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Title: Simultaneous oxidation of arsenic and antimony at low and circumneutral pH, with and without microbial catalysis

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Abstract: Arsenic and antimony are common mine-water pollutants and their toxicity and fate are strongly influenced by redox processes. In this study, simultaneous Fe(II), As(III), and Sb(III) oxidation experiments were conducted to obtain rates under laboratory conditions similar to those found in the field for mine waters of both low and circumneutral pH. Additional experiments were performed under abiotic sterile conditions to determine the biotic and abiotic contributions to the oxidation processes. Our results showed that under abiotic conditions in aerated Fe(III)-sulfuric acid solutions, Sb(III) oxidizes slightly faster than As(III). The oxidation rates of both elements were accelerated by increasing As(III), Sb(III), Fe(III), and chloride concentrations in the presence of light. For unfiltered circumneutral water from the Giant Mine (Yellowknife, NWT, Canada), As(III) oxidized at 15-78 μmol/L/h whereas Sb(III) oxidized at 0.03-0.05 μmol/L/h during microbial exponential growth. In contrast, As(III) and Sb(III) oxidation rates of 0.01-0.03 and 0.01-0.02 μmol/L/h, respectively, were obtained in experiments performed with acid unfiltered mine waters from the Iberian Pyritic Belt (SW Spain). These results suggest that the Fe(III) formed from microbial oxidation abiotically oxidized As(III) and Sb(III). After sterile filtration of both mine water samples, neither As(III), Sb(III), nor Fe(II) oxidation was observed. Hence, under the experimental conditions, bacteria were catalyzing arsenic and antimony oxidation in the Giant Mine waters and iron oxidation in the acid waters of the Iberian Pyrite Belt.

Keywords: arsenic, antimony, iron, oxidation rates, AMD

Merced, 08/30/11

Professor Ron Fuge

Executive Editor Applied Geochemistry

Please find enclosed the requested revised version of our manuscript APGEO-D-11-00045R2 ”Simultaneous oxidation of arsenic and antimony at low and circumneutral pH, with and without microbial catalysis" by Maria P. Asta, D. Kirk Nordstrom, and R. Blaine McCleskey and a cover letter explaining in detail how the comments and changes suggested by the reviewer have been taken into account in the new version of the paper.

The main modifications proposed by the reviewer (remove figure 2a and 2b and combine figures 3a and 3b) have been carried out in the revised manuscript, as well as the majority of minor comments and criticisms expressed in the revisions.

We expect that this version of the manuscript clarifies the main drawbacks encountered by the reviewer.

Thank you in advance,

Maria P. Asta

Ms. Ref. No.: **APGEO-D-11-00045R1**

Title: **"*Simultaneous oxidation of arsenic and antimony at low and circumneutral pH, with and without microbial catalysis*"** Applied Geochemistry

Reviewers' comments:

Reviewer #1: Asta et al. provide a substantially improved manuscript detailing their work on the bacterially-catalyzed) oxidation of aqueous As and Sb species. That the body of work was valuable has never been in dispute, and the changes made address the issues raised about the presentation.

I do think it would be worthwhile including a table as supplementary information. While it "may not be read by many people", such a table should prove invaluable to anyone wishing to extend or repeat your experiments. It would also mean that Figures 2a and 2b could be removed, but I leave that to the Editor's discretion (I also think Figures 3a and 3b could be combined). Otherwise, apart from some minor points, listed below, I see no reason why this paper should not be accepted for publication in Applied Geochemistry.

Following the reviewer's comment the figures 3a and 3b have been combined and figures 2a and 2b of previous manuscript have been deleted in the paper. However, regarding the fact of including a supplementary table we think that it would be redundant since the main results are shown in the numerous figures of the paper.

Data throughout the document would be easier to understand if SI prefixes were added to the units, ie 18 µmol/L instead of 1.8 x 10-5 mol/L.

Done.

Second line of the abstract, "simultaneous" should come before the list of elements (ie simultaneous Fe…. Oxidation"

Done.

The second research highlight: "catalyze needs a "d" to make catalyzed.

Done.

Page Three, Paragraph Three: The sentences relating to Sb should be moved down to the paragraph relating to Sb on Page Four.

Done.

In addition, the sentence about Sb III and Sb V being adsorbed by Fe- and Mn-precipitates needs some expansion to demonstrate that there are differences between the two states - i.e. which form of Sb is "best" adsorbed?

Although the assessment of the Sb(III) and Sb(V) sorption onto Fe and Mn precipitates is a very interesting issue, this is not the scope of this study for that reason we had already included some references about this issue. See

page 3 of the reviewed manuscript:*"Antimonite and Sb(V) are sorbed onto Fe and Mn precipitates immobilizing dissolved Sb* ***(Belzile et al., 2001; Leuz et al., 2006; Casiot et al., 2007)****."*

Page Nine, First sentence in Section 3.1 is redundant (the table is already described in the methods).

Done.

Page Ten, second paragraph. UV oxidation of SbIII has been demonstrated by Brihaye et al (1983, Analytica Chemica Acta v 148 51-57). Indeed, in a soon to be submitted manuscript, we will also present evidence for the (relatively slow) oxidation of SbIII to SbV in the presence of light. A comment explaining that you think such processes should be relatively minor compared to Fe-mediated photo-oxidation would help here.

Following the reviewer's suggestion we have included a comment about the Fe-mediated photo-oxidation in page 10 of the reviewed manuscript: ***"Therefore, oxidation of those elements in the presence of light is relatively slow compared to Fe- mediated photo-oxidation."***

Page 11 First paragraph: The 54 and 87 rations need (As) and (Sb) or something similar added to clarify which ratio is for which element.

Done.

Page 11 Second Paragraph (Opening paragraph of 3.2.1): Capability, rather than capacity is a more appropriate term.

Done.

Page 11,Second Paragraph "removal of total dissolved…" the "of total" is unnecessary.

Done.

Page 12: Why are two moles of H+ produced per mole of As oxidised? This should be explained, or at least a reference added.

We consider that we do not need to reference a chemical reaction.

Page 16, first paragraph "bacterially mediation" should be "bacterially catalyzed". Indeed, mediated should probably be replaced throughout the document. In the next paragraph, for example, "bacteria accelerate Fe(II) oxidation" would be more accurate.

Done.

Page 17 Opening paragraph "quantification……is essential" [not are essential]

Done.

Page 17 Third paragraph "…As(III) and Sb(III) were…" [were is missing]. In addition, this paragraph could be combined with the one above.

Done.

Research Highlights

- The quantification of the As(III) and Sb(III) oxidation rates and their mechanisms are essential for understanding and predicting As and Sb geochemistry in natural waters.
- At the circumnetural pH of the Giant Mine waters (Yellowknife, NWT, Canada) As(III) and Sb(III) oxidation was catalyzed by microbes whereas in the acid mine waters from the Iberian Pyrite Belt (SW Spain) As(III) and Sb(III) are oxidized abiotically by the Fe(III) formed from microbial oxidation.
- Under abiotic conditions in aerated Fe(III)-sulfuric acid solutions, Sb(III) oxidizes slightly faster than As(III). The oxidation rates of both elements were accelerated by increasing As(III), Sb(III), Fe(III), and chloride concentrations in the presence of light.

Simultaneous oxidation of arsenic and antimony at low and circumneutral pH, with and without microbial catalysis

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Abstract

Arsenic and antimony are common mine-water pollutants and their toxicity and fate are strongly influenced by redox processes. In this study, simultaneous Fe(II), As(III), and Sb(III) oxidation experiments were conducted to obtain rates under laboratory conditions similar to those found in the field for mine waters of both low and circumneutral pH. Additional experiments were performed under abiotic sterile conditions to determine the biotic and abiotic contributions to the oxidation processes. Our results showed that under abiotic conditions in aerated Fe(III)-sulfuric acid solutions, Sb(III) oxidizes slightly faster than As(III). The oxidation rates of both elements were accelerated by increasing As(III), Sb(III), Fe(III), and chloride concentrations in the presence of light. For unfiltered circumneutral water from the Giant Mine (Yellowknife, NWT, Canada), As(III) oxidized at 15-78 µmol/L/h whereas Sb(III) oxidized at 0.03-0.05 µmol/L/h during microbial exponential growth. In contrast, As(III) and Sb(III) oxidation rates of 0.01-0.03 and 0.01-0.02 µmol/L/h, respectively, were obtained in experiments performed with acid unfiltered mine waters from the Iberian Pyritic Belt (SW Spain). These results suggest that the Fe(III) formed from microbial oxidation abiotically oxidized As(III) and Sb(III). After sterile filtration of both mine water samples, neither As(III), Sb(III), nor Fe(II) oxidation was observed. Hence, under the experimental conditions, bacteria were catalyzing arsenic and antimony oxidation in the Giant Mine waters and iron oxidation in the acid waters of the Iberian Pyrite Belt.

Keywords: arsenic, antimony, iron, oxidation rates, AMD

1. Introduction

Mining and smelting activities are a major worldwide source of metal contamination of soils, sediment, and water. Among other elements, arsenic and antimony are common constituents of mine waters and can reach very high concentrations (up to 53 mmol/L, e.g. Adriano, 1986; Ragaini et al., 1977; Ainsworth et al., 1990; Nordstrom and Alpers, 1999; Baroni et al., 2000; Flynn et al., 2003; Clark and Raven, 2004).

Elevated As concentrations arise from oxidative dissolution of arsenopyrite (FeAsS) and As sulfosalts (e.g. tennantite ($Cu_{12}As_4S_{13}$), Cu_3AsS_3) in waste rock and tailings and dissolution of arsenolite (As_2O_3) from smelter emissions, flues, stockpiles, contaminated soils and sediments (Smedley and Kinniburgh, 2002; Sarmiento et al., 2005, 2007). Similarly elevated Sb concentrations result from oxidative dissolution of Sb sulfide minerals (stibnite, Sb_2S_3), and other minerals such as famatinite (Cu_3SbS_4), Cu_3SbS_3 and Sb_2O_3 (see e.g., Verplanck et al., 2008). The dissolution of these minerals mainly release As(III) and Sb(III). Once the reduced As and Sb metalloids are released from their source, the oxidation process is important because the resulting As(V) and Sb(V) have different sorption, solubility, toxicity, and bioavailability properties from each other and from their reduced forms. For example, it is well known that the ability of some minerals (such as Fe and Mn oxyhydroxides) to sorb As depends on the oxidation state of As (Stollenwerk, 2002; Dixit and Hering, 2003; Giménez et al., 2007; Cheng et al., 2009; Zhu et al., 2009). For Sb, far fewer studies have focused on its behavior (Filella et al., 2002, 2009). Antimonite and Sb(V) are sorbed onto Fe and Mn precipitates immobilizing dissolved Sb (Belzile et al., 2001; Leuz et al., 2006; Casiot et al., 2007).

Because microbes could play a significant role in all of the aforementioned processes, there are many studies reporting the existence of As-oxidizing bacteria found in different environments (Santini et al., 2000; Gihring and Banfield, 2001; Gihring et al., 2001; Langner et al., 2001; Casiot et al., 2004). The presence of As-oxidizing bacteria in streams affected by AMD (Acid Mine Drainage) has been reported (Wakao et al., 1988; Leblanc et al., 2002; Bruneel et al., 2003; Casiot et al., 2003; Duquesne et al., 2007; Nakazawa and Hareyama, 2007), and some authors have proposed that Fe oxidizers (such as *Acidithiobacillus ferrooxidans*) oxidize As(III) to As(V), which is immediately sorbed by Fe(III) oxyhydroxides (Leblanc et al., 1996). However, the

ability of Fe-oxidizing bacteria to oxidize As(III) is still in contention. Whereas some studies found that Fe-oxidizers are not capable of oxidizing As(III) to As(V) (Wakao et al., 1988; Duquesne et al., 2003), other works suggest that Fe-oxidizing bacteria may be involved in As(III) oxidation (Seith and Jekel, 1997). Under circumneutral conditions Osborne et al. (2010) reported the detection and isolation, for the first time, of aerobic psychrophilic arsenite-oxidizing bacteria, designated as GM1, in the cold environment found underground (groundwater temperatures are 1.5-6 ºC) at the Giant Mine, Yellowknife, Northwest Territories, Canada. According to the phylogenetic analysis of its full 16S rRNA gene sequence carried out by Osborne et al. (2010), GM1 seems to be a member of the Betaproteobacteria related to *Polaromonas* species. GM1 is closely related (98% sequence identity) to *Polaromonas* sp. JS666, a *cis*-dichloroethene-degrading bacterium isolated from granular activated carbon from Dortmund, Germany (Coleman et al., 2002), and to *Polaromonas napthalenivorans* CJ2, a naphthalene-degrading bacterium isolated from a coal-tar contaminated aquifer in New York state, USA (Jeon et al., 2003). Because there is negligible Fe in the Giant Mine circumneutral waters, acidophilic Fe-oxidizers should not be active.

Whereas arsenic has been widely studied, little is known about microbe-Sb interactions (Lehr et al., 2007). Some studies have focused on microbial oxidation of Sb (Ehrlich, 2002; Lehr et al., 2007). Oxidation of dissolved Sb has been reported under acidic conditions by *A. ferrooxidans* or *Stibiobacter senarmontii* isolated from an AMD (Bryner et al., 1954; Lyalikova, 1978).

