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8 **ALKALI AND ALKALINE EARTH METAL CHLORIDE SOLUTIONS**
9 **INFLUENCE SULFIDE MINERAL DISSOLUTION**
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12 Hariprasad Parthasarathy, David A. Dzombak, Athanasios K. Karamalidis*
13 Department of Civil and Environmental Engineering,
14 Carnegie Mellon University, Pittsburgh, PA - 15213
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18 * Corresponding author:
19 Athanasios K. Karamalidis
20 Department of Civil and Environmental Engineering
21 Carnegie Mellon University,
22 Pittsburgh, PA – 15213
23 Phone: 412-268-1175
24 Email: akaramal@andrew.cmu.edu
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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.

Keywords: sulfide minerals, arsenopyrite, sodium chloride, mineral dissolution

Highlights:

- $NaCl$, $CaCl_2$, $MgCl_2$ influence sulfide mineral dissolution under anoxic conditions.
- Dissolution of arsenic from arsenopyrite increases with an increase in cation activity
- Dissolution of sulfur decreases with increasing chloride ion activity in solution
- Sulfide mineral dissolution under anoxic conditions is dependent on anionic species in the mineral, and cations and anions in solution.

1. Introduction

Traditionally, alkali and alkaline earth metal chlorides such as NaCl, MgCl₂ and CaCl₂ 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 Fe³⁺ and dissolved oxygen (Barrett and Anderson, 1982; Ohmoto et al., 1994) or reactants such as acids (Nunez et al., 1990; Awakura et al., 1980). 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, 2005). 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 (Nunez et al., 1990; Awakura et al., 1980; Barrett and Anderson, 1982). 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 (Walker et al., 2006, Lin and Zheng, 1996). 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., 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.

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126 The objective of this study was to determine the effect of NaCl, CaCl₂, and MgCl₂
127 solutions on the dissolution of FeS₂(s), FeAsS(s), and PbS(s) under anoxic conditions. Of
128 particular interest was the influence of positively charged species (H⁺, Na⁺, Ca²⁺, and
129 Mg²⁺), on the release of the negatively charged sulfur and arsenic species (in
130 arsenopyrite) from these minerals. For this purpose, dissolution experiments were
131 conducted in a column plug-flow reactor and anoxic influent solutions at a low pH to
132 avoid precipitation and mass transfer complications. Effluent concentrations of
133 constituent elements for each mineral were measured and compared to variables in the
134 experiments to determine the parameters that influenced the dissolution of these minerals
135 under anoxic conditions.

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137 **2. Materials and Methods**

138 *2.1 Mineral preparation and characterization*

139 Arsenopyrite, galena, and pyrite were obtained from Wards Sci. Inc. (Rochester, NY) and
140 were crushed in a porcelain mortar and pestle and size fractionated using nylon sieves to
141 a range of 150- 250 µm. The mortar and pestle as well as sieves were soaked overnight in
142 10% (w/V) HNO₃ prior to use. The crushed minerals were then sonicated in 50% ethanol
143 and washed with HCl (12N for arsenopyrite and pyrite, and 1N for galena) based on the
144 method described by Parthasarathy et al., (2014). This enabled the removal of fine
145 particles adhering to the mineral surface and removal of oxide layers that may affect
146 dissolution measurement. The size-segregated, clean particles were analyzed by X-ray

diffraction (XRD). XRD analyses confirmed 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).

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

Mineral	SEM-EDS Stoichiometry
Arsenopyrite (FeAsS)	$\text{Fe}_{1.03 \pm 0.05} \text{As}_{1.01 \pm 0.05} \text{S}_{0.87 \pm 0.05}$
Galena (PbS)	$\text{Pb}_{0.97 \pm 0.01} \text{S}_{1.14 \pm 0.08}$
Pyrite (FeS ₂)	$\text{Fe}_{1.03 \pm 0.03} \text{S}_{1.94 \pm 0.06}$

2.2 Reagents and dissolution experiments

Ultra high pure NaCl (99.9999%, metal basis), CaCl₂ (99.99%, metal basis), and MgCl₂ (99.99%, metal basis) purchased from Alfa Aesar, USA, were used to make influent solutions for dissolution experiments. 1 molar 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, MgCl₂, and CaCl₂ 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 1N HCl to 2L 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 Mg²⁺ and Ca²⁺ in 10 mM MgCl₂ and CaCl₂ 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 2. List of dissolution experiments conducted (every row represents an experiment conducted with each sulfide mineral). T= 25 °C, P= 1bar, 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	0.0052
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.

