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REVIEW

Distribution of arsenic in the natural environment with emphasis on rocks and soils

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Arsenic is ubiquitous in the environment. Although the average arsenic concentrations in rocks (~2 mg kg^{-1}), soils (~2 mg kg^{-1}), freshwater (~1 μg dm^{-3}), seawater (~2 μg dm^{-3}) and organisms is generally low, high arsenic concentrations in limited areas are not uncommon. Whereas terrestrial organisms appear not to accumulate arsenic, marine organisms effectively concentrate arsenic to levels thousand of times higher than in ocean waters. The geochemical cycle and mineralogy of arsenic are reviewed with some emphasis towards Japanese locations and arsenic concentrations (averages, ranges) found in samples from the lithosphere, pedosphere, hydrosphere and biosphere are tabulated and discussed.

Keywords: Arsenic, geochemical cycle, lithosphere, pedosphere, hydrosphere, atmosphere, biosphere, geochemical prospecting

INTRODUCTION

Arsenic is ubiquitous in the atmosphere, hydrosphere, pedosphere, lithosphere and biosphere of the earth. Volcanic activity and the weathering of arsenic-containing sulfidic minerals are the primary sources of arsenic. Plants and animals take up arsenic from the environment and thus become part of the arsenic cycle operating in nature. Many environmental samples have been analyzed for total arsenic and lately for arsenic compounds. This paper summarizes the results of these analyses and addresses the use of arsenic in geochemical prospecting for ore bodies.

GEOCHEMISTRY AND MINERALOGY OF ARSENIC

Arsenic is the third member of Group 15 (Group VA) of the Periodic System that also includes nitrogen, phosphorus, antimony and bismuth. In some of its chemical reactions arsenic behaves much like phosphorus and antimony. Arsenic (atomic number 33) has only one stable isotope (mass number 75) in nature.[1,2] Arsenic abundance in the earth's crust is 2 mg kg^{-1}.[3] Thus, arsenic is as abundant as tin, tungsten, and tantalum, but much less abundant than copper, lead and zinc. Arsenic is ubiquitous in nature and concentrates in many types of mineral deposit, particularly those containing sulfides and sulfosalts. Arsenic is associated in these deposits with elements such as copper, silver, gold, zinc, cadmium, mercury, uranium, tin, lead, phosphorus, antimony, bismuth, sulfur, selenium, tellurium, molybdenum, tungsten, iron, nickel, cobalt and the platinum-group metals. Arsenic also occurs in nature in the form of oxides, complex oxides, arsenates, arsenate-sulfates, arsenites and other complex oxygen-containing compounds. The biophilic character of arsenic is manifested by its presence, usually in small amounts, in a wide variety of living and fossilized organisms.

Geochemical cycle of arsenic

The generalized geochemical cycle for arsenic is shown in Fig. 1. The atmosphere, hydrosphere, pedosphere and biosphere receive arsenic as a result of anthropogenic industrial, domestic and mining activities in addition to naturally mobilized arsenic.

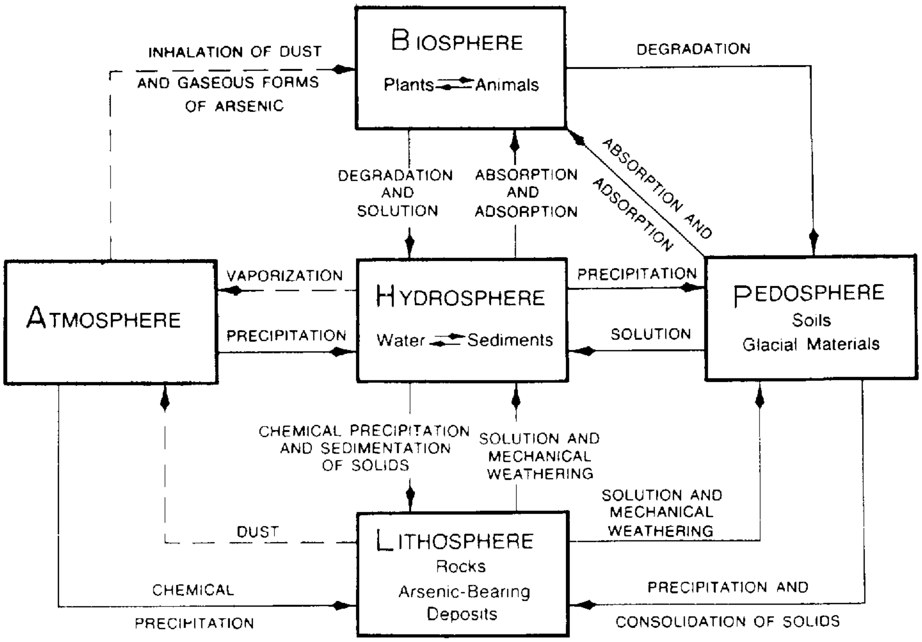


Figure 1 Generalized geochemical cycle for arsenic.[3]

Mineralogy of arsenic

Arsenic is the main constituent of 206 species of minerals such as elemental arsenic (1), alloys and arsenides (23), sulfides and sulfosalts (49), oxygen-containing compounds (except arsenites, arsenates, silicates) (5), arsenites (7), arsenates (119), and silicates (3).[4] The frequency of the combinations of arsenic with other elements (including OH and H_2O) in these arsenic minerals is summarized in Fig. 2, which also contains an example for the calculations of these frequencies. Metallic elements most frequently found in arsenic minerals are silver, aluminum, copper, iron, magnesium, manganese, nickel and lead. The preference of arsenic for heavy metals such as copper and lead justifies the classification of arsenic as a chalcophile.[5]

The principal arsenic minerals in endogene (hypogene) deposits are arsenopyrite (FeAsS), niccolite (NiAs), cobaltite (CoAsS), tennantite [$(Cu,Fe)_{12}(As_4S_{13})$], enargite (Cu_3AsS_4), native arsenic (As), orpiment (As_2S_3), realgar (As_4S_4) and proustite (Ag_3AsS_3). The principal supergene arsenic minerals, formed by oxidation of the hypogene minerals, are scorodite [$(Fe,Al)(AsO_4).2H_2O$], beudantite [$PbFe_3(OH)_6(SO_4)(AsO_4)$], olivenite [$Cu_2(OH)AsO_4$], mimetite [$Pb_5Cl(PO_4,AsO_4)_3$], arsenolite [$As_2O_3$], erythrite [$Co_3(AsO_4)_2.8H_2O$] and annabergite [$Ni_3(AsO_4)_2.8H_2O$].