The main objectives of this research are: (1) to determine biotic versus abiotic contributions to As and Sb oxidation in natural waters and (2) to estimate their oxidation rates. With these aims, unfiltered water types obtained from two very different mine environments have been used to study the simultaneous oxidation of As and Sb under laboratory conditions. The first type corresponds to waters collected from the Giant Mine where roasting of As-bearing gold ores produced As trioxide, which has left substantial As and Sb contamination (Hutchinson et al., 1982; Douglas et al., 2000; Clark and Raven, 2004; Andrade et al., 2010). Giant Mine waters are circumneutral pH and are rich in Ca, sulfate and As (exceeding 50 mmol/L in some mine waters from the dissolution of As trioxide stored underground) but have low concentrations of Mg and Fe (<18 µmol /L; Clark and Raven, 2004). In contrast, the second type of high-Fe (up to 0.14 mol/L; Sanchez-España et al., 2005) acid mine waters were collected from the Iberian Pyritic Belt (IPB, in the SW of the Iberian Peninsula). In the IPB very high As

concentrations (up to 500 µmol /L; Sanchez-España et al., 2005) can be found in acid mine drainage (AMD) and acid rock drainage (ARD) as a result of the weathering of As-bearing sulfides (Sánchez-España et al., 2005; Sánchez-Rodas et al., 2005; Acero et al., 2006; Sarmiento et al., 2007; Asta et al., 2010a). These mine waters transport high concentrations of acidity, sulfate, Fe, and other metal(loid)s (e.g., As, Co, Ni, Cu, Pb, Sb and Mn).

2. Materials and Methods

2.1. Field sampling

The Giant Mine is located near Yellowknife in the North West Territories, Canada, in the Archean Slave geological province of the Canadian Shield (Jenner et al., 1981). Gold ore was extracted from 1948 to 1999 (Cullen et al., 2005) and the host mineral for the gold was arsenopyrite. Nearly 7 million ounces of gold had been produced by the time the mine closed. A mineralogical study of the tailings revealed the main waste minerals to be quartz, dolomite, and calcite with minor pyrite and arsenopyrite (unpublished report by John Jambor, 2000 cited in Clark and Raven, 2004). Beginning in 1951, electrostatic precipitation was used to remove most of the arsenic that formerly was released into the atmosphere from smelting (Cullen et al., 2005). The recovered arsenic trioxide dust was stored underground in the mine and amounted to a total of 237,000 tons (Clark and Raven, 2004). Groundwater seeping into the storage chambers has high dissolved concentrations of arsenic, exceeding 0.05 mol/L in some local areas (Clark and Raven, 2004). On July 12, 2007 samples of both bacterial slime (unfiltered) and groundwater were collected from underground seeps and roof drippings and stored at 4ºC in the dark. Details on the water chemistry can be found in Clark and Raven (2004) and a microbiological study can be found in Osborne et al. (2010).

The Iberian Pyritic Belt (IPB), located in the SW of Spain, has been described as one of the largest massive sulfide deposits in the world, containing original reserves of the order of 1700 Mt (Sáez et al., 1999) divided up into more than 80 massive sulfide deposits. Over several centuries of mining activity this area has generated huge amounts of mining waste that continue to generate acidity and metal pollution affecting streams and rivers in the Tinto and Odiel drainage basins (Olías et al., 2004; Nieto et al., 2007; Sarmiento et al., 2009). Unfiltered water samples with bacterial slime were collected at

two IPB abandoned mines (San Telmo and Mina Esperanza) in July 2007 and June 2008, respectively, to be used in our laboratory experiments. Water samples from the San Telmo abandoned mine were collected from water emanating from a sulfidic waste pile and water samples from Mina Esperanza were taken from water emerging from the adit mouth. Water samples were stored in the dark at 4ºC until used in the experiments. The location and the main features of the waters of those abandoned mines can be found in Sanchez-España et al. (2005, 2007, 2008).

2.2. Reagents

All the reagents used to prepare the experimental and analytical solutions were of purity at least equal to the reagent-grade standards of the American Chemical Society. Double-distilled water and re-distilled or trace-metal grade acids were used in all preparations. Arsenite and antimonite stock solutions were prepared by dissolving $NaAsO_2$ and Sb_2O_3 in double-distilled water, respectively. The following reagents were used for hydride generation atomic-absorption spectrometry (HG-AAS) analytical determinations: 10 percent (weight per volume) KI from Aldrich; 10 percent (weight per volume) L-Ascorbic Acid from Aldrich; NaOH, $NaBH_4$, $NaAsO_2$, and Sb_2O_3 and trace metal grade HCl from Fisher scientific; 0.013 mol/L As(III) and 0.013 mol/L As(V) from High Purity Standards.

2.3. Analyses

Concentrations of total dissolved As (As(T)) and Sb (Sb(T)) and As(III) and Sb(III) were determined by HG-AAS in water samples according to the methodology described in McCleskey et al. (2003). The As(V) and Sb(V) was calculated as the difference between As(T) and Sb(T) and As(III) and Sb(III), respectively. An atomic absorption spectrophotometer (Perkin-Elmer (PE) - AAnalyst 300) with an electrically heated quartz cell and a path length of 15 cm inline with a flow-injection analysis system (FIAS; PE - FIAS 100), an autosampler (PE - AS90), and a hallow cathode lamp for Sb and an As electrodeless discharge lamp (EDL) attached to an EDL power supply (PE - EDL System 2) were used. The following spectrometer parameters were used: lamp current—380 mV, wavelength—193.7 nm for As and 217.6 nm for Sb, slit—0.7 nm. Peak height was used for data processing. Sodium borohydride was prepared daily and filtered through a 0.45-μm polyvinylidene fluoride filter membrane using a vacuum

pump. The detection limits of the HGAAS analytical procedure used at the USGS National Research Program Laboratory in Boulder (Colorado, USA), were 0.0013 µmol /L for As(T), 0.011 µmol /L for As(III), 0.0041 µmol /L for Sb(T) and 0.0082 µmol /L for Sb(III).

Ferrous and total dissolved Fe concentrations were determined by colorimetry using the FerroZine method (Stookey, 1970; To et al., 1999) in a Hewlett-Packard model 8452 diode array spectrometer with 1-cm path-length cells at room temperature. The concentration of dissolved Fe(III) was determined by computing the difference between total dissolved Fe and dissolved Fe(II). The detection limits are 0.0180 µmol/L and 0.036 µmol /L for total and ferrous Fe, respectively. However, if Fe(III) exceeds 95% of the total Fe in a sample, Fe(II) is overestimated. On completion of our experiments, the quantity of dissolved Fe(III) was very high compared to dissolved Fe(II). Subsequently, when the Fe(III) concentration was higher than 95% of total Fe, the colorimetric determination by Herrera et al. (1989) was used. This method is suitable for Fe(II) determination in bacterial leaching systems, where Fe(II) might be as low as 1% of total Fe.

The concentrations of total dissolved As, Sb and Fe were also measured with an inductively coupled plasma atomic emission spectrometer (ICP-AES) Leeman Lab-Direct Reading Echelle. The detections limits were 0.4 µmol /L for As, 0.25 µmol /L for Sb and 0.13 µmol /L for Fe.

Sulfate and chloride concentrations were determined using a Dionex model 600 ion chromatograph with AG4A guard and AS4A separator columns and Anion Self-Regenerating Suppressor-II. Detection limits were 5.2 µmol /L and 2.8 µmol /L for sulfate and chloride, respectively.

Solution pH measurements were carried out on an unstirred aliquot of solution using an Orion Ross pH electrode after calibration with standard buffer solutions of pH 1.68, 4.01, and 7.00.

The mineralogical composition of the precipitates formed during the experiments was determined by X-ray diffractometry (XRD) using a Bruker D5005 diffractometer with Cu Kα radiation at the Institute of Earth Sciences "*Jaume Almera*" CSIC (Barcelona,

Spain). Powered samples were scanned from 0º to 60º 2θ with a continuous scan speed of 0.0014 degrees 2θ per second. Samples of precipitates were observed under field-emission scanning electron microscopy (SEM) using a Hitachi H-4100FE with an intensity current of 10 kV.

2.4. Kinetic study

Biotic and abiotic batch experiments were performed in transparent and brown-dark polyethylene flask bottles of 250 mL and 125 mL. Bottles were immersed in water baths at ambient temperature (20 ± 2ºC) and at 4ºC (±1) under atmospheric conditions.

2.4.1. Abiotic experiments

Abiotic experiments were carried out in Fe(III)-SO_4 solutions, which were prepared by dissolving $Fe_2(SO_4)_3$ at pH 2.3. In these experiments Fe(III) was quickly mixed into 125 or 250 mL of the pH-adjusted solution which already contained Sb(III) and/or As(III). Initial concentration of As(III) and Sb(III) in the experiments ranged from 0.3 to 33 and 0.2 to 21 µmol/L, respectively. Experiments were carried out with 18 to 6270 µmol/L of Fe(III), added as ferric sulfate, and 2 to 177 mmol/L of sulfate. Chloride was added as NaCl to seven experiments (L10-Cl, L5-Cl, L14-Cl, L15-Cl, NL2-Cl, NL5-Cl and NL6-Cl, Table 1) after being run for a period of time (from 265 to 890 h). Photoirradiation was carried out by using a conventional lamp with light in the visible spectra. Experimental conditions of the abiotic experiments are shown in Table 1.

2.4.2. Biotic experiments

Two types of biotic experiments were conducted: AMD-inoculated synthetic acid medium and neutral pH groundwater (Table 2). In the first type of experiments, performed in acid conditions, common bacteria from AMD water from the Iberian Pyritic Belt (SW Spain) were cultivated in a synthetic medium (9K medium) used to grow *Acidithiobacillus ferrooxidans*. This medium was prepared according to the composition of Silverman and Lundgren (1959), adjusting its pH to 2.3. In those experiments, 5 mL of field water sampled from the Iberian Pyritic Belt (containing bacterial slime) were incubated in 250 mL of 9K medium. Maximum oxidation rates were measured in 9K media (IPB-ST-1, IPB-ST-2, and IPB-ST-3) and additional experiments were carried out adding 0.25 (experiments IPB-ME-1, IPB-ME-2, IPB-

ME-3, IPB-ME-4) and 0.1 mL (experiment IPB-ME-5 and IPB-ME-6) of this enriched solution to 250 mL of solutions prepared with the desired Fe(II), As(III) and Sb(III) concentrations. The second type of biotic experiments was performed in unfiltered field water samples from the Giant Mine, Yellowknife (Canada), which already showed very high As(III) and Sb(III) concentrations (up to 40 mmol/L and 5.4 µmol/L, respectively) at temperature of 20ºC and 4ºC. Control experiments were carried out in parallel by using duplicates filtered through 0.2-µm syringe filters.

Bottles were periodically stirred to provide oxygenation and the incubation of bacteria in the culture medium. At appropriate time intervals, samples (1-5 mL) for Sb(III), Sb(T), As(III), As(T), Fe(II), and Fe(III) analysis were collected and filtered through a 0.2-µm filter and preserved at 4ºC in the dark until being analyzed.

2.5. Geochemical calculations

Speciation-solubility calculations were made with the geochemical code PHREEQC (Parkhurst and Appelo, 1999) using the WATEQ4F thermodynamic database (Ball and Nordstrom, 1991).

3. Results and discussion

3.1. As and Sb abiotic oxidation in the presence of Fe(III)

The aqueous oxidation of As(III) and Sb(III) in the range of 0.3 to 33 and 0.2 to 21 µmol/L, respectively, were measured in acid Fe(III)-SO_4 in the presence of visible light. As shown in Figure 1, after 800 hours 30-100% of As(III) was oxidized and Sb(III) was completely oxidized, depending on the initial Fe(III) concentration.

To verify the effect of the photochemical processes on the As and Sb oxidation some experiments were carried out under the same initial experimental conditions (Table 1). The results show no oxidation in dark conditions (data not shown), which is in good agreement with those reported by earlier studies (Kocar and Inskeep, 2003; Dutta et al., 2005; Li et al., 2006). These results suggest, as described previously by Emett and Khoe (2001), Dutta et al. (2005), Leuz et al. (2006) or Li et al. (2006) that the reactive species produced from the hydrolysis of Fe(III), $^{\bullet}OH$, are thus responsible for the oxidation of

As and Sb. The Fe(III) hydrolysis produces $Fe^{III}(OH)^{2+}$ species which is an effective source of hydroxyl free radicals ($^{\bullet}OH$) in the presence of light (hν, photons, equation 1) (Brihaye et al., 1983; Khoe et al., 1986; Emett and Khoe, 2001; Quentel and Filella, 2002; Kocar and Inskeep, 2003). These free radicals react with As(III) and Sb(III) to produce As(V) and Sb(V).

(1) $Fe(III)(OH)^{2} + h\nu \rightarrow Fe(II) + {}^{\bullet}OH$

Direct photochemical oxidation of As or Sb should be negligible or very slow, since As(III) and Sb(III) do not absorb terrestrial sunlight (Oldenburg et al., 1997; Emett and Khoe, 2001). Therefore, oxidation of those elements in the presence of light is relatively slow compared to Fe- mediated photo-oxidation.

