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Short Communication

The role of rainwater-borne hydrogen peroxide in the release of arsenic from arsenopyrite

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HIGHLIGHTS

- Arsenopyrite weathering was markedly complicated by H_2O_2 in the synthetic rainwater solutions.
- Arsenic release was enhanced by H_2O_2 at the concentration range set in the experiment.
- H_2O_2 played an indirect role in the transformation of arsenite into arsenate in the solution.
- Fate of liberated arsenic species may be affected due to the formation of $FeAsO_4$ precipitates.
- This sheds some light on a previously overlooked natural process worthy of further investigation.

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ABSTRACT

A microcosm experiment was conducted to examine the effects of hydrogen peroxide (at a concentration range of 5–50 μM) on the release of arsenic from the dissolution of arsenopyrite, a dominant arsenic-bearing mineral occurring in natural environments. This was to simulate the reaction between rainwater-borne hydrogen peroxide and arsenopyrite grains exposed on the land surfaces during rainfall events. The results showed that the release of arsenic from arsenopyrite was enhanced by the H_2O_2 at this concentration range. It was also evident that H_2O_2 played an indirect role in the transformation of arsenite into arsenate in the solutions, which might affect the fate of the liberated arsenic species due to the formation of $FeAsO_4$ precipitates. The preliminary study sheds some light on the possible role of rainwater-borne H_2O_2 in the weathering of arsenopyrite, which could complicate the geochemical processes governing the release, transport and fate of arsenopyrite-derived arsenic in natural environments. This provides a rationale for conducting additional laboratory-based investigations to obtain further insights into the chemical mechanisms and kinetics, and the subsequent field-scale study to validate the research findings.

1. Introduction

Arsenopyrite (FeAsS) is an important source of aqueous arsenic (As) species (Smedley and Kinniburgh, 2002) that pose a significant threat to aquatic ecosystems and human health (WHO, 2001). Release of As from oxidation of arsenopyrite has been investigated using molecular oxygen as an oxidant at circumneutral pH (Yu et al., 2007) and ferric ion (Fe^{3+}) as a major oxidant under acidic conditions (Yu et al., 2004, 2007). These previous researches have allowed an accumulation of knowledge regarding the mobilization of As from the dominant As-bearing rocks.

Hydrogen peroxide (H_2O_2) is a common constitute of rainwater (up to 200 μM) (Willey et al., 1996). It has much stronger oxidizing capacity, as compared to molecular oxygen. In particular, an even more powerful oxidant (i.e. hydroxyl radical) may be generated through Fenton reaction (Barbusinski, 2009) since aqueous ferrous ion (Fe^{2+}) is readily available during oxidation of arsenopyrite. This represents a potential natural process that may significantly affect the course of arsenopyrite oxidation in field conditions but has so far been overlooked.

We have conducted microcosm experiment to examine the oxidation of arsenopyrite in the presence of H_2O_2 at a concentration range of 5–50 μM, which can be frequently encountered in storm scenarios (Zuo and Deng, 1999; Yuan and Shiller, 2000; Gonçalves et al., 2010). Our experiment was limited to a single exposure event (e.g. from addition of H_2O_2 to nearly complete consumption

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of H_2O_2 for the highest-dose treatment) to allow a better comparison between the different treatments.

2. Materials and methods

The arsenopyrite specimen was obtained from a commercial source. The sample was crushed and ground to pass a 0.149 mm sieve and stored in an airtight plastic bag prior to being used in the experiment. The surface area of the powdered arsenopyrite was 1.1498 $m^2\,g^{-1}$ (determined by the BET method).

All chemical reagents used in the experiments were of analytical reagent grade. Ultrapure water (18.2 $M\Omega\,cm^{-1}$) was used throughout the entire course of all the experiments.

Three treatments (T5, T20 and T50) were set for the experiment with the concentration of H_2O_2 ranging from 5 to 50 μM. The aqueous system without added H_2O_2 served as the control (C). 500-mL glass beakers were used as batch reactors. For each reactor, 0.2 g of the arsenopyrite powders was added into the beaker, followed by adding 200 mL of a relevant reacting solution. The experiment was performed in triplicate in a room with the temperature being controlled at 25 ± 1 °C. Repeatability analysis of the analytical data gives a mean relative standard deviation (RSD) of 4.4% for pH, 0.42% for DO, 11.3% for total As, 3.8% for total Fe, 19.6% for As^{3+} and 15.3% for As^{5+}.

Immediately after addition of all the ingredients, the contents in each reactor were manually stirred with a glass rod for 5 s. In-situ measurements of pH and dissolved oxygen (DO) were made at the following times after the commencement of the experiment: 5, 60, 120, 180, 240, and 300 min. A solution sample (20 mL) was also taken from each reactor (after measuring pH and DO) for determinations of H_2O_2, total As, As^{3+}, As^{5+}, total Fe, Fe^{2+} and total S, and then 20 mL of ultrapure water were added to the reactor to compensate the solution loss due to sample taking.

