

## TRACE METAL SUBSTITUTION IN AND RELEASE FROM JAROSITE

**JASON ANTHONY**, Whitman College

**Research Advisor:** Bryn Kimball

### INTRODUCTION

Jarosite,  $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ , is a mineral commonly found in acid mine drainage (AMD), acid sulfate soils, and even found on Mars (Milliken et al., 2008). Because of its association with AMD, jarosite was anticipated to be found in Blackbird Creek. Blackbird Creek is a cobalt mining affected stream in the Idaho Cobalt Belt, the largest cobalt resource in the United States (Johnson et al., 1998). The presence of jarosite would impact the concentration of trace elements because trace metals commonly substitute into the mineral structure (Hudson-Edwards et al., 2008; Welch et al., 2007).

Jarosite is a hexagonal mineral with  $\text{K}^+$  in highly coordinated sites and  $\text{Fe}^{3+}$  in octahedral sites. Hudson-Edwards et al. (2008) found that trace metals substituted for Fe in the octahedral site in the crystal structure of jarosite. These substitutions may result in local charge imbalances and strain on the unit cell. For example, when Cu substituted for Fe, natural and synthetic jarosite showed differences in unit cell dimensions (Hudson-Edwards et al., 2008). These differences were most likely related to differing proportions of hydronium, Fe, and Pb in the mineral structure. Substitutions can either increase or decrease the solubility of the mineral. For example, a  $\text{Cr}^{3+}$  and  $\text{Pb}^{2+}$  substitution decreased jarosite solubility (Smith et al., 2006), whereas  $\text{Na}^+$  or  $\text{H}_3\text{O}^+$  substitution increased solubility (Drouet & Navrotsky, 2003). Phosphorus and As may substitute for S in jarosite, and this substitution may affect rates of dissolution and bioaccessibility (Burger et al., 2009; Desborough et al., 2010).

This study investigated the mobility of trace metals, specifically cobalt, in aqueous environments as they were substituted into the mineral structure of jarosite. It also investigated how cobalt substitution affects the stability of jarosite. This research improves our understanding of the effects of trace metal substitution in secondary minerals in mining environments.

### METHODS

Jarosite (Jr) was synthesized according to Baron and Palmer (1996). Cobalt-substituted jarosite (CoJr) was synthesized in a similar manner, except the starting solution contained dissolved  $\text{Co}^{2+}$ . Before experimentation, synthesized CoJr was additionally rinsed twice with 1 mM  $\text{HNO}_3$  (15 min. each). Laboratory and field samples were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and inductively coupled plasma mass spectrometry (ICP-MS). Other methods used in this study are outlined in this issue (Kimball, 2016).

### RESULTS

XRD patterns for both jarosite (Jr) and cobalt-substituted jarosite (CoJr) were best matched with synthetic jarosite (PDF#00-022-0827) both before and after 20 days of leaching. Each well-defined peak for both experiments matched with synthetic jarosite. The peak locations did not shift along  $2\theta$  during 20 days of leaching in either experiment.

SEM images showed that both Jr and CoJr grains exhibited similar size and shape both before and after 20 days of leaching. A lack of statistical difference

