Chemical evolution of groundwater quality in the southern foot of Mount Fuji

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IKEDA, K. (1989) Chemical evolution of groundwater quality in the southern foot of Mount Fuji. Bull. Geol. Surv. Japan, vol. 40(7), p. 331-404.

Abstract: This study was conducted in an area at the southern foot of Mt. Fuji in Shizuoka Prefecture, Japan.

The aim of the study is to clarify the relation between the chemical constituents in groundwater and the lithology of aquifer, as well as the relation between the groundwater flow in an aquifer and the changes in chemical composition of groundwater by means of field surveys and laboratory experiments. This is based on the assumption that the formation and evolution of groundwater quality reflects the three-dimensional distribution and flow of groundwater.

The surveyed area covers a land area of approximately 180 km² extending from the slope area of the southern foot of Mt. Fuji to the coastal lowland facing the Suruga Bay. Ejecta of Old-Fuji, New-Fuji and Ashitaka volcanoes are distributed in the area. In the coastal plain these layers are covered with fluvial deposits of the Fuji River. Up to 103 samples of ground-water from each layer were analyzed. Also, laboratory experiments on the water-rock interaction were conducted for 11 samples from outcrops or drilled 'cores of Fuji and Ashitaka volcanoes. These experiments are conducted for clarifying the relation between the aquifer lithology and the groundwater chemistry, as well as the relation between the duration of water-rock contact under specific conditions and the concentrations of chemical constituents.

Groundwater in each layer contains bicarbonate of Ca^{2+} , Mg^{2+} , Na^+ and K^+ , and is characterized by K/Na ratio, Na/SiO₂ ratio, SiO₂ to total cation ratio and SO₄/Cl ratio, which differ from one aquifer to another. This groundwater character is a result of the water-rock interaction which reflects the physical and chemical property of aquifer rocks. The results of the laboratory experiments on the water-rock interaction also corroborate this. These results indicate that the groundwater quality can be used for the classification of aquifer system.

The anion which resulted from the water-rock interaction is mostly HCO_3^- . The patterns of groundwater flow were examined by a distribution chart of the HCO_3^- concentrations in groundwater in aquifer on the assumption, that the HCO_3^- concentration in groundwater is related to the duration of water-rock contact. The groundwater flow patterns estimated from the HCO_3^- concentration were conformable to hydrological data such as the distribution of hydraulic head and specific capacity.

In the laboratory experiment on the water-rock interaction, too, the total contents of dissolved solids and the concentration of HCO_3^- were expressed as a function of a logarithm of the period of contact time. This relationship indicates that the groundwater flow in an aquifer can be traced by its chemical composition.

Salinization of fresh groundwater in volcanic ejecta was observed in the coastal area of the district. The salinization of groundwater is closely related to the draw-down of the groundwater level. It appears to have been caused by sea water intrusion, which occurred in accordance with Ghyben Herzberg's law and as a result of the reversal of hydraulic gradient which was caused by a large scale draw-down to below the sea level in the inland area.

The oxygen and hydrogen isotopic composition for 12 samples of typical salinized groundwater suggests that salinization has been caused by sea water intrusion. But all samples of salinized groundwater showed a Ca-Na-Cl type chemical character and contained

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Bulletin of the Geological Survey of Japan, Vol. 40, No. 7

remarkably more Ca^{2+} than the calculated value assuming the simple mixing of sea water and groundwater. Laboratory experiments showed that these chemical characteristics resulted mainly from the cation exchange reaction between sea water and geological materials.

The velocity of the salt water flow entering the aquifer was calculated on the basis of the changes of the Cl⁻ concentration. The velocity of the salt water in the New Fuji lava aquifer was calculated as 11 meters per day. On the other hand, the velocity of the groundwater flow in the same aquifer was calculated on a hydrological basis using the hydraulic conductivity, hydraulic gradient, and effective porosity. Calculated velocities were 5.0-10.1 meters per day. Both of these calculated values are reasonably close, and this seems to indicate that the mechanism of groundwater flow is conformable to hydrological interpretation based on Darcy's formula.

It can be conducted that the study of the process of the formation of and the change in groundwater quality are a successful way to clarify the hydrological phenomena, such as flow and mixing of water, and to identify the complex of groundwater systems.

1. Introduction

1.1 Previous Studies

In groundwater hydrology, the groundwater quality is thought to be a key to investigate the groundwater flow system, especially in respect to flow and stagnation of groundwater.

The concept that the groundwater qualicorresponds to the geochemical tv character of water-bearing sediments was set forth by MOORE (1949). He maintained that the chemical process between the rocks and minerals in aquifer affects the groundwater quality, and defined "hydrochemical facies" as water quality, which reflects the geochemical character of water-bearing sediments.

SEABER (1962), MORGAN and WINNER (1962), BACK (1966) and others classified the groundwater in New Jersey, Louisiana and New Jersey Atlantic coastal area on the basis of the hydrochemical facies. They showed a possibility to distinguish groundwater flow systems on the basis of the quality of groundwater.

As regards the groundwater chemistry changes with depth or along flow path, SUGISAKI and SHIBATA (1961) conducted a study in the Nobi Plain in Japan. In their study of the groundwater quality from the upper to lower reaches, the change in groundwater quality due to flow is characterized by the increase in the concentration of HCO_3^- to total anion ratio and the Na⁺ to total cation ratio. A similar result was obtained by BACK (1966) conducted in the Atlantic coastal area and by KURATA *et al.* (1958) conducted in the eastern Tokyo area. These studies indicate that the change in water quality can be expressed by means of a key diagram and that water quality changes from the Ca-HCO₃ type to the Na-HCO₃ type and in some cases, to the Na-Cl type in the coastal area influenced by salt water.

These results show that increase of bicarbonate and consequent cation exchange reaction can be chemical indicators of the groundwater flow in Quaternary sediments. Other studies indicate that the change in the water quality during the groundwater flow is accompanied by the decrease in concentrations of SO_4^{2-} and $NO_{\overline{3}}$ as a result of reduction and so on. This reflects the reducing environment of an aquifer (FOSTER, 1942). Furthermore, the SO_4/Cl ratio decreases during a flow of groundwater through a reducing environment.

As to the groundwater quality in sediment layers, the tendencies of the change in water quality have so far been clarified to some extent. But their theoretical substantiation is still insufficient. On the other hand, the study of the origin of the chemical constituents in groundwater is thought to form the base of the study of the formation of groundwater quality. GARRELS and CHRIST (1965) formulated a system of chemical thermodynamic theories of chemical equilibrium, solubility, complex ion effects. etc. which are related to the reactions of minerals and water under conditions of low temperature low pressure near the earth's surface. These studies are thought to have provided an important suggestion to the formation of the quality of natural water.

FETH et al. (1964) analyzed the groundwater in granite areas in California and Nevada, and pointed out that the chemical constituents in groundwater originate from the weathering products, which are produced when the minerals composing granite weather and are altered into kaolinite and montmorillonite. GARRELS and MACKENZIE (1967)provided а stoichiometric explanation for the mechanism of formation of Ca²⁺, Mg²⁺, Na^+ , K^+ , SiO_2 in water and so on, using an assumptive equation for chemical reaction for weathering of the water containing CO_2 and typical minerals in igneous rocks in the groundwater in the same areas.

These chemical reactions for weathering occur when CO₂ is dissolved in water. Accordingly, in a closed system it is expected that, as the chemical reaction for weathering progresses, the amount of CO_2 will decrease and pH value will increase. Eventually, however, the water-rock interaction will reach an equilibrium state. ICHIKUNI et al. (1982) studied alkaline mineral spring water and as a result made clear that mineral spring water has reached an equilibrium state of the water-rock interaction. And they assumed that, in this stage, montmorillonite is formed in connection with the water rich in SiO_2 and Ca^{2+} with a high pH, and kaolinite-montmorillonite system reaches its equilibrium. This concept appears to have provided an important suggestion concerning the condition for the formation of water quality in situations where groundwater keeps contact with rocks for a very long time.

