Chemical Geology 294-295 (2012) 165–172

Contents lists available at SciVerse ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Research paper

Experimental study of the kinetics of ligand-promoted dissolution of stibnite (Sb_2S_3)

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ARTICLE INFO

Article history:
Received 4 March 2011
Received in revised form 4 November 2011
Accepted 7 November 2011
Available online 19 November 2011

Editor: Dr. J. Fein

Keywords:
Stibnite dissolution
Antimony mobilisation
Low molecular mass organic ligands
Ligand-promoted dissolution

ABSTRACT

Batch reactor experiments were carried out in order to investigate the influence of organic ligands in aqueous solution on the rate of dissolution of stibnite (Sb_2S_3). Ligands that may be regarded as representative of those occurring naturally in the soil solution were chosen, namely acetic, oxalic, citric, and salicylic acids, EDTA, glycine, cysteine, glucose, catechol, desferrioxamine-B, and standardized natural chestnut leaf litter extract. Millimolar concentrations of the ligands dissolved in inert buffers at $pH = 4$, 6, and 8 were added to powdered stibnite in a stirred, thermostatted reactor (25 °C) and the rate of increase in antimony concentration over time was monitored by ICP-OES. Dissolution rates were initially parabolic and settled into a linear regime. Comparison of initial and steady state rates achieved with different ligands with the blank experiments gives a very complex picture. Both rate enhancements and retardations are observed, and in some cases the net effect of a ligand at a given pH may be either an increased or a decreased mobilization with respect to the blank experiment, depending on the time of contact of the solution with the mineral. Rationalisations in terms of known principles of surface complexation are attempted. The extent of solution phase complexation of Sb(III) with the ligand under investigation is not found to be a decisive factor in the cases of those systems for which complexation constants are known. There is evidence suggesting that a linear free energy relationship may exist between the rates of ligand-promoted dissolution and pK_a values of the ligands under investigation.

1. Introduction

The present work is part of a broader study of the dissolution behaviour of antimony minerals, particularly stibnite (antimony(III)-sulfide, Sb_2S_3), in the context of the abandoned mining site of Goesdorf, Luxembourg. In the light of antimony's character as an emerging, global pollutant (Filella et al., 2002), there is a need to understand the factors governing its rate of mobilisation from its natural sources as well as from polluted environmental compartments. The geological setting of the Goesdorf mine was described in detail elsewhere (Filella et al., 2009a, 2009b). The deposit consists of hydrothermal lenticular stibnite veins in faults within Devonian siltstone. The area above the mine comprises farmland, meadows, and deciduous forests, with soil of the dystric cambisol type (Filella et al., 2009b). Water coming from precipitation and percolating through the soil, and thence through the fault system in the mineralized area, where it comes into contact with the antimony ore, can thus be expected to contain organic matter of pedogenic origin. Analyses did indeed reveal the presence of amino acids (up to 0.6 μM), hexoses (up to 0.4 μM) and refractory organic matter (ROM) (up to 9 mg l^{-1}) in water samples collected at the deepest point of the drainage adit, the only part of the mine presently accessible. Amino acids and carbohydrates were determined by literature methods (Chatigny et al., 2008) and ROM by a voltammetric method (Chanudet et al., 2006)). The aim of the present study is to investigate possible effects of typical soil organic carbon species on the dissolution kinetics of stibnite over an environmentally representative pH range.

Ligand-promoted dissolution of oxides and silicates has been studied extensively (Furrer and Stumm, 1986; Biber et al, 1994; Sposito, 2004 and references therein), while fewer data exist on the dissolution of sulfides (Davis et al, 1995). The same general principles are expected to hold, since surfaces of sulfides behave in a similar way to those of oxides, by forming amphoteric surface hydroxo groups (Rönngren et al, 1991; Davis et al, 1995). Low molecular weight organic acids (LMWOA) occur in soils as a result of microbial breakdown of humic substances, leaching of plant detritus, and root exudation. Commonly found LMWOA in the soil solution comprise carboxylic acids, e.g. formic and acetic acids (2–5 mmol l^{-1}), oxalic and tartaric acids (0.05–1 mmol l^{-1}), citric acid (<0.05 mmol l^{-1}), aromatic acids (0.05-0.3 mmol l^{-1}), amino acids (e.g. glycine, alanine, aspartic acid, glutamic acid, arginine, lysine, 0.05-0.6 mmol l^{-1}) and carbohydrates (e.g. glucose, glucosamine, galactose, mannose, xylose), which, together with their polymerised forms, can account for up to one half of a soil's organic carbon (Sposito, 2008). Davis and co-workers examined the effect of citric, oxalic, benzoic, salicylic, phthalic acids, as well as EDTA, NTA and catechol on the photo-oxidative rate of dissolution of cadmium sulfide (Davis et al, 1995). The effect of citric, oxalic, phthalic and salicylic acids on the dissolution of

