# Geological Sources of As in the Environment of Greece: A Review

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**Abstract** This review summarizes the existing data about the geological sources of As in Greece; their variety and the relevant concentrations make Greece a peculiar territory to generalize and better understand the methodology for their assessment. These sources concern As-containing ores in active and abandoned mining areas, geothermal/hydrothermal waters, lignites in exploited and unexploited deposits, As-minerals in various rock types such as metamorphic rocks, and mineral dust originating in Sahara desert. It is considered that As release from the above sources, in conjunction with various anthropogenic As fluxes, occasionally creates distinct areas with contaminated groundwater, soils, marine and atmospheric environment.

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To the memory of Constantine Zenghelis (1870–1957, Professor of Chemistry and Metallurgy in Technical University of Athens, Professor of Chemistry and Rector in University of Athens) and Constantine Ktenas (1884–1935, Professor of Mineralogy in University of Athens) who first studied As minerals in Greece at the beginning of the twentieth century.

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A. Scozzari and E. Dotsika (eds.), *Threats to the Quality of Groundwater Resources: Prevention and Control*, Hdb Env Chem, DOI 10.1007/698_2013_230,
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In general, Greece has been reported as a global As “hot spot” and it is argued that a significant amount of the Hellenic population might be affected by As pollution. The most important and permanent As source seems to be geothermal/hydrothermal fluids, due to faults and volcanic activity, affecting the underground, surface, and marine aquatic environment.

**Keywords** Arsenic, Geothermal, Greece, Minerals, Ores, Volcanoes

**Contents**

## Abbreviations

| | |
|---|---|
| BAB | Back-arc basin |
| MLC | Megalopolis lignite center |
| MOR | Mid-ocean ridge |
| P-ALC | Ptolemais-amynteon lignite center |
| SAAVA | South aegean active volcanic arc |
| SWAT | Soil and water assessment tool |
| UCC | Upper continental crust |

## 1 Introduction

Greece is considered to face significant environmental problems related to elevated As concentrations in groundwater, soils, and the marine environment [1, 2]. In fact, Greece is included among the As-polluted “hot spots” of the entire world [3]. According to the Geochemical Atlas of Europe [4], the As-polluted soils are mainly located in northern Greece (Macedonia), as well as in Attica including the Cycladic Islands. On the other

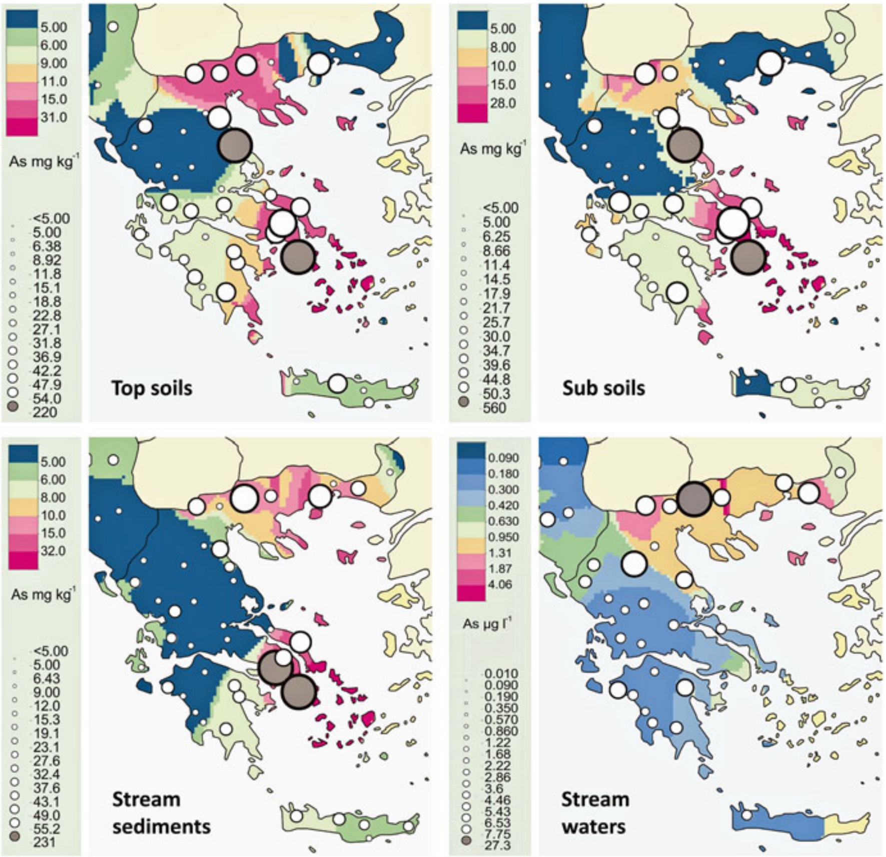

**Fig. 1** Part of the Geochemical Map of Europe (modified after the EuroGeoSurveys – FOREGS Geochemical Baseline Database [4]) showing the distribution of As in top and sub-soils (*upper left map*: top layer soils; *upper right map*: sub layer soils) as well as in stream sediments (*lower left map*) and in stream waters (*lower right map*) in Greece. The lowest As concentrations are represented by the *smallest-open-circle* symbol, contracting to the highest As concentrations that are shown by the *biggest-gray-circle* symbol (dot size scale size). The multiple-grade color scale is based on the measured As concentration levels. All the values of As concentrations, in soils and sediments, below 9.60 ppm are called "background" [137]

hand, the highest concentrations of As in stream waters are observed in northern Greece (Fig. 1). The population in Greece exposed to As pollution is estimated to be 150,000 people [5]. The sources of As are both anthropogenic and natural. Of note, thermal springs (geothermal waters) and mining areas are of great significance [5]. The data, in the literature, about anthropogenic sources of As in Greece are still not extended. These sources are presumably related to fertilizers, pesticides, municipal wastes, and coal combustion in thermal power plants. Also, there are facts indicating that serious contamination of the environment in Greece, with regard to As, is attributed to combustion of fossil fuels [e.g., 6]. However, it is believed that the natural (geological) sources of As are equally significant and mainly concern As-containing ores in active and abandoned mining areas, geothermal/hydrothermal waters due to faults (northern Greece) and volcanic activity (southern Greece), coals (mainly lignites in exploited and unexploited deposits), As-minerals in various rock types such as metamorphic rocks, and, certainly, the mineral dust flux derived from Sahara desert (Fig. 3). Consequently, the scope of this review is to summarize all of the existing data about geological sources of As in Greece and to serve as the basis of future scientific research on this issue.

Arsenic, as a chemical element, has been known in Greece since Prehistoric times. In particular, most of the Early Bronze Age in Greece (4000–2500 BC) was actually an age of arsenical copper. Arsenical copper was an advantageous Cu–As alloy, with nominally 1–6 wt% As, which allowed the manufacturing of harder tools in the prehistoric world. Relevant artifacts have been found all over the Aegean, and particularly in Crete, as well as in Evia (3.12 wt% As) dated 4000 BC and Thessaly (average 2.9 wt% As) dated 3700–3300 BC. The geological source of As in Prehistoric Greece might be in Cyclades, perhaps in Kythnos island, but this hypothesis is still questionable [7–9]. Another hypothesis is that the prehistoric sources of As could be related to primitive mining in Anatolia (Asia Minor). Later, the historical Lavrion (or Laurium) mines, located at Attica peninsula, were used in Classical Greece as the principal source of Ag and wealth for the Athenian State. In Lavrion mines there are many As minerals but perhaps they were not given appropriate attention by the ancient Greek philosophers and scientists inasmuch Theophrastus (known as the Father of Mineralogy, 371–287 BC) mentioned only native As and realgar ($As_2S_3$), of unknown origin, in his treatise "*On Stones*" (*Περί Λίϑων*) (Caley and Richards [10] and Eichholz [11] referring to Latin translation – 1495–1498 AC in Venice and 1578 AC in Paris – and first English translation – 1746 in London – of Vaticanus 1302 and 1305 Codices). The Lavrion mines were also operated during the nineteenth century and Zenghelis [12] reported analyses for As in minerals from this area, as well as from Greek islands. In the same report [12] there is also a map indicating As in eastern Thessaly. Moreover, Ktenas [13] approved the occurrence of realgar ($As_2S_3$) in the same area (see Fig. 2). On the basis of the data of the Ministry of Economy of Greece, 659 and 14 t of As-oxide ($As_2O_3$: 99.40 wt %) were produced on 1931 and 1947, respectively, in Lavrion mines [14, 15]. It seems that after the 1950s there was no further production of As from Greek mines. Nowadays, the Lavrion mines are abandoned and mainly secondary As minerals can be found (e.g., annabergite, adamite, see Fig. 2 and Table 1), but important As ores (Au-containing arsenopyrite/As-pyrite, see Fig. 2 and Table 1) are exploited in Kassandra Pb–Zn–Ag–Au active mines in eastern Chalkidiki (Macedonia, northern Greece). Finally, it should be emphasized that the magnitude of Greek geological sources of As is evident from a variety of As minerals discovered in the country for the first time in the world (Table 2). Very recently, peculiar As-sulfides of possible biogenic origin were also discovered in the floor of the submarine crater of Kolumbo volcano located north of Santorini at the Hellenic Volcanic Arc [16–18].

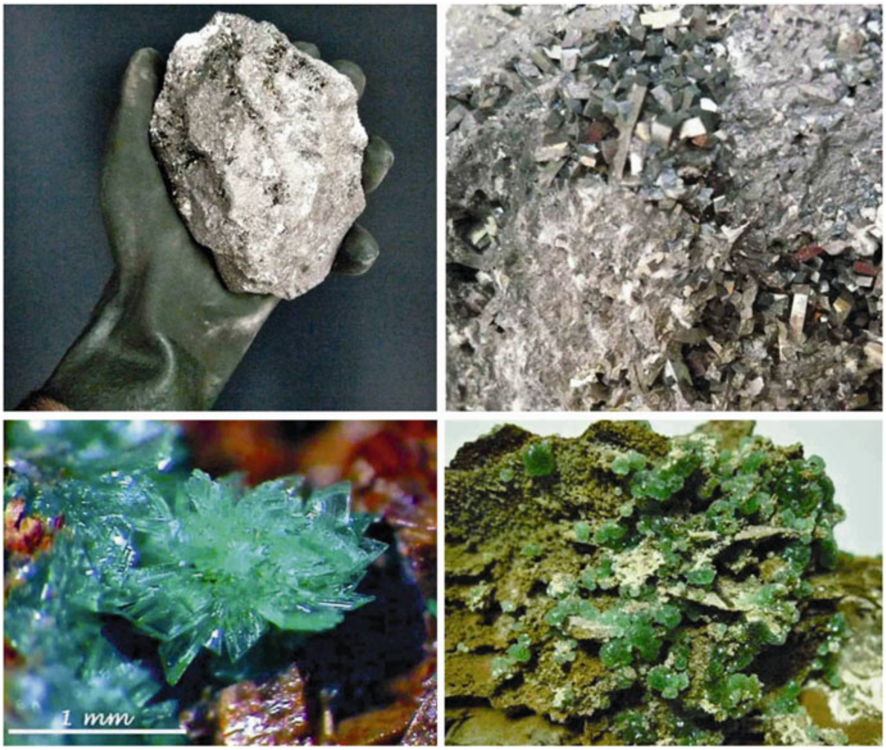

**Fig. 2** Representative As minerals from Greece. *Upper photos*: Typical mm-sized arsenopyrite ($FeAsS$) crystals in massive As-ore from Kassandra Mines (Olympias), eastern Chalkidiki; *lower left photo*: annabergite ($Ni_3(AsO_4)_2 \cdot 8H_2O$) from Lavrion mines, Attica [http://www.mindat.org/photo-15308.html]; *lower right photo*: adamite ($Zn_2(AsO_4)OH$) mm-sized crystal aggregates from Lavrion mines, Attica