Arsenic is found in traces in practically all common sulfides and in a great variety of other minerals, particularly in sulfates, phosphates and vanadates. The principal carrier of arsenic in rocks and in many types of mineral deposits is pyrite, FeS_2. This mineral may contain arsenic at concentrations reaching 6000 mg kg^{-1}. Arsenic is apparently present in lattice sites substituting for sulfur.[3]

Arsenic concentrations in ore minerals from various deposits in Japan are compared with literature values in Table 1. Mineral deposits of the xenothermal type, considered to be formed at high temperatures, have higher arsenic concentrations than deposits of other types.

ARSENIC IN THE LITHOSPHERE

The concentration of arsenic in the rocks of the lithosphere varies with the abundance of arsenic-carrying minerals. The arsenic concentration in igneous rocks is relatively constant at 1.0–4.3 mg kg^{-1}, whereas the concentrations in sedimentary rocks vary considerably from 2.6 mg kg^{-1} in limestone to

Table 1 Arsenic concentrations (mg kg^{-1}) in Japanese ore minerals[6,7]

	Type of ore deposit															
	Vein			Xenothermal			Network			Black ore			Onishi[8]		Boyle and Jonasson[3]	
Ore	Number of values	Range	Mean	Number of values	Range	Mean	Number of values	Range	Mean	Number of values	Range	Mean	Range	Remarks	Range	Remarks
Pyrite	29	80–1000	176	10	80–5000	1438	16	80–5000	928	3	250–500	383	<80–5000 110–20000	Japan USSR, Canada, Norway	100–1600 5–5600	In rocks In mineral deposits
Galena	1	250	250	—	—	—	—	—	—	—	—	—	<80–1000 <5–10000	Japan USA, Canada	<5–60	In mineral deposits
Sphalerite	3	80–200	127	6	200–5000	1400	—	—	—	—	—	—	<80–1000 <5–15	Japan Canada	<5–400	In mineral deposits
Chalcopyrite	30	80–250	106	20	80–5000	1717	27	80–2500	533	7	100–500	257	<80–5000 110–3800	Japan Silesia, Canada	10–1000	In mineral deposits

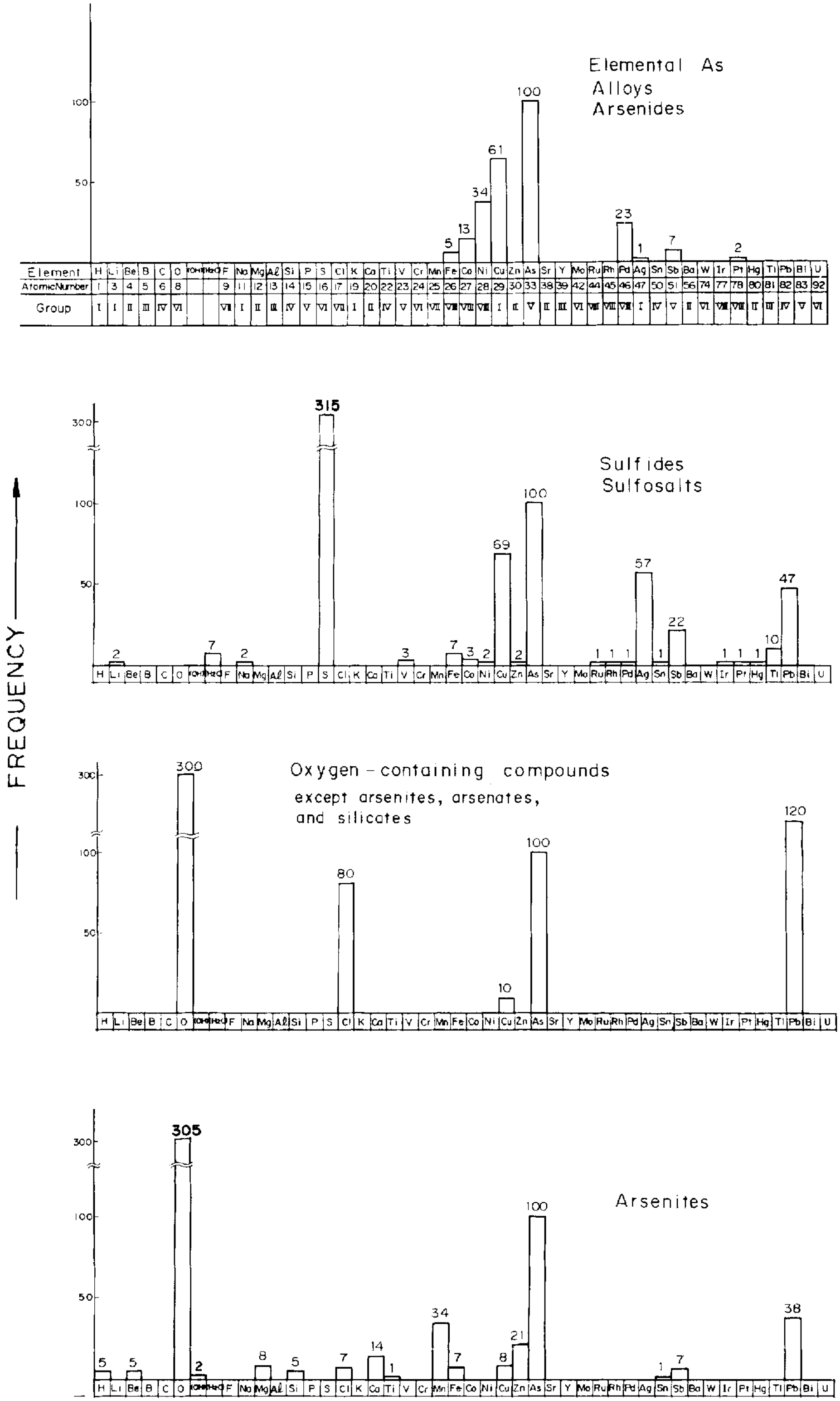
17.0 mg kg^{-1} in shale. Arsenic, a relatively mobile element in endogenic processes, tends to form broad primary halos and dispersion trains in the vicinity of arseniferous ore bodies, and may serve as a good indicator element (pathfinder element) in geochemical prospecting for some twenty elements of commercial importance.

