



The mineral and aqueous phase evolution of sulfur and nickel with weathering of pyrrhotite in a low sulfide, granitic waste rock

Jeff B. Langman^{a,b,*}, David W. Blowes^b, Harish Veeramani^b, David Wilson^b, Leslie Smith^c, David C. Segó^d, Dogan Paktunc^e

^a University of Idaho, Department of Geological Sciences, Moscow, ID, USA

^b University of Waterloo, Department of Earth and Environmental Sciences, Waterloo, ON, Canada

^c Department of Earth and Ocean Sciences, University of British Columbia, Vancouver, BC, Canada

^d Department of Civil and Environmental Engineering, University of Alberta, Edmonton, AB, Canada

^e Canada Centre for Mineral and Energy Technology, Mining & Mineral Sciences Lab, Ottawa, ON, Canada

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ABSTRACT

The release of S and metals from the weathering of waste rock pyrrhotite [Fe_(1-x)S] is affected by oxidation pathways, the presence and concentration of Fe-substitution metals (e.g., Ni), and Fe (oxyhydr)oxide products. A 4C (monoclinic) pyrrhotite [Fe₇S₈, Ni:Fe substitution of about 1:200] in a low sulfide waste rock was weathered in the laboratory and at a field site to identify the evolution of S oxidation, distribution and coordination of Ni, and possible adsorption of Ni on secondary Fe minerals. Mineral phase S was present in the -2, -1, 0, +4, and +6 oxidation states prior to its release as SO₄²⁻ into solution. The thiosulfate [S₂O₃²⁻] pathway of sulfide oxidation was indicated by the presence of polythionates and S₂O₃²⁻. Sulfur as S₂O₃²⁻ was more persistent than sulfite [SO₃²⁻] prior to oxidation to SO₄²⁻. The release of Ni during the oxidative dissolution of pyrrhotite was influenced by its distribution in the grain: diffuse throughout the grain (solid solution mineral) or concentrated in exsolved pentlandite [(Fe,Ni)₉S₈] lamellae within the pyrrhotite. With the oxidation of S, Ni coordination changed from bonding with reduced S species to bonding with oxygen prior to its release with SO₄²⁻. Sulfur as SO₄²⁻ typically stayed in solution with release from the pyrrhotite, but the solubility of released Ni was dependent on leachate pH. A near-neutral pH induced the adsorption of Ni onto Fe (oxyhydr)oxides, which formed during oxidation of the pyrrhotite. In some grains, Ni was found concentrated in Fe distal precipitates as opposed to the closer alteration layers/zones of the sulfide grain. Subsequent dissolution of the Fe (oxyhydr)oxides or desorption of Ni with a change in pH provides a delayed release of Ni into solution. This improved understanding of the oxidation pathway of S, coordination and release of Ni, and influence of Fe (oxyhydr)oxides in the weathering of pyrrhotite will assist in determining appropriate reaction-rate factors and element release rates for prediction of acid rock drainage.

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1. Introduction

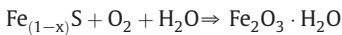
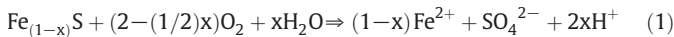
Weathering of waste rock proceeds rapidly by partial oxidation of sulfide minerals, but further oxidative dissolution may be constrained by the availability of oxygen to sustain oxidation and water for hydrolysis and leaching of elements into solution (Nordstrom and Southam, 1997; Nordstrom and Alpers, 1999; Blowes et al., 2003). The variable element composition, crystal structure, and substitution metals associated with pyrrhotite [Fe_(1-x)S] also affect its rate of weathering (Yakhontova et al., 1983; Orlova et al., 1989; Janzen et al., 2000; Belzile et al., 2004; Chen et al., 2006). Pyrrhotite occurs in various crystal