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

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 5cm 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 1mL/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 hours 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 280L 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 0.01mg/L (dissolved oxygen). All dissolution experiments were conducted at ambient temperature (22 °C) and pressure (1.01×10^5 pa). Effluent samples were collected at 2-hour intervals and analyzed for dissolution products by inductively coupled plasma mass spectrometry (ICP-MS) and ion chromatography (IC).

Samples collected were preserved with 5% HNO₃ (trace metal grade). Samples were diluted (5x) with 5% HNO₃ and analyzed for iron and arsenic (arsenopyrite), iron (pyrite), and lead (galena) using an Agilent 7700x ICP-MS equipped with a collision-reaction-chamber. Polyatomic interference for Fe and As were reduced by conducting the analysis in Helium-collision mode. A four point calibration curve for each analyte was constructed before every set of samples with $r^2 > 0.99$. A multi-element standard mixture from Agilent Technologies Inc. was used to prepare standard solutions and a midrange

standard was used to check the calibration after every 10 samples. The detection limits were 0.15 ppb for Fe, 0.04 ppb for As, and 0.003 ppb for Pb.

Total sulfur was measured as sulfate by exposing the collected samples to air for 48 hours prior to analysis. Sulfate was measured using an ion-suppressed chromatography system. The high-pressure liquid chromatography (HPLC) system consisted of an anion suppressor (AERS 500, Dionex), an anion separation column (AS-14A, Dionex) and a conductivity detector (ED40 Electrochemical detector, Dionex). The eluent was 0.8mM NaHCO_3 /10mM Na_2CO_3 at a flow rate of 1.2 mL/min at 35 °C. The same temperature (35 °C) was used for the detector. The injection volume was 100 μL . A four-point calibration was used and calibration curves were developed with $r^2 > 0.99$ for SO_4^{2-} . The sulfate concentration was determined according to USEPA (USEPA, 1992) and Standard Methods (APHA, AWWA, and WEF, 1998). The calibration curve for sulfate was constructed each time a fresh eluent was used or otherwise every 20 injections. Standard solutions, prepared daily with dilutions of a stock standard sulfate solution with respective salts were used. The method detection limit was found to be matrix dependent and varied from 1- 20 ppb.

2.4 Data analysis

Effluent concentrations of S, As, and Fe for arsenopyrite, S and Pb for galena, and S and Fe for pyrite were monitored with respect to time, and steady-state concentrations were obtained for each experiment. Since parameters such as mass of mineral, specific surface

area, flow rate, and residence time were constant for experiments with each mineral, the steady state concentrations were directly compared for each mineral. The specific surface areas of each mineral was measured in triplicate using the B.E.T analysis with Kr absorption isotherm before and after dissolution, and was found to not vary significantly for all three minerals. The surface areas were found to be 0.330 m²/g, 0.125 m²/g, and 0.009 m²/g for galena, arsenopyrite, and pyrite respectively.

Steady state concentrations were determined to be reached after 12 hours of dissolution, if the effluent concentration was within $\pm 15\%$ of the average over 8 hours. It must be noted that effluent concentrations can be influenced by dissolution mechanisms (such as a shrinking core model for galena dissolution), resulting in a broad definition of steady state as detailed above. To overcome any mechanistic effects on effluent concentrations, steady state values were determined by determining average concentrations over the same time period for experiments with each mineral.