Although photochemical reactions with $Fe^{III}(OH)^{2+}$ may represent a substantial contribution to As(III) and Sb(III) oxidation at low pH, the rate of As(III) and Sb(III) oxidation was considerably faster (up two orders of magnitude) in the presence of chloride (Figure 2). Emett and Khoe (2001) attribute this catalytic effect to the formation of Fe-chloride-complexes ($Fe(III)Cl^{2+}$), which absorb photons (hν) to produce highly oxidizing dichlororadicals. In contrast, no oxidation was observed without light even in the presence of chloride because photoreactions were totally inhibited. On the other hand, sulfate, which is present in the studied solutions, has been found to exert an inhibitory effect on As(III) oxidation in the presence of light. This inhibition is caused by Fe(III)-sulfate complexes ($FeSO_4^{+}$), which do not produce the reactive free-radicals necessary to the As(III) oxidation (Emett and Khoe, 2001).

3.1.1 Oxidation rate dependence on initial As(III), Sb(III) and Fe(III) concentrations

Iron, As, and Sb coexist together in acidic environments (e.g. acid mine waters). Therefore, the dependence of As(III) and Sb(III) oxidation rate on the initial concentration of Fe(III) was tested. Likewise, the rate of As(III) and Sb(III) oxidation was evaluated as a function of initial As(III) and Sb(III) concentration, respectively, under constant conditions (Fe(III) and SO_4 concentration and pH). The results show (Figure 3) that increasing initial As(III) and Sb(III) concentrations result in an increase of the oxidation rates.

Oxidation of As(III) and Sb(III) in the presence of different Fe(III) concentrations in the presence of visible light experiments is illustrated in Figure 1. Oxidation rates increased with increasing Fe(III) or, in other words, with increasing Fe:As and Fe:Sb ratios (Figure 4). At Fe:As and Fe:Sb molar ratios of 0.5 and 0.9 only 18 and 44 % of the initial As and Sb were oxidized after 800 hours, respectively, whereas increasing the Fe:As and Fe:Sb molar ratios to 54 and 87, respectively, about 34% of As and 100% of Sb were oxidized at the end of the experiments. As observed in Figure 4, in experiments with initial Fe:As and Fe:Sb molar ratios lower than 54 and 87**,** respectively, a gradual As(III) and Sb(III) oxidation was observed. However, a fast initial As(III) and Sb(III) oxidation occurred at the start of the experiments with a high Fe:As and Fe:Sb molar ratios.

3.2. Microbial-catalyzed oxidation of As(III) and Sb(III)

3.2.1 Giant Mine, Yellowknife, NWT (Canada) field waters

Biotic and abiotic control experiments were carried out in order to demonstrate the capability of microorganisms to oxidize As(III) and Sb(III) in the groundwaters of the Giant Mine (GM-1, GM-2 and GM3 in Table 2). Batch experiments were conducted with the unfiltered field water at 20 and 4 ºC. No significant oxidation of As(III) was observed in the filtered (0.2 µm) field water sample, confirming that As(III) oxidation rates from other oxidizing agents were not important.

The results of two biotic laboratory experiments carried out under atmospheric conditions and 20ºC are shown in Fig. 5. The initial As(III) concentration was 40000 µmol/L and both experiments were performed from the same initial unfiltered water sample. Total arsenic and antimony concentrations remained constant during the experiments, therefore removal of dissolved As and Sb can be ruled out. The results showed two different trends: in the experiment GM-1, biological oxidation occurred, after a lag period of 400 h, to a maximum rate of 53 µmol/L/h of As(III) during exponential growth coinciding with the main pH shift (Fig. 5). Whereas in the experiment GM-2 oxidation took place at the beginning of the experiment and an oxidation rate of 78 µmol/L/h was obtained during the main linear drop in pH. After that, a lag period of around 300 h took place followed by an acceleration of the oxidation rate at the end of the experiment GM-2 (oxidation rate was 54 µmol/L/h).

This second stage of oxidation could represent (1) the growth of another As-oxidizing strain, (2) a revitalized growth of the same strain, or (3) an alleviation of a toxicity effect that might relate to (1) or (2). Main differences between GM-1 and GM-2 are due to the lag time (600 h in GM-1 and 150 h in GM-2) and are probably caused by a higher initial population density in GM-2.

In parallel to oxidation, the pH decreased as the As(III) decreased (Fig. 5). Therefore, the effect of Fe oxidation/precipitation processes can be discarded due to the low dissolved Fe concentrations (<18 μmol/L; Clark and Raven, 2004), and the pH decrease reflects the acidity generated by the As oxidation process according to the reaction:

(2) $H_3AsO_3 + ½O_2 \rightarrow H_2AsO_4^- + H^+$

for pH values of 2.3 – 7 (Nordstrom and Archer, 2003). For values below 2.3 there is no change in pH because the protons consumed during oxygen reduction are exactly balanced by those produced in arsenite oxidation. Hence, a pH of 2.3 becomes the limit of pH decrease by arsenite oxidation alone. For pH values above 7, 2 moles of protons are produced for every mole of As oxidized and the pH will decrease more rapidly. Consequently, if the buffer capacity of the solution is low, pH is a measure of arsenite oxidation at circumneutral pH values as well as As(III) determinations. Therefore, to obtain the As oxidation rates, only the data points that show a substantial linear or near-linear drop in pH have been considered. As stated above, this decrease indicates that As oxidation was the dominant process.

Additional biotic experiments were performed to study the effects of temperature on the oxidation of As(III) and Sb(III). The experiments were performed with the same initial unfiltered water sample with 4000 μmol/L of As(III) and 5.4 μmol/L of Sb(III) and at two different temperatures, 20 and 4ºC, simultaneously. Within 120 h, 50% of As(III) and Sb(III), was oxidized in the batch experiments performed at 20 ºC (Fig. 6a). For experiments conducted under cold conditions (4 ºC), 50% and 57% of the initial As(III) and Sb(III), respectively, were oxidized within 120 hours (Fig. 6b). As observed in experiments GM-1 and GM-2 the pH decreased as As(III) and Sb(III) oxidized (Fig. 6). Total concentrations of arsenic and antimony were constant during the experiments indicating no losses from precipitation or sorption. The initial rates were slower at 4ºC than at 20ºC but the overall rates were similar. Although the oxidation rate of As is

shown slower at 4ºC than at 20ºC in Figure 6, how one determines the rate is sensitive to what points on the curve are used. When the rate decreases with time (non-linear exponentially decreasing) it usually means that the growth rate is declining and this part of the curve is not used. No oxidation was observed in batch studies conducted after filtration of the sample (data not shown), indicating that bacteria are required to catalyze As(III) and Sb(III) oxidation in Giant Mine waters. Therefore, the ability of some microbes in Giant Mine waters to oxidize As and Sb, even under the extreme conditions found in Giant Mine waters has been demonstrated. However, further research could distinguish whether the same strain of microbe oxidizes As and Sb simultaneously or if there is a diversity of microbes involved.

3.2.2 Iberian Pyritic Belt (SW Iberian Peninsula) AMD waters

Laboratory experiments were conducted at pH 2.3 to examine As(III) and/or Sb(III) oxidation in AMD stream waters of the Iberian Pyritic Belt (IPB-ST and IPB-ME experiments, Table 2). Results showed that within 25-40 hours after inoculation As(III) and Sb(III) oxidation started and accelerated, whereas Fe(II) oxidation demonstrated a lag of ~50-300 h, but was completely oxidized by 300-750 h (Figure 7). It is well known that Fe(II) oxidation does not occur at observable rates at pH 2.3 without microbial catalysis (Nordstrom, 2003).

A lag period of slow oxidation during the first 100 h of incubation was followed by rapid As(III), Sb(III), and Fe(II) oxidation likely coinciding with the exponential phase of growth (Fig. 7). Within 200-250 hours, 100% of Sb(III) and between 50 to 100% of As(III) were oxidized to Sb(V) and As(V), respectively, during exponential growth at rates in the range of 0.01 to 0.02 µmol/L/h and 0.01 to 0.03 µmol/L/h, respectively. In all experiments, As(III) and Sb(III) concentrations decreased rapidly (Fig. 7). Nonetheless, two trends were observed. First, in the experiments carried out with the highest As(III) and Fe(II) concentrations (9K medium), As oxidation appeared to start after 100-150 h, in contrast Fe oxidized after 300-400 h (Fig. 7a). Second, in the experiments conducted with lower Fe(II) concentrations (Fig. 7b), the oxidation of Fe, As and Sb seems to start at the same time after 50 h and the curves indicated that the As(III), Sb(III) and Fe(II) oxidation took place simultaneously. Although we do not have direct evidence, these differences could be explained by the existence or two or more competing microbial species, different metabolism in one strain, or a toxicity

effect. In contrast, in the abiotic control experiments there was no obvious As(III), Sb(III), and Fe(II) oxidation.

Although the presence of As- and Sb-oxidizing bacteria appears to be a reasonable hypothesis to account for As(III) and Sb(III) oxidation, it is worth noting that the analytical uncertainty of the Fe(II) concentration during the first hours is ca. ±5%. Hence, high concentrations of Fe(III), even greater than 5 mmol/L, would not have been detected. This undetected amount of Fe(III) may have been able to oxidize As(III) and Sb(III) under these experimental conditions. To ascertain whether the AMD water contained some As(III) and/or Sb(III) oxidizer capable of growth by arsenite oxidation, supplementary experiments were performed using very low Fe(II) concentrations (about 40 µmol/L). At this low ferrous Fe concentration, As(III) and Sb(III) oxidation was substantially less than in the experiments performed at higher Fe(II) concentrations, whereas Fe(II) was completely oxidized (Fig. 8), indicating that Fe-oxidizing microbes in AMD are not As- or Sb-oxidizing microbes. Thus, As(III) and Sb(III) oxidation could be catalyzed by the Fe(III) formed by the Fe-oxidizers and oxidation would then result from a coupling of microbial and abiotic processes. Connections between Fe and As redox reactions have been previously suggested (Daus et al., 2002; Bednar et al., 2005; Sarmiento et al., 2007) but no attempt was made to distinguish between Fe(III) oxidation of As(III) and independent microbial oxidation of As(III). As far as we know, no other studies have determined the simultaneous oxidation of Fe(II), As(III), and Sb(III) oxidation in sulfuric acid or comparable AMD systems.

The pH and the total concentrations of Fe, As, and Sb were constant during the experiments indicating that no precipitation or sorption took place except for those in 9K medium. In those experiments, pH increased during the first 400 h from 2.4 to 2.8, followed by a pH decrease to 2.2. The pH increase is a consequence of Fe(II) oxidation to Fe(III) observed by the Fe(III) increase in the solution (Fig. 9a), which consumes protons, whereas the pH decrease is due to Fe(III) hydrolysis and Fe(III) precipitation (Nordstrom, 2003; Kupka et al., 2007) causing a decrease in total dissolved Fe concentration (Fig.10a). X-ray diffraction examinations of the retrieved precipitate in this experiment showed that it was jarosite ($XFe_3(SO_4)_2(OH)_6$) where X is usually Na^+, K^+ and H_3O^+. Wang et al. (2006) argue that schwertmannite ($Fe_8O_8(OH)_{5.5}(SO_4)_{1.25}$) is produced by biological oxidation of ferrous Fe in cultures of Fe-oxidizing bacteria, and

owing to its instability, it can spontaneously transform to other phases including jarosite ($XFe_3(SO_4)_2(OH)_6$). This transformation is favored by aging, temperature, and ammonium concentration in acid media. Although the 9K solution is supersaturated with respect to schwertmannite and jarosite as indicated by the PHREEQC calculations (Parkhurst and Appelo, 1999), direct precipitation of jarosite is not likely because its formation at low temperature is slow (weeks to months) (Brown 1970; Babcan, 1971; Stahl et al., 1993; Zhai et al., 2010). Furthermore, the precipitation of jarosite as the only Fe-phase present does not account for the As behavior, because arsenate sorption capacity of jarosite in the presence of such high concentrations of sulfate (about 0.18 mol/L) is practically negligible. By contrast, schwertmannite transformation into jarosite would account for the behavior in the total As concentration in the experiments performed in 9K medium (Fig. 9b). Aqueous As(V) could be partially sorbed as schwertmannite precipitated. When schwertmannite transformed to jarosite, As(V) could have been released back to the solution as jarosite has a lower arsenate sorption capacity than schwertmannite in the presence of high sulfate concentrations (Asta et al., 2009). Alternatively, schwertmannite or jarosite could have started to precipitate as the pH increased, sorbing or co-precipitating some As, and then redissolved or desorbed as the pH decreased. However, no direct evidence supporting these explanations has been found and this interpretation is speculative at present.

4. Comparison of oxidation rates

The oxidation rates obtained in this study and previous works are presented in Table 3. The results show that at circumneutral pH, As(III) and Sb(III) oxidize simultaneously in the unfiltered Giant Mine waters. However, the microbial oxidation rate for As is about 3 orders of magnitude faster than for Sb. Oxidation rates for As(III) were typically 15-78 µmol/L/h and for Sb(III) typically 0.03-0.05 µmol/L/h during the exponential growth. These As(III) oxidation rates are close to those reported by Gihring and Banfield (2001) and Gihring et al. (2001) under biotic conditions but several orders of magnitude higher than abiotic rates (Table 3; also see Nordstrom, 2003).

