

## VARIATIONS AND CONTROLS ON THE COPPER/ARSENIC RATIOS IN WATERS AT THE FURTEI GOLD MINE, SARDINIA, ITALY

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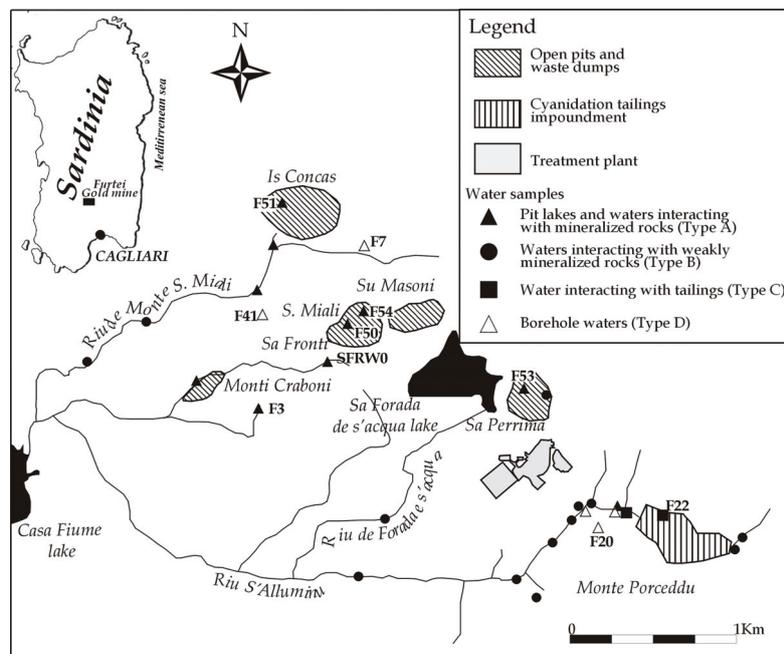
### Abstract

Waters draining the area of the epithermal high sulfidation gold deposit at Furtei, Sardinia (Italy) show the typical trend of increasing “heavy metal” load with decreasing pH. In the primary (hypogene) assemblage, pyrite and enargite/luzonite are the most abundant sulfides. Therefore, the copper and arsenic contents of waters interacting with highly mineralized rocks could be controlled by enargite. However, in such waters, Cu/As molar ratios are different from those of enargite. In surface, oxygenated waters, they are much higher. Hence, copper is more mobile than arsenic in these conditions. This is in agreement with 1) the composition of secondary minerals found at the mine, the Cu-bearing minerals being in general more soluble than the As-bearing ones; 2) laboratory experiments suggesting that under some conditions acidic solutions remove more easily copper than arsenic from enargite. On the other hand, in subsurface, reduced waters, Cu/As ratios are lower, probably because reducing conditions do not allow the formation of iron oxy-hydroxy-sulfates that may act as adsorbent media for arsenic species.

### Introduction

The Furtei gold mine is located in southern Sardinia (Italy), about 40 kilometers north of the regional capital city, Cagliari (Fig. 1). It has been operating between 1997 and 2002 for exploitation of an epithermal “high-sulfidation” deposit. The mine is currently in standby; plans for restarting activities are under consideration. The deposit is hosted in a Tertiary calc-alkaline volcanic complex. Alteration facies (vuggy and/or massive silica; advanced argillic; argillic; propylitic) are typical of this class of deposits (Ruggieri et al., 1997).

The primary (hypogene) sulfide mineral assemblage includes pyrite and enargite (with intergrown luzonite) as main minerals; other sulfides occur in lesser amounts. Gold occurs as native metal, subordinately in tellurides. Before exploitation, this hypogene assemblage was covered by a 10-50 meter thick oxidized cap, composed of Fe oxyhydroxides, gypsum, clay minerals, relic quartz, with subordinate iron-bearing sulfates and scorodite. Gold grades were economic (in the order of 1 gram/tonne), and this oxidized cap was the first target of exploitation.



**Figure 1.** Map showing the Furtei area with location of sampling sites. Labelled samples have As concentration greater than 0.1  $\mu\text{mol/L}$ .

