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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.

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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 ($\text{Sb}_3\text{O}_6\text{OH}$), 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 dystic 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 Shoty (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 (pK) 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)	$\text{pK}_1(\text{CO}_2\text{H}) = 1.40$ $\text{pK}_2(\text{CO}_2\text{H}) = 4.26$	$\text{Sb}(\text{OH})_2\text{Oxa}^- (3.8 \pm 0.2)$ $\text{Sb}(\text{Oxa})_2^- (5.9 \pm 0.1)$	Neaman et al. (2006). Tella and Pokrovski (2009)
Citric acid (H_3L)	$\text{pK}_1(\text{CO}_2\text{H}) = 3.13$ $\text{pK}_2(\text{CO}_2\text{H}) = 4.76$ $\text{pK}_3(\text{CO}_2\text{H}) = 6.40$ $\text{pK}_4(\text{OH}) \sim 16$	$\text{Sb}(\text{OH})_2(\text{HCit})^{2-} (0.1 \pm 0.2)$ $\text{Sb}(\text{OH})_2(\text{H}_2\text{Cit})^- (4.6 \pm 0.3)$ $\text{Sb}(\text{H}_2\text{Cit})_2^- (-3.9 \pm 0.3)$	Neaman et al. (2006), Tella and Pokrovski (2009)
Tartaric acid (H_4Tar)	$\text{pK}_1(\text{CO}_2\text{H}) = 3.04$ $\text{pK}_2(\text{CO}_2\text{H}) = 4.37$ $\text{pK}_3(\text{COH}) \sim 14.0$ $\text{pK}_4(\text{COH}) \sim 15.5$	$\text{SbTar}^+ (9.855)$ $\text{SbTar}^{2-} (17.184)$ $\text{SbTar}(\text{OH})^- (9.408)$ $\text{Sb}_2\text{H}_{-2}(\text{OH})_2\text{Tar}_2^{2-} (22.17)$	Tella and Pokrovski (2009), Filella and May (2005)
EDTA (H_4L)	$\text{pK}_1(\text{CO}_2\text{H}) = 2.0$ $\text{pK}_2(\text{CO}_2\text{H}) = 2.7$ $\text{pK}_3(\text{CO}_2\text{H}) = 6.1$ $\text{pK}_4(\text{CO}_2\text{H}) \sim 10.2$	$\text{SbEDTA}^- (26.77)$ $\text{SbHEDTA} (28.00)$ $\text{SbEDTA}(\text{OH})^{2-} (20.760)$ $\text{SbEDTA}(\text{OH})_2^{3-} (12.676)$	Filella and May (2005)
Phthalic acid (H_2L)	$\text{pK}_1(\text{CO}_2\text{H}) = 2.95$ $\text{pK}_2(\text{CO}_2\text{H}) = 5.41$	–	Neaman et al. (2006)
Salicylic acid (H_2L)	$\text{pK}_1(\text{CO}_2\text{H}) = 2.97$ $\text{pK}_2(\text{OH}) = 13.7$	–	Neaman et al. (2006)
Glycine (HGly)	$\text{pK}_1(\text{CO}_2\text{H}) = 2.34$ $\text{pK}_2(\text{NH}_3) = 9.58$	$\text{SbGly}^{2+} (11.240)$	Tella and Pokrovski (2009), Filella and May (2005)
Thiolactic acid (H_2ThLac)	$\text{pK}_1(\text{CO}_2\text{H}) = 3.63$ $\text{pK}_2(\text{SH}) = 10.24$	$\text{SbLac}^{2+} (8.717)$ $\text{SbLac}_2^+ (13.476)$	Filella and May (2005)
Xylitol (Xyl)	$\text{pK}(\text{OH}) = 13.7$	–	Wu and Ke (1986)
Glucose	$\text{pK}(\text{OH}) = 12.43$	–	Dean (1973)
Catechol (H_2L)	$\text{pK}_1(\text{OH}) = 9.45$ $\text{pK}_2(\text{OH}) = 13.0$	$\text{SbCat}(\text{OH})^0 (3.119)$ $\text{SbCat}_2^- (0.543)$	Tella and Pokrovski (2009), Filella and May (2005)

