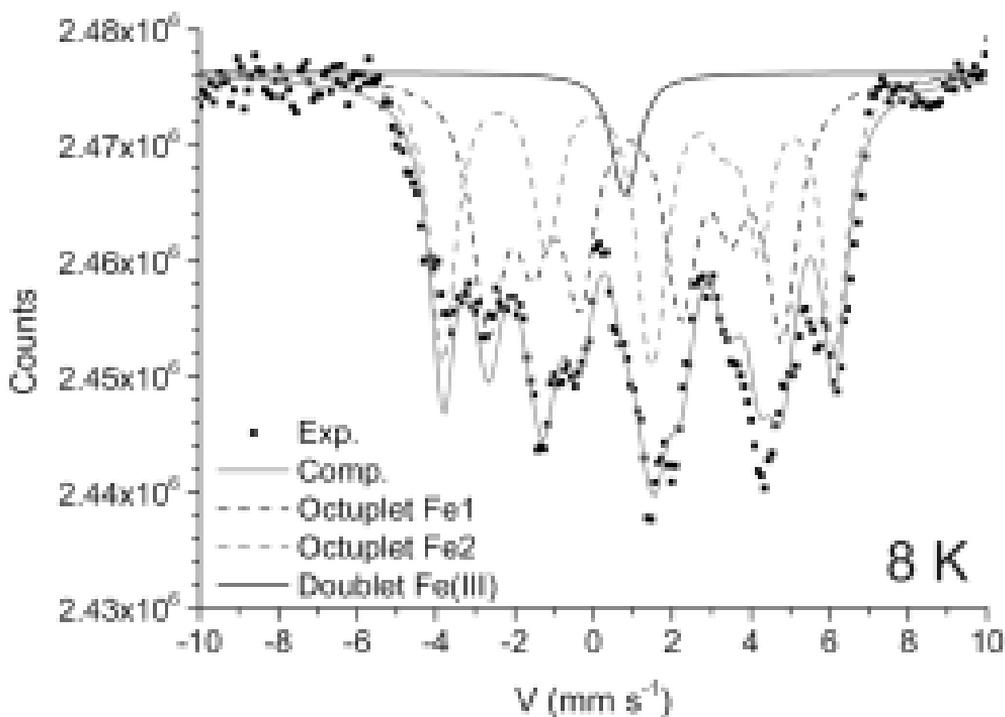
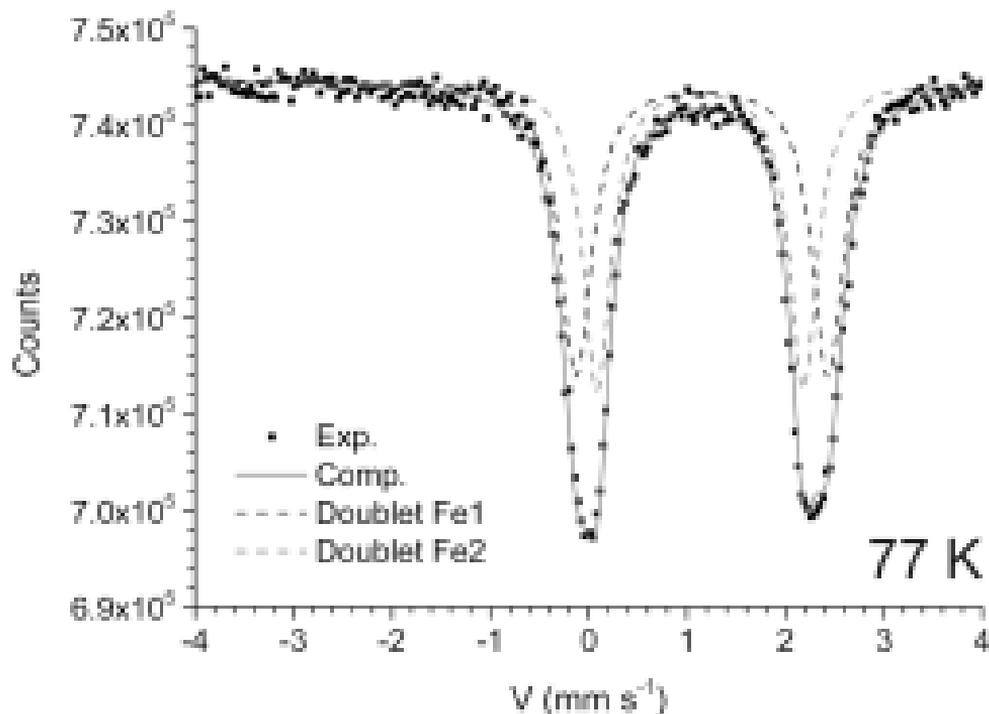
Table 4. Lattice parameters of chukanovite and phase composition (wt.%) of oxidized samples of chukanovite CF0 after 9-10 months of ageing. Ck = chukanovite, M = magnetite and G = goethite. The error was estimated via the analysis of two XRD patterns of each sample. The values given for  $\chi^2$  and  $R_{wp}$  are those of the best fit.