This oxidized ore was treated on site by cyanide heap leaching. After exhaustion of this ore type, exploitation went on by open pit mining of sulfide ore. This was floated on site to obtain an enargite-rich concentrate, that was shipped overseas for further processing.

Exploitation at Furtei was preceded and accompanied by studies of the potential environmental impact and plans for reclamation (see e.g. Cidu, 2000; Nicol et al., 2002 and references therein). A typical environmental risk associated with this type of deposit is the generation of acid, metal-rich drainage. Given the mineralogy of the primary ore, the “heavy metals” most likely to occur in dangerous concentrations are copper and arsenic. In this communication, we discuss the contents of these elements in waters draining the mineralized areas, and the possible control(s) on their ratio.

## Methods

Water chemistry at Furtei has been continuously monitored from 1994 (i.e., prior to exploitation) to 2005 (e.g., Cidu et al., 1997; Cidu, 2000; Da Pelo et al., 2005). For this study, a specific sampling was carried out in October 2006. Water samples were filtered in situ through a 0.4  $\mu\text{m}$  pore-size polycarbonate filter with an all-plastic filtration assembly, and acidified upon filtration for metal analyses. At each sampling site, temperature, pH, alkalinity, redox potential (Eh), and conductivity were measured. The Eh was measured by platinum electrode, and the value corrected against the Zobell’s solution (Nordstrom, 1977). Anions were determined by ion chromatography (IC Dionex DX-120), and cations by ICP-AES (ARL-3520B) and ICP-MS (ELAN 5000). The ionic balance was always in the range of  $\pm 5\%$ ; both precision and accuracy were estimated at  $\pm 10\%$  or better, using randomly duplicate samples and a standard reference solution (SRM1643e).

## Results and Discussion

The full data set for the sampled waters is reported by Musu (2007). For the following discussion, waters were divided into four types depending on the nature of material they interact with: A = waters interacting with highly mineralized rocks, including waters from open pit lakes and seepages from sulphide-rich rock piles; B = waters interacting with weakly mineralized rocks; C = waters interacting with tailings; D = waters flowing out from boreholes, presumably interacting with mineralized rocks at depth. In a modified Ficklin plot (Ficklin et al., 1992; Fig. 2), the four types of waters appear well distinguished: type A shows a low pH and a very high metal content, type B ranges from weakly acidic to weakly alkaline pH and from moderate to low metal content, whereas type C and D waters have an intermediate character. The overall chemistry of waters collected in 2006 does not show remarkable changes with respect to previous samplings; the most noticeable variation is the increasing acidity of water in the tailing pond (current pH = 3.3), in agreement with the trend observed since 2001, when the initial material discharged in the pond, represented by tailings of the alkaline cyanide heap leaching process, was replaced by sulphide-rich tailings from the flotation plant.

