Geogenic arsenic in groundwaters in the western Alps

Delphine Tisserand [a,*], Eric Pili [b,c], Roland Hellmann [a], Anne-Marie Boullier [a], Laurent Charlet [a]

[a] ISTerre, University of Grenoble 1, CNRS, Observatory for Earth, Planetary, and Space Sciences (OSUG), F-38041 Grenoble, France
[b] CEA, DAM, DIF, F-91297 Arpajon, France
[c] Institut de Physique du Globe de Paris-Sorbonne Paris Cité, CNRS, Université Paris Diderot, 1 rue Jussieu, F-75238 Paris cedex 05, France

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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.

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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

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.
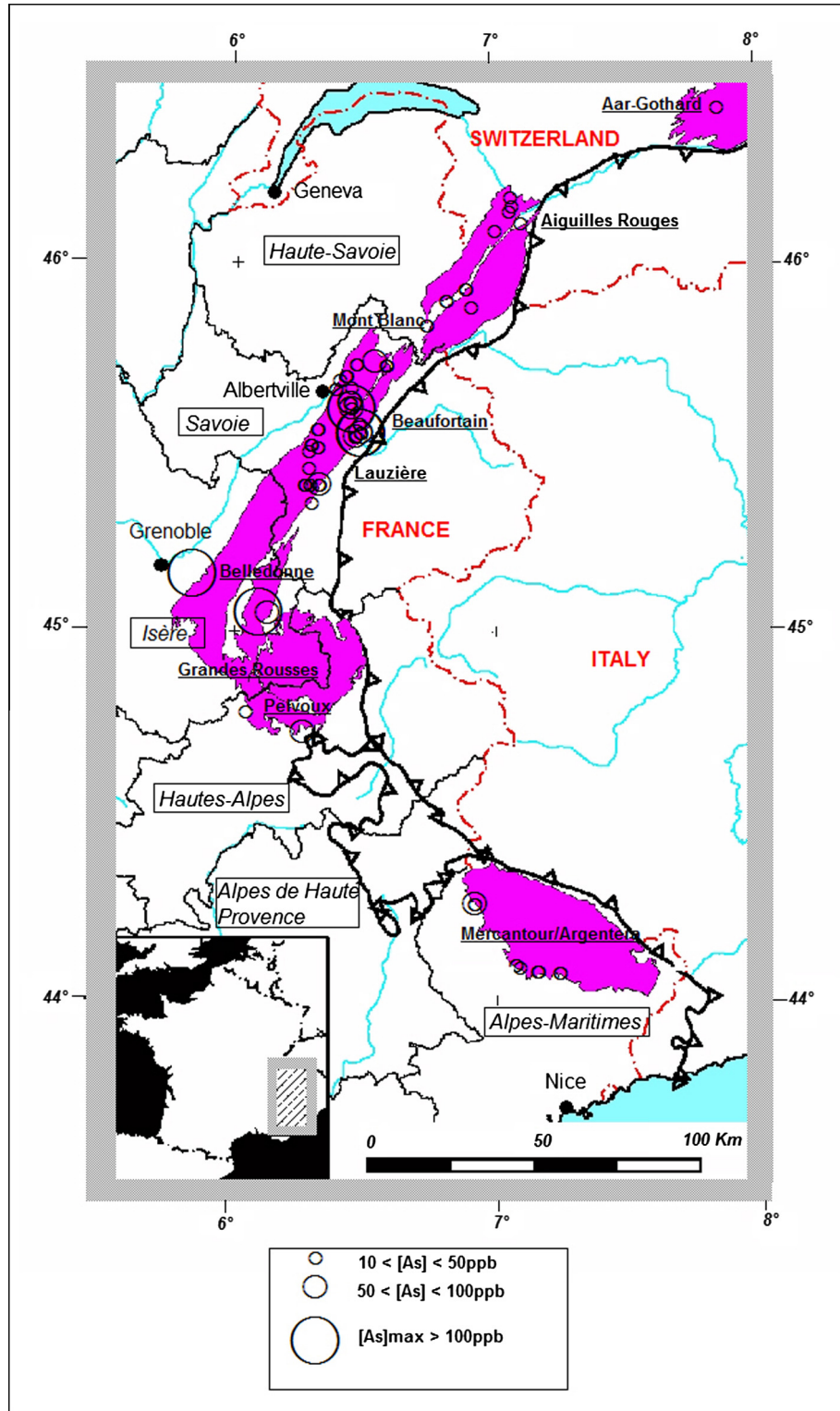

Fig. 1. Arsenic (As) occurrences in the External Crystalline Massifs (ECM) measured over the period 1996–2011 (see Table 1). The black line with barbs represents the Pennic front that separates the autochtonous External Alps in the west from the allochtonous Internal Alps in the east. The ECM are in 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.

These reservoirs have a heterogeneous geographic distribution (e.g. Pili et al. (2013)), and combined with a general dispersal of the local populations, results in water distribution costs that increase rapidly with distance. The consequence of this has been the recognized need to develop and use many local water sources. This, in turn, leads to a potentially higher risk of potable water having As concentrations above the drinking water guideline fixed at 10 µg/l.

In this study we discuss As-bearing crystalline rocks in the western Alps, and in particular, the geographic occurrence of As in groundwaters in the ECM. Even though elevated As values associated with certain localities occasionally show up in local media coverage, only a very limited number of scientific investigations concerning elevated As groundwaters in the ECM have been carried out. Here we have compiled and evaluated a published data set based on about 500 natural water sources. In addition to this, we present some of our own As measurements from one thermal source in the French ECM. And finally, since the ECM have a relatively large population for a mountainous region, we discuss the potential effects of external factors, such as climate change and land usage practices, on As mobilization.

