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Organic ligand-induced dissolution kinetics of antimony trioxide

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ABSTRACT

The influence of low-molecular-weight dissolved organic matter (LMWDOM) on the dissolution rate of Sb_2O_3 was investigated. Some representative LMWDOMs with carboxyl, hydroxyl, hydrosulfuryl and amidogen groups occurring naturally in the solution were chosen, namely oxalic acid, citric acid, tartaric acid, EDTA, salicylic acid, phthalandione, glycine, thiolactic acid, xylitol, glucose and catechol. These LMWDOMs were dissolved in inert buffers at pH = 3.7, 6.6 and 8.6 and added to powdered Sb_2O_3 in a stirred, thermostatted reactor (25°C). The addition of EDTA, tartaric acid, thiolactic acid, citric acid and oxalic acid solutions at pH 3.7 and catechol at pH 8.6 increased the rate of release of antimony. In the 10 mmol/L thiolactic acid solution, up to 97% by mass of the antimony was released after 120 min reaction. There was no effect on the dissolution of Sb_2O_3 for the other ligands. A weak correlation between dissolution rate with the dissociation constant of ligands and the stability of the dissolved complex was also found. All the results showed that the extent of the promoting effect of ligands on the dissolution of Sb_2O_3 was not determined by the stability of the dissolved complex, but by the dissociation constant of ligands and detachment rate of surface chelates from the mineral surface. This study can not only help in further understanding the effect of individual low-molecular-weight organic ligands, but also provides a reference to deduce the effect of natural organic matters with oxygen-bearing functional groups on the dissolution of antimony oxide minerals.

Introduction

Antimony (Sb) is a potentially toxic trace element, which is classified as a priority pollutant by the USEPA and the EU (CEC, 1976; USEPA, 1979). In light of antimony's character as an emerging, global pollutant (Amarasiriwardena and Wu, 2011; He et al., 2012; Maher, 2009; Reimann et al., 2010; Shotyk et al., 2005), it is necessary to understand the factors governing its rate of migration rate from its natural sources as well as from polluted environmental compartments. The ore mineral stibnite (Sb_2S_3), associated with its principal weathering products senarmontite (cubic Sb_2O_3), valentinite (orthorhombic Sb_2O_3) and stibiconite (Sb_3O_6OH), is the most important natural source of antimony in the supergene environment (Filella et al., 2009). It is believed that the dissolution of these phases dramatically contributes to the Sb pollution in water draining zones. The dissolution behaviors of stibnite and the release kinetics of Sb from the dissolution of Sb_2O_3 under environmental conditions have been investigated widely (Biver and Shotyk, 2012a, 2012b, 2013; Hu et al., 2014, 2015, 2016a, 2016b). Although antimony

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oxide is the primary natural source of antimony, only thermodynamic solubility data (Zotov et al., 2003) and dissolution kinetics at different pH values are available, while nothing is known on its dissolution kinetics in the presence of ligands. Yet the presence of ligands is thought to contribute significantly to the dissolution of oxide, sulfide and silicate minerals (Aiken et al., 2011; Biber et al., 1994; Brantley, 2008; Davis et al., 1995; Furrer and Stumm, 1986; Gulley-Stahl et al., 2010; Liang et al., 2000; Sposito, 2004; Waples et al., 2005). Because mine areas might comprise deciduous forests, meadows, and farmland, with soil of the dystric cambisol type, when water coming from precipitation and percolating through the soil and the fault system comes into contact with the ores, it can thus be expected to contain organic matter of pedogenic origin. Among the organic carbons in the soil solution, low-molecular-weight organic acids (LMWOA), such as carboxylic acids (*e.g.*, acetic acids, oxalic, tartaric acids, citric acid and aromatic acids), amino acids (*e.g.*, glycine, arginine and lysine) and carbohydrates, along with their polymerized forms, can take up to more than one half of the organic carbons (Sposito, 2008). Biver and Shotyk (2012b) have examined the effect of acetic, oxalic, citric, and salicylic acids, EDTA, glucose, catechol, glycine, cysteine, desferrioxamine-B, and natural chestnut leaf litter extract on the dissolution of stibnite. Both enhancement and retardation of the dissolution rate of Sb_2S_3 were observed, and a linear relationship was found between the rates of ligand-promoted dissolution and the pK_a values of the ligands. In addition, the stability and structure of aqueous complexes formed by Sb(III) and Sb(V) with carboxylic acids, catechol, and amino acids having O- and N-functional groups typical of natural organic matter were determined from solubility, *in situ* potentiometry and X-ray absorption fine structure spectroscopy measurements (Anderegg and Malik, 1970; Filella and May, 2005; Tella and Pokrovski, 2009, 2012; Tserenpil and Liu, 2011). However, the effect of organic ligands on the dissolution rate of antimony oxides is unknown.