# 2 Geological Sources of As in Mining Areas

## *2.1 Arsenic in Kassandra Active Mines (Chalkidiki)*

The Kassandra mines (Olympias, Madem Lakkos/Mavres Petres) massive sulfide –Pb–Zn–Ag–Au– ore deposits, in eastern Chalkidiki peninsula (Macedonia, Greece; see Fig. 3 and Table 1), are developed as strata bound and/or fracture controlled and in places stratiform within the calcitic-rhodochrositic marbles, biotite-hornblende gneisses, and amphibolites that have been regionally deformed and metamorphosed [19, 20]. The Madem Lakkos ores can be divided into three different types: a massive sulfide ore, a disseminated sulfide ore as well as a skarn ore, due to geochemical and mineralogical characteristics [20]. Massive sulfide ore deposits, exploited at Kassandra mines, accommodate arsenopyrite (As: 29–33 wt% [21]; see Fig. 2 and Table 3) together with pyrite (and/or As-pyrite), sphalerite,

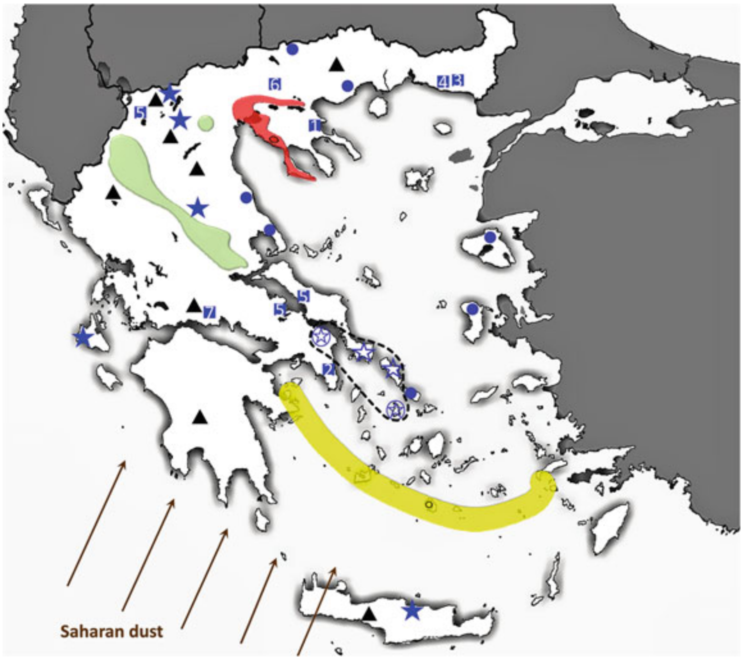

**Fig. 3** Geological sources of As in Greece (see also Tables 1, 2, and 4) concerning mining areas, ore occurrences (in non-Ophiolitic rocks), coals, As-containing rock-forming minerals in metamorphic rocks of the Attico-Cycladic Crystalline Complex (included into "*dashed-line*"), and Neogene phosphate deposits. Areas in northern Greece where sediments, soils, cave deposits, and underground waters contain As due to geothermal fluids circulating through deep faults, are marked with a "*red transparent curve*" (the spot of highest As release – western Chalkidiki – is also mentioned). The South Aegean Active Volcanic Arc (SAAVA), known also as Hellenic Volcanic Arc, where high amounts of As are released due to hydrothermal fluids originating in intense volcanic activity, is designated by a "*yellow transparent curve*" (the spot of highest As release – Santorini – is also mentioned). The Ophiolitic rocks of Greece, hosting occasionally As-bearing minerals associated with massive sulfide ores, are marked with "*transparent green curves*." The Saharan dust supply, mainly in southwestern and south Greece, is also indicated by *brown arrows*

chalcopyrite, galena, and various Sb-minerals (e.g., boulangerite) [19, 20]. Arsenopyrite and pyrite occur mainly as coarse, idiomorphic grains. As-pyrite grains were measured by Nebel et al. [20] to contain 2,600–4,900 ppm (massive sulfide ore samples), 1,400–5,000 ppm (disseminated sulfide ore samples) and 810 ppm (skarn ore samples) of As, respectively. Cabri and Chryssoulis [22] gave more details about Au in pyrite (As-poor pyrite), As-pyrite and arsenopyrite from Olympias mine [22]. Recently, Hahn et al. [23] performed geochronology in Olympias arsenopyrite and concluded an age of 26.1 ± 5.3 Ma related to metamorphic core complex exhumation [23]. Additionally, the trace elements analysis [20] revealed that also sphalerite derived from Madem Lakkos massive sulfide ore contains elevated As amount (55–1,700 ppm), while sphalerite from the disseminated sulfide

**Table 1** Location of geological sources of As in Greece and their relevant symbols shown in Fig. 3

| Symbols of geological sources | Location of geological sources |
|---|---|
| *Blue solid squares*: mining areas | (1) Kassandra Pb–Zn–Ag–Au active mines, at Olympias and Stratoni (eastern Chalkidiki, Macedonia, northern Greece); (2) Lavrion abandoned Pb–Zn–Ag mines, Lavrion (Attica, Greece); (3) Kirki Pb–Zn abandoned mines, including (a) the hydrothermal Pb–Zn Aghios Philippos deposit, north of Kirki flotation plant, and (b) the Pagoni Rachi polymetallic deposit, south of the Pb–Zn Aghios Philippos deposit, both hosted at the abandoned Kirki mining area, between Sappes and Esymi (Thrace, northeastern Greece); (4) Perama Ag–Au active mines, Perama Hill, northeastern of Petrota graben (Thrace, Greece); (5) Ni-laterite active mines that are mainly situated (a) at Agios Ioannis mines at Kokkino area, Larymna (Fthiotida, central Greece) (b) at Agios Ioannis area (central Evia) and (c) Kastoria (western Macedonia, Greece); (6) Lachanas Sb-W abandoned mine (NNE of Thessaloniki city, Macedonia, Greece); (7) Bauxite active mines at Parnassos-Ghiona Mts. (central Greece) |
| *Blue solid circles*: ore occurrences in non-Ophiolitic rocks | Asimotrypes area (Pangeon Mt. Serres-Kavala, Macedonia); Agistro area (Serres, Macedonia); Agria area (Volos/Pelion Mt, Thessaly); Agia area (Ossa/Kissavos Mt, Thessaly); Tinos Island at Panormos and Apigania Bay; Chios Island at Keramos area; Lesvos Island at Kalloni gulf |
| *Black solid triangles*: coals | Megalopolis lignite-bearing basin (Peloponnese), Florina-Ptolemais-Servia lignite-bearing basin (western Macedonia), Drama lignite-bearing basin (eastern Macedonia), Domeniko lignite deposit (Elassona, Thessaly), Ioannina lignite basin (Epirus), Plakia lignite deposit (Crete Island), and Pera-Lakkos mine at Parnassos-Ghiona bauxite mines (central Greece) |
| *Blue open* and *circled stars*: metamorphic rocks of Attico-Cycladic Crystalline complex | *Blue open stars* represent southern Evia and at Andros Island occurrences, while blue circled stars represent occurrences at Syros Island (Cyclades) and Varnavas area (Attica) |
| *Blue solid stars*: Neogene phosphate deposits | Palliki peninsula (Kefalonia Island), Heraklion area (Crete Island), Komnina area and Vegora lignite quarry (Florina-Ptolemais lignite basin, western Macedonia), Drymos area (Sarantaporo-Elassona basin, Thessaly) |

**Table 2** As-minerals that have been found in Greece for the first time in the literature; source: Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA) (International Mineralogical Association (IMA), personal communication)

| As-mineral[a] | CNMNC approved formula | Year/IMA No. | Locality |
|---|---|---|---|
| Agardite-(Nd) | $Nd(Cu^{2+})_6(AsO_4)_3(OH)_6 \cdot 3H_2O$ | 2010-056 | Lavrion |
| Attikaite | $Ca_3Cu_2Al_2(AsO_4)_4(OH)_4 \cdot 2H_2O$ | 2006-017 | Lavrion |
| Georgiadesite | $Pb_4(As^{3+}O_3)Cl_4(OH)$ | 1907 | Lavrion |
| Hilarionite | $Fe_3^{+2}(SO_4)(AsO_4)(OH) \cdot 6H_2O$ | 2011-089 | Lavrion |
| Kamarizaite | $Fe_3^{+3}(AsO_4)_2(OH)_3 \cdot 3H_2O$ | 2008-017 | Lavrion |
| Kirkiite | $Pb_{10}Bi_3As_3S_{19}$ | 1984-030 | Kirki |
| Nealite | $Pb_4Fe(AsO_3)_2Cl_4 \cdot 2H_2O$ | 1979-050 | Lavrion |
| Zincolivenite | $CuZn(AsO_4)(OH)$ | 2006-047 | Lavrion |

[a] According to Dunn and Rouse [134] thorikosite from Lavrion mines has chemical formula of $(Pb_3Sb_{0.6}As_{0.4})(O_3OH)Cl_3$ and seems to accommodate low As amount. On the other hand, IMA/CNMNC (International Mineralogical Association (IMA), personal communication) does not accept the argument that thorikosite is an As-containing mineral. Thus, IMA has decided to include thorikosite, with the given chemical formula of $Pb_3O_3Sb^{3+}(OH)Cl_2$, in the official IMA/CNMNC list of minerals as a non-As-containing mineral

ore accommodates As content between 76 and 400 ppm as well. Moreover, high concentrations of As also were measured [20] in galena either from the massive or from the disseminated Madem Lakkos sulfide ore (3.6–510 ppm), respectively. Furthermore, As-sulfominerals (Table 3) are represented by tennantite [19, 20] and colusite (in selected disseminated sulfide ore samples from Madem Lakkos; [20]). It is noteworthy that for the first time in Greek territory seligmannite was reported to be hosted in these sulfide ores and especially to coexist with enargite in Madem Lakkos orebody by Nicolaou [24]. The presence of seligmannite was also reported by Nebel et al. [20].

Except Olympias and Madem Lakkos/Mavres Petres Pb–Zn–Ag–Au mines, Skouries Cu–Au porphyry [25, 26] is also located in Kassandra mining area, containing very low As amounts (1–6 ppm). However, a similar porphyry-Cu system exists in Fissoka area [26] possessing high As concentration (up to 21,000 ppm) in contrast to other sampling sites of the porphyry-Cu systems.