In the case of Fe release from arsenopyrite and pyrite, a large variability in effluent concentration was observed, potentially due to the presence of Fe hotspots or/and amorphous iron phases in natural mineral samples. However, Fe concentrations were averaged over the same time frame as As and S, which resulted in large error bars for Fe steady state concentrations.

The calculated steady state concentrations were then compared against the different experimental parameters (electrolyte concentration, cation activity, ionic strength, anion

activity, and electron affinity of the cation) to determine the variable with which steady-state dissolution rate was most strongly correlated.

3. Results

The concentrations of sulfur released from each mineral and arsenic release concentrations from arsenopyrite, as a function of time, are depicted in Figure 1 and Figure 2 respectively. The plots follow similar trends: a high initial release of S or As occurred, which gradually decreased to reach an average steady state value. Similar trends have been observed with other flow-through experiments, with the high initial release potentially due to preferential dissolution from cracks and surface irregularities (Walker et al., 2006).

With PbS (s) (Figure 1A) and FeAsS(s) (Figure 1C), the highest sulfur effluent concentrations were observed in the absence of chloride salts in solution (i.e. HCl solution at pH 2.56). However, in the case of pyrite, the release rate of sulfur was highest with 10mM NaCl (Figure 1B). Experiments with 10mM MgCl₂ and 10mM CaCl₂, with similar chloride ion activities resulted in similar effluent concentrations of S for all three minerals.

The dissolution of FeAsS(s) was found to follow two distinct trends. While the effluent sulfur concentrations decreased in the presence of chloride salts (Figure 1C) in solution,

309 the steady state concentrations of As increased in the presence of chloride salts in
310 solution (Figure 2). In experiments with the same cation activity, (Na^+ in 5.6mM NaCl,
311 and Mg^{2+} and Ca^{2+} in 10mM MgCl_2 and CaCl_2 respectively) similar steady state As
312 concentrations were observed.

Figure 1. Effluent concentrations (μM) of S released from (A) Galena, (B) Pyrite, and (C) Arsenopyrite, as a function of time. $T=25\text{ }^{\circ}\text{C}$, $P=1\text{ bar}$, $\text{pH}=2.56$.

Figure 2. Effluent concentration (μM) of As released from arsenopyrite as a function of time. $T = 25\text{ }^{\circ}\text{C}$, $P = 1\text{ bar}$, $\text{pH} = 2.56$.

The dissolution of all three sulfide minerals was found to be non-stoichiometric, i.e., the molar ratios in solution of elements dissolved from the solids were not the same as the ratios in the solids. The effluent concentrations of individual elements of the three minerals were plotted against each other as depicted in Figure 3 (A-D). As seen in Figure 3A, the dissolution of arsenopyrite resulted in a higher release of Fe as compared to As, in all cases except for the experiment with 10mM MgCl_2 for which nearly stoichiometric release quantities were observed. In general, the release ratios moved closer to the 1:1 (Fe:As) ratio upon addition of chloride salts in solution. In the case of sulfur and arsenic release from arsenopyrite (Figure 3B), in the absence of chloride salts in solution (i.e. with HCl solution at a pH of 2.56), sulfur was preferentially released from arsenopyrite. On

the addition of chloride salts, this ratio tended towards 1, consistent with an increase in arsenic release and decrease in effluent S concentration. While a relatively similar trend was observed with galena dissolution (Figure 3C), a large scatter in dissolution stoichiometry was observed with pyrite dissolution (Figure 3D). These trends suggest preferential dissolution of arsenic from arsenopyrite, and a reduction of S dissolution from galena and pyrite when chloride salts were added to solution.

Figure 3. Stoichiometry of dissolution of (A and B) Arsenopyrite, (C) Galena, and (D) Pyrite with chloride salts in solution. The blue line in each plot represents the solid phase stoichiometric ratio for the mineral.