2. Materials and methods

2.1. French Regional Health Agency (ARS) and other databases

We collected As concentration data measured in groundwaters occurring within the ECM in France and the western-most part of Switzerland, the two countries that host most of the ECM. For the French ECM, we exploited a comprehensive database from the French Regional Health Agency (Agence Régionale de Santé, henceforth denoted as "ARS"). The goal of the ARS is the measurement of the quality of potable water sources in France, and for this reason, As is one of the critical elements that has been measured and reported for natural springs and groundwater sources. The ECM in France encompass the following départements (from north to south, time period of measurements given in parentheses, see Fig. 1 and Table 1): Haute–Savoie (2005–2011), Savoie (1997–2011), Isère (1996–2012), Hautes–Alpes (1994–2012), Alpes–Maritimes (2000–2012). Most of the data represent spring water sources, with the remainder representing wells. The Swiss As data were obtained from Pfeifer (2010) and Pfeifer (pers. comm., 2012). The time periods corresponding to the Swiss analyses are not known. In addition, a recent study of 122 groundwaters in contact with crystalline basement rocks collected in the northern part of the Gotthard rail tunnel (eastern Aar Massif, Switzerland; Bucher et al., 2012) provides a unique data set of in situ cation (including As) and anion concentrations, at depths up to 2200 m.

All As concentrations reported here are from natural waters that have not undergone any particular pre-treatments, in particular those that remove As from water. The ECM water sources reported in this study total 493 springs and wells that are associated with 101 localities (see Table 1 and Fig. 1). Water sources for which As concentrations were measured over time periods of several years generally show concentrations with varying degrees of variability on a year-to-year basis, with some of them showing concentration peaks that far exceed the mean concentrations. We have chosen to classify each water source based on the absolute maximum measured As concentration. Based on this criterion, we considered maximum As concentrations that fall in the following ranges: 10–50, 50–100, >100 µg/l. Sources with As occurences <10 µg/l are also included in the data shown in Table 1. The upper and lower limits of 50 and 10 µg/l correspond, respectively, to the past (1963–1993) and present (since 1993) critical As values established by the WHO (WHO, 2011). It should be noted that thermal waters with As concentrations exceeding the 10 µg/l limit are exempt from regulations, considering that they are not used for potable water.

2.2. Case study in the French ECM

From September 2004 to November 2005, we carried out a geochemical study on a thermal spring located in the French ECM. The hydrogeological context of this site is characterized by deep fluid circulation within a crystalline massif (Courtois and Vigouroux, 2005a). The As concentrations that we measured are most probably completely geogenic, as there are no large-scale fruit orchards or other agricultural activities using As-bearing pesticides or herbicides in the recharge area. In addition, we are not aware of any other anthropogenic activities that could lead to surface As release in the catchment or recharge zone. The thermal waters at this site were sampled on a weekly basis; the water temperatures were concomitantly recorded. The thermal water samples were filtered on site (0.22 µm cellulose acetate membrane filters), stored in polyethylene bottles (with no acidification), and kept at 4 °C until analysis. Total As concentrations were determined by coupling an HPLC (high performance liquid chromatography, Varian Prostar 230) to an AFS (atomic fluorescence spectroscopy, Millenium Excalibur). Coupling HPLC with AFS permits very low quantitative analyses of As, down 0.5 µg/l, even in highly mineralized solutions. HPLC-AFS also allowed determination of As speciation (i.e. As^{III}, As^V). Even though the storage conditions were not optimal for As speciation analysis, we assumed that the slow oxidation kinetics of As^{III} (Kim and Nriagu, 2000; Smedley and Kinniburgh, 2002) allowed for a qualitative determination of in situ As speciation (for a detailed study on $As^{III,V}$ analytical protocol, see e.g., McCleskey et al., 2004). The instrumental parameters for the HPLC-AFS analyses are shown in Table 2, Supplementary Information.

3. Results

3.1. Results from ARS database and published studies

Fig. 1 shows the western Alpine arc with the ECM and other geological units, and overlain on this are the measured As concentrations, differentiated according to the three concentration ranges described earlier. This figure clearly indicates that many ECM groundwaters are enriched in As and that concentrations in specific localities exceed 10 µg/l in five French ECM départements and in the Swiss canton of Valais. It should be noted that As concentrations from areas completely external to the ECM are not considered here, and thus have not been mapped (e.g., exceptionally high As concentrations in certain thermal springs in the Massif Central, France). Therefore, the indicated distribution of As occurrences in Fig. 1 only concerns the ECM zone.

Table 1 lists the number of water sources with As concentrations classified according to the three concentration ranges considered. The data are subdivided into groups corresponding to the five French alpine départements, whereas all of the Swiss cantons considered here have been grouped together. Within each group, we have listed both the number of towns (villages) and the number of water sources associated with them. The pH values of the individual water sources generally range from 7.0 to 8.95, and the temperatures vary from 4 to 27 °C. The specific water type (surface water, groundwater, thermal water) associated with each group's maximum As concentration is also indicated. The maximum As concentrations range from 26 to 370 µg/l, and have been measured in all three types of waters. A detailed look at Table 1 reveals that As occurrences with concentrations in the range of 10–50 µg/l predominate, with a total of 83 sites, representing ~17% of all

Table 1
Groundwater data pertaining to the External Crystalline Massifs (ECM), obtained from the French Regional Health Agency (ARS), and from Pfeifer (2010) and Pfeifer (2012, pers. comm.) for western Switzerland (canton Valais). In France, the ECM is located in five French départements (Alpes–Maritimes, Savoie, Haute–Savoie, Hautes–Alpes, and Isère). The grouping of As occurrences is based on the maximum As concentrations measured for each specified time period and concentration range. Water type associated with maximum As concentrations: S = surface water, G = groundwater, T = thermal water). ni = no information available. Note: ppb equivalent to µg/l.