Due to mining activity in Kassandra mines region, As can be detected in surface waters of three local separated sub-basins (i.e., Kokkinolakkas, Kerasia, and Piavitsa sub-basins) [27]. The results showed that the enriched As concentration in stream waters is mainly influenced by the sulfide mineralization on the hydrogeochemistry of the corresponding streams (As content in Kerasia stream waters: 7–42 ppb and in Piavitsa stream waters: 4–141 ppb) and secondarily is affected by the mining activity (As content in Kokkinolakkas stream waters: 8–45 ppb). On the other hand, As in soils of Stratoni village [28] seems to be immobilized in insoluble secondary phases probably preventing its migration to underground waters. Up to now, there are no references in the literature about elevated As concentrations in potable water of the area. Nevertheless, the As distribution in waters and soils of Kassandra mines region is not extended, despite the huge As

**Table 3** As-minerals involved in ores from Greek mining areas [with ideal chemical formulas based on: IMA Database of Mineral Properties, created and maintained by the RRUFF Project [135] in partnership with the IMA/CNMNC List of Mineral Names [136] compiled by Ernest H. Nickel and Monte C. Nichols, March 2007, supplied through the courtesy of Material Data, Inc. and based on the database MINERAL, which MDI makes available as a free download to the mineralogical community (http://rruff.info/about/about_IMA_list.php)]

| Mine/ore | As-bearing minerals (in alphabetical order) |
|---|---|
| Kassandra Mines (Olympias and Stratoni), eastern Chalkidiki, Macedonia, northern Greece (active)/Pb–Zn–Ag–Au sulfides | Arsenopyrite; As-pyrite; Colusite; Enargite; Tennantite; Seligmannite |
| Lavrion, Attica, central Greece (abandoned)/Pb–Zn–Ag sulfides | Adamite; Agardite-(Nd); Annabergite; Arsenic (native arsenic); Arseniosiderite; Arsenocrandallite; Arsenogoyazite; Arsenopyrite; Arsenpolybasite; Attikaite; Austinite; Beudantite; Conichalcite; Duftite; Enargite; Georgiadesite; Gersdorffite; Hilarionite; Löllingite; Luzonite; Nealite; Pearceite; Proustite; Rammelsbergite; Realgar; Scorodite; Tennantite; Zincolivenite |
| Kirki mining area, Thrace, northeastern Greece (abandoned)/Pb–Zn-sulfides | Arsenopyrite; Beudantite; Bukovskyite; Enargite; Jordanite; Kirkiite; Luzonite; Pearceite; Selligmanite; Scorodite; Tennantite; As-bearing Tetrahedrite[a]; Zincian tennantite/tetrahedrite |
| Perama Hill, Thrace, northeastern Greece (active)/Au–Ag | Enargite; Luzonite; Tennantite |
| Aghios Ioannis, Larymna and Aghios Ioannis, Evia, central Greece; Kastoria, western Macedonia, Greece (active)/Ni-laterite | As in goethite[b] |

(continued)

**Table 3** (continued)

| Mine/ore | As-bearing minerals (in alphabetical order) |
|---|---|
| Lachanas area, Thessaloniki, Macedonia, northern Greece (abandoned)/Sb-W | Arsenopyrite |
| Parnassos-Ghiona Mts., Central Greece (active)/bauxite | As in Al-oxyhydroxides[c]; As in Fe–Cr–Ti-bearing phases[d] |

Ideal chemical formulas of As-bearing ore minerals: Adamite: $Zn_2(AsO_4)OH$; Agardite-(Nd): $Cu^{2+}{}_6Nd(AsO_4)_3(OH)_6{\bullet}3H_2O$; Annabergite: $Ni_3(AsO_4)_2{\bullet}8H_2O$; Arsenic (native arsenic): As; Arseniosiderite: $Ca_2Fe^{3+}{}_3O_2(AsO_4)_3{\bullet}3H_2O$; Arsenocrandallite: $CaAl_3(AsO_4)(AsO_3OH)(OH)_6$; Arsenogoyazite: $SrAl_3(AsO_4)(AsO_3OH)(OH)_6$; Arsenopyrite: FeAsS; Arsenpolybasite: $[Ag_9CuS_4][(Ag,Cu)_6(As,Sb)_2S_7]$; Attikaite: $Ca_3Cu_2Al_2(AsO_4)_4(OH)_4{\bullet}2H_2O$; Austinite: $CaZnAsO_4(OH)$; Beudantite: $PbFe^{3+}{}_3(AsO_4)(SO_4)(OH)_6$; Bukovskyite: $Fe^{3+}{}_2(AsO_4)(SO_4)(OH){\bullet}7H_2O$; Colusite: $Cu_{13}VAs_3S_{16}$; Conichalcite: $CaCuAsO_4(OH)$; duftite $PbCuAsO_4(OH)$; Enargite: $Cu_3AsS_4$; Georgiadesite: $Pb_4(As^{3+}O_3)Cl_4(OH)$; Gersdorffite: NiAsS; Hilarionite: $Fe^{3+}{}_2(SO_4)(AsO_4)(OH){\bullet}6H_2O$; Jordanite: $CuPbAsS_3$; Kirkiite: $Pb_{10}Bi_3As_3S_{19}$; Löllingite: $FeAs_2$; Luzonite: $Cu_3AsS_4$; Nealite: $Pb_4Fe(AsO_3)2Cl_4{\bullet}2H_2O$; Pearceite: $Cu(Ag,Cu)_6Ag_9As_2S_{11}$; Proustite: $Ag_3AsS_3$; Rammelsbergite: $NiAs_2$; Realgar: $As_4S_4$; Scorodite: $Fe^{3+}AsO_4{\bullet}2H_2O$; Selligmanite: $CuPbAsS_3$; Tennantite: $Cu_{12}As_4S_{13}$; Zincian tennantite/tetrahedrite: $(Cu_{9.80}Ag_{0.05}Au_{0.03})(Zn_{1.88}Fe_{0.14})(As_{2.78}Sb_{1.29})S_{13.01}$; Zincolivenite: $CuZn(AsO_4)(OH)$

Empirical formula of specific As-bearing ore minerals: Agardite-(Nd) [48]: $[(Nd_{0.19}La_{0.14}Y_{0.12}Pr_{0.05}Gd_{0.02}Ce_{0.02}Sm_{0.02}Dy_{0.02})_{\Sigma REE0.58}Ca_{0.39}]_{\Sigma 0.97}(Cu_{5.49}Zn_{0.44})_{\Sigma 5.93}(AsO_4)_3(OH)_{5.38}{\bullet}2.64H_2O$; Atticaite [43, 44]: $Ca_{2.94}Cu^{2+}{}_{1.93}Al_{1.97}\ Mg_{0.04}Fe^{2+}{}_{0.02}[(As_{3.74}S_{0.16}P_{0.12})_{\Sigma 4.02}O_{16.08}](OH)_{3.87}{\bullet}2.05H_2O$; Kamarizaite [45, 46]: $Ca_{0.03}Fe^{3+}{}_{2.86}(AsO_4)_{1.90}(SO_4)_{0.10}(OH)_{2.74}{\bullet}3.27H_2O$; Tennantite [58]: $(Cu_{9.91}Ag_{0.01})(Zn_{1.75}Fe_{0.18})(As_{3.97}Sb_{0.06}Te_{0.03})S_{13.}09$; Zincolivenite [42]: $Cu_{0.94}Zn_{1.03}Fe_{0.02}[(AsO_4)_{0.98}(PO_4)_{0.02}](OH)_{0.98}(H_2O)_{0.10}$

[a] According to the literature [58] the empirical formula of As-bearing tetrahedrite (As: 3.06 wt%) has been calculated to be $(Cu_{9.64}Ag_{0.23})(Zn_{1.89}Fe_{0.08})(As_{0.68}Sb_{3.43})S_{13.04}$. This mineral obviously belongs to the tennantite-tetrahedrite series: $(Cu,Ag,Fe,Zn)_{12}As_4S_{13} – (Cu,Fe,Ag,Zn)_{12}Sb_4S_{13}$

[b] As hosted in rounded fragments of goethite [69]

[c] As associated with Al-oxyhydroxides [69]

[d] As associated with Fe–Cr–Ti-bearing phases [75, 76]

mineralization, in contrast to western Chalkidiki where there is no apparent As mineralization but severe contamination occurs due to the rise of geothermal fluids. As in the environment of Kassandra mines is probably not widely distributed in the environment due to natural immobilization mechanisms such as the formation of insoluble Fe-arsenate phases (scorodite). The natural scavenging of As into Fe(III)-oxy-hydroxy-sulfate phases, as happens in the case of mine water [29], can be another explanation of relatively low As pollution in Kassandra mines and eastern Chalkidiki.

## 2.2 *Arsenic in Lavrion Pb–Zn–Ag Abandoned Mine (Attica)*

The carbonate-hosted massive sulfide Pb–Zn–Ag ores of Lavrion abandonded mine (Fig. 3 and Table 1), which is mainly related to the detachment fault resulting from the separation and superposition of the Cycladic "Blueschist" and the "Basal" units, accommodates several As-bearing minerals [30, 31]. The first documented attendance reported the existence of bulk As elevated concentration in the ores of Lavrion, which was published in the beginning of twentieth century [12] referring to specific As value of 0.3 wt% in Sounion (Attica) ore and up to 1.71 wt% in neighboring Legraina (Sounion, Attica).

Mineralogical investigations thoroughly both determined the sulfide mineral assemblages (Table 3), generating and hosting in the entire massive sulfide Pb–Zn–Ag ores of Lavrion [30, 31] and focused on the polymetallic Plaka ore system, but especially on a late Pb–As–Sb–Cu–Ag-rich banded vein [31, 32]. In addition, relevant investigations focusing on an adjacent ore at Kamariza area [31, 33], and on other neighboring mines situated in the district of Lavrion [31] were also carried out. All of the above studies [31] confirmed the presence of arsenopyrite [30, 32, 33], occurring as euhedral rhomb-shaped to subhedral grains that usually interlock with euhedral to subhedral pyrite (hosting As with mean value of 0.64 wt%) and sphalerite [30], or as idiomorphic crystals up to 200 μm in length [32]. Microprobe analyses indicate that pyrite grains can host an average of 0.64 wt% As [30]. In addition, the existence of several primary sulfarsenides [31], such as gersdorffite (associated with sulfides and fluorite; [30]) hosting av. 49.82 wt% As [33] and realgar (mainly related to calcite and base metal sulfides; [30]), as well as arsenides, such as löllingite (As mean values: 70.55 wt% [30]; 69.46 wt% [32]) and rammelsbergite [34] were also reported. Moreover, the existence of proustite (As: 13.8–14.9 wt%) always together with pyrargyrite and usually associated with pearcite-arsenpolybasite (As: 5.3–7.5 wt%), enargite (As: 19.4 wt% [30]; 17.13 wt% [33]) was proved [30]. Especially native arsenic (As: 91.1–97.2 wt% [30]; 95.58 wt% [32]) was observed as dendritic inclusions in galena crystals forming botryoidal crusts up to 5 cm wide on open cracks of carbonate minerals and spatially associated with silver sulfosalts in the investigated ores [30, 32]. Finally, fahlore (tennantite-tetrahedrite series) with a relatively high As content (As in fahlore/freibergite: 3.5–8.9 wt% and in fahlore/tetrahedrite: 3.6–8.5 wt%, respectively) is an abundant sulfosalt in the mines

[30]. Ag-Bi-tetrahedrite/tennantite aggregates in the Plaka deposit were measured to contain between 8.76 and 17.56 wt% As amount [32], whereas tetrahedrite/tennantite group minerals, accommodated in Kamariza deposit, were probed to host significant (0.88–19.45 wt%) arsenic concentration [33]. According to electron microprobe analyses [32], other secondary non As-minerals were also found to accommodate, in their structure, remarkable As concentrations, such as bournonite (As: 0.76 wt%), Ag-tetrahedrite (As: 1.75 wt%), heteromorphite (As: 1.28 wt%), falkmanite (As: 0.57 wt%), veenite (As: 1.22 wt%), miargyrite (As: 1.12 wt%), and pyrargyrite (As: 0.64 wt%).