The aim of the present work is to investigate the possible effects of common low-molecular-weight dissolved organic matters on the dissolution kinetics of Sb_2O_3 over an environmentally representative pH range and at different dosage levels. The present work, as part of a broader study of the dissolution behavior of antimony minerals, can help clarify the geochemical cycle and fate of Sb in the environment.

1. Materials and methods

1.1. *Organic matters*

Common low-molecular-weight dissolved organic matters (oxalic acid, citric acid, tartaric acid, EDTA, salicylic acid, phthalandione, glycine, thiolactic acid, xylitol, glucose and catechol) were selected. They exhibit a wide range of molecular structures that could affect their coordination chemistry with surface-bound and aqueous-phase metals (Furrer and Stumm, 1986), and acidity constants that span a wide range (Table 1). In the experiments on the effect of pH, the concentration of the eleven ligands was adjusted to 1 mmol/L. To study the effect of ligand dosages, their concentrations were increased to 5 mmol/L and 10 mmol/L. All organic matters were purchased from Sinopharm Chemical Reagent Beijing Co. Ltd. (Beijing, China). All reagents used were analytically pure grade or better.

Table 1 – Organic ligands used in this study and stepwise dissociation constants (p*K*) of their functional groups and stability constants of Sb(III)-ligand complexes ($\log\beta_n$).

Ligands	Acidity constants	Stability constants of Sb(III)-ligand complexes	References
Oxalic acid (H_2L)	$pK_1(CO_2H) = 1.40$	$Sb(OH)_2Oxa^-$ (3.8 ± 0.2)	Neaman et al. (2006). Tella and Pokrovski (2009)
	$pK_2(CO_2H) = 4.26$	$Sb(Oxa)_2^-$ (5.9 ± 0.1)	
Citric acid (H_3L)	$pK_1(CO_2H) = 3.13$	$Sb(OH)_2(HCit)^{2-}$ (0.1 ± 0.2)	Neaman et al. (2006), Tella and Pokrovski (2009)
	$pK_2(CO_2H) = 4.76$	$Sb(OH)_2(H_2Cit)^-$ (4.6 ± 0.3)	
	$pK_3\ (CO_2H) = 6.40$	$Sb(H_2Cit)_2^-$ (−3.9 ± 0.3)	
	$pK_4\ (OH) \sim 16$		
Tartaric acid (H_4Tar)	$pK_1(CO_2H) = 3.04$	$SbTar^+$ (9.855)	Tella and Pokrovski (2009), Filella and May (2005)
	$pK_2(CO_2H) = 4.37$	$SbTar^{2-}$ (17.184)	
	$pK_3(COH) \sim 14.0$	$SbTar(OH)^-$ (9.408)	
	$pK_4(COH) \sim 15.5$	$Sb_2H_{-2}(OH)_2Tar_2^{2-}$ (22.17)	
EDTA (H_4L)	$pK_1(CO_2H) = 2.0$	$SbEDTA^-$ (26.77)	Filella and May (2005)
	$pK_2(CO_2H) = 2.7$	SbHEDTA (28.00)	
	$pK_3(CO_2H) = 6.1$	$SbEDTA(OH)^{2-}$ (20.760)	
	$pK_4(CO_2H) \sim 10.2$	$SbEDTA(OH)_2^{3-}$ (12.676)	
Phthalic acid (H_2L)	$pK_1(CO_2H) = 2.95$	–	Neaman et al. (2006)
	$pK_2(CO_2H) = 5.41$		
Salicylic acid (H_2L)	$pK_1(CO_2H) = 2.97$	–	Neaman et al. (2006)
	$pK_2(OH) = 13.7$		
Glycine (HGly)	$pK_1(CO_2H) = 2.34$	$SbGly^{2+}$ (11.240)	Tella and Pokrovski (2009), Filella and May (2005)
	$pK_2(NH_3) = 9.\ 58$		
Thiolactic acid (H_2ThLac)	$pK_1(CO_2H) = 3.63$	$SbLac^{2+}$ (8.717)	Filella and May (2005)
	$pK_2(SH) = 10.24$	$SbLac_2^+$ (13.476)	
Xylitol (Xyl)	$pK(OH) = 13.7$	–	Wu and Ke (1986)
Glucose	$pK(OH) = 12.43$	–	Dean (1973)
Catechol (H_2L)	$pK_1(OH) = 9.45$	$SbCat(OH)^0$ (3.119)	Tella and Pokrovski (2009), Filella and May (2005)
	$pK_2(OH) = 13.0$	$SbCat_2^-$ (0.543)	