1.2. Methods

The antimony trioxide (Sb_2O_3) (99.999%) used, with specific surface area $0.873 \text{ m}^2/\text{g}$, has been described in our previous study (Hu et al., 2014). Rates of dissolution of Sb_2O_3 were measured in 500 mL beakers in the dark. For every run, 250 mL buffer solution with organic matter was introduced into the reactor and an accurately weighed mass of 50 mg ($7.86 \text{ mmol/m}^2 \text{ Sb}$) Sb_2O_3 was added. The solutions were stirred using a magnetic stirrer. Approximately 1 mL aqueous solution was taken at certain intervals for 120 min, using disposable PP/PE syringes (Zhiyu medical equipment Co., Ltd., Shanghai, China) fitted with CME $0.22 \mu\text{m}$ hydrophilic syringe filters (Jinteng Laboratory Equipment Co., Ltd., Tianjin, China). Each experiment was conducted in triplicate. The following buffering agents were used: pH 3.7: sulfanilic acid ($\text{pK}_a = 3.3$), pH 6.6: MES (2-(N-morpholino)-ethanesulfonic acid, $\text{pK}_a = 6.2$) and pH 8.6: MOPS (3-(N-morpholino)-propanesulfonic acid, $\text{pK}_a = 7.2$). These buffers were used because they are known to have scant tendency to form complexes with metal ions (Good et al., 1966). The total buffer concentration was 0.05 mol/L and the pH was adjusted to the desired value with 1 mol/L NaOH solution using a pH meter (Sartorius (Shanghai) Trading Co., Ltd., China). The ionic strength of each solution was adjusted to 0.1 mol/L using NaClO_4 . Control experiments were performed using only the buffer solutions with different pHs. The pH values of the solutions were measured at the beginning and end of the experiments. No drift in pH was observed within experimental error; thus, only the initial pH value was reported for each experiment. All reagents were purchased from Sinopharm Chemical Reagent Beijing Co. Ltd. (Beijing, China). All reagents used were analytically pure grade or better.

1.3. Analysis of Sb_{tot} and Sb(III)

The analysis of Sb_{tot} and Sb(III) , calculation of the dissolution rate of Sb_2O_3 and normalization of the total released amount Sb_{tot} with respect to the specific surface area of Sb_2O_3 refer to our previous method (Hu et al., 2014). For all experiments, the concentration of Sb_{tot} was almost equal to the corresponding concentration of Sb(III) in the solution, so we only provide the concentration of Sb_{tot} in the subsequent sections.

2. Results and discussion

2.1. Ligand trends on release rate of Sb at different pH

The release of antimony in the solution was linear during the first 60 min, followed by a parabolic rate law after 60 min for some ligands (EDTA, thiolactic acid and catechol). In the subsequent discussion, the dissolution rate of Sb_2O_3 was evaluated using the concentration of mobilized antimony in the linear range from 0 to 60 min only (Table 2).

Strikingly, at pH 3.7, the promotion effect observed for the aliphatic ligands decreased in the order: EDTA > tartaric acid > thiolactic acid > citric acid > oxalic acid after 100 min, but the aromatic ligands had little effect on the release of Sb (Fig. 1a). After 60 min reaction, the amount of Sb was almost unchanged in the EDTA and thiolactic acid solutions, while it still increased linearly in the tartaric acid solution even after 90 min, and finally surpassed the concentration of Sb in the thiolactic acid solution.

The release of Sb at pH 6.6 showed a different result from that at pH 3.7 (Fig. 1b). All released concentrations of Sb in the presence of ligands were lower than that at pH 3.7. Only thiolactic acid and catechol had a considerably larger effect on the enhancement of Sb release. The other ligands had little effect on the release of Sb. In the thiolactic acid solution, similar to the results at pH 3.7, the release of Sb increased linearly for the first 60 min and then reached a plateau.

At pH 8.6, the trends of ligands on the release extent of Sb present an entirely different result from acidic conditions (pH 3.7 and 6.6) (Fig. 1c). Firstly, catechol and thiolactic acid had a considerably large promoting effect on the release of Sb, but the effect of other ligands was slight. Secondly, unlike the trend of ligands at pH 6.6, the release rate and concentration of Sb in the presence of catechol were much larger than those in the thiolactic acid solution.

Furthermore, it can be found from Fig. 1d that: (1) the presence of EDTA, thiolactic acid, tartaric acid, citric acid and catechol could enhance the release of Sb, while the effect of other ligands was very slight; (2) with the increase of pH, the release rate of Sb decreased sharply in the presence of EDTA, thiolactic acid and tartaric acid; (3) the release rate of Sb

Table 2 – Dissolution rates of Sb_2O_3 in the first 60 min in the presence of organic acids at different pH and ligand dosage (unit: $\text{mg/m}^2/\text{min}$).