Arsenic in rocks

The abundance of arsenic in common igneous, sedimentary and metamorphic rocks is summarized in Tables 2, 3 and 4. Among the igneous rocks (Table 2), ultrabasic rocks have the lowest average arsenic concentration and extrusive faces of acid rocks the highest. Arsenic concentrations are generally higher in sedimentary rocks (Table 3) than in igneous rocks. Arsenic is considered to have become concentrated in sedimentary rocks through sedimentation processes. The fine-grained clastic sediments have higher arsenic concentrations than the coarse-grained sediments. Metamorphic rocks have arsenic concentrations similar to the concentrations in rocks from which they are derived. Thus, metamorphic rocks of sedimentary origin (quartzite, slate, phyllite) have higher arsenic concentrations that other metamorphic rocks formed by contact or regional metamorphism. The rather high concentration of arsenic in skarn may be due to heavy metal-containing minerals in this rock.

Geochemical prospecting using arsenic in rocks

Approximately 30 years ago, arsenic began to attract attention as an indicator element in geochemical prospecting. Arsenic was found to be an effective indicator element in pedogeochemical prospecting for gold, silver, cobalt and tungsten deposits, for which other indicator elements were not available at that time. Now, arsenic often serves as a valuable indicator for deposits of metals such as gold, silver, copper, lead, zinc, mercury, tin, molybdenum, tungsten, iron, cobalt, nickel and platinum. Certain types of uranium deposits, particularly those enriched in Ni–Co arsenides, are recognizable by their high arsenic concentrations. The aureoles of arsenic in the rocks adjoining gold veins in Rhodesia were investigated by James.[9] The arsenic content of unweathered rock collected from underground workings showed very marked pseudo-logarithmic decay curves extending into the wallrock from the shear zones (Fig. 3). In the Bell Mine, in which the surrounding country rock is sandstone, the aureole is only 8 m wide (Fig. 3A),


FREQUENCY
Elemental As
Alloys
Arsenides
100
50
5
13
34
61
100
23
1
7
2
Element
AtomicNumber
Group
H Li Be B C O (OH) H₂O F Na Mg Al Si P S Cl K Ca Ti V Cr Mn Fe Co Ni Cu Zn As Sr Y Mo Ru Rh Pd Ag Sn Sb Ba W Ir Pt Hg Tl Pb Bi U
1 3 4 5 6 8 9 11 12 13 14 15 16 17 19 20 22 23 24 25 26 27 28 29 30 33 38 39 42 44 45 46 47 50 51 56 74 77 78 80 81 82 83 92
Sulfides
Sulfosalts
300
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50
315
2
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2
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69
2
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1 1 1
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22
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10
47
Oxygen-containing compounds
except arsenites, arsenates,
and silicates
300
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80
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Arsenites
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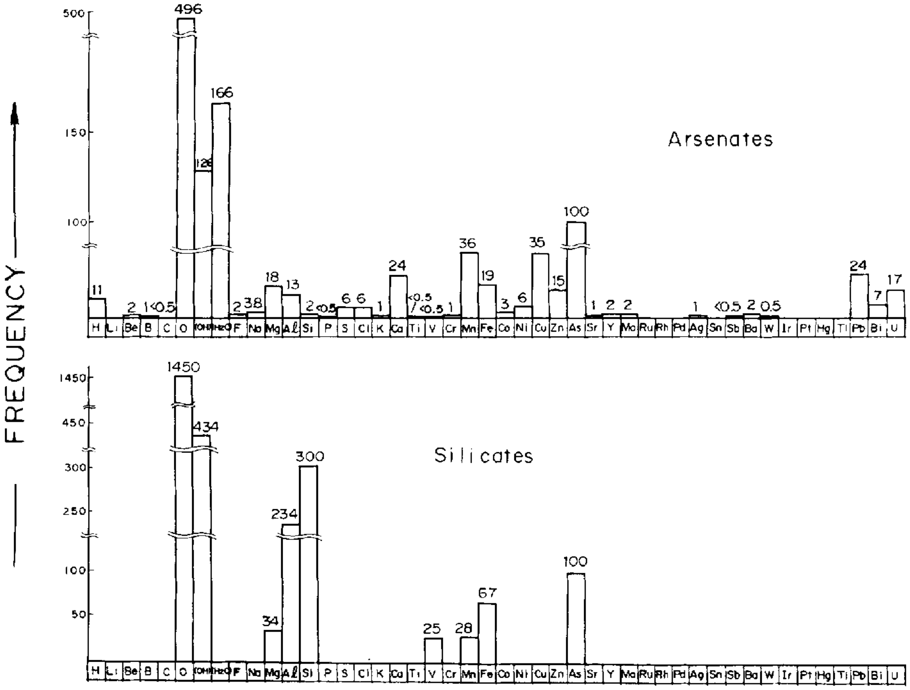