In the manner of Garrel's way of thinking the chemical character of rocks and minerals, which are in contact with groundwater, plays an important role in the formation of groundwater quality. The change in water quality during the groundwater flow is probably due to the increases in ion concentration of the reaction product and pH value.

Apart from the above-mentioned change in water quality in the natural system, sometimes there occurs a change in water quality as a result of intrusion of a different water which has a different quality. A typical example of this phenomenon is the salinization of groundwater which accompanies an artificial drawdown of the groundwater level. In Japan, this phenomenon is often observed in coastal areas (MURASHITA, 1982). Generally. this phenomenon is closely related to the decline of the hydraulic head of groundwater and it is expected as a result of sea water intrusion, but in fact the salinized groundwater does not show water quality of the mere mixture of groundwater and sea water (IKEDA, 1967). This means that this phenomenon involves problems which cannot be solved on the basis of analysis of water quality of such a mixture alone. In fact, isotopic studies of this phenomenon have been conducted (ANDO and IKEDA, 1980; IKEDA and ANDO, 1980).

1.2 Objectives of the Study

The study of groundwater quality started with qualitative evaluation of groundwater as a water resource. Then the concept of the evolution of water quality was introduced in this field of study and attempts were made to assume reaction of groundwater upon geological materials. Studies by GARRELS and MACKENZIE (1967), WALLICK (1981) and ICHIKUNI *et*

Bulletin of the Geological Survey of Japan, Vol. 40, No. 7

al. (1982) discussed the groundwater quality as a result of the water-rock interaction. The results of their studies are highly suggestive as to the change in groundwater quality, when the water-rock interaction reaches its equilibrium state. But these arguments are not directly related to hydrological phenomena.

Although it is considered very important to study the formation of groundwater quality by relating it to the hydrological cycle, it appears that studies conducted along this line are too scarce. This is because the water-rock interaction still has many aspects which remain to be clarified. The chemical reactions in which the chemical constituents in rocks are dissolved in water are affected by the complicated mechanism of weathering of rock-forming minerals, as well as the cation dissolution, e.g. Ca²⁺, and its partly recombination with weathering products.

In this study, the formation of groundwater quality in relationship to the waterrock interaction was examined through field surveys and laboratory experiments. Its objective is to verify the hypothesis that the direction and degree of the evolution of groundwater quality correspond to the flow and behavior of groundwater as it moves from the recharge area to the discharge area. The evolution of groundwater quality chemically means the approach to an equilibrium state during the flow in a continuous aquifer. It is possible, therefore, to argue about the correlation of aquifers based on the continuity of the changes in groundwater quality and about classification of aquifers, which reflect the chemical properties of aquifer rocks, on the basis of the findings of this study.

The phenomenon of contamination by salt water, which is often observed in coastal areas of Japan, causes serious problems and has to be investigated by means of hydrogeological methods. To clarify the origin of salt water and the mechanism of salinization, it is necessary to consider such problems as the water-rock/sediment interaction. Unfortunately, thus far no study has been conducted to consider such problems.

This study was conducted for the purpose of examining the relationship between the groundwater cycle and the groundwater quality through analysis of the formation of groundwater quality, which includes the problem of salinization of groundwater, and clarifying the above-mentioned hydrological phenomena through analysis of the groundwater quality. For this purpose, the process of the formation of groundwater quality was studied in a volcanic area in Japan, extending from the southern foot of Mt. Fuji to the coastal plain, where many geological, lithological and hydrological studies, including those on the recharge and discharge areas, have been conducted.

Groundwater at the southern foot of Mt. Fuji is recharged directly by the precipitation at Mt. Fuji, Mt. Ashitaka and their environs. The recharged groundwater flows through the lava or the volcanic gravel, ejected from Mt. Fuji and Mt. Ashitaka, both of which range under the alluvial plane extending from the southern foot of Mt. Fuji to the coast. The chemical constituents in this groundwater include a relatively small quantity of chemical species, stemming from the rainwater and the chemical constituents which were dissolved in groundwater as a result of the water-rock interaction in volcanic ejecta. Since many lithological studies of volcanic ejects have already been published, it is possible to interprete the relationship between the formation of groundwater quality and the hydrological environment in its ideal form.

In this area, the phenomenon of salinization of groundwater has been observed since 1960's. Since a large amount of data on the quality of the groundwater in this area is available as a result of the groundwater quality research work conducted at the initial stage of salinization, the characteristics of the salinized groundwater and the mechanism of the formation of groundwater quality could be examined sufficiently on their basis. The results of the laboratory experiments on water-rock/ sediment were also examined in conjunction with the above mentioned investigation.

2. Description of the Study Area

The area investigated in this study is the Fuji area in the Shizuoka Prefecture, a central part of Japan. This area consists of a gentle slope at the southern foot of Mt. Fuji facing the northern coast of the Suruga



Fig. 1 Location of the study area, contours are at 100 m interval.

-335-

Bay and a lowland along the Suruga Bay extending southward. It covers a land area of approximately 180 km².

2.1 Topography

Figure 1 shows the outline of the geographical features of this area. This area is broadly divided into a gentle slope spreading between Mt. Fuji and Mt. Ashitaka and a lowland. The lowland is subdivided into an alluvial fan, a coastal sand dune and a swampland. The alluvial fan was formed by the Fuji River which rises at the western edge of the lowland and runs southward, and the Urui River, which rises at the southwestern foot of Mt. Fuji. It inclines from northwest to southeast with a gradient of approximately 1/500. The coastal sand dune at the mouth of the Fuji River extends from east to west along the coastline. It is about 10 meters high above sea level. The swampland, located at the eastern side of the Wada River, is a back marsh between the foot of Mt. Ashitaka and the coastal sand dune, with a width of 2 km and a height of 0.5 to 2.5 meters. It is called Ukishimagahara.

The rivers in this area include the Fuji River which runs southward along the western edge of the area, the Urui River which runs southeastward in the western part of the area, and two small rivers—the Wada River and the Taki River—which rise in the central part of the area and run southward. Also, between Mt. Fuji and Mt. Ashitaka runs the Akabuchi River, which meets the Wada River and the Taki River and then flows into the harbour of Tagonoura. All these rivers flow into the Suruga Bay.

The harbour of Tagonoura is a dug-in harbour, facing the mouths of the Urui River and the Numa River (Fig. 1).

The gentle slope at the southern foot of Mt. Fuji is covered mainly with lava. The northern edge of the study area has a height of 200 to 800 meters. It inclines at a gradient of about 3/100 and borders on the

lowland at its southern end. Many eroded landforms, resulting from erosion by rainwater and snowmelt water are seen in this area (TSUYA, 1971). The Tenmazawa (a valley), the Dempo Zawa and other valleys which spread from the northern edge of the area to the southwest are valleys formed through erosion by water. At the lower course of these valleys are fans.

2.2 Hydrogeology

As shown in Table 1, the basement of the study area belongs to the Misaka group (Miocene), on which Fuji and Ashitaka volcanoes were formed.

The Fuji Volcano consists of the Old-Fuji Volcano, formed in the Pleistocene, and the New-Fuji Volcano, erupted in the Recent epoch, and covers the former (TSUYA, 1971).

Deposits of the Old-Fuji Volcano are of basaltic composition and mostly appear as volcanic mud flows, layers of volcanic sand and gravel and pyroclastic rocks, such as breccia. Some part of its mid-slope contains lava layers.

