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REVIEW

Geochemical Conditions Enhancing the Solubilization of Arsenic into Groundwater in Japan

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The geochemical behavior of arsenic-bearing groundwaters from four areas—Fukuoka, Kumamoto, Fukui, and Takatsuki—has been reviewed and considered from the viewpoints of the chemical composition of the water, the geological setting of the host formation, and the arsenic content in sediments and rocks. In all the areas except Fukui, arsenic-bearing water is concluded to have come from a specific aquifer during water–sediment interactions. Stagnant groundwater, having reducing and alkaline properties, played a significant role in the release of arsenic from such Quaternary sediments as silt–clay layers and brownish-colored gravel beds.

Keywords: geochemical; groundwater; arsenic; aquifer; wells; depth

INTRODUCTION

Recently, the detection of arsenic in drinking groundwater has attracted considerable attention in such areas as Fukuoka,[1] Kumamoto,[2] Fukui[3] and Takatsuki[4] in Japan (Fig. 1). Since the Ministry of Health and Welfare, Japan, revised the Water Quality Standard for Drinking Water Supply Act, effective after December 1993, which lowered the criterion of arsenic content from 0.05 to 0.01 mg l^{-1}, it is still possible that arsenic-bearing groundwater will be identified in other areas.

This work is a Review of reports on the behavior of arsenic-bearing groundwater in Japan, and is intended to assess natural environmental conditions enhancing the solubilization of arsenic into groundwater. Arsenic analysis was performed for both groundwater and sediment according to the method of the Japanese Industrial Standard. The method has hydride generation and atomic absorption spectrometry.

OCCURRENCE OF ARSENIC-BEARING GROUNDWATER

Case 1: Groundwater in the South Chikugo Plain, Fukuoka[1]

In the South Chikugo Plain, Fukuoka Prefecture, through which both the Chikugo River and the

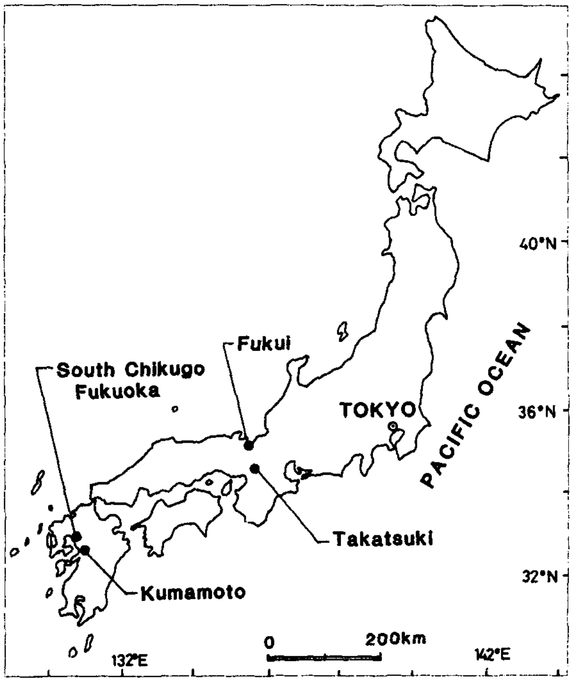

Figure 1 Localities of the arsenic-bearing groundwaters studied.