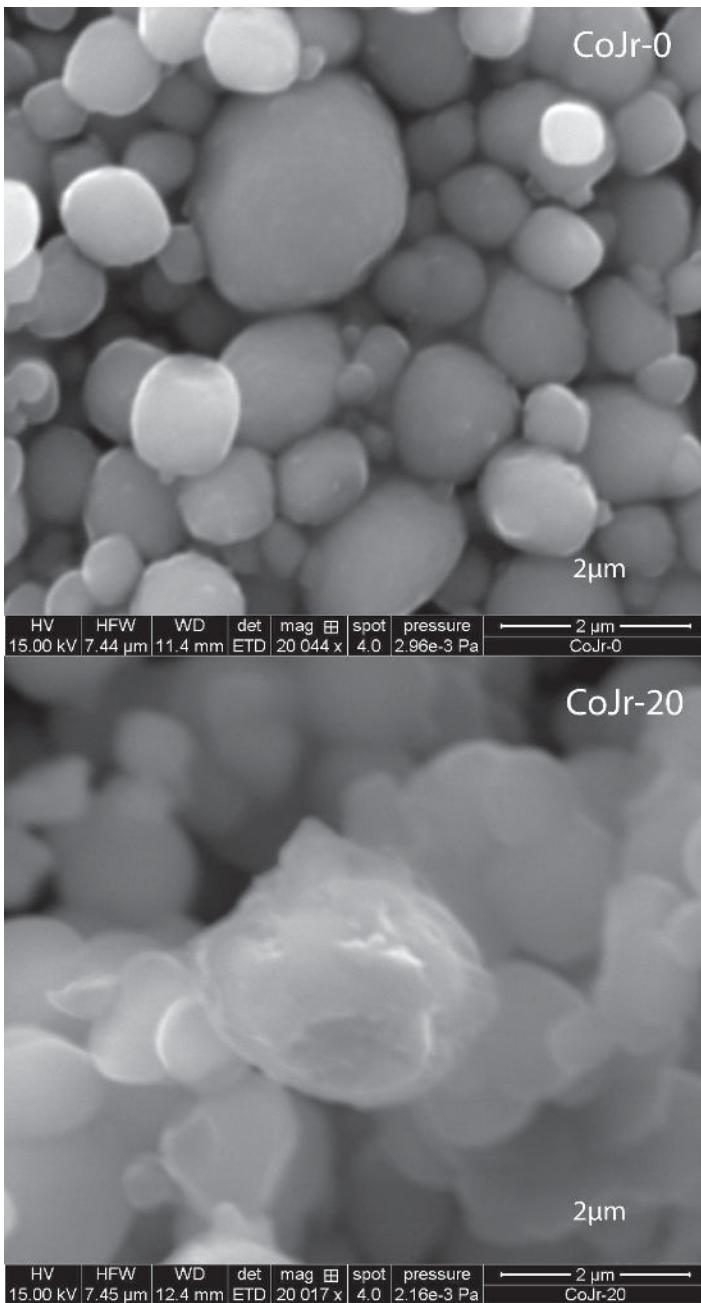


Figure 1. CoJr-0 and CoJr-20 SEM images at 20,000x magnification. Grain etching was pronounced in the CoJr-20 samples as apparent in more surface roughening compared to the CoJr-0 samples

in grain size amongst all groups was confirmed with ANOVA. However, Figure 1 shows that the CoJr grains that had been leached for 20 days exhibited etching, which was absent in SEM images of leached Jr grains.

The pH and total dissolved solids (TDS) of the Jr and CoJr solutions showed important differences. During the experiment, the pH of Jr, CoJr, and the Blank