For the first time in the literature, extremely rare secondary As-mineral species (Table 2) named as agardite-(Nd), attikaite, georgiadesite, hilarionite, kamarizaite, nealite, and zincolivenite were discovered in the Lavrion mines (Greece). In particular, a Pb-arsenate chloride, named georgiadesite (Tables 2 and 3), was discovered by Lacroix and Schulten at the beginning of twentieth century, in the Lavrion mines formed by action of seawater on Pb-bearing phases at Vrissaki point slags [35, 36]. A later chemical and crystallographic study described the georgiadesite as monoclinic with no twinning relationship [37]. More recently, a structural study [38] of this As-bearing lead mineral from the type locality showed that arsenic occurs as $As^{3+}$ and not as $As^{5+}$, revealing its revised chemical formula as $Pb_4(As^{3+}O_3)Cl_4(OH)$, approved by IMA/CNMMN (Table 2). A similar worldwide discovery was the detection of another bright orange, transparent lead chloride arsenite ($As^{3+}$) mineral in the ancient slags of Lavrion mines, named as nealite (Tables 2 and 3) from Dunn and Rouse [39], with As content measured up to 17.30 wt% in the studied crystal (always twinned with the twofold twin axis in {001}) [39]. Furthermore, nealite crystal formula was determined as $Pb_4Fe(AsO_3)2Cl_4•2H_2O$, and also the As atoms were observed to form $AsO_3$ pyramids [40]. XRD studies on nealite crystal, from type locality, were additionally elaborated [41]. Nealite is the first mineral found to contain ferrous iron atom [39] coordinated with oxygen and chlorine atoms simultaneously [40]. Nevertheless, another totally new mineral analog of olivenite and of adamite, observed as green or greenish blue translucent crystals with vitreous luster, with streaks and conchoidal fracture, and finally named as zincolivenite (Tables 2 and 3) was found for the first time in Kamariza mining area, Lavrion [42]. Zincolivenite has been found in association with adamite (Voudouris P, personal communication) (see Table 3 and Fig. 2) and with arseniosiderite (Table 3), as well [42]. Besides, new As-minerals named attikaite and kamarizaite (see Tables 2 and 3) were discovered for the first time in Kamariza deposit (Lavrion) in 2007 [43, 44] and in 2009 the latter mineral [45, 46], respectively. Attikaite was observed as light blue to greenish blue color crystals, with a pale black streak, to form spheroidal segregations consisting of thin flexible orthorhombic crystals [43, 44], whereas kamarizaite yellow to beige crystals, with light yellow streak, occur as fine-grained monomineralic aggregates composed of platy crystals and submicron kidney-shaped segregations [45, 46] as well. Attikaite was measured to contain 45.45 wt% $As_2O_5$, and has been found together with other As-bearing minerals in Kamariza (i.e., arsenocrandalite and arsenogoyazite [44]; see Table 3). On the other hand, kamarizaite was also measured to contain 39.89 wt% $As_2O_5$ and has found in association with scorodite in the dump of the Kamariza mine ([45, 46]; see Table 3). Recently, at Hilarion mine (Kamariza deposit, Lavrion) were also found two more As-mineral named hilarionite [47] and agardite-(Nd) [48, 49] (see Tables 2 and 3), respectively. In particular, agardite-(Nd) was observed as transparent, light bluish green, with white streak, and luster vitreous in crystals and silky in aggregates [48]. Hexagonal crystals of agardite-(Nd) have been found associated with zincolivenite in the locality [48] and were measured to contain 33.65 wt% $As_2O_5$. Additionally, in Kamariza and/or Hilarion mines (Lavrion) annabergite, austinite, duftite, beudantite, and conichalcite were also found (Voudouris P, personal communication).

Herein, it is constructive to note that other As-bearing phases are also formed in the Lavrion coastal area, due to seawater reaction with metals remaining in cavities of the dumped old metallurgical slags. According to IMA/CNMNC these new phases cannot be referred to as new minerals due to anthropogenic impact that possibly affects the mineralization. Such materials are also new Pb–chlorite–arsenite phases ($Pb_5(As^{3+}O_3)Cl_7$ and $Pb_2(As^{3+}O_2OH)Cl_2$) that were collected from historic black metallurgical slags of Punta Zeza area south of Lavrion [50, 51].

## 2.3 *Arsenic in Kirki Pb–Zn Abandoned Mines (Thrace)*

The environmental impact of the past mining activities neighboring with the Eirini local river (e.g., at the abandoned Kirki mining area including the hydrothermal Pb–Zn Aghios Philippos deposits at the northern part of Kirki) resulted in the exposure mainly to the rain and to the drainage water, of mining wastes together with the residues of the mining concentrates, due to their late disclosure, as they still remain displayed at plant's location (e.g., cracked tailing ponds, open pits). In the related Pagoni Rachi deposit located south of the Pb–Zn Aghios Philippos deposits, there was no mining activity in the past, and therefore no mining wastes. Thus, the existing mining wastes comprise a potential source of toxic and heavy metals (e.g., As), which through their transportation by rain, drainage waters, and also by Eirini local river (discharges into Aegean sea at a distance of 23 km, on the east coast of Alexandroupolis town) could be finally dispersed into the surrounding area [52] and subsequently could originate the hypothetical contamination of the hydrologic system of the entire investigated area. In the case of the potential As source in abandoned Kirki mines, several studies [52–56] were carried out. Results of these works reveal that the As concentration in the investigated remaining solid materials of the tailing ponds is extreme highly enriched (up to 944 ppm), whereas chemical analyses of the piles of concentrates as well as in the soil and the surface sediments around the flotation plant remarked that As enrichment is up to 5,243 and 1,732 ppm, respectively [52, 54]. Nevertheless, the chemical analyses of the detected As-bearing secondary minerals (beudantite, bukovskyite, scorodite; see Table 3) that form, together with other several secondary minerals, thin layers covering the floor of the highly acidic pit lake, confirmed the presence of highly As concentration (497–1,582 ppm) and the highly acidic and oxidative conditions [53, 55, 56], as well. Potential results of this highly acidic pit lake formation could be the forthcoming release and the subsequent load of high concentrations of As to the environment. A recent unpublished diploma thesis [57] applied the hydrological model SWAT (Soil and Water Assessment Tool) at the Eirini stream watershed, located nearby the Kirki abandoned mixed sulfide mine (Evros, Thrace, Greece) that situated upstream in the river basin, in order to monitor the flow-rate and the water quality.

Arsenic-bearing mineralization (Table 3) in hydrothermal Pb–Zn Aghios Philippos deposit (north of Kirki flotation plant), and in Pagoni Rachi polymetallic deposit (south of the Pb–Zn Aghios Philippos deposit), both hosted at the abandoned Kirki mining area (see Fig. 3 and Table 1), between Sapes and Esymi (Thrace, Greece), has been described be several authors [58–64], respectively. Aghios Philippos is developed in the periphery of the Pagoni Rachi prospect.

The mineral kirkiite (see Tables 2 and 3), worldwide, was firstly discovered in Kirki mining areas (Greece) by Moëlo et al. [59] to exist in the hydrothermal polymetallic Pb–Zn deposit of Aghios Philippos [59]. Recently, a published article [65] referring to the kirkiite from the type locality, describes in details a highly pseudosymmetric structure, overloaded with heavy atoms and prone to multiple twinning. This study also found that the structure contains split As position, and two additional sites that could accommodate both As and Bi atoms. Moreover, the kirkiite empirical formula was presented once again ($Pb_{10}Bi_{2.16}As_{3.84}S_{19}$) slightly different with that of $Pb_{10.08}Bi_{2.55}Sb_{0.13}As_{2.91}S_{19}$ [59]. Also, concerning the As-mineralization in Pb–Zn Aghios Philippos deposit, evidences about the presence of minor primary As-sulfide minerals such as arsenopyrite, together with the sulfosalt $Cu^{2+}$-bearing pearceite (As content: 6.91–7.50 wt%; [58]) rich in Cu (up to 16 wt%; [58]) associated with $Pb^{4+}$-bearing tennantite (As content: 21.88 wt%; [58]) rich in Pb (up to 2.3 wt%; [58]), and related to an unrecognized phase (As content: 21.09–22.95 wt%; [58]) with similarities to watanabeite, as well as to $Pb^{4+}$-bearing enargite (As content: 21.13 wt%; [58]). Besides jordanite (and/or Bi-jordanite; [60]), luzonite and selligmanite (see Table 3) were demonstrated in the past [58, 60–64]. On the other hand, the authors [58] using EPMA microprobe, alternatively, detected almost similar to the previous paragenesis the occurrence of As-minerals in the Pagoni Rachi deposit (Kirki mining area; see Table 3), such as As-bearing tetrahedrite with As content 3.06 wt%, tennantite with As content 20.16 wt% and a solid solution between tennantite-tetrahedrite classified as zincian tennantite/tetrahedrite due to its high Zn content up to 8.0 wt% (As: 13.51 wt%) respectively.

## *2.4 Arsenic in the Perama Hill Au–Ag Active Mine (Thrace)*

In the Perama Hill high-intermediate sulfidation epithermal Au–Ag deposit, located on the northeastern part of Petrota graben, nearby to the Kirki mining area (Thrace, Greece, see Fig. 3 and Table 1), arsenic-bearing mineralization [66–68] consists of enargite, luzonite, and tennantite (see Table 3). Tennantite is distinguished by means of microprobe investigation [67]. Thus, crystals of Bi,Zn-rich tennantite

(As: 18.08 wt%) have been found to intergrow with pyrite crystals, together with bismuthinite and lillianite homologues, whereas Fe-rich tennantite crystals seem to be associated with enargite crystals as well. Furthermore, Zn-rich tennantite crystals measured to contain up to 20.38 wt% As. Enargite (As: 18.15–21.88 wt %) seems to have a close association with tellurides whereas, together with its polymorph luzonite both coexist also with bismuthinite and Fe-rich tennantite. Nevertheless, the early-stage high sulfidation pyrite-enargite-bearing ores, proving by the coexistence of early pyrite together with and/or replaced by enargite surrounding by late tennantite, have been mentioned [68] to be crosscutting by the late-stage barite-tennantite-galena veins in the Perama Au–Ag deposit. The late-stage veins also include tellurides, and not only the earlier enargite ores. The potential effect of As-containing mineral phases in Perama Hill active mines on the groundwater has not been clarified yet and future research is needed. Actually concerning the local aquatic systems there are no previous papers focusing on As (and not only on minerals, ores, etc.).

## *2.5 Arsenic in Ni-Laterite Active Mines (Central and Northwestern Greece)*

Investigation of As distribution in Ni-laterite deposits in active mining areas from Greece (Aghios Ioannis mines at Kokkino area, Larymna, Fthiotida, Central Greece; Aghios Ioannis area, central Evia; Kastoria, western Macedonia) was recently performed [69, 70], (see Fig. 3 and Table 1). In particular, the study of As, existing in individual Greek Ni-laterite deposits, indicates the elevated high content of the element especially in laterite samples derived from the lowermost part of the Aghios Ioannis bauxitic laterite deposit, Larymna (up to 2,600 ppm with an average of 573.3 ppm, in bulk), whereas the amount either in laterites from Aghios Ioannis (central Evia) or in laterites from Kastoria region is quite low (As in laterites from Aghios Ioannis, Evia: 2–3 ppm and As in deposit from Kastoria: 3–14 ppm, both in bulk). This dissimilarity in As concentration revealed the wide variation of the element's content in the laterite deposits [69]. This could be probably due to the different sources of the Greek deposits and/or of different spots into the same deposit (i.e., parent ophiolite complexes, local conditions of re-deposition, and involvement of the organic matter [70]) that supply the Ni-laterite deposits with As. Besides, SEM-EDS analyses of the investigated samples revealed that As in the studied laterite deposits is mostly associated with goethite (Fe-oxyhydroxide with $As_2O_3$: 0.75–1.2 wt%, see Table 3) [69, 70]. Regardless of the high As concentration in samples from different laterite deposits and/or of different spots into the same deposit (e.g., Aghios Ioannis exploitable deposits, Larymna, central Greece), the mean average value of As in Greek laterites has been measured and it seems to be rather low ($<10$ ppm). Also the great variation in As hosted in Greek laterite deposits is in line with the measuring As existing in the metallurgical product (ferro-nickel alloy) of the smelting plant located in Larymna, central Greece [69]. Thus, and also taking into account the assumption of the As-adsorption by goethite [70], the possible impact of the As on the ferronickel smelting in the metallurgical industry, as well as in the environment and in the human health seems to be controlled [69, 70].