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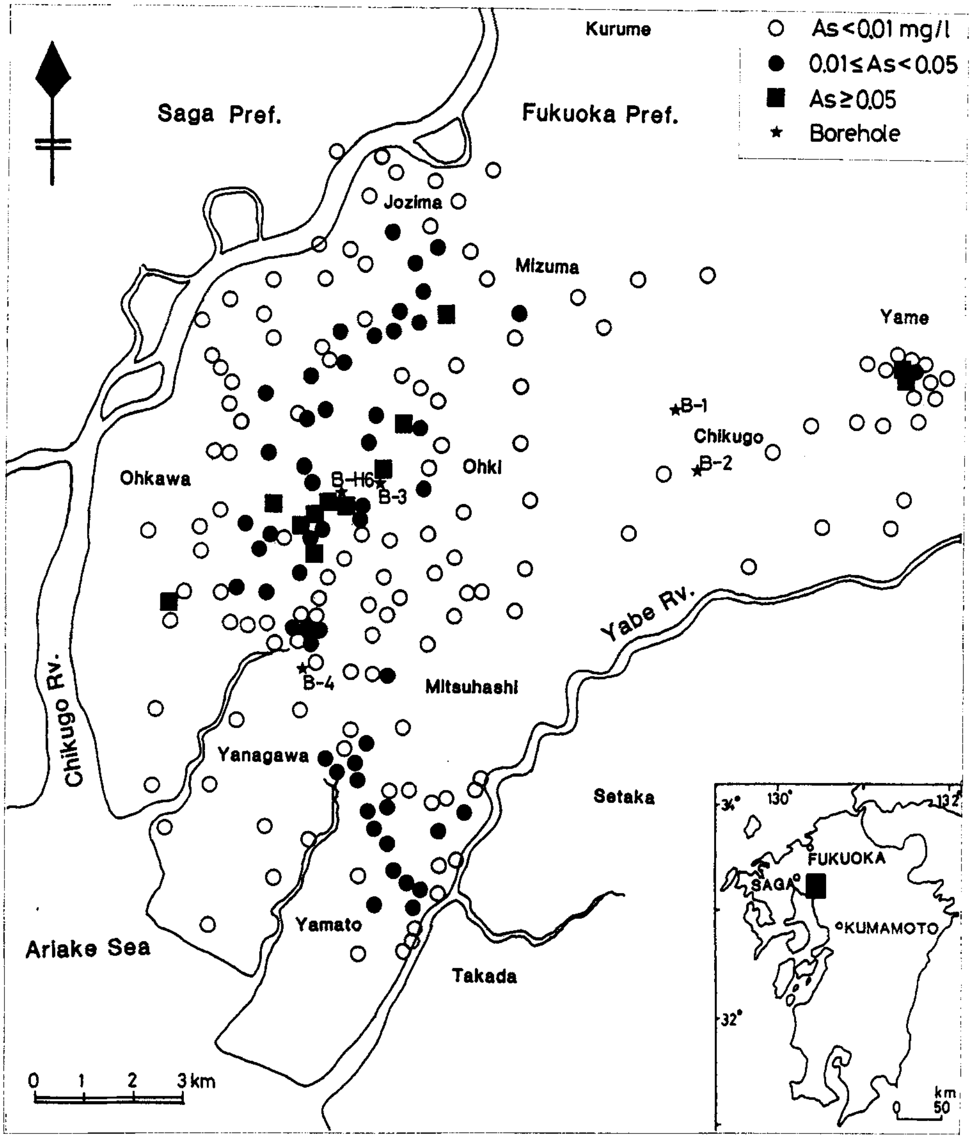

Figure 2 Distribution of wells in South Chikugo Plain, Fukuoka Prefecture (Case 1).

Yabe River meander before entering the Ariake Sea (Fig. 2), wells have been exploited for drinking and farming since about 1910.[5] It was in February 1994 when arsenic (0.01–0.19 mg l^{-1}) was first detected in groundwaters of Ohkawa. Since then, the number of wells whose groundwater has been chemicaly analyzed has rapidly increased and it attained 11 673 in October 1994. Among these, 22.6% of the wells were identified as containing more than 0.01 mg l^{-1} As. The maximum concentration showed the very high value of 0.37 mg l^{-1}. Figure 2 shows the distribution of representative wells in the area and the level of arsenic concentrations. The depth of wells in the area usually ranges from 15 to 60 m, and high arsenic concentrations were detected in wells of approximate depths as 30–50 m, as shown in Fig. 3.