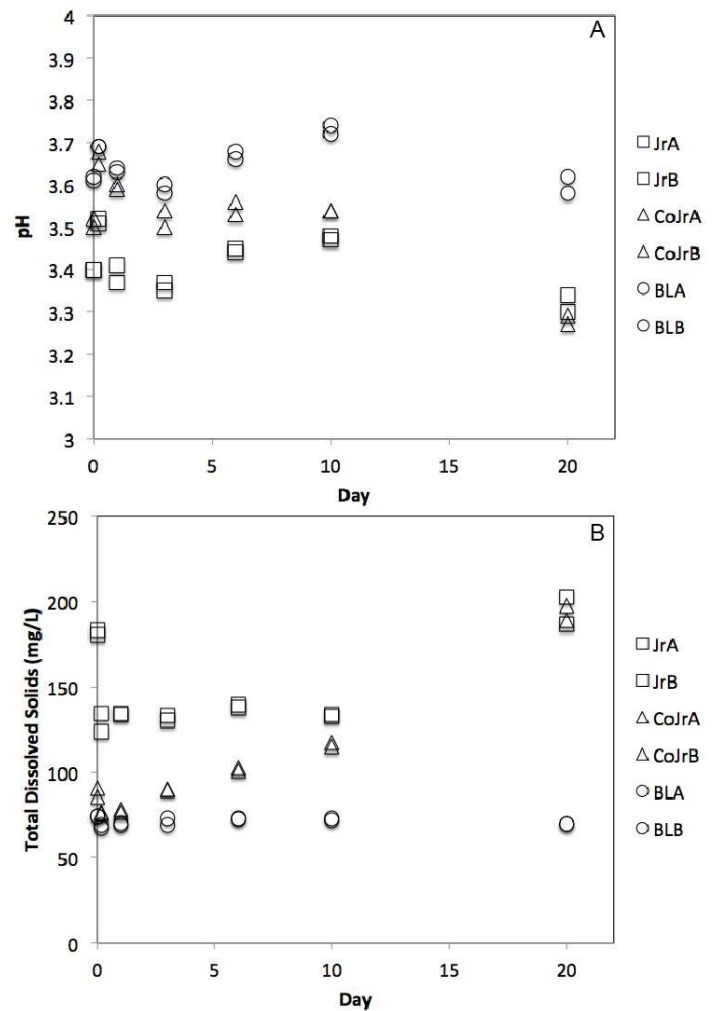


Figure 2. Time versus pH (A) and total dissolved solids (TDS) (B) for batch leach experiments with Jr, CoJr, and Blanks (BLA and BLB). Most likely due to a failing conductivity probe, the TDS values for day 20 were unexpectedly low, so the day 20 values plotted here represent those calculated with PHREEQC based on known concentrations of ions in solution.

fluctuated slightly (Fig. 2a). The pH of Jr and CoJr solutions were always below the Blank, and showed the greatest pH decrease between days 10 and 20 (Fig. 2a). The pH of the CoJr solution was always higher than the Jr solution, except on day 20 (Fig. 2a). TDS was unexpectedly low for day 20, most likely due to a failing conductivity probe. As a result, we used PHREEQC to calculate TDS for day 20 based on the known concentrations of ions in solution. The TDS of the Jr solutions was always well above the Blank (Fig. 2b). Solutions in the CoJr experiment showed a slight increase in TDS relative to the Blank at the beginning of the experiment, then increased linearly (Fig. 2b).

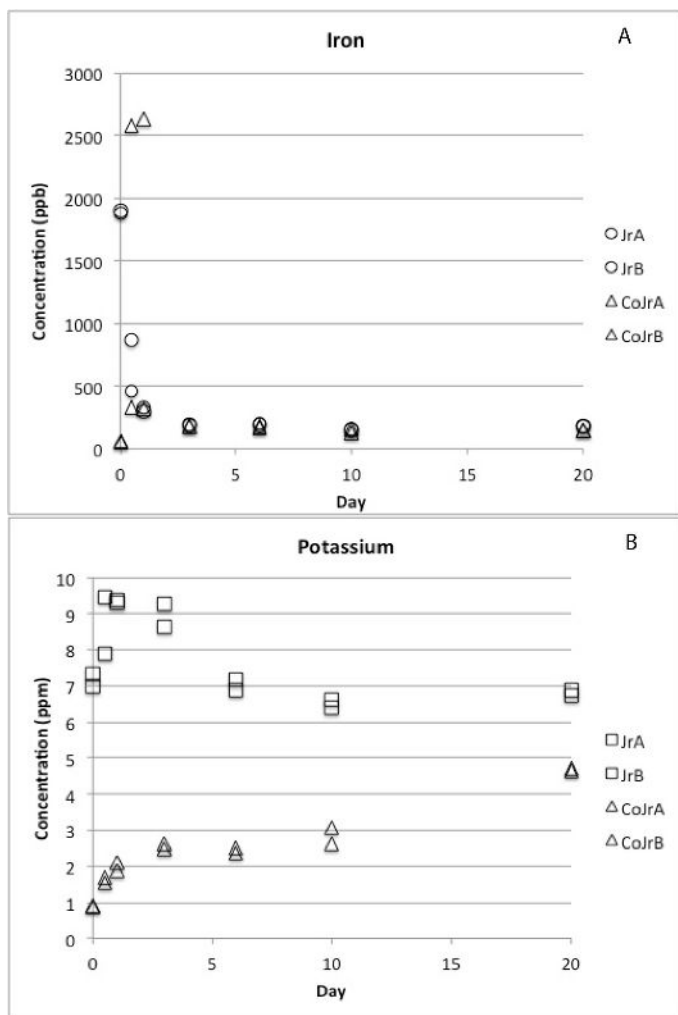
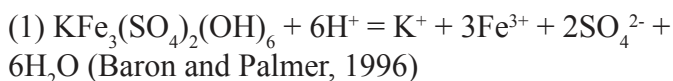


Figure 3. Time versus dissolved Fe (A) and K (B) for batch leach experiments with Jr and CoJr: The concentration of Fe (A) increased and decreased dramatically during the first day, followed by relative stability from day 3 onwards in both Jr and CoJr experiments. Potassium concentrations (B) were on average 4 mg/L higher in the Jr experiment compared to the CoJr experiment.