Many studies have been focused on the behavior of As and Sb and their natural attenuation in acid mine drainage (Nordstrom and Alpers, 1999; Casiot et al., 2003**;** Frau and Ardau, 2003; Lee et al., 2005; Acero et al., 2006; Lee and Chon, 2006; Pfeifer

et al., 2007; Casiot et al., 2007; Manaka et al., 2007; Asta et al., 2010a,b). However, as far as we know, this is the first study determining simultaneous oxidation of Fe(II), As(III), and Sb(III) in sulfuric acid solutions similar to those found in acid mine drainage. Under our experimental conditions the As and Sb oxidation rates obtained at low pH in the presence of Fe(II) oxidizing microbes are lower than the abiotic oxidation by Fe(III), suggesting abiotic As(III) and Sb(III) coupled to microbial Fe(II) oxidation is the primary oxidation process. The resulting Fe(II) oxidation rate was around 500 μmol/L/h/ and is comparable to reported data for bacterially catalyzed Fe(II) oxidation in AMD (Kirby and Elder Brady, 1998; Nordstrom, 2003; Sánchez-España et al., 2007).

The lack of oxidation observed in batch experiments after filtration of the field samples suggest that bacteria accelerate the Fe(II) oxidation in AMD waters and As(III) and Sb(III) oxidation in the Giant Mine groundwaters. In the latter case, it remains to be determined whether the same microbes are responsible for the As(III) and Sb(III) oxidation or different species are involved.

Regarding the abiotic results obtained in Fe(III)-SO_4 aerated acid solutions, the Sb oxidation rates were close or even higher than biotic ones. In contrast, the abiotic As oxidation rates in acid solutions without Fe are many orders of magnitude slower than those obtained by microbial mediation or with Fe. These results are consistent with those of McCleskey et al. (2004) who found that properly filtered water samples that were also acidified with HCl would maintain constant As(III/V) ratios for many months (at least 18 months for one sample).

According to our results, the As and Sb abiotic oxidation rates by Fe(III) increased when the initial concentration of Fe(III), chloride, As(III), and Sb(III) increased and in the presence of light as observed in earlier studies (Hug et al., 2001; Brihaye et al., 1983; Emett and Khoe, 2001, Hug and Leupin, 2003; Kocar and Inskeep, 2003; Buschmann et al., 2005a,b; Dutta et al., 2005; Leuz et al., 2006). However, the Sb(III) oxidation rate in Fe(III) solutions was faster than As(III) oxidation as previously reported by Leuz et al. (2006).

5. Conclusions

The quantification of the As(III) and Sb(III) oxidation rates and their mechanisms is essential for understanding and predicting As and Sb geochemistry in natural waters. In particular, it is important to distinguish abiotic from biotic mechanisms. In this paper the simultaneous oxidation of Fe(II), As(III), and Sb(III) was studied under acid conditions similar to acid mine drainage. The simultaneous oxidation of As(III) and Sb(III) was studied under circumneutral conditions. Both conditions were studied with and without microbes and circumneutral conditions were studied at 4ºC and at 20ºC.

Our results showed that at the circumneutral pH of the Giant Mine groundwaters the As(III) oxidation rate, which is much faster than Sb(III) oxidation, increased by several orders of magnitude compared to abiotic rates with little or no Fe(III).

In contrast, under sulfuric acid conditions similar to those found in acid mine waters of the Iberian Pyritic Belt, As(III) and Sb(III) were oxidized abiotically, at low oxidation rates, by the microbially formed Fe(III).

In the absence of microbes but with Fe(III)-sulfuric acid aerated solutions, As(III) and Sb(III) oxidized faster than with microbes and the abiotic oxidation rates were accelerated by increasing Fe(III), As(III), Sb(III), and Cl concentrations in the presence of light. Oxidation of Sb(III) by Fe(III) in acid aerated solutions was found to be faster than As(III) oxidation and the rate of oxidation of either is highly dependent on the ratio of Fe(III)/As(III) or Fe(III)/Sb(III).

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TABLE CAPTIONS

Table 1. Experimental conditions of the As(III) and Sb(III) abiotic oxidation experiments in the presence of Fe(III).

Table 2. Experimental conditions of the microbial-catalized oxidation of As(III) and Sb(III) experiments.

Table 3. As(III) and Sb(III) oxidation rates obtained in this study and previous studies.

FIGURE CAPTIONS

Figure 1. Abiotic oxidation of 0.3 µmol/L of As(III) (a) and 0.2 µmol/L of Sb(III) (b) by Fe(III) in SO_4 acid-aerated solutions and in the presence of visible light. Initial As(III)/$As(III)_0$ and Sb(III)/$Sb(III)_0$ values for B1, B2 and B3 are 1.0. Error bars correspond to 10% resulting from the propagation of the ±5% analytical error.

Figure 2. Effect of chloride on the oxidation of 33 µmol/L of As(III) (a) and 2 µmol/L Sb(III) (b) by Fe(III) in SO_4 aerated and in the presence of visible light. Error bars correspond to 10% resulting from the propagation of the ±5% analytical error.

Figure 3. Effect of initial As(III) and Sb(III) on the oxidation rates. As(III) oxidation in the experiments: B1, B5 and B9 (a); Sb(III) oxidation in the experiments: B1, B5 and B9 (b). Error bars correspond to the ±5% analytical error.

Figure 4. Abiotic As(III) and Sb(III) (b) oxidation at different Fe(III):As(III) (a) and Fe(III):Sb(III) molar ratios (b). Initial As(III)/$As(III)_0$ and Sb(III)/$Sb(III)_0$ values for all experiments are 1.0. Error bars correspond to 10% resulting from the propagation of the ±5% analytical error.

Figure 5. Evolution of the ratio As(III)/$As(III)_0$ and pH during two batch experiments performed in unfiltered Giant Mine water at 20ºC. Initial arsenic concentration ($As(III)_0$) is 40000 µmol/L. Error bars correspond to 10% resulting from the propagation of the ±5% analytical error.

Figure 6. Evolution of the ratios of As(III)/$As(III)_0$ and Sb(III)/$Sb(III)_0$ and pH during two batch experiments performed in unfiltered Giant Mine water at 20ºC (a) and 4 ºC (b). Initial arsenic ($As(III)_0$) and initial antimony ($Sb(III)_0$) concentrations are 4000 µmol/L and 5.4 µmol/L, respectively. Error bars correspond to 10% resulting from the propagation of the ±5% analytical error.

Figure 7. Evolution of Fe(II), As(III) and Sb(III) concentration during the IPB-ST-1 (a) and IPB-ME-2 (b) biotic oxidation experiments carried out at pH 2.3. Error bars correspond to the analytical error (±5% for As(III) and Sb(III); ±10% for Fe(II)).

Figure 8. Evolution of the molar ratio of As(III)/$As(III)_0$, Sb(III)/$Sb(III)_0$, and Fe(II)/$Fe(II)_0$ during unfiltered experiments carried out with initial concentrations of $As(III)_0$ = 6.4 µmol/L and $Sb(III)_0$ = 1.8 µmol/L and $Fe(II)_0$ = 0.04 mmol/L. Error bars correspond to 10% resulting from the propagation of the ±5% analytical error.

Figure 9. Variation in Fe(III) and Fe(T) concentration (a) and in As(III) and total arsenic (As(T)) concentration (b) during the experiments conducted in 9K media. Error bars correspond to the analytical error of 10% for Fe(II) and Fe(T) and ±5% for As(III).

TABLES.

Table 1. Experimental conditions of the As(III) and Sb(III) abiotic oxidation experiments in the presence of Fe(III).

Initial experimental conditions*								
			As(III)	Sb(III)	Fe(III)	Sulfate		
Exp.	Light	Cl	μmol/L			mmol/L	Fe:As	Fe:Sb
L10	y	n	33	-	2500	26	75	-
L10-Cl	y	y	13	-	2500	26	188	-
L5	y	n	27	-	6270	177	235	-
L5-Cl	y	y	13	-	6270	177	470	-
L14	y	n	-	2	36	2	-	17
L14-Cl	y	y	-	2	36	2	-	17
L15	y	n	-	2	180	5	-	87
L15-Cl	y	y	-	2	180	5	-	87
L17	y	n	29	-	6270	177	215	-
B1	y	n	0.3	0.2	18	5	54	87
B2	y	n	0.3	0.2	180	5	540	872
B3	y	n	0.3	0.2	1800	8	5400	8720
B4	y	n	3	2	18	5	5	9
B5	y	n	3	2	180	5	54	87
B6	y	n	3	2	1800	8	540	872
B7	y	n	33	21	18	5	0.5	0.9
B8	y	n	33	21	180	5	5.4	9
B9	y	n	33	21	1800	8	54	87
NL1	n	n	33	-	3350	42	100	-
NL2	n	n	32	-	3580	42	113	-
NL2-Cl	n	y	33	-	3580	42		-
NL7	n	n	18	-	3350	177	186	-
NL5	n	n	-	2	180	5	-	87
NL5-Cl	n	y	-	2	180	5	-	87
NL6	n	n	-	2	36	2	-	17
NL6-Cl	n	y	-	2	36	2	-	17

***** Temperature (ºC): 20 ± 2; pH: 2.3-2.4

"-": 0 or not applicable

Table 2. Experimental conditions of the microbial-catalized oxidation of As(III) and Sb(III) experiments.

Initial experimental conditions							
Experiment	**pH**	**T (ºC)**	**As(III) µmol/L**	**Sb(III) µmol/L**	**Fe(II) mmol/L**	**Fe:As**	**Fe:Sb**
GM-1	7.2	20 ± 2	40000	*n.a*	-	-	-
GM-2	7.2	20 ± 2	40000	*n.a*	-	-	-
GM-3	4.7	20 ± 2	4000	5.4	-	-	-
GM-4	4.7	4 ± 1	4000	5.4	-	-	-
IPB-ST-1	2.3	20 ± 2	10.7	-	152	14250	-
IPB-ST-2	2.3	20 ± 2	10.7	-	152	14250	-
IPB-ST-3	2.3	20 ± 2	10.7	-	152	14250	-
IPB-ME-1	2.3	20 ± 2	6.7	1.1	1.8	330	1161
IPB-ME-2	2.3	20 ± 2	3.3	1.8	1.5	456	642
IPB-ME-3	2.3	20 ± 2	3.3	1.7	0.9	349	387
IPB-ME-4	2.3	20 ± 2	3.3	1.2	0.4	258	260
IPB-ME-5	2.3	20 ± 2	6.5	1.6	0.04	6.1	18
IPB-ME-6	2.3	20 ± 2	6.4	1.8	0.04	6.1	16

n.a.: not analyzed

"-": 0 or not applicable

Table 3. As(III) and Sb(III) oxidation rates obtained in this study and previous studies.

Oxidant	Experimental conditions			Oxidation rates			Reference
	pH	T (ºC)	Fe(III) (µmol/L)	Fe(II)	As(III) (µmol/L/h)	Sb(III) (µmol/L/h)	
Microbial oxidation	~ 7	20 ± 2	-	-	53-78	0.04 - 0.05	*This study*
		4 ± 1	-	-	15	0.03	
	7 - 8	70	-	-	120♦	-	*Gihring and Banfield (2001); Gihring et al. (2001)*
Fe(III) formed by microbial oxidation	2.3-2.4	20 ± 2	-	500	0.01 - 0.03†	0.01 - 0.02	*This study*
Abiotic Fe(III)	2.3	20 ± 2	18-6300	-	≤ 0.2	≤ 0.8	*This study*
	1.3	20 ± 2	180	-	0.011+	-	*McCleskey et al. (2004)*
			18	-	0.005+	-	
			18	-	0.004	-	
	2	25	5000	-	0.015	-	*Cherry et al. (1979)*
	5		0.01	-	0.0014	-	
	7		0.001	-	0.00008	-	
	2.2	25	90	-	-	~ 2×10^{-4}	*Leuz et al. (2006)*

♦ This value is 100-fold greater than the abiotic oxidation rate of 0.8 µmol/L/h obtained by Gihring and Banfield (2001) and Gihring et al. (2001)