To further analyze this non-stoichiometric behavior, the mean effluent concentrations for

the minerals, averaged over the last 8 hours of each experiment, were calculated and compared to different experimental parameters. Correlation between the effluent elemental concentrations and experimental parameters was analyzed by determining the Spearman's rank correlation coefficient (ρ), and the corresponding p-value to test if the correlation coefficient was significantly different from zero. Plots for sulfur release from the three minerals, and arsenic release from arsenopyrite depicting the parameter with strongest correlation to dissolution rates are shown in Figure 4. Each point on the plots represents a single experiment, with the error bars depicting $\pm 1\sigma$ uncertainty in steady state concentrations. Since H^+ activity, temperature and pressure were constant for all experiments, they were not considered in the correlation analysis.

The results show that dissolution of the three sulfide minerals under anoxic conditions was affected by the presence of alkali and alkaline earth metal chlorides in solution. In general, the steady state release concentrations of sulfur for all three minerals decreased in the presence of alkaline metal chlorides, while the effluent concentrations of As increased in arsenopyrite dissolution, as depicted in Figure 4. A table summarizing these steady state concentrations is also presented (Table 3).

Table 3. Steady state effluent release concentrations of Sulfur for all three minerals and As for arsenopyrite.

Electrolyte	Steady State Effluent Sulfur Concentration (micro M)			Steady state As concentration (micro M)
	Galena	Arsenopyrite	Pyrite	
D.I Water (pH 2.56)	3.93	3.89	0.69	0.091
5.6 mM NaCl	-	0.65	-	0.154
10mM NaCl	2.93	0.06	1.19	0.404
10mM CaCl ₂	0.07	BDL	BDL	0.141
10mM MgCl ₂	0.25	BDL	BDL	0.149

365 BDL: Below Detection Limit

366 The steady state sulfur concentrations for dissolution of all three minerals showed a
 367 correlation to the ionic strength of the solution. In particular, the Spearman's correlation
 368 analysis revealed that the steady-state S concentrations exhibit strong monotonic
 369 correlations with calculated chloride ion activity (Figure 4A, 4B, and 4C). Spearman's ρ
 370 was found to be -0.933 (p-value < 1E-04) for S release from arsenopyrite, -0.847 (p-value
 371 < 1E-04) for S release from galena, and -0.792 (p-value < 3E-04) for S release from
 372 pyrite, which suggests a decrease in S release with increasing chloride ion activity in
 373 solution.

374

375 The steady state arsenic release from arsenopyrite, on the other hand, did not exhibit a
 376 strong correlation to chloride ion activity, but displayed a strong positive correlation to
 377 the activity of cations (Figure 4D) in solution (Spearman's $\rho = 0.757$, with a p-value <
 378 1E-04) suggesting that the dissolution of arsenic increases with an increase in the activity

379 of cations in solution.

380

381 In addition, while the steady state concentrations of Pb also showed a strong negative,
382 monotonic correlation to chloride ion activity (Spearman's $\rho = -0.853$, with a p-value <
383 $2E-04$), Fe release from arsenopyrite and pyrite did not correlate with any of the
384 experimental parameters in this study, potentially due to the dissolution of iron from
385 amorphous Fe phases in these naturally sourced mineral samples.

Figure 4. Dissolution of sulfide minerals is dependent on solution species activity. (A) Steady state S release from PbS(s) as a function of chloride ion activity. (B) Steady state S release from FeAsS(s) as a function of chloride ion activity (C) Steady state S concentration from FeS₂(s) as a function of chloride ion activity, and (D) Steady state As concentration from FeAsS(s) as a function of cation activity. T= 25 °C, P= 1 bar, pH

=2.56

4. Discussion

From the results obtained, it is clear that alkali and alkaline metal chloride salts in solution can affect the dissolution of sulfide minerals. One approach to interpretation of these dissolution results is to consider the reaction of sulfide minerals with solutions of alkali and alkaline metal chlorides as interactions between the anions on the mineral surface and the cations in solution. A schematic depicting these interactions is presented in Figure 5. The anions on the mineral surface (S^{2-} , S_2^{2-} , S^- , and As^-) exhibit nucleophilic properties arising from the availability of lone pairs of electrons, while the cations in solution (H^+ , Na^+ , Mg^{2+} , Ca^{2+}) can act as electrophiles due to their ability to accommodate an electron pair from donor atoms (Pearson, 1968). We hypothesize that the dissolution process is based on interactions between nucleophilic anions on the mineral surface and electrophilic cations in solution and depends on two factors: (i) nucleophilic reactivity of the anions on the surface, and (ii) activity of other anions in solution that may compete with the surface nucleophiles.