The Old Fuji's volcanic mud flow deposits consist of volcanic blocks, ash and sand. It was generally thought that the volcanic mud flow deposits are impermeable (TSUYA, 1971). In fact, the spring water of the Wakitamaike Pond in Fu-

| Table 1 | Stratigraphic units of the southern part |
|---------|--|
| | of Mt. Fuji area. |

| | | Chiefly fluvial deposits of | Fuji River |
|-------|-------------|-----------------------------|------------|
| | Description | New Fuji volcano ejecta | upper |
| гу | Recent | - | middle |
| cerna | | | lower |
| puant | | Old Fuji volcano ejecta | |
| Ø | Distance | Ashitaka volcano ejecta | upper |
| | Pleistocene | - | middle |
| | | _ | lower |
| gene | Pliocene | (Iwabuchi volcanics) | |
| Neo | Miocene | Misaka formation | |

Chemical evolution of groundwater quality (K. Ikeda)



Fig. 2 Generalized geologic map of the study area. Circles show the location of observation wells.

jinomiya at the southwestern foot of Mt. Fuji and that in Sugita and Ishihara spring out from the boundary surface between the agglomeratic mud flow and the New Fuji lava above it (Fig. 2). Since 1970, however, it has been made clear that there exists a large quantity of groundwater in the Old Fuji's deposits under the black soil layer beneath the New Fuji's lava at the southern foot of Mt. Fuji and in the lowland.

As shown in Fig. 2, in the study area only a part of the Old Fuji's volcanic mud flow is exposed and most part of it is covered with the New Fuji's lava, which is divided into older, middle and younger lava by TSUYA (1971). The New Fuji's lava in the study area belongs to the older basaltic lava.

The New Fuji's lava has many joints and cracks, as well as caves formed during its solidification, which serve as good paths for groundwater (KURATA, 1966; MURASHITA and KISHI, 1967; YAMAMOTO, 1971).

Mt. Ashitaka is a volcano consisting of layers of pyroclastic material. These ejecta

Bulletin of the Geological Survey of Japan, Vol. 40, No. 7



Fig. 3 Geological sections along A-A', B-B' and C-C' lines.

are broadly classified into a basalt layer and an andesite layer. No wells have been bored at the foot of this mountain and accordingly, no data available about the groundwater in this area. Topographically, however, it is certain that Mt. Ashitaka is one of the most important groundwater recharge areas in the study area. To investigate the groundwater in the study area, therefore, this fact must be taken into account.

Figure 3 shows the geological sections at A-A', B-B' and C-C' (in Fig. 2), based on

the geological columnar sections. The lowland is composed mainly of river sediments of the Recent epoch of the Fuji River and the Urui River. At its northwestern end, the low land has the form of a fan, where coarse sands and gravels are abundant. As it approaches the harbour of Tagonoura, sand and clay become more abundant.

The alluvium is underbedded by the volcanic ejecta of Mt. Fuji and Mt. Ashitaka. The Fuji lava is distributed beneath the lowland between the Fuji



Fig. 4 Well log cross sections at the slope area of Mt. Fuji. Number are shown in Figure 2.

- 339 -

River and the Wada River at a gradient of about 3/100. Near the habour of Tagonoura its surface is about 100 meters deep. The lava layer has either a single layer or 2 to 3 layers with volcanic ash and gravel between them. Its whole thickness ranges from several meters to 40 meters.

The New Fuji lava is underbedded by the volcanic ejecta of the Old Fuji. At the lowland, the black soil layer is referred by YAMAMOTO (1971) as deposited between the activities of Old and New Fuji volcanoes. The lowest volcanic sand and gravel layer is made up of mud flow deposits of the Old Fuji. It is so thick that even a well with a depth of 250 meters does not pass through this layer. It seems to have a thickness of more than 150 meters. Near Obuchi at the southern foot of Mt. Fuji it has a thickness of about 200 meters (SAWAMURA, 1955).

As shown in the left half of the profile A-A' of Fig. 3 beneath the New Fuji lava are, in descending order, loam layer, volcanic sand and gravel (scoria of YAMAMOTO, 1971), black soil layer and volcanic sand and gravel layer with large blocks.

At the Wada River and eastward there exists a volcanic sand and gravel layer, but no lava layer beneath the alluvial deposits. Thickness of the layer seems to exceed 200 meters. This layer includes 2 or 3 loam layers of 1 to 2 meters in thickness. One of the loam layers, characterized by yellowish brown color, is a hypersthene andesite. According to MURASHITA (1977), they are distributed concentric to the summit of Mt. Ashitaka and therefore these volcanic sand and gravel layers are considered to be ejecta of Mt. Ashitaka.

Figure 3 shows the boundary between the ejecta of Mt. Fuji and those of Mt. Ashitaka by a discontinuity of patterns considering the discontinuous changes in groundwater which nearly parallels with the course of the Wada River, as will be explained later (3.3.4).

At Mt. Fuji, valleys are formed in a radial pattern. The valleys at the mid-slope and foot of Mt. Fuji were formed as a result of erosion by water (IWATUKA and MACHIDA, 1962). In many of these valleys

water flows only when it rains heavily. They are usually gullies. This suggests that rainwater permeates into the mountain and then changes into groundwater.

The geological columnar sections (Fig. 4) of the well in the slope (see Fig. 2) show that the Fuji lava is exposed or distributed near the surface. This layer has a thickness of 50 to 60 meters on the average and about 100 meters at the thickest. The volcanic sand and gravel layer beneath the lava layer is thought to be the Old Fuji's mud flow layer (TSUYA, 1971). It seems that the groundwater flows down through fissures and cracks of the New Fuji lava layer or where it crops out in the underlying Old Fuji mud flow layer.

A small portion of the groundwater which flows down the lower slopes reaches the surface as spring water. YAMAMOTO (1971) made a detailed study of the spring water and broadly classified it into two types. The first type is a relatively small one where the relatively shallow groundwater springs out after flowing down on an impermeable layer. The second type is a large one where groundwater springs out through cracks in lava tunnels. The spring waters in Ishihara and Sugita surveyed in this study are thought to belong to the first type and the Wakitamaike Pond to the second type.

Most part of the groundwaters are recharged in the New Fuji lava layer and the Old Fuji mud flow layer at the lower slope of the mountain and reaches below the lowland flowing down through them.

Table 2 shows the classification of the aquifers of the lowland by MURASHITA (1977). Hydraulic conductivity as calculated by the pumping test of these aquifers are also shown in the table. As can be seen from the table, the New Fuji lava layer is the most permeable, followed by the upper part of the Ashitaka volcanic sand and gravel layer, the Fuji River/the Urui River sedimentary layer, the Old Fuji Table 2 Aquifers and hydraulic conductivity.

Aquifers of the southern foot of Mt. Fuji area Hydraulic conductivity (cm/sec)

| Sand and gravel in fluvial deposits of Fuji River | Allu | |
|--|---------------|-----------------------------------|
| Fuji lavas with cracks | \mathbf{FL} | $(0.25{\sim}11.3){\times}10^{-1}$ |
| Old Fuji mud flow, volcanic sand and gravel | OF | $6.6 	imes 10^{-2}$ |
| Upper part of Ashitaka volcanic sand and gravel | AU | $(1.1 \sim 1.4) \times 10^{-2}$ |
| Lower part of Ashitaka volcanic sand and gravel | AL | $(1.1{\sim}7.3){	imes}10^{-2}$ |
| | | |

mud flow and the lower part of the Ashitaka volcanic sand and gravel layer.