Organic acids	pH 3.7	pH 6.6	pH 8.6	pH 6.6	
		1 mmol/L		5 mmol/L	10 mmol/L
Ligand-free	0.043	0.160	0.126	0.160	0.160
Oxalic acid	0.060	0.163	0.134	0.157	0.163
Citric acid	0.417	0.231	0.191	0.682	1.455
Tartaric acid	2.537	0.160	0.157	0.263	0.442
EDTA	4.806	0.191	0.154	0.265	0.525
Salicylic acid	0.080	0.157	0.143	0.137	0.163
Phthalandione	0.120	0.154	0.131	0.157	0.163
Glycine	0.066	0.151	0.131	0.137	0.131
Thiolactic acid	3.830	1.507	0.916	5.574	8.071
Xylitol	0.088	0.143	0.114	0.160	0.126
Glucose	0.060	0.163	0.106	0.148	0.114
Catechol	0.203	0.531	2.451	1.926	2.586

Fig. 1 – (a–c) Surface-normalized amount of Sb_{tot} mobilized as function of time at pH 3.7, pH 6.6 and pH 8.6 and (d) variation of dissolution rates with pH for various ligands.

increased sharply in the presence of catechol with the increase of pH; (4) on the whole, the dissolution rate of Sb_2O_3 (4.806, 3.830 and 2.537 mg/m²/min) in the EDTA, thiolactic acid and tartaric acid solutions under the acidic condition was larger than that (2.451 mg/m²/min) in the catechol solution under the alkaline condition. Thus, the discussion below will focus on the effects of EDTA, thiolactic acid, tartaric acid, citric acid and catechol.

2.1.1. Effect of EDTA

As we know, the rate of ligand-promoted dissolution is, in the general case, proportional to the surface concentration of the surface complex (Furrer and Stumm, 1986; Sposito, 2004). Both of the 1st two pK_a values ($pK_{a1} = 2.0$ and $pK_{a2} = 2.7$) of EDTA are below 3.0, so that at pH = 3.7, two fully and one incompletely deprotonated carboxyl group are available for multidentate chelation with Sb (Biver and Shotyk, 2012b). Moreover, the stability constant ($\log K$) values of $SbEDTA^-$, $SbHEDTA$, $SbEDTA(OH)^{2-}$ and $SbEDTA(OH)_2^{3-}$, published as 26.77, 28.00, 20.76 and 12.68, respectively (Filella and May, 2005), are higher than the stability constants of other Sb-ligand complexes, so at pH 3.7, EDTA exhibited excellent promoting ability on the dissolution of Sb_2O_3 . By contrast, a decrease in the dissolution rate was found at pH 6.6 and 8.6. This is because pH 6.6 is close to the $pH_{PZC} = 5.98$ (pH at point of zero charge) of

Sb_2O_3 (Xu and Schoonen, 2000). Stumm and Morgan (1996) emphasized that the pH-dependent surface charge of minerals is an important factor in their dissolution, because the polarization affects surface chemical bonds and causes generalized minimum dissolution rates of minerals at the pH_{PZC} . In addition, previous research on equilibria of Sb(III)–polyaminocarboxylic acids has shown that when $pH > 7$, surface precipitation would occur (Filella and May, 2005), so that little dissolved Sb could be detected in the alkaline solution.

2.1.2. Effect of thiolactic acid

Similar to the effect of EDTA, the rate of thiolactic acid-promoted dissolution is related to the concentration of the surface Sb-thiolactate complex. The pK_1 (CO_2H) and pK_2 (SH) of thiolactic acid are equal to 3.63 and 10.24 (Tella and Pokrovski, 2009). The studied pH range was 3.7–8.6, so the sulfhydryl group ($-SH$) was unavailable for chelation with Sb. Thus, the effect of thiolactic acid may be understood as analogous to the interaction between $Sb(OH)_3$ and lactic acid (HLac), with pK_1 (CO_2H) = 3.86 (Neaman et al., 2006). Previous research (Tella and Pokrovski, 2009) showed that at $pH < 4$, a bidentate complex, $SbLac_2^-$, formed according to the reaction:

When $\text{pH} > 4$, in addition to SbLac_2^- , Sb(OH)Lac_2^- also formed according to the reaction below:

In addition, the dosage of thiolactic acid was found to have an important influence on the release rate of Sb. When the concentration of thiolactic acid increased to 5 and 10 from 1 mmol/L, the release rate of Sb increased to 5.574 and 8.071 from 1.507 mg/m²/min. Thus, as the pH increased, the free thiolactic acid concentration (undeprotonated carboxyl group) decreased, fewer surface complexes of Sb-thiolactic acid were formed, and the dissolution rate of Sb_2O_3 was weakened.