Example of freqcncy calculation: element, alloys arsenides

Native element, alloys, arsenides		As	Sb	Co	Ni	Cu	Ag	Fe	Pd	Pt
Arsenic	As	1								
Stibarsen (allemontite)	AsSb	1	1							
Modderite	CoAs	1		1						
Safflorite	$CoAs_2$	1		0.5						
Skutterudite	$CoAs_{2-3}$	1		0.4						
Langisite	$Co_{0.8}Ni_{0.2}As$	1		0.8	0.2					
Whitneyite	(Cu,As)	0.5				0.5				
Paxite	Cu_2As_3	1				0.67				
Domeykite	Cu_3As	1				3				
Novakite	$(Cu,Ag)As_3$	1				0.17	0.17			
Koutekite	Cu_5As_2	1				2.5				
Algodonite	$Cu_{6-7}As$	1				6.5				
Löllingite	$FeAs_2$	1						0.5		
Chathamite	$(Fe,Co,Ni)As_3$	1		0.11	0.11			0.11		
Nickeline (niccolite)	NiAs	1			1					
Rammelsbergite	$NiAs_2$	1			0.5					
Para-rammelsbergite	$NiAs_2$	1			0.5					
Chloanthite	$NiAs_3$	1			0.33					
Maucherite	$Ni_{11}As_8$	1			1.38					
Orcelite	$Ni_{<5}As_2$	1			2.5					
Oregonite	Ni_2FeAs_2	1			1			0.5		
Arsenopalladinite	$Pd_5(As,Sb)$	0.5	0.5						5	
Sperrylite	$PtAs_2$	1								0.5
		22.0	1.5	2.81	7.52	13.34	0.17	1.11	5.0	0.5
		100	6.8	13	34	61	0.8	5.0	2.3	2.3

Figure 2 Frequency of combinations of arsenic with other elements including OH and H_2O in arsenic materials.

Table 2 Arsenic concentrations (mg kg^{-1}) in igneous rocks

Rock type		Onishi[8]			Boyle and Jonasson[3]		
		Number of values	Range	Mean	Number of values	Range	Mean
Ultra-basic rocks	Periodotite, pyroxenite, dunite, kimberlite, etc.	19	0.3–3.0	1.0	40	0.034–15.8	1.5
	Serpentinite	8	0.8–6.6	2.8	—	—	—
Basic rocks	Extrusives (basalt, etc.)	113	0.1–9.0	1.4	78	0.18–113	2.3
	Intrusives (gabbro, diabase, etc.)	32	0.066–5.6	1.4	112	0.061–28	1.5
Intermediate rocks	Extrusives (latite, trachyte, andesite, dacite, etc.)	33	0.5–5.8	2.2	30	0.5–5.8	2.7
	Intrusives (granodiorite, syenite, diorite, etc.)	6	0.59–2.3	1.4	39	0.091–13.4	1.03
Acid rocks	Extrusives (rhyolite, pitchstone, etc.)	52	0.2–12.2	3.1	2	3.2–5.4	4.3
	Intrusives (granite, granodiorite, aplite, etc.)	148	0.0–8.5	1.9	116	0.18–15.0	1.29

Table 3 Arsenic concentrations (mg kg^{-1}) in sedimentary rocks

Rock type		Onishi[8]			Boyle and Jonasson[3]		
		Number of values	Range	Mean	Number of values	Range	Mean
Recent sediments	Stream, river, lake silts, etc.	—	—	—	9691	<1–13000	14.1
	Ocean sediments	30	<0.4–60.0	13.7	75	<0.4–455	33.7
Clastic sedimentary rocks	Shales, black shales, pyritic shales, etc.	—	—	—	75	<3–500	17
	Shale, argillite, slate, etc.	304	0.3–59	12.3	116	0.3–500	14.5
	Sandstone, arkose, conglomerate	(10)[a]	(0.6–9.7)	(2.3)	15	0.6–120	4.1
		98	—	15.5			
Chemical sedimetary rocks	Limestone, dolomite, etc.	37	0.1–23.5	3.5	40	0.1–20.1	2.6
	Iron formations, iron-rich sediments, etc.	—	—	—	45	1–2900	—
Evaporites	Gypsum, anhydrite, etc.	—	—	—	5	0.1–10	3.5
	Phosphorite	195	0.4–188	17.4	41	3.4–100	14.6

[a] 88 samples of Chinle formation, Colorado Plateau, USA, are excluded from the values in parentheses.

Table 4 Arsenic concentrations (mg kg^{-1}) in metamorphic rocks

Rock type		Onishi[8]			Boyle and Jonasson[3]		
		Number of values	Range	Mean	Number of values	Range	Mean
Sedimentary origin	Quartzite	40	2.2–70	6.4	4	2.2–7.6	5.5
	Slate, phyllite, etc.	32	0.5–70	16.5	75	0.5–143	18.1
Contact metamorphism	Hornels	1	0.7	0.7	2	0.7–11	5.9
	Skarn	6	5–20	11.0	—	—	—
Regional metamorphism	Schist	13	0.4–15	3.9	9	0.0–18.5	1.1
	Gneiss	4	0.5–2.2	1.3	7	0.5–4.1	1.5
	Amphibolite, greenstone, etc.	1	2.2	2.2	45	0.4–45	6.3

whereas in the Motapa Mine the aureole is almost 70 m wide in a greenstone country rock (Fig. 3B). This difference is probably related to the chemical reactivity and the permeability of the two rock types, and to the duration of the hydrothermal activity.