## 2.6 Arsenic in Lachanas Sb-W Abandonded Mine (Thessaloniki)

The Sb and Sb-W ore deposits, related to Ternary volcanic intrusions, situated in Lachanas area (Pilaf-Tepe and Tasch-Kapou location sites) at the NNE of Thessaloniki city, have been examined in the past [71, 72]. Studies of these ores detected the presence of arsenopyrite together with major Sb and W minerals (antimonite and wolframite) coexisting with other minerals (quartz, pyrite, sericite, chlorite calcite, dolomite), as well as with some other Sb-sulfides (bournonite, boulangerite, and jamesonite). It should be noted that As from Lachanas area was measured in bulk [72] and found to vary from 100 ppm up to 1,800 ppm, whereas chemical analyses of Sb and Sb-W ore deposits [71] recorded very high As contents (0.03 wt% in mixed Sb-W ore), and up to 0.18 wt% (in Sb ore).

## 2.7 Arsenic in Bauxite Active Mines (Central Greece)

Parnassos-Ghiona allochthonous karst-type bauxite deposits are hosted within carbonate formations and divided into three bauxite horizons (from bottom to top: B1, B2 and B3) separated by limestones. The B3 horizon, locally and occasionally, underlies from a thin layer of As-rich coal (mean value of 18 ppm approximately, please see the relevant paragraph; [73]). Measurements of the As concentration of selected nontypical and nonindustrial black-gray Fe-rich bauxite sample, deriving beneath the contact between the coal and the B3 horizon, and situating in the Peralakkos mine [73] which is located in the Parnassos-Ghiona active mining areas (central Greece; see Fig. 3 and Table 1), were recently reported [69, 74]. These studies demonstrate the enrichment of As content in the black-gray Fe-rich bauxite sample (up to 300 ppm, in bulk; [74]), whereas the extremely highly elevated As concentration in yellow-gray bauxite samples is also reported (up to 890 ppm, in bulk; [69]). Black–gray Fe-rich bauxite sample consists mainly of pyrite ($FeS_2$) and also Al-oxyhydroxide (diaspore: AlOOH). Minor hematite ($Fe_2O_3$) and/or goethite (FeOOH) are also observed. Additionally, SEM-EDS analyses provide the information that the As is hosted in areas dominated by Al-oxyhydroxides ($As_2O_3$: 1.39 wt%; [69]) of the bauxite samples (especially the "yellow-colored type") and thus, the authors conclude that As is mostly associated with Al-oxyhydroxides (diaspore and/or boehmite: AlOOH polymorphs) in bauxite (see Table 3; [69]). Moreover, they maintain that As enrichment of black–gray Fe-rich bauxite sample, from distinct sites beneath the As-rich thin coal layer in the B3 horizon, is probably related to the organic matter of the coal, assuming that the amount of the As accommodated in the bauxite can be influenced by the existence of this organic layer [69, 74]. However, according to very recent studies based on advanced analytical, microscopic and spectroscopic characterization techniques [75, 76], As in Greek bauxites, sampled from active mines of Parnassos-Ghiona area, may not be related to Al-oxyhydroxides (and also to S-phases) but to Fe–Cr–Ti-phases into relevant pisoliths.

## 3 Other Occurrences of As Ore Minerals in Greece

Ore occurrences in the Greek mainland, as well as in Greek islands, of remarkable concentrations of As, tightly associated with As-bearing ore minerals (e.g., arsenopyrite: FeAsS) and/or arsenic sulfides/sulfosalts (e.g., realgar: AsS in Agria, Volos, Pelion Mt.–unpublished data) have been thoroughly reported by several authors [12, 71, 72, 77–86] (see Fig. 3 as well as Tables 1 and 4).

A very recent study [77] on gold-bearing sulfide mineralization at Asimotrypes area, Pangeon Mt. (Serres-Kavala, Macedonia, Greece) revealed that Au-bearing sulfide precipitation (at $T \approx 270°\mathrm{C}$; $P = 1{,}800–2{,}000$ bars) formed an Au-bearing hypogene mineralization that consists of arsenopyrite (As: 41.7–43 wt%) together with traces of arsenian-pyrite (As: 0.01–3.8 wt%) and Cu,As-sulfosalt (tennantite: $Cu_{12}As_4S_{13}$) dispersed into the Au-ore body, originating an As-ore occurrence (mean average As amount of unoxidized auriferous samples of 25,000 ppm; maximum As value of 496,250 ppm), as well (see Fig. 2, Table 4). Arsenopyrite was found to dominate minor chalcopyrite, galena, and sphalerite in the mineralized bodies. This hydrothermal alteration, associated with the auriferous bodies and veins, occurs within amphibolites facies rocks of the Southern Rhodope core complex. This is attributable to the leaching of the Paleozoic marine metasedimentary (marble) core complex, and interlayered mafic metavolcanic (amphibolites) and Miocene granitic rocks through fluid/rock interaction [77]. Nearby the Mount Pangeon in a neighboring region of Serres at Agistro area, Macedonia (unpublished data; see Fig. 3 as well as Tables 1 and 4) auriferous veins of arsenopyrite together with pyrite and pyrrhotite are also occurring.

Massive sulfide ore associated with Greek ophiolite complexes occurring in the Othrys Mt. to Pindos Mt., consisting mainly of pyrite, chalcopyrite, and less amount of sphalerite and bornite, were found to accommodate relative high contents of As and Au [79]. In particular, elevated arsenic concentration was found at different sulfide ore samples from the Pindos ophiolite complex (Ioannina-Grevena, Epirus-western Macedonia; see Fig. 3 and Table 1). These samples were taken from the Perivoli region (SE slope of Smolikas Mt.), and in particular from a “Cyprus-type” sulfide ore occurrence situated at Kondros Hill area (mineral assemblages: pyrite, chalcopyrite, sphalerite and bornite) which shows an increased arsenic content up to

**Table 4** Occurrences of As-minerals in Greece (non-mining areas)

| Locality | As-minerals | References |
|---|---|---|
| Asimotrypes area, Pangeon Mt., Serres-Kavala, Macedonia | Arsenopyrite, As-pyrite, tennantite | [77] |
| Agistro area, Serres, Macedonia | Arsenopyrite[a] | – |
| Trilofon area, Veria, Macedonia | Cobaltite | [78] |
| Pindos ophiolite complex, Pindos Mt. | As-pyrite | [79] |
| Paliouri area, Karditsa, Western Thessaly | Arsenopyrite | [80] |
| Agia area, Ossa/Kissavos Mt., Eastern Thessaly | Arsenopyrite, Scorodite[b] | [81–84] |
| Agria area, Volos, Pelion Mt., Eastern Thessaly | Arsenopyrite, Realgar[c] | [81] |
| Panormos Bay, Tinos Island | Niccolite/Nickelite, Luzonite, Gersdorffite, Laggisite | [87] |
| Apigania Bay, Tinos Island | Arsenopyrite, Xanthoconite, Proustite, Rammelsbergite, Laggisite, Polybasite, Native As[d] | [88] |
| Keramos area, Chios Island | (–)[e] | [84] |

[a] Unpublished data

[b] Reported only by Chatzidiakos et al. [84] in the area of Bourboulithra (Melivoia, Agia, Ossa/Kissavos Mt., Eastern Thessaly)

[c] Unpublished data of a study [81] though presented a map did not mention the As-hosted phase)

[d] Reported as native As nanoparticles into pyrite crystals [88]

[e] There is no indication for As-hosted phase [84]

150 ppm (in bulk), and also from a “Fe–Cu–Ni–Co” sulfide ore occurrence situated at Tsoumes area (mineral assemblages: pyrrhotite, pyrite, pentlandite, chalcopyrite, and magnetite) with its As concentration varying between 20 and 27 ppm (in bulk), respectively. Additionally, chemical analysis of samples derived from the “Cyprus-type” sulfide ore occurrence at the Aspropotamos region (east of Perivoli region, SE slope of Smolikas Mt.) indicates a decreased As content from 15 to 25 ppm (in bulk) in regarding to the Neropriona area’s samples (consist mainly of disseminated pyrite and chalcopyrite) and moreover to 22 ppm (in bulk) concerning the Aspropotamos area’s quartz veins samples comprise mainly of disseminated pyrite, chalcopyrite, and pyrrhotite, as well. On the other hand, “Cyprus-type” sulfide ore samples from the Othrys ophiolite complex (Aghioi Theodoroi and Limogardi areas, Fthiotida, central Greece; see Fig. 3 and Table 1) revealed a significant low content of As (20 ppm, in bulk). Furthermore, advanced microbeam technique (SIMS) adequately illustrates the quantitative chemical composition of As in selected minerals from the sulfide ore occurrences from Pindos ophiolite complex [79]. The SIMS analyses confirmed the relative high As contents in coarse- and fine-grained As-bearing pyrite associated with bornite + covellite + siegenite assemblage. Thus, the variation of As concentration in the coarse-grained pyrite is between 110 and 3,080 ppm av. 1,290 ppm), in the fine-grained pyrite is between 170 and 12,900 ppm av. 1,610 ppm), and in very fine intergrowth with bornite is

between 130 and 2,710 ppm av. 1,180 ppm), respectively. Similarly, the elevated amount of As in selected coarse- and fine-grained As-bearing pyrite is also associated with chalcopyrite (As variation in coarse-grains: 72–1,552 ppm with an average value of 817 ppm; As variation in fine-grained: 205–311 ppm with an average value of 275 ppm) and with sphalerite (As variation in very fine intergrowths with sphalerite: 272–915 ppm with an average value of 585 ppm). Finally, pyrite associated with bornite was measured to have significant As content in coarse-grained crystals (As: 39–198 ppm; av. 105 ppm), in fine-grained crystals (As: 84–378 ppm; av. 225 ppm) as well as in very fine intergrowths with bornite (As: 373–1,279 ppm; av. 790 ppm), respectively. Conclusively, coarse- and fine-grained pyrite associated with chalcopyrite, bornite, and with assemblages of bornite, covellite, and siegenite seems to incorporate significant amount of As in micro-scale, assuming that the presence of arsenian pyrite (Table 4) is present in the massive sulfide ores occur in Pindos ophiolite complex [79].

As-bearing sulfides existing in Ophiolite-hosted ore deposit are thoroughly described [78] also at the area between Trilofon and Fitia villages, Eastern part of Vermion Mt. (NW of the city of Veria). In particular, the presence of cobaltite (theoretical formula: CoAsS) was identified. Special emphasis was given to its chemical composition ($Co_{0.84}Ni_{0.11}Fe_{0.05}As_{0.98}S_{1.02}$). Microprobe analyses from the cobaltite euhedral small crystals intergrowing within pyrrhotite demonstrated that As was varying between 44.40 and 45.93 wt%. The ore occurs in an area of ophiolites and flysch and situated within diabases and serpentinites forming lenses, bands, and disseminations. The mineralogical paragenesis of the ore is cobaltite, pyrrhotite, chalcopyrite, pyrite, and sphalerite (crystallization order). The authors concluded that cobaltite was crystallized at 500–600°C.

