# Arsenic in Mining Environments: Evidences from Sardinia (Italy)

Ardau Carla, Cidu Rosa, Da Pelo Stefania, Dadea Claudia, Fanfani Luca, Frau Franco, Musu Elodia, Lattanzi Pierfranco

*Dipartimento di Scienze della Terra, Via Trentino 51, 09127 Cagliari, Italy*
*e-mail: lfanfani@unica.it*

## Abstract

In Sardinia, the dispersion of arsenic in the environment appears strictly linked with mineralised bodies and mining activities. Currently, the areas of main concern are the active gold mine at Furtei, and the abandoned Pb-As mine at Baccu Locci. At Furtei, the main sources of arsenic are enargite, and arsenian pyrite; an ongoing monitoring program of water quality in the area around the mine documented so far no major changes with respect to pre-mine conditions, except for the formation of extremely acid, As-rich pit lakes. At Baccu Locci, the main primary source is arsenopyrite; arsenic dispersion is essentially due to the past unwise practice of discarding mine tailings into the nearby creek. Arsenic is slowly released from residual arsenopyrite and temporary secondary mineral traps such as Fe-oxyhydroxides, causing contamination of soils and waters as far as 10 km downstream of the mine.

**Key words:** water contamination, arsenic, past and present mining, Sardinia

## Introduction

Arsenic is long recognised as one of the most dangerous inorganic chemicals. High arsenic contents in drinking water were identified as the cause for several diseases, including cancer, in many regions of the world. Arsenic is not abundant in the Earth's crust (usually less than 6 mg/kg, except for shales, Fe-rich sediments and coals). However, contaminated groundwaters at a regional scale are documented in aquifers with relatively low arsenic amounts, when associated to specific geological environments (volcanogenic sediments of closed basins in arid to semi-arid climates; young alluvial sediments in strongly reducing aquifers with low hydraulic gradient). Though thermal springs and sulphide–bearing rocks may occasionally contaminate water resources, most cases of local contamination are connected with mineral exploitation, metal smelting and fossil fuel burning (i.e., a combination of "geogenic" and "anthropogenic" sources). Entirely anthropogenic sources are now rare, because arsenic use is being continuously reduced over the world. In mined areas, wastes from ore extraction and processing are dissemination sources of arsenic, since significant amounts of arsenic from sulphide minerals (especially pyrite) still remain in the wastes; eventually, arsenic may be concentrated in hydrous iron oxides through supergene processes.

## Arsenic in Sardinia, Italy: regional overview

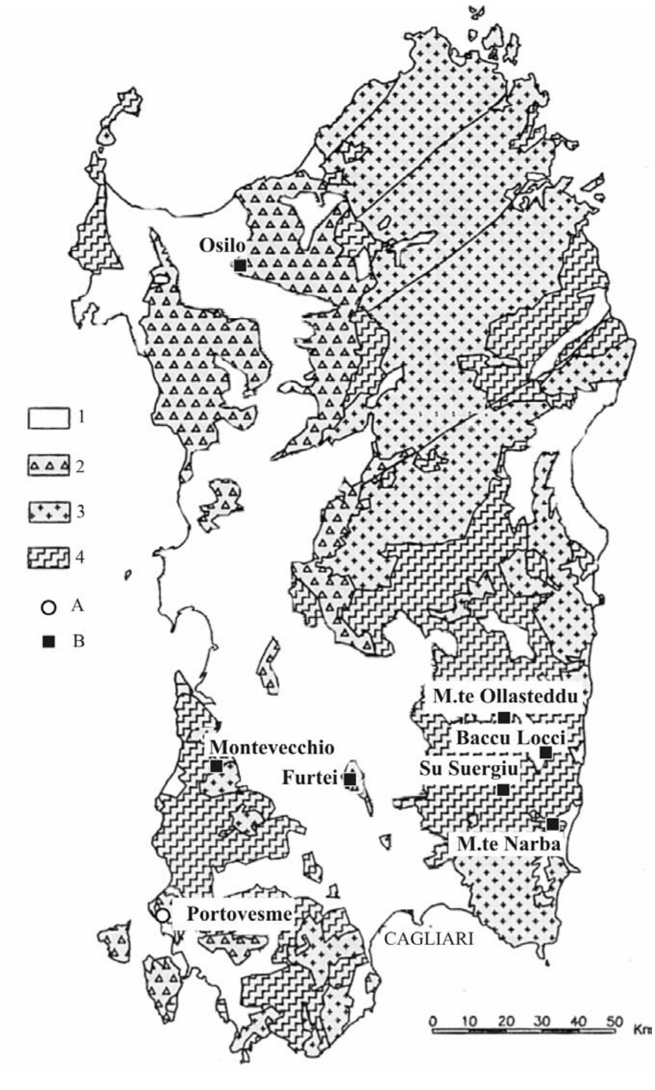
There are no systematic data on arsenic distribution in rocks at the regional scale. Data on stream sediments (De Vivo et al., 2001; Marcello et al., 2003) cover a good portion, but not all, of the region.

