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Hydrogeochemistry in the abandoned mining area of Tafone Graben (Italy): Environmental implications

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ABSTRACT: In Southern Tuscany the Triassic "Calcare Cavernoso" limestone hosts important sulphide deposits. In the Tafone area mineralization consists of stibnite with minor Fe, Cu, Zn, Pb and Hg sulphides. The end of mining works left tailings and waste deposits along the Tafone valley, and two exploited pits are now filled with water. Relatively high amounts of Sb, Zn and As in the tailings were postulated to be the source of a potential contamination in the Tafone hydrological system.

A hydrogeochemical study, based on 40 samples, including lake, stream, spring and well waters, was carried out in an area of approximately 130 km^2. A survey of chemical characters in waters revealed high salinity of waters with dominant sulphate, and anomalies in Li and B, and contaminants such as Sb and As, in the Tafone stream system. Anomalous concentrations are due to tailings, waste disposal and mining works, but high concentrations of Sb and As in solution have additional sources, such as the interaction processes between waters and the ore-body. The left-hand tributaries to the Tafone stream dilute the concentration of the above species, but Sb and As are available all along the Tafone banks.

1 INTRODUCTION

The study area is located in Southern Tuscany (Italy) and covers some 130 km^2. In the Tafone graben, the exploitation of antimony mineralization up to few years ago left several tailings and waste deposits; nowadays, imported Sb mineral concentrates are still processed. The products of mining activity are thought to represent potential contaminant sources of pollution to the hydrosphere. A hydrogeochemical study was carried out to assess contaminant processes and define their environmental impact.

2 GEOLOGY AND MINERALIZATION

The study area shows a complex tectonic situation, mainly characterised by the metamorphic basement of Southern Tuscany outcropping in tectonic contact with the reduced Tuscan series and the allochthonous Ligurian Nappe with overlying Mio-Pliocene and Quaternary sediments (Dessau et al 1972, Moretti et al 1990). The stratigraphic sequence may be summarised as follows: 1) the Carnian "Verrucano" phyllites representing the Tuscan basement; 2) the Tuscan, Carnian to Norian "Calcare Cavernoso" comprising an alternation of limestone, dolostone and gypsum-anhydrite; 3) the Tuscan, Oligocene "Macigno" formation composed of sandstone and, occasionally, nummulitic breccia; 4) the Cretaceous-Eocene flysh-type sediments and clastic deposits of the S. Fiora and Pietraforte sandstones of the allochthonous Ligurian Nappe; 5) the Mio-Pliocene and Quaternary clay and sand with local presence of carbonate and, also, travertine associated with hydrothermal activity (Fig. 1).

The antimony deposits of southern Tuscany are located at the top of the highly porous Calcare Cavernoso, in tectonic contact with the impermeable flysh-type formations, behaving as a cap-rock for the mineralised fluids. Ore deposits are found on the edge of a well-developed, NW-SE trending horst-graben system, that was formed during the tensional phase of the Alpine post-orogenesis, to which the Pleistocene magmatism of Southern Tuscany is related (Peccerillo et al 1987). The deposits are thought to be related to hydrothermal activity during the Pleistocene. The possible origin of elements from the magma (Dessau et al 1972) and from the leaching of host rocks or Pre-Carbonifer basement (Dehm et al 1983) has been argued. The most important deposits (Poggiofuoco, Monteauto and Tafone), exploited until recently, are on the edge of the Tafone graben.