structures (polytypes) that differ according to the level of Fe vacancy (Becker et al., 1997; Wang and Salveson, 2005; de Villiers et al., 2009; de Villiers and Liles, 2010; Elliot, 2010). Differences in Fe vacancies produce nonstoichiometric composition, multiple crystal systems (monoclinic, hexagonal, or orthorhombic), and metal substitutions, such as the inclusion of Co and Ni (Orlova et al., 1989; Janzen et al., 2000; Pósfai et al., 2000; Harries et al., 2013). A low sulfide, granitic waste rock containing a common Fe-deficient pyrrhotite (Fe₇S₈ or 4C (monoclinic) pyrrhotite) that included traces of Ni and Co [(Fe_{0.852}Ni_{0.004}Co_{0.001})_{Σ0.857}S] was weathered during laboratory and field experiments. The objectives of these experiments were to examine the formation of weathering products and observe the evolution of the oxidation, retention, and release of S and Ni. A better understanding of the oxidation state and coordination of S and Ni in the pyrrhotite grains will assist in determining appropriate reaction-rate factors and element release rates for prediction of acid rock drainage (ARD).

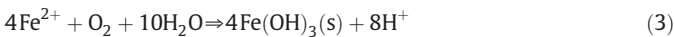
* Corresponding author at: University of Idaho, Department of Geological Sciences, Moscow, ID, USA.

E-mail address: jlangman@uidaho.edu (J.B. Langman).

The weathering of pyrrhotite commonly produces secondary oxidation products that form alteration layers (or discontinuous zones) of Fe_7S_8 + Fe_2S_3 , FeS_2 , and Fe (oxyhydr)oxides, where S is not expected to migrate from the FeS_2 (marcasite or enriched S layer) to the outer ferric Fe layer (Mycroft et al., 1995; Cruz et al., 2005). Under oxidative conditions, the formation of Fe (oxyhydr)oxides provides an external barrier to pyrrhotite dissolution (Mycroft et al., 1995; Thomas et al., 1998, 2001). The loss of S (Eq. (1)) and retention of Fe (Eqs. (2) and (3)) in the weathered layers can produce various Fe (oxyhydr)oxides, such as goethite [α -FeO(OH)], lepidocrocite [γ -FeO(OH)], magnetite [$\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$], ferrihydrite [$\text{Fe}_2\text{O}_3 \cdot 0.5\text{H}_2\text{O}$], and hematite [Fe_2O_3]. The oxidative dissolution of pyrrhotite produces greater S release early in the weathering process followed by the potential for greater release of Fe with dissolution of the alteration layers (Thomas et al., 1998). The different element release periods create a variable end product depending on pH and the extent of oxidation and dissolution (Eq. (2)).



and/or FeOOH and/or Fe_yS_z (unbalanced)



The alteration layers of oxidized pyrrhotite can be composed of various Fe-deficient sulfides, polysulfides, elemental S, and sulfoxyanions as stable or metastable intermediaries along with SO_4^{2-} and Fe (oxyhydr)oxide products (Steger and Desjardins, 1977, 1978; Buckley and Woods, 1985; Davis and Ritchie, 1986; Blowes and Jambor, 1990; Plysunin et al., 1990; Kalinkin et al., 2000; Mikhlina et al., 2002; Belzile et al., 2004). The evolution of the pyrrhotite reaction rate and development of the alteration layers can be described conceptually and mathematically by the shrinking core concept (Levenspiel, 1972; Cathles, 1979; Davis and Ritchie, 1986, 1987; Davis et al., 1986; Wunderly et al., 1996; Mayer et al., 2002), but accurate modeling of ARD using this concept requires adjustments to modeling variables to account for the variability in crystal structure, heterogeneity of secondary mineral formation, and presence and behavior of substitution metals.

The point at which Ni is released during pyrrhotite weathering is not well constrained but represents a potential weathering indicator because of its greater solubility in near-neutral pH compared to Fe. Nickel substitutes for Fe in pyrrhotite at trace levels (Arnold, 1966; Janzen et al.,

2000), but it may be unevenly distributed. Within pyrrhotite, Ni can be diffusely distributed as a common Fe substitute or in discontinuous layers or fine lamellae (basal parting) of pentlandite [$(\text{Fe,Ni})_5\text{S}_8$] (Naldrett et al., 1967; Janzen, 1996). Pentlandite likely forms during exsolution of a nickeliferous pyrrhotite, which produces concentrated Ni in pentlandite lamellae with lower Ni abundance distributed throughout the pyrrhotite grain (Hawley, 1962; Naldrett et al., 1967; Etschmann et al., 2004). The release of Ni into solution from oxidative dissolution of pyrrhotite is primarily dependent upon the local pH, which controls the mobility of trace metals such as Ni (Nordstrom, 2011); however, the release of Ni may be influenced by its distribution within the pyrrhotite (diffusely distributed or as pentlandite lamellae) and the presence of various Fe (oxyhydr)oxides in the alteration zones.