† Obtained in 9K media

+ Experiment performed with HCl

Figure 1a

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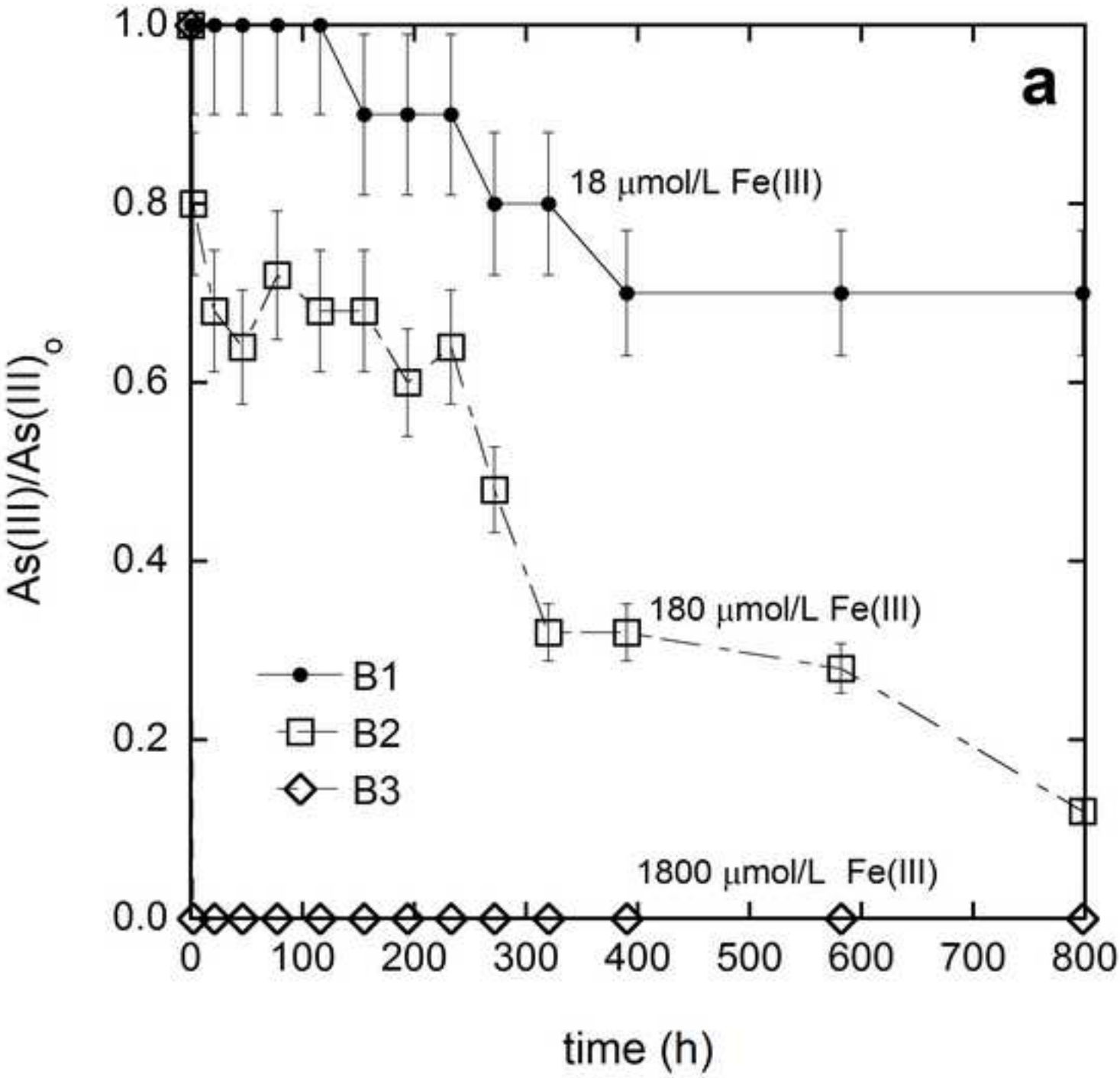

Figure 1b

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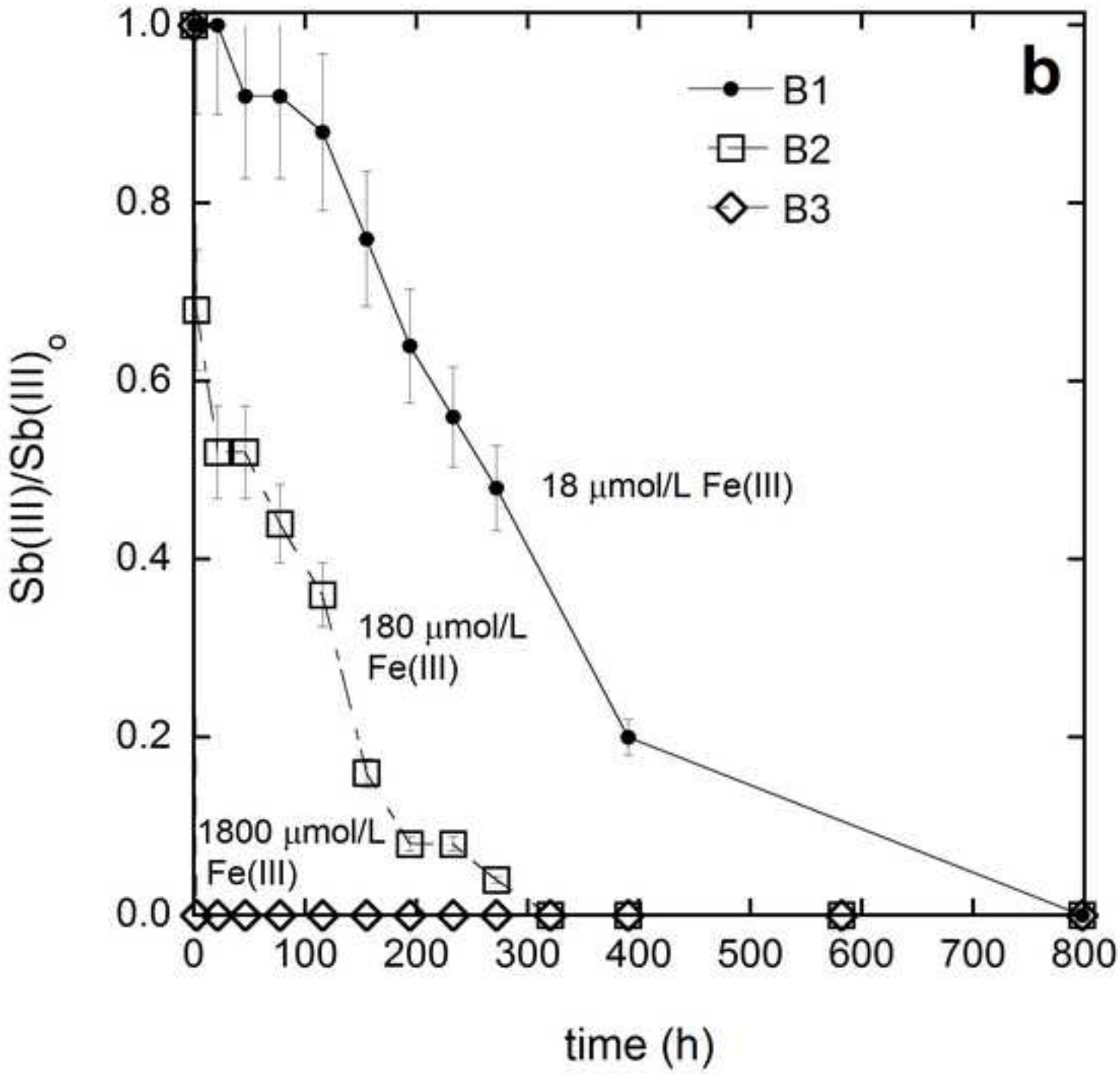

Figure 2

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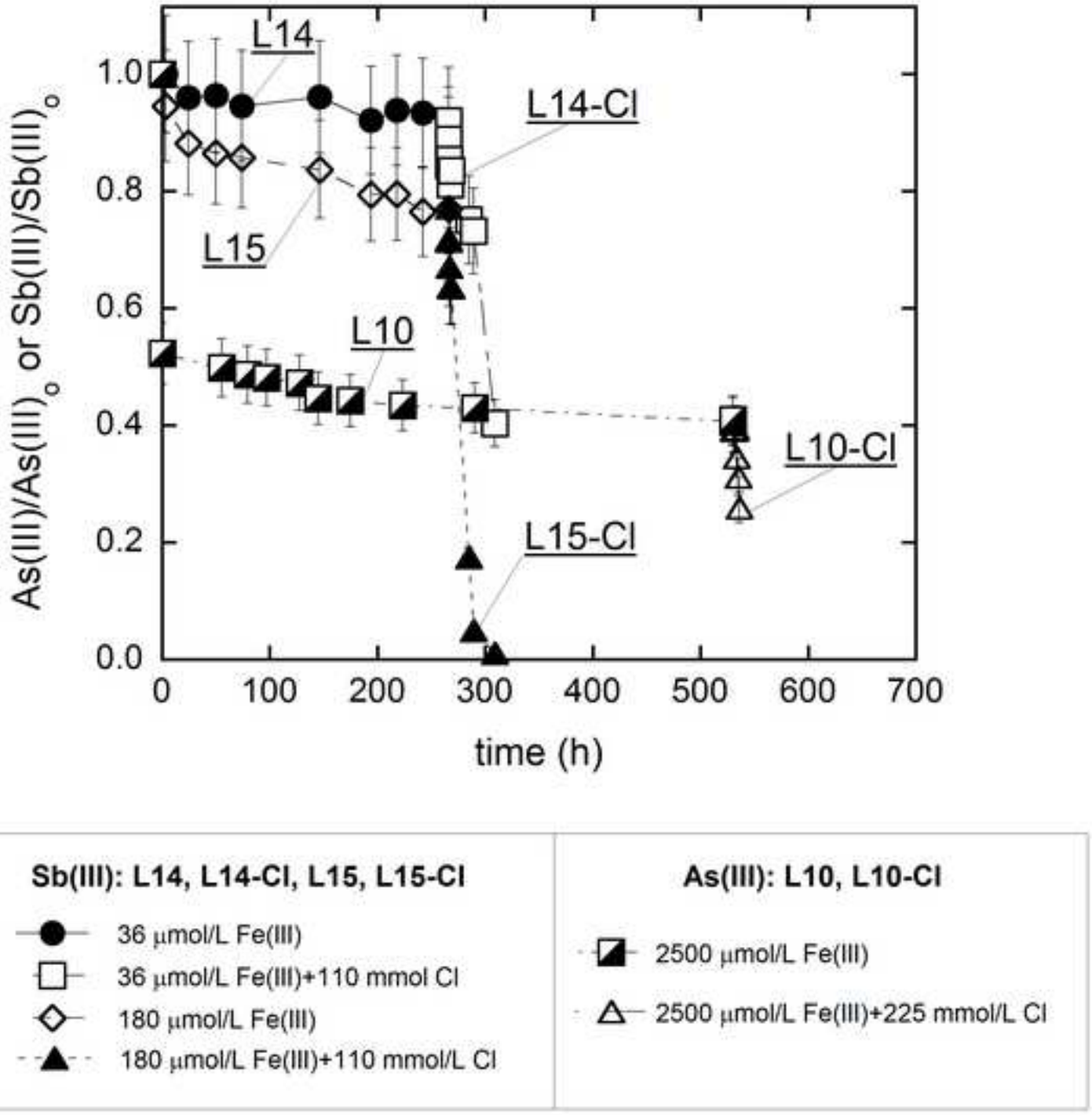

Figure 3a

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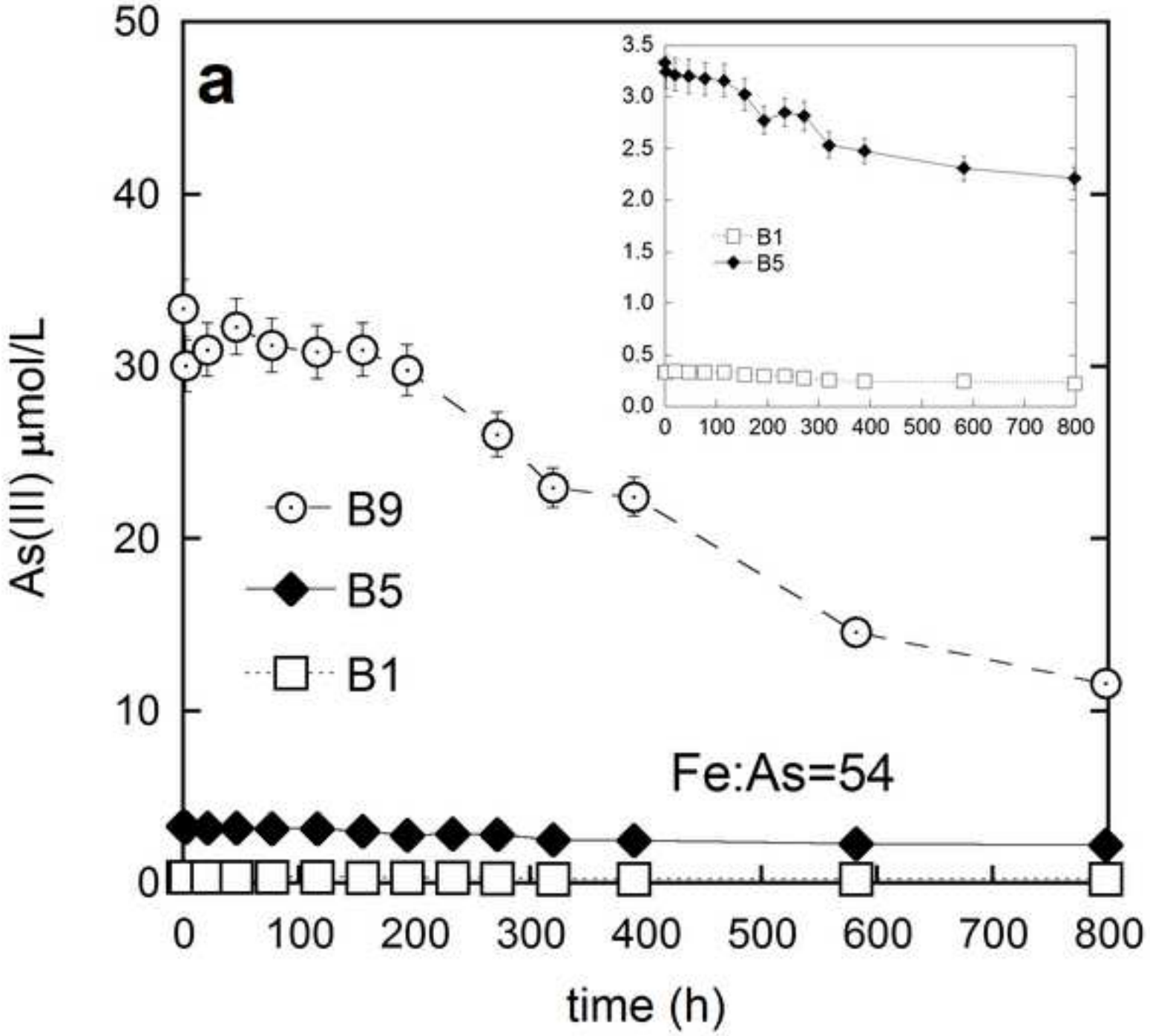