Département or canton	Number of towns	Number of water sources	Number of sources [As] 10–50 ppb	Number of sources [As] 50–100 ppb	Number of As sources [As] >100 ppb	[As] max (ppb)	Water type with respect to [As]max	Sampling period
Valais, Switzerland	6	6	6	0	0	38	G	ni
Haute-Savoie (F)	5	34	8	0	0	25.8	S	2005–2011
Savoie (F)	42	257	57	9	5	187	G	1997–2011
Isère (F)	31	144	0	1	2	370	T	1996–2012
Hautes-Alpes (F)	3	3	1	1	0	76	G	1994–2012
Alpes-Maritimes (F)	14	49	11	1	0	62	G	2000–2012
Total	101	493	83	12	7			

measured sources. Twelve sources are in the range 50–100 µg/l, representing ~2.4% of the total, and seven sources have concentrations >100 µg/l, which represent ~1.4% of the total. These results underline the fact that roughly 79% of the water sources have maximum As concentrations below 10 µg/l. This reflects the heterogeneous nature of As mobilization in the aquifers, as well as the fact that water sources serving towns and villages in the ECM have been, in many cases, specifically chosen for low As concentrations.

Due to the large scale of Fig. 1, and because the exact locations of all water sources are not always precisely known (or are proprietary information), the true locations of water sources are not always accurately represented in Fig. 1. In addition, some of the values reported in Fig. 1 do not appear to be strictly associated with the crystalline ECM, but rather are located in adjacent border regions. To address this, in Fig. 2 we show at much higher resolution a map of the regional geology of a part of the Savoie with corresponding As levels (differentiated by concentration as in Fig. 1, data from ARS and SCERCL, 2006). The crystalline rocks constituting this département originate from two different parts of the same European basement, and have undergone various degrees of metamorphism and deformation during the Alpine orogeny. They are juxtaposed with sedimentary units (Debelmas, 1980). It appears that most of the elevated As concentrations are observed with groundwaters from crystalline rock. As an example, in two particular cases near Albertville and near Champagny en Vanoise,

elevated As concentrations are associated with groundwaters hosted in crystalline rocks, whereas all groundwaters hosted in nearby sedimentary rocks have As concentrations below 10 µg/L (Fig. 2). However, in some cases elevated As levels are associated with sedimentary lithologies that are in close proximity to crystalline rocks. In such cases, it is not known which geological units are the ultimate source of As.

Quite surprisingly, the 122 groundwater samples from the northern part of the Gotthard rail tunnel were found in general to be devoid of As (see on-line Supplementary data from Bucher et al., 2012), even though pyrite and pyrrhotite were frequent accessory minerals. Moreover, the in situ temperatures are elevated (45 °C) and the groundwater is characterized by high pH (pH 8–10). Only eight samples revealed As concentrations ranging from 5 to 12 µg/l, with iron (Fe) concentrations ranging from 0 to 1.027 mg/l.

3.2. Results from the ECM case study

The thermal water at this ECM site is circumneutral (pH = 6.75, based on one measurement). The water temperatures ranged from 23.7 to 26.3 °C, with a mean value at 25.1 °C. The concentrations of As over one year (2004–2005) are presented in Fig. 3. During the period studied, total arsenic concentrations were variable, with a mean value of 396.8 µg/l ± 76.6 µg/l (1 SD). The minimum and
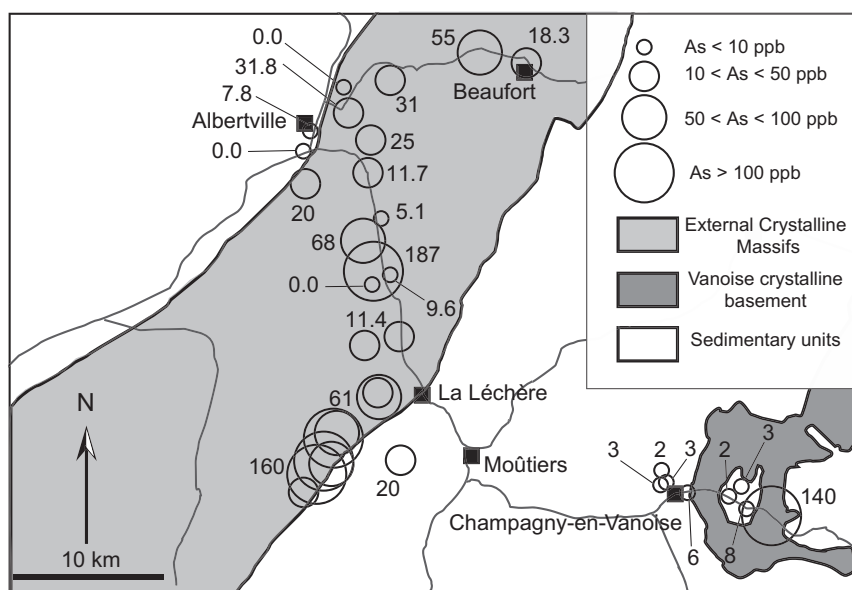