Additionally, copper ore deposit studied [80] in the area Paliouri area, near Karditsa (Western Thessaly) consists mainly of pyrite, sphalerite, and chalcopyrite as well as of gangue minerals (e.g., quartz and calcite), although the existence of euhedral and elongated crystals of arsenopyrite together with pyrite crystals was also proven. The entire area that Cu-ore occurs consists of basic and ultrabasic igneous rocks (e.g., serpentinites, spilites).

It is already well known that mineralogical and geochemical investigations in the region of Eastern Thessaly were undertaken far away in the past [12], reporting As mineralization in ore occurrences with no mining activity. A brief report of these occurrences in Eastern Thessaly [81] succinctly describes the ternary hydrothermal sulfides of As related to granitic intrusions in the area of Melivoia village, Agia, Ossa/Kissavos Mt. as well as in the area of Agria village, Volos, Pelion Mt. (see Fig. 3), concerning that the As hosting mineral is arsenopyrite. This As-sulfide mineral is accommodated within the metamorphic basic ophiolitic rocks (amphibolites, prasinites) as well as within the metamorphic rocks of sedimentary origin (mica-chlorite schists, quartz-chlorite-mica schists) [82, 83]. Arsenopyrite (FeAsS) together with galena (PbS), chalcopyrite ($CuFeS_2$), pyrite ($FeS_2$), sphalerite ((Zn,Fe)S), and stibnite ($Sb_2S_3$) used to form sulfide mineralization paragenesis in the entire investigated area [81]. Crystals of scorodite ($FeAsO_4 \cdot 2H_2O$) with length of 50 μm were also found in rocks from Bourboulithra area (Melivoia) by

Chatzidiakos et al. [84]. Relevant work implied that the As and the Sb mineralization are both related to each other [82]. Moreover, the authors [82–84] suggested that the extended occurrence of arsenopyrite in the area lying between Melivoia, Velika, Skiti, and Ano Polydendri (cultivated region of Agia, Eastern Thessaly) is probably the natural source of As contamination either in the groundwaters or in the soils. The relevant studies revealed that the Agia's groundwaters have relatively elevated As concentration (mean value of 12 ppb; maximum value of 125 ppb), as well as Agia's soils are characterized by relatively increased concentration (As: 5–242 ppm) with much higher mean average (As: 13 ppm) in comparison with that of the average of the global soil composition of (As: 2–20 ppm) mentioned by Yan-Chu [85] and lately re-noted by Hughes et al. [86], respectively. Decisively, Chatzidiakos et al. [84] predicted the trivalent oxidation state of the As in the groundwaters and implied that the $As^{3+}$ natural pollution reflects mainly the influence of arsenopyrite mineralization and, thus, is due to the dissolution of FeAsS. Nevertheless, they assumed a direct combination of the As natural pollution with some anthropogenic inputs in the cultivated area of Agia (Eastern Thessaly) [82]. Additionally, this natural groundwater As contamination is also well reflected by the existence of hydrothermally altered zones in the investigated area.

Besides, recent studies [87, 88] on Tinos island, Greece, thoroughly represent an abundant ore mineralization due to the presence of epithermal ore systems in Panormos [87] hosting in Mesozoic marbles and Apigania Bay [88] hosting in Mesozoic marbles and schists, as well. Bulk chemical analysis of the hosting rocks, complementary, affirmed the high As composition in the island (marbles, schists of blueschists belt and milky quartz veins were found to contain 66, 67 and 41 ppm As in bulk, respectively). Both ore occurrences are characterized by numerous ore and gangue minerals associated with arsenic. The Panormos Bay ore system, among others (precious metals, ore and gangue minerals), also was identified arsenide minerals (e.g., niccolite or nickelite: NiAs), sulfosalts (e.g., luzonite: $Cu_3AsS_4$), Ni, As-sulfides [e.g., gersdorffite (NiAsS)], and other such as laggisite ($Co_{0.8}Ni_{0.2}As$), whereas the Apigania Bay mineralization exhibit some differences. The latter As-enriched epithermal mineralization consists mainly of arsenopyrite and minor of As-sulfides/sulfosalts, such as xanthoconite ($Ag_3AsS_3$), proustite ($Ag_3AsS_3$), rammelsbergite ($(Ni,Co,Fe)As_2$), laggisite ($Co_{0.8}Ni_{0.2}As$), and/or As-bearing polybasite ($[(Ag,Cu)_6(Sb,As)_2S_7][Ag_9CuS_4]$). Also, pyrite crystals measured contain up to 2.24 wt% As, assuming that this is due to the existence of native As nanoparticles into it, while specks or laths of proustite and xanthoconite are intergrown with pyrite and sphalerite crystals [88]. Finally, electron microprobe analyses in selective grains and characteristic crystals from Tinos island confirmed the abundant existence of As in sulfides and sulfosalts, resulting that pyrite, arsenopyrite, xanthoconite, proustite, rammelsbergite, and laggisite are rich in As (1.85, 44.85, 15.02, 14.99, 68.28, and 55.03 wt%, respectively).

On the other hand, preliminary studies of the oxidation state of As in groundwaters from the island of Chios (Keramos area, NW part of Chios, Eastern Aegean sea, Greece) suggested, on the basis of theoretical calculations, that the dominant species of As are trivalent and the concentration of As increases up to

6.13 ppb. A relevant geochemical study [89] examining the possible influence of geology on As concentration in groundwater, stream water, and stream sediments in Keramos gulf of Lesvos Island (NE Aegean sea, Greece), assumed that the measurement of the elevated As concentration cannot be attributed to the geothermal activity of the investigated area, but ascribed to the presence of the adjacent ophilitic ultramafic formations, which possibly accommodate As-bearing minerals. The study concluded that these formations are apparently the predominant factor of the corresponding As geochemical behavior.

## 4 Arsenic in Areas with Geothermal Fluids and Volcanic Activity

Arsenic in groundwaters and soils, influenced by geothermal activity (possibly mixed with geothermal fluids in deep horizons) due to faults, is intensively observed in northern Greece (see Fig. 3 and Table 1; [90–98]), and in particular at greater Thessaloniki (including Axios river and western Chalkidiki). This highly populated area has very limited water resources, and subsequently As-contaminated groundwaters have minimized the water supply potential for people and animals. In groundwaters, derived from specific wells of greater area of Thessaloniki and the Axios river delta, rather elevated As concentrations were measured (4–130 ppb), attributed to the possible effect of pH on As mobilization, as positive correlation of As with the pH values was also estimated [93]. On the other hand, elevated As concentrations were also recorded near Volvi Lake [92]. However, according to Kouras et al. [95] and Voutsa et al. [96] the As contamination of groundwaters is really severe in western Chalkidiki near Nea Triglia area. In this area As concentrations were recorded to be up to 1,840 ppb with EU permission level for potable water to be 10 ppb. Arsenic seems to be correlated with U [94] as well as with B [96]. The sources of As, released to the surface by geothermal fluids (33–42°C) circulating through faults, may be related to igneous rocks underlying thick sedimentary formations. This assumption is also supported by the geochemical fact that As was also correlated with K, Mn, and Fe, indicating geogenic origin and the presence of hydrothermal conditions resulted in enhancements of their mobility [95]. A study of hydrothermal waters from springs and boreholes with an average As concentration of 36 and 70 ppb, respectively, that are enriched in several constituents (e.g., $H_2S$, K, B, $NO_2$, Mn) was also carried out for Anthemous basin (between western Chalkidiki and Thessaloniki) [91]. This study provides also a representative model of As enrichment of waters from springs and boreholes, attributable to the local hydrothermal fluids circulation, influenced by the presence of a specific geological basement (e.g., existence of granodiorite that probable is leached by water circulation through fracture zones) and by hydrothermal conditions (e.g., $T = 23\text{–}28°\text{C}$, pH: 6.2–7.3, Eh from −0.21 to −0.88 mV, TDS up to 5,850 ppm, $H_2S$: 60–70 vol.%, etc.), causing the further enrichment of groundwater in As and other metals. Thus, hydrothermal fluids enhanced the groundwater in As, which then deposits As-rich metalliferous sediments av. 147 ppm in As) and rich in As travertine av. 235 ppm in As) due to its discharge through WNW–ESE faults in the western Chalkidiki peninsula [91]. In a very recent study by Winkel et al. [98], alkaline groundwaters in western Chalkidiki containing up to 3,760 μg/L As, were found to be associated with arsenate ($As^{5+}$)-rich (As: up to 913 mg/Kg) travertine according to Synchrotron radiation spectroscopic study (micro-XRF and -XAS). Thus, the influence of the reported geothermal activity results in the natural pollution of the underground water and consequently of the soils of the investigated areas.

Herein, it is noteworthy to report a rare example of As-mineralization as a consequence of the influence of hydrothermal fluids in the caves of Aghia Paraskevi (SW of Kassandra peninsula, western Chalkidiki). Orpiment ($As_2S_3$) crystals, with specific amount of As between 60.7 and 61.32 wt%, are formed very closed to the surface of thermal Na–Cl type spring waters ($T = 35.0$–$39.2°C$, pH: 6.35–7.00 and TDS: 35.964–43.521 mg $L^{-1}$) in these active sulfuric acid caves, due to the hydrothermal influence as a result of the mixing of seawater with the meteoric origin of geothermal waters of the cave [99].

The enrichment of As in sediments situated in areas of volcanic activity in South Aegean Active Volcanic Arc (SAAVA, also known as Hellenic Volcanic Arc) (Fig. 3 and Table 1), is suspended as a possible influence of hydrothermal fluids. In particular, measurements of As concentrations in surface siliceous (As: 10.1–27.0 ppm) and in carbonate sediments (2.4–27 ppm) derived from Methana Island [100] reveal an average of 20.45 ppm and of 6.67 ppm, which are both rather elevated compared to the As concentration of the upper continental crust – UCC [101], respectively (see Fig. 4). Furthermore, the geochemical investigation elaborated on submarine hydrothermal fields of Milos Island (south Aegean Hellenic Volcanic Arc) significantly showed that the corresponding sediment cores, derived from Voudia Bay (average of 9 ppm in As content), Palaeochori (average of 57 ppm in As content) as well as from Rivari (average of 108 ppm in As content), accommodate a relative high As amount [102, 103], contrast to UCC As content (Fig. 4). A very recent study [104] just discovered poorly crystalline orpiment ($As_2O_3$), in the bottom of the sea at Palaeochori and Spathi Bays (off the southeast coast of Milos Island), yielded by the abundant hydrothermal venting of acidic and highly sulfidic fluids occurring in this shallow-sea environment. These fluids are characterized by an extremely high As concentration, up to 300 times higher than of the seawater, and indeed far exceed to the mid-ocean ridge (MOR) and back-arc basin (BAB) fluids As content, respectively. They suggest that unique orpiment phase is derived by the mixing of the overlying seawater with these hydrothermal fluids moving from the leachate metamorphic basement – due to water–rock interaction – upwards, through an abundant vein system, towards to the surface of the bottom of the sea in critical boiled conditions. They also believe that the source of the extremely elevated amount of As is the combination of the leaching phenomena of the greenschist facies metamorphic basement due to the water–rock interaction, and of the directly partition of the As into the vapor phase (under critical conditions) in this local hydrothermal system.

