

## Behavior of Toxic Elements in Hydrothermal Systems: As and Hg in the Thermal Waters of the Phlegraean Fields (Italy)

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In the last years, many studies have dealt with the distribution of the arsenic and mercury in natural waters, in order to evaluate the environmental problems connected to anomalous concentrations of As and Hg in the shallow waters. In particular, As occurs in elevated concentrations in geothermal areas, as it is selectively mobilized in hydrothermal conditions. In the case of the Phlegraean Fields (P.F.) hydrothermal system, the study of the evolutionary trends of As phases in solution results are very interesting, since this element appears to be sensible to the chemical and physical changes of the deep system (Celico et al. 1992). In the waters of the P.F., the concentrations of As range from 225 ppb to 5200 ppb, therefore they are in good agreement with the mean contents (3000-6000 ppb) of the acid volcanic rock of the reservoir and with the characteristic values of other geothermal areas, maximum values being similar to the most elevated concentrations registered in the world (Stauffer and Thompson 1984). There are three main processes causing As increasing in the shallow waters: 1) the direct feeding of fluids coming from the magmatic chamber, 2) uprising of As bearing fluids generated by As gas-phase partition in deep boiling waters at temperatures ranging from 235 to 280 °C (Allard et al. 1991, Panichi & Volpi 1999), 3) water-rock interaction processes, enhanced by elevated temperatures of the thermal waters. The feeding by deep As enriched hot fluids is the prevalent As source in boiling pools located on the external side of the Solfatara crater, whereas, the elevated mobility of the arsenic, for leaching of the glassy portion of the pyroclastic rocks, gives the reason for high As contents found in all the studied waters. In the sampled area and mainly in the crater of the Solfatara, particularly elevated As concentrations cause the formation of As bearing minerals, like Realgar. Sulfurs and sulphates of arsenic are the most common minerals as a consequence of the big affinity of As with the sulphur. Controlling factors on the behaviour of As in aqueous solutions are: 1) high S contents in fluids that lead to a precipitation of As in sulphur phases, 2) variable quantities of Cl, F and O in gas and waters that enhance As mobilization in volatile form and 3) physico-chemical parameters (as pH and Eh) controlling oxidation state and stability of neoforming minerals. The pH and Eh values of the

Phlegraean waters favour the mobility of the arsenic in the trivalent form. In the specific case, thermodynamic data lead to define  $H_3AsO_3$  as the stable As phase in studied thermal waters (Vink 1996). Mixing processes with meteoric water occur when hydrothermal waters rise from the deep reservoir to the shallow aquifer. Such phenomena produce a decrease in salinity and changes in the chemico-physical conditions, causing, therefore, in some cases the As loss from the solution. In fact, in some samples, it has been observed a shift versus more oxidizing conditions and As losses following dilution and oxidation in the form  $As^{5+}$ .  $As(V)$  is a relatively insoluble phase, as it precipitates with hydrated oxides of Fe and Mn, with clayey mineral and with organic material. In all the area, mercury shows a different evolutionary trend from that of arsenic. The high levels found in studied thermal waters accord to the normal contents of the other geothermal areas (Cellini Legittimo et al., 1986), where sediments and fine-grained mud are often greatly enriched in mercury. In the P.F. waters, Hg concentrations range between 1 and 230 mg/l and appear to be higher than that of ground water (1 mg/l). Observing Hg distributions, it can be deduced that this element is associated with the ascent of deep fluids from the magma chamber, likely as  $HgCl_2$ . As a matter of fact, cold waters display very low Hg levels, as a consequence of the absence of direct inflow of volcanic gases. In this case the only source of Hg must be the rocks of the volcanic cover, from which it is unlikely removed.

- Allard P., Maiorani A., Tedesco D., Cortecchi G. and Turi B., *J. Volcanol. Geoth. Res.*, **48**, 139-159, (1991).  
Celico P., Dall'Aglio M., Ghiara M. R., Stanzione D., Brondi M. & Prospero M., *Boll. Soc. Geol. It.*, **111**, 409-422, (1992).  
Cellini Legittimo, P., Piccardi, G. and Martini, M., *Chem. in Ecol.*, **2**, 219-231, (1986).  
Panichi C and Volpi G., *J. Volcanol. Geoth. Res.*, **91**, 321-328, (1999).  
Stauffer RE & Thompson JM, *Geochim. Cosmochim. Acta.*, **48**, 2540-2561, (1984).  
Vink BW, *Chem. Geol.*, **130**, 21-30, (1996).