Fig. 2. Arsenic occurrences in groundwaters in Savoie. Most, if not all elevated As concentrations are associated with crystalline rocks, rather than sedimentary lithologies. The two geological units shown in grey represent crystalline rocks from Hercynian basements of the European plate: the Beaufortain massif is in light grey, which is a component of the autochtonous External Crystalline Massifs, and the allochtonous Vanoise basement is in dark grey. Sedimentary units adjacent to the ECM and Vanoise are indicated in white. Note: ppb equivalent to µg/l.

maximum As concentrations that we measured were 150.9 and 598.9 µg/l, respectively. Although the exact causes for the temporal variation of the As concentrations are unknown, we assume that short term (hours to days) precipitation events in the recharge area, local climate variations that include dry and wet periods (time scale of months), and local seismicity all contribute to the measured variations. The measurement of As speciation revealed the presence of As^{III} in the range 0–434.8 µg/l. As was the case for total As, the As^V and As^{III} concentrations were not stable over the period of measurement. Based on the 59 analyses of As speciation realized over the year-long period, only eight samples had As^{III}/As^V ratio >1. Considering that our storage conditions were not optimal for preserving the reduced As state in the water samples, the quantification of As^{III} is probably not too reliable. Nonetheless, the detection of As^{III} can be used as a tool to provide some insights into redox conditions where water-rock interactions take place.

We compared our results with another study of As in a Maine (USA) watershed by Sidle et al. (2001), where the As^{III}/As^V ratio varied in the range of 0.01–4.45 (with the majority of values <1). This was interpreted by these authors in terms of 'some reduced conditions' existing in the groundwater. In addition, the study of Pili et al. (2013) in the French ECM (Savoie) revealed As^V, as the principle As species, but the presence of As^{III} shows that reducing conditions exist at depth. Arsenic speciation may not always be in accordance with measured pH and redox potentials (Eh); i.e., disagreement between measured and calculated potentials. This statement has been demonstrated by Holm and Curtiss (1989) who showed that even when As^V/As^{III} increases with increasing Eh, the calculated redox potentials from the As^V/As^{III} couple, compared to the measured Eh, always has a negative bias, that can attain +200 mV. These authors conclude that groundwaters are not in redox equilibrium, and that As speciation values indicate a qualitative estimation of redox conditions. With respect to the thermal ECM source that we monitored, we can only deduce that the presence of As^{III} allows us to infer the existence of reducing conditions at depth.

4. Discussion

4.1. Arsenic mobilization mechanisms: Arsenic-rich sulfides in the ECM

Sulfide minerals are a common source of natural geogenic arsenic. Arsenic mobilization is associated with oxidation processes
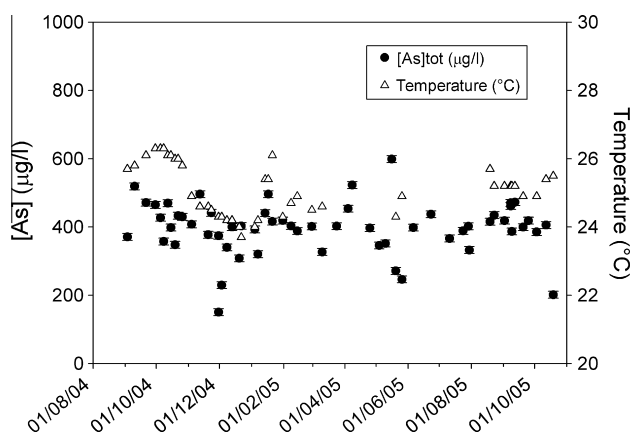

Fig. 3. Temporal evolution of total dissolved As concentrations (µg/l) and temperatures (°C) in a thermal spring within the ECM over a one-year period from September 2004 to November 2005. Temperatures range from 23.7 to 26.3 °C with a mean value at 25.1 °C. Arsenic concentrations range from 150.9 µg/l to 598.9 µg/l, with a mean value of 396.8 µg/l. The error bars are proportional to the estimated accuracy of the measurements (<10%). The cause for the variability in As and temperature are potentially the result of many factors- see text for details.

that lead to leaching of As, causing its release in groundwaters (Sidle et al., 2001; Pfeifer et al., 2007). Arsenic-bearing sulfides such as pyrite (FeS_2), arsenian pyrite ($Fe(S_{1-x}As_x)$) (Fleet et al., 1993), arsenopyrite (FeAsS), and pyrrhotite ($Fe_{1-x}S$) are recognized as common accessory minerals in crystalline rocks in the western Alps and the ECM (e.g., Negga et al., 1986; Pili et al., 2013). Other sulfide phases, though of minor importance in most of the ECM, contain As in high proportions: realgar (AsS) and orpiment (As_2S_2). Pyrite can incorporate up to 9.5 wt.% As in its structure (Abraitis et al., 2004), in part because the ideal stoichiometry of pyrite does not exist in natural systems (Griffin et al., 1991; Cepedal et al., 2008). Arsenopyrite, with an ideal formula range given by $FeAs_{0.9}S_{1.1}$ to $FeAs_{1.1}S_{0.9}$, incorporates up to 46 wt.% As (Abraitis et al., 2004). In addition, As-bearing pyrite is commonly associated with the presence of arsenopyrite, where As is incorporated into the pyrite structure via a non-stoichiometric substitution mechanism (Abraitis et al., 2004). These sulfide minerals therefore constitute potential sources of As that are released into groundwaters if the in situ redox conditions promote the oxidation and dissolution of sulfide minerals, which then allows As mobilization. Because of the ubiquity of sulfides phases, elevated geogenic As concentrations are often associated with groundwater sources in crystalline rocks (Sidle, 2002). Several important mountain ranges can even be considered to be "high As belts", e.g. the Appalachians (Peters, 2008), the "Iberic pyrite belt" (Maia et al., 2012). The French–Swiss ECM may thus also be considered as an "As belt", given that As levels up to several hundreds of µg/l have been measured in groundwaters.