2.3 Hydrology

Precipitation and Evapotranspiration

The hydrological environment of the study area as described in 2.2 suggests that the recharge of groundwater in this area is directly related to precipitation. To obtain the outline of precipitation and evapotranspiration in the study area data were collected and calculated, as shown in Fig. 5.

The values for precipitation are based on the 1966–1983 precipitation record (Japan Meteorological Agency, 1967–1984) for Yoshiwara, Fuji City, which is located in the central part of this area. The annual precipitations during this period range from 1,644 to 2,699 mm, averaging 2,194 mm; the standard deviation is 299 mm. In this area there is a seasonal fluctuation in precipitation, much rain from June to September, while scarce rain from January to February.

Potential evapotranspiration was calculated by Thornthwaite's method (THORNTHWAITE, 1948) on the basis of temperature and latitude. Although this method is an empirical one tailored to the actual measurement requirements in the United States of America, it can be used approximate calculating annual for hydrological balance in Japan (ICHIKAWA, 1973: KAYANE. 1980). The monthly





Fig. 5 Annual precipitation and evapotranspiration at Yoshiwara in Fuji during 1966–1983.

average temperature in Yoshiwara for the 1966–1983 period was used for calculating the annual potential evapotranspiration. The minimum value for the period is 746.2 mm, maximum 866.2 mm, average 807.8 mm and the standard deviation is 32.9 mm. Figure 5 shows the annual precipitation (P), the annual potential evapotranspiration (Et) and the time-serial fluctuation of the difference of them (P–Et). The P–Et value is thought to be directly related to the recharge of groundwater in this area. The mean P–Et value is 1,386 mm/year and the standard deviation is 313 mm/year, which means a fluctuation rate of 22.6%.

Groundwater Level

In the study area are groundwater level observation wells prepared by the Gakunan Groundwater User's Counter-Measure Association and Shizuoka Prefectural Government, as shown in Fig. 2. A total of 7 groundwater level observation wells—G-

| | Table 3 Obse | ervation | wens in this are | ea |
|--------------------------|-------------------------------------|----------------------|------------------------|---------------|
| Obser- vation well | Well head above sea level (m) | Well depth (m) | Screen depth (m) | Aquifer |
| G-1 | 5.30 | 106.0 | 94.0-106.0 | FL |
| G2 | 6.19 | 180.0 | 153.0 - 177.0 | OF |
| G-3 | 5.04 | 100.0 | 87.4 - 100.0 | FL |
| G-4 | 3.11 | 180.0 | 156.0 - 177.0 | AL |
| G-N3 | 5.50 | 103.4 | 85.9 - 102.4 | \mathbf{FL} |
| G-N4 | 4.34 | 200.0 | 156.0 - 200.0 | AL |
| G5 | 6.63 | 200.0 | 170.0-200.0 | AL |

1, 2, 3, 4, 5, N3 and N4 have been set up since 1969 when the groundwater level observation program was started. Some of them are now discarded. Table 3 shows the depth, the altitude of well head (T.P.) and the screen depth for each well. The groundwater level observation wells G–N3 and G–N4 were prepared because the wells G–3 and G–4 became incapable of observing groundwater levels due to spontaneous



Bulletin of the Geological Survey of Japan, Vol. 40, No. 7

Fig. 6 Secular changes of the groundwater level in the observation wells. Locations of the wells are shown in Figure 2. Nos. 1, 3, a and b are groundwater levels in the New Fuji lava aquifer. No. 2 is one in the Old-Fuji aquifer and No. 4 is in Ashitaka-lower aquifer.

water rise. The well G–5 was bored because the well G–N4 had become a flowing well. Figure 6 shows the results of observation by the wells G–1 and G–2, continued observation by the wells G–3 to G–N3 and G–4, G–N4 to G–5.

According to these records the water levels of the G–1 and G–3 wells, which have screens in the New Fuji lava layer, drop around March and April and rise around September and October every year. Indicating this annual cyclic change in water level, the G–1 well recorded an altitude of 0.70 meters in April 1970 and the G–3 well recorded the lowest water level -0.30meters since the start of the observation program in March 1972, but the water levels of both wells rose by about 3 meters in the autumn of 1973. Since 1974, they have remained at 3 to 4.5 meters. The records of the water levels of the G-2 and G-4 wells, which have screens in the Old Fuji agglomeratic mud flow layer and the Ashitaka volcanic sand and gravel layer do not show a clear annual cyclic change. The G-2 and G-4 wells recorded the lowest water levels of 0.88 and -1.90 meters, respectively, in April 1970, but since 1972 the water levels of both wells have been rising steadily. The G-2 well recorded an average annual water level (altitude) of 5.2 meters in 1984 and the G-5 well which had replaced the G-4 well recorded a altitude of well head of 6.63 meters and as of March 1985 it had become an flowing well.

Although none of these groundwater level observation wells existed before 1968, there are records of the water levels of the points a and b in Fig. 2. The points a and b are located 1.2 km and 2.7 km away Chemical evolution of groundwater quality (K. Ikeda)

| Periods | Water level change | Amount of pumping (m ³ /day) | Pumping area | Event |
|-----------|-------------------------------|---|--|--------------------------------|
| 1959~1965 | rapid fall | rapid increase from 600,000 to 1,170,000 | estimated to be 20 km ² | salinization occur in 1960 |
| 1966~1971 | lowest level | 1,000,000 | | salinization increase |
| 1972~1974 | steady recovery | 850,000~920,000 | estimated to be larger than 50 km ² | salinization not remarkable |
| 1972~1983 | constant (keep high level) | 850,000~920,000 | | salinization decrease |

Table 4 Characteristic changes of groundwater level in the New Fuji lava aquifer.

Table 5characteristic changes of groundwater levels in the Old Fuji aquifer and the Ashitaka-lower aquifer in
observation wells.

| Periods | Water level change | $\begin{array}{c} \text{Amount of pumping} \\ (\text{m}^3/\text{day}) \end{array}$ | Event |
|--------------------|--------------------------|--|---|
| G-2 (aquifer D) | F) | | |
| $1968{\sim}1971$ | steady fall | unknown | $Cl^{-} 10 \sim 30 \text{ mg}/l$ |
| $1971 {\sim} 1977$ | steady recovery | unknown | $Cl^{-} 30 \sim 50 \text{ mg}/l$ |
| 1978~1985 | constant (high level) | 310,000* (Mar. 1985) | $Cl^- 35 \pm mg/l$ |
| G-4 (aquifer Al | L) | | |
| 1968~1971 | steady fall | unknown | rapid salinization increase Cl ⁻ from 10 mg/ <i>l</i> to 1,000 mg/ <i>l</i> |
| $1971 {\sim} 1979$ | steady recovery | unknown | $\mathrm{Cl^-} \mathrm{~from~} 1,000 \mathrm{~mg}/l \mathrm{~to~} 15,000 \mathrm{~mg}/l$ |
| 1980~1985 | constant (high level) | 310,000* (Mar. 1985) | rapid salinization decrease Cl ⁻ from 15,000 mg/l to 5,000 mg/l |

* This value is the sum of pumping volume both from the aquifers DF and AL.

from the coastline respectively (Fig. 2) and are used for observation of groundwater level in the New Fuji lava layer at the depths of 106 meters and 80 meters and furthermore of the screen depths of 90–106 meters and 40.0–62.0 meters, respectively. Since 1960, the water levels of both wells have dropped significantly, reaching nadir in 1965. In 1960–1965 both wells recorded average annual water level drawdown rates of 0.6 meters and 0.8 meters per year respectively.

As seen from Fig. 6, it is possible to classify the whole period since 1956 into 4 characteristic periods of change in groundwater in the New Fuji lava layer as shown in Table 4.