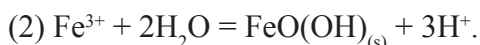
During the first day, dissolved [Fe] increased then decreased dramatically, then remained approximately constant at around 180  $\mu\text{g Fe/L}$  until day 20 in both experiments (Fig. 3a). Cobalt concentrations increased linearly throughout the CoJr experiment (data not shown), with a slope of 4.5  $\mu\text{g Co/L}$  ( $R^2 = 0.95$ ). Dissolved [K] was always higher in the Jr experiment, and remained relatively constant at around 7 mg/L from day 6 onwards (Fig. 3b) Dissolved K in the CoJr solutions increased rapidly during the first 3 days, remained constant until day 10, then resumed increasing to day 20 (Fig. 3b). Calculated sulfate concentrations generally mirrored those measured for K in both experiments.

## DISCUSSION

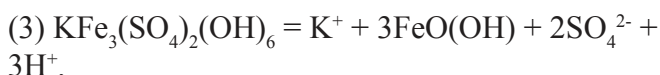
Jarosite dissolution is commonly described by the reaction:



where  $\text{H}^+$  is presumed to be a reactant. While these leach experiments are consistent with production of dissolved  $\text{K}^+$ ,  $\text{Fe}^{3+}$ , and  $\text{SO}_4^{2-}$ , they are inconsistent with consumption of  $\text{H}^+$  because the solution pH for all experiments decreased over time (Fig. 2a). An increase in  $\text{H}^+$  may result from the hydrolysis of dissolved  $\text{Fe}^{3+}$ , which forms more stable goethite by the reaction:



A more appropriate reaction for these experiments may be the overall reaction of (1) and (2), leading to:



Goethite [ $\text{FeO}(\text{OH})$ ] is a presumed product that we have yet to prove, but it has been shown to form during other jarosite leach experiments (Welch et al., 2008).

Pure Jr underwent rapid dissolution on day 1. TDS and [Fe] rapidly increased before stabilizing around day 3, while [K] increased, then decreased before stabilizing around day 6. The sharp increase, followed by decrease in [Fe] was also observed in earlier jarosite leach experiments (Kimball and Seal, 2014). At this time, it is unclear why this trend occurs. Rapid dissolution of smaller grains is an unlikely explanation because the grain size remained statistically similar from day 0 to 20 from analysis of SEM images.

The CoJr experiment exhibited a gradual increase in TDS and [K], and decrease in pH, which is consistent with CoJr dissolving according to reaction (3). CoJr also showed a rapid increase then decrease in [Fe] initially. This trend in [Fe] is not explained by the rapid release of sorbed Fe because the synthesized CoJr was rinsed with acid prior to the experiment, removing ions sorbed to the grains. The rate of

dissolution of CoJr appeared to increase between days 10 and 20, as revealed by accelerated pH decrease (Fig. 2a), and increase in TDS (Fig. 2b) and [K] (Fig. 3b). The nearly constant [Fe] from day 3 onward suggests that dissolution was nonstoichiometric, where some Fe remained in the solid phase. The continual increase of Co while Fe remained unchanged was similar to results with Cu- and Zn-substituted jarosite, where dissolved Cu and Zn also increased linearly over time (Kimball and Seal, 2014). Welch et al. (2008) also observed that dissolved [Fe] was lower than [SO<sub>4</sub>] and [K] in solution during leaching of jarosite. In each of these cases, the system seems stable with respect to Fe, but not with respect to K, SO<sub>4</sub>, and substituted trace metals.

