



# Assessing the influence of humic acids on the weathering of galena and its environmental implications

Qingyou Liu<sup>a</sup>, Heping Li<sup>a,\*</sup>, Guoheng Jin<sup>a,b</sup>, Kai Zheng<sup>a,b</sup>, Luying Wang<sup>a,b</sup>

<sup>a</sup> Key Laboratory of High-Temperature and High-Pressure Study of the Earth's Interior, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China

<sup>b</sup> University of Chinese Academy of Sciences, Beijing 100039, China

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## ABSTRACT

Galena weathering often occurs in nature and releases metal ions during the process. Humic acid (HA), a critical particle of natural organic matter, binds metal ions, thus affecting metal transfer and transformation. In this work, an electrochemical method combined with spectroscopic techniques was adopted to investigate the interfacial processes involved in galena weathering under acidic and alkaline conditions, as well as in the presence of HA. The results show that the initial step of galena weathering involved the transformation  $Pb^{2+}$  and  $S^0$ , regardless of whether the solution was acidic or alkaline. Under acidic conditions,  $S^0$  and  $Pb^{2+}$  further transform into anglesite, and HA adsorbs on the galena surface, inhibiting the transformation of sulfur. HA and Pb (II) ions form bridging complexes. Under alkaline conditions without HA, the sulfur produced undergoes no transformation, whereas  $Pb^{2+}$  will transform into PbO. The presence of HA changes the galena weathering mechanism via ionization effect, and  $Pb^{2+}$  is ultimately converted into anglesite. Higher acidity in acidic conditions or higher alkalinity in alkaline conditions causes galena corrosion when the electrolyte does not contain HA. Conversely, higher pH always accelerates galena corrosion when the electrolyte contains HA, whether the electrolyte is acidic or alkaline. At the same acidity/alkalinity, increasing the concentration of HA inhibits galena weathering. Galena will release  $134.7 \text{ g m}^{-2} \text{ y}^{-1} Pb^{2+}$  to solution at pH 2.5, and the amount decreases to  $28.09 \text{ g m}^{-2} \text{ y}^{-1}$  in the presence of 1000 mg/L HA. This study provides an in situ electrochemical method for the assessment of galena weathering.

## 1. Introduction

Galena, one of the most common lead-bearing sulfide minerals, can easily weather when exposed to oxidizing conditions and form more stable secondary lead species (Benvenuti et al., 2000; Keim and Markl, 2015). In natural geologic environments, anglesite and cerussite are most often transformed during galena weathering (Lara et al., 2011; Szczerba and Sawlowicz, 2009). During the galena weathering process, heavy metals, such as Pb, As, and Cr, are released and cause ecological risk to the soil-plant system and the sediment-water column (Azhari et al., 2017). In a laboratory setting, Hsieh and Huang (1989) were the first to systematically study the dissolution of PbS(s) in dilute aqueous solutions. The results show that the dissolution reaction is pH dependent, enhanced by dissolved oxygen and slightly affected by photo-irradiation. The overall dissolution processes is controlled by surface reaction. Based on this study, Fornasiero et al. (1994) used Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy to investigate the surface oxidation of galena subject to various conditioning environments. They proposed a mechanism of oxidation

involving the dissolution of lead and sulfide ions, the formation of lead sulfoxy species and lead carbonate, and their subsequent adsorption or precipitation on the galena surface. Similarly, they determined the oxidation reaction is pH dependent, and the oxidative dissolution of PbS(s) occurs primarily by the reaction (1), as Hsieh and Huang (1989) reported. In recent years, isotope technique has been a useful tool for the investigation of galena oxidation. Heidel and Tichomirowa (2011) investigated galena oxidation mechanisms via oxygen and sulfur isotopes. The oxygen isotope composition of sulphate produced from galena oxidation could be determined for the first time. Sulfur isotopes of sulphate showed an enrichment of  $(32) S^0$  in sulphate (relative to galena), which increases with increasing pH. Moreover, its enrichment processes may be associated with the formation of anglesite.