On the other hand, the level of the

groundwater at a depth of more than 150 meters, which exists beneath the New Fuji lava layer and the Ashitaka volcanic sand and gravel layer continued drawdown until 1971 at the G–2 well and until 1969 at the G–4 well, reflecting the rapid increase in the quantity of groundwater utilized as a result of salinization of the New Fuji lava groundwater. The whole period of change in the level of the deep layer groundwater since 1968 can be divided into 3 characteristic periods (Table 5).

When the level of the deep layer groundwater and that of the New Fuji lava layer groundwater are compared, using the average annual water levels at the G-2 and the G-1 wells as yardsticks, both remained almost the same as each other until 1974, but the level of the deep layer groundwater has been apparently higher than that of the New Fuji lava layer groundwater since 1975. The water level at the G-4 well remained lower than that of the New Fuji lava layer groundwater from 1968 to 1975, in 1970 the difference being 3.0 meters. Since 1976, however, the water level at the G-4 well has been higher than that of the New Fuji lava layer groundwater by about 3.0 meters.

The relationship between the lava layer groundwater and the deep layer one will affect the vertical groundwater flow from shallow zone to deeper zone. Salinization of groundwater at the G-4 well since 1970 suggests the salinized groundwater vertically percolates from the shallow lava layer to the deeper one.

2.4 Groundwater Use

The groundwater in the study area had been used mainly by paper mills until 1955. In 1964, the quantity of the groundwater utilized increased rapidly, reflecting the marked increase in production at paper mills and other factories. Figure 7 shows the chronological change in groundwater withdrawal in Fuji City since 1955. For 1955–1970, only the quantity of the groundwater pumped up for industrial use is shown. From 1971 on, those for industrial, domestic, agricultural-fisheris and other



Fig. 7 Secular changes of the amount of groundwater use in Fuji City, 1955-1985.

use are shown.

A breakdown of the total annual quantity pumped up in 1971 indicates 5.6% for domestic use, 3.3% for agricultural and fisheries, 89.5% for industrial and 1.6% for other use. In 1985, however, it indicates 11.8% for domestic, 4.5% for agricultural and fisheries, 80.9% for industrial and 2.8% for other use, reflecting some decrease in the industrial use.

The quantity of groundwater utilized has rapidly increased since 1955-from 560,000 m³/day in 1955 to 770,000 m³/day in 1960 and 1,170,000 m³/day in 1964 (see Fig. 7). The temporary decrease in the quantity of groundwater utilized in 1965 is mainly due to the fact that groundwater in some parts of this area was salinized and therefore could not be supplied for industrial use in that year. The salinization of groundwater first occurred in a part of the coastal area in 1960 and has since spread. By 1965, the salinized area had covered a land area of about 10 km². The decrease in the quantity of groundwater utilized is attributable to the above mentioned fact, as well as to the self-regulation by groundwater users and of surface water (181,000 m^3/day) as industrial water-supply.

Since 1970, the quantity of groundwater utilized has once again been on the increase. This is because exploitation of the groundwater at a depth of more than 150 meters (in the Old Fuji mud flow and the Ashitaka volcanic sand and gravel laver) and the groundwater at the foot of Mt. Fuii, which had hardly been utilized until around 1964, made a significant progress and their use has increased rapidly since around 1970. The rapid decrease in the quantity of groundwater utilized seems to be due to the effect of the Fujigawa/ Higashisuruga industrial water supply, which started in 1975. The quantity of groundwater utilized as of March 1985 was $1,152,602 \text{ m}^3/\text{day}$, of which the groundwater at a depth of more than 150 meters accounted for $310,000 \text{ m}^3/\text{day}$.

The recent decrease in the quantity of groundwater utilized has resulted in the rise in the groundwater level and the decrease in the concentration of chloride ion in salinized groundwater.

3. Water-Rock Interaction in the Aquifer

The chemical composition of natural water is formed through its contacts with solids and gases in the hydrological cycle. It reflects the environment around it and the characters of the rocks and gases (mainly carbon dioxide) with which it came into contact, and shows the result of the waterrock interaction.

In this chapter, the groundwater samples collected from each aquifer are analyzed and the quality of groundwater and its distribution in each aquifer are studied. Furthermore. the relation with the lithological characteristics and chemical compositions of aquifer rocks, as well as the water-rock interaction in the aquifer are studied. Also, classification of groundwater systems by chemical characteristics of the groundwater, as well as the relationship between the distribution of groundwater quality and the mechanism of formation of groundwater quality are explained in this chapter.

3.1 Chemical Characteristics of Groundwater

Volcanic ejecta of Old Fuji, New Fuji and Mt. Ashitaka in the study area have different lithological characteristics, as stated in 2.1. According to the comparative study by FUJII and YUI (1985) of the chemical compositions of the ejecta of Mt. Fuji and those of Mt. Ashitaka, the rocks of Mt. Ashitaka are low in FeO, TiO₂ and especially K₂O, compared with those of Mt. Fuji. There is a distinct difference in chemical composition between the rocks of Mt. Fuji and Mt. Ashitaka. Each of these volcanic layers spreads with fairly high lithological continuity. Each layer is bounded by clay layers or loam layers and forms a distinct aquifer.

Due to the above-mentioned hydrological conditions, the chemical composition of groundwater in aquifers in this area is thought to be the result of a distinct waterrock interaction, showing a distinct characteristic.

Aquifers in this area are the Old Fuji agglomeratic mud flow layer (OF layer), the New Fuji lava layer (FL layer), the Ashitaka volcanic sand and gravel upper layer (AU layer), Ashitaka volcanic sand and gravel lower layer (AL layer) and the alluvial deposits of Fuji River layer (Allu Layer) classified by MURASHITA (1977).

(1) Sampling and Analytical Method

Concerning the wells in this area, two major groups are distinguished. One is a group of relatively shallow wells (less than 150

meters deep) which were bored by around 1965, and the other is that of deep wells (more than 150 meters deep) bored in and after 1965. The shallow wells (called the shallow layer groundwater wells) have screens in the Fuji River alluvial deposits layer and the New Fuji lava layer at the west side of the Wada River. They reach the groundwater at depths of less than 100 meters. The deep wells (called the deep layer groundwater wells) have screens in the Old Fuji agglomeratic mud flow layer beneath the lava layer or the Ashitaka volcanic sand and gravel laver. They reach the groundwater at depths of more than 150 meters. The deep wells were bored because the shallow layer groundwater had been salinized since 1960 and their upper portions were cemented to prevent the influx of groundwaters from the shallow laver.

Wells with known screen depth and



Fig. 8 Locations of samples for the chemical analyses of groundwater and rock in the study area.

geological columnar sections were selected out of these and groundwater samples were collected. Samples were taken from pumping wells or from spring out. The sampling locations are shown in Fig. 8.

Chemical analyses of the samples were conducted on the basis of the method of IKEDA and NAGAI (1973).Water temperature, pH, electric conductivity, dissolved oxygen and HCO_3^- were analyzed at the sampling site. The constituents such as Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁺, NO₃⁻. SiO_2 , PO_4^{3-} , I^- , Br^- , total iron and were analyzed manganese in the laboratory.

Seven samples were collected from the Fuji River alluvial deposit layer. 20samples from the New Fuji lava layer, 16 samples from the Old Fuji agglomeratic mud flow layer, 12 samples from the Ashitaka volcanic sand and gravel upper layer, 32 samples from the Ashitaka volcanic sand and gravel lower layer and 16 samples from the slope at the foot of Mt. Fuji (30 to 400 meters high). Judging from the geological columnar sections (Fig. 4), almost all of the samples collected at the foot of the mountain are thought to be those of groundwater in the Old Fuji agglomeratic mud flow layer. Table 6 shows a part of the results of the analyses of these samples.

