



Silicate mineral dissolution in the presence of acidophilic microorganisms: Implications for heap bioleaching

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ABSTRACT

Silicate minerals are found with sulfide minerals and therefore, can be present during heap bioleaching for metal extraction. The weathering of silicate minerals by chemical and biological means is variable depending on the conditions and microorganisms tested. In low pH metal rich environments their dissolution can influence the solution chemistry by increasing pH, releasing toxic trace elements, and thickening of the leach liquor. The amenity of five silicate minerals to chemical and biological dissolution was tested in the presence of either *Ferroplasma acidarmanus* Fer1 or *Acidithiobacillus ferrooxidans* with olivine and hornblende being the most and least amenable, respectively. A number of the silicates caused the pH of the leach liquor to increase including augite, biotite, hornblende, and olivine. For the silicate mineral olivine, the factors affecting magnesium dissolution included addition of microorganisms and Fe²⁺. XRD analysis identified secondary minerals in several of the experiments including jarosite from augite and hornblende when the medium contained Fe²⁺. Despite acidophiles preferentially attaching to sulfide minerals, the increase in iron coupled with very low Fe²⁺ concentrations present at the end of leaching during dissolution of biotite, olivine, hornblende, and microcline suggested that these minerals supported growth. Weathering of the tested silicates would affect heap bioleaching by increasing the pH with olivine, fluoride release from biotite, and production of jarosite during augite and hornblende dissolution that may have caused passivation. These data have increased knowledge of silicate weathering under bioleaching conditions and provided insights into the effects on solution chemistry during heap bioleaching.

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1. Introduction

Silicate minerals such as micas, feldspars, olivines, chain silicates, and pyroxenes are found with sulfide minerals and therefore, can be present during heap bioleaching of sulfide minerals for metal extraction. The weathering of silicate minerals by chemical and biological means is variable depending on the conditions and microorganisms present. In low pH and metal rich environments their dissolution can influence the conditions by altering the pH, releasing elements such as fluoride into solution, and increasing the viscosity of the leach liquor (Dopson et al., 2008). The release of fluoride from ore samples obtained from the Aitik mine containing biotite and muscovite is responsible for inhibition of bioleaching whereas, an ore containing lower amounts of fluoride is not inhibited (Dopson et al., 2008). Silicates are also present in tailings impoundments that

produce pH neutral products (Strömberg and Banwart, 1999a; Strömberg and Banwart, 1999b).

Weathering of silicates is catalyzed by heterotrophic bacteria and fungi via the production of acidic metabolites (Jain and Sharma, 2004) as well as by the action of acidophilic microorganisms. At pH 2.0, oxidation of Fe²⁺ by *Acidithiobacillus ferrooxidans* results in the formation of jarosite (KFe₃(SO₄)₂(OH)₆) and its precipitation was responsible for the partial alteration of phlogopite (KMg₃AlSi₃O₁₀(OH)₂) to vermiculite ((Mg,Fe,Al)₃(Al,Si)₄O₁₀(OH)₂·4H₂O) (Bigham et al., 2001). This transformation resulted in an increased distance between the stratified layers such that the physical size of the mica increased from a unit layer of 10.0 to 14.3 Å (Štyriaková et al., 2004). However, at pH <1.5 no jarosite was formed and phlogopite weathering did not result in any structural changes (Bigham et al., 2001). The weathering of mica minerals by *A. ferrooxidans* contained in a black schist ore also resulted in the formation of vermiculite from phlogopite, although phengite (K(Mg,Fe)_{0.5}Al_{1.5}(Si_{3.5}Al_{0.5})O₁₀(OH,F)₂) underwent structural changes at a much lower rate (Bhatti et al., 1993). Black shale samples containing quartz (SiO₂) and orthoclase (KAlSi₃O₈) are weathered by cultures of *A. ferrooxidans* without addition of Fe²⁺ before precipitation reactions lower the soluble Si

