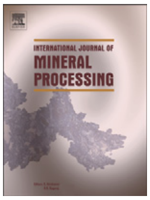
International Journal of Mineral Processing 98 (2011) 30–34

Contents lists available at ScienceDirect

International Journal of Mineral Processing

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



Weathering of phlogopite in simulated bioleaching solutions

Tariq M. Bhatti [a,b,1], Jerry M. Bigham [c], Antti Vuorinen [d], Olli H. Tuovinen [a,b,*]

[a] Department of Microbiology, Ohio State University, Columbus, OH 43210, USA
[b] Department of Chemistry and Bioengineering, Tampere University of Technology, FI-33101 Tampere, Finland
[c] School of Environment and Natural Resources, Ohio State University, Columbus, OH 43210, USA
[d] Department of Geology, P.O. Box 64, FI-00014 Helsinki University, Finland

ARTICLE INFO

Article history:
Received 5 April 2010
Received in revised form 16 September 2010
Accepted 6 October 2010
Available online 14 October 2010

Keywords:
Acidithiobacillus ferrooxidans
Iron oxidation
Jarosite precipitation
Lattice expansion
Mica alteration
Phlogopite weathering

ABSTRACT

The purpose of this study was to examine structural alterations of finely ground phlogopite, a trioctahedral mica, when exposed to acid, iron- and sulfate-rich solutions typical of bioleaching systems. Phlogopite suspensions were supplemented with ferrous sulfate and incubated with iron- and sulfur-oxidizing bacteria (*Acidithiobacillus ferrooxidans*) at 22 °C. As bacteria oxidized ferrous iron, ferric iron thus formed partially precipitated as K-jarosite. K-jarosite precipitation was contingent on the preceding ferrous iron oxidation by bacteria and the release of interlayer-K from phlogopite. This chemically and microbially induced weathering involved alteration of phlogopite to a mixed layer structure that included expansible vermiculite. The extent of phlogopite weathering and structure expansion varied with duration of the contact, concentration of ferrous iron and phlogopite, and the presence of monovalent cations (NH_4^+, K^+, or Na^+) in the culture solution. NH_4^+ and K^+ ions (100 mM) added to culture suspensions precipitated as jarosite and thereby effectively prevented the loss of interlayer-K and structural alteration of phlogopite. Additional Na^+ (100 mM) was insufficient to precipitate ferric iron as natrojarosite and therefore the precipitation was coupled with interlayer-K released from phlogopite. When ferrous iron was replaced with elemental sulfur as the substrate for *A. ferrooxidans*, the weathering of phlogopite was based on chemical dissolution without structural interstratification. The results demonstrate that iron oxidation and the concentration and composition of monovalent ions can have an effect on mineral weathering in leaching systems that involve contact of phlogopite and other mica minerals with acid leach solutions.

1. Introduction

Micas are common layer silicates in soils, sediments, and many ore deposits. In soils, micas constitute a long-term nutrient reservoir of K and Mg that are released to the soil solution upon weathering (Kalinowski and Schweda, 1996; Taylor et al., 2000; Arocena and Velde, 2009). Micas differ greatly in their susceptibility to natural weathering processes (Nagy, 1995). In general, trioctahedral micas are more readily weathered through chemical dissolution and structural alterations as compared to dioctahedral micas. Our previous work with phlogopite, biotite, muscovite and phengite (Bhatti et al., 1993, in press; Bigham et al., 2001; Tasa et al., 1995) showed that phlogopite and biotite were most readily weathered under acid bioleaching conditions. Micas sometimes contain potentially toxic trace elements and thus weathering may release these species into the environment. Advanced weathering results in the formation of expansive structures such as vermiculite and smectite found in diagenetic environments.

Previously we have observed structural alterations in the mica component of a black schist ore due to enhanced weathering by acidophilic iron-oxidizing bacteria (*Acidithiobacillus ferrooxidans*), which produced ferric iron by oxidation of pyrrhotite ($Fe_{1-x}S$) and pyrite (FeS_2) (Bhatti et al., 1993, 1994). Mica minerals were also subject to dissolution by sulfuric acid that bacteria produced upon oxidation of tetrathionate as the substrate (Bigham et al., 2001). Phlogopite in the black schist ore was shown to be particularly susceptible to structural alteration when bacteria oxidized Fe-sulfides or ferrous iron (Bigham et al., 2001; Bhatti et al., 2010). The results of the previous work demonstrated that iron oxidation resulted in the precipitation of K-jarosite (ideal formula $KFe_3(SO_4)_2(OH_6)$) whereby K was provided by release of interlayer-K in the mica (Bigham et al., 2001). The purpose of this work was to identify factors that affect the weathering of phlogopite in cultures of *A. ferrooxidans*. This bacterium is common in bioleaching systems where accessory micas in the gangue may be exposed to the action of acidophilic bacteria and iron- and sulfur-compounds for extended periods of time.