(2) Water Quality of Groundwater of the Alluvial Formation

The Fuji River alluvial deposits are composed mainly of sand, gravel and clay and spread from the Fuji River to the vicinity of the harbour of Tagonoura. The quantity of dissolved matters in the groundwater in this formation tends to increase eastward. The pH ranges from 6.4 to 7.4. It is low at the northwestern side where fans are developed, and is relatively high near the harbour of Tagonoura. The HCO₃ concentration ranges from 80 to 150 mg/*l*. The concentration of Cl⁻, Na⁺, Ca²⁺ and Mg²⁺, as well as that of HCO₃, tends to increase. The increase in concentration of these dissolved matters coincides with the change of the prevalent constituent of this aquifer from gravel to sand and then to clay. Near the harbour of Tagonoura the groundwater contains little oxygen, and instead, contains Fe^{2+} and Mn^{2+} which are chemically stable under a reducing environment. The concentration of SiO₂ ranges from 14 to 42 mg/l. In most cases it is less than 30 mg/l.

(3) Water Quality of Groundwater in the Volcanic Ejecta

As stated in 2.2, ejecta of Mt. Fuji and Mt. Ashitaka occur in this area in the form of lava, volcanic sand and gravel, agglomeratic mud flow and so on. The water quality of the groundwater in these volcanic ejecta is characterized by bicarbonate with less than 5 to 6 mg of Cl⁻ in it. It also contains Ca²⁺, Mg²⁺, Na⁺ and K⁺ as cations. The equivalent concentration of these cations is characterized by the following relationship:

 $Ca^{2+} > Na^{2+} > Mg^{2+} > K^+$

for all samples of groundwater, except those of groundwater in Old Fuji, for which the relationship is as follows:

 $Na^+ > Ca^{2+} > Mg^{2+} > K^+.$

The concentration of SiO₂ ranges from 34 to 42 mg/l. On the whole, groundwater contains much dissolved oxygen. Assuming the quantity of dissolved oxygen in the water which is in equilibrium with the atmosphere to be 100%, then the average quantity of oxygen in groundwater in the Fuji lava layer is 85%, that in the Ashitaka volcanic sand and gravel layer 81%. And that in the Old Fuji agglomeratic mud flow layer is 62%. Since the hydraulic conductivity of the volcanic ejecta in this area is more than 1×10^{-2} cm sec⁻¹, this implies that the volcanic ejecta contain such a quantity of oxygen-consuming small organic substances that the groundwater in these aquifers is under a relatively oxidizable environment. The groundwater in

| Table 6 | Chemical | analyses | of fresh | groundwater. |
|---------|----------|----------|----------|--------------|
| | | | | |

Alluvial aquifer

| Well N | 0. | | A | -1 | A | -2 | A | -3 | A | -4 | A | -5 | A | -6 | A | 7 |
|---------------------|-------------------|-----------------|-------|------|-------|------|-------|------|------|------|------|------|-------|------|------|------|
| Depth o | of | | 23- | -60 | 55 | -82 | 24 | -60 | 38 | -56 | 20 | -40 | | | | |
| Screen Total F | (m) Depth (m) | | 7 | 1 | 8 | 5 | 6 | 0 | 6 | 0 | 4 | 0 | | n | 3 | 0 |
| 10121 L | | | | L | 0 | | | 0 | 0 | | - | | | | | |
| Temp. | (C) | | 1 | 6.1 | 1 | 7.6 | 18.0 | | 17.8 | | 16.8 | | 16.4 | | 1 | 6.8 |
| EC (S. | 25C) | | 26 | 0 | 41 | 4 | 29 | 5 | 21 | 9 | 22 | 9 | 26 | 6 | 23 | 8 |
| pH | 7.1 | | 7.1 | | 7.4 | | 7.2 | | 7.4 | | 7.0 | | 6.9 | | 7.0 | |
| RpH | | | | 7.9 | | 7.8 | | | | 7.9 | | 7.9 | | 7.8 | | |
| HCO ₃ | (mg/ <i>l</i>) | (me/ <i>l</i>) | 120.8 | 1.98 | 155.9 | 2.56 | 129.3 | 2.12 | 85.4 | 1.40 | 86.0 | 1.41 | 100.0 | 1.64 | 87.2 | 1.43 |
| Cl- | (mg/l) | (me/ <i>l</i>) | 15.7 | 0.44 | 32.2 | 0.91 | 12.8 | 0.36 | 7.7 | 0.22 | 7.4 | 0.21 | 8.3 | 0.23 | 8.4 | 0.24 |
| SO_4^{2-} | (mg/l) | (me/ <i>l</i>) | 4.0 | 0.08 | 46.6 | 0.97 | 33.7 | 0.70 | 28.1 | 0.59 | 29.7 | 0.62 | 39.5 | 0.82 | 30.5 | 0.63 |
| NO_{3}^{-} | (mg/l) | (me/ <i>l</i>) | 0.1 | 0.00 | 0.0 | 0.00 | 3.7 | 0.06 | 4.3 | 0.07 | 5.5 | 0.09 | 8.7 | 0.14 | | |
| TOt. A: | nions | (me/ <i>l</i>) | | 2.50 | | 4.44 | | 3.24 | | 2.28 | | 2.33 | | 2.83 | | 2.30 |
| Na | (mg/ <i>l</i>) | (me/ <i>l</i>) | 11.1 | 0.48 | 36.7 | 1.60 | 10.7 | 0.47 | 7.0 | 0.30 | 7.6 | 0.33 | 9.7 | 0.42 | 7.6 | 0.33 |
| K | (mg/l) | (me/ <i>l</i>) | 2.9 | 0.07 | 3.4 | 0.09 | 2.1 | 0.05 | 1.9 | 0.05 | 1.9 | 0.05 | 2.4 | 0.06 | 1.8 | 0.05 |
| Ca | (mg/l) | (me/ <i>l</i>) | 25.1 | 1.25 | 41.6 | 2.08 | 40.0 | 2.00 | 28.2 | 1.41 | 29.5 | 1.47 | 35.9 | 1.79 | 30.0 | 1.50 |
| Mg | (mg/l) | (me/ <i>l</i>) | 9.5 | 0.78 | 9.0 | 0.74 | 8.3 | 0.68 | 6.0 | 0.49 | 5.3 | 0.40 | 6.5 | 0.49 | 5.2 | 0.43 |
| TOt. Ca | ations | (me/ <i>l</i>) | | 2.58 | | 4.51 | | 3.20 | | 2.25 | | 2.25 | | 2.70 | | 2.51 |
| Dis. O ₂ | (mg/l) | | 0.05 | | | | | | | | 3.11 | | 4.98 | | 7.06 | |
| Free CO | $O_2 (mg/l)$ | | 15.7 | | 9.82 | | 12.9 | | 5.38 | | 13.8 | | 20.0 | | 14.0 | |
| NO_2^- | (mg/l) | | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | |
| NH_4^+ | (mg/l) | | 0.81 | | | | | | 0.0 | | 0.1 | | 0.1 | | 0.1 | |
| Fe^{2+} | (mg/l) | | 2.02 | | 0.20 | | | | 0.07 | | 0.10 | | 0.02 | | 0.05 | |
| TOt. Fe | e (mg/ <i>l</i>) | | 2.26 | | 0.20 | | | | 0.07 | | 0.16 | | 0.03 | | 0.11 | |
| Mn | (mg/l) | | 0.56 | | | | | | 0.00 | | 0.00 | | 0.00 | | 0.00 | |
| PO_4^{3-} | (mg/l) | | 0.07 | | | | 0.10 | | 0.01 | | 0.01 | | 0.00 | | 0.05 | l |
| SiO ₂ | (mg/l) | (m mol) | 42.3 | 0.70 | 29.8 | 0.50 | 26.5 | 0.44 | 16.7 | 0.28 | 19.8 | 0.33 | 20.9 | 0.35 | 37.1 | 0.62 |