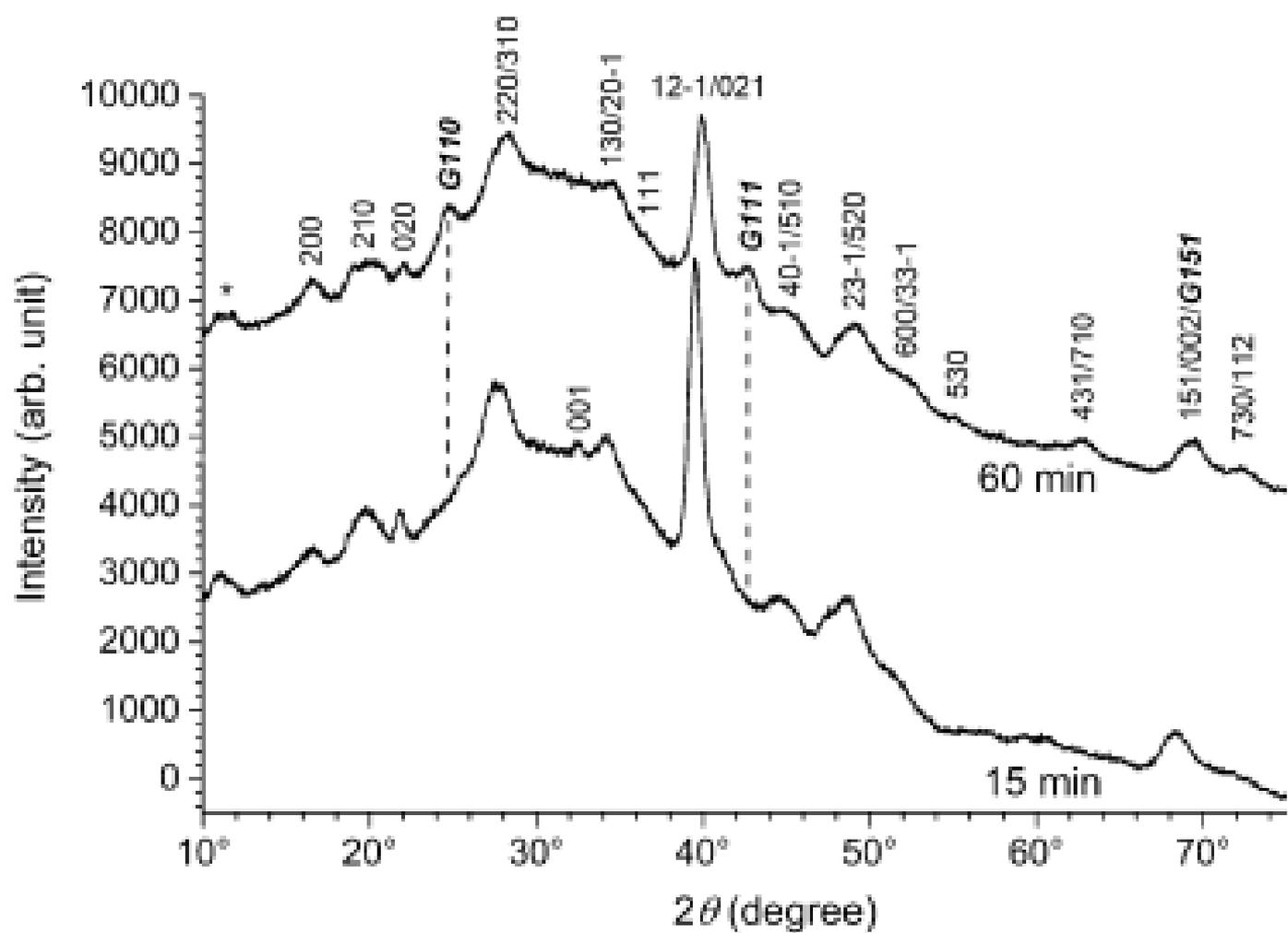
Ox. time	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\beta$ (degree)	%Ck	%M	%G	$\chi^2$	$R_{wp}$ (%)
15'	12.28 $\pm$ 0.01	9.34 $\pm$ 0.01	3.197 $\pm$ 0.003	98.1 $\pm$ 0.4	98 $\pm$ 1	2 $\pm$ 1	0	1.3	1.8
30'	12.30 $\pm$ 0.03	9.33 $\pm$ 0.03	3.196 $\pm$ 0.001	97.87 $\pm$ 0.01	95 $\pm$ 1	5 $\pm$ 1	0	1.1	3.5
60'	12.35 $\pm$ 0.02	9.30 $\pm$ 0.02	3.196 $\pm$ 0.02	97.88 $\pm$ 0.05	79 $\pm$ 4	12 $\pm$ 2	9 $\pm$ 2	1.6	2.6