Although single values as high as 4,500 mg/kg were reported, the regional background (median value) is <10 mg/kg with 75% samples <23 mg/kg. Marcello et al. (2003) explicitly refer most anomalous high values to proximity with mineralized areas, although they suggest that a single "high isolated value" north of Portovesme may be related to the local metallurgical industry. Moreover, there are no other important anthropogenic sources of this element, and there is no evidence of any geological environment where a significant arsenic mobilisation to water may occur from rocks with low arsenic concentration.

A survey of the main rivers and streams of Sardinia (35 samples) indicated dissolved arsenic contents $\leq 5$ µg/L (Cidu and Biddau 2007). In a more detailed (101 superficial and 22 groundwater samples) study of an area (620 km$^2$) in southeastern Sardinia, Cidu et al. (in press) found significant (>10 µg/L) arsenic contents only in streams draining the mining areas of Baccu Locci, Su Suergiu (Gerrei Sb district), and Monte Narba (Sarrabus "silver lode"), and the mineralised veins of the gold prospect at Monte Ollasteddu.

Therefore, in Sardinia the dispersion of arsenic in the environment appears to be strictly linked with mineralised bodies and mining activities. Previous studies suggest that the main areas of concern are the gold deposit of Furtei, and the abandoned Pb-As mine of Baccu Locci (see below). Importantly, in the two large historical Pb-Zn-Ag districts of Montevecchio-Ingurtosu and Iglesiente, the As dispersion is modest, and confined to specific point sources (Cidu and Fanfani, 2002; Cidu et al. 2007). Localisations of the main areas concerned by arsenic anomalies are reported in Figure 1.

***Figure 1*** *Simplified geological sketch map of Sardinia with localization of the main areas affected by arsenic anomalies. 1 Undifferentiated sedimentary and volcanic rocks (Mesozoic to Quaternary); 2 Tertiary calc-alkaline volcanic rocks; 3 Hercynian granitoid rocks; 4 Palaeozoic metamorphic basement; A Industrial site; B Mining and mineralized areas.*



## Impacted areas

### *Furtei.*

The Furtei gold deposit, a high sulphidation epithermal precious metal deposit, was discovered at the end of the1980s, and has been exploited since 1997. The deposit is hosted by a Tertiary volcano-sedimentary complex. Wall rock alteration comprises propylitic, argillic, and silica-rich facies, whereas in the orebodies the primary (hypogene) minerals are mainly pyrite and enargite/luzonite, with minor amounts of other sulphides. An oxidized cap, mostly consisting of iron oxyhydroxides, clays, and gypsum, with iron sulphates and scorodite, covered the sulphide bodies. The cyclic formation of secondary minerals (mostly cuprian iron sulphates) is observed today during dry periods.