4.2. Primary sources: Arsenic mobilization

Elevated As concentrations in geothermal waters are well documented in many localities around the world: USA, Japan, New Zealand, Chile, Mexico, Iceland, Kamchatka, and France, for example (Smedley and Kinniburgh, 2002; Planer-Friedrich et al., 2007; Nordstrom et al., 2009; Birkle et al., 2010). Taking a specific example of geothermal waters within the French ECM, Courtois and Vigouroux (2005a) realized a detailed study of a thermal water source at the external boundary of the ECM. This site is located at the boundary between crystalline rocks composed of amphibolites, schists, gneisses, and serpentinites, and younger sedimentary units of Jurassic age composed of organic rich marls and shales. According to these authors, fluids circulate to an estimated depth of 4000 m along a fault system and fractures, where they attain a maximum temperature of roughly 150 °C, and then resurface at 25–27 °C. According to the same authors, the thermal water has a meteoric origin (rainwater infiltration in the recharge area), based on oxygen ($\delta^{18/16}O_{H2O} = -11.9‰$) and hydrogen isotopes ($\delta^{2/1}H_{H20} = -82.9‰$). These isotopic signatures fall directly on the meteoric water line (SMOW).

These ECM thermal waters are especially characterized by high concentrations of NaCl, sulfate, and reduced sulfur species (Courtois and Vigouroux, 2005a). The presence of elevated sulfate is attributed to the dissolution of gypsum and anhydrite-rich lithologies of Triassic age. Dazy and Razack (1989), based on an isotopic analysis of sulfur, confirm the sedimentary origin of the sulfate-rich waters. The notable presence of trace elements, such as Sr, Li, Rb, F, B, I, are thought to be additional evidence for mineralization of the waters at considerable depth as they percolate both in the crystalline basement and the Triassic evaporite deposits. According to Courtois and Vigouroux (2005a), the presence of As most probably has its origin in iron sulfide minerals present in the crystalline basement. However, we cannot exclude other lithologies as a source for As. For example, As may also be present in the evaporites (see, e.g., As-evaporite correlation in Birkle et al., 2010).

We also cannot discount the potential presence of As in the organic-rich marls that border the crystalline rocks at this site.

It is very interesting to note that a similar study by the same authors of another thermal water source in the ECM (Courtois and Vigouroux, 2005b) reveals that the hydrogeochemistry and regional geology are very similar. However, for reasons not specified, the thermal waters at this second site are low in As (<10 μg/l). Further on we discuss possible reasons why these similar sites have very different As concentrations.

The mobilization of As can be represented via a myriad of reactions. A very common set of generalized reactions that describe the oxidation of pyrite in the presence of water and oxygen are represented by reactions (1–3). These reactions do not include intermediate sulfoxyanion species that form (Nordstrom, 2011; and references therein):

$$2FeS_{2(s)} + 7O_{2(g)} + 2H_2O_{(l)} \rightarrow 2Fe^{2+}_{(aq)} + 4SO^{2-}_{4(aq)} + 4H^+_{(aq)} \qquad (1)$$
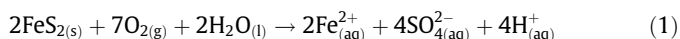
The protons produced during the oxidation of sulfide to sulfate serve to oxidize Fe^{2+} to Fe^{3+}:

$$4Fe^{2+}_{(aq)} + O_{2(g)} + 4H^+_{(aq)} = 4Fe^{3+}_{(aq)} + 2H_2O_{(l)} \qquad (2)$$
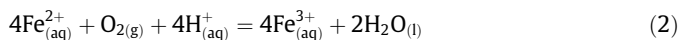
In turn, the ferric ions produced further oxidize pyrite, releasing ferrous ion and protons:

$$FeS_{2(s)} + 14Fe^{3+}_{(aq)} + 8H_2O_{(l)} \rightarrow 15Fe^{2+}_{(aq)} + 2SO^{2-}_{4(aq)} + 16H^+_{(aq)} \qquad (3)$$
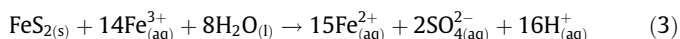
Reaction (3) is particularly important at pH < 3. The net result is the production of very low pH waters, and because of the low pH, the precipitation of ferric iron oxyhydroxides is greatly reduced. The above reactions (especially reaction 2) are generally recognized to be catalyzed by biotic processes (Nordstrom, 2011), since organisms such as certain bacteria (in particular, *Acidithiobacillus ferrooxidans*) use the oxidation reactions as a source of energy.

Eqs. (1)–(3) above show the relation between iron sulfide oxidation and dissolution, and the implied release of As from the primary Fe-sulfide. It is therefore interesting to note that there is no evident positive correlation between As and Fe concentrations in groundwaters from the Gotthard rail tunnel (Supp. Info, Bucher et al., 2012), as might expected from reactions (1)–(3) above. This may imply that oxidation/dissolution of primary iron sulfides (which are prevalent) is hindered. According to Bucher et al. (2012), O_2 levels are very low in the Gotthard rail tunnel, and for this reason, they postulate that bicarbonate plays a key role. Bucher and colleagues suggest that oxidation of pyrrhotite produces hematite and sulfate, and reduction of bicarbonate leads to elemental carbon, according to reaction 4. The precipitation of hematite (and goethite) may be the reason why so little Fe was measured in the tunnel waters.

$$4FeS_{(s)} + 8HCO^-_{3(aq)} \rightarrow 2Fe_2O_{3(s)} + 4SO^{2-}_{4(aq)} + 7C_{(s)} + 1CH_{4(g)}$$
$$+ 2H_2O_{(l)} \qquad (4)$$
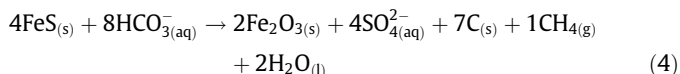
Reaction 4 implies a direct relation between FeS dissolution (and release of As) and production of sulfate. However, we were not able to deduce any obvious positive relation between the concentrations of As and sulfate measured in the tunnel waters, based on data given in Bucher et al. (2012). One possible reason for this may be As sequestration in the secondary oxidized iron phases.