2. Materials and methods

The phlogopite studied was a research grade sample that was ground to −200 mesh (Φ <74 µm) and stored dry until used. The sample

---

* Corresponding author. Department of Microbiology, Ohio State University, 484 West 12th Avenue, Columbus, OH 43210, USA. Tel.: +1 614 292 3379; fax: +1 614 292 8120.
E-mail address: tuovinen.1@osu.edu (O.H. Tuovinen).

[1] Present address: Department of Chemical and Materials Engineering, Pakistan Institute of Engineering and Applied Sciences, P.O. Nilore-45650, Islamabad, Pakistan.

0301-7516/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.minpro.2010.10.004

contained 43.50% SiO_2, 10.61% Al_2O_3, 2.83% Fe_2O_3, 4.66% FeO, 22.87% MgO, 0.773% CaO, 0.161% Na_2O, 11.31% K_2O, 0.034% MnO, and 0.19% TiO_2 (Bigham et al., 2001).

A. ferrooxidans was used as the test organism in all weathering experiments. The culture was maintained with ferrous sulfate in a medium that contained 120 mM $FeSO4 \cdot 7H_2O$ and 0.4 g/L each of $(NH_4)_2SO_4$, $MgSO_4 \cdot H_2O$, and K_2HPO_4. The medium was adjusted to pH 2.0 with sulfuric acid.

The time course experiments with inoculated phlogopite suspensions were designed to test the effect of (a) the concentration of phlogopite (0.1 to 2.5% w/v); (b) ferrous sulfate concentration (0 to 120 mM Fe^{2+}); (c) varying monovalent cations (100 mM K^+, NH_4^+ and Na^+ as respective sulfates); and (d) the substitution of 10 g S^0/L for $FeSO_4$ as the source of energy for the bacteria. Cultures were incubated on a shaker (150 rpm) at 22 ± 2 °C. Evaporation losses were compensated for by addition of distilled H_2O. In long time courses, fresh mineral salts solution was added after 60 days of incubation.

At intervals, samples were removed for chemical and mineralogical analysis. Chemical analysis of solution samples and leach residues was based on inductively coupled plasma atomic emission spectroscopy (Bhatti et al., 1993). Samples of solids for X-ray diffraction (XRD) analysis were air dried at 22 ± 2 °C followed by manual grinding with a mortar and pestle. Samples were analyzed as powder mounts using CuKα-radiation and a vertical, wide-range goniometer equipped with a diffracted-beam monochromator and a Θ-compensating slit. Samples were scanned from 2 to 70° 2Θ in increments of 0.05° 2Θ with 4 s counting time.