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Table 1
Formula and composition of the major elements present in the mineral samples

Silicate	Major elements (% wt/wt)											
	Si	Al	Fe	Mg	Ca	Na	K	Ti	Mn	Cr	P	S
Augite	24.5	0.7	7.4	7.4	15.3	0.5	0.2	<0.1	0.2	0.1	<0.1	<0.1
Biotite	17.7	5.9	13.7	8.4	1.2	0.4	8.1	1.6	0.5	<0.1	<0.1	<0.1
Hornblende	20.4	6.4	12.7	10.3	4.0	1.3	0.3	0.3	0.2	0.1	<0.1	0.1
Microcline	29.5	9.7	0.4	0.2	0.3	2.6	9.1	<0.1	<0.1	<0.1	0.3	<0.1
Olivine	19.7	0.2	5.8	28.1	0.2	<0.1	0.1	<0.1	0.1	0.2	<0.1	<0.1

concentration (Tasa et al., 1995). Surface changes of a fayalite olivine (Fe_2SiO_4) occur during natural chemical weathering at pH 2 and olivine weathering was reduced in the presence of *A. ferrooxidans* or Fe^{3+} (Welch and Banfield, 2002). Finally, the ability of *A. ferrooxidans* to utilize Fe^{2+} produced during dissolution of fayalite was demonstrated and its dissolution is inhibited by Fe^{3+} interaction with the mineral surface (Santelli et al., 2001; Welch and Banfield, 2002).

The acidophiles '*Ferroplasma acidarmanus*' Fer1 (Dopson et al., 2004; Edwards et al., 2000b) and *A. ferrooxidans* (Hallberg and Johnson, 2001) both oxidize Fe^{2+} . However, '*F. acidarmanus*' Fer1 is a heterotroph (Dopson et al., 2005) while *A. ferrooxidans* is an autotroph that also oxidizes reduced inorganic sulfur compounds (Hallberg and Johnson, 2001). Both of these acidophiles have been implicated in biomining (Rohwerder et al., 2003) where they come into contact with both sulfide and silicate minerals. To date, the role of acidophilic microorganisms in silicate mineral dissolution has been virtually limited to *A. ferrooxidans* grown in the presence of Fe^{2+} and the effect of other microorganisms and growth conditions is largely ignored. In this study, we report silicate mineral dissolution rates for a range of silicates that may be present during heap bioleaching for *A. ferrooxidans* and '*F. acidarmanus*' Fer1 grown under various conditions.

2. Materials and methods

2.1. Minerals used in the study

The silicate minerals used in the study were the pyroxene chain silicate augite, the mica magnesium-biotite, the chain silicate magnesio-hornblende, the feldspar microcline, and the orthosilicate olivine all purchased from Ward's (Rochester, NY, USA). The silicates were ground and sieved to $<125 \mu\text{m}$ and analyzed for chemical contents by inductively coupled plasma (ICP) emission spectrometry (Table 1). The silicate minerals were divided into multiple portions in a sample divider (Retsch, Haan, Germany) for the bioleaching experiments.

2.2. Microorganisms and silicate mineral leaching conditions

Initial shake flask experiments (100 mL) were carried out with 5% (wt/vol) silicate mineral in minimal salts medium (MSM) containing trace elements (Dopson and Lindström, 1999) and growth substrates. Duplicate shake flasks were inoculated with 3.125×10^9 cells of either *A. ferrooxidans* (ATCC 23270; MSM at pH 2.0) or '*F. acidarmanus*' Fer1 (Dopson et al., 2004; Edwards et al., 2000b) in MSM at pH 1.2. The substrate for '*F. acidarmanus*' Fer1 was 50 mM Fe^{2+} and 0.02% (wt/vol) yeast extract or 0.02% (wt/vol) yeast extract alone whereas, the substrate for *A. ferrooxidans* was 50 mM Fe^{2+} or 5 mM tetrathionate. The flasks were incubated shaking at 30° and 37 °C, respectively. Silicate mineral leaching was indicated by increased pH and release of soluble magnesium (Mg_{Sol}) by atomic absorption spectrometry (AAS) (Dopson and Lindström, 1999). Soluble Fe^{2+} was tested by titration with ceric sulfate (Kolthoff and Sandell, 1963). pH and redox potential (Pt electrode against a Ag^0/AgCl reference) were also measured. Shake flask results are presented as means \pm SD (number of replicates (n)=2).