Case 2: Groundwater in the Kumamoto Plain[2]

From 1989 to 1991, 22 wells in the southern part of Kumamoto City and such neighboring towns

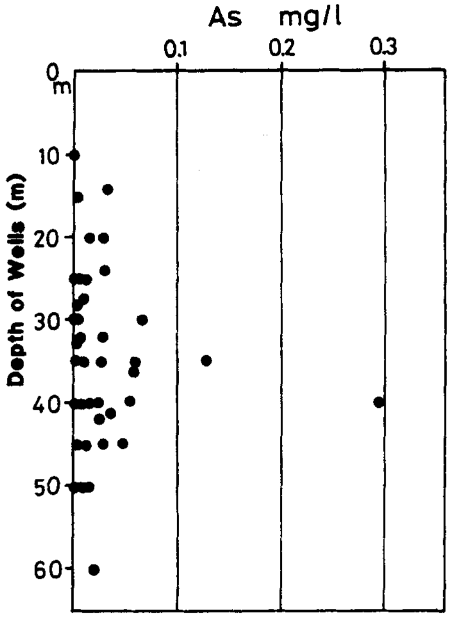

Figure 3 Arsenic concentrations versus depth of wells, in the South Chikugo Plain, Fukuoka (Case 1).

as Tomiai were demonstrated to contain fairly detectable amounts of arsenic in groundwater. They ranged from 0.005 to 0.066 mg l^{-1} As. The wells are distribued in an area of 20 km wide from east to west and 10 km long from north to south in the Kumamoto Plain. Among 46 wells whose depths are known to be from 5 to 110 m, 19 wells having depths of 30–50 m contain arsenic-bearing water (0.005 to 0.066 mg l^{-1}). It is noteworthy that the majority (54%) of arsenic-bearing wells have depths of 30–50 m, although deeper wells down to 110 m do not always contain detectable amounts of arsenic.

Case 3: Groundwater in Fukui[3]

Groundwater from 14 wells in the extreme western area of Fukui Prefecture have proved to contain arsenic ranging from 0.011 to 0.050 mg l^{-1} in 1990. The area is situated along the Sea of Japan coast, extending about 2.5 km east to west and 0.5 km north to south. The depth of each well has not been reported but they are believed to be shallow.

Case 4: Groundwater in Takatsuki

During periodic monitoring by the Takatsuki City authorities, substantial amounts of arsenic (0.011–0.060 mg l^{-1}) were detected in 1990 from 10 wells distributed in the eastern part of the city. The well depth varies from about 50 to 300 m. It was obvious that high arsenic concentrations were detected only from wells having slotted screens installed and having averaged depths of 49–68 m, as shown in Fig. 4.

CHEMICAL FEATURES OF ARSENIC-BEARING GROUNDWATER

Case 1

The chemical compositions of 67 representative samples of groundwater in the area are shown in the key diagram (Fig. 5A). The water was collected from March to May, 1994 and analyzed by the Fukuoka Institute of Health and Environmental Sciences.[1] The various types of water are defined as follows: Type I, non-calcium carbonate type (e.g. hot spring, fossil waters); II, calcium carbonate type (e.g. shallow and free surface groundwater, river water); III, sodium carbonate type (e.g. confined and/or stagnant groundwaters); IV, non-sodium carbonate type

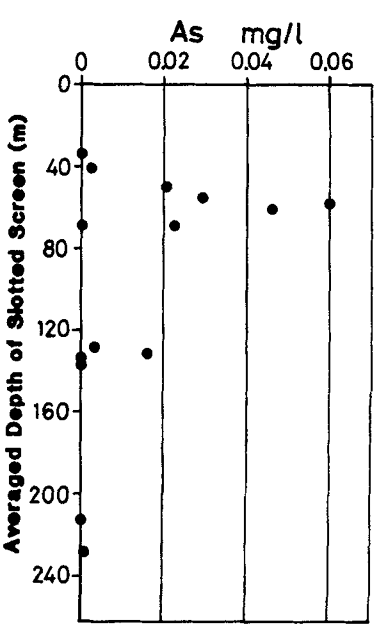

Figure 4 Arsenic concentrations versus average depth of slotted screens installed in the wells of Takatsuki (Case 4).

(e.g. seawater, brackish water); V, intermediate type. Arsenic-free water in the area is classified into Types II, III and V, but arsenic-bearing water (>0.01 mg l^{-1}) is closely related to Type III (water rich in Na^+ and HCO_3^- species) which generically presupposes stagnant groundwater. Statistically, no strong correlations have been observed between arsenic and other ions analyzed.