1.1. Mine site and waste rock

Samples of a low sulfide waste rock containing pyrrhotite were collected from the Diavik Diamond Mine (Diavik), located on an island in Lac de Gras in the Northwest Territories, Canada (Fig. 1), as part of the Diavik Waste Rock Project. The site is in the Canadian Arctic: a permafrost, polar climate area with an annual precipitation of less than 300 mm (40% as rain, 60% as snow) and average minimum, mean, and maximum temperatures of -31 , -9 , and 18 °C, respectively (Environment Canada, 2013). An active freeze-thaw zone extends 4 m into the bedrock at the site, and deeper into unconsolidated materials (Pham et al., 2013). The waste rock is composed of about 75% granite, 14% pegmatitic granite (pegmatite), 10% biotite schist, and 1% diabase (Blowes and Logsdon, 1998). The granites are primarily quartz [SiO_2], K-feldspar [KAlSi_3O_8], and albite [$\text{NaAlSi}_3\text{O}_8$], with greater albite in the granite and greater K-feldspar in the pegmatite (Jambor, 1997). The biotite schist is composed primarily of albite (35–55%), quartz (20–50%), and biotite [$\text{K}(\text{Mg,Fe})_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$] (10–25%) and has a mean sulfide content of 0.24 wt.% S (range of 0.02 to 0.42 wt.% S). The sulfide in the schist is primarily composed of pyrrhotite ranging from 50 to 200 μm in diameter (Jambor, 1997).

2. Materials and methods

Waste rock was collected for weathering under laboratory conditions (humidity cell) and to construct field-site, experimental, waste-rock piles (test piles) to examine weathering under natural conditions as part of the Diavik Waste Rock Project. The humidity cell experiment is described in Langman et al. (2014), and the construction of the two

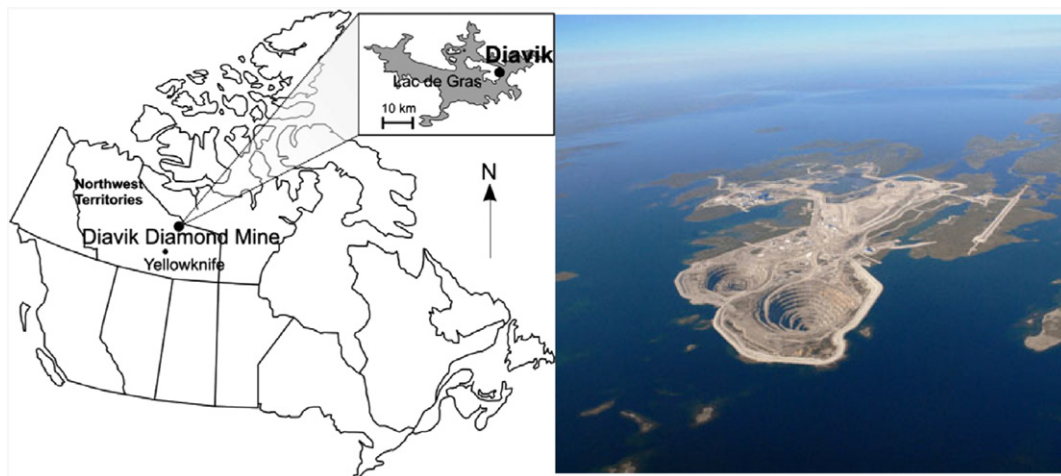


Fig. 1. The Diavik Diamond Mine is located on East Island in Lac de Gras—300 km northeast of Yellowknife, NT, 220 km south of the Arctic Circle—and is the location of the Diavik Waste Rock Project (Smith et al., 2013c; photo courtesy of Diavik Diamond Mines, Inc.).

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