The crystal structure and Gibbs free energy of formation of chukanovite as an oxidation product of carbon steel in human liver

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ABSTRACT

Chukanovite has been identified as an oxidation product of carbon steel in a human liver through powder X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Steel oxidation products include siderite, chukanovite, vivianite, magnetite, goethite, 2-line ferrihydrite. Hydroxylapatite and amorphous silica surrounding the oxidized steel are precipitated from body fluid. The Rietveld refinement of the chukanovite structure shows it is as expected monoclinic, space group of $P2_1/a$, with $a = 12.402(2)$, $b = 9.414(1)$, $c = 3.216(1)$ Å, $\beta = 97.73(3)°$. The standard Gibbs free energy of formation of chukanovite is estimated at $-1167.2 \pm 1.2 \, kJ \, mol^{-1}$ from the equilibrium between siderite and chukanovite. By using linear free energy relationship, the Gibbs free energy of formation for other isostructural phases of pokrovskite, parádsasvárite, and nullaginite are predicted. The results of this study could improve the mineralogical and geochemical properties of chukanovite which is an oxidation product of carbon steel relevant also in radioactive waste containers and oil/gas pipes. Furthermore, the combined method of experimental measurements and geochemical modeling could be a useful tool to study the formation of inorganic solid precipitates and bio-materials in biofluids, and is especially important in medical mineralogy field.

1. Introduction

Chukanovite was described as a new mineral by Pekov et al. (2007), occurring as a terrestrial alteration product of the Dronino iron meteorite. Chukanovite is an iron hydroxide-carbonate mineral "$Fe_2(CO_3)(OH)_2$" which is isostructural with the malachite-rosasite group, with general formula $Me_2^{2+}(CO_3)(OH)_2$. Several studies reported chukanovite as a metastable corrosion product of carbon steels (Peev et al., 2001; Lee and Wilkin, 2010; Azoulay et al., 2014; Pandarinathan et al., 2014). Recently, the formation of chukanovite has been recognized as an important oxidation product of long-term corrosion in oil/gas pipeline steels (Ko et al., 2014) and nuclear waste disposal (Hill et al., 2015). Chukanovite was also observed in corrosion layers of iron archaeological artifacts (Saheb et al., 2008; Remazeilles et al., 2009) and zerovalent iron permeable reactive barriers (Lee and Wilkin, 2010). Biogenic chukanovite was reported as a microbial reduction product of Fe^{2+}-excess magnetite (Kukkadapu et al., 2005).

There are not many structural reports and thermodynamic data for chukanovite, because it is generally precipitated as a microcrystalline phase mixed together with other iron minerals (e.g. siderite and goethite) (Nishimura and Dong, 2009; Azoulay et al., 2014; Ko et al., 2014; Pandarinathan et al., 2014). The crystal structure of chukanovite was

firstly determined through X-ray synchrotron diffraction data by Pekov et al. (2007), and subsequently refined through electron diffraction data by Pignatelli et al. (2014). The standard Gibbs free energy of formation of chukanovite was also reported in several studies (Nishimura and Dong, 2009; Lee and Wilkin, 2010; Azoulay et al., 2012; Kim et al., 2017). However, their equilibrium condition and the Gibbs free energy differ from each other due to their different experimental conditions or experimental errors. In this study, we provide a crystal structure refinement and Gibbs free energy of formation of chukanovite formed in an oxidized steel that interacted with body fluid in human liver. In addition, we predict the standard Gibbs free energy of formation of chukanovite and other isostructural minerals (malachite-rosasite group) using the Sverjensky-Molling equation (Sverjensky and Molling, 1992). The new results will help us to better understand the mineralogical and geochemical characteristics of chukanovite and associated minerals.

2. Sample and methods

2.1. Oxidized carbon steel in human liver

The sample is a surgery product from a middle-aged man's liver. The steel was discovered as an unusual magnetic material in the patient's

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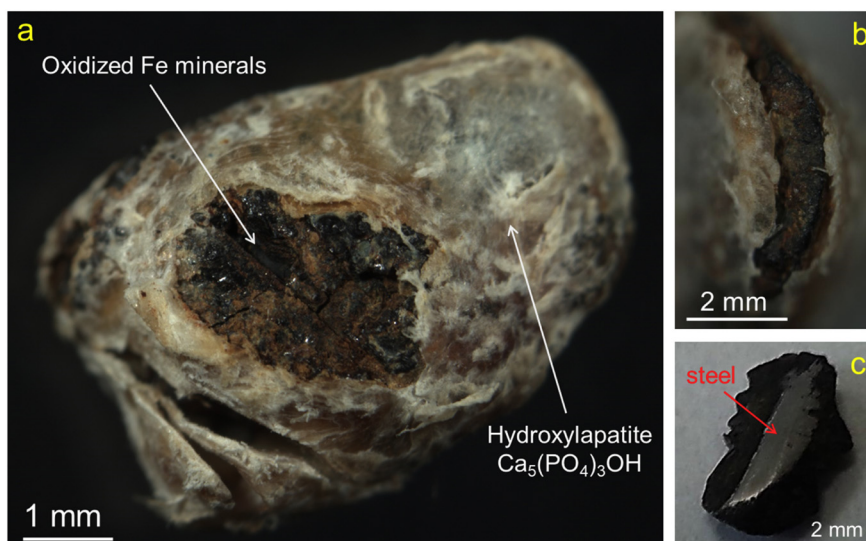*E-mail address:* hfxu@geology.wisc.edu (H. Xu).