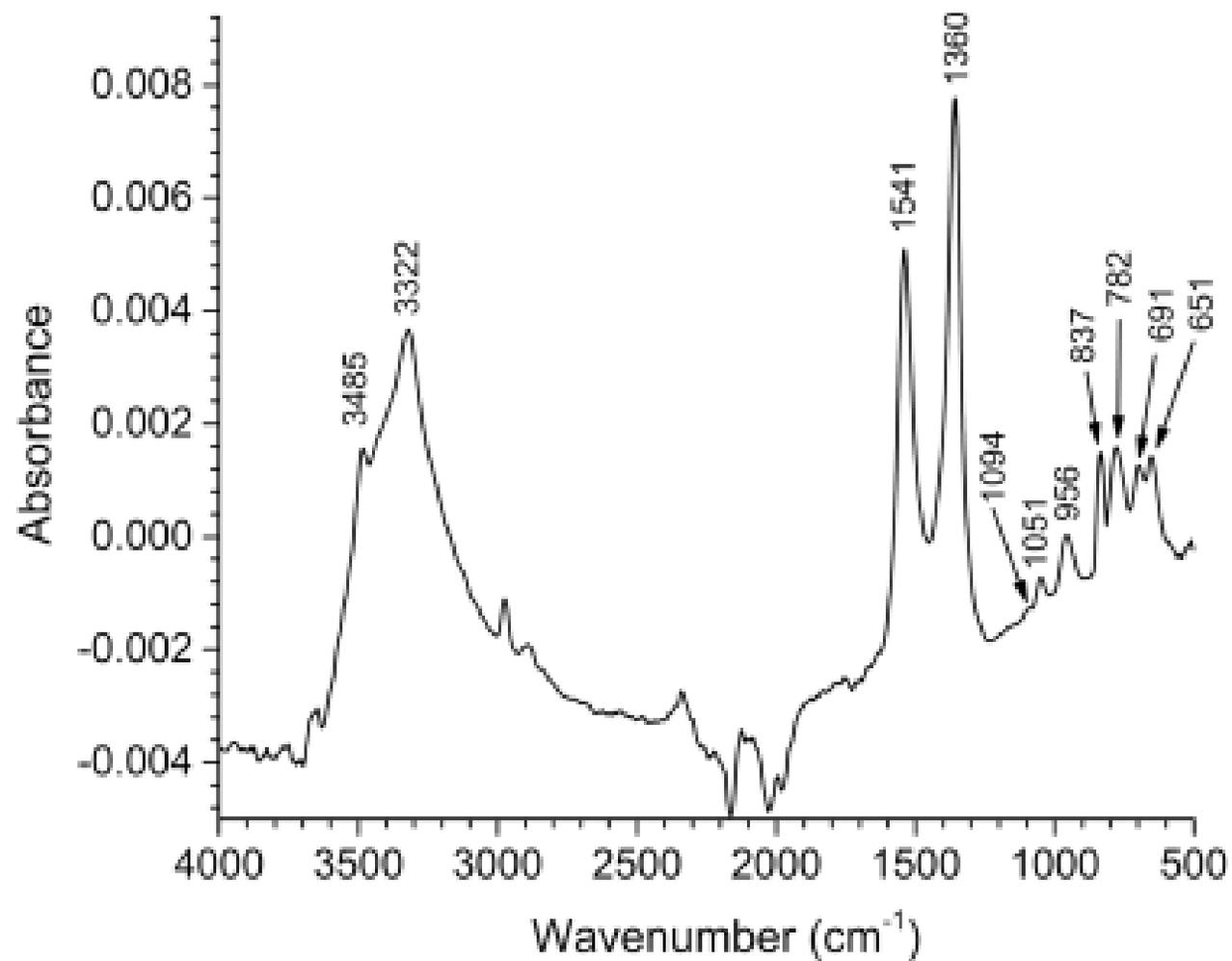
12

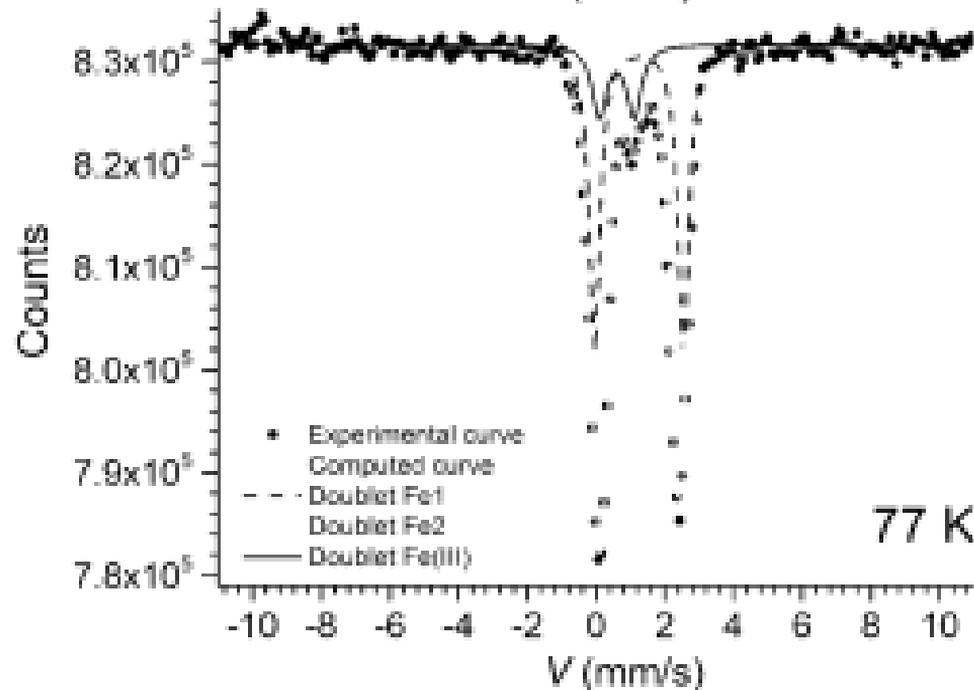
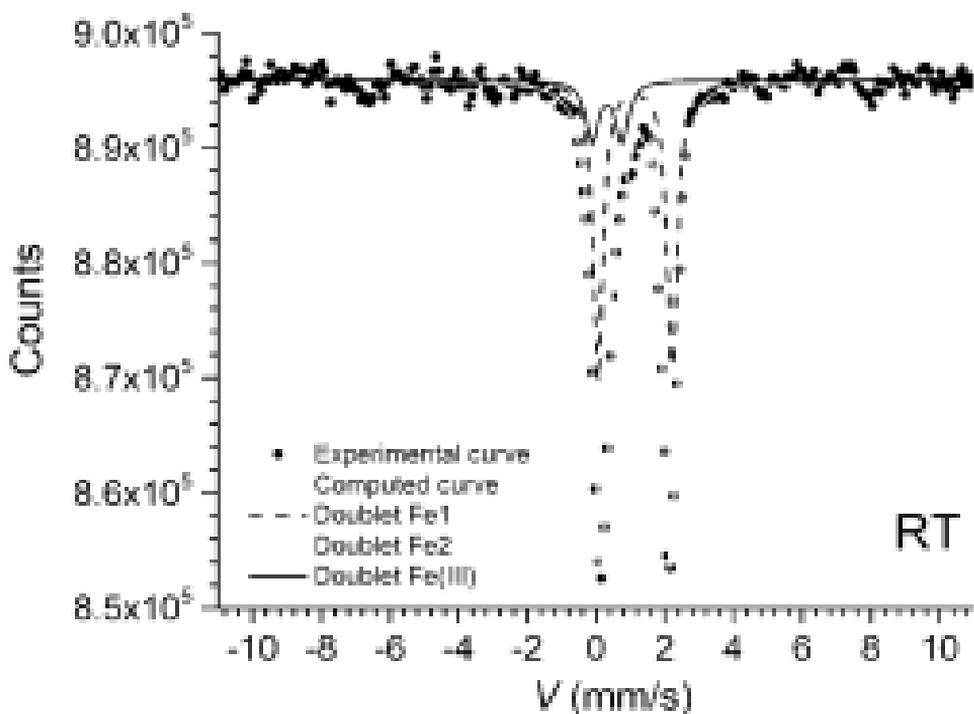