In order to clarify the sources of arsenic-bearing groundwater, borehole B-H6 was drilled in 1994 at a distance of 20 m from the well representing the highest arsenic concentration in the area (Fig. 2). As a result, six aquifers were confirmed to exist within the depth of 55 m, as shown in Fig. 6. Groundwater samples were obtained only from a specific depth using a pumping sampler and an inflatable packer in the borehole. During the process of boring, groundwater was sampled at 12 horizons, after checking continuously that pH, redox potential (E_h), electroconductivity, concentration of dissolved oxygen and water temperature were stable. This method entirely avoided the groundwater sample coming into contact with air. The groundwater temperature ranged from 17.7 to 21.4 °C.

It is remarkable that chemical compositions of arsenic-rich (>0.010 mg l^{-1}) groundwater in the fourth, fifth and sixth aquifers lie entirely in the field of Type III on the key diagram, and those of arsenic-free groundwaters in other aquifers are plotted in the field of Types II and V. Thus, Fig. 5(A) indicates not only water quality differences between arsenic-rich and arsenic-poor types, but also the depth difference of the acquifers. Beneath the fourth aquifer, pH values range from 7.2 to 8.0 and E_h values from +0.1 to −0.1 V. It is concluded that arsenic-rich water occurs only in deeper aquifers and is characterized by stagnant groundwater containing predominant Na^+ and HCO_3^- species.

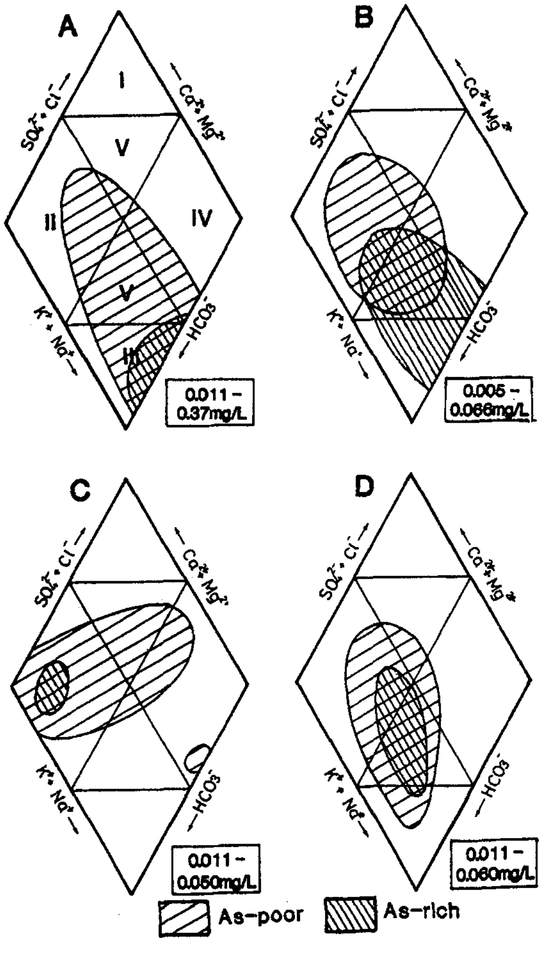

Figure 5 Key diagrams showing the chemical composition of groundwater. A, South Chikugo, Fukuoka (Case 1); B, Kumamoto (Case 2); C, Fukui (Case 3); D, Takatsuki (Case 4). The values in the boxes show the ranges of arsenic concentration. The Roman numeral indicates the classification of the water, as explained in the text.

Case 2

As shown in Table 1, the arsenic-rich water ($\geqq 0.005$ mg l^{-1}) has a tendency to have a higher pH, higher concentrations of Fe^{3+}, PO_4^{3-} and NH_4^+ ions, and lower NO_3^- ions compared with arsenic-poor water (As <0.005 mg l^{-1}).[2] When plotted on the key diagram shown in Fig. 5(B), the chemical compositions of the arsenic-rich groundwaters lie mostly in the fields of Types V and III. The arsenic-rich groundwater of Kumamoto has a simiar composition to Case 1.