Geochemical prospecting using arsenic is being applied at several geothermal fields. Arsenic concentrations in rocks of the Fushime geothermal field, South Kyushu, Japan,[10] are shown in Table 5. The arsenic concentrations in the igneous and pyroclastic rocks are

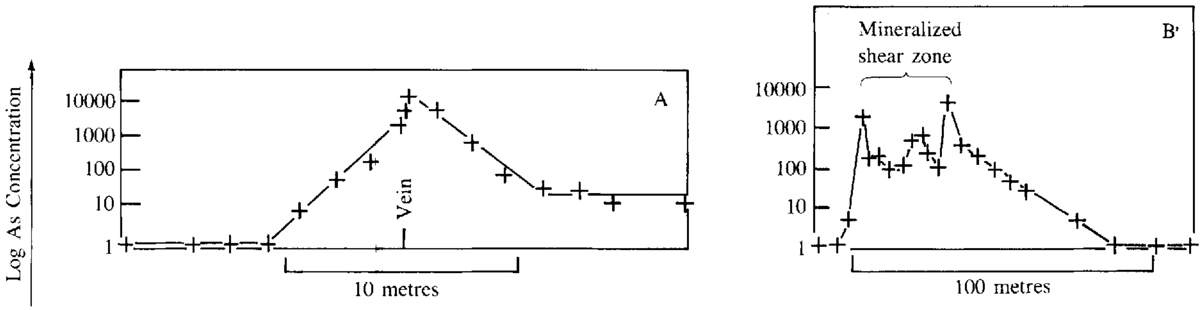


Figure 3 Wall rock aureole defined by the arsenic concentration in (A) sandstone adjoining a gold vein in the Bell Mine, Rhodesia, and in (B) a greenstone adjoining a mineralized shear zone in the Motapa Gold Mine, Rhodesia.[9]

Table 5 Arsenic concentrations (mg kg^{-1}) in rocks of the Fushime geothermal field, Japan[10]

Rock type		Number of values	Range	Mean
Recent sediments	Sand, gravel	2	3–4	3.5
Igneous rocks (extrusives)	Andesite lava	27	<1–102	15.5
	Dacite lava	24	<1–48	15.5
Igneous rocks (intrusives)	Porphyrite	7	10–74	29.1
	Granite, granite porphyry	12	<1–34	9.8
Pyroclastic rocks	Andesitic	35	<1–42	14.6
	Dacitic	55	<1–48	17.5
Sedimentary rocks	Sandstone, mudstone, siltstone	4	8–20	15.0

considerably higher than the average concentrations in rocks listed in Table 2. Hot water and hot gases, which are capable of transporting arsenic compounds, are probably responsible for the arsenic enrichment in the rocks of the geothermal field.

ARSENIC IN THE PEDOSPHERE

Arsenic concentrations in normal soils range from 0.1 to 55 mg kg^{-1} with an average of 7.3 mg kg^{-1} (Table 6) but vary considerably with location, parent material from which the soil was formed, soil type and degree of pollution. Arsenic tends to form in soils in well-defined secondary dispersion halos and trains in the vicinity of arseniferous deposits, particularly where iron-rich horizons are well developed. Arsenic concentration in soils in the vicinity of arsenic-containing deposits is naturally high and is most favorable for geochemical prospecting.

Arsenic in soils

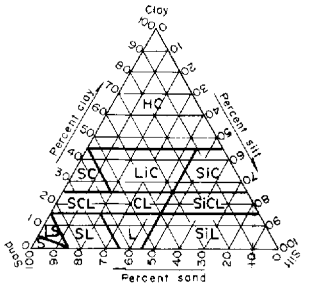
Arsenic concentrations in soils worldwide and in Japan are listed in Table 6. Soils formed from sedimentary rocks have higher arsenic concentrations than soils from igneous or metamorphic rocks, as expected from the arsenic concentrations in these rock types (Tables 2, 3, 4). Arsenic is generally enriched in the B horizon of most normal soils. This enrichment is caused by the strong sorption of arsenic by hydrous iron oxides that predominate in this horizon. In soils near arsenic-bearing deposits, marked enrichments were noted in the B and C horizons. The arsenic concentrations in the soil horizons near the Chitose Mine, Hokkaido, Japan,[14] are shown in Table 7.

Among soils used for particular purposes, orchard soils show the highest arsenic concentrations, no doubt because arsenicals were sprayed for insect or weed control. Arsenic concentrations in soils are not clearly correlated with soil character or clay content. The

Table 6 Arsenic concentrations (mg kg^{-1}) in soils

Soil type	Number of values	Range	Mean	Ref
Normal soils (worldwide)	327	0.1–55	7.2	3
Normal soils (worldwide)				3
A-horizon	25	1.5–9.6	3.57	
B-horizon	20	0.4–22	4.9	
C-horizon	10	0.4–11	4.0	
Soils near arseniferous deposits (worldwide)				3
A-horizon	8	20–1035	375	
B-horizon	8	190–2400	855	
C-horizon	3	98–1491	953	
Soils formed from: (Japan, 27 localities)				11
Igneous rocks (extrusive)	2	8.0–31.9	20.0	
Igneous rock (intrusive)	2	13.9–16.9	15.4	
Sedimentary rocks of volcanic ash origin	5	20.3–31.6	24.8	
Sedimentary rocks (clastic)	14	14.0–51.3	25.6	
Sedimentary rocks (chemical)	1	22.8	22.8	
Metamorphic rocks	3	10.9–25.8	16.9	
Average	27	8.0–51.3	23.2	
Soils formed from:				12
Andesite	4	3.8–10.6	7.7	
Sandstone	4	4.3–6.4	5.5	
Green and Black schist	4	6.0–16.4	10.8	
Soil horizons				13
L-horizon	0	—	—	
F-horizon	3	3.8–6.0	5.0	
H-horizon	3	6.4–7.7	6.8	
A-horizon	3	5.9–13.0	9.6	
AB-horizon	2	4.3–10.6	7.5	
B-horizon	1	16.4	16.4	
Soils				12
Plain	45	5.8–28.7	11.7	
Forest	58	0.44–53.4	9.4	
Orchard	213	tr–179	23.2	
Farm	58	2.1–54.7	12.1	
Ricefield	98	1.8–35.8	9.0	
Soils classified by textural class[a]				12
SL (clay 12.5–25.0%)	3	1.8–11.2	6.9	
L (clay 25.0–37.5%)	7	2.4–6.0	4.1	
SiL	1	14.2	14.2	
SCL	1	3.0	3.0	
CL (clay 37.5–50.0%)	6	3.4–9.6	6.9	
LiC	4	4.6–9.6	7.3	