2.1.3. Effect of tartaric acid

The pH-dependent trend in the tartaric acid (H_2Tar) solution is the same as the case of EDTA: pH has a great effect on the dissolution rate of Sb_2O_3 under the acidic condition because of large stability constants of Sb-Tar^{2-} complexes formed in Eqs. (3)–(7) (Filella and May, 2005), but almost no effect on the release of Sb at pH 6.6 and 8.6. In addition to above-mentioned reasons for the effect of EDTA and thiolactic acid on the release rate of Sb, as a multidentate chelator at pH = 6.6 and 8.6 (Tella and Pokrovski, 2009), the steric hindrance effect of Sb-tartaric acid complexes might be also a main factor.

2.1.4. Effect of citric acid

Citric acid has only a slight effect on the release of Sb. The pH-dependent trend is the same as the case of the above ligands: a promoting effect at pH 3.7, a retarding effect at pH = 6.6 and little effect in basic solution. According to the complex model, however, at pH = 6.6 and 8.6 the third protolysis of citric acid is almost complete ($\text{pK}_{\text{a}1} = 3.16$, $\text{pK}_{\text{a}2} = 4.76$ and $\text{pK}_{\text{a}3} = 6.40$) (Tella and Pokrovski, 2009), so that it should act as a multidentate chelator and promote the release of Sb. All the above is ascribed to the concentration of the surface Sb-citrate complex (Eqs. (8)–(10) (Tella and Pokrovski, 2009), the free citric acid concentration and the pH_{PZC} of Sb_2O_3 . At pH 3.7, more deprotonated citric acid was consumed, and more Sb-citrate complexes were formed than those at other pH values, so more Sb was released. At pH = 6.6, just as with EDTA, the impact of the pH_{PZC} of Sb_2O_3 played a decisive role. In the alkaline solution, surface precipitation would occur (Filella and May, 2005), so that little dissolved Sb was detected.

2.1.5. Effect of catechol

The presence of catechol (H_2Cat) inhibits the release of Sb at pH 3.7 and pH 6.6, while accelerating it at pH 8.6. A possible reason for this lies in the relatively high $\text{pK}_{\text{a}1}$ of the 1st (phenolic) deprotonation of catechol ($\text{pK}_{\text{a}1} = 9.45$) (Tella and Pokrovski, 2009). At pH = 8.7, at least part of the chelating functional groups are deprotonated, so that catechol can develop its chelating ability when the 1st pK_{a} is approached. The chelating reaction between Sb(OH)_3 and catechol can be written as:

As suggested by Filella and May (2005), and the stability constant ($\log K$) value of SbCat_2^- is 5.44 (Anderegg and Malik, 1970). According to Eq. (11), with the increase of pH, the reaction shifted to the right and then more Sb_2O_3 dissolved. At pH 3.7 and 6.6, catechol seems to act as a monodentate ligand with a decelerating effect on the dissolution rate. In addition to the effect of the pH_{PZC} (5.98) of Sb_2O_3 and the concentration of free ligand, as pointed out by Furrer and Stumm (1986), monodentate ligands frequently have no effect on or even retard dissolution by blocking access to the surface.

2.1.6. Effects of other ligands

The other organic ligands had virtually no effect on the release of Sb in the studied pH range (3.7–8.6) in spite of having greater complex stability constants with Sb (III). For example, the complex stability constant of glycine with Sb (SbGly^{2+}) is 11.24 (Filella and May, 2005), which is much larger than that of the catechol-Sb complex (SbCat(OH)^0) ($\log K = 3.119$). However, the former ligands showed a considerably smaller effect on the enhancement of release of Sb in comparison to the latter ligands.