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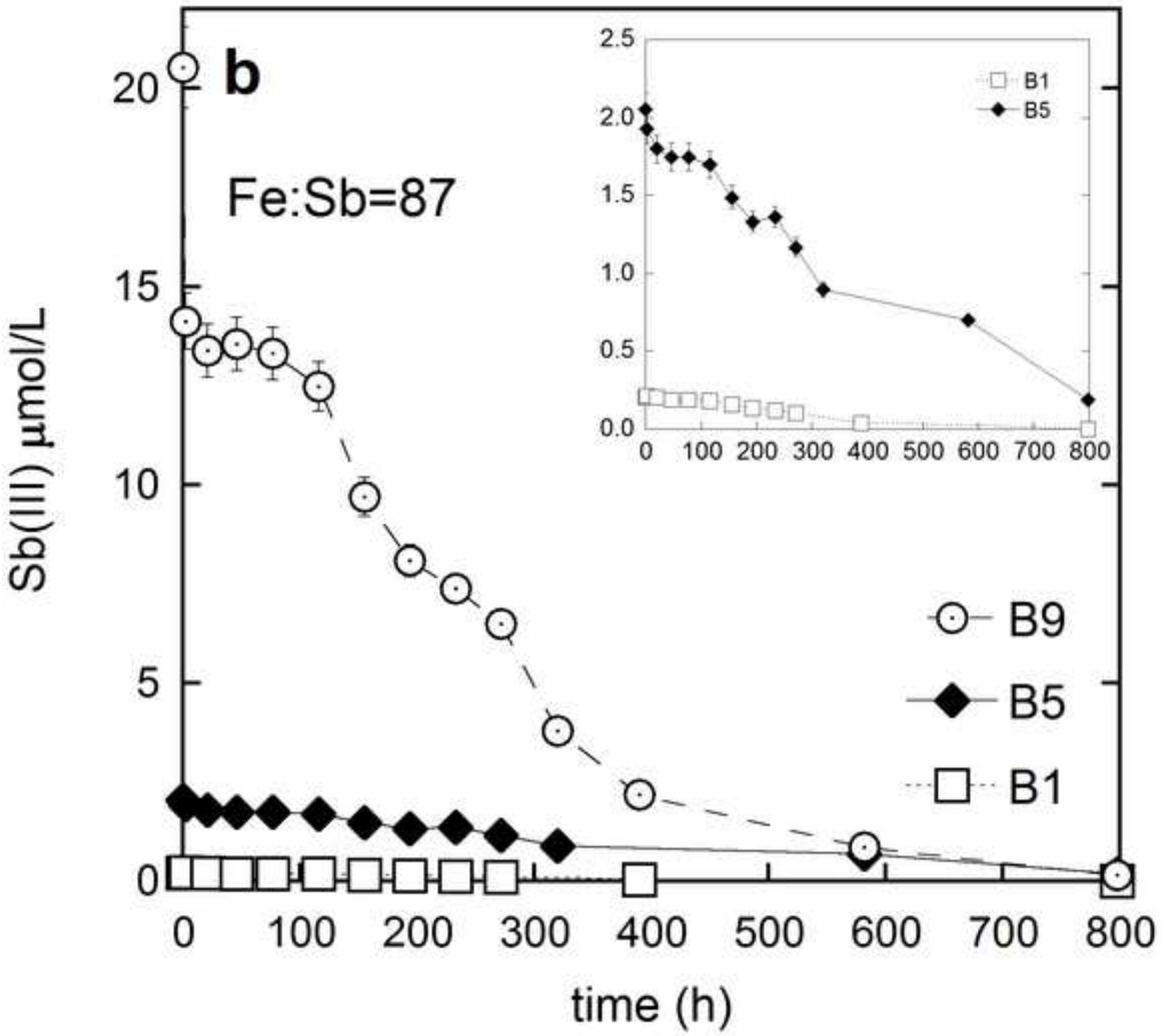

Figure 4a

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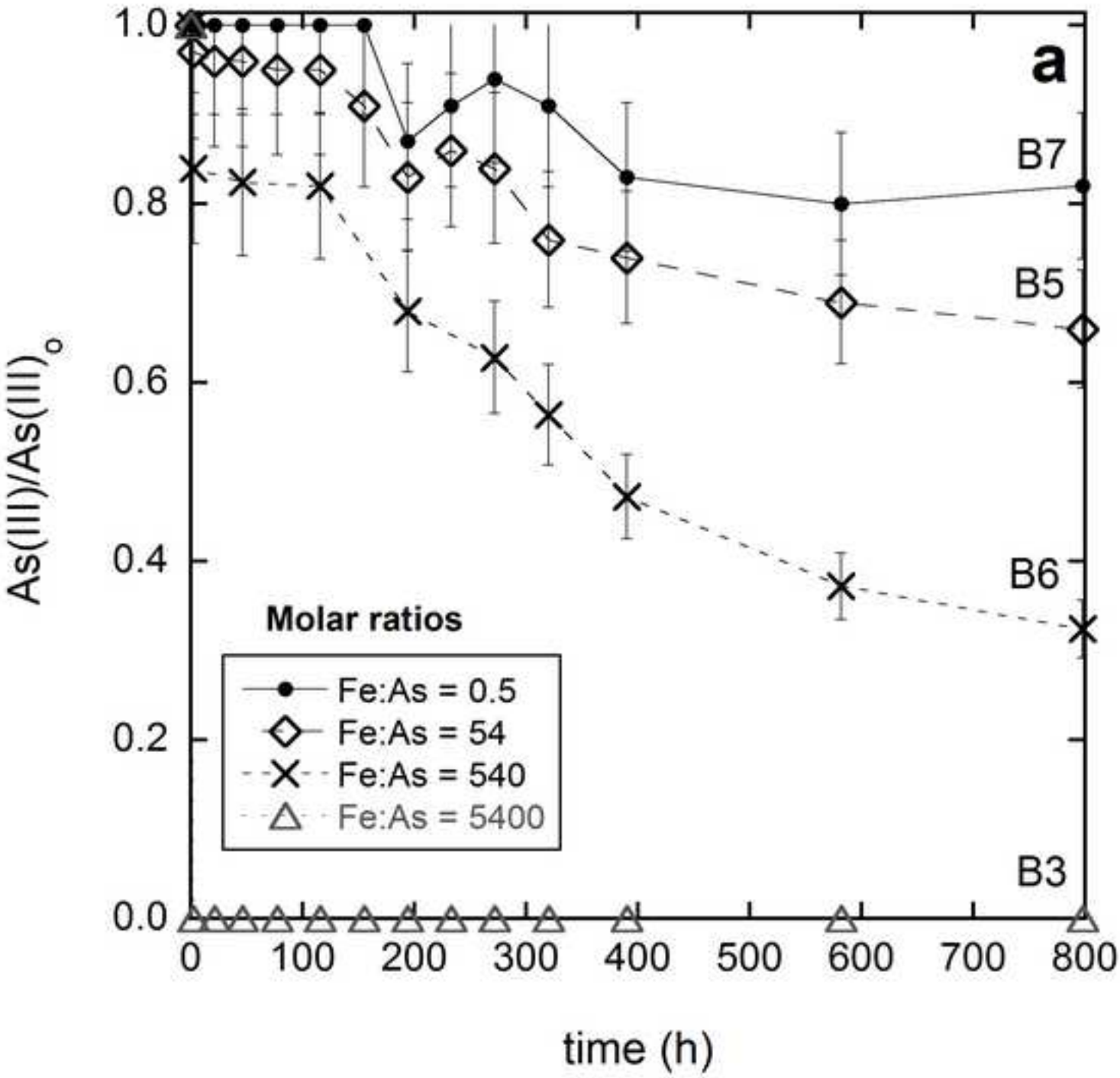

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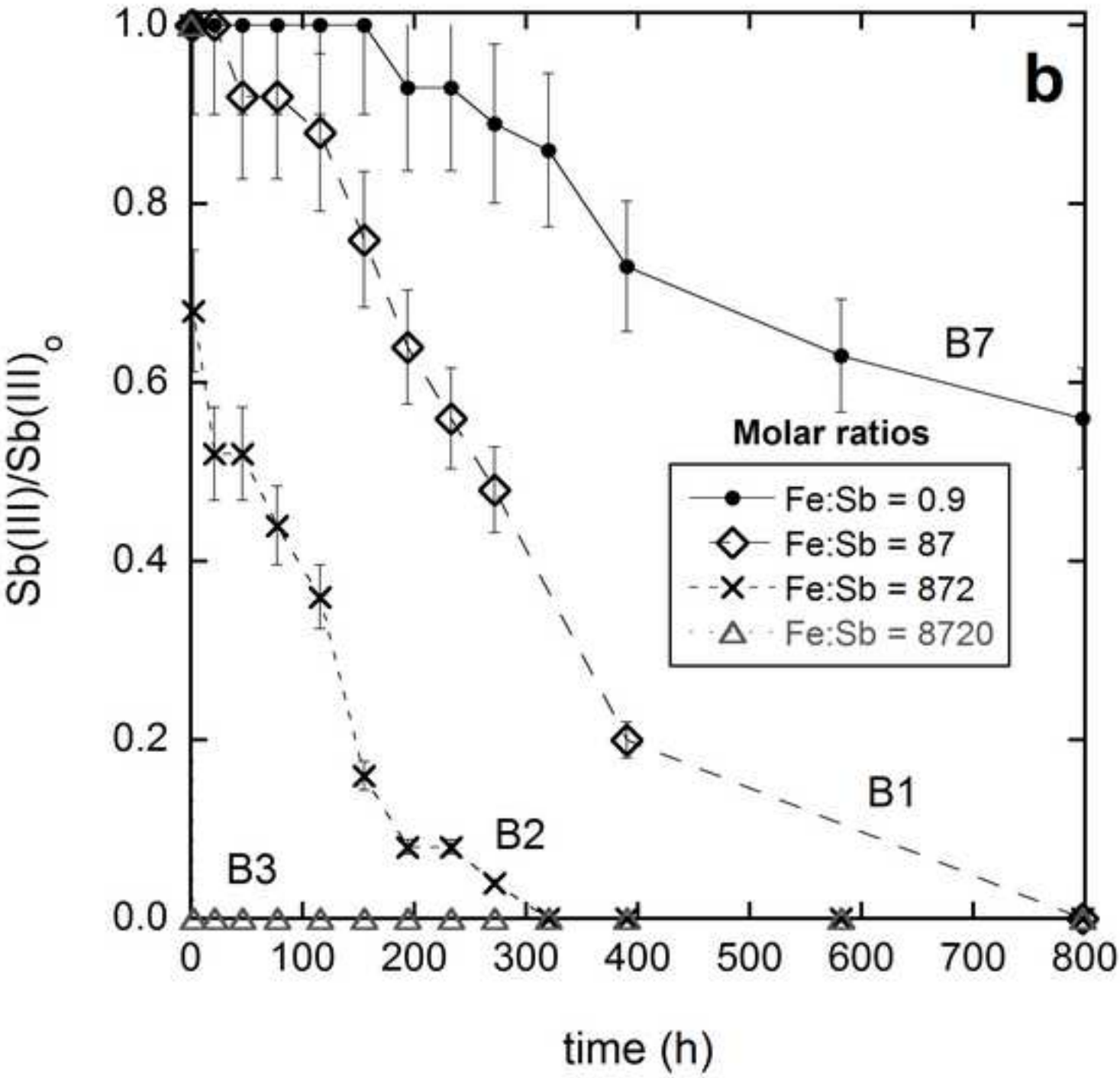