[a] Textural class is defined by the triangular diagram:

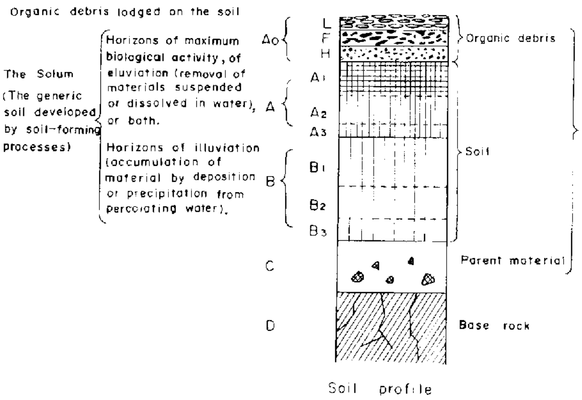


chemical forms of arsenic in soils have not yet been unequivocally identified. Koyama *et al.*[15] found that only a small percentage of the total arsenic in soils is soluble in water. Most of the arsenic appears to exist in the form of arsenates of calcium, aluminum and iron, in organic form, and in the form of other insoluble arsenic-containing compounds (Fig. 4). Calcium bis(dihydrogen arsenate) (extractable with 2.5% acetic acid), aluminum tris(dihydrogen arsenate) (extractable

Table 7 Arsenic concentrations (mg kg^{-1}) in soil horizons near the Chitose Mine, Japan[14]

Depth (cm)	Horizon[a]	Background[b]	Anomalous part (Above veins)
0			
10	A	12	12
20			
30	——		16
40			
50	B	14	18
60	——		
70			
80		10	56
90	C		
100		12	

[a] Horizon: See the diagram below (hypothetical soil profile showing the principal horizons).
[b] Background: soils far away from ore veins.



with 1 mol dm^{-3} sodium fluoride solution), and iron tris(dihydrogen arsenate) (extractable with 0.1 mol dm^{-3} sodium hydroxide solution) were suggested as the predominant arsenates, with iron arsenate the most and calcium arsenate the least important.

Geochemical prospecting using arsenic in the soils

Table 8 Arsenic concentrations (mg kg^{-1}) in unweathered rocks, weathered rocks, and soils formed from these rocks[16]

				Background (rock)	
Rock	Unweathered	Weathered	Soil	Range	Mean
Granite	1.8	1.7	40	N.D.[a]–5.3	1.8
Diabase	2.3	—[b]	10–110	N.D.–6.3	3.1
Shale	7.9	7.9	14–26	9.5–14	12
Slate	4.2	13	48	N.D.–22	9.4
Chert	7.2	—	12	N.D.–17	6.1

[a]N.D., not detected. [b]–, no data.

In general, heavy metals in ore deposits are dispersed to soils or weathered zones of rocks, mainly by the action of water. The arsenic concentration tends to increase during the weathering process,[16] with the lowest concentration in the unweathered rock and the highest in the soil (Table 8). Arsenic-based geochemical prospecting using soils is more frequently carried out than using rocks. As one of many examples, the results of a geochemical survey[17] using arsenic and silver for the Aokusa gold–silver vein deposit in the outer part of the Ikeno mining area, Hyogo Prefecture, Japan, are shown in Fig. 5. Both elements indicate clear anomalies associated with known veins such as the Sakura and Kanaya veins. The survey led to the discovery of new gold–quartz veins by drilling at the anomaly in the vicinity of the north-western front of the Sakura vein, proving the effectiveness of geochemical prospecting using arsenic in soils for gold–silver deposits.[17]

Pedogeochemical prospecting using arsenic is also carried out at some geothermal fields. For example, arsenic concentrations in soils of the Hachimantai geothermal field, North-Eastern Honshu, Japan,[18] are given in Table 9. Arsenic is enriched in the B and C horizons.

Table 9 Arsenic concentration (mg kg^{-1}) in soils of the Hachimantai geothermal field.[18]

Horizon[a]	Number of values	Range	Mean
G	1	9.91	9.9
A	22	2.51–21.82	7.9
AB	1	9.70	9.7
B	16	1.98–51.76	16.7
C	20	1.47–103.64	21.3

[a]Horizon: see footnote (a) of Table 7.

ARSENIC IN THE HYDROSPHERE, ATMOSPHERE AND BIOSPHERE

The migration of arsenic from the hydrosphere, pedosphere and atmosphere to the biosphere[3] is outlined in Fig. 6.