Case 3

Representative analyses of the arsenic-rich (>0.010 mg l^{-1}) groundwaters are characterized by such major components as Ca^{2+}, Mg^{2+}, and HCO_3^-, having the ratio of $Mg^{2+}/(Na^++K^+)$ in meq $l^{-1}>1$, and lie in the field of Type II, while those of arsenic-poor groundwaters in other districts in the Fukui Prefecture lie widely within Types II, V and IV (Fig. 5C). From the key diagram, it can be seen that the arsenic-bearing water of Fukui originates in typical groundwaters in a shallow aquifer.

Case 4

Chemical compositions of arsenic-rich (0.011–0.060 mg l^{-1}) waters indicate that the concentrations of (Na^{+}+K^{+}) vary from 0.99 to 1.47 meq l^{-1} and those of Ca^{2+}+Mg^{2+} from 1.03 to 2.68 meq l^{-1}, while HCO_3^- concentrations (meq l^{-1}) comprise 56–74% of total anions.[4] The Mg^{2+} concentrations are always lower than Na^{+}, which is different from Case 3. On the key diagram, both arsenic-rich and arsenic-poor groundwaters lie completely within the same field as Types II and V (Fig. 5D). The pH values of the arsenic-bearing water ranged mostly from 5.9 to 6.8. The measured temperature of groundwaters in the area was 17.1 to 22.8 °C, showing no difference between arsenic-rich and arsenic-poor waters. From Fig. 4, the arsenic-rich groundwater is estimated to occur originally within a limited aquifer, although the depth of most wells ranges from about 50 to 300 m.

GEOLOGICAL SETTING

The geologies of the South Chikugo Plain (Case 1) and Kumamoto Plain (Case 2) are similar to each other, and consist of thick Quaternary sediments.

In Case 1, arsenic-bearing groundwater principally occurs in the fourth, fifth and sixth aquifers, which are within the Pleistocene Kawazoe Member (stratigraphic unit of subordinate rank, comprising some part of a formation), mainly composed of dark greenish gray- to brownish gray-colored alternate layers of gravel-bearing sand and semi-consolidated clay.[6] The Kawazoe Member is unconformably covered by the Nakabaru Formation which sometimes intercalates a thin layer of Aso-3 pyroclastic flow deposits