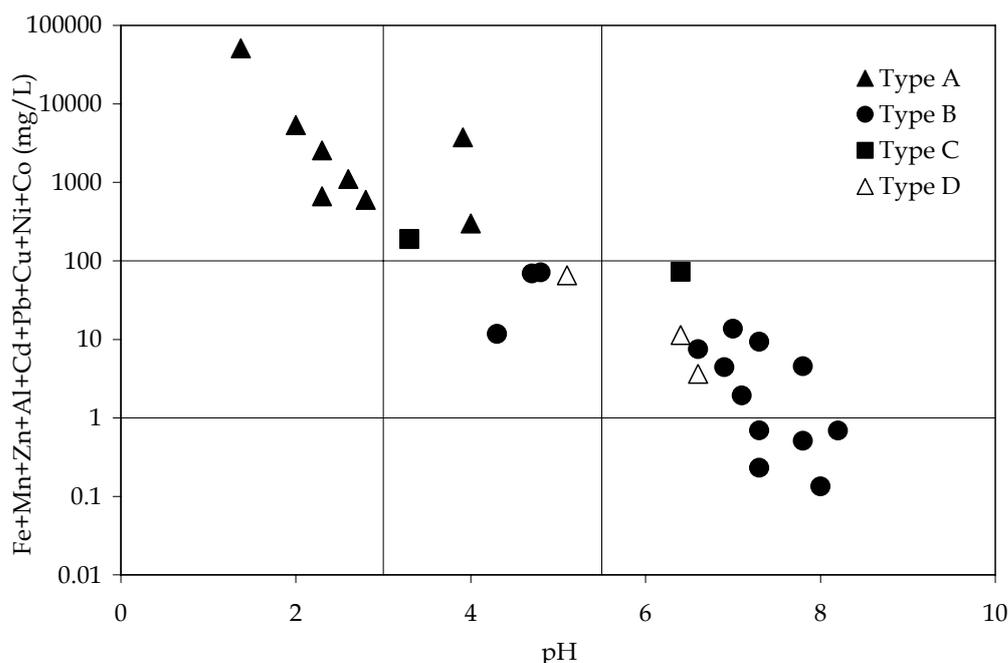
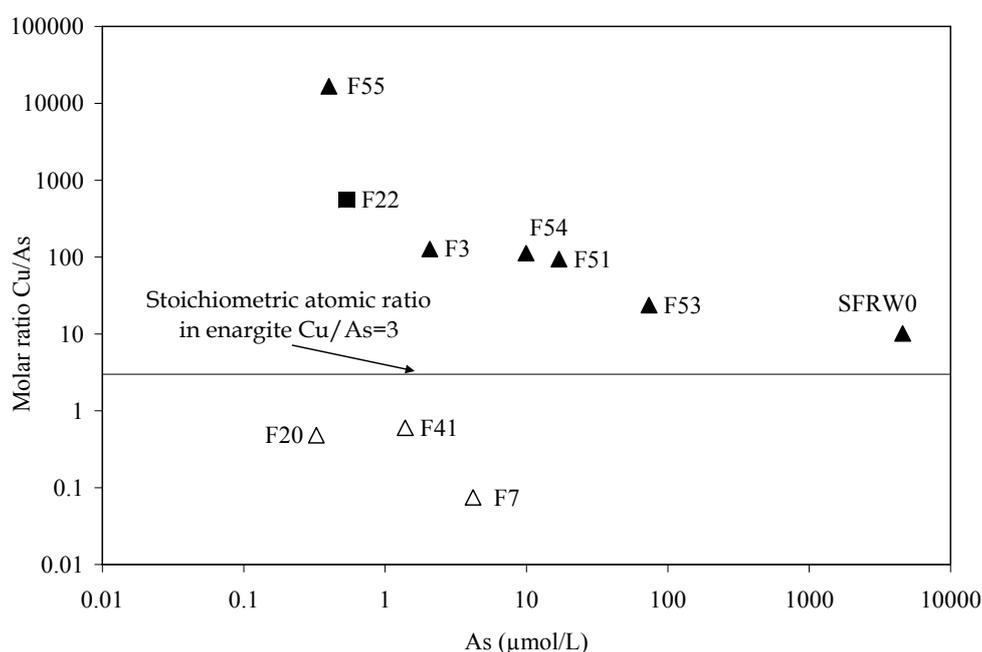


Figure 2. Modified Ficklin plot of the studied waters.

We now consider in detail waters of the A and D types, that is, those that interact with mineralized rocks. For the reasons explained above, we can now include in this discussion the water from the tailing impoundment. All these waters are characterized by As contents higher than  $0.1 \mu\text{mol/L}$ . Their location in the area is shown in Figure 1. As previously stated, enargite and its polymorph luzonite are the main carriers of copper and arsenic in the primary ore. In these minerals, the Cu/As atomic ratio is 3. Another common Cu-As mineral at Furtei is tennantite: ignoring substitutions, also in this mineral the Cu/As ratio is 3. Minor copper contributions arise from small amounts of chalcopyrite, digenite and tetrahedrite; and arsenic contributions from pyrite, that contains tens of mg/kg As (Musu, 2007). Hence, we expect that rocks containing significant proportions of primary ore have a bulk Cu/As atomic ratio not far from 3. Analyses of a few samples of mineralized rocks and tailings give values in the range from about 1 to 12, with most values between 2 and 6 (Da Pelo et al., 2005). Departures from the enargite-luzonite ratio may be ascribed to the previously mentioned phases, and/or the occurrence of secondary minerals (e.g., for arsenic, scorodite). Leachates (24 hour batch extraction in Milli-Q water) of these solid samples show Cu/As ratios much higher than in the corresponding solids (Da Pelo et al., 2005). Figure 3 shows that also in surface waters collected in 2006 Cu/As ratios are much higher than those expected by enargite stoichiometry and those observed in solid samples.



