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Alkali and alkaline earth metal chloride solutions influence sulfide mineral dissolution

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ABSTRACT

Alkali and alkaline metal chlorides have been considered as inert electrolyte species with respect to sulfide mineral dissolution in the presence of oxidizing agents such as O_2 and Fe^{3+}. Under anoxic conditions in the laboratory or the field, as exist in most saline subsurface environments, the potential reactivity of alkali and alkaline metal chlorides with sulfide minerals has typically been ignored. Arsenopyrite (FeAsS(s)), galena (PbS(s)), and pyrite (FeS_2(s)) are commonly encountered sulfide mineral phases, the dissolution of which affects many ecosystems. In this study, dissolution experiments with these minerals were conducted under anoxic conditions with 10 mM solutions of NaCl, $CaCl_2$, and $MgCl_2$ at constant pH of 2.56. Results show that these electrolytes affect sulfide mineral dissolution under anoxic conditions, either increasing or decreasing the rate. The extent to which sulfide mineral dissolution is affected is small but measurable and depends on the anionic species in the mineral and cationic species in solution. Specifically, the dissolution of arsenic from arsenopyrite increased with an increase in cation activity in solution, while the dissolution of sulfur decreased with an increase in chloride ion activity. These results suggest that sulfide mineral dissolution under anoxic conditions is caused by an interaction of cations in solution with anions on the mineral surface, and inhibited by the presence of competing anions in solution.

1. Introduction

Traditionally, alkali and alkaline earth metal chlorides such as NaCl, $MgCl_2$ and $CaCl_2$ have been used to control bulk solution ionic strength while studying mineral dissolution with higher-energy reactants. These chloride reagents typically are considered inert and with little influence on dissolution aside from effect on the activity of reactants through ionic strength. This is particularly true with the study of sulfide mineral dissolution for which usually involve experiments conducted with oxidants such as Fe^{3+} and dissolved oxygen (Barrett and Anderson, 1982; Ohmoto et al., 1994) or reactants such as acids (Awakura et al., 1980; Nunez et al., 1990). In strongly reacting environments, effects of background electrolytes on dissolution typically are negligible as compared to that caused by the reactants, and hence not observable. Therefore the effect of these electrolytes as possible reactants for dissolution has not been explored. With the emergence of interest in aqueous environments that are anoxic and have high concentrations of alkali metal chlorides, such as brines in deep saline formations, the potential for these salt solutions to influence mineral dissolution merits examination.

The ability of sulfide minerals to react with waters and contribute to acid mine drainage (AMD) and toxic metal mobilization (As, Pb, Cd, Hg, etc.) has driven study of the factors and conditions controlling their dissolution (Vaughan, 2006). The dissolution of sulfide minerals has been studied under varying solution conditions including in the presence of alkaline metal chlorides in solution. Non-oxidative acidic dissolution of sphalerite ((Zn, Fe)S(s)) and galena (PbS(s)) has been studied in the presence of sodium and magnesium chloride solutions. The reported increases in dissolution were attributed to a change in H^+ ion activity, and not determined to be an effect of the electrolyte itself (Awakura et al., 1980; Barrett and Anderson, 1982; Nunez et al., 1990). Limited studies have been conducted on the dissolution of pyrite (FeS_2(s)) in the presence of sodium chloride in solution (Ohmoto et al., 1994), and on oxidative dissolution of pyrite and arsenopyrite (FeAsS(s)) in electrolyte solutions (Lin and Zheng, 1996; Walker et al., 2006). These studies assume the only reactants in dissolution to be H^+ or the oxidant species, namely O_2 and Fe^{3+}, but the potential interaction of the mineral surfaces with cations in solution, which could affect dissolution, has not been investigated.