Published thermodynamic data for jarosite vary over five orders of magnitude (Fig. 4), most likely because of variable composition (Welch et al., 2008). Figure 4 shows log[Fe<sup>3+</sup>] versus pH values over a range where jarosite is often observed in the environment. Solubility lines separate where jarosite is expected to be stable (above the line) from where the solution is expected to be stable (below the line)

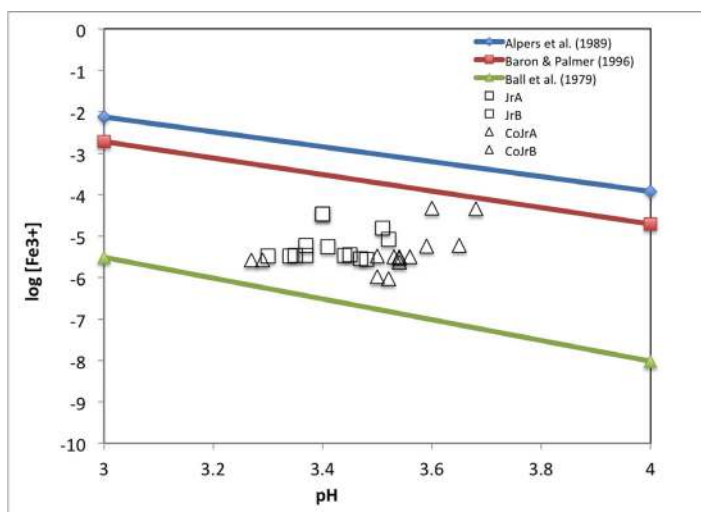


Figure 4. Plot of  $\log[\text{Fe}^{3+}]$  versus  $\text{pH}$  for a system containing jarosite and its dissolved components. Jarosite solubility lines are also represented by the following equation:  $\log[\text{Fe}^{3+}] = (1/3)\log K - x\log[\text{K}^+] - (2/3)\log[\text{SO}_4] - y(\text{pH})$ , where  $x = 0.257$  and  $y = 1.8$  (Alpers et al., 1989;  $\log K = -9.83$ ),  $x = 0.333$  and  $y = 2$  (Baron and Palmer, 1996;  $\log K = -11$ ), and  $x = 0$  and  $y = 2.5$  (Ball et al., 1979;  $\log K = -5.39$ ). Jarosite solutions evolved towards equilibrium at a constant rate, while CoJr evolved slowly at first, then quickly between days 10 and 20.

under equilibrium conditions. The data from these experiments lie between two possible solubility lines. Over time pH decreased and the data evolved towards the equilibrium line established by Ball et al. (1979). The data lie above this equilibrium line, indicating that if the system were at equilibrium, jarosite would be the most stable phase. The system was not at equilibrium, however, because no dissolved jarosite constituents were present at the beginning of the experiment. Over time, the experiment evolved toward stability, as indicated by the data moving towards equilibrium. On day 20, CoJr began to overtake Jr in evolving towards equilibrium, supporting an increase in the dissolution rate of CoJr.

Comparison of leach experiments in this study to those of goethite (Penprase, 2016) and schwertmannite (Schonberger, 2016) show that jarosite leaching was between goethite and schwertmannite in terms of released [Co] and TDS. Cobalt release from jarosite increased linearly at 4.5  $\mu\text{g/L}$  per day reaching 90  $\mu\text{g/L}$  on day 20, while the [Co] in solution of the Co-schwertmannite (CoSwt) leach experiment remained nearly constant around 30  $\mu\text{g/L}$  (Schonberger, 2016). During leaching of Co-goethite (CoGt), dissolved Co concentrations increased rapidly and remained at approximately 250  $\mu\text{g/L}$  for the duration of the experiment (Penprase, 2016). During leaching of CoJr, TDS was 30 mg/L higher than the blank, whereas during leaching of CoSwt, TDS was approximately 50 mg/L higher than the blank (Schonberger 2016). During leaching of CoGt, on the other hand, TDS was lower than the blank (Penprase 2016), suggesting sorption or precipitation of ions in solution. These comparative TDS results are consistent with what might be expected based in mineral stability at the experimental conditions, which would increase from schwertmannite, to jarosite, to goethite. These results also suggest that the ability of jarosite to sequester Co through substitution in its mineral structure is between that of schwertmannite and goethite.

## CONCLUSION

Results from this study show that when Jr and CoJr samples were leached under conditions where Jr was expected to be stable, Jr and CoJr underwent

dissolution. Additionally, Co was released from the mineral structure throughout the duration of the experiment, despite the relative stability of Fe in the solid phase. Release of Co from jarosite, even under stable conditions, suggests that jarosite may be a long-term source of trace metals in the environment. Jarosite was not detected in the Blackbird Creek precipitates, which were likely amorphous based on XRD (Penprase, 2016). Because this leach experiment was conducted over a 20-day period, additional research is needed to understand the stability of Co-substituted jarosite over a longer time frame. Understanding the fate of Co-substituted jarosite under conditions where it is expected to be stable furthers our knowledge of secondary Fe minerals, which are common mining affected streams.