**Figure 3. Molar Cu/As ratios in selected waters (full symbols: surface waters; empty symbols: subsurface waters, as in Figs. 1 and 2)**

Therefore, high Cu/As ratios in the water do not reflect solely the Cu/As ratio in parent solid materials. Overall, the Cu/As ratio shows a decreasing trend with increasing As in solution. In turn, As in solution increases with decreasing pH and increasing Eh (Figs. 4 and 5). Hence, mobilization of arsenic from solids is in general lesser than that of copper, although is favored under low pH and/or high Eh conditions.

This trend is in agreement with the findings by Musu (2007): at the laboratory scale, dynamic (flow-through reactor) dissolution experiments of enargite at pH 1 and 4 show that in most cases the Cu/As ratios in the reacted solution are higher than stoichiometric values in enargite (i.e., acidic fluids remove more easily copper than arsenic from the mineral); at the deposit scale, recent copper secondary minerals at Furtei are represented by easily soluble species such as sulfates (e.g., cuprian melanterite and chalcantite), whereas arsenic is hosted in somewhat less soluble phases (scorodite and/or iron oxy-hydroxy-sulfates onto which arsenic is adsorbed, presumably as arsenate). Hence, secondary minerals are more likely to immobilize arsenic than copper. Similar high Cu/As ratios have been reported from other high sulfidation deposits (see Lattanzi et al., 2007; Musu, 2007), suggesting that this behaviour may be a general rule for this type of deposits.

Subsurface (type D) waters show, on the other hand, a different trend, with Cu/As molar ratios consistently lower than in enargite. This may simply mean that they interact with an As-bearing, Cu-poor material (e.g., arsenian pyrite-bearing, enargite-poor rocks). However, an alternative/additional explanation can be linked to much lower Eh values than surface waters (Fig. 5). Under these conditions, iron oxyhydroxides, that in the surface environment act as adsorbers for As, thereby limiting its mobility, do not form. Indeed, in a previous

sampling (2003), it was observed that water flowing out from the F7 borehole precipitated, a few meters away from the outflow point, significant amounts of iron oxyhydroxides, thereby lowering pH to 4.2, with a concomitant decrease of As in solution of about one order of magnitude.

