Jarosite quantification in soils: An enhanced sequential extraction procedure

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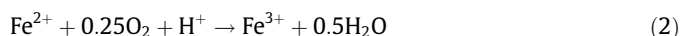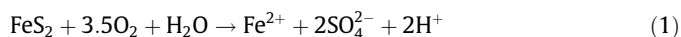
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ABSTRACT

A two-step sequential extraction procedure established for the quantification of acidity producing ferric and ferrous sulfate minerals such as melanterite and jarosite in acid mine wastes was evaluated for quantification of jarosite spiked in soils. The procedure involves in sequence anoxic water extraction, roasting the solid residue after anoxic water extraction at 550 °C for 1 h, and 4 M HCl extraction of the roasted solid. Soil and quartz samples were spiked with known amounts of synthetic and natural jarosite and their recovery was measured using the suggested two-step sequential extraction procedure. The recoveries of synthetic and natural jarosite were calculated on the basis of the S contents of the initially spiked jarosite in soil and quartz samples. Less than 50% of the spiked jarosite was recovered. The missing S is partially attributable to the retention of jarosite by the Teflon filter membrane used during the filtration of the anoxic water extract. Further investigations also demonstrated a lower 4 M HCl-S extractability from jarosite samples roasted at 550 °C than those roasted at 450 °C. S recovery from jarosite-spiked quartz samples increased to 45–70% by replacing the Teflon filter membrane with the Cellulose Acetate filter membrane and including this filter paper in the second step roasting. This modified method is a step forward in the development of methods to accurately and reliably quantify jarosite in soil materials.

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1. Introduction

Jarosite is a secondary Fe(III) mineral commonly found in acid sulfate soils (ASS) (Welch et al., 2007; Johnston et al., 2011a,b) and acid mine drainage (AMD) sites (Bigham et al., 1996; Norlund et al., 2010). Jarosite is a member of the alunite group with the standard molecular formula of $AB_3(SO_4)(OH)_6$, where A is a monovalent cation such as K^+, Na^+, H_3O^+ and NH_4^+ and B position is occupied by trivalent cations like Fe^{3+} and Al^{3+} (Baron and Palmer, 1996; Bigham and Nordstrom, 2000; Smith et al., 2006; Bigham et al., 2010; Desborough et al., 2010).

In natural environments, jarosite forms as a result of partial oxidation of pyrite (FeS_2) (which forms a solution rich in Fe^{2+} and SO_4^{2-}) (Eq. (1)), a process generally catalysed by iron-oxidising bacteria (Bigham and Nordstrom, 2000) (Eqs. (1)–(3)).

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (1)$$

$$Fe^{2+} + 0.25O_2 + H^+ \rightarrow Fe^{3+} + 0.5H_2O \qquad (2)$$

$$3Fe^{3+} + K^+ + 2SO_4^{2-} + 6H_2O \rightarrow KFe_3(SO_4)_2(OH)_6 + 6H^+ \qquad (3)$$

Jarosite is stable under oxic, acidic (pH 1–3) and SO_4^{2-} rich (>3000 mg L^{-1}) conditions (Bigham and Nordstrom, 2000; Smith et al., 2006). However, in the long term and under less favorable environmental conditions (i.e. reducing, near-neutral conditions), jarosite will transform to other iron minerals such as goethite (α-FeOOH/Fe(OH)$_3$) as shown in Eq. (4) (White et al., 1997; Welch et al., 2007).

$$3H_2O + KFe_3(SO_4)_2(OH)_6 \rightarrow 3Fe(OH)_3 + 2SO_4^{2-} + 3H^+ + K^+ \qquad (4)$$
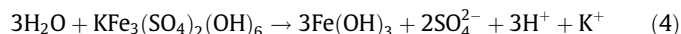
In oxidised ASS and AMD environments, jarosite exists with other meta-stable secondary Fe(III) minerals such as schwertmannite ($Fe_8O_8(OH)_6SO_4$) and discharges acidity to the environment as they hydrolyse (Ahern et al., 2004; Li et al., 2007; Welch et al., 2007; Johnston et al., 2009a,b). In addition to being an important source of acidity, jarosite can scavenge and influence the mobility of trace metals (Smith, 2004; Welch et al., 2007). However, these scavenged trace metals are likely to be re-mobilized as jarosite weathers (Acero et al., 2006; Welch et al., 2007). Therefore the presence of secondary Fe(III) minerals such as jarosite in ASS is a potential hazard to terrestrial and aquatic environments (Sullivan et al., 2012).