- 348 -

Bulletin of the Geological Survey of Japan, Vol. 40, No. 7

| Fuji lava aquifer | | | | | | | | | | | | | | | | | | |
|---------------------|-------------------|-----------------|------|------|------|------|------|------|------|------|------|------|--------|------|------|------|--------|------|
| Well N | 0. | | FI | L-1 | FI | L-3 | FI | L-6 | FI | ·9 | FL | -11 | FL | -13 | FL | -15 | FL-18 | |
| Depth of Screen | of (m) | | 67 | -85 | 15 | -33 | 48 | -63 | 19 | -60 | 70- | -100 | 54–115 | | 4050 | | 80-125 | |
| Total D | epth (m) |) | 8 | 5 | 3 | 3 | 6 | 3 | 6 | 60 | | 100 | | 0 | 50 | | 130 | |
| Temp. | (C) | | 1 | 5.6 | 1 | 4.7 | 17.5 | | 1 | 6.3 | 1 | 16.2 | | 5.0 | 16.0 | | 15.2 | |
| EC (S. 25C) | | 116 | | 137 | | 17 | 9 | 18 | 0 | 16 | 5 | 11 | 1 | 12- | 4 | 10 | 1 | |
| pH | | 7.2 | | | 6.9 | | 6.7 | | 7.0 | | 7.0 | | 7.5 | | 7.2 | | 7.8 | |
| RpH | | | | 7.6 | | | 7.3 | | 7.6 | | 7.8 | | 7.9 | | | | | |
| HCO ₃ | (mg/ <i>l</i>) | (me/ <i>l</i>) | 58.4 | 0.96 | 43.3 | 0.71 | 83.0 | 1.36 | 51.2 | 0.84 | 48.2 | 0.79 | 53.7 | 0.88 | 66.5 | 1.09 | 63.4 | 1.04 |
| C1- | (mg/l) | (me/l) | 5.0 | 0.14 | 5.7 | 0.16 | 7.2 | 0.20 | 7.0 | 0.20 | 7.6 | 0.21 | 3.7 | 0.10 | 5.6 | 0.16 | 4.1 | 0.12 |
| SO_4^{2-} | (mg/ <i>l</i>) | (me/ <i>l</i>) | 5.0 | 0.10 | 9.5 | 0.20 | 15.5 | 0.32 | 17.6 | 0.37 | 18.0 | 0.38 | 5.1 | 0.11 | 9.8 | 0.20 | 14.8 | 0.31 |
| NO ₃ | (mg/l) | (me/ <i>l</i>) | 7.5 | 0.12 | 13.8 | 0.22 | | | 16.1 | 0.26 | 12.3 | 0.20 | 9.8 | 0.16 | 5.7 | 0.09 | 1.6 | 0.03 |
| TOt. A | nions | (me/ <i>l</i>) | | 1.32 | | 1.29 | | 1.88 | | 1.67 | | 1.58 | | 1.25 | | 1.54 | | 1.50 |
| Na | (mg/ <i>l</i>) | (me/ <i>l</i>) | 6.0 | 0.26 | 7.8 | 0.34 | 9.5 | 0.41 | 8.5 | 0.37 | 19.0 | 0.50 | 8.3 | 0.36 | 7.6 | 0.33 | 9.4 | 0.41 |
| К | (mg/l) | (me/l) | 2.4 | 0.06 | 2.0 | 0.05 | 2.6 | 0.07 | 2.7 | 0.07 | 2.1 | 0.05 | 1.4 | 0.04 | 2.9 | 0.07 | 1.5 | 0.04 |
| Ca | (mg/l) | (me/l) | 12.0 | 0.60 | 11.4 | 0.57 | 17.6 | 0.88 | 17.3 | 0.81 | 15.0 | 0.75 | 10.0 | 0.50 | 12.7 | 0.64 | 11.5 | 0.57 |
| Mg | (mg/l) | (me/ <i>l</i>) | 4.3 | 0.35 | 4.6 | 0.38 | 6.3 | 0.52 | 6.0 | 0.49 | 5.8 | 0.48 | 3.5 | 0.29 | 5.1 | 0.42 | 4.7 | 0.39 |
| TOt. Ca | ations | (me/ <i>l</i>) | | 1.27 | | 1.34 | | 1.88 | | 1.74 | | 1.57 | | 1.19 | | 1.46 | | 1.41 |
| Dis. O ₂ | (mg/ <i>l</i>) | | 7.64 | | 7.96 | | | | 8.55 | | 8.59 | | 7.71 | | | | | |
| Free CO | $O_2 (mg/l)$ | | 5.8 | | 8.66 | | 20.9 | | 8.19 | | 7.71 | | 2.69 | | 6.65 | | 1.59 | |
| NO_2^- | (mg/l) | | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | |
| $\mathrm{NH_4^+}$ | (mg/l) | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.2 | | 0.0 | | 0.0 | | 0.0 | |
| Fe ²⁺ | (mg/l) | | 0.00 | | 0.05 | | 0.05 | | 0.01 | | 0.02 | | 0.02 | | 0.01 | | 0.30 | |
| TOt. Fe | e (mg/ <i>l</i>) | | 0.02 | | 0.07 | | 0.07 | | 0.08 | | 0.03 | | 0.02 | | 0.02 | | 0.47 | |
| Mn | (mg/l) | | 0.00 | | 0.00 | | 0.00 | | 0.02 | | 0.00 | ļ | 0.00 | | | | | |
| PO_4^{3-} | (mg/l) | | 0.12 | | 0.05 | | 0.06 | | 0.09 | | 0.08 | | 0.14 | | 0.08 | | 0.08 | |
| SiO ₂ | (mg/ <i>l</i>) | (m mol) | 45.0 | 0.75 | 35.6 | 0.59 | 49.1 | 0.82 | 46.0 | 0.77 | 43.9 | 0.73 | 41.5 | 0.69 | 47.5 | 0.79 | 34.1 | 0.57 |

Chemical evolution of groundwater quality (K. Ikeda)