4.3. Temporary sinks and secondary sources of arsenic

Groundwaters containing high concentrations of ferrous and ferric iron have the potential to precipitate HFO, in particular if certain geochemical factors lead to an increase in pH (solubility minima for HFO are in the circum-neutral pH range). Common HFO minerals include ferrihydrite, schwertmannite, microcrystalline goethite, and lepidocrocite (Nordstrom, 2011). HFO are known to efficiently scavenge aqueous As (Dixit and Hering, 2003), a process that immobilizes As and therefore reduces its concentration in groundwaters. Roman-Ross et al. (2005) showed that As^V can also be adsorbed onto gypsum surfaces, resulting in the formation of $Ca_3(AsO_4)_2$. Organic matter has also been determined to be an important scavenger of As (Huang and Matzner, 2006; Wang and Mulligan, 2006).

Arsenic sorbed on HFO phases should not be considered to be permanently sequestered, since As can be rapidly released to groundwaters when chemical conditions are such that the HFO are thermodynamically unstable, leading to their dissolution, under both oxic and anoxic conditions (Smedley and Kinniburgh, 2002; Charlet and Polya, 2006; Pfeifer et al., 2007). HFO phases should be most stable under circumneutral pH conditions, and dissolve more readily in the acid and basic pH range. It has also been observed that As is preferentially desorbed with increasing pH, from values above 8 (termed alkaline desorption), independent of dissolution processes (Pfeifer et al., 2007). The pH of most groundwaters in the ECM tend towards values that are between circumneutral and basic, with an upper limit of approximately pH 9 (ARS database), or up to 10.4 for the specific case of the Gotthard rail tunnel. These conditions are favorable for As mobility. Other processes can also lead to As remobilization. For example, high concentrations of phosphate, silicate, carbonates, and organic matter can also enhance As desorption from iron or manganese oxides due to competitive adsorption effects (Voegelin and Hug, 2003; Stollenwerk et al., 2007; Pili et al., 2013). Based on the processes described above, As can be considered as an ubiquitous element in groundwaters, irrespective of the redox conditions (Casiot et al., 2003; Zheng et al., 2004; Chauhan et al., 2012; Paikaray, 2012).

With respect to the parameters discussed above, it is difficult to ascertain which processes are responsible for As-rich ECM groundwaters. The fact that the ECM are almost entirely composed of crystalline rock is nonetheless important, because the total amount of iron sulfide accessory minerals contained therein is very substantial. The measureable presence of trace elements such as Sb in waters within the ECM (ARS database), an element frequently present in As-bearing sulfides (Smedley and Kinniburgh, 2002), may in fact be evidence that crystalline ECM rocks are the primary source of As leaching. Thus, even though sulfide phases are the most likely candidates as the primary source of As, we cannot rule out the role of organic carbon, whose presence has been shown to be of high importance in the microbiologically-mediated reductive dissolution of HFO that contain sorbed As (McArthur et al., 2001, 2004; Akai et al., 2004). Indeed, a known process for mobilizing As is the oxidation of organic matter via the reduction of HFO (Bhattacharya et al., 2002a,b; Zheng et al., 2004). Thus, As and Fe concentrations are not correlated due to redox processes of iron after As mobilization (Dhar et al., 2008). Even though organic matter is generally not present in fractured crystalline rock (Peters, 2008), the presence of carbon-rich marls and shales, found very often in sedimentary units bordering the ECM, may play a role in As mobilization. In addition, estimating the competitive effect of anions present in ECM groundwaters, e.g., anion leaching from evaporites, also cannot be quantified at present.

The question that arises concerns understanding the geographic and temporal heterogeneity of As concentrations in the ECM. The two thermal water sources in the French ECM described by Courtois and Vigouroux (2005a, b) are a case in point. One of them is arsenic poor, while the other has elevated arsenic levels, and yet both are located in geological environments that are very similar. This possibly points to differences in hydrogeochemical transport conditions, local source geology, water circulation depth (i.e., T), or perhaps the presence of rock lithologies containing HFO that

sequester As. Thus, the hetereogeneity of As occurrences is a very complex question that cannot be answered in a simple manner, mainly because so much more research needs to be done.