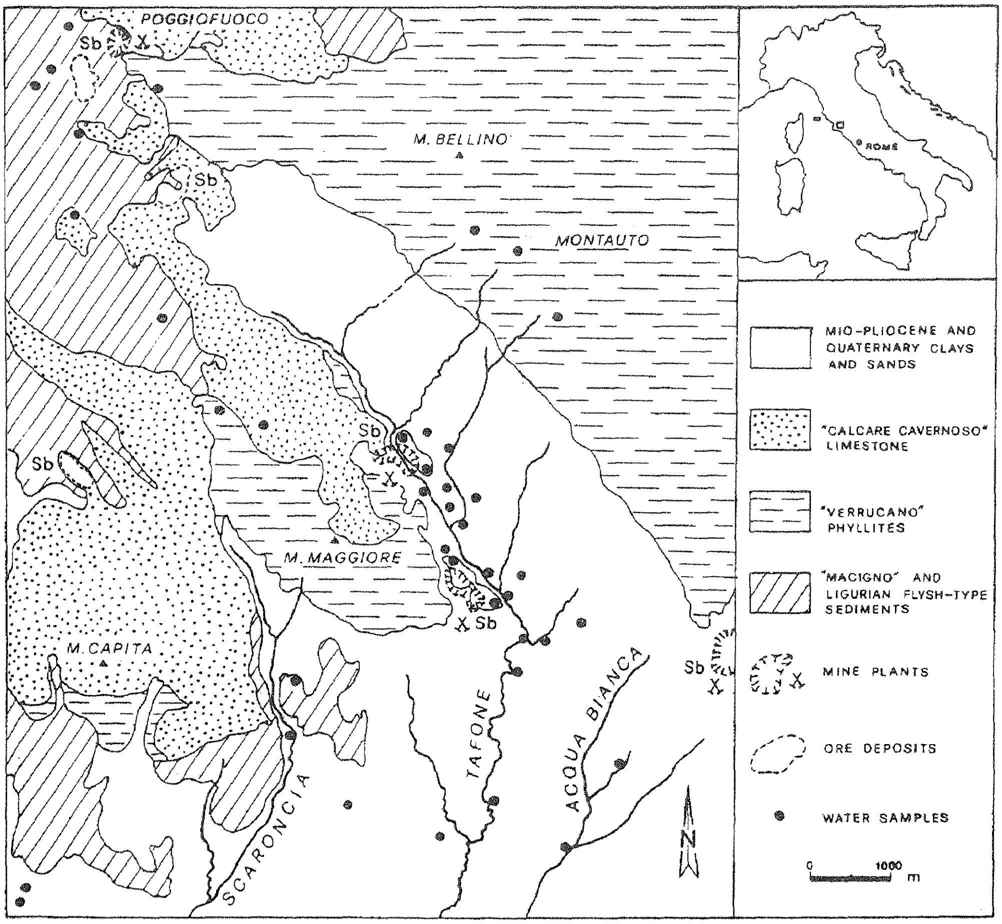

Fig. 1. Schematic geological map with location of mineral deposits and water samples.

Differently from most antimony deposits in Tuscany, where the host limestone is strongly silicised, in the Tafone deposit, stibnite is associated with marcasite and pyrite. Disseminated traces of cinnabar, sphalerite and galena and widespread baryte have been reported (Dessau 1972). In this area, the flotation tailings and waste materials, left from the mining activity, show a large variability in metal concentration due to the variable composition of the deposits exploited and the different processing techniques used over time; concentrations of up to 7% antimony, 1% zinc, 0.4% arsenic and lower amounts of lead, mercury and copper have been reported (Massoli-Novelli et al., 1994).

3 HYDROGEOCHEMICAL STUDY

The hydrogeochemical study was based on 36 samples, including spring, well and stream waters, and 4 samples derived from two previous exploited pits, which now also collect water from metallurgy plant and flow in the Tafone stream. Sample locations are given in Fig. 1. The main aquifers of the area are hosted in the Calcare Cavernoso formation and the Quaternary sediments which are the most permeable formations.

Temperature, pH, conductivity, redox potential and alkalinity were measured at the sampling site. Water samples were filtered through a 0.4 µm pore-size filter and acidified for metal analyses. The anions were determined by ionic chromatography, Ca Mg, Na, K by AAS Li, Rb, Cs by AES, Sr, Ba, Fe, Mn, B, Si by ICP-AES, Al, Zn, Cd, Pb, Co, Ni by GF-AAS, As, Sb by AAS after hydride generation.

Water temperature was about 16 °C, a value close to the mean annual temperature in the area, and the pH was always higher than 6.0. Most of waters samples

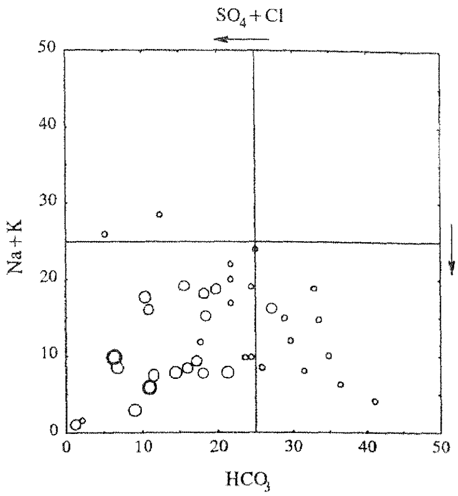

Fig. 2 Langelier-Ludwig diagram. The circles are proportional to the salinity.

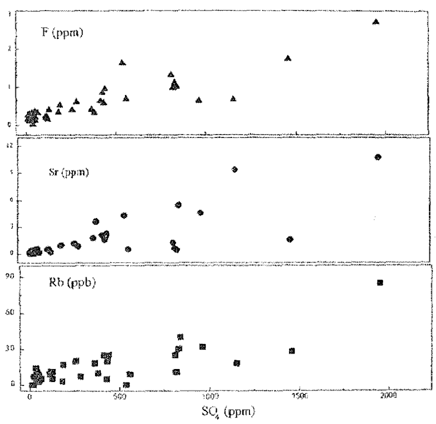

Fig. 3. Plot of F, Sr and Rb versus SO_4 concentrations.

showed oxidising conditions except 5 groundwater samples, where reduced S-species were observed.

