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Geogenic arsenic in groundwaters in the western Alps

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SUMMARY

Groundwater arsenic (As) of geogenic origin in the western Alps is generally associated with aquifers in crystalline rock. The External Crystalline Massifs (ECM) are in particular noted for occurrences of elevated concentrations of As in groundwaters. The present study is based on As in groundwaters that have been measured in the ECM in both France and Switzerland. Arsenic-bearing sulfide minerals, such as pyrite, arsenian pyrite, and arsenopyrite, are the most likely sources of As leached within the crystalline ECM rocks. While it is not known how As concentrations vary with time at all of the reported water sources, we measured on a weekly basis the concentration of As at one thermal source over a period of one year and found the As concentrations to be variable; however, the cause of the variability is at present not understood. Even though many studies have applied $\delta^{34}S_{SO4}$ as a tool for understanding As mobilization in the ECM, there is no consensus at present. Finally, we present some perspectives on the possible effects of climate change and anthropogenic activities on As mobility in the ECM. In particular, droughts have the potential to increase As concentrations in groundwaters.

1. Introduction

1.1. Arsenic in the environment

An increasing awareness of arsenic (As) toxicity led the World Health Organization (WHO) to reduce the critical value of As in potable water from 50 to 10 μg/l in 1993 (WHO, 2011). This action was taken in parallel with worldwide efforts to reduce anthropogenic inputs to potable water sources. Moreover, geogenic As concentrations exceeding WHO critical values have been measured in many countries, Asia being at present the most impacted area (Charlet and Polya, 2006; Vaughan, 2006).

Arsenic is a very common element in the environment, occurring in rocks, soils, water, and air. Native As is known to occur in intrusive magmatic rocks, often in veins associated with Co–Ni–Ag–U (Ramdohr, 1975). Sulfide minerals, such as arsenian pyrite and arsenopyrite, are very common and well-known primary geogenic As-containing minerals (Pfeifer et al., 2007). These sulfide minerals are commonly associated with metals (Pb, Zn) of economic interest. Mining activities leading to their extraction can lead to As mobilization via leaching under oxidizing conditions. Hydrous ferric oxides (HFO) are known to be efficient secondary traps for As after its mobilization from sulfide minerals (Devitre et al., 1991; Pfeifer et al., 2007; Root et al., 2007). The subsequent dissolution of HFO can therefore lead to As remobilization. Phosphates, carbonates, dissolved silica, and organic matter are also known to increase As mobility (Smedley and Kinniburgh, 2002; Voegelin and Hug, 2003; Stollenwerk et al., 2007).

1.2. Geographical and geological background

In the western Alps As is commonly associated with crystalline basement lithologies, and in particular, in relation with Au-, Pb-, Sb-, U-, W- and Zn-sulfide mineralization (Negga et al., 1986; Bondietti et al., 1994; Pfeifer and Zobrist, 2002; Pfeifer et al., 2007). Ground and surface waters in such areas very often have high As concentrations, e.g., (i) Pfeifer et al. (2007) reported locally elevated As concentrations in waters percolating through mine wastes in the Aiguilles Rouges Massif (French–Swiss border); (ii) Féraud et al. (2009) reported high As concentrations in rivers in the crystalline basement of the Mercantour–Argentera Massif (border of French–Italian Alps); (iii) Pili et al. (2013) reported high As concentrations in groundwaters of the Beaufortain Massif (French Alps). All three of these occurrences, the Aiguilles Rouges, the Beaufortain, and the Mercantour–Argentera, are in mountain ranges that in a geological and structural context belong to the External Crystalline Massifs (ECM). The ECM form the backbone of the Alpine arc and represent the Hercynian-age basement of the European plate that was uplifted during the collisional stage of the Alpine orogeny (Ceriani et al., 2001). The following massifs also belong to the ECM: Aar-Gotthard (Switzerland), Mont Blanc

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Massif (France, Italy), Grande-Rousses (France), and Pelvoux (France). The ECM account for a total surface area of approximately 10,000 km^2 (see Fig. 1), with a population of several hundred thousand. This population may locally be increased by one to two orders of magnitude in association with seasonal tourism.

Water in the ECM is a critical resource. Even though a significant portion of water recharge occurs by rain and snowmelt in the ECM and Alps in general, the rough alpine topography of this region leads to much runoff. In addition, the crystalline rocks that characterize the ECM are characterized by low reservoir capacities.

