Available online at www.sciencedirect.com

ScienceDirect

Geochimica et Cosmochimica Acta 188 (2016) 393–406

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

Effect of biofilm coatings at metal-oxide/water interfaces II: Competitive sorption between Pb(II) and Zn(II) at *Shewanella oneidensis*/metal-oxide/water interfaces

Yingge Wang[a,*], Alexandre Gélabert[a,b], F. Marc Michel[a,c,1], Yongseong Choi[d], Peter J. Eng[e], Alfred M. Spormann[f], Gordon E. Brown Jr.[a,c,g]

[a] *Surface & Aqueous Geochemistry Group, Department of Geological Sciences, School of Earth, Energy, and Environmental Sciences, Stanford University, Stanford, CA 94305-2115, USA*
[b] *Department of Earth Sciences, University of Paris 7, IMPMC, IPGP, CNRS, UMR 7590, F-75015 Paris, France*
[c] *Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, MS 69, 2575 Sand Hill Road, Menlo Park, CA 94025, USA*
[d] *Advanced Photon Source, Argonne National Laboratory, 9700 South Cass Ave., Argonne, IL 60439, USA*
[e] *Consortium for Advanced Radiation Sources, University of Chicago, Chicago, IL 60637, USA*
[f] *Department of Chemical Engineering, Stanford University, Stanford, CA 94305, USA*
[g] *Department of Photon Science, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025, USA*

Received 19 March 2013; accepted in revised form 22 April 2016; available online 7 May 2016

Abstract

Competitive sorption of Pb(II) and Zn(II) on *Shewanella oneidensis* MR-1 biofilm-coated single-crystal α-Al_2O_3 $(1\,\bar{1}\,0\,2)$ and α-Fe_2O_3 $(0\,0\,0\,1)$ surfaces was investigated using long-period X-ray standing wave-florescence yield (LP-XSW-FY) spectroscopy. *In situ* partitioning of aqueous Pb(II) and Zn(II) between the biofilms and underlying metal-oxide substrates was probed following exposure of these complex interfaces to equi-molar Pb and Zn solutions (0.01 M $NaNO_3$ as background electrolyte, pH = 6.0, and 3-h equilibration time). At higher Pb and Zn concentrations ($\geqslant 10^{-5}$ M), more than 99% of these ions partitioned into the biofilms at *S. oneidensis*/α-Al_2O_3 $(1\,\bar{1}\,0\,2)$/water interfaces, which is consistent with the partitioning behavior of both Pb(II) or Zn(II) in single-metal-ion experiments. Thus, no apparent competitive effects were found in this system at these relatively high metal-ion concentrations. However, at lower equi-molar concentrations ($\leqslant 10^{-6}$ M), Pb(II) and Zn(II) partitioning in the same system changed significantly compared to the single-metal-ion systems. The presence of Zn(II) decreased Pb(II) partitioning onto α-Al_2O_3 $(1\,\bar{1}\,0\,2)$ substantially (~52% to ~13% at 10^{-7} M, and ~23% to ~5% at 10^{-6} M), whereas the presence of Pb(II) caused more Zn(II) to partition onto α-Al_2O_3 $(1\,\bar{1}\,0\,2)$ surfaces (~15% to ~28% at 10^{-7} M, and ~1% to ~7% at 10^{-6} M). The higher observed partitioning of Zn(II) (~28%) at the α-Al_2O_3 $(1\,\bar{1}\,0\,2)$ surfaces compared to Pb(II) (~13%) in the mixed-metal-ion systems at the lowest concentration (10^{-7} M) suggests that Zn(II) is slightly favored over Pb(II) for sorption sites on α-Al_2O_3 $(1\,\bar{1}\,0\,2)$ surfaces under our experimental conditions. Competitive sorption of Pb(II) and Zn(II) at *S. oneidensis*/α-Fe_2O_3 $(0\,0\,0\,1)$/water interfaces at equi-molar metal-ion concentrations of $\leqslant 10^{-6}$ M showed that the presence of Pb(II) ions decreased Zn(II) partitioning onto α-Fe_2O_3 $(0\,0\,0\,1)$ significantly (~45% to <1% at 10^{-7} M, and ~41% to 3% at 10^{-6} M), whereas adding Zn(II) caused only small changes in Pb(II) partitioning (~59% to ~47% at 10^{-7} M, and ~26% to ~23% at 10^{-6} M), suggesting that Pb(II) strongly outcompetes Zn(II) for sorption sites on *S. oneidensis*-coated α-Fe_2O_3 $(0\,0\,0\,1)$ surfaces. Our study implies that caution should be taken when applying

---

[*] Corresponding author. Tel.: +1 650 223 3711; fax: +1 650 729 2199.
E-mail address: wang.yingge@gmail.com (Y. Wang).

[1] Present address: Department of Geosciences, Virginia Tech, Blacksburg, VA 24061, USA.

http://dx.doi.org/10.1016/j.gca.2016.04.054

results obtained from partitioning studies of single-metal-ion systems to mixed-metal-ion systems at complex biofilm/mineral interfaces.