Figure 5. Schematic of the dissolution of sulfide minerals under anoxic conditions with alkali and alkaline metal chlorides in solution. Three kinds of nucleophilic anions on sulfide minerals are depicted – (A) Monosulfides; (B) Disulfides/Polysulfides; and (C) Sulfur-Arsenic polyanion.

4.1 Nucleophilic reactivity of anions on the surface

The nucleophilic reactivity of a species is measured by the rate of reaction with a specific

electrophilic substrate (Larson and Weber, 1994; Edwards and Pearson, 1962). Generally, nucleophilic reactivity is correlated to basicity, or the ability of a species to take up a proton, and the polarizability of the species (Metzler and Metzler, 2001; Larson and Weber, 1994; Edwards and Pearson, 1962). The relationship of nucleophilic reactivity to basicity is implicit in the fact that nucleophile-electrophile interactions are generalized acid-base type reactions (Larson and Weber, 1994; Edwards and Pearson, 1962), and hence an increase in basicity is expected to lead to an increase in nucleophilic character. However, the proton is unique in that it does not face any restrictions in its interactions with a nucleophile. Any other electrophile will be restricted by its additional electrons due to the constraints of the Pauli's exclusion principle (Edwards and Pearson, 1962). The polarizability, or the ease with which the electron distribution around a chemical group can be distorted (Metzler and Metzler, 2001), enables the nucleophilic species to accommodate the additional electrons of electrophiles, thereby reducing the constraints of the Pauli's principle.

The effect of polarizability is evident in the release of As from FeAsS(s). The polarizability of bonding and nonbonding electrons away from the nucleophiles reduces repulsions due to Pauli's exclusion and increases nucleophilic character (Metzler and Metzler, 2001; Edwards and Pearson, 1962). Owing to the opposing trends of polarizability and electronegativity in the periodic table (Carey and Sundberg, 2007), arsenic is a better nucleophile than the sulfur species. This polarizability of As⁻ enables greater interaction with electrophiles (e.g. Na⁺, Ca²⁺, Mg²⁺) (Figure 5C) in solution, which results in an increase of As release with an increase in cation activity (Figure 4D).

440 However, it is possible for a species to exhibit low nucleophilic reactivity towards metal
441 cations but be strongly binding to the proton (Pearson, 1963), as observed in the S
442 species, which is more reactive to H^+ than to the other cationic species (Na^+ , Ca^{2+} , Mg^{2+})
443 (schematically depicted in Figure 5A). Previous dissolution experiments under anoxic
444 conditions and in the absence of cations other than H^+ report that rates of dissolution of
445 galena, pyrite, and sphalerite are dependent on H^+ activity (Sun et al., 1991;
446 Weerasooriya and Tobschall, 2005). Proposed reaction mechanisms involve the
447 protonation of the negatively charged surface resulting in a charged surface complex that
448 subsequently dissociates leading to mineral dissolution (Sun et al., 1991; Weerasooriya
449 and Tobschall, 2005).

450
451 Although the minerals have a common electron donor atom in sulfur, different sulfur
452 groups can exhibit slightly different nucleophilic reactivities due to differences in charge
453 of the sulfur atom (-1 in disulfides and -2 in sulfides) and polarizability (Metzler and
454 Metzler, 2001; Pearson, 1968). This difference in sulfur speciation can result in
455 differences in polarizability of the S species on these sulfide minerals. The marginal
456 increase in S release from pyrite upon reaction with 10mM NaCl (Figure 4B) may be
457 attributed to the difference in polarizability of the disulfide species on pyrite as compared
458 to the sulfide species on galena. However, a more detailed set of experiments on pyrite
459 dissolution needs to be conducted to examine this effect further and test the polarizability
460 difference hypothesis.

