ARSENOPYRITE SURFACE REACTIVITY: A LABORATORY INVESTIGATION ON pH ROLE

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Abstract
The reactivity of arsenopyrite in acidic and oxygen-saturated solutions was investigated in laboratory by solution chemistry and surface techniques such as Scanning Electron Microscopy (SEM) and micro-Raman Spectroscopy (μRS). The overall reactivity was evaluated by measuring arsenopyrite dissolution rates at pH values of 1, 2 and 4 at three different temperatures (298, 323 and 348 K). Surface speciation was investigated by μRS, and surface features were observed by SEM. This work provides evidences for pH dependence of both dissolution rates and surface speciation.

Introduction
The toxicity of As and environmental processes of As dispersion are known since several decades. Also for this reason, the As geochemical and mineralogical behaviour has attracted the attention of scientific community. Dissolution of arsenopyrite is generally considered one of the main causes of the mobilization of As in mine environment (Welch, 2000; Nordstrom, 2002; Smedley and Kinninburg, 2002). As observed for many other metal sulphides (Legrand et al., 2005; De Giudici et al., 2007, and references therein), the behaviour of arsenopyrite surface exposed to the interaction with air and water is usually characterized by the formation of a surface coating (Jones et al., 2003). The composition of surface coating depends on solution pH (Nesbitt et al., 1995), however, the reactivity of arsenopyrite and the role of surface coating are debated in the literature (Nesbitt et al., 1995; Richardson and Vaughan, 1989; Craw et al., 2003).

This work is aimed to investigate kinetics and reactivity of arsenopyrite in contact with acidic and oxidative solutions during long-duration experimental runs. Under these conditions the arsenopyrite surface is coated by a thin layer whose composition depends on solution pH.

Methods
Specimens of natural arsenopyrite were selected from the abandoned Baccu Locci mine (Sardinia, Italy). Before dissolution runs, arsenopyrite grains were cleaved, pre-treated in diluted hydrochloric solutions (10%), then washed in Milli-Q water, and immediately used in the experiments.

The arsenopyrite surfaces were investigated by Scanning Electron Microscopy (SEM, ESEM FEI QUANTA 200) and by micro-Raman Spectroscopy (μRS). μRaman measurements were carried out in back scattering geometry by using the polarized 514.5 nm line of an Argon-ion-laser, a triple spectrometer Jobin-Yvonne Dilor integrated system with a spectral resolution of 1 cm⁻¹. A confocal microscope Olympus B-201 has been used with a spatial resolution of 1 μm. Table 1 illustrates Raman active modes derived from literature.

The dissolution experiments were carried out in a flow through reactor made of Teflon. Two kinds of experimental runs were carried out in this study, long time (6 months) experimental runs, and short time (1 month) experimental runs. Each run was carried out using a freshly cleaved and pre-treated arsenopyrite grain. The flow rate, Q, was 70 μl per min, being controlled by a peristaltic pump. The residence time of solution is about 3 min. The reactor was sealed and held at a fixed temperature by using a thermostatic bath. Output solutions were sampled, filtered (0.4 μm) and analysed by ICP-MS (Perkin Elmer DRCe). The rates of the overall process of arsenopyrite dissolution were measured by the following equation:

\[ R_{asp} = C \frac{Q}{A} \]

where C is As concentration in output solutions, and A is the mineral geometric surface area.
Table 1. Raman active modes of arsenopyrite and secondary phases. * Diagnostic (strong) peak.

<table>
<thead>
<tr>
<th>Vibrations</th>
<th>Raman shift (cm⁻¹)</th>
<th>References</th>
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<tbody>
<tr>
<td>As-O symmetric and antisymmetric</td>
<td>790; 850</td>
<td>Martens et al. 2003</td>
</tr>
<tr>
<td>stretching</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AsO₄ + AsOH</td>
<td>750-850 (broad)</td>
<td>Wayde et al. 2003</td>
</tr>
<tr>
<td>Fe₂O₃ Hematite</td>
<td>226; 245; 293; 300; 413; 498; 612.</td>
<td>Bersani et al. 2003</td>
</tr>
<tr>
<td>Pyrite</td>
<td>342; 348</td>
<td>Ushioda 1972, McGuire et al. 2001</td>
</tr>
<tr>
<td>Arsenopyrite</td>
<td>198, 313, 337,404, 412</td>
<td>McGuire et al. 2001</td>
</tr>
<tr>
<td>Fe-O</td>
<td>203; 241</td>
<td>Edwards and Russel 1998</td>
</tr>
<tr>
<td>Fe-OH</td>
<td>913</td>
<td>Edwards and Russel 1998</td>
</tr>
<tr>
<td>As₂S₃</td>
<td>181; 204; 244;311; 345; 355; 382</td>
<td>Flynn et al. 1976</td>
</tr>
<tr>
<td>As-Fe</td>
<td>136; 150</td>
<td>McGuire et al. 2001, Flynn et al. 1976</td>
</tr>
<tr>
<td>As₂-O₃</td>
<td>217; 260; 285; 331;357; 426; 461</td>
<td>Martens et al. 2003, Flynn et al. 1976</td>
</tr>
<tr>
<td>SO₂</td>
<td>1100-1200; 1300-1400</td>
<td>Colthup et al. 1990</td>
</tr>
<tr>
<td>S</td>
<td>150; 219*; 472*</td>
<td>Mycroft et al. 1990</td>
</tr>
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Results and Discussion