## ACKNOWLEDGEMENTS

I would like to acknowledge the Keck Geology Consortium for making this research possible. I would like to thank Dr. Bryn Kimball for her constant guidance and tireless support throughout the project and Angela McGuire for her assistance with XRD and SEM. I would also like to acknowledge fellow Keck students, Sam Schonberger and Shanti Penprase, and Whitman student Lena Goss. Laboratory experiments, SEM, and XRD analysis were conducted at Whitman College. Further SEM and XRD were conducted at Carleton College.

## REFERENCES

- Alpers, C.N., Nordstrom, D.K., Ball, J.W., 1989, Solubility product of jarosite from acid mine water at Iron Mountain, California, U.S.A.: *Sciences Geologiques*, v. 42, p.281-298.
- Ball, J.W., Jenne, E.A., Nordstrom, D.K., 1979, WATEQ2-A computerized chemical model for trace and major element speciation and mineral equilibria of natural waters, in Jenne, E.A., ed., *Chemical modeling in aqueous systems. Speciation, sorption, solubility, and kinetics*: Washington, D.C.: American Chemical Society Symposium Series, v. 93, p. 815-836.
- Baron, D., and Palmer, C.D., 1996, Solubility of jarosite at 4–35 °C: *Geochimica et Cosmochimica Acta*, v. 60, p. 185–195.
- Burger, P.V., Papike, J.J., Shearer, C.K., and Karner, J.M., 2009, Jarosite growth zoning as a recorder of fluid evolution: *Geochimica et Cosmochimica Acta*, v. 73, p. 3248–3259.
- Desborough, G.A., Smith, K.S., Lowers, H.A., Swayze, G.A., Hammarstrom, J.M., Diehl, S.F., Leinz, R.W., and Driscoll, R.L., 2010, Mineralogical and chemical characteristics of some natural jarosites: *Geochimica et Cosmochimica Acta*, v. 74, p. 1041–1056.
- Drouet, C., and Navrotsky, A., 2003, Synthesis, characterization, and thermochemistry of K-Na-H<sub>3</sub>O jarosites: *Geochimica et Cosmochimica Acta*, v. 67, p. 2063–2076.
- Hudson-Edwards, K. A., Smith, A. M. L., Dubbin, W. E., Bennett, A. J., Murphy, P. J., Wright, K., 2008, Comparison of the structures of natural and synthetic Pb-Cu-jarosite-type compounds: *European Journal of Mineralogy*, v. 20, p. 241-252.
- Johnson, R., Close, T., Mchugh, E., 1998, Mineral Resource Appraisal of the Salmon National Forest, Idaho: US Geological Survey. Open-File Report 98-478.
- Kimball, B. E., Seal R. R. II., 2014, Trace copper and zinc release from jarosite. The V. M. Goldschmidt Conference, Sacramento, CA.
- Milliken R. E., Swayze G. A., Arvidson R. E., Bishop J. L., Clark, R. N., Ehlmann B. L., Green R. O., Grotzinger J. P., Morris R.V., Murchie S. L., Mustard J. F. and Weitz C., 2008, Opaline silica in young deposits on Mars: *Geology* v. 36, p. 847–850.
- Smith, A.M.L., Hudson-Edwards, K.A., Dubbin, W.E., and Wright, K., 2006, Dissolution of jarosite [KFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>] at pH 2 and 8: Insights from batch experiments and computational modeling: *Geochimica et Cosmochimica Acta*, v. 70, p. 608–621.
- Welch, S.A., Christy, A.G., Kirste, D., Beavis, S.G., and Beavis, F., 2007, Jarosite dissolution I—Trace cation flux in acid sulfate soils: *Chemical Geology*, v. 245, p. 183–197.
- Welch, S.A., Kirste, D., Christy, A.G., Beavis, F.R., and Beavis, S.G., 2008, Jarosite dissolution II—Reaction kinetics, stoichiometry and acid flux: *Chemical Geology*, v. 254, p. 73–86.