4.2 Activity of competing anions in solution

As described earlier, the dissolution of sulfur from sulfide minerals can be understood as an interaction of the sulfur nucleophile with protons in solution. Since the pH of all electrolyte solutions was fixed, the dissolution of sulfur from any particular mineral was not expected to vary, irrespective of the electrolyte in solution. However, results depicted in Figures 4A, 4B, and 4C show a decreasing monotonic relationship between effluent sulfur concentrations and chloride ion activity in solution. This suggests that the interactions between electrophilic cations in solution and the anions on the mineral surface may also be dependent on other anions present in solution.

The presence of chloride ions in solution reduces the interaction of protons with the mineral surface, resulting in a decrease in dissolution of sulfur. As depicted in Figures 4A, 4B, and 4C, highest effluent sulfur release is observed in the absence of chloride salts in solution (D.I water, pH 2.56), where the protons are relatively free to interact with the mineral surface. With NaCl solutions, the interaction of protons and the mineral surface is inhibited by the presence of chlorides in solution leading to lower sulfur release. The release of sulfur from all three minerals is lowest in the presence of CaCl_2 , and MgCl_2 , due to the excess chloride ions in solution that strongly shield the interaction of protons and surface.

The shielding effect of Cl^- is observed only with the interaction of protons with the mineral surfaces. The high electronegativity of Cl^- limits its nucleophilicity and its effect

of inhibiting the interactions between the cations and As^- is low in the range of concentrations studied. Hence, similar cation activities yield similar steady state dissolution concentrations, even with differences in the activity of Cl^- (Figure 4D). At higher Cl^- activities, the inhibitory effect on dissolution may be higher.

5. Conclusions and implications

From study of sulfide mineral dissolution under anoxic conditions in the presence of different concentrations of the alkali and alkaline metal chloride salts NaCl , MgCl_2 , and CaCl_2 , it is clear that the composition and abundance of such electrolytes affect sulfide mineral dissolution. The rate of dissolution of sulfide minerals under anoxic conditions is controlled by the relative activities of the reactive cation(s) (H^+ for galena and pyrite, $\text{H}^+/\text{Na}^+/\text{Ca}^{2+}/\text{Mg}^{2+}$ for arsenopyrite in this study) and the inhibitory anion(s) (Cl^- in this study) in solution. The propensity of a sulfide mineral surface to react with a cation is dependent on the nucleophilicity of the anionic species in the mineral surface. In general, the rate of dissolution of sulfur decreased in the presence of alkali and alkaline metal chlorides. The case of arsenic release from arsenopyrite was an exception as FeAsS(s) contains a second and stronger nucleophilic group in As^- .

While this study offers insights into the interaction of electrolytes with sulfide mineral surfaces under low electrolyte concentration conditions, high concentration conditions

505 remain unexplored. However, certain implications of this work can be extended to
506 geologic systems. The effect of brines on mineral dissolution will be driven by their
507 compositions. With Na-Ca-Cl brines, the extent to which sulfide mineral dissolution
508 occurs will depend on the relative concentrations of Cl^- , Na^+ , and Ca^{2+} . Further, an
509 approach based on electrophile-nucleophile interactions is not necessarily limited to
510 sulfide minerals but could be valid for any solid surface that contains potential donor
511 atoms including but not limited to cyanides, thiocyanides, and carbides.

512
513 In this study, an inhibitory effect of Cl^- on cation-stimulated sulfide mineral dissolution
514 was observed. This inhibitory effect will likely vary depending on the anion and its
515 tendency for interaction with protons and other cations in solution. Such interactions are
516 dependent on the basicity and nucleophilicity of the specific electrolyte anion. For
517 instance, with respect to halides, basicity decreases but nucleophilicity increases down
518 the group of the periodic table (Carey and Sundberg, 2007). Therefore, F^- is expected to
519 have a higher inhibitory effect on H^+ while I^- ion would inhibit other cations to a larger
520 extent.

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