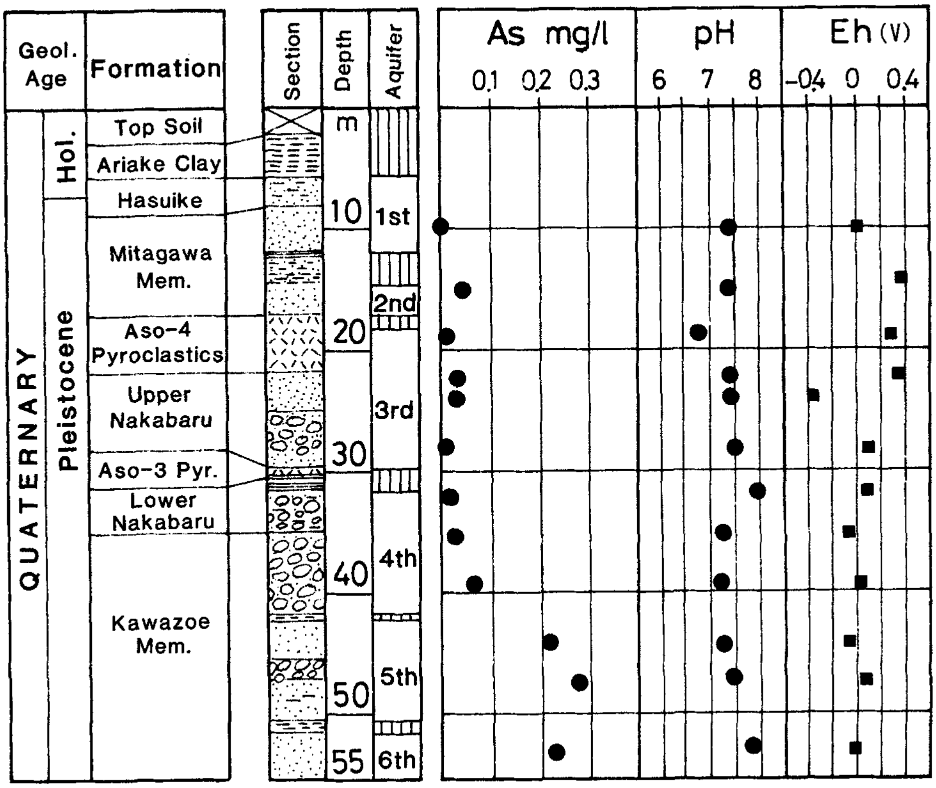

Figure 6 Columnar section showing geology of the B-H6 borehole, South Chikugo, Fukuoka (Case 1). The arsenic concentration, pH and E_h of groundwater collected at a specific depth of the aquifers are plotted.

Table 1 Compositon differences between arsenic-rich and arsenic-poor groundwater in Kumamoto (Case 2).[2]

	Groundwater content			
	As-rich ($n=46$)		As-poor ($n=54$)	
	Range	Av.	Range	Av.
pH	7.3–9.1	8.2	6.5–8.2	7.1
As[a] ($\mathrm{mg\,l^{-1}}$)	0.005–0.066	0.032	<0.005	0.001
Fe ($\mathrm{mg\,l^{-1}}$)	<0.03–1.3	0.58	<0.03–0.57	0.07
PO_4^{3-} ($\mathrm{mg\,l^{-1}}$)	<0.05–11	5.50	<0.05–11	0.50
NO_3^- ($\mathrm{mg\,l^{-1}}$)	<0.05–16	1.02	<0.05–52	10.20
NH_4^+ ($\mathrm{mg\,l^{-1}}$)	<0.01–1.08	0.12	<0.01–0.28	0.03

[a] Arsenic analysis for both groundwater and sediments were performed according to the Japanese Industrial Standards method, using hydride generation and atomic absorption spectrometry.

(1.2×10^5 years BP). Both Kawazoe Member and Nakabaru Formation are regarded as overbanked and fluvial deposits formed in the interglacial stage.[6] Thus it is plausible that iron hydroxides as weathered products were initially accumulated in the strata. In fact, the occurrence of 'Red Soil' beneath the Aso-4 pyroclastic flow deposit is widely known in North Kyushu.[7]

In Case 2, arsenic-bearing groundwater is considered to originate from the first aquifer emplaced in the marine silt and sand bed of the Shimabara Bay Formation of the Pleistocene, overlying the Aso-4 pyroclastic flow deposits (8.0×10^4 years BP).[2,8] Because the formation forms a nearly horizontal stratum filling a submerged valley, groundwater emplaced in the formation is inferred to flow extremely slowly.

In Case 3, an aquifer of arsenic-bearing groundwater may exist in Quaternary alluvial deposits, which are composed mainly of fluvial gravel and sand and also coastal dune sand. The basement consists of Yakuno Intrusive rocks (gabbro and diorite) and Ultrabasic rocks (peridotite and serpentinite), Triassic to Jurassic in age.[9,10] In the Ultrabasic rock body, a small nickel deposit in weathered parts of residual origin, which contained no arsenic minerals, had been mined in the 1940s.[10]

In case 4, most groundwater occurs in the Osaka Group, which is composed of Plio–Pleistocene marine and non-marine sediments and is divided into two formations, Senriyama and Ibaraki. The Senriyama Formation consists mainly of sand with several volcanic ash layers about 200 m in thickness, and is conformably overlain by the Ibaraki Formation. The Ibaraki Formation, more than 100 m thick, consists mainly of sand beds intercalating eight key beds of marine clay. The basement is made up largely of the Mesozoic formations (Tamba Terrane).[4]