Keywords: *Shewanella oneidensis*; Biofilm; Metal-oxide surface; Competitive sorption; Pb; Zn; Hematite; Alumina; X-ray standing wave; LP-XSW-FY; Metal partitioning

---

1. INTRODUCTION

Although metal-ion sorption on Fe- and Al-(oxyhydr) oxides minerals has been well studied at the molecular level (e.g., Bargar et al., 1997a,b; Brown and Sturchio, 2002), the mobility and bioavailability of metal ions in natural environments are still largely unknown due to the fact that mineral surfaces in soils can be extensively colonized by microbes or coated by natural organic matter (NOM) (Mayer, 1994; Barker et al., 1998; Ransom et al., 1999; Bonneville et al., 2009; Ganor et al., 2009; Lalonde et al., 2012). Minerals, microbial biofilms, and NOM have been shown to have strong affinities for metal ions and are good natural sorbents for heavy metal toxins (e.g., Kinniburgh et al., 1996; Fein et al., 1997; Brown et al., 1999; Tipping, 2002). Extensive studies have focused on metal-ion sorption on mineral surfaces (e.g., Brown and Sturchio, 2002), bacterial surfaces (e.g., Fein et al., 1997; Johnson et al., 2007), and/or soil NOM (e.g., Kinniburgh et al., 1996; Tipping, 2002). However, most of these studies investigated metal-ion sorption in single-substrate systems (e.g., mineral, bacteria, or NOM). As a result, metal cycling in more complex systems composed of a combination of microbial, organic, and mineral constituents remains under-explored and relatively poorly understood. This is due mainly to the inherent complexity of such systems and the lack of analytical tools capable of probing the partitioning of metal ions between different pools of reactive sites.

Recent advances in the use of high intensity synchrotron radiation, combined with the long period X-ray standing wave fluorescence yield (LP-XSW-FY) method, now enable studies of elemental distributions at a variety of buried interfaces and multi-layered substrates (e.g., Bedzyk et al., 1986, 1988, 1990; Abruna et al., 1989; Wang et al., 1991, 1992, 2013, 2016; Templeton et al., 2001, 2003; Yoon et al., 2005; Kitts et al., 2009; Levard et al., 2011). The LP-XSW-FY technique uses the superposition of incoming and reflected X-ray beams on a reflecting surface under total external reflection conditions to generate a well-defined periodic electric field intensity variation known as an X-ray standing wave (XSW). Fluorescence yield of specific elements of interest is measured as a function of incident X-ray angle and quantified by XSW modeling to obtain the distribution and relative abundance of elements present both within a layer (film) and at an interface. The LP-XSW-FY technique has been reviewed in detail previously (Bedzyk and Cheng, 2002; Trainor et al., 2006) and several prior studies have demonstrated the utility of this approach for probing mineral substrates coated with biofilms/organic matter (Templeton et al., 2001, 2003; Yoon et al., 2005; Wang et al., 2013, 2016). In the first LP-XSW-FY study of its kind, Templeton et al. (2001) evaluated the *in situ* partitioning of Pb(II) at *Burkholderia cepacia* biofilm-coated single-crystal metal-oxide surfaces. They found that the *B. cepacia* coating provided additional sorption sites and did not block reactive sites on the metal-oxide surfaces. We recently carried out LP-XSW-FY experiments on the partitioning of Pb(II) and Zn(II) at more environmentally realistic *Shewanella oneidensis* MR-1 biofilm/metal-oxide interfaces and obtained similar results (Wang et al., 2016), which suggests that these conclusions may be more general.

However, natural soil and aqueous systems have complex solution compositions; in many cases, a wide range of dissolved metals are present simultaneously and may interfere with each other for uptake and accumulation on mineral surfaces, in microbial biofilms, or in NOM (Benjamin and Leckie, 1981a; Fowle and Fein, 1999; Burnett et al., 2007). One can expect that various metal ions could compete to a greater or lesser extent for the available sorption sites. Therefore, studying competitive sorption effects in multi-component systems is essential for understanding metal-ion sorption in complex natural systems. Failure to account for competitive effects could lead to errors in predicting the fate and transport of the metal ions and, therefore, the toxicity to humans and biota in natural systems, as well as the efficiency of many engineered systems for heavy metal removal (Benjamin and Leckie, 1981a; Burnett et al., 2007).

A few studies to date have focused on competitive metal-ion sorption on bacterial surfaces (see, e.g., Mullen et al., 1989; Fowle and Fein, 1999; Burnett et al., 2007; Claessens and Van Cappellen, 2007). Mullen et al. (1989) investigated the adsorption of Ag(I), La(III), Cu(II), and Cd(II) by *Bacillus cereus*, *Bacillus subtilis*, *Escherichia coli*, and *Pseudomonas aeruginosa* and found that metal-ion affinity to bacterial surfaces decreased in the order Ag(I) > La(III) > Cu(II) > Cd(II) (Mullen et al., 1989). Fowle and Fein (1999) studied mixed-metal-ion sorption of Cd (II), Cu(II), Pb(II), and Ca(II), by two Gram positive bacteria (*Bacillus subtilis* and *Bacillus licheniformis*) and found that the chemical equilibrium approach for single-metal-ion systems could be used to predict competitive sorption behavior in these multi-metal-ion systems (Fowle and Fein, 1999). Burnett et al. (2007) performed multi-metal-ion competitive sorption experiments in which aqueous Cd(II), Cu(II), Mn(II), Ni(II), and Pb(II) ions were reacted simultaneously with the surfaces of the thermophile bacterium *Anoxybacillus flavithermus*, and found the following order of affinity for the bacterial surface: Mn(II) ~ Ni(II) < Zn(II) < Cd(II) < Pb(II) ~ Cu(II). They found that metal-ion stability constants obtained from single-metal-