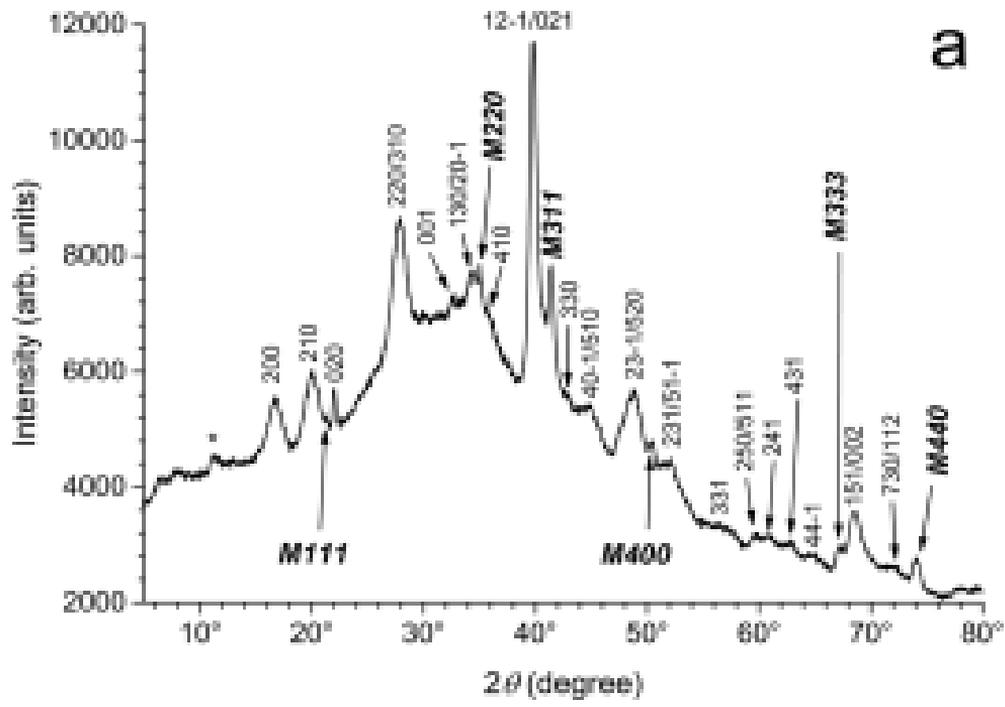
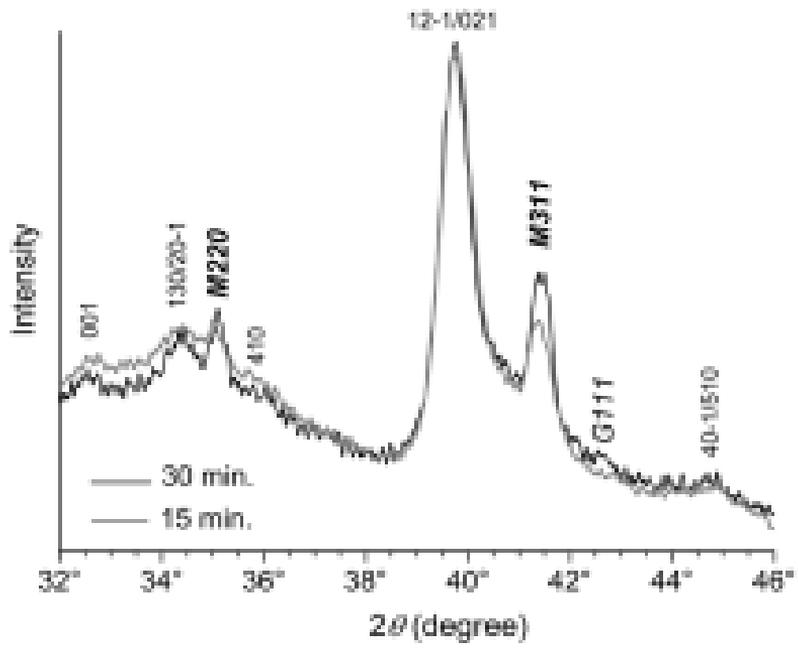