Under natural conditions, many studies (Acero et al., 2007; Gerson and O'Dea, 2003; Keim and Markl, 2015; Mikhlín et al., 2006; Ryan et al., 2001) have revealed the mechanism of galena weathering via

\* Corresponding author.

E-mail address: [liheping123@yahoo.com](mailto:liheping123@yahoo.com) (H. Li).

electrochemical methods and surface observation. The products include (1) the formation of chloropyromorphite by the addition of phosphate to Pb-contaminated soil, which has been proposed as a remediation technology to reduce the mobility and bioavailability of Pb; (2) acidic aerobic dissolution to form  $\text{H}_2\text{SO}_4$  and  $\text{Pb}^{2+} \cdot 6\text{H}_2\text{O}$  (Gerson and O'Dea, 2003); (3) the formation of acceptor-type cation vacancies  $\text{Pb}_{1-x}\text{S}$  (Mikhlin et al., 2006); and (4) the formation of a lead-deficient and sulfur-rich surface layer, which is consistent with the observed non-stoichiometry between dissolved sulfur and lead in acidic environments. Acero et al. (2007) revealed that galena dissolution is controlled by diffusion processes or by the mixed-controlled diffusion of reactants and products between the bulk solutions and the reacting surfaces. Based on the above research, Keim and Markl (2015) explained the weathering of galena in detail, and they presented hydro-geochemical models of Pb dissolution and re-precipitation during the weathering of ore deposits containing galena. Generally, galena weathering is an electrochemical process. Different lead or sulfur intermediate products may occur, but the consensus is galena oxidative dissolution occurs first via reactions (1) (Paul et al., 1978). Then,  $\text{Pb}^{2+}$  or  $\text{S}^\circ$  further transform, depending on the conditions.

HA is known to comprise supra-molecular structures of small biomolecular fragments bound together through cation bridging, hydrogen bonding and hydrophobic interactions (Sutton and Sposito, 2005). HA has two polar functional groups, a phenolic group and a carboxylic group, and the dissociated groups can easily bind to metal ions (Ondrasek et al., 2018). Thus, these groups might control metal transfer and transformation (Liu and Gonzalez, 2000) and affect the mobility, toxicity and bioavailability of metal ions in the environment (Koopal et al., 2005; Schulten and Schnitzer, 1997). It is important to understand the nature of organic functional groups of HA in the process of determining the stability of metal complexes and the effects on environmental detoxification (Pandey et al., 2000). HAs may enhance or diminish heavy metal adsorption, depending on the relative stabilities of metal-humate binary and metal-humate-surface ternary complexes as a function of pH (Apak, 2002). It is known that HA forms negatively charged complexes with heavy metal ions (Yang and Van Den Berg, 2009). In accordance with hard and soft acid/base theory, Cu(II) and Pb(II) ions react with HA via O and N atoms and form stable complexes (Hizal and Apak, 2006). Most heavy metals are known to share common binding sites in humic substances (Tipping et al., 2002). Heavy metals and HA may form different complexes. For example,  $\text{Pb}^{2+}$  and HA can form bridging (Fig. 1a) or unidentate (Fig. 1b) HA-Pb(II) complexes (Jerzykiewicz, 2004).

For these reasons, the study of HA has attracted the attention of scientists in various fields (Genc-Fuhrman et al., 2016; Huang et al., 2017; Martin et al., 2017). In the geochemical processing of Au, Chotpantarat et al. (2015) revealed that HA can dissolve and transport Au because Au and HA can form a complex. Bergeron and Harrison (1989) confirmed the significance of humic substances in the chemical transport of Au and revealed an increase in Au solubility according to the following order: humic acid < fulvic acid < potassium humate. In the environmental field, acid mine drainage and heavy metal ion pollution from sulfide mineral oxidation are serious issues; the passivation of sulfide minerals prior to oxidation has been an efficient means to prevent these issues (Sahoo et al., 2013). HA is interesting because it has a relatively environmentally friendly way to block electrochemical

activity through passivation of the electrode surface (Acai et al., 2009), and it participates in high-affinity interactions with oxide surfaces (Li et al., 2015). It should be noted that HA itself is potentially toxic to humans, due to its acidity when partly dissolved in water, and thus, HA is not a suitable adsorbent without pre-treatment. The use of different physical-chemical methods to modify HA is one of the most common pre-treatment measures (Celebi and Erten, 2010; Jiang et al., 2014; Lei et al., 2016).