Stirred tank reactors (STRs) were carried out with 5% (wt/vol) biotite in 1.5 L MSM pH 1.2 containing 50 mM Fe^{2+} and 0.02% (wt/vol) yeast extract. Where indicated, the STRs were inoculated with 1.7×10^9 '*F. acidarmanus*' cells incubated at 37 °C and sparged with 300 mL air min^{-1} . Soluble metals, pH, and redox potential were analyzed

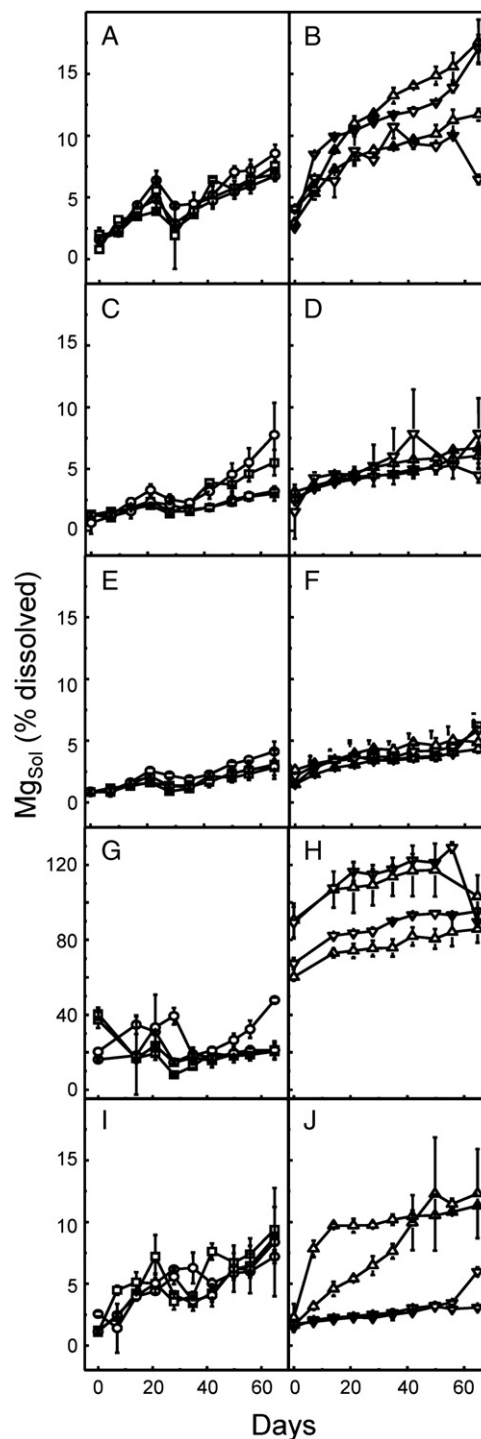


Fig. 1. Dissolution of augite (A and B), biotite (C and D), hornblende (E and F), microcline (G and H), and olivine (I and J) in batch cultures (data are means \pm SD ($n=2$)). The silicates were leached in the presence (filled symbols) and absence (open symbols) of microorganisms. The graphs are '*F. acidarmanus*' Fer1 (A, C, E, G, and I) grown under mixotrophic (■, □) or heterotrophic (●, ○) conditions or *A. ferrooxidans* (B, D, F, H, and J) grown on Fe(II) (▲, △) or tetrathionate (▼, ▽) media.

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