Galena, pyrite, and arsenopyrite represent three different types of sulfide minerals based on their anionic sulfide groups. Multiple experiments aimed at understanding the surface speciation for these minerals have revealed the major anionic groups to be sulfide (S^{2-}) for galena (Hernan et al., 1995), disulfide (S_2^{2-}) for pyrite (Nesbitt et al., 1998), and As^- and S^- as a polyanion ($[AsS]^{2-}$) for arsenopyrite (Corkhill and Vaughan, 2009). Studies conducted to determine the isoelectric points ($pH_{i.e.p}$) of galena, pyrite, and arsenopyrite under anoxic conditions have revealed a $pH_{i.e.p} < 2$ for all three minerals (Bebie et al.,

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1998). As a result, at a pH greater than 2, the mineral surface is negatively charged and could interact electrostatically with positively charged alkali and alkaline earth metal cations supplied by chloride salts in solution.

The objective of this study was to determine the effect of NaCl, $CaCl_2$, and $MgCl_2$ solutions on the dissolution of $FeS_2(s)$, FeAsS(s), and PbS(s) under anoxic conditions. Of particular interest was the influence of positively charged species (H^+, Na^+, Ca^{2+}, and Mg^{2+}), on the release of the negatively charged sulfur and arsenic species (in arsenopyrite) from these minerals. For this purpose, dissolution experiments were conducted in a column plug-flow reactor and anoxic influent solutions at a low pH to avoid precipitation and mass transfer complications. Effluent concentrations of constituent elements for each mineral were measured and compared to variables in the experiments to determine the parameters that influenced the dissolution of these minerals under anoxic conditions.

2. Materials and methods

2.1. Mineral preparation and characterization

Arsenopyrite, galena, and pyrite were obtained from Wards Sci. Inc. (Rochester, NY) and were crushed in a porcelain mortar and pestle and size fractionated using nylon sieves to a range of 150–250 μm. The mortar and pestle as well as the sieves were soaked overnight in 10% (w/V) HNO_3 prior to use. The crushed minerals were then sonicated in 50% ethanol and washed with HCl (12 N for arsenopyrite and pyrite, and 1 N for galena) based on the method described by Parthasarathy et al. (2014). This enabled the removal of fine particles adhering to the mineral surface and removal of oxide layers that may affect dissolution measurement. The size-segregated, clean particles were analyzed by X-ray diffraction (XRD). XRD analyses confirmed that the primary mineral phases were arsenopyrite, pyrite, and galena for the corresponding samples. No secondary mineral phases were detected in any of the mineral samples. Average mineral stoichiometry was measured using a scanning electron microscope (SEM)–energy dispersive X-ray spectroscopy (EDS) system. The measured stoichiometries are presented in Table 1. While XRD analyses confirmed the presence of a single mineral phase and SEM analyses revealed near theoretical stoichiometry, the absence of amorphous phases could not be confirmed. As noted later, the solution phase Fe concentrations measured in some of the dissolution experiments suggest the possible presence of some amorphous Fe phase(s).

2.2. Reagents and dissolution experiments

Ultra high pure NaCl (99.9999%, metal basis), $CaCl_2$ (99.99%, metal basis), and $MgCl_2$ (99.99%, metal basis) purchased from Alfa Aesar, USA, were used to make influent solutions for dissolution experiments. 1 M ultra pure HCl (Fisher Scientific Inc., USA) was used to adjust the pH. All solutions were made with deionized water (18.2 MΩ; Barnstead, USA).

Dissolution of galena, arsenopyrite, and pyrite was studied with 10 mM concentrations of NaCl, $MgCl_2$, and $CaCl_2$ in de-oxygenated, carbonate-free solutions under nitrogen atmosphere (Table 2). The pH was adjusted to 2.56 ± 0.01 by the addition of 6 ± 0.4 mL of 1 N HCl to 2 L of solution to maintain a constant H^+ activity. The pH was measured using an Accumet XL 60 (Fisher scientific) pH meter. To provide for direct comparison between electrolytes, an additional experiment with NaCl, with Na^+ activity similar to that of Mg^{2+} and Ca^{2+} in 10 mM $MgCl_2$ and $CaCl_2$ respectively, was conducted for arsenopyrite. The activities in solution were calculated using the Extended Debye–Hückel equation (Benjamin, 2010), and the corresponding concentration of NaCl was calculated to be 5.6 mM (Table 2). Control experiments with nitrogen-purged deionized water (pH 2.56, HCl) were also conducted.