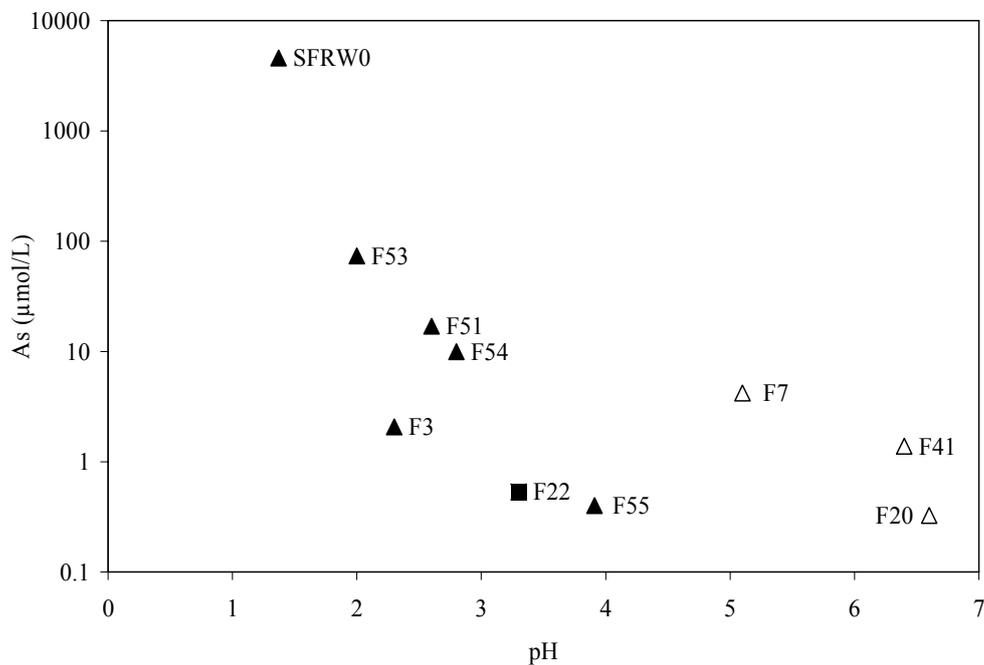


Figure 4. Arsenic content as a function of pH in selected waters (symbols as in Figs. 1 and 2).

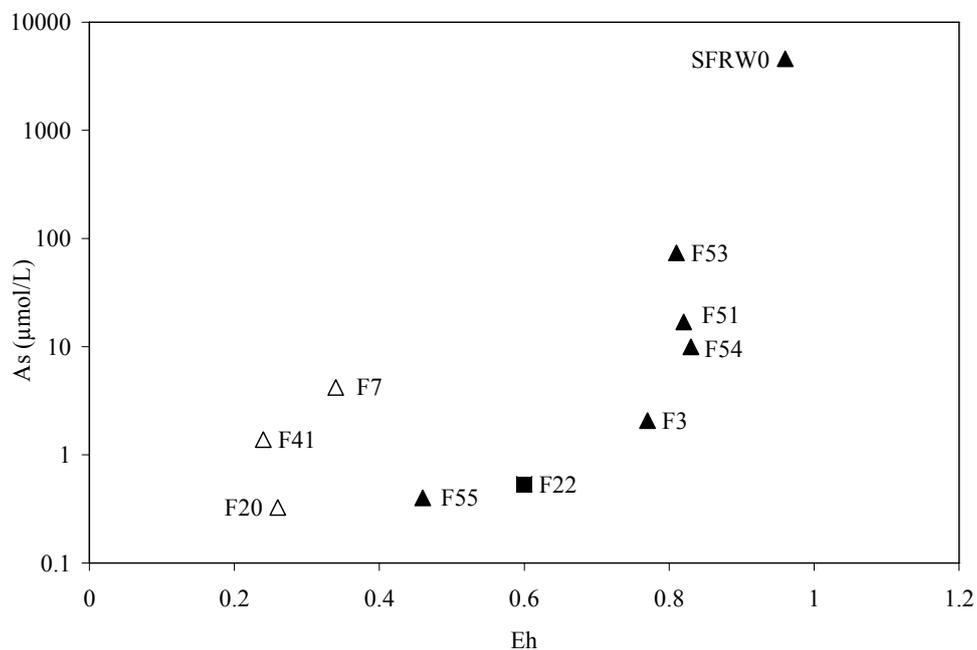


Figure 5. Arsenic content as a function of Eh (Volts) in selected waters (symbols as in Figs. 1 and 2).

### Conclusions

Copper to arsenic ratios in surface waters interacting with highly mineralized rocks at Furtei are much higher than those expected by stoichiometric dissolution of the main copper-arsenic mineral in the primary assemblage, i.e. enargite. The ratios are also higher than known bulk copper-arsenic ratios of mineralized rock samples.

Hence, in the Furtei environment, copper is more mobile than arsenic. This can be explained by a) a higher solubility of the secondary minerals hosting copper with respect to those hosting arsenic, and b) a greater reluctance of arsenic to be released from enargite during interaction with acidic fluids. The trend observed at Furtei is common to waters draining other high sulfidation deposits, suggesting that it may represent a general rule for this class of deposits. Subsurface waters on the contrary show low ( $\leq 1$ ) Cu/As molar ratios. This may be, at least in part, explained by the fact that these are reduced ( $E_h \leq 0.4$  V) waters, hence formation of iron oxyhydroxides and the consequent adsorption of arsenic does not take place.

### **Acknowledgements**

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