The long time run (six months) was carried out through different steps, and investigated the pH conditions of 1, 2 and 4, and temperature conditions of 298, 323 and 348 K. The As concentration increased after each temperature increase, and tends to reach a stationary state after several hundreds of hours of interaction. Table 2 shows the stationary rate values of overall arsenopyrite dissolution process. Dissolution rates show dependence on temperature, but the pH dependence was observed only between pH 2 and 4, while between pH 1 and 2 there is not a noticeable change in dissolution rates.

Figure 1 shows the arsenopyrite surface features after reaction with acidic solution at pH 1. The SEM images illustrate that dissolution takes place via formation of etch pits elongated along [110] traces of arsenopyrite. In addition, surface coating can appear in SEM imaging as small size powder that partially covers the imaged surface.

Figure 2a shows the μR spectra of arsenopyrite after short-experimental-duration-run (1 month) at pH 1 and 298 K, and Figure 2b after a short experimental duration at pH 4 and 298 K. μRS clearly indicates that the surface speciation is dependent on pH. In fact native sulphur occurs at arsenopyrite surface after reaction with solution at pH 1, but it does not occur after interaction with solution at pH 4. In addition, Raman analysis indicates the presence of significative amounts of Fe₂O₃ only at pH 4. This contrasts with Eh-pH diagrams presented in Craw et al. (2003) that predict the formation of iron oxides only above pH 5. Eh-pH diagrams (Brookins, 1988) indicate that stability fields of the different iron oxy-hydroxides species can significantly change, and depend on total iron activity and the particular species. As a consequence, experimental knowledge of both structure and chemical composition of dissolving arsenopyrite surface as well as surface coating is crucial to the understanding of dissolution process.

Table 2. Measured dissolution rates.

<table>
<thead>
<tr>
<th>pH</th>
<th>298 K</th>
<th>323 K</th>
<th>348 K</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>1.60±0.3×10⁻⁸</td>
<td>7.06±1.4×10⁻⁸</td>
<td>1.69±0.3×10⁻⁷</td>
</tr>
<tr>
<td>2</td>
<td>1.69±0.3×10⁻⁸</td>
<td>7.53±3.8×10⁻⁸</td>
<td>1.23±0.2×10⁻⁷</td>
</tr>
<tr>
<td>4</td>
<td>7.37±1.47×10⁻⁸</td>
<td>2.31±0.46×10⁻⁷</td>
<td>3.00±0.6×10⁻⁷</td>
</tr>
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</table>

Conclusions

This work investigates the overall process of arsenopyrite dissolution in acidic and oxygen-saturated solutions. The results clearly indicate that overall dissolution rates are pH dependent between pH 2 and 4, while their values do not show noticeable differences at pH between 1 and 2.
μRaman spectroscopy indicates that surface speciation is pH dependent between pH 1 and 4, in fact the presence of native sulphur at arsenopyrite surfaces was revealed only at pH 1, and iron oxides were predominant only at pH 4. SEM investigation revealed the presence of non uniform distribution of secondary phases and coexistence of different surface features such as fine powders (secondary phases) and etch pits.

The pH dependence of surface speciation was observed also for the dissolution of other metal sulphides such as galena (De Giudici et al., 2005, 2007). In this case, however, native sulphur was observed also at pH 4, and disappeared at pH 5.6. In agreement with previous literature studies (see for the instance Walker et al., 2006), present study points out that the mechanism ruling arsenopyrite dissolution process is mainly electrochemical. However, there is a need for detailed experimental investigations on surface speciation at dissolving metal sulphides such as arsenopyrite.

![SEM images of reacted arsenopyrite.](image)

![Raman spectra of arsenopyrite after reaction at pH 1 (a), and pH 4 (b).](image)

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**References**