From the Langelier-Ludwig diagram (Fig. 2) it is possible to distinguish three main groups: 1) calcium-bicarbonate waters with low salinity (< 1 g/l); 2)sodium-calcium-chloride-bicarbonate waters of comparable salinity; 3) calcium-magnesium-sulphate waters with salinity up to 4g/l. Groups 1) and 2) represent waters with relatively shallow circulation into the carbonate and/or phyllites formations, with an increasing Na-Cl character for waters interacting with alluvial sediments. Waters belonging to group 3) evolve to higher sulphate and magnesium concentrations with increasing salinity; this behaviour

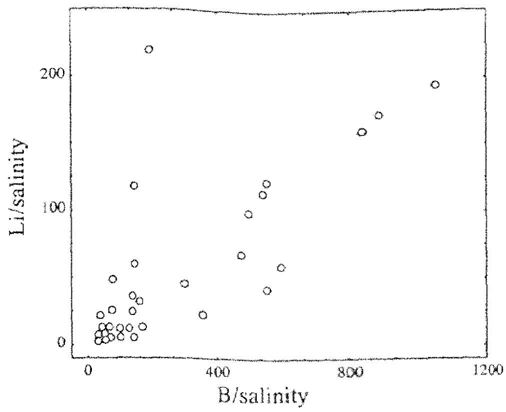

Fig. 4. Plot of lithium versus boron concentrations normalised to salinity.

is due to interaction with gypsum and dolomite present either in the evaporitic formation or in the tailings and mining waste. Two samples from water settled on the waste after rainy periods showed high sulphate but low salinity.

In the studied waters, a strong positive correlation of F, Rb, Sr with SO_4 concentrations was observed (Fig. 3), confirming that these elements are associated with the Calcare Cavernoso formation hosting the mineral deposits.

The plot of B/salinity versus Li/salinity (Fig. 4) shows that the majority of samples were grouped together at low Li and B concentrations. Relative lithium enrichment is related to interaction with the phyllites while boron enrichment is observed in waters leaching Miocene sediments. A strong increase in Li and B concentrations was observed in water flowing out of the mining plant and along the Tafone stream. This trend makes it possible to follow the dilution effect of the stream water by unpolluted tributaries: a decreasing of about 70% in Lithium, Boron and sulphate concentrations was observed at about 2 km downstream from the mining works.

The maps of Fig. 5 report the areal distribution of Sb and As in solution for the studied water samples. Anomalous concentrations of these elements are found in proximity of known mineral occurrences and mining areas. The Tafone valley is shown to be a widely polluted area with relatively high concentrations of antimony and arsenic all along the stream. The erosion of tailings and mining waste and their remobilisation, along the Tafone banks, do not favour an attenuation process.

The concentrations of others metals, such as Pb, Cd, Cu, Co and Ni, which were considered in this study, were generally low and often below the detection limit (about 1μg/l) of the methods used.

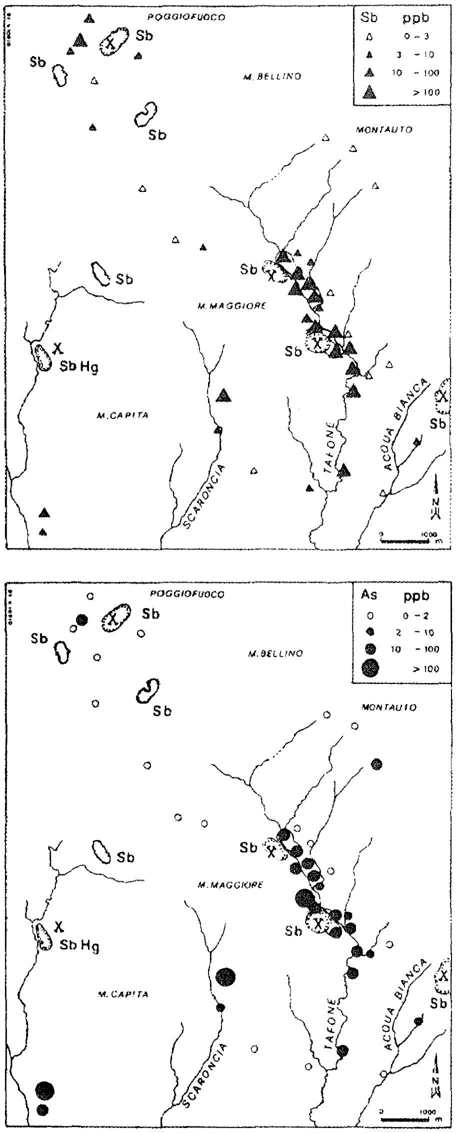

Fig. 5. Map showing the antimony and arsenic distribution.

4 CONCLUSIONS

In order to verify the presence of contaminant processes over an area of Southern Tuscany, covering about 130 km^2, 40 water samples were analysed for a large set of major, minor and toxic components in solution. The chemical composition of water samples revealed high concentrations of SO_4, Mg, Sr, and F, anomalies in Li and B and the presence of contaminants, such as Sb and As, in areas of known mineral deposits. Anomalous concentrations of Sb and As are enhanced in the Tafone valley by the presence of tailings and mining waste.

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