4.4. $^{34}S_{SO4}$ and As in groundwaters

Sulfide mineral oxidation, as well as gypsum and anhydrite dissolution, do not involve significant S isotope fractionation (Szynkiewicz et al., 2012). For this reason, the use of S isotopes can be useful for distinguishing the mineralogical provenance of groundwaters. In particular, the sulfur isotope signature of dissolved sulfates ($\delta^{34}S_{SO4}$) allows a better understanding of As mobilization (Xie et al., 2009). Pili and colleagues (2013) report $\delta^{34}S_{SO4}$ in As-containing groundwaters percolating through crystalline rocks in the Beaufortain (Savoie ECM, France), with values ranging from −0.1‰ to +11.0‰. Moreover, this same study also measured $\delta^{34}S$ for three sulfide minerals: arsenopyrite, +8.25‰; chalcopyrite, +7.80‰; and pyrite, +15.00‰. The French ECM site studied by Courtois and Vigouroux (2005a) reports two sulfur isotope values based on analyses by Dazy and Razack, 1989: $\delta^{34}S_{SO4}$ = +14.7‰ and $\delta^{34}S_{H2S}$ = −5.3‰. According to Bosch et al., 1976, the measured value of $\delta^{34}S_{SO4}$ = +14.7‰ points to a sulfate source in the Triassic gypsum and anhydrite units that are leached by circulating groundwaters. The other French ECM thermal spring studied by Courtois and Vigouroux (2005b) reports $\delta^{34}S_{SO4}$ = +20.2‰ (avg. of two values), this value also having been measured by Dazy and Razack (1989).

Even though $\delta^{34}S_{SO4}$ can potentially serve as an indicator for the source of sulfate, the use of isotopic signatures must be interpreted with caution. In particular with respect to the French ECM sites discussed immediately above, the measured values may reflect a combination of two signals, one from oxidation of pyrite and other Fe-bearing sulfides, and the second from dissolution of gypsum present in the Triassic evaporite sequence. Because the mixing proportions of the two sources, the fractionation factors, and the temperature of isotope exchange are not known, it is probably not possible to unequivocally determine the source of the sulfate based only on the isotopic sulfate signature of groundwaters. On the other hand, in aquifers where the lithology is simple, the sulfate isotope signature may be used to determine provenance. As an example Sidle et al. (2001) determined $\delta^{34}S_{SO4}$ to range from +4.05 to +4.61‰, with a mean of approximately +4.2 ‰. These authors attribute this to local oxidation of arsenian pyrite associated with groundwater that only circulates in igneous and metamorphic rocks.

One major question is to what degree does $\delta^{34}S$ fractionate during oxidation of S to sulfate. According to Shelton and Rye (1982) and Robertson and Schiff (1994), low degrees of fractionation of metal sulfides are commonplace. Insignificant fractionation of $\delta^{34}S$ was determined in the study by Sidle et al. (2001). These authors show that $\delta^{34}S_{SO4\text{-sulfide}}$ fractionation is minor, averaging about 0.42‰. Other workers have found $\delta^{34}S$ fractionation to lie in the range −1.8‰ to + 0.8‰ (Balci et al., 2007; Heidel and Tichomirowa, 2011).

In a recent study, Pili et al. (2013) make a case for Rayleigh-type sulfur isotope fractionation and find a negative correlation between $\delta^{34}S_{SO4}$ and total As in solution (see Fig. 4). They postulate that this mechanism can result in a large overall fractionation, based on a series of small fractionation factors during each oxidation step of sulfide minerals. On the other hand, other data sets do not show this negative correlation. For example, the two French ECM sites studied by Courtois and Vigouroux (2005a,b) do not show any correlation between $\delta^{34}S_{SO4}$ and total As (Fig. 4) even if only 3 data are available. Moreover, when the data from Sidle et al. (2001) are plotted (Fig. 4), there is also no correlation between $\delta^{34}S_{SO4}$ and total As in solution. These contradictory results

point out the need for more laboratory and field research on $\delta^{34}S$ fractionation.

4.5. Possible impact of redox, climatic, and anthropic oscillations

Intrusion of oxygen in fractured rocks leads to increased pyrite oxidation, in particular associated with dry summer conditions. Following the first rain events in early fall, fracture systems are re-filled with water, leading to a rapid discharge (i.e., pulse) with elevated sulfate concentrations in groundwater sources (Pili et al., 2013). This can potentially lead to a concomitant increase in geogenic As in groundwaters. Classical mechanisms for mobilization and increased groundwater concentrations of As include : (i) oxidation of sulfide minerals, (ii) reductive dissolution of iron and manganese hydroxides, which are a common sink of As associated with coatings, (iii) oxidation of organic material linked to the previous two processes, (iv) biological transformations (bacteria can increase oxidation rates) (Charlet and Polya, 2006), (v) alkaline desorption (Bundschuh et al., 2004; Bhattacharya et al., 2006; Niccoli et al., 2010).

Climate change is expected to drastically affect hydrological systems and water quality. As an example, in the Beaufortain Massif in France, the droughts in the summer of 2003 and in the winter of 2004–2005 are thought to be responsible for increased concentrations of As in groundwaters (Pili et al., 2013). Temperatures have risen by up to 2 °C since 1900, particularly at higher elevations. Morevoer, precipitation is projected to increase in winter and sharply decrease in summer (Beniston, 2010). Hydrological systems will respond to changing precipitation patterns and to the timing of snow-melt in the Alps, with an earlier peak in runoff occurring at the end of the winter (Beniston, 2010), and a decrease in water availability for agriculture in the spring, when agricultural needs are at a maximum. Most significant will be the decline in the hydraulic head associated with fractured rock systems as well as valley aquifer groundwaters during severe droughts. The impacts of these climatic changes will affect both the natural environment and a number of economic activities such as tourism. As a result,
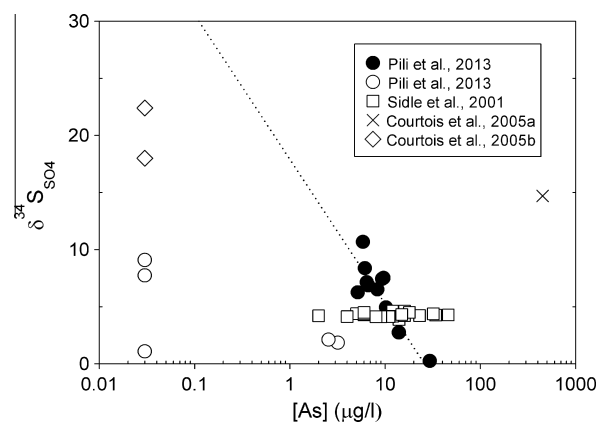