2.2. Ligand trends on release rate of Sb at different dosages

The increase of ligand dosage, such as for thiolactic acid, catechol, citric acid, EDTA and tartaric acid, enhanced the dissolution rate of Sb_2O_3 (Fig. 2), especially in the thiolactic acid, catechol, and citric acid solutions. When the dosage of

Fig. 2 – Ligand trends in which the dissolution rates vary monotonically with the dosage of various ligands.

thiolactic acid increased to 5 and 10 mmol/L, the release rate of Sb was 4 times and 6 times greater, respectively, than that in the 1 mmol/L thiolactic acid solution, which was the case for catechol and citric acid as well. These results illustrated that the dissolution rate of Sb_2O_3 was related to the ligand concentration. With increasing ligand dosage, more dissolved Sb was chelated, which then promoted the dissolution of Sb_2O_3 . However, the increase ratio of the dissolution rate was found to be less than the increase ratio of the ligand dosage. This could be due to steric hindrance, which could occur when a high concentration of LMWDOMs were adsorbed to the surface of Sb_2O_3 . Meanwhile, this also could explain why the release rate of Sb in the 1 mmol/L thiolactic acid solution was larger in the first 60 min than that at 60–120 min. This occurred because the depletion of limited thiolactic acid over time resulted in insufficient ligand concentration for chelation with Sb(III) at 60–120 min, which was true for catechol as well. In addition, all the results illustrated that in the case of thiolactic acid, catechol and citric acid, the dosage exhibited a considerably larger effect on the enhancement of release of Sb from Sb_2O_3 compared with the effect of pH.

2.3. Ligand trends on release percentage of Sb

The release percentage of Sb to the total Sb contained in the original Sb_2O_3 at the end of the experiment under different conditions is summarized in Table 3. On the one hand, generalizing for pH 3, the promoting effect and extent of dissolution observed for the aliphatic ligands decreased in the order: EDTA > tartaric acid > thiolactic acid > citric acid > oxalic acid, but the aromatic ligands had only a slight effect on release. With the increase of pH (pH 6.6 and 8.6), the promoting effect and extent of dissolution for the aliphatic ligands was lessened on the whole compared to that at pH 3.7. For catechol, the release percentage of Sb (3.15%, 9.00% and 30.0% at pH 3.0, 6.6 and 8.6, respectively) increased noticeably with the increase of pH. Generalizing for increasing ligand dosage (5 and 10 mmol/L), a promoting effect on dissolution was observed for all ligands and decreased in the order: thiolactic acid > catechol > citric acid > EDTA. On the other hand, the release percentage of Sb increased from 20.4%, 9.00% and 3.29% to 97.0%, 59.8% and 22.3% when the dosage of thiolactic acid, catechol and citric acid increased from 1 to 10 mmol/L at pH 6.6, respectively. That is,

Fig. 3 – Correlation between logarithms of measured ligand-promoted dissolution rates and pK_a values of some ligands.

almost all Sb was released from Sb_2O_3 in the 10 mmol/L thiolactic acid solution. All the above results are explained by the effect of pH and dosage on the dissolution rate of Sb_2O_3 in the presence of ligands.

2.4. Correlation of acid dissociation constants and extent of complexation with dissolution rate

In some cases, there is a correlation between the $\log(r)$ and the pK_a of the dissociation step of a polyprotic acid believed to be relevant for complex formation, irrespective of whether the ligand exerts a promotive or an inhibitory effect (Biver and Shoty, 2012b; Ludwig et al., 1995). In this study, the $\log(r)$ shows a linear dependence on the pK_a in the six organic ligand solutions (Fig. 3), which suggests a potential relationship between the rate of ligand-promoted dissolution and the acid dissociation constants of the organic ligands (Eqs. (12)–(14)). The result confirmed the relationship between the dissolution rate of Sb_2O_3 and the dissociation of polyprotic acids. This is also consistent with most studies on the effects of ligands on dissolution rates of (hydr-) oxides: the rate of ligand-promoted dissolution (r) is proportional to the surface concentration of the surface complex. As we know, the surface concentration of a

Table 3 – Release percentage (wt%) of Sb at the end of experiments in the presence of various ligands at different pH and ligand dosage.