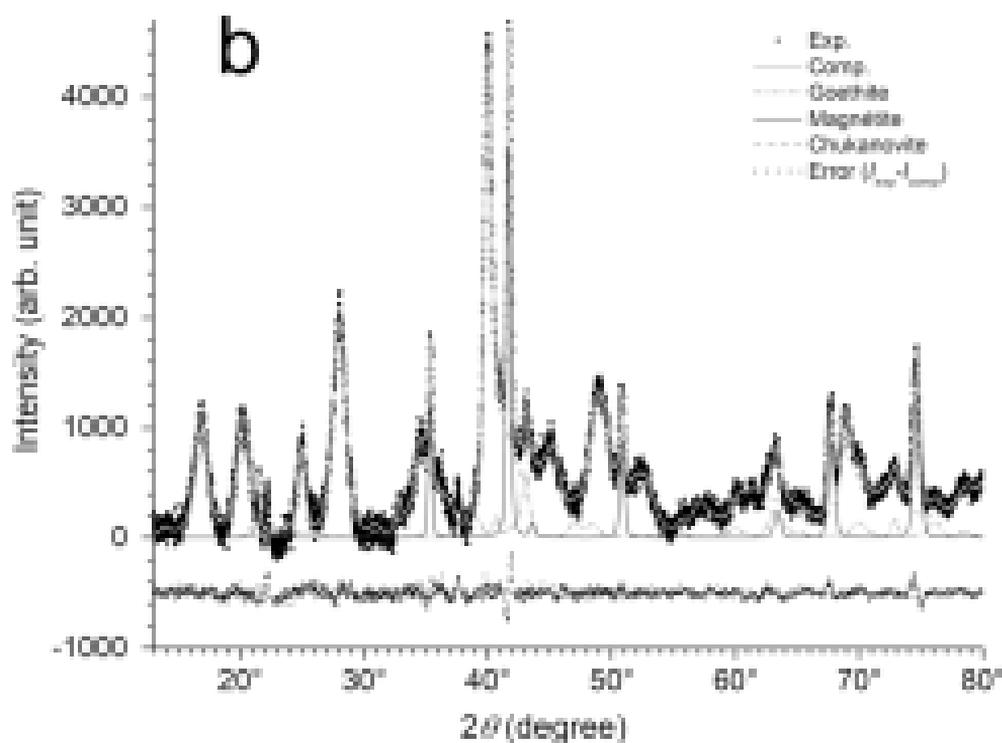
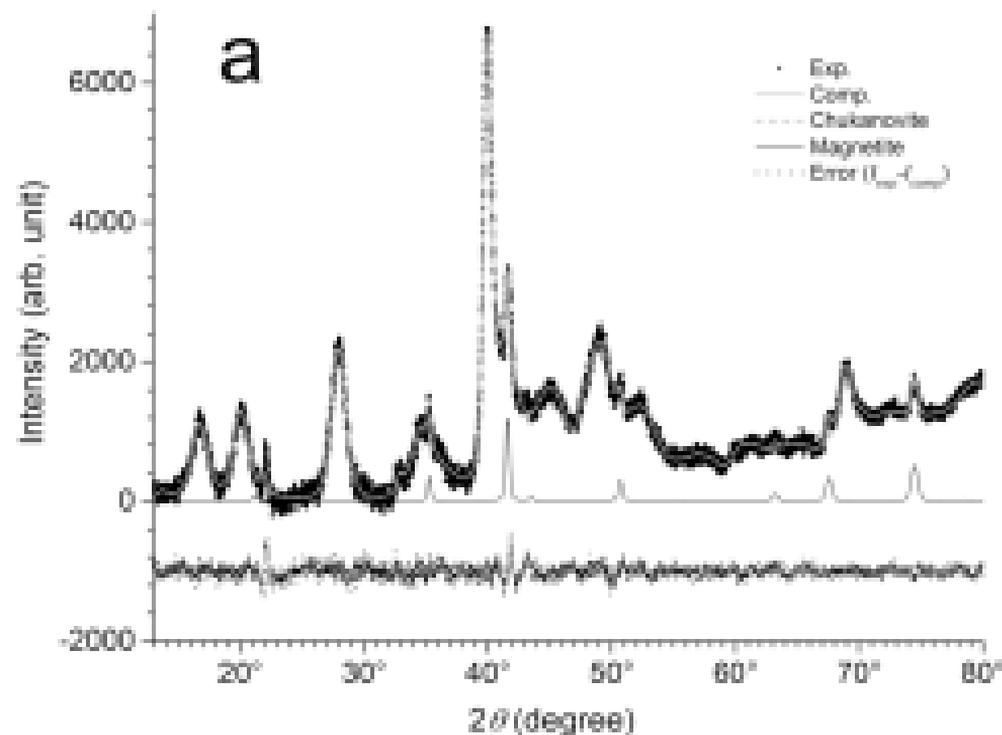