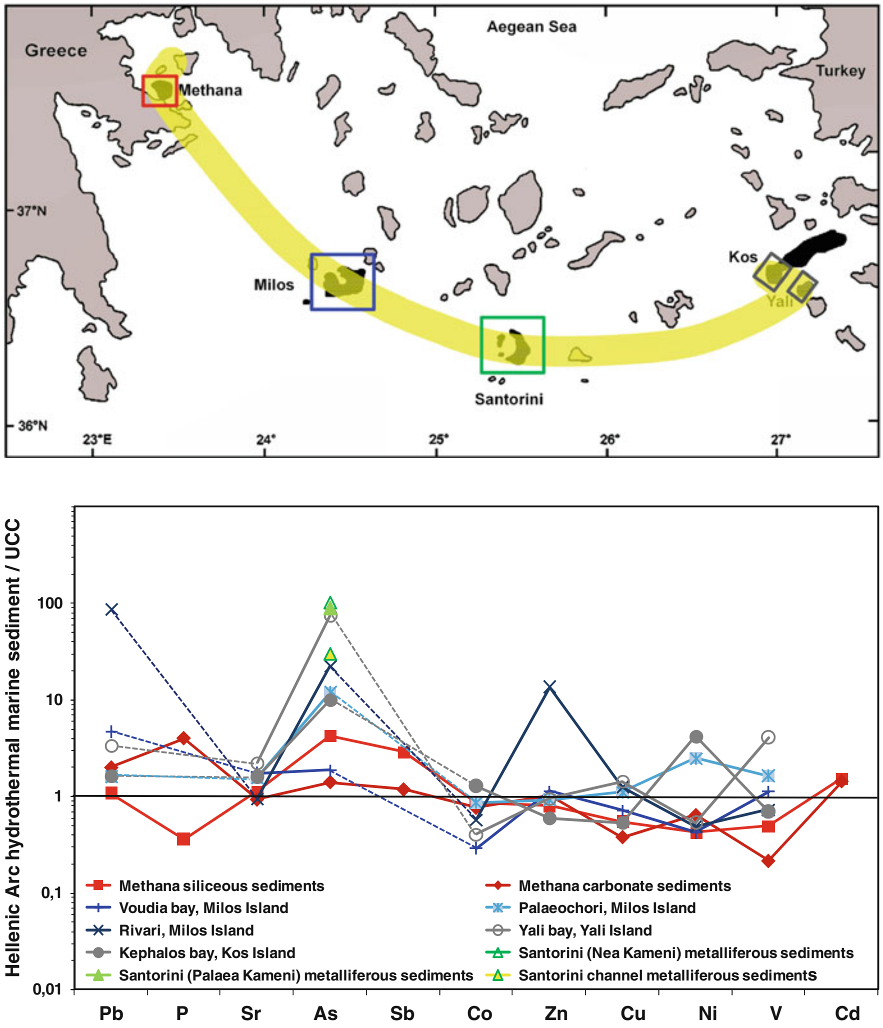

**Fig. 4** *Upper image*: simplified map indicating the Methana (NE Peloponesse), Milos, Santorini, Yali and Kos volcanic centers, acting as significant As sources in the Hellenic Volcanic Arc. *Lower image*: Upper Continental Crust (UCC)-normalized (according to Rudnick and Gao [101]) spider diagram of trace elements in marine hydrothermal precipitates showing an extreme As geochemical positive anomaly in the whole Hellenic Volcanic Arc. Average values of Methana siliceous sediments [100]: *red thick line* and *solid square*; Average values of Methana carbonate sediments [100]: *darker red-brown thick line* and *solid lozenges*; Milos Island sediment [102, 103]: *blue thick line* and *plus symbol* correspond to Voudia Bay samples, *light blue thick line* and *asterisk in lighter blue* background correspond to Palaeochori, *dark blue thick line and cross* correspond to Rivari, respectively; Yali Island (Yali Bay) sediments [103, 105]: *gray thick line* and *open circle*; Kos Island (Kephalos Bay) sediments [101, 103] *gray thick line* and *closed circle*; Average values of Santorini caldera metalliferous marine sediments [106]: *green thick line* and *open triangle* correspond to Nea Kameni islet, *light green thick line* and *closed triangle* correspond to Palaea Kameni islet, *yellow thick line* and *green triangles* with *yellow filling color* correspond to Santorini “channel” situated between Palaea and Nea Kameni islets

Another intense As enrichment phenomenon was alternative found in sediments from Yali Bay, Yali Island (average of 356 ppm in As content) and from Kephalos Bay at Kos Island sediments (average of 48 ppm in As content), respectively [103, 105]. On the other hand, chemical analyses conducted in selected areas of Santorini Island, and especially measuring the As concentration in metalliferous sediments from Nea Kameni (As: av. 493 ppm), Palaea Kameni (As: av. 425 ppm) and from the area of the channel (As: av. 145 ppm) located between the latter two small islets, exposed again the hydrothermal enrichment of As, together with Sb. Moreover, this investigation described the impact of the formation of freshly precipitating Fe-oxides resulting the scavenge of the hydrothermal As into the sediments [106]. Therefore, all of the above studies indicate an extreme As enrichment in the hydrothermally influenced sediments, compared to UCC (Fig. 4), either associated with a relative elevated Sb concentration (e.g., in the case of Methana sediments [100]) or related to Fe–Mn rich layers (e.g., in the case of Santorini [106] and Milos [102, 103] sediment cores). These findings suggest a relatively recent hydrothermal activity, as a result of the volcanic activity in the Hellenic Volcanic Arc. Finally, in a recent investigation, peculiar As-sulfides of possible biogenic origin were also discovered in the floor of the submarine crater of Kolumbo volcano located north of Santorini [16–18].

## 5 Arsenic in Coals

Lignites, as the most common type of coals in Greece, are mainly situated at the three lignite-bearing main coal deposits (e.g., [107–109], see Fig. 3 and Table 1) in Ptolemais and Florina (Florina-Ptolemais-Servia main basin in western Macedonia, NW Greece), in Megalopolis (Megalopolis basin in Peloponnese, southern Greece) as well as in Drama lignite deposit (Drama basin in eastern Macedonia, NE Greece). Similar to the above, smaller coal deposits such as Domenico lignite deposit [110] in Elassona lignite basin (Larissa district, Northern Thessaly), lignite-bearing strata [107, 111] in Ioannina basin (Ioannina, Epirus), and Plakia lignite deposit [111] in Plakia basin (Crete Island) have also been geochemically examined in the past. Moreover, the As content of all of these coal deposits has been measured, concerning that the mentioned deposits in Greece could be potential sources of this hazardous element.

Recently, a new occurrence of a nonindustrial thin layer of coal, at the Pera-Lakkos mine located in the Parnassos-Ghiona bauxite mining area, overlying bauxite horizon B3 (please see relevant paragraph and Fig. 3 as well as Table 1) has discovered and a relevant article [73] demonstrates that accommodate an average of 18 ppm of As content, approximately.

Geochemical investigation of Lava xylite/lignite deposit (a sub-basin at the Servia basin – southeast of Kozani, northern Greece – situated in the southern part of the elongated intermontane Florina-Ptolemais-Servia main basin) has revealed [107, 112] that As can be considered as a highly enriched element. Estimation of arsenic in air-dried lignite samples reveals an average value at

9.32 ppm with maximum at 27.83 ppm [112]. It is mentioned that part of the As may be organically bound, while the rest probably occurs as a solid solution or as As-purite. Similar study [107] calculated the As concentration either to air-dried lignites or to lignite ashes (heated at 1,000°C) derived from Kozani (Lava and Anatoliko), Ptolemais (Kardia), and Florina (Anargyri and Achlada) lignite sub-basins. The results concluded with the As enrichment in all of the investigated samples (Kozani: av. 58.45 ppm for air-dried lignites and av. 293.9 ppm for lignite ashes; Ptolemais: av. 22.2 ppm for air-dried lignites and av. 104 ppm for lignite ashes; Florina: av. 10.7 ppm for air-dried lignites and av. 48.6 ppm for lignite ashes), respectively. The entire coal deposit from the Florina-Ptolemais-Servia main basin, which is divided into several lignite-bearing sub-basins, is belonging to the Ptolemais-Amynteon Lignite Center (P-ALC) in Northern Greece.

On the other hand, other opencast mines at Domenico lignite deposits, Elassona basin, Larissa, Thessaly [110], as well as at Lofoi lignite-bearing deposit, Florina lignite-bearing basin [113] were also examined for their trace elements composition in the lignite ashes (lignitic samples that prior heated at 850°C). The results showed the As concentration at the lignite ashes, compared to that of the earth crust's average of 1.8 ppm [114], is strongly enriched. The As mean average content is 46.5 ppm with a maximum value of 104 ppm corresponding to Florina basin's lignitic samples, whereas the composition of As at the lignitic samples from Elassona basin is up to 150 ppm (mean average at 32.06 ppm). This is ascribed to the existence of olivinite and granitic rocks regarding the Florina lignite-bearing deposit, and it is strongly believed that these silisic and mafic-ultramafic surrounding rocks in the area actively contributed to the formation of the deposit. Correspondingly, the As enrichment occurs at the samples from Elassona lignite basin is attributed to the geothermal activity that had affected the area during the past, confirming the presence of travertine in the overburden sediments. Nevertheless, strong positive correlation between Mo and As is observed at both Florina and Elassona lignite samples [110, 113] that can be explained due to the existence of sulfide minerals, as well as an intermediate to strong positive correlation of Cr and As is also notable concerning the Florina lignite samples [113].

Lignites from the Ptolemais Basin have similarities to those of Drama basin with regard to their deposition under similar geologic conditions [112]. The Drama basin consists mainly of peat and lignite and minor of clay, sands, and muds. The lignite deposit can be divided into three lignite seams A, B, and C (from the bottom to the top). Seam A can also separated into three sub-seams A3, A2, and A1 (from the bottom to the top), respectively [108, 115, 116]. In accordance with a previous study [107] reporting a range of As concentration at air-dried lignites (sampling site near Pangeon Mt.: 34–124 ppm; sampling at the main lignite deposit: 13.2–90.3 ppm) as well as at heated (1,000°C) lignite ashes (sampling site near Pangeon Mt.: 856–1,131 ppm; sampling at the Dipotama lignite deposit: 50.9–1,675.0 ppm), a newly detailed geochemical study [116] also analyzed several composited samples (air-dried lignites and lignite ashes heated at 1,000°C) from the Drama lignite basin. The latter study showed that As is highly enriched to the air-dried lignites av. 62 ppm) as to their corresponding heated lignite ashes av. 185 ppm), compared to the crustal abundances and also to the surrounding rocks (<2 ppm at metamorphic rocks; up to 2.7 ppm at igneous rocks), as well. It is noteworthy that As concentration exhibits a vertical variation between different sampling sites at different seams of the lignite basin (i.e., As content of air-dried lignites of seam C is approximately 25 ppm and remarkable increasing up to 149.0 ppm for the seam A3 samples; also, As average content of heated lignite ashes varies from 78.45 ppm (for seam C samples) up to 399.5 ppm for seam A3 samples, respectively). Analogous works related to the main Drama lignite [115], and to the Philippi peatland [117] have been evaluated, as well. These latter studies affirmed the highly As enrichment to the air-dried lignites from Drama main lignite deposit (up to 138 ppm; [115]), as well as to the air-dried lignites derived from the nearby Philippi peatland (82.27–259.80 ppm; [117]). Conclusively, arsenic in the Drama lignite deposit has an increasing trend from the surrounding rocks to the air-dried lignites up to the heated (1,000°C) ashes. Additionally, authors [115] suggested that arsenic from the surrounding crystalline rocks is initially mobilized and transferred by the surface water, and whereupon is deposited in the peat swamp and subsequently incorporated in the lignite. Finally, they indicated that As does not emit to the atmosphere due to the existence of high amounts of Fe, Ca-oxides, which trap most of this hazardous element at the final lignite's residue (fly ash) during combustion.