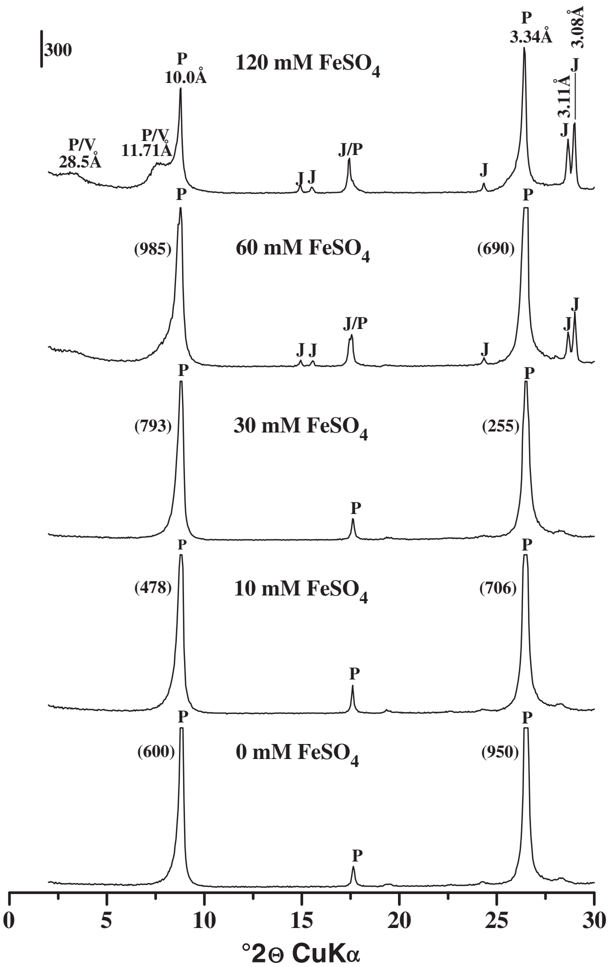


Fig. 1. X-ray diffraction patterns from phlogopite (2.5% w/v) and precipitates following 10 days contact in *A. ferrooxidans* cultures that were supplemented with 0–120 mM $FeSO_4$ as the substrate. The vertical bar indicates the scale of relative counts. The numbers in parentheses indicate the counts that were off scale. The diagnostic peaks of jarosite and interstratified phlogopite/vermiculite are identified with the corresponding *d* values (1 Å = 0.1 nm). Letter designations: J = jarosite, P = phlogopite, V = vermiculite.

3. Results and discussion

3.1. Effect of Fe^{2+} and S^0 on phlogopite weathering

Weathering of phlogopite (2.5% w/vol) was tested in iron-oxidizing bacterial cultures that were supplemented with 0, 10, 30, 60, or 120 mM Fe^{2+}. The cultures were incubated for 10 days, and supplemental ferrous iron was completely oxidized by *A. ferrooxidans* within two days. XRD patterns did not indicate any structural alteration of phlogopite in the absence of iron, and the oxidation of 10 and 30 mM concentrations of Fe^{2+} also did not affect the structure of phlogopite (Fig. 1). Interstratification of phlogopite with an expansible component was apparent following the oxidation of 60 and 120 mM Fe^{2+}. The 10.0 Å phlogopite peak was broadened (Fig. 1), and a mixed layer structure of phlogopite and vermiculite was formed after bacterial oxidation of 120 mM Fe^{2+}. Distinct jarosite peaks with the characteristic doublet at 3.08 and 3.12 Å were present in suspended solids sampled from cultures grown with 60 and 120 mM Fe^{2+} (Fig. 1).

Phlogopite interlayers did not expand within 30 days when S^0 (10 g/L) was initially substituted for 120 mM Fe^{2+} in *A. ferrooxidans* cultures (Fig. 2). Under these conditions, bacteria oxidize S^0 to sulfuric acid, which enhances the chemical dissolution but does not cause selective loss of K^+ from the structure. Similarly, structural alterations of phlogopite were not detected in *A. ferrooxidans* cultures grown with K-tetrathionate (5 mM $K_2S_4O_6$) (results not shown). In this case,

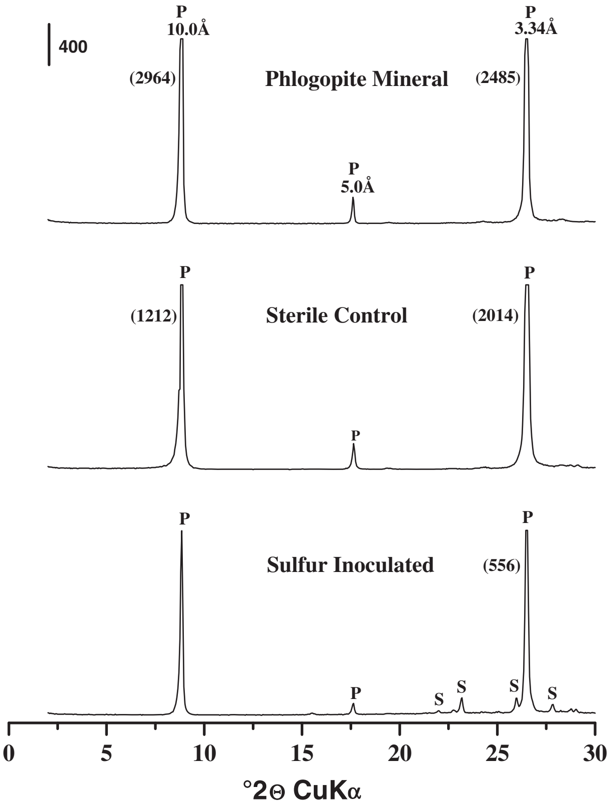


Fig. 2. X-ray diffraction patterns from original (untreated) phlogopite, from phlogopite (2.5% pulp density) incubated as a sterile control for 30 days, and from phlogopite (2.5% w/v) and S^0 (10 g/L) inoculated with *A. ferrooxidans* and incubated for 30 days. The vertical bar indicates the scale of relative counts. The numbers in parentheses indicate the counts that were off scale. The diagnostic peaks of phlogopite are identified with the corresponding *d* values (1 Å = 0.1 nm). Letter designations: P = phlogopite, S = elemental sulfur.