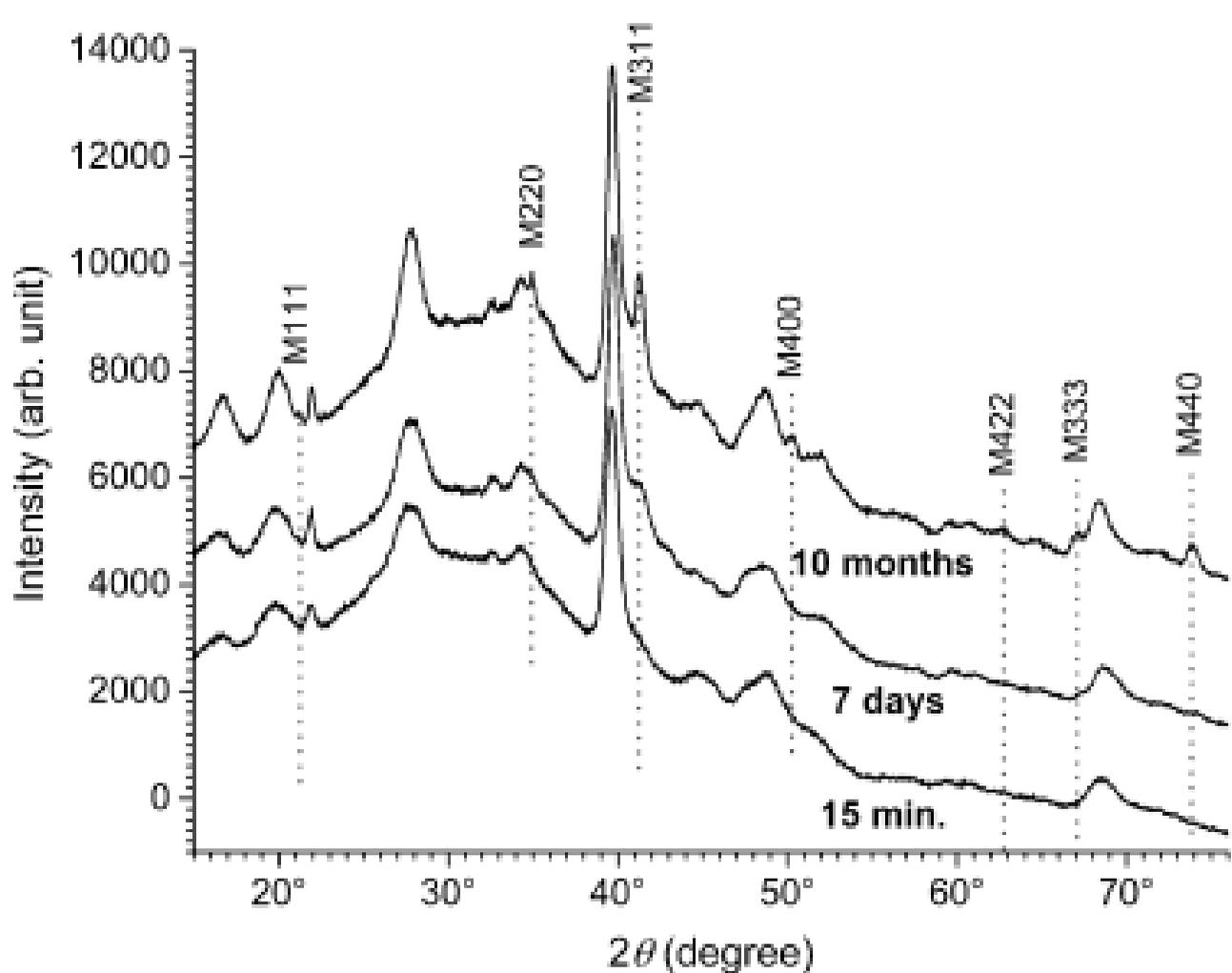


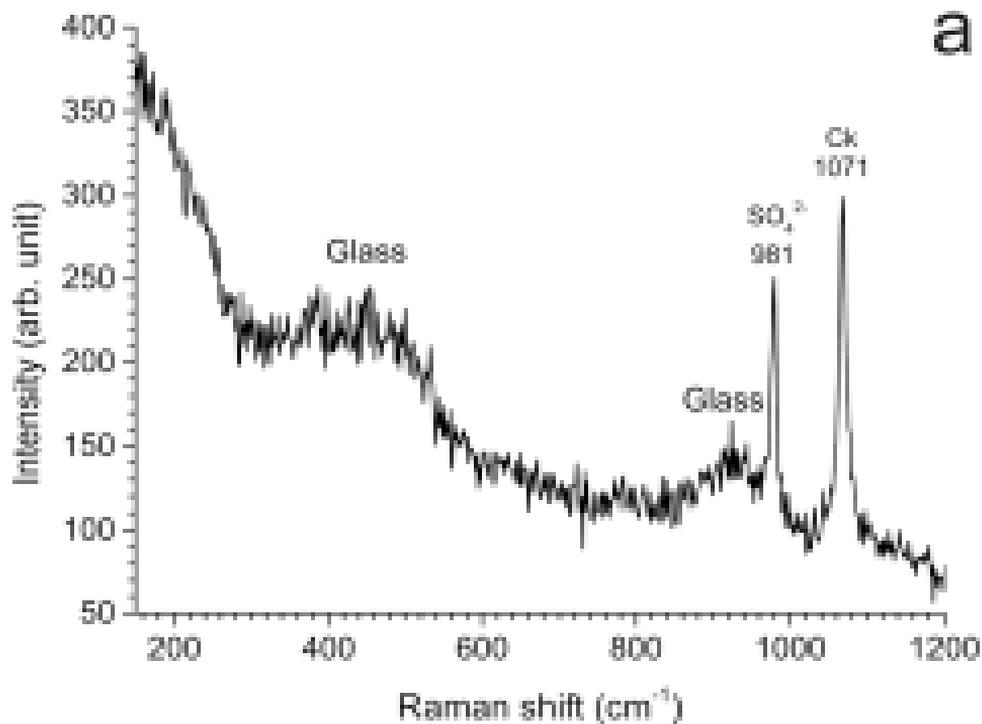
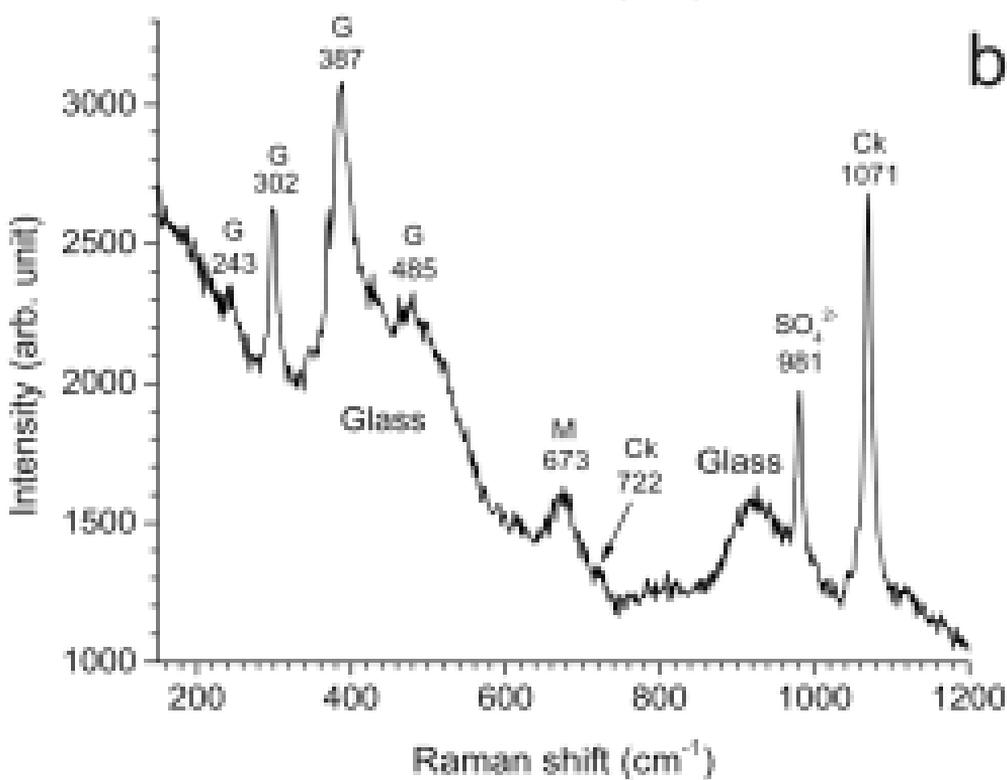