Solution pH and DO were measured by a HACH HQ30d FLEXI Portable Meter; H_2O_2 was determined using a titanium sulfate colorimetric method (Liu et al., 2010); Total As, Fe and S were determined by ICP-MS (7500cx, Agilent, USA); arsenic species (As^{3+} and As^{5+}) in the solution were separated by high-performance liquid chromatography (HPLC) (Agilent technologies 1200 Series) with an anion-exchange column (G3154-65001, Agilent) protected by an Agilent guard column (G3154-65002), and then quantified by ICP-MS (Agilent Technologies 7500cx); Ferrous iron (Fe^{2+}) was determined following the method of Tamura et al. (1974).

3. Results and discussion

3.1. Temporal changes in H_2O_2 and DO in the solutions

After mixing the arsenopyrite powders with the H_2O_2 solutions, H_2O_2 underwent degradation. Approximately 71%, 27% and 40% of the H_2O_2 decomposed after just 60 min in T5, T20 and T50, respectively. At 180 min, H_2O_2 was not detectable for both T5 and T20 while over 50% of the H_2O_2 in T50 was lost. The concentration of H_2O_2 in T50 continued to decrease and dropped to below 5 $mg\,L^{-1}$ (<10% of the added H_2O_2) at the 300 min (Fig. 1a). This suggests that under the set experimental conditions, extended time was required for the completion of reaction between H_2O_2 and the arsenopyrite grains at the highest dose (50 μM).

In contrast, there was no significant difference in the dissolved oxygen (DO) among the control and all the three treatments; DO concentrations showed little temporal variation with values around 8.3 $mg\,L^{-1}$ during the entire period of the experiment (Fig. 1b).

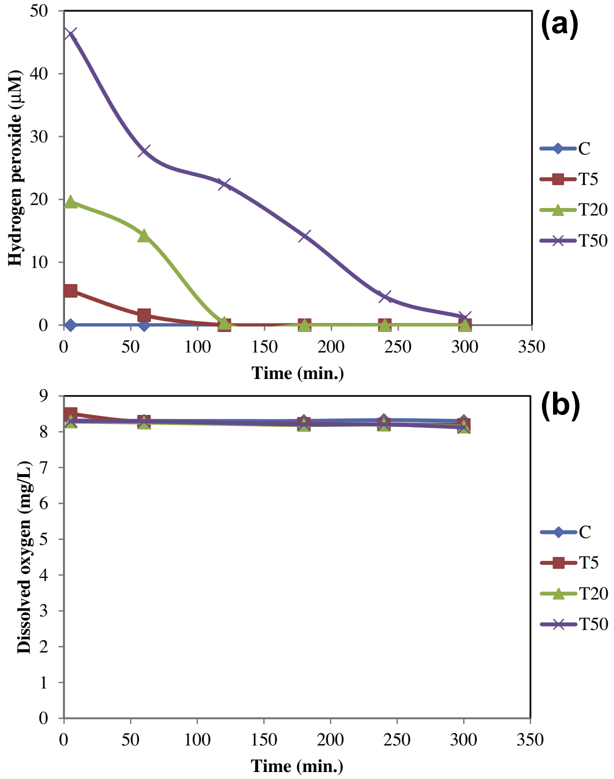

Fig. 1. Temporal variation in (a) hydrogen peroxide (H_2O_2) and (b) dissolved oxygen (DO) in the solution during the period of experiment.

Hydrogen peroxide can undergo spontaneous decomposition to generate dissolved oxygen according to the following chemical equation:

$$2H_2O_2 \rightarrow O_2 + 2H_2O \qquad (1)$$

The insignificant difference in DO between the control and the treatments appears to suggest that spontaneous decomposition of H_2O_2, if any, was negligible. This implies that the added H_2O_2 was predominantly consumed by reacting with the mineral surfaces of arsenopyrite.

3.2. Arsenic dynamics during the course of the experiment

There was a clear trend that total As in the solution increased over time for the control and all the three treatments. At any given time, total As was in the following decreasing order T20 > T5 > C. Total As was higher in T20 than in T50 for the earlier part of the experiment and the opposite was observed for the later part of the experiment (Fig. 2). In the control where molecular oxygen was the only oxidant, release of As from the mineral surfaces can be described by the following chemical equation (Eq. (2)):

$$FeAsS + 11/4O_2 + 3/2H_2O \rightarrow 2Fe^{2+} + 2H_3AsO_3 + 2SO_4^{2-} \qquad (2)$$

The As^{3+} in the form of arsenous acid (H_3AsO_3) can be further oxidized by molecular oxygen to produce As^{5+}, as shown below (Eq. (3)):

$$H_3AsO_3 + 1/2O_2 \rightarrow H_2AsO_4^- + H^+ \qquad (3)$$

However, Eq. (3) is kinetically slow. The predominant presence of As^{3+} in the control of this experiment (Fig. 3a) was consistent with what was reported in the reaction systems with molecular oxygen as the main driving oxidant. The addition of H_2O_2 facilitated the oxidation of As^{3+}, as can be seen in Fig. 3b–d. In spite of the higher total As in T20 and T50 than in C and T5, the