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The assessment of acidity is a key tool for managing ASS and AMD landscapes. The challenge lies in quantitatively discriminating the different sources of acidity, particularly the fraction associated with jarosite (Ahern et al., 2004). Sequential extraction techniques often aim to quantitatively recover separate phases mixed with other mineral phases. These separate phases are usually operationally defined such as: water soluble, exchangeable, carbonate bound (Tessier et al., 1979; Dold, 2003; Claff et al., 2010). In these sequential extraction techniques, a variety of extractants such as 4 M to 12 M HCl, acidified AAO (extraction for about 1 h), 0.3 M NaOH and citrate buffer dithionite (CBD) (some of which also require heating the solution up to 80–90 °C) have been used to dissolve jarosite (Dold, 2003; Yin and Catalan, 2003; Claff et al., 2010). However, these extractants are unable to specifically recover only jarosite. In 2007, Li et al. introduced a simple two-step sequential extraction method and they obtained a 100% recovery of jarosite spiked in mine tailing samples by using this method.

In 2004, Ahern et al. introduced two measurements termed "Net Acid Soluble Sulfur" (S_{NAS}) and "Residual Acid Soluble Sulfur" (S_{RAS}) for the assessment of the acidity present in these iron minerals in ASS. Both S_{NAS} and S_{RAS} employ the recovery of S from such minerals and are stoichiometrically able to estimate their content. The jarosite content is therefore estimated based on the "ideal" jarosite composition (e.g. Eq. (4)). S_{NAS} content is obtained by subtracting the 1 M KCl extractable sulfur content from the 4 M HCl extractable sulfur content. S_{RAS} content is determined from the soil residue by extracting with 4 M HCl after the peroxide oxidation (Ahern et al., 2004). However, a recent evaluation (Vithana et al., 2013) revealed that neither measurement provides a reliable estimate of the jarosite content in ASS. That study found that S_{NAS} content underestimated the initially spiked jarosite content in soil materials and quartz, accounting only for 50–60% of the initially spiked jarosite content. The S_{RAS} content also greatly underestimated the initially spiked jarosite content in soil materials and quartz due to its partial dissolution during the peroxide oxidation procedure.

Li et al. (2007) proposed a sequential extraction procedure to quantify jarosite in acid mine wastes. Li et al's (2007) method consists of two extraction steps and involves sequential removal of water soluble sulfate, pyrite and organic sulfur from the sample, leaving jarosite for final extraction using 4 M HCl. We note that the second step is a pre-treatment for the final extraction and is not an extraction step. The authors identified three sequential steps in the procedure as follows:

(1) Anoxic water extraction (3 min) – In this step, water soluble Fe(II) sulfate minerals such as melanterite ($FeSO_4 \cdot 7H_2O$) and other soluble sulfate minerals such as epsomite ($MgSO_4 \cdot 7H_2O$) and gypsum ($CaSO_4 \cdot 2H_2O$) are removed from the sample leaving pyrite and jarosite.

(2) Roasting step – The solid residue left after anoxic water extraction is roasted at 550 °C for 1 h in air. Organic sulfur, pyrite and pyrrhotite ($Fe_{(1-x)}S$, where $x = 0$–0.2) are removed as SO_3 gas during the roasting step.

(3) 4 M HCl extraction (30 min) of the roasted sample – In this step, the sulfur (as sulfate) content in the roasted sample is recovered. Sulfur recovered in this step is assumed to have originated only from jarosite via transformation to yavapaiite.