Fig. 4. Sulfur isotope signatures, expressed in terms of $\delta^{34}S_{SO4}$ (‰/CDT), as a function of total dissolved As concentration (μg/l), measured at various sites (ECM, France and Maine, USA). The X and diamond symbols refer to measurements from thermal springs in the French ECM, and the squares represent data from crystalline rocks in Maine (USA). The shaded and non-shaded circles refer to data from the Beaufortain (French ECM). The Beaufortain data show a negative correlation between $\delta^{34}S_{SO4}$ and total As (the non-shaded circles are not included in the correlation since they are associated with iron oxide precipitation). The negative correlation is interpreted by Pili et al. (2013) as evidence for Rayleigh-type sulfur isotope fractionation. On the other hand, the data from Maine, USA (Sidle et al., 2001) and the French ECM show no correlation, corresponding to a lack of fractionation.

more water is being pumped out of aquifers to make artificial snow in many ski resorts throughout the ECM.

As a response to these climate change impacts on water resources, ASR (aquifer storage and recovery) geo-engineering technology is currently being developed. The focus of this technology is to temporarily store surface water in porous geological reservoirs, in order to adjust to the availability of surface water resources at the end of winter, rather than in the spring. In the European Alps, all possible river dams have already been built. In the USA, about 330 ASR wells have been set up, and 6 billion liters per day are stored in such a manner (Maliva et al., 2006). This technology is just now being introduced to Europe. However, a combination of both drought conditions induced by climate change (see, e.g., Pili et al. (2013)), excessive depletion of aquifers to produce artificial snow, and ASR technology will have important impacts on water quality. One reason for this will be a potentially greater intrusion of oxygen into aquifers during summer droughts, or into geological reservoirs during their ASR-refill at the end of winter. As a consequence of oxygen intrusion, water–rock interactions will be directly affected, which in turn has implications for water quality, and in particular with respect to increasing concentrations of As, Fe, Mn, U, and even Ni, V, and Mo (NRC, 2008) in groundwaters. Thus, the effects of repeated climate-induced droughts and ASR cycles on the quality of aquifer waters, as well as the relationship among ASR storage interval properties in lower valleys, recovery rates, and recharge volumes, must be evaluated.

Excess input of organic matter will further affect water quality. Most importantly, dissolved organic matter is known to mobilize As by way of biogeochemical reactions. Organic matter sources include agricultural practices in mountainous regions that include the ECM. This could potentially enhance the mobility and concentration of As in groundwaters. Moreover, in mountain valleys, increased amounts of landfill material also can lead to an increase in the release organic matter (Peters, 2008). In addition, Pili et al. (2013) showed that biomass degradation in groundwater results in a significant mobilization of manganese oxides (possibly along with As), illustrating redox changes.

All the above-described situations may have potentially dramatic effects on the concentrations of As observed in groundwaters, in particular because the volume of crystalline rock that serves as a possible As-source in the ECM is extremely important. In the western Alps, As in crystalline rocks has been measured at concentrations in the range 1–30 mg/kg (Pfeifer and Zobrist, 2002; Pili et al., 2013). This large As reservoir can lead to As concentrations in groundwaters up to 400 µg/l (Table 1) in the ECM. Slight perturbations of an entire aquifer system can suffice to dramatically change and increase As mobility. Aside from the saturated zone, it is possible that the vadose zone may be even more sensitive to these perturbations, given that is located in the critical zone between the surface and the saturated zone. It is the first zone to be subject to increased O_2 penetration during droughts. In general, natural and anthropogenic perturbations will first affect the vadose zone, before affecting groundwaters located at deeper depths. Moreover, groundwaters that circulate to great depths, such as thermal waters, may in fact behave in a more stable manner compared with shallower systems. This may be due in part to water–rock interactions, in particular partial pyrite oxidation and As release, occurring at elevated temperatures and in a poral network that is characterized by long residence times.

5. Conclusions

Arsenic concentrations that have been measured in groundwaters within the ECM over a period of several years in five French départements and in western Switzerland show a high variability of As concentrations, ranging from values lower than the critical 10 µg/l value fixed by WHO, to values of several hundred µg/l. Sulfide minerals, such as pyrite and arsenopyrite that are present in crystalline rocks, are most probably the major source of As in ECM groundwaters. Nonetheless, the role played by organic rich marls and other sedimentary units that are in direct contact with the crystalline ECM rocks needs to be elucidated. The high variability in As groundwater concentrations within the ECM is quite surprising, and may be due to differences in local source geology, hydrogeochemical transport conditions, and depth (T) of groundwater circulation. In addition to this, the presence or absence of rock units containing iron and manganese oxyhydroxides may play an important role in sequestering and removing As from groundwaters. Based on important differences in published isotope data, the use of $\delta^{34}S$ for determining the source(s) of As is not always straightforward. Arsenic groundwater levels in the ECM are also potentially sensitive to climate changes and anthropogenic activities. The increased frequency of droughts may be responsible for higher As concentrations that have been recorded in the ECM (e.g. Beaufortain). Increased oxygen intrusion leading to higher rates of metal sulfide oxidation and As release may be the direct result of such drought conditions.

Acknowledgments

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhydrol.2013.06.023.

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