Table 1
Stoichiometry of mineral samples for dissolution experiments measured by SEM–EDS.

Mineral	SEM–EDS stoichiometry
Arsenopyrite (FeAsS)	$Fe_{1.03 \pm 0.05}As_{1.01 \pm 0.05}S_{0.87 \pm 0.05}$
Galena (PbS)	$Pb_{0.97 \pm 0.01}S_{1.14 \pm 0.08}$
Pyrite (FeS_2)	$Fe_{1.03 \pm 0.03}S_{1.94 \pm 0.06}$

Table 2
List of dissolution experiments conducted (every row represents an experiment conducted with each sulfide mineral). T = 25 °C, P = 1 bar, pH 2.56.

Electrolyte	Concentration (M)	[HCl] (M)	Ionic strength (M)	Anion activity	Cation activity
D.I. water	–	0.003	0.0030	0.0028	0.0028
NaCl	0.01	0.003	0.0130	0.0115	0.0089
$CaCl_2$	0.01	0.003	0.0330	0.0192	0.0053
$MgCl_2$	0.01	0.003	0.0330	0.0192	0.0056
NaCl (Arsenopyrite only)	0.0056	0.003	0.0085	0.0076	0.0051

2.3. Experimental setup and analytical methods

Experiments were conducted in a small-scale plug-flow column system described by Parthasarathy et al. (2013), under nitrogen atmosphere. Although most mineral dissolution experiments are conducted in batch or mixed flow reactor systems, plug-flow reactors have some advantages for study of mineral dissolution, including inherently high solid–liquid ratios (Rimstidt and Newcomb, 1993). While plug flow reactor systems are less desirable to determine rate laws and constants, they are useful in determining relative rates (Rimstidt and Newcomb, 1993), as in the case of this study.

Plug flow systems are typically not used in dissolution experiments, as the resulting data can be hard to interpret (Rimstidt and Newcomb, 1993). However, for very slow reactions, the analysis of data from plug flow reactor systems can be simplified, as demonstrated by Parthasarathy et al. (2013). Briefly, Parthasarathy et al. (2013) showed that when the rate of reaction is much slower than the rate of mass transfer, the plug-flow system is under reaction rate control and the rate of a dissolution reaction can be determined directly from the effluent elemental concentrations using Eq. (1).

$$k' = \frac{(C_{out} - C_{in})}{\tau} \qquad (1)$$

where, k' (mol/L.s) is the apparent rate of arsenic dissolution, C_{out} (mol/L) is the steady state effluent arsenic concentration, C_{in} (mol/L) is the influent arsenic concentration, and τ (s) is the residence time of the fluid in the column. The same equation (Eq. (1)) was used to determine dissolution rates of galena, and pyrite.

The small-scale plug flow system consisted of a 5 cm poly ether–ether ketone (PEEK) column connected to a HPLC pump capable of delivering influent solution at a constant flow rate. The column was packed with mineral and influent solution was fed at a constant flow rate of 1 mL/min. The average pore volume in the column was 0.45 ± 0.05 mL. The masses of specific solid phase packed were 2.5 ± 0.1 g, 2.7 ± 0.05 g, and 1.7 ± 0.1 g of arsenopyrite, galena, and pyrite respectively. The reactant solutions were purged with nitrogen for 20 h prior to the experiments, to remove any dissolved oxygen and carbonate in the system. Nitrogen pumping was continued through the entire duration of each experiment to prevent oxygen intrusion. The entire system was placed in a 280 L glove bag (Sigma Aldrich USA), which was filled with nitrogen. The oxygen concentration inside the glove bag and the dissolved oxygen in the influent solution were measured using an Accumet XL 60 Dissolved Oxygen meter (Fisher scientific). The detection limits were 0.1% saturation (atmospheric oxygen) and 0.01 mg/L (dissolved oxygen). All dissolution experiments were conducted at