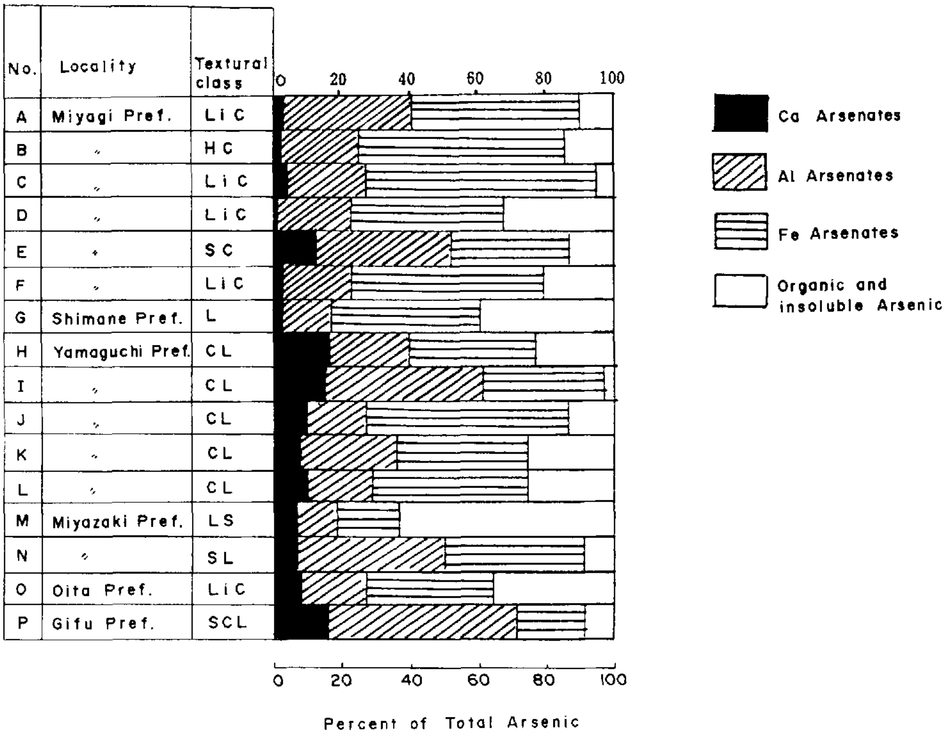


Figure 4 The forms of arsenic in Japanese soils.[15]

Table 10 Arsenic concentrations (μg kg^{-1}) in natural waters

	Onishi[8]			Boyle and Jonasson[3]		
Water type	Number of values	Range	Mean	Number of values	Range	Mean
Rain and snow	53	0.01–13.9	1.52	48	0.01–13.9	1.44
Normal stream, river	—[a]	0.2–25	N.C.[a]	88	0.25–22400	3.08
Normal lake waters	18	0.16–54.5	8.98			
Normal groundwaters	18	0.08–22	2.56	45	0.01–800	17.9
Groundwaters and mine waters near polymetallic sulfide deposit	—	—	—	102	3–400000	N.C.
Oilfield and other saline waters	7	0.00–243000	63.3	11	10–243000	N.C.
Hot springs	86	0.00–137000	847	92	0.2–40000	2090
Condensed water from volcanic gases	—	—	—	11	63–812	486
Spring waters; mainly cold carbonated waters in volcanic terrains	—	—	—	17	120–37500	22200
Spring waters depositing travertine	—	—	—	4	30–500	307
Thermal waters associated with epithermal mineral deposits	—	—	—	4	50–200	117
Ocean and sea	92	0.15–6.0	1.59	183	0.0056–11.24	2.57

[a]N.C., not calculated.

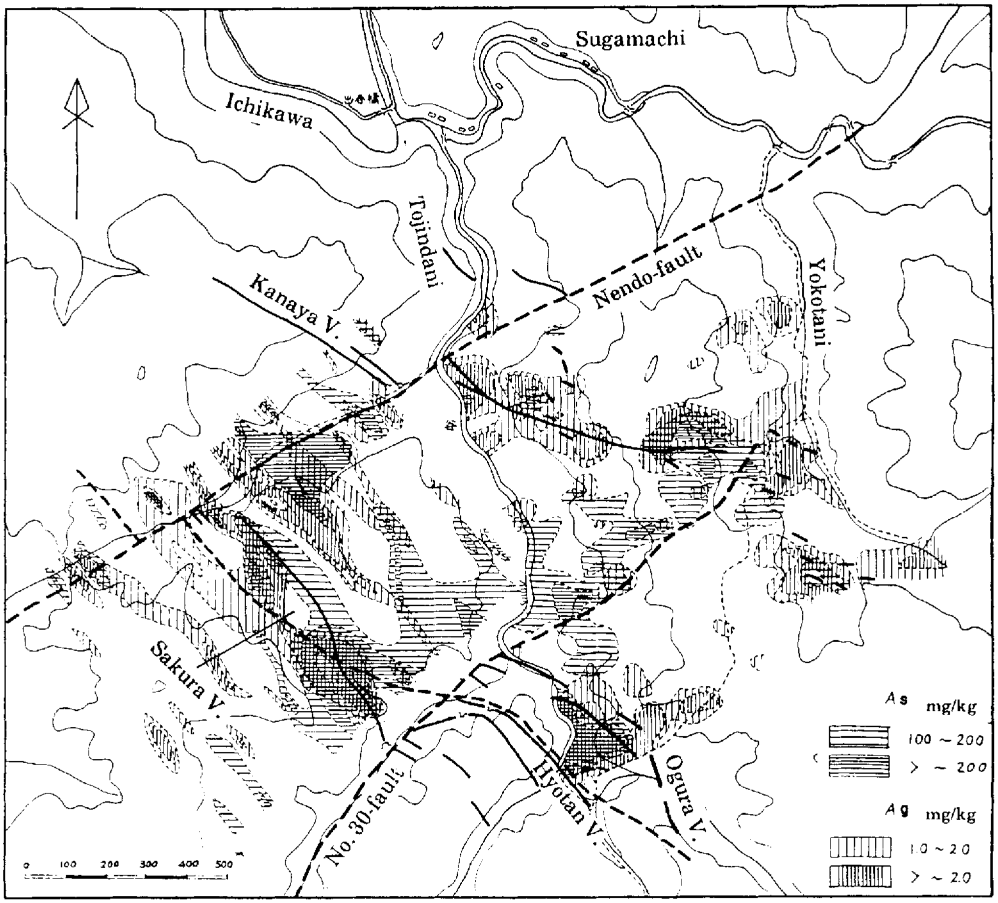


Figure 5 Pedogeochemical survey map of the Ikeno Mine area, Japan.[17]