ARSENIC CONTENTS IN HOST FORMATIONS

The arsenic contents in host formations of groundwater in the four cases aforementioned are summarized as follows. In Case 1, 80 samples from the drill hole core (B-1, B-2, B-3, B-4, and B-H6 in Fig. 2) range from 0.8 to 33 $\mathrm{mg\,kg^{-1}}$ as shown in Fig. 7. It is remarkable that samples of mud (clay and silt) and brownish to reddish brown-colored gravel contain higher arsenic concentrates than those of volcanic ash, sand and dark grayish-colored gravel. Brownish to reddish brown-colored gravel is filled and coated by goethite and/or amorphous iron hydroxide. In Case 2, the arsenic contents of the host formation of wells take a 4.2 $\mathrm{mg\,kg^{-1}}$ average, ranging from less than 0.5 to 20.6 $\mathrm{mg\,kg^{-1}}$. The arsenic contents of Case 3 were analyzed in rock samples of peridotite, slate and conglomerate cropping out in the area, and they show levels of <0.5, 14 and 12 $\mathrm{mg\,kg^{-1}}$, respectively. In Case 4, arsenic amounts in clay samples of the Osaka Group from a drill hole core range from 2 to 386 $\mathrm{mg\,kg^{-1}}$, taking an average of 148 ± 121 $\mathrm{mg\,kg^{-1}}$.

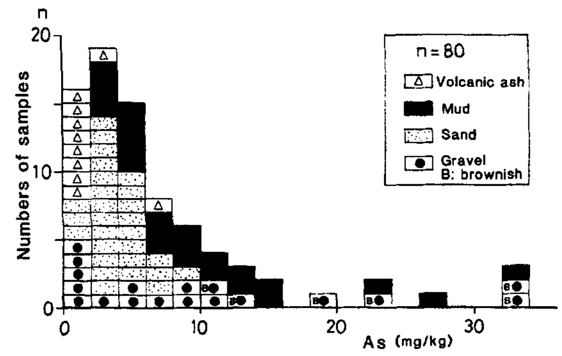

Figure 7 Histograms of arsenic contents in the drilled core from B-H6, B-1, B-2, B-3, and B-4 (Fig. 2) in South Chikugo (Case 1).

DISCUSSION AND CONCLUSION

Arsenic content in rocks and sediments

The average amounts of arsenic in the Earth's crust, granite and diabase are known to be 1.8, 0.5 and 1.9 ppm, respectively.[11] Terashima and Ishihara[12] reported 3.8 ppm as the average amount of arsenic in Japanese granitic rocks (310 samples). For sedimentary rocks, abundances of arsenic in shale, sandstone and carbonate rocks are reported to be 13, 1 and 1 ppm, respectively.[11] The arsenic content in the Shimanto Group of Cretaceous and Paleogene in Miyazaki Prefecture was 9.9±3.7 ppm in shale (21 samples) and 4.5±2.0 ppm in sandstone (13 samples).[13] The Tertiary sedimentary rocks (300 samples) composing the hanging wall and foot wall of a coal bed in 12 Japanese coal basins show the arsenic content to be from 0 to 280 ppm, while coal itself (less than 30% ash component) contains from 2 to 64 ppm.[14, 15]

Comparing these values with those in the four cases, it can be pointed out that in those areas above there are neither unusual rocks nor sediments which contain abnormally high arsenic contents. In any case, clastic sediments and rocks such as dark-colored clay–silt and black shale tend to contain relatively high arsenic levels. This can be due to the large cation-exchange capacities of the clay minerals contained there, while Mok and Wai[16] regarded suspended fine particles in water to be good scavenging agents for arsenic.

Source of arsenic in groundwater

From the fact that arsenic-rich groundwater occurs in wells distributed over a very wide area (up to 75 km^2, Case 1) and is also found in deeper aquifers bearing stagnant water, and the fact that no sediments containing abnormal amounts of arsenic have been found, arsenic is considered to be a component dissolved from the host formation into groundwater, but not necessarily from anthropogenic sources. Other cases (Cases 2, 3 and 4) also support this as a natural phenomenon for similar reasons to Case 1.

In Cases 1 and 2, it is concluded that considerable amounts of arsenic species adsorbed on both iron hydroxide minerals in gravel layers and clay minerals in clay–silt layers (which had been formed during the sedimentation period) were easy to solubilize when the formations encountered stagnant groundwater under reducing and faintly alkaline conditions. Furthermore, in Case 2, the high concentrations of competing anions such as PO_4^{3-} for precipitation play an important part in releasing and solubilizing arsenic from the sediments into the overlying water.[16]

In Case 3, although detailed chemical compositions of the groundwater have not been reported, the water quality appears to be quite different from the other cases (Fig. 5C), so that there may exist other factors controlling the solubilization of arsenic. Further study is required, especially on the arsenic content in various sedimentary featues of the alluvial sediments, because the arsenic-rich water is considered to have originated during water–sediment interactions. Generally, along such beach sand dunes as in this case, it is probable that a peat or black-mud layer such as backmarsh (which is suitable for the sorption and solubilization of arsenic) will be found in the sediment.