Organic ligands	pH 3.7	pH 6.6	pH 8.6	pH 6.6	
		1 mmol/L		5 mmol/L	10 mmol/L
Ligand-free	2.18	2.23	2.20	2.23	2.23
Oxalic acid	3.16	2.21	2.19	2.66	2.53
Citric acid	6.90	3.29	2.73	9.74	22.3
Tartaric acid	49.2	2.55	2.30	4.65	6.14
EDTA	53.4	2.85	2.20	4.26	9.63
Salicylic acid	1.90	2.28	2.13	2.23	2.56
Phthalandione	2.19	2.38	2.07	2.81	2.60
Glycine	1.69	2.34	2.26	2.13	2.52
Thiolactic acid	41.7	20.4	12.3	82.9	97.0
Xylitol	2.18	2.29	2.03	3.02	2.10
Glucose	1.76	2.35	1.96	2.17	2.31
Catechol	3.15	9.00	30.0	40.1	59.8

Fig. 4 – Ligand-promoted dissolution processes of Sb_2O_3 . SbL^+ refers to a series of Sb and low weight dissolved organic matter complexes.

complex is related to the solution phase concentration of the ligand via an adsorption isotherm. Thus, ultimately, the ligand-induced dissolution rate of Sb_2O_3 has a relationship with the solution-phase concentration of the ligand.

$$\text{pH } 3.7: \log(r) = -0.161\text{pK}_a + 1.03 (R^2 = 0.965) \quad (12)$$

$$\text{pH } 6.6: \log(r) = -0.098\text{pK}_a + 0.574 (R^2 = 0.974) \quad (13)$$

$$\text{pH } 8.6: \log(r) = 0.263\text{pK}_a - 2.24 (R^2 = 0.851) \quad (14)$$

However, no correlation between the extent of complexation in solution and the reaction rate was found. For instance, nearly all of the Sb present in solution was complexed by EDTA, oxalate and citrate under the conditions of the experiments; however, the dissolution rates and the observed trends of the rates as a function of pH differed widely for these three ligands. The simple principle of a correlation between dissolution rate and the stability of the dissolved complex (Ludwig et al., 1995) may not be generally applicable: the concept of the similarity between the surface complex and the aqueous complex present in solution, for instance, does not at all take into account the possibility of surface passivation resulting from polynuclear surface complexes, which may be of similar stability as the aqueous complexes, but quite reluctant to detach from the surface (Furrer and Stumm, 1986). Mechanistically, the ligand-promoted dissolution process of Sb_2O_3 (Fig. 4) can be deduced from the bioxalate ligand on a trivalent metal oxide (Furrer and Stumm, 1986): the first step is the reversible, rapid formation of a surface chelate, which in step 2 (the slow, rate-determining step) is detached by nucleophilic attack of water. Step 3 represents the rapid reprotonation of the fresh layer. The pK_a value of a ligand and stability constant of the Sb-ligand complex are key factors in the formation of a surface chelate, but not decisive factors in promoting the dissolution of Sb_2O_3 . Ultimately, the detachment rate of the surface chelate dominates the dissolution of Sb_2O_3 .

3. Conclusions

The effect of low-molecular-weight dissolved organic matter on the dissolution of Sb_2O_3 is part of a broader study of the dissolution behavior of antimony oxide minerals. EDTA,

tartaric acid, thiolactic acid, citric acid and oxalic acid as multidentate ligands have an overall promotive effect under acidic conditions, while catechol has an overall promotive effect under alkaline conditions. Comparing the dissolution rate of Sb_2O_3 with the initial dissolution rates of Sb_2S_3 in the presence of 1 mmol/L catechol, citrate and EDTA (Biver and Shoty, 2012a), we found the values of dissolution rates of Sb_2O_3 and Sb_2S_3 were of the same order of magnitude (10^{-5} mol/m²/min). Also, the trend of pH-dependent dissolution rates in the presence of the above ligands was similar between Sb_2O_3 and Sb_2S_3 . In addition, we found that the effect of some ligands on the dissolution of Sb_2O_3 was much larger than the effect of light at a similar pH level (Hu et al., 2014). Some ligands, such as EDTA, thiolactic acid, tartaric acid, citric acid and catechol have more influence on the dissolution rates of Sb_2O_3 than those at acidic pH values in the presence of light. A linear dependence of the logarithm (r) on pK_a was found for the six organic ligands, suggesting a potential relationship between the rate of ligand-promoted dissolution of Sb_2O_3 and acid dissociation constants of the organic ligands. No correlation was found between the complexation extent of Sb-ligands in solution and the release rate of Sb. In conclusion, the promotive extent of ligands on the dissolution of Sb_2O_3 was determined by the detachment rate of surface chelate from the mineral surface. These results in this paper help us to further recognize the geochemical implications of Sb. The effect of natural organic matters on the dissolution of Sb_2O_3 will be studied in future work.

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