The sulfur content extracted from 4 M HCl extraction step is then used to calculate the jarosite recovery (Section 2.10). Using this method Li et al. (2007) reported a 100% recovery from a mixture of 5% jarosite in quartz, and from lateritic nickel tailing waste of varying jarosite contents.

During the roasting step, jarosite is thermally decomposed to yavapaiite ($KFe(SO_4)_2$) and hematite (Fe_2O_3) (Eq. (5)).

$$KFe_3(SO_4)_2(OH)_6 \rightarrow KFe(SO_4)_2 + Fe_2O_3 + 3H_2O \qquad (5)$$
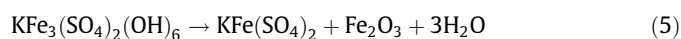
Li et al. (2007) emphasised the importance of keeping the roasting temperature strictly at 550 °C or below as yavapaiite formed decomposes above 550 °C resulting in liberation of S as SO_3 (Eq. (6)).

$$2KFe(SO_4)_2 \rightarrow K_2SO_4 + Fe_2O_3 + 3SO_3 \qquad (6)$$
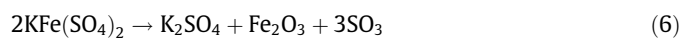
Jarosite decomposes via several weight loss stages which involved the removal of water (200–320 °C), crystallisation of yavapaiite (350–450 °C) (Eq. (5)), and the decomposition of yavapaiite associated with the removal of SO_3 (550–800 °C) (Eq. (6)) (Baron and Palmer, 1996; Drouet and Navrotsky, 2003; Smith, 2004; Forray et al., 2005). However, both Frost et al. (2005) and Xu et al. (2010) have reported widely varying temperatures at which these weight loss stages occur depending on either composition or crystallinity.

Roasting of jarosite enhanced S recovery in the subsequent 30 min 4 M HCl extraction step (Li et al., 2007). The composition of jarosite is highly variable in natural environments and therefore, their stabilities will also likely vary (Baron and Palmer, 1996; Dutrizac and Jambor, 2000). Hence, the suggested 30 min time frame for the maximum amount of S recovery from the roasted sample through the 4 M HCl extraction may not hold for all jarosite types.

Li et al.'s (2007) study did not examine jarosite from ASS materials which is predominantly K-jarosite (Keene et al., 2010; Johnston et al., 2009a, 2012). These natural types of jarosite are common and known to have a significant impact on the environment, yet it has not been systematically examined. It is very likely that both the thermal behavior and the solubility kinetics of K-jarosite from ASS behave differently from AMD type jarosites after roasting and in subsequent 4 M HCl extraction. The objective of this study is to systematically evaluate the utility of the two-step sequential extraction procedure of Li et al. (2007) for quantification of jarosite spiked (at already known rates) in soil materials.

2. Materials and methods

2.1. Sampling

Soil samples were collected from two regions previously confirmed as non-sulfuric (Isbell, 2002), in north-eastern New South Wales (NSW) Australia: (1) Tuckean Swamp on the Richmond River catchment (28°58′38″S, 153°24′15″E) and; (2) Shark Creek on the Clarence River catchment, Australia (29°31′52″S, 153°12′35″E). Soils in both sites were classified as Sulfidic Oxyaquic Hydrosols (confidence level 2) according to "The Australian Soil Classification" (Isbell, 2002). Samples were collected from the upper layer (0–30 cm) and placed into plastic bags and then sealed. Within 24 h of sampling, the two soil samples were placed in a fan forced oven at 80 °C and dried for two weeks until a constant weight was reached. Dried soil samples were sieved (<2 mm) and then ground using a ring mill (Rock Labs, New Zealand). A fine river pure (washed) quartz sand (<64 μm) sample was used as a soil reference material.

2.2. Synthesis of jarosite

Jarosite was synthesised by the method of Baron and Palmer (1996). A beaker containing a mixture of 56 g of KOH, 172 g of $Fe_2(SO_4)_3 \cdot 5H_2O$ and 1000 mL of deionised water was heated at 95 °C for 4 h with continuous stirring. After jarosite settled on the