In Case 4, the mechanism of arsenic solubilization is assumed to be the same as that in Cases 1 and 2, becuase the arsenic contents in the host are very high. The arsenic contents in samples of the host formations vary widely from 2 to 386 mg kg^{-1}, so that such analyses will be a great help in solving the arsenic solubilization questions, as they will provide more detailed descriptions of sedimentary features and constitutional analyses for clay minerals, iron hydroxides and organic matters contained therein.

Factors controlling the sorption and solubilization of arsenic

Figure 7 shows that goethite- and amorphous iron hydroxide-bearing brownish gravel contains a relatively high arsenic content. This fact coincides with the experimental result that the adsorptive capacity of amorphous iron hydroxide is very high for arsenic.[17] As shown in Fig. 8, iron hydroxide is stable in the oxidizing conditions in the pH range 6 to 8, found commonly in groundwater. As redox potential is considered to be the most important factor for arsenic adsorption on to iron hydroxide, groundwater samples from a specific aquifer at B-H6 (Case 1) are plotted in Fig. 8. As the total dissolved iron concentrations range from 2×10^{-4} to 1×10^{-5} mol l^{-1}, most arsenic-bearing water

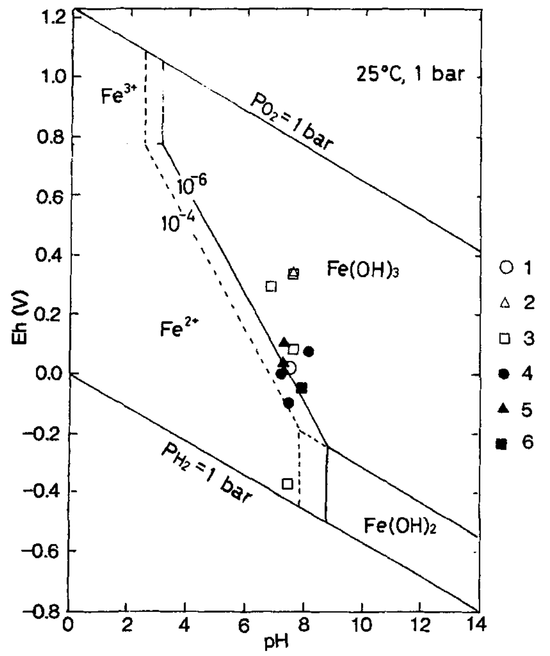

Figure 8 E_h–pH diagram for the system Fe–O–H.[19] Assumed activity of total dissolved iron = 10^{-6} and 10^{-4} mol l^{-1}. The numbers 1 to 6 correlate with those of the first to sixth aquifers, respectively.

samples are plotted in the field of $Fe(OH)_3$ at 25 °C and 1 atm. However, due to the slow kinetics of the Fe^{2+}–$Fe(OH)_3$ transformation aqueous iron species exist in thermodynamically metastable states, implying that coprecipitation of arsenic species with iron hydroxide is obstructed by the presence of anions like PO_4^{3-}.

In an investigation of arsenic concentrations in the groundwater of Sendai City, Kaneko[18] showed that the most important factor for arsenic solubilization from the sediment is the change of pH from 6 to 9, on the basis of a leaching experiment with arsenic-adsorbing iron hydroxide. However, it is clear from Fig. 8 that the redox potential in groundwater entirely controls an area of predominance of each iron species, which largely affects sorption and solubilization of arsenic species. According to Mok and Wai,[16] solubilization of arsenic from sediments is controlled by pH, E_h and arsenic concentration in the interstitial water of sediments, as well as by changes in the total iron, extractable iron, extractable manganese, mineral oxides and hydroxides.

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