Moreover, lignite-bearing strata have been observed in the northern part of the intermontane Ioannina basin, Epirus [111], consisting mainly of a deeper lignite formation (comprising of one solid layer) and a shallower interval (splitting into 3–4 thin layers). Relevant to the previous results statement [111] was carried out through the geochemical and mineralogical investigation of selected samples derived from this lignite-bearing deposit in point of the arsenic content of it. The study noted that As may be associated inorganically with pyrite (probably due to the absence of phosphate minerals in the lignite deposit), organically with clays or even with carbonates, as well. In general, the vertical variation of As (from 1.93 to 46.40 ppm) is strongly remarkable, and obviously is highly enriched in the shallower interval, compared to its almost depleted concentration at the deeper interval in the lignite-bearing strata of Ioannina basin. Relevant work [107] calculated the high As concentration to the air-dried lignite samples av. 46.6 ppm) and to the heated (1,000°C) ashes av. 165 ppm), as well.

Nevertheless, analogous geochemical investigation [118] at the lignite samples from Plakia deposit located at the Plakia lignite basin (Crete Island) showed an enrichment of the As concentration (16.7–47.7 ppm) comparing to that of the word's coals [119]. The authors mentioned that there is positive correlation between the As, Mo, U, and the S in the lignite samples, as well as among the S-bearing minerals and the total concentration of these chalcophile elements in the lignite, indicating directly that the As, Mo, and U, most probable, are associated with sulfur-bearing minerals.

Additionally, geochemical investigation of derived lignite samples from Megalopolis lignite basin in Peloponnese [107], southern Greece (Megalopolis Lignite Center – MLC) indicated that they also incorporate As. Arsenic concentrations were detected in air-dried lignites av. 11.8 ppm), as well as in 1,000°C heated lignitic ashes av. 24.95 ppm).

It is well known that the combustion of the coal (e.g., lignite) produces the fly ash (i.e., coal's residue), and also that the concentration of the elements of the fly ash and their potential leachability are closely related to the coal's composition burned in the power plants and the relevant technological processes. Thus, as coal (lignite and/or xylite) from the main mining districts (i.e., Ptolemais-Amynteon Lignite Center (P-ALC) in northern Greece and Megalopolis Lignite Center (MLC) in the Peloponnese) is consumed for the electric power production, several tonnes of fly ash are produced annually. Thus, it was strongly recommended to examine the potential transfer of As source from the parent coal deposit to the residue and finally possibly to the environment, as well. Except the above investigations of heated lignite samples at 850°C [110, 113], several other published articles [120, 121] have been examined primarily the lignite industrial residue (fly ash) from the power stations of Greece (Megalopolis A, Amynteon, Agios Dimitrios, Ptolemais, and Kardia) concerning the potential passing of major and trace elements from the coal to the environment, through the exposing fly ash to the groundwater, during the subsequent landfilling of it. All of the relevant works measured the As amount that passes from the coal to the fly ash (20.5–38.8 ppm, [120, 121]) and also have calculated the As content at the fly ashes' leachates. They concluded that the As cannot easily be released from the fly ash, due to the low mobility of the element at the investigated leachating samples. Thus, As content in the fly ash of lignites has a relative low potential hazard for the environment [120, 121].

## 6 Potential Arsenic Sources in Metamorphic Rocks

The nature of As in metamorphic rocks of Greece differs to that of other geological sources, due to different hosting minerals. Arsenic in metamorphic rocks prefers to incorporate in several As-bearing Mn-silicates and not in sulfide minerals. These As sources are mainly located in Eocene blueshist belt of the Attico-Cycladic Crystalline Complex of the Hellenides, Aegean sea, Greece (see Fig. 3 and Table 1) and especially at Mili area, near Karystos (southern Evia) [122], at the areas of Akra Bouri and Mili [123] as well as at Andros Island in the areas of Vasilikon Mt. and Vourkoti [124], of Apikia [122] and of Apikia, Petalon, Rdisa, and Vitali [123].

In particular, on the Island of Andros, piemontite-spessartine and piemontite quartzites are the ferromanganoan metasediments that markedly accommodate As quantities [123]. These metamorphic – As enriched – rocks are derived from Mn-nodule-bearing sediments consisting of a mixture of terrigenous illitic clays with biogenic radiolarian ooze. They usually form layers of significant lateral extension intercalated within piemontite-free muscovite-chlorite quartzites and schists with scattering oxide-rich lenses. Mineralogical investigation [122, 124] not only showed the presence of quartz, piemontite, spessartine, braunite, Mg-chlorite, hematite, phengite, phlogopite, and rutile but also proved the existence of As-bearing ardennite as accessory mineral, together with other accessories (Na-amphibolite, clinopyroxene, albite, apatite, and tourmaline), but in different quantities (mainly $< 2$ vol.%, and rarely between 2 and 20 vol.%). In contrast to Andros assemblages, the mineral composition of southern Evvia is quartz, piemontite, sursassite, braunite, Mg-chlorite, hematite, rutile, and titanite in coexistence with the essential accessory mineral of As-bearing ardennite [122], too. Trace element analysis of Fe,Mn-metasediments, from Andros island, confirmed the general enrichment of As (mean average: 434 ppm). It should be noted that the maximum content of As measured at 2,500 ppm. This strong enrichment was attributed [123, 124] to the allochemical processes during diagenesis and/or early high-$P$ – low-$T$ metamorphism (>11 kbar and 360–420°C) under highly oxidizing conditions. These processes resulted in the decomposition of the oxyhydroxides from the Mn nodules and micronodules, releasing the relative trace elements (such as As) and therefore effected to the As mobilization from the sedimentary column, which obviously taken up by hydrous pore fluids, accumulated in newly formed mineral assemblages that can accommodate selectively these elements and conclusively the subsequent concentration of the arsenic in the Mn-silicate minerals, such as ardennite. More recent work [123] examined $As^{5+}$-$V^{5+}$-bearing silicate ardennites from southern Evia (Akra Bouri and Mili, near Karystos) and Andros Island (Apikia, Petalon, Rdisa, Vitali area), revealing that the Andros' ardennites are commonly Ca–$Mn^{3+}$–$As^{5+}$-rich silicate minerals. Furthermore, Pasero et al. [123] suggested that the $As^{5+}$ incorporates in isolated T4 tetrahedron (Andros Island), whereas $As^{5+}$ occupies sites at T4 tetrahedron together with $V^{5+}$ (Akra Bouri, Southern Evia) as well as with $Si^{4+}$ (Mili, Southern Evia). They recommended that $Si^{4+}$-(As, V, P)$^{5+}$ substitution in T4 is maintained by variations in the overall hydrogen content. Conversely, $As^{5+}$ (or $V^{5+}$ plus some $Si^{4+}$) predominates in the less rigidly bounded and slightly larger T4 tetrahedron in most ardennites.

Finally, according to very recent research [125] unique As-bearing rock-forming minerals also occur in metamorphic rocks of Varnavas area (NE Attica) and Syros Island (Cyclades).

## 7 Arsenic in Phosphate Deposits

Neogene phosphate deposits have been well described [126] as notable As hosting rocks in Greece. Phosphate rocks, containing elevated amount of As, occur in several locations in Greece (see Fig. 3). In particular, phosphates of marine origin appearing as a thick-bedded, whitish to yellowish-brown phosphatic limestone outcrop, formed at an outer shelf-upper slope environment (Palliki peninsula, southwestern part of Kefalonia Island). Their arsenic content is varying between 5.0 and 15.0 ppm. Phosphates formed at a hemipelagic environment, occur in the northern part of the Karteros basin (Prassas Hill, Heraklion, Crete Island), embedding into a yellowish-brown sandstone beds. Chemical analysis of Cretan phosphates revealed the highest value of As (up to 35.6 ppm) comparing to the rest of Greek phosphate deposits. On the other hand, phosphates developed in a lacustrine environment are present in Komnina area and in Vegora lignite quarry (Florina-Ptolemais lignite basin, western Macedonia) as well as in Drymos area (Sarantaporo-Elassona basin). Similar to the marine origin, but not as high amount as the Cretan deposit has, the latter phosphates exhibit a detectable As amount (Komnina deposit: 7.6 ppm; Vegora deposit: 10–15 ppm; Drymos deposit: 1.0–6.8 ppm). In all of the presented cases, As is mainly attributed to the existence of the organic matter of the hosting deposits [126].

## 8 Arsenic in Desert (Saharan) Dust and "Red Rain"

Huge quantities of mineral dust are transported every year from the arid desert regions of northern Africa over the Mediterranean areas ($3.9 \times 10^6$ t year$^{-1}$). Sahara desert is responsible for the global emission of 50% of the total mass of mineral aerosols to the atmosphere. Aeolian transport of Saharan dust influences significantly the rain acidity and furthermore the climate to the Mediterranean, causing among others, intense "red (or mud) rain" and even "red snow" episodes. During these episodes geological material from Sahara is deposited to the aquatic, terrestrial, and urban environment [127–129] (see also Fig. 3). This material, transported from N. Africa to Greece, hosts both inorganic nutrients (e.g., K, Ca, Mg, Fe) and contaminants, including metals (e.g., Pb, Cr, Cu, Ni) and metalloids (mainly As). Arsenic in the dust particles is not detectable by conventional point analyses techniques such as SEM-EDS. However, recent Synchrotron-based reports revealed that As, together with other very hazardous elements such as Pb, are concentrated in specific phases of Saharan dust from "red rain" precipitated over Athens, Greece [130, 131]. It has been mentioned that the mean annual atmospheric mass fluxes are severe in south Greece, and particularly in Crete Island, reaching the value of 21 g m$^{-2}$, one of the highest in Mediterranean [132]. In the case of western Mediterranean, it has been estimated that the atmospheric input of As is 95–132 t year$^{-1}$ [133]. There is no specific indication for eastern Mediterranean in the literature, up to now, but it is presumed that there is a permanent supply of significant quantities of As in Greece due to annual Saharan dust deposition.

## 9 Conclusion

Geological sources of arsenic in the environment of Greece include As-containing ores in active and abandoned mining areas, geothermal/hydrothermal waters, lignites in exploited and unexploited deposits, As-minerals in various rock types such as metamorphic rocks, and mineral dust originating in Sahara desert. These sources, as well as various anthropogenic As fluxes, may create distinct areas of contaminated groundwater, soils and marine environments. The most important and persisting source of As exposure to the Greek populace appears to be the geothermal and hydrothermal fluids arising from faults as well as the volcanic activity which, in turn, affect underground, surface, and marine aquatic environments. On the other hand, past mining in Greece does not affect significantly the aquatic systems, compared to the permanent supply of As in geothermal and volcanic areas. The only exception might be the Lavrion past mining area, although further research is needed to confirm this statement. The methodological approach presented in this chapter may represent a useful example for similar analyses with regard to the other areas of the world affected by As pollution.

**Acknowledgements** We would like to kindly thank Prof. Thomas J. Walsh, MD (Professor of Medicine in Microbiology and Immunology, Weill Cornell Medical College, USA) for critical reading and fruitful comments on the manuscript. We also thank Assist. Prof. Panagiotis Voudouris (Faculty of Geology & Geoenvironment, University of Athens, Greece) for critical discussion and comments concerning As-minerals in Lavrion historical mines and Perama Hill epithermal Au–Ag deposit (Thrace).

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