Fig. 1. Optical images of the oxidized steel sample. The metallic steel is coated with dark brown iron minerals and white fiber-like hydroxylapatite. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

liver during a pre-NMR magnetic check. The steel sample about $6.1 \times 3.8 \times 1.8$ mm (Fig. 1) was oxidized in the liver over the years. The metallic steel is coated with dark brown oxidized iron minerals and fiber-like hydroxylapatite (outermost) (Fig. 1). The carbon steel had derived from outside of the body, however, we don't know exactly where the sample originated from. It could be a broken part of drill bit due to its strength and hardness.

2.2. X-ray powder diffraction (XRD)

We scratched and separated the particles from the core to the outermost zones and then divided into the magnetic and nonmagnetic zones. We acquired the XRD results of powdered samples placed inside polyimide tube (1 mm diameter). XRD patterns were recorded on a 2-D image-plate detector using a Rigaku Rapid II instrument (Mo-$K\alpha$ radiation) in the Geoscience Department at the University of Wisconsin-Madison. Two-dimensional diffraction patterns were converted to conventional 2θ vs. intensity patterns using Rigaku's 2DP software. Synthetic silicon powder was used as the standard for calibration of diffraction line positions. Data were collected between 5 and 40° 2θ range in a spin mode with exposure time of 15 min per pattern.

For Rietveld refinement, the pure chukanovite was separated from the nonmagnetic middle zone. The Rietveld refinement analysis was performed with TOPAS 5 software (Bruker, MA, USA) to determine the detailed crystal structure of chukanovite and quantitative analysis of oxidized iron minerals in the sample. We used previous chukanovite model (Pekov et al., 2007) as the initial structure with $Fe_2(CO_3)(OH)_2$ chemical formula based on TEM-EDS analysis (Supplementary Fig. S1). The space group of $P2_1/a$ setting of chukanovite in the Rietveld refinement is in good agreement with isostructural malachite-rosasite group minerals. A pseudo-Voigt function was used for fitting the peak profiles.

2.3. Scanning electron microscope (SEM)

Samples for SEM analysis were put on glass slides, coated with carbon (~100 Å). To prevent the oxidation reaction, air exposure was minimized during the sample preparation. All SEM images were obtained using a Hitachi S3400N variable pressure microscope with an X-ray energy-dispersive spectroscopy (EDS) attachment. High-resolution Ge detector and imaging was used in backscattered electron image mode to study morphology and chemical variations.

2.4. Transmission electron microscopy (TEM)

TEM samples were prepared by dropping suspensions of crushed samples onto lacy-carbon-coated 200-mesh Cu grids. TEM imaging and selected-area electron diffraction (SAED) analysis were carried out using a Philips CM200-UT microscope operated at 200 kV in the Materials Science Center at the University of Wisconsin-Madison. The chemical composition was obtained using TEM-EDS system equipped with a Li-drifted Si detector (Oxford instruments Link ISIS). An electron beam diameter of ~50 nm was used for collecting X-ray EDS spectra.

2.5. pH-Eh diagram

Geochemist's Workbench 11 (Rockware Inc., Golden, CO, USA) software package was used to construct Eh-pH diagrams. Body fluid compositions ($Na^+ = 142$ mM, $K^+ = 5$ mM, $Mg^{2+} = 1.5$ mM, $Ca^{2+} = 2.5$ mM, $Cl^- = 148.8$ mM, $HCO_3^- = 27$ mM, $HPO_4^{2-} = 1$ mM, and $SO_4^{2-} = 0.5$ mM) were used for modeling equilibrium reactions at 37 °C (Bigi et al., 2005; Waugh and Grant, 2010). The potential surface water condition (Fe = 10^{-4} M, $HCO_3^- = 10^{-2}$ M, $HPO_4^{2-} = 10^{-6}$ M) were used for modeling equilibrium reactions at 25 °C (Lee and Wilkin, 2010). The total dissolved iron (ΣFe) is estimated to be 10^{-4} M based on mineral assemblage from XRD analysis. All calculations were conducted with the thermos database that includes new chukanovite data from this study.

3. Results

3.1. XRD

Four distinct zones can be recognized in the studied sample, namely a core zone, two magnetic middle zones, two nonmagnetic middle zones and two outmost zones. X-ray diffraction results from the selected zones suggest that the oxidized sample is composed of solid iron, siderite, chukanovite, vivianite, magnetite, goethite, and hydroxyapatite (Fig. 2). The XRD pattern of core zone shows that the initial material is zero-valent metallic iron (Figs. 1c and 2). The chukanovite coexists with the siderite and goethite phase in the sample (Fig. 2). The magnetic phase of the middle zone is magnetite (Fig. 2). The outermost zones consist of poorly crystallized goethite and hydroxylapatite (Fig. 2). The goethite is the final oxidation product of carbon steel (Fig. 2). The concentration of goethite increased from the core to the