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doi:10.1016/j.chemgeo.2011.11.009

chalcopyrite was studied by Goyne et al. (2006), without analysis of the reaction kinetics. Antimony(III) is known to form complexes with all of the above mentioned organic acids, and for some of them complexation constants are known (Anderegg and Malik, 1970; Filella and May, 2005, Tella and Pokrovski, 2009). It also forms a complex with guanosine (Klüfers and Mayer, 1997), which suggests that carbohydrates may have an effect on the rate of dissolution of stibnite. A special class of biomolecules found in soils are the siderophores. These are synthesised by bacteria, fungi and graminaceous plants under conditions of iron deficiency in oxic environments, where the bioavailability of iron is severely limited by the poor solubility of Fe(III) containing minerals. Siderophores form soluble Fe(III) complexes, in which form the Fe(III) becomes accessible to organisms. Some 500 siderophores have been characterised today (Sposito, 2008). For recent literature on the different classes of siderophores and their characteristics see for instance Duckworth et al., 2009b; Müller et al., 2009; Duckworth and Sposito, 2005a; Duckworth and Sposito 2005b; Ma et al., 1993; Smith et al., 1985.

The most extensively studied siderophore is desferrioxamine-B (DFOB, deferoxamine), a trihydroxamic acid (Fig. 1). DFOB is commercially available as the mesylate salt under the trade name Desferal (Novartis). It is medicinally used in the treatment of iron poisoning. DFOB has been shown to promote the dissolution of the iron minerals goethite, α-FeOOH, (Simanova et al, 2010), hematite, α-Fe$_2$O$_3$, (Hersman et al, 1995), but also manganite, γ-MnOOH (Duckworth and Sposito, 2005b), hausmannite, Mn$_3$O$_4$ (Pena et al, 2007), and cobalt hydroxides (Bi et al, 2010) by forming an exceptionally stable Co(III) complex (more stable than the Fe(III) complex) (Duckworth et al, 2009a). Similarly, Mn(III) is stabilised in aqueous solution by complexation with DFOB (Duckworth and Sposito, 2005a). A large number of stability constants of DFOB-metal complexes is known (Anderegg et al, 1963; Hernlem et al, 1996), unfortunately, no constant is available for antimony. Cornejo-Garrida et al. (2008) conducted a kinetic study on the effect of DFOB on arsenopyrite and galena dissolution.

We thus chose a number of representative substances, which either occur as such in the soil solution, or which may serve, by virtue of structural and functional similarities, as proxy compounds for a class of common soil solution components (Table 1 and Fig. 1). An experiment was also carried out using DFOB in conjunction with citric acid, as synergistic kinetic effects had been reported between DFOB and LMWOA (Duckworth et al, 2009b and references therein ; Cheah et al, 2003). A synergistic kinetic effect between a reductant (ascorbate) and a chelator (oxalate) in the dissolution of hematite has also been reported (Banwart et al, 1989). The synergistic effect observed in the dissolution of goethite in the presence of both DFOB and oxalate is described by Loring et al. (2008). More importantly, these authors proffer a novel interpretation of the molecular-scale mechanism of synergistic dissolution in which the readsorbed, inner-sphere metal-oxalate complex plays a decisive role.