As mentioned above, galena is often weathered under natural conditions and releases metal ions during this process. Meanwhile, HA binds metal ions and, thus, affects metal transfer and transformation. Therefore, HA must affect galena weathering when both are exposed to the same near-surface oxidizing conditions, and these conditions are often present in Pb-Zn ore mines. To our knowledge, no data have been reported on the effects of HA during galena weathering. In this work, polarization spectroscopy and electrochemical impedance spectroscopy (EIS) were used to investigate galena weathering under different concentrations of HA with different pH values, with aimed to (1) reveal the galena electrochemical behaviors in the presences of HA and (2) quantitatively determine how HA concentration and pH affect galena weathering.

## 2. Materials and methods

### 2.1. Galena electrode

Galena samples were collected from the Huize Pb-Zn deposit (Yunnan Province, China). X-ray powder diffraction analysis showed that the samples were composed of PbS and ZnS, and the electron microprobe tests revealed the percentages of the elements Pb, Zn and S (wt%) were 86.53%, 0.0064% and 13.39%, respectively. The galena samples were cut into an approximately cubic shape to guarantee their bottom surface, namely the working area, was  $0.25 \text{ cm}^2$ . Then, the samples were connected to a copper wire using silver paint on the upper surface and sealed with epoxy resin, keeping only the working surface exposed to the solution (Liu et al., 2017; Wang et al., 2016). Muñoz et al. (1998) reported this detailed electrode preparation method. Prior to each test, the mineral electrode was polished with 1200-grit carbide paper to obtain a fresh surface, degreased using alcohol, rinsed with deionized water and dried in a stream of air.

### 2.2. HA electrolyte

HA (CAS 1415-93-6, Shanghai Aladdin Bio-Chem Technology Co., LTD), with more than 90% (wt%) as fulvic acid (FA,  $\text{C}_9\text{H}_9\text{NO}_6$ ), was used as the electrolyte. First, HA was dissolved in water to obtain 0, 10, 100 and 1000 mg/L electrolyte solutions. Then,  $\text{HNO}_3$  and NaOH solutions were used to adjust the pH of the electrolyte solutions to 2.5, 4.5, 8.5 and 10.5, respectively.

### 2.3. Electrochemical measurements

As stated previously, galena weathering is an electrochemical process. Therefore, its weathering character and parameters were evaluated through electrochemical test. Electrochemical measurements were performed using a computer-controlled electrochemical measurement system (PARSTAT 2273, Princeton Applied Research) with a conventional three-electrode electrolytic cell that included a platinum auxiliary electrode, a pyrite working electrode and a saturated calomel reference electrode (SCE). All other potentials in this study are quoted with respect to the SCE (0.242 V vs. standard hydrogen electrode), if not otherwise stated. To minimize the resistance of the solution between the working electrode and the reference electrode, the reference electrode was connected to a Luggin capillary.

In this work, polarization curve and electrochemical impedance spectroscopy (EIS) were used to investigate the electrochemical

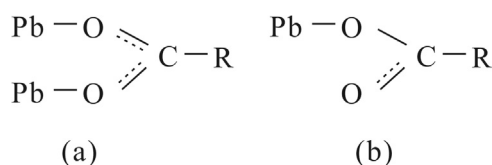


Fig. 1. Modes of coordination of Pb(II) ions to carboxyl groups in HA. (a) bridging complexes, (b) unidentate complexes.

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