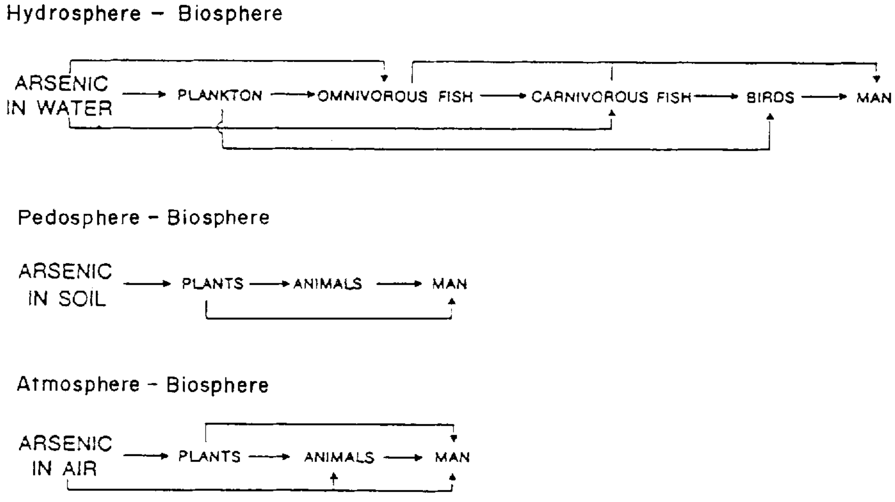


Figure 6 Transfer of arsenic from the hydrosphere, pedosphere and atmosphere to the biosphere.[3]

Arsenic in the hydrosphere

The concentrations of arsenic in rain, snow, rivers, lakes, groundwater and spring water are summarized in Table 10. In geothermal regions, arsenic appears to concentrate in river sediments and thermal waters. For instance, the arsenic concentrations in river sediments and thermal waters of the Nishi–Kirishima geothermal field, South Kyushu, Japan (Table 11) are at least 1000 times higher than in river water.

Watanuki *et al.*[20] reported a high correlation between pH and the negative logarithm of the arsenic concentrations in the waters of Tamagawa, Akita Prefecture, Japan. In these waters the arsenic does not precipitate from aqueous solution. Low arsenic concentrations are the result of dilution of arsenic-rich waters by arsenic-poor waters.

Table 11 Arsenic concentrations (mg kg^{-1}) in rivers, river sediments, hot springs and thermal waters of the Nishi–Kirishima geothermal field, Japan[19]

Sample	Number of values	Range	Mean
River water	8	N.D.[a]–0.004	0.001
River sediments	2	2.4–3.1	2.8
Hot spring water	3	0.009–0.69	0.236
Thermal water	3	3.4–7.9	5.2

[a] N.D., not detected.

Arsenic in the atmosphere

Arsenic in the atmosphere is mainly the result of human activities with minor contributions from active volcanic areas that emit gases rich in arsenic (Table 10). Bacteria acting on arseniferous compounds in soils and sediments[3] are known to form volatile arsines (arsine, methylarsines) that may escape into the atmosphere and contribute to its arsenic load.

Table 12 Arsenic concentrations (mg kg^{-1}) in plants and animals

Sample	Onishi[8]			Boyle and Jonasson[3]		
	Number of values	Range	Mean	Number of values	Range	Mean
Marine plants	7	1–12	3.6	7	1–12	3.7
Marine animals	20	<0.0036–50	11.88	62	0.002–50	5.85
Terrestrial plants	49	0–5	0.60	204	0.002–10	0.45
Phytoplankton, Columbia River	—	—	—	5	0.36–2.85	1.31
Terrestrial plants in areas without arseniferous deposits	—	—	—	8	3–100[a]	N.C.[b]
Terrestrial plants near arseniferous deposits	—	—	—	91	<1–10000	N.C.
Terrestrial freshwater animals	841	0.02–10.7	0.51	9	0.016–5.2	N.C.
Terrestrial land animals (mainly organs; wet weight)	—	—	—	173	0.001–10	N.C.

[a] Concentrations in the ash obtained from plant materials. [b]N.C., not calculated.

Table 13 Arsenic concentrations (mg kg^{-1}) in fossil fuels

Example	Onishi[8]			Boyle and Jonasson[3]		
	Number of values	Range	Mean	Number of values	Range	Mean
Coal	—	0–200	N.C.[a]	205	0.3–75	4
Coal ash	—	<80–10000	N.C.	650	5–8000	N.C.
Canadian (Nova Scotia) coal ash	—	—	—	7	<20–270	91
Petroleum	—	—	—	10	0.04–1.11	0.26
Petroleum	—	—	—	18	<0.003–0.188	0.100
Petroleum ash	—	—	—	13	Up to 10%	N.C.

[a] N.C., not calculated.

Arsenic in the biosphere

All plants and animals contain arsenic, but the concentrations are generally low (Table 12). Fossilized plant materials, especially coal, have relatively high concentrations of arsenic (Table 13). Much of the arsenic in coal is present in pyrite and occasionally in other sulfides such as arsenopyrite, marcasite and galena. Some arsenic is probably also present in organic form in certain types of coal.

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