Exploitation was preceded and accompanied by studies on the potential environmental impact, including a baseline study of waters in the area prior to exploitation, their systematic monitoring from 1997 to 2004, and mineralogical and geochemical characterization on environmentally relevant solid materials, such as tailings and waste rocks. Though enargite/luzonite are important repositories of arsenic in the primary mineral assemblage, a single analysis of As in pyrite (~ 50 mg/kg, Musu et al. 2007a) suggests that this mineral may be another major arsenic source. Surface waters in the area show generally low content of arsenic (<5 µg/L). When draining the mineralised bodies, waters reach extreme conditions of acidity (pH ~2-4), and become metal-rich (total dissolved Al+Fe+Mn+Zn+Cu+As+Ni+Co up to ~ 4 g/L); pit lakes and seepages from waste rock dumps show arsenic content up to 5 mg/L. Significant arsenic contents (up to 300 µg/L) have been recorded in water from boreholes. Arsenic in surface waters is apparently less mobile than copper (most Cu/As ratios in waters are much higher than required by enargite stoichiometry and arsenian pyrite analysis). The main explanation for this phenomenon is that secondary minerals hosting copper are very soluble, whereas arsenic release is slowed down by retention in comparatively more stable phases, such as Fe oxyhydroxides and/or scorodite. Groundwaters show lower Cu/As ratios. The trend observed at Furtei is common to waters draining other high sulphidation deposits, suggesting that it may represent a general rule for this class of deposits. Up to now, no major change in water chemistry with respect to pre-mine conditions was recorded by the ongoing monitoring program in the area around the Furtei mine. However, the occurrence of extreme acid waters with high metal contents stored in pit lakes, and seepages percolating out of waste rock dumps in rainy periods, have to be considered by the mining company for correct environmental management.

### *Baccu Locci*

The deposit of Baccu Locci is hosted by metasedimentary Paleozoic rocks. It is characterized by a complex mineral assemblage, where galena and arsenopyrite in about equal amounts represent the main ore minerals (see references in Conti et al., 1998).

The deposit was exploited for about a century (1873–1965) for Pb and As, and produced a visible environmental impact within the hydrological catchment draining the mine. Nevertheless, only in the last decade environmental studies aimed to establish the level of contamination in the area were conducted (Fanfani & Pilia, 2007; Frau et al., 2008; and references therein). These studies pointed out a diffuse, severe arsenic contamination affecting surface and ground waters, stream sediments and soils. Only recently a first management plan for risk mitigation in the whole area is in preparation.

The main sources of As contamination are represented by the waste-rock dumps (containing As up to 95 g/kg in the <2 mm fraction) along the banks of several streamlets draining the mining area, and by the flotation tailings (As up to 24 g/kg) discharged into the main water course of the area. Stream sediments contain up to ~ 0.5 g/kg As. In such waste materials arsenic, though present in residual arsenopyrite, and in its secondary products, such as scorodite and As-bearing ferrihydrite (Frau & Ardau 2004; Frau et al. 2005), is significantly released to surface waters only by desorption from As-bearing ferrihydrite (Frau & Ardau 2004). As a consequence, As concentration tends to gradually increase along the stream course (up to ~900 µg/L) as far as the coastal plain of Quirra, about ten kilometres away from the mining area. Groundwaters in the coastal plain show concentrations up to ~850 µg/L, due to interaction of water with overflooded contaminated sediments (As up to 1.3 g/kg; Fanfani & Pilia, 2007). Temporary arsenic mitigation processes occur in the area downstream the mine (As adsorption onto hydrous ferric oxides, and/or removal by scorodite and/or "anionic clays" such as woodwardite/glaucocerinite). They are however reversible, and do not ensure any long-time mitigation. Currently, As in soils and waters represents a serious health hazard, especially in the cultivated coastal plain.

Indeed, several studies (see references in Falchi, 2005) document that in the area a contamination of some vegetal species, both cultivated and wild, is associated with high amounts of arsenic in waters and soils. Specifically, levels of arsenic that may induce chronic diseases in livestock and humans are documented in forage plants (up to 120 mg/kg) and leaf vegetables (up to 13 mg/kg), whereas arsenic levels in fruits, and goat and sheep milk are low (<10 µg/L in milk, with a single value of 23 µg/L). However, in spite of the modest amounts of arsenic directly ingested with food, long term exposure may represent a significant health risk for humans and livestock.

### *Other areas*

As mentioned above, a certain extent of arsenic dispersion has been documented in connection with other mineralised areas in Sardinia. These include: the epithermal gold prospect at Osilo, where surface waters show low (<15 μg/L) As contents, but values as high as 290 μg/L have been determined in groundwaters (Biddau & Cidu, 2005); the Sb district of Gerrei, the main Sb producer in Italy in the XX century (see Cidu et al., this volume); and the large gold deposit at the Monte Ollasteddu prospect (Dini et al., 2005), that mainly consists of quartz-arsenopyrite veins. Indeed, a large arsenic anomaly has been detected in soils surrounding this deposit (Ministero della Difesa, 2004). Downstream of Monte Ollasteddu, the Riu Gruppa creek shows >10 μg/L As for several kilometres down to the confluence with the Flumendosa (the largest Sardinian river). In this river, a weak As anomaly (>5 μg/L) persists for a few kilometres downstream of the confluence (Cidu et al., in press).