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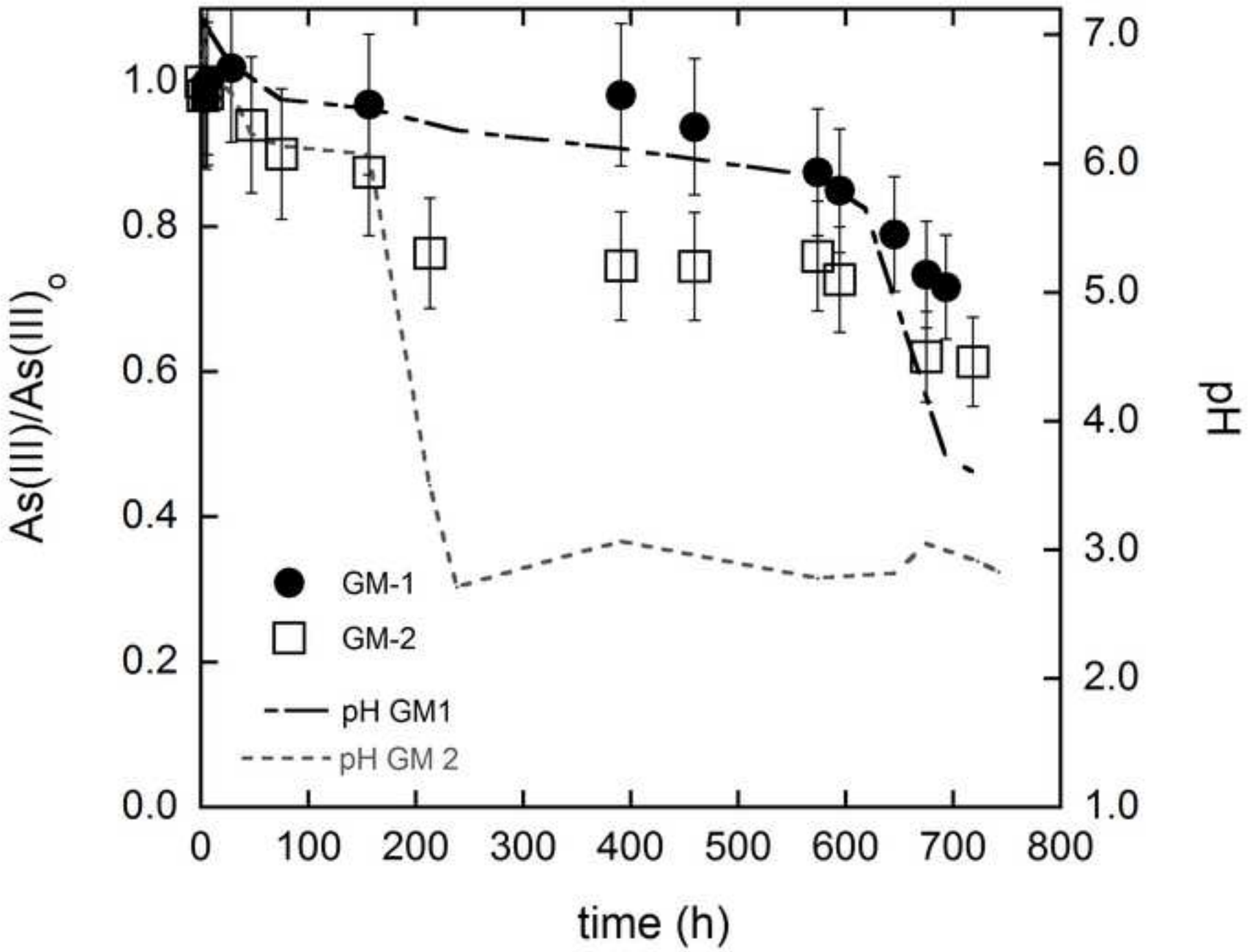

Figure 6a

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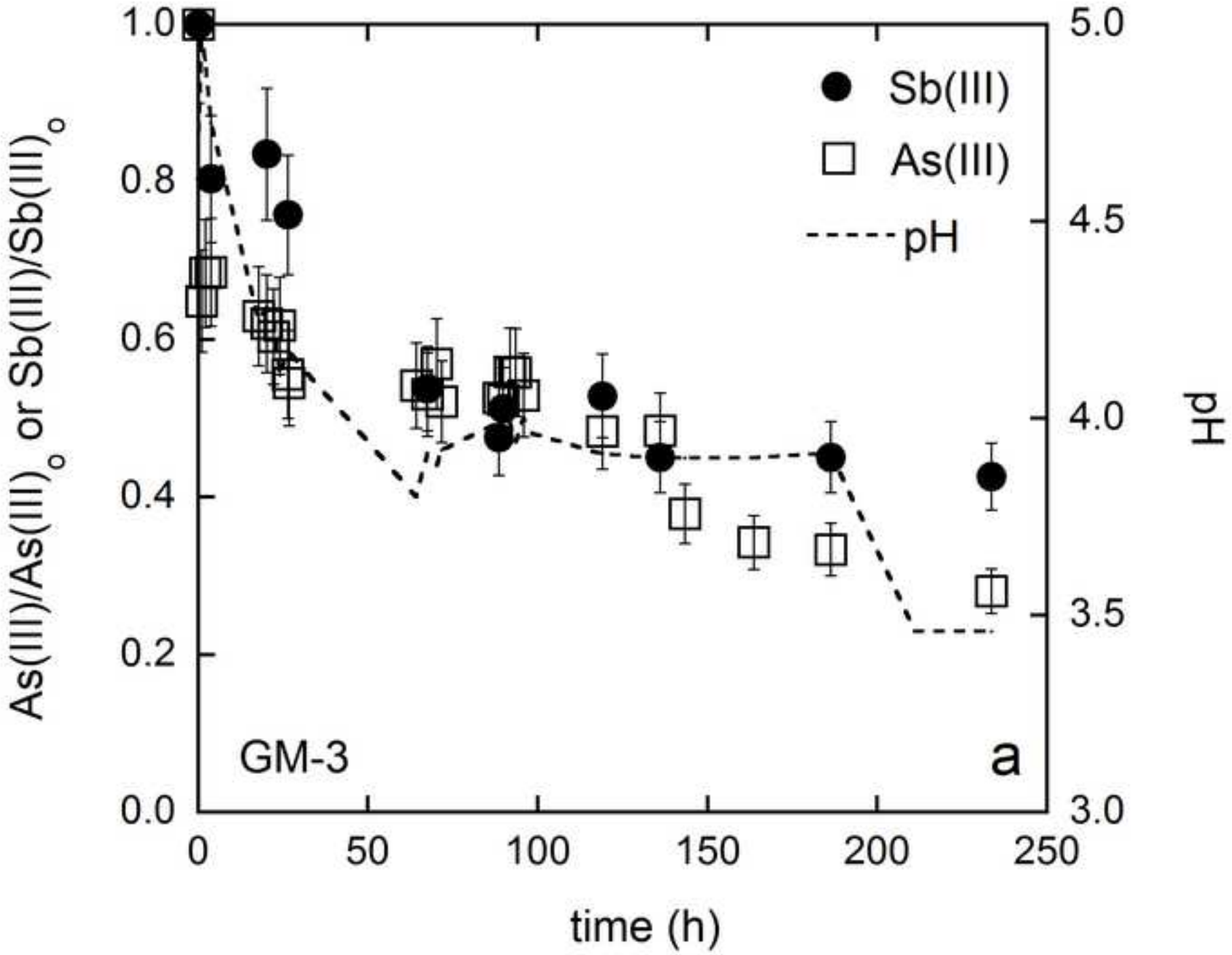

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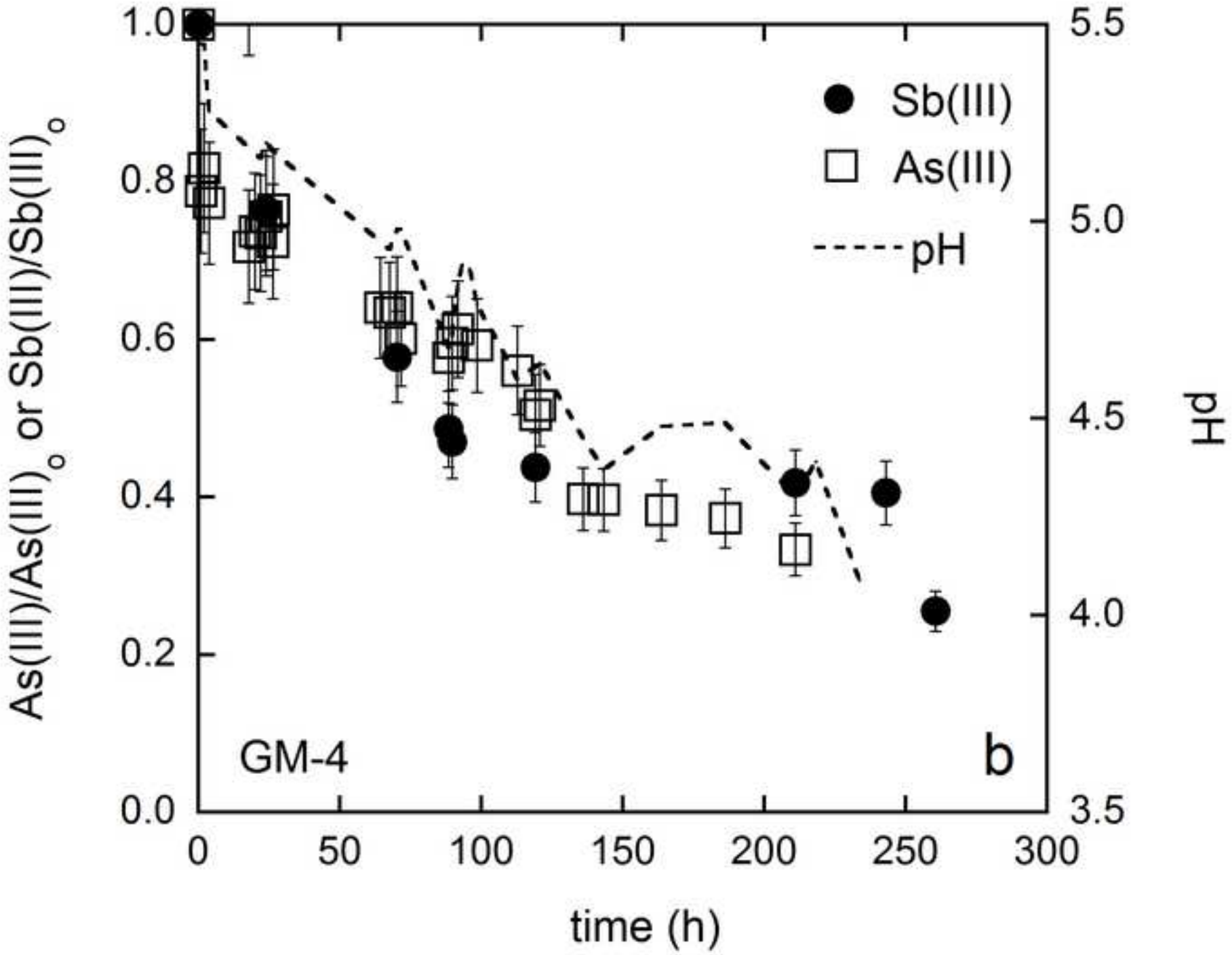

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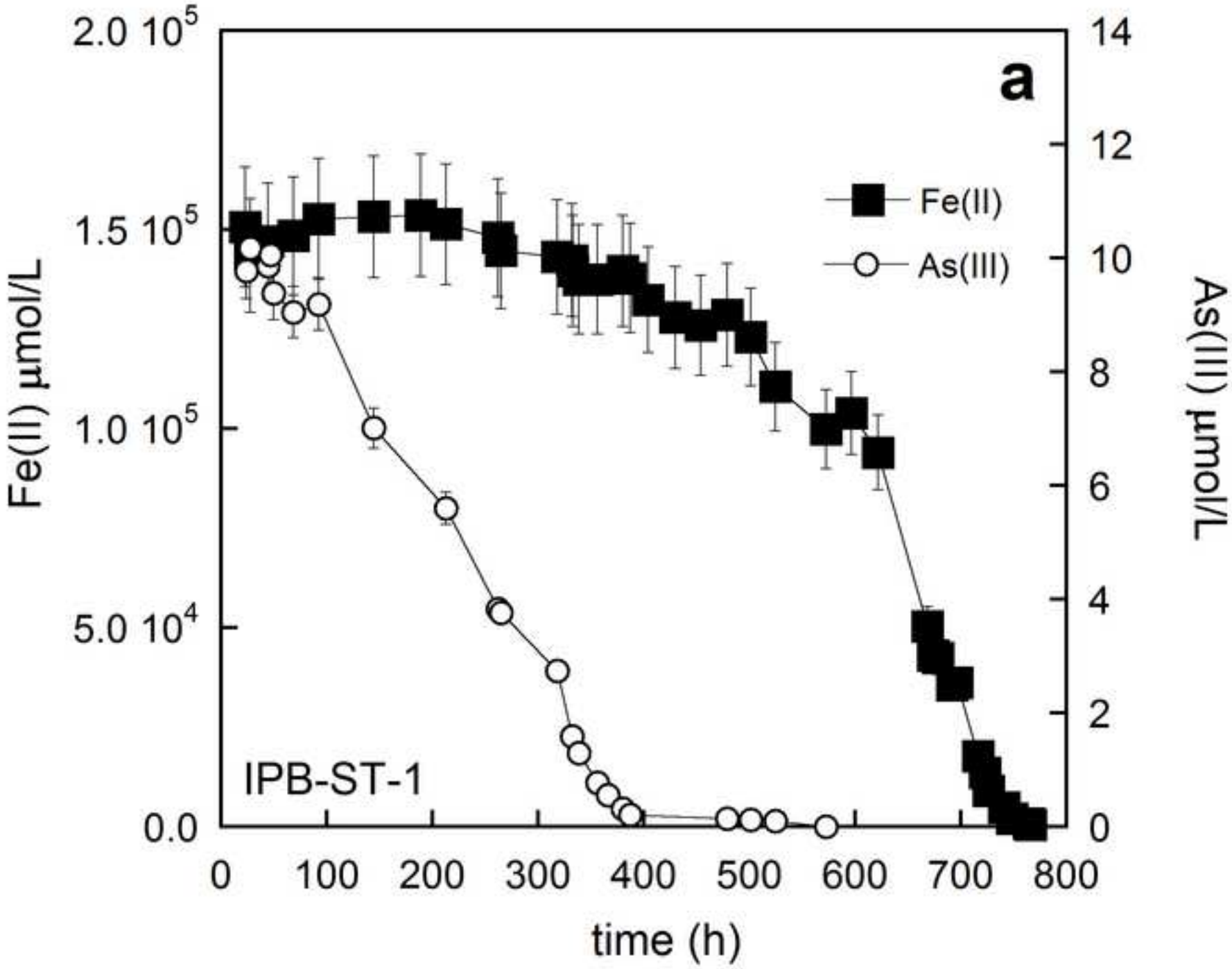