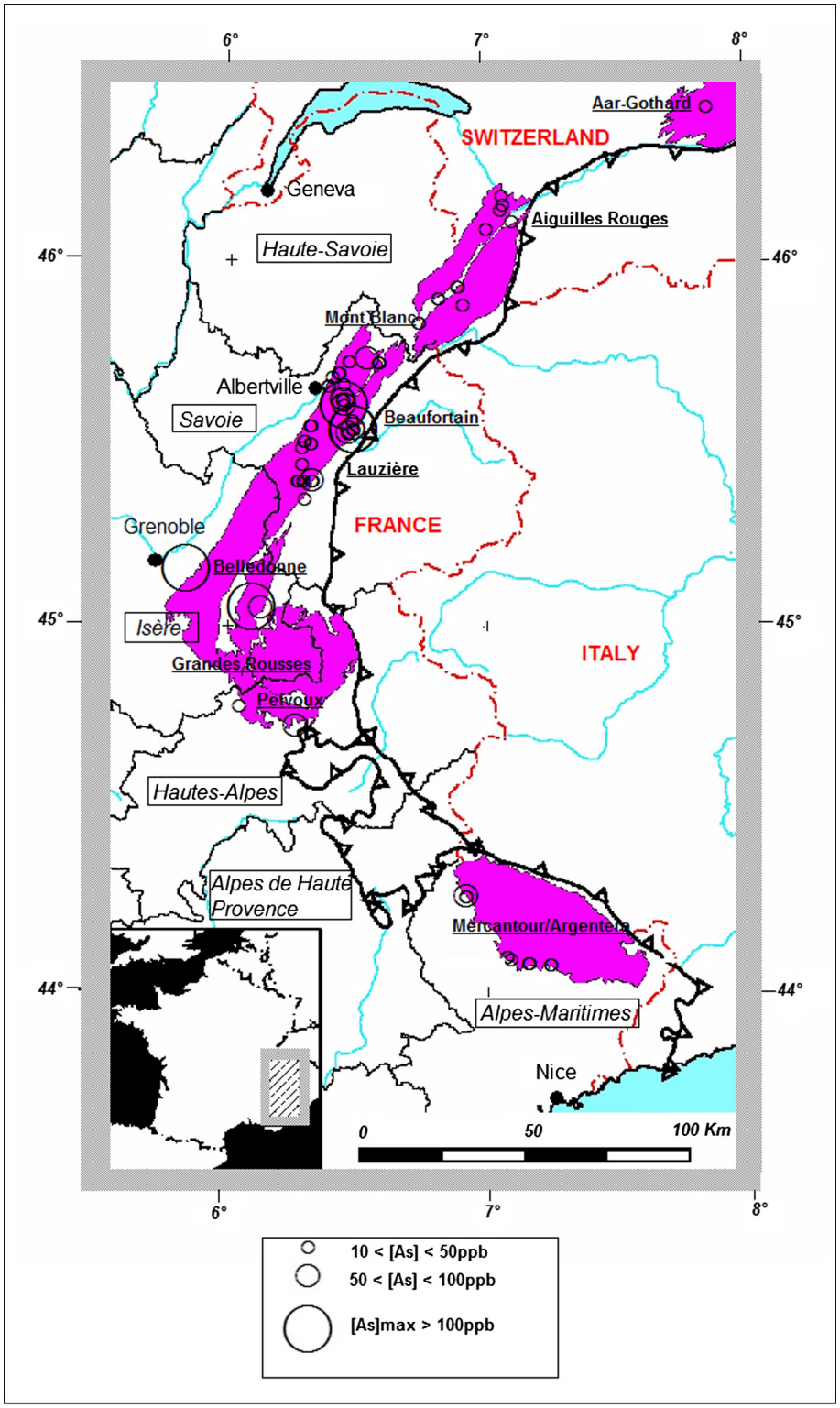

Fig. 1. Arsenic (As) occurrences in the External Crystalline Massifs (ECM) measured over the period 1996–2011 (see Table 1). The black line with barbs represents the Pennic front that separates the autochtonous External Alps in the west from the allochtonous Internal Alps in the east. The ECM are in dark rose, and the names of massifs within the ECM are underlined (names of French départements are enclosed in boxes). The circles and the corresponding As concentration ranges are based on the absolute maximum As concentrations measured for a particular water source. Note: ppb equivalent to μg/l.