## Acknowledgements

This work was financially supported by the Italian Ministry of Education, University and Research (PRIN 2006, Scientific Coordinator: L. Fanfani) and Fondazione Banco di Sardegna.

## References

Biddau R, Cidu R (2005) Hydrogeochemical baseline studies prior to gold mining. A case study in Sardinia (Italy). J. Geochem. Expl. 86: 61—85

Cidu R, Fanfani L (2002) Overview of the environmental geochemistry of mining districts in southwestern Sardinia, Italy. Geochemistry: Exp. Environ. Anal. 2: 243—251

Cidu R, Biddau R (2007)Transport of trace elements under different seasonal conditions: effects on the quality of river water in a Mediterranean area. Appl. Geochem. 22: 2777—2794

Cidu R, Biddau R, Nieddu G (2007) Rebound at Pb-Zn mines hosted in carbonate aquifers: influence on the chemistry of ground water. Mine Water Environ. 26: 88—101

Cidu R. et al. (2008) Caratterizzazione idrogeochimica ed isotopica e valutazione della qualità delle acque superficiali e sotterranee campionate nel foglio 549 Muravera. In: Ottonello G. (ed), Geochemical baselines of Italy, 149—183 (in press).

Conti P, Funedda A, Cerbai N (1998) Mylonite development in the Hercynian basement of Sardinia (Italy). J. Struct. Geol. 20(2/3): 121—133.

De Vivo B, Boni M, Costabile S (2001). Cartografia geochimica ambientale della Sardegna. Carte d'intervento per l'uso del territorio. Mem. Descr. Carta Geol. d'It. LVII (2001), p 7—32

Dini A, Di Vincenzo, Ruggieri G, Rayner J, Lattanzi P (2005) Monte Ollasteddu, a new gold discovery in the Variscan basement of Sardinia (Italy) - first isotopic ($^{40}$Ar-$^{39}$Ar, Pb) and fluid inclusion data. Mineral. Deposita 40: 337—346

Falchi M (2005) Contenuto di "metalli pesanti" in latte di ovini e caprini della piana di Quirra, Sardegna sud-orientale. Degree Thesis in Natural Sciences, Università di Cagliari.

Fanfani L, Pilia A (2007) Arsenic mobilization in groundwater at Quirra Plain (Sardinia, Italy). In: Bullen & Wang (eds), 2007 Water-Rock Interaction, p 1227—1230.

Frau F, Ardau C (2004) Mineralogical controls on arsenic mobility in the Baccu Locci stream catchment (Sardinia, Italy) affected by past mining. Mineral. Mag. 68(1): 15—30.

Frau F. et al. (2005) Determination of Arsenic Speciation in Complex Environmental Samples by the Combined Use of TEM and XPS. Microchimica Acta 151: 189—201.

Frau F, Ardau C, Fanfani L (2008). Environmental geochemistry and mineralogy of lead at the old mine area of Baccu Locci (south-east Sardinia, Italy). J. Geochem. Expl. (accepted).

Marcello A, Pretti S, Valera P (2003) The Cagliari, Nuoro, Sassari sheets of the geochemical map of Italy: explanatory notes In: Ottonello G, Serva L (eds), Geochemical baselines of Italy, p 261—285

Ministero della Difesa (2004) Relazione finale sullo studio geochimico svolto nel poligono di Perdasdefogu. http:\\www.difesa.it\NR\exeres\8373F092-ICA2-4379-9BC4-5105D378CDE8.htm

Musu E, Da Pelo S, Lorrai M, Lattanzi P (2007a) - Variations and controls on the Cu/As ratios in waters at the Furtei gold mine, Sardinia. Proceedings IMWA Symposium, R. Cidu & F. Frau eds., Cagliari, p 441—445

Musu E, Da Pelo S., Lattanzi P Lorrai M (2007b) - Secondary mineralogy at Furtei, Sardinia, Italy: controls on toxic elements mobility. In: Bullen & Wang (eds), 2007 Water-Rock Interaction, p 625—628