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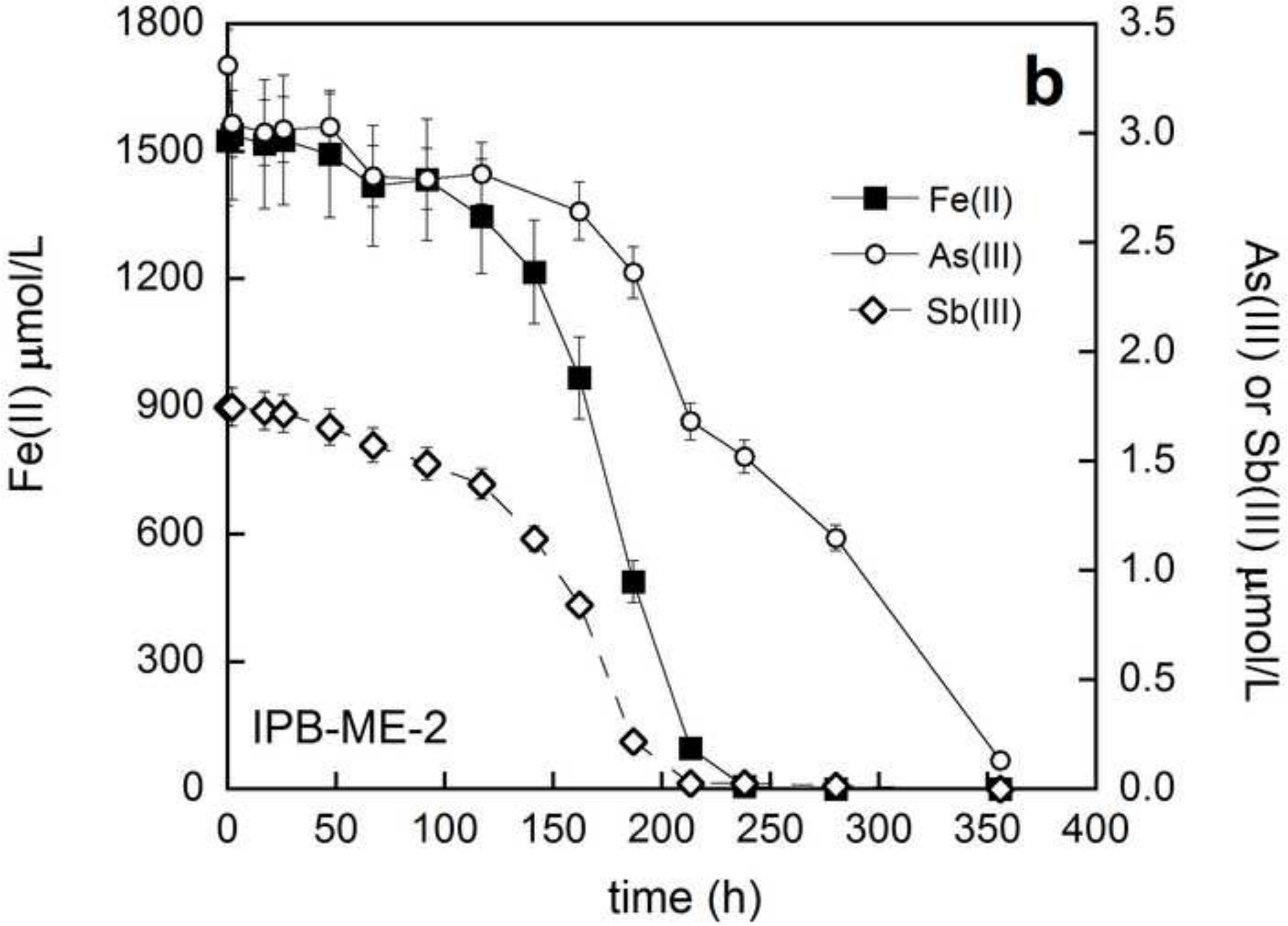

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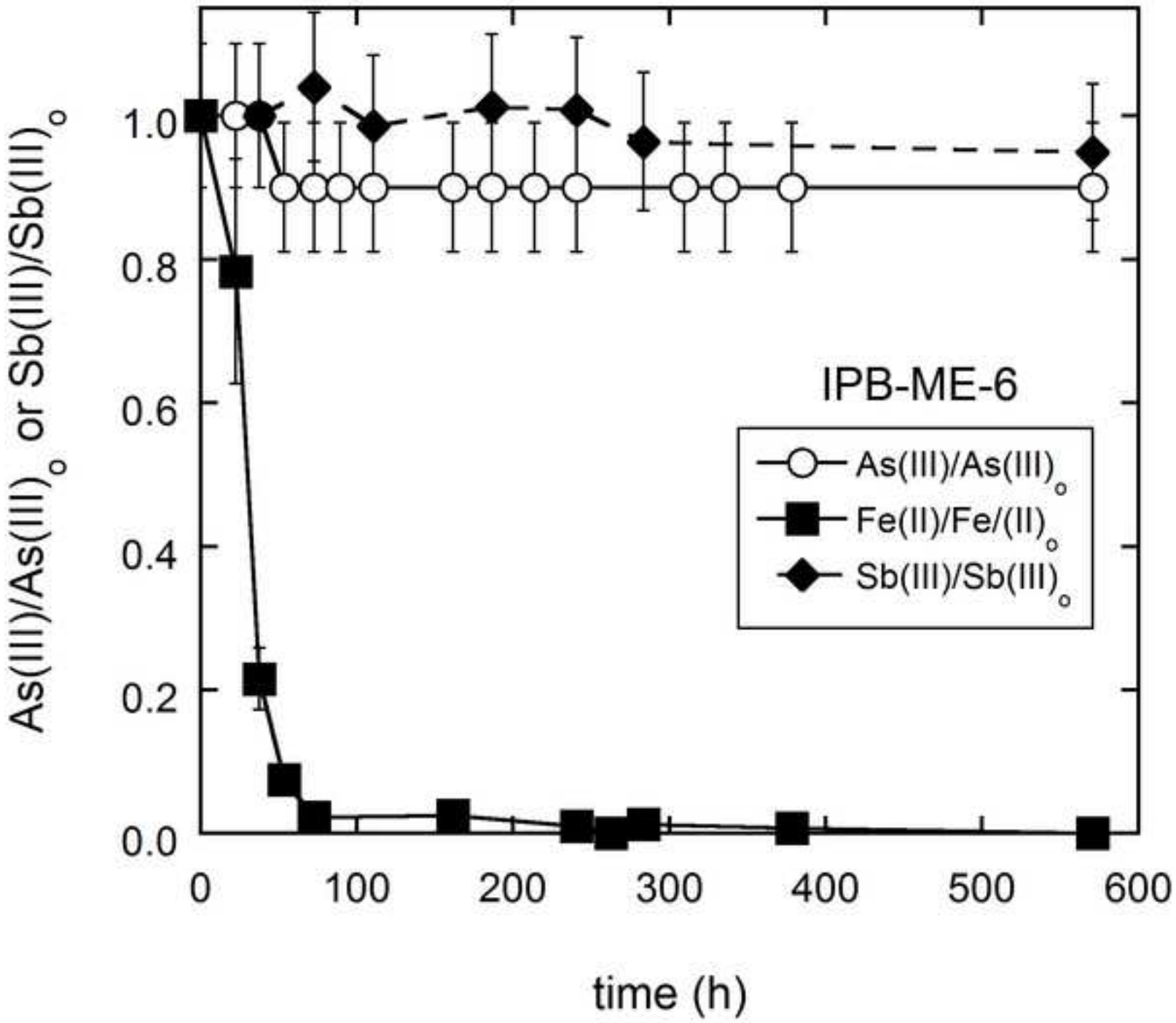

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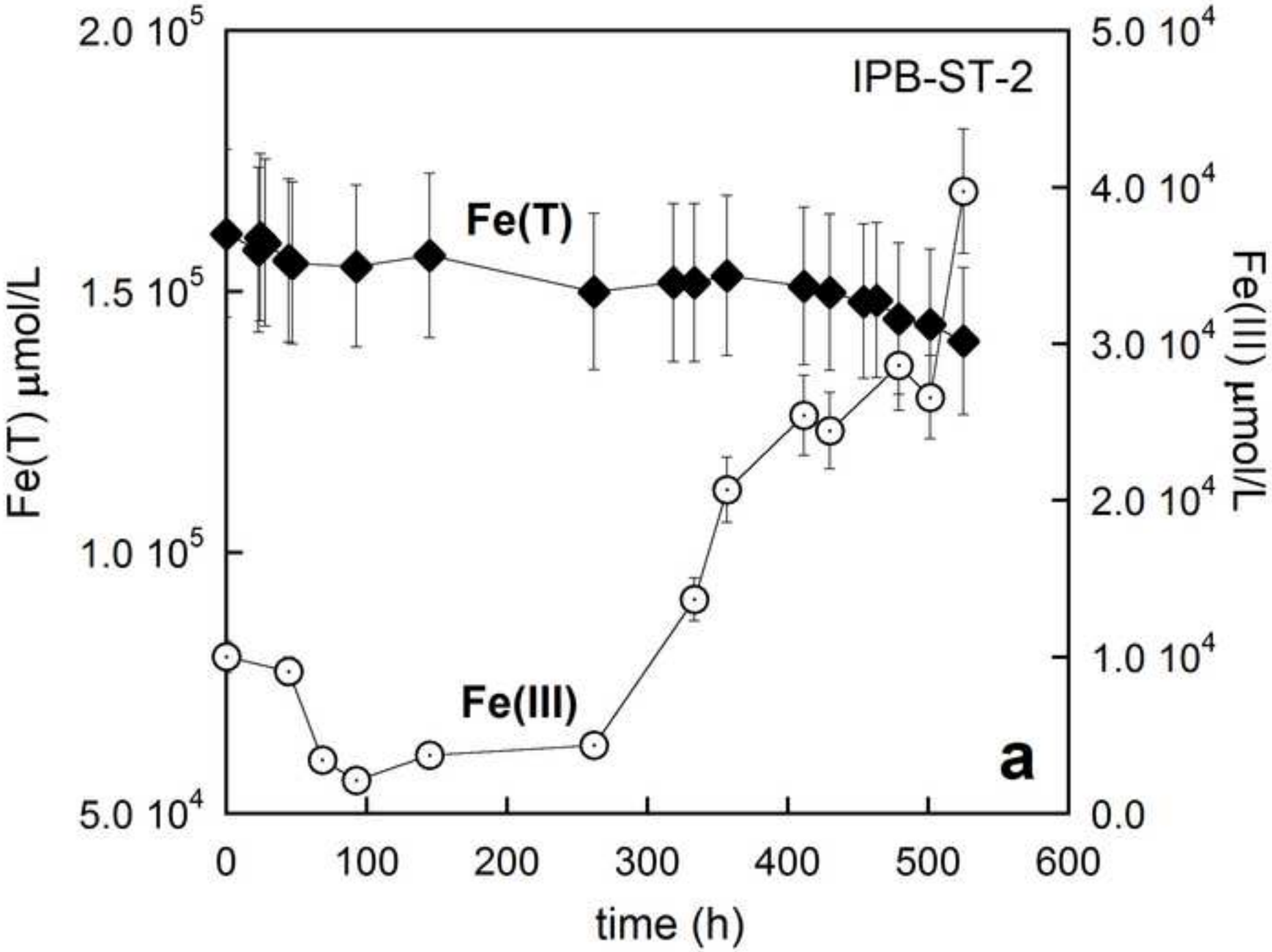

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