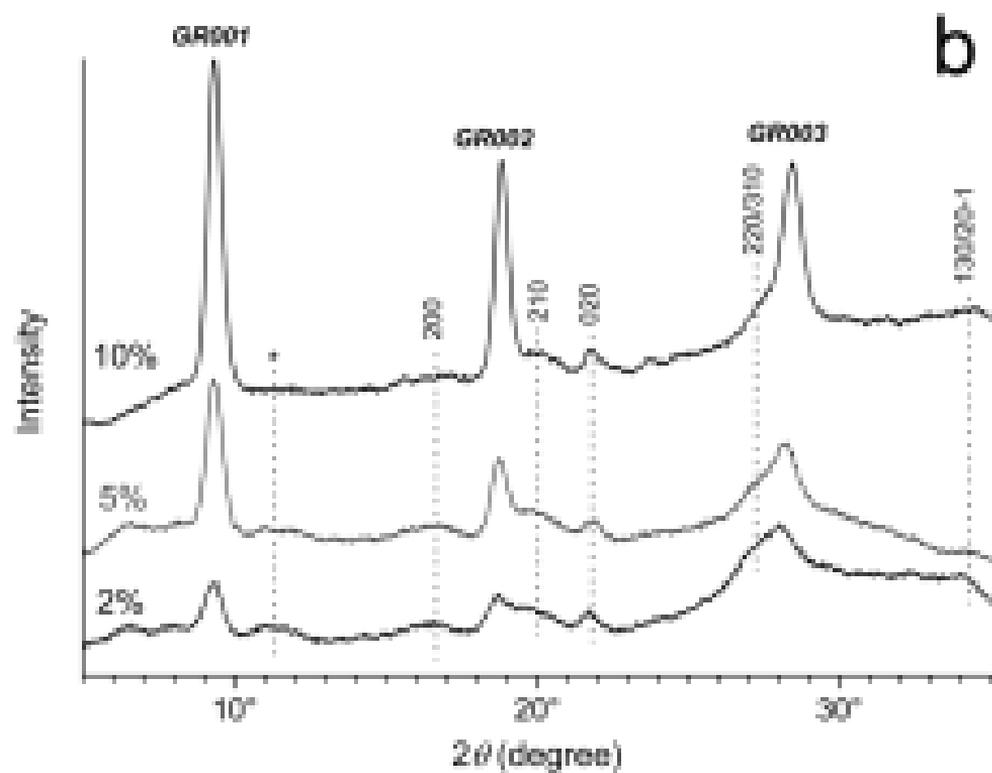
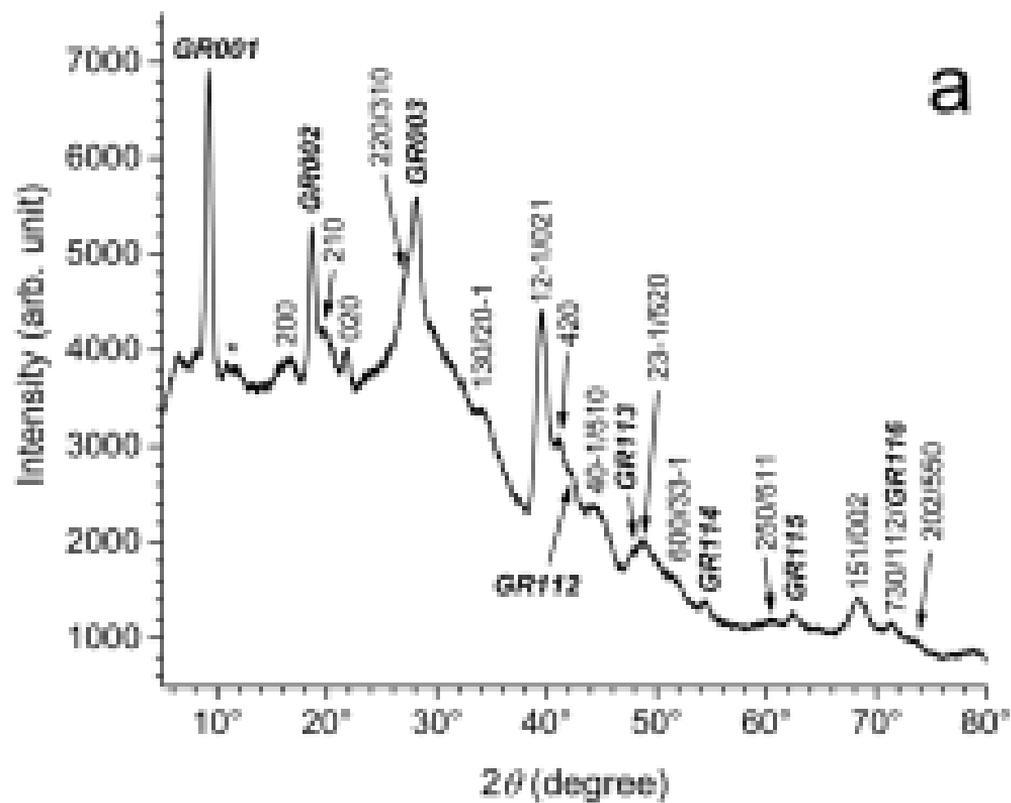