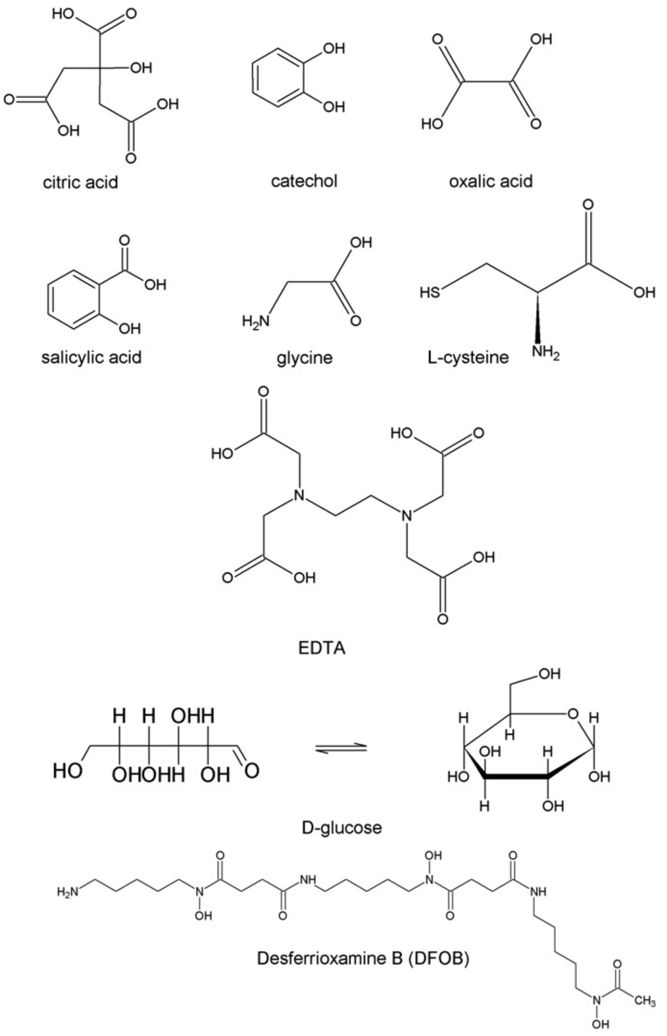

Fig. 1. Structures of the ligands used in the kinetic experiments. 1 mM of these ligands was applied (in separate experiments) to a 1 l suspension of *circa* 100 mg stibnite in biological buffer solutions (pH 4, 6 and 8).

2. Experimental

Rates of dissolution of stibnite were measured in a batch reactor. This consisted of a conventional, 1 L two-necked, round-bottom flask immersed in a constant temperature water bath set to 25 °C. Through the central neck, a ground glass stopper with a plastic axle carrying a magnetic stirrer bar was fitted, so that the stirrer did not touch the bottom of the flask, in order to avoid grinding of the mineral. The second neck remained open to the atmosphere and was used as a sampling port. The following buffer agents were used: pH 4: sulfanilic acid (pK$_a$ = 3.3), pH 6: MES (2-(N-morpholino)-ethanesulfonic acid, pK$_a$ = 6.2) and pH 8: MOPS (3-(N-morpholino)-propanesulfonic acid, pK$_a$ = 7.2). The so called 'Good's buffers' MES and MOPS were chosen because they are known to complex metal ions to a negligible extent (Good et al, 1966). The suitability of sulfanilic acid for the present purpose was tested by control experiments at pH = 4 without buffer, showing that a sulfanilic acid/sulfanilate buffer did neither promote nor inhibit the stibnite dissolution rate. The total buffer concentrations were 0.05 M and the pH adjusted to the desired value with 1 M NaOH solution under potentiometric control (pH meter:

Table 1
List of ligands used in the kinetic experiments.

Class	Representative substance	Concentration in the experiment	Concentration in the soil soln.
Carboxylic acids	Acetic acid	1 mM	2–5 mM
	Oxalic acid	1 mM	0.05–1 mM
	Citric acid	1 mM	<0.05 mM
Aminocarboxylic acids, aminocarboxylate siderophores	EDTA	1 mM	
Aromatic acids	Salicylic acid	1 mM	0.05–0.3 mM
Amino Acids	Glycine	1 mM	0.05–0.6 mM
S-bearing amino acid	Cysteine	1 mM	
Carbohydrates	Glucose	1 mM	
Phenols, catecholate siderophores	Catechol	1 mM	Nanomolar, up to 0.25 mM in the rhizosphere
Hydroxamic Siderophores	Desferrioxamine-B (DFOB)	1 mM	
	DFOB + citric acid	1 mM each	
Leaf Litter extract		1 mM total acidity	