**a****b**

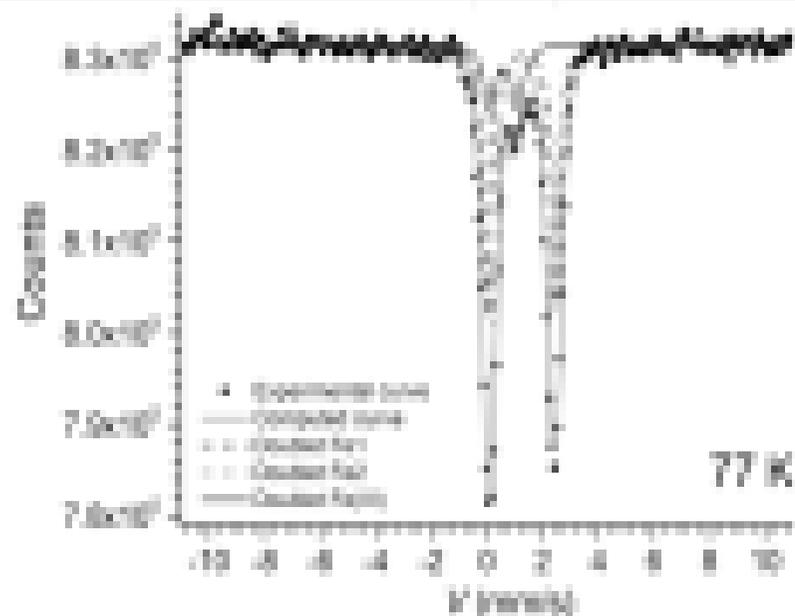
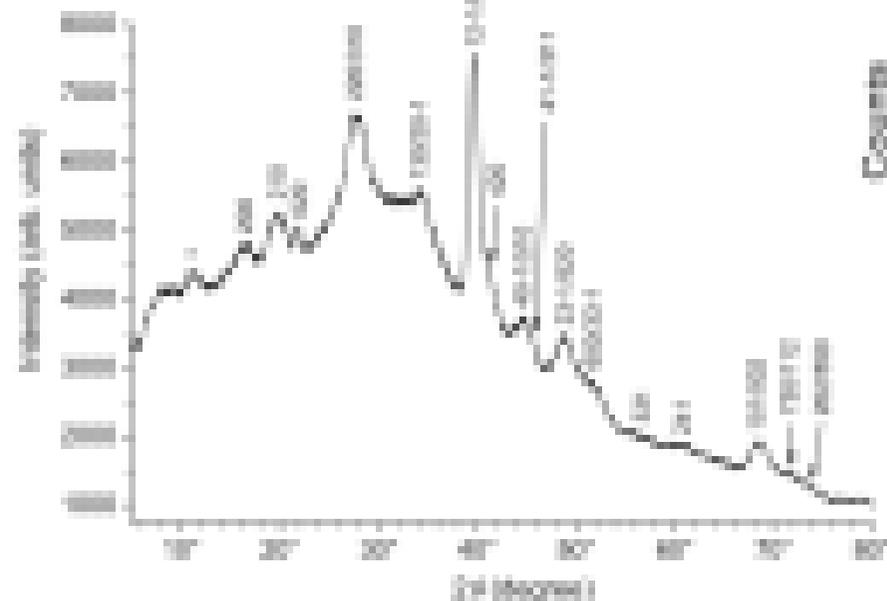




**a****b**

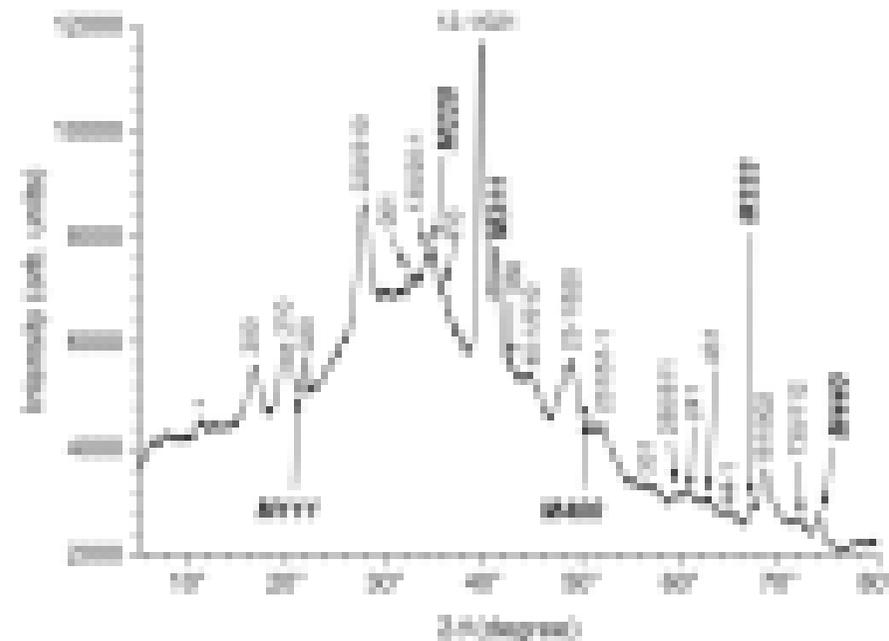


XRD



TMS

XRD



Ageing 10 months



Fe(II)-chukanovite + magnetite

in anoxic conditions