| Ashitaka upper aquifer | | | | | | | | | | | | | | | | | | |
|------------------------|----------------|-----------------|------|------|------|--------------|------|-------------|------|--------------|------|------|------|------|------|------|------|------|
| Well No. | | | AU | U–1 | AU | IJ -2 | A | J -4 | A | IJ 5 | A | U–7 | A | U-8 | AU | J–10 | AU | J–11 |
| Depth of Screen (m | 1) | | | | 42 | -83 | 110 | -135 | 25 | -27 | 120 | -150 | 120 | -160 | 50 | -58 | 80- | -135 |
| Total Dep | th (m) | | 3 | 0 | 83 | 3 | 15 | 0 | 4 | 0 | 150 | | 160 | | 90 | | 13 | 5 |
| Temp. (C) |) | | 1 | 6.0 | 15 | 15.0 15.3 | | 5.3 | 1 | 17.3 | | 16.0 | | 6.6 | 16.8 | | 1 | 5.9 |
| EC (S. 25C) | | | 120 | | 70 | | 14 | 3 | 14 | 4 | 10 | 2 | 10 | 5 | 11 | 0 | 85 | i i |
| pH | | | | 7.8 | 7.6 | | | 7.4 | | 7.1 | 5 | 7.6 | | 7.5 | | 7.7 | | 7.9 |
| RpH | | | 8.0 | | | 7.9 | 1 | 7.6 | | 7.7 | 1 | 7.9 | | 8.0 | | | | 8.0 |
| HCO ₃ (r | mg/l) | (me/ <i>l</i>) | 60.4 | 0.99 | 39.7 | 0.65 | 89.7 | 1.47 | 37.8 | 0.62 | 55.5 | 0.91 | 47.0 | 0.77 | 50.0 | 0.82 | 53.1 | 0.87 |
| Cl- (r | mg/l) | (me/ <i>l</i>) | 3.7 | 0.10 | 3.1 | 0.09 | 3.0 | 0.08 | 6.3 | 0.18 | 3.0 | 0.08 | 4.1 | 0.21 | 5.3 | 0.15 | 3.2 | 0.09 |
| SO_4^{2-} (r | mg/l) | (me/ <i>l</i>) | 1.7 | 0.04 | 6.5 | 0.14 | 2.0 | 0.04 | 23.7 | 0.49 | 9.5 | 0.20 | 6.2 | 0.13 | 8.5 | 0.18 | 0.9 | 0.02 |
| NO ₃ (r | mg/ <i>l</i>) | (me/ <i>l</i>) | 0.0 | 0.00 | 1.1 | 0.02 | 0.0 | 0.00 | 8.2 | 0.13 | 1 | | 0.95 | 0.02 | 1.0 | 0.02 | 0.03 | 0.00 |
| TOt. Anio | ns | (me/ <i>l</i>) | | 1.13 | | 0.90 | | 1.59 | | 1.42 | | 1.19 | | 1.04 | | 1.17 | | 0.98 |
| Na (r | mg/ <i>l</i>) | (me/ <i>l</i>) | 7.0 | 0.30 | 5.4 | 0.23 | 16.5 | 0.72 | 6.4 | 0.28 | 6.3 | 0.27 | 6.5 | 0.28 | 6.2 | 0.27 | 5.7 | 0.25 |
| K (r | ng/l) | (me/ <i>l</i>) | 0.7 | 0.02 | 0.8 | 0.02 | 5.0 | 0.13 | 1.3 | 0.03 | 2.1 | 0.05 | 1.7 | 0.04 | 2.2 | 0.06 | 1.2 | 0.03 |
| Ca (r | ng/l | (me/l) | 9.4 | 0.47 | 7.6 | 0.38 | 6.4 | 0.32 | 13.2 | 0.66 | 9.8 | 0.49 | 8.3 | 0.41 | 8.9 | 0.44 | 8.5 | 0.42 |
| Mg (r | mg/l | (me/ <i>l</i>) | 3.8 | 0.31 | 2.5 | 0.21 | 4.6 | 0.38 | 4.3 | 0.35 | 3.9 | 0.32 | 3.7 | 0.30 | 4.1 | 0.34 | 2.9 | 0.24 |
| TOt. Catio | ons | (me/ <i>l</i>) | | 1.10 | | 0.84 | | 1.55 | | 1.32 | | 1.13 | | 1.03 | | 1.11 | | 0.94 |
| Dis. O ₂ (| (mg/l) | | 7.64 | | 8.83 | | | | 7.96 | | | | 8.24 | | | | 8.62 | |
| Free CO ₂ (| (mg/l) | | 1.51 | | 1.59 | | 5.65 | | 4.91 | | 2.22 | | 2.35 | | 1.60 | | 1.06 | |
| NO_2^- (| (mg/l) | | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | |
| NH_4^+ (| (mg/l) | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| Fe ²⁺ (| (mg/l) | | 0.01 | | 0.02 | | 2.72 | | 0.04 | | 0.02 | | 0.00 | | 0.18 | | 0.10 | |
| TOt. Fe | mg/l | | 0.02 | | 0.02 | | 2.72 | | 0.34 | | 0.03 | | 0.01 | | 0.21 | | 0.18 | |
| Mn (| VIn (mg/l) | | | | 0.00 | | | | 0.00 | | 0.00 | | 0.00 | | | | 0.00 | |
| PO_4^{3-} (| mg/l | | 0.07 | | 0.08 | | | | 0.05 | | 0.20 | | 0.12 | | | | 0.05 | |
| SiO_2 (| mg/l | (m mol) | 39.5 | 0.64 | 39.7 | 0.64 | 33.1 | 0.55 | 37.6 | 0.61 | 40.3 | 0.65 | 40.0 | 0.67 | 38.6 | 0.64 | 36.6 | 0.61 |

— 350 —

Bulletin of the Geological Survey of Japan, Vol. 40, No. 7

| Ashit | aka lowei | aquifer | | | | | | | | | | | | | | | | |
|---------------------|--|-----------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| Well N | о. | | AI | 1 | AL | ,10 | AI | -16 | AL | -18 | AL | -24 | AL | -28 | AL | -29 | AL | |
| Depth Screen | of (m) | | 215 | -237 | 138 | -160 | 200 | -250 | 150 | -200 | 142 | -250 | 170 | -200 | 210- | -254 | 200- | -240 |
| Total I | Depth (m) |) | 25 | 0 | 16 | 0 | 25 | 0 | 20 | 0 | 25 | 0 | 20 | 0 | 254 | 1 | 240 | |
| Temp. | (C) | | 1 | 5.1 | 1 | 5.1 | 15.6 | | 15.7 | | 13.9 | | 13.9 | | 13.7 | | 13.3 | |
| EC (S. | 25C) | | 7 | 7 | 10 | 101 | | 88 | | 3 | 9 | 3 | 10 | 0 | 99 |) | 125 | |
| pH | | | 8.1 | | | 7.6 | | 8.2 | | 8.4 | | 8.2 | | 8.3 | ; | 8.3 | | 7.8 |
| RpH | | | 9.1 | | | | | 8.2 | | | | | | 8.3 | | | | 8.0 |
| HCO ₃ | (mg/ <i>l</i>) | (me/ <i>l</i>) | 42.1 | 0.69 | 45.8 | 0.75 | 54.3 | 0.89 | 51.2 | 0.84 | 47.0 | 0.77 | 47.0 | 0.77 | 48.8 | 0.80 | 61.0 | 1.00 |
| Cl- | (mg/l) | (me/ <i>l</i>) | 3.3 | 0.09 | 7.5 | 0.21 | 3.0 | 0.09 | 3.5 | 0.10 | 2.4 | 0.07 | 2.8 | 0.09 | 2.7 | 0.08 | 3.7 | 0.10 |
| SO_4^{2-} | (mg/l) | (me/l) | 2.2 | 0.05 | 6.5 | 0.14 | 3.0 | 0.06 | 2.6 | 0.05 | 7.2 | 0.15 | 8.0 | 0.17 | 7.3 | 0.15 | 9.8 | 0.20 |
| NO_3^- | (mg/l) | (me/ <i>l</i>) | 0.9 | 0.01 | 0.6 | 0.01 | 0.18 | 0.00 | 0.43 | 0.01 | 0.30 | 0.00 | 0.44 | 0.01 | 0.85 | 0.01 | 0.60 | 0.01 |
| TOt. A | nions | (me/ <i>l</i>) | | 0.84 | | 1.11 | | 1.04 | | 1.00 | | 0.99 | | 1.03 | | 1.04 | | 1.31 |
| Na | (mg/ <i>l</i>) | (me/ <i>l</i>) | 6.6 | 0.29 | 7.6 | 0.33 | 5.3 | 0.23 | 5.6 | 0.24 | 7.1 | 0.31 | 7.6 | 0.33 | 7.6 | 0.33 | 10.7 | 0.47 |
| K | (mg/l) | (me/ <i>l</i>) | 0.7 | 0.02 | 2.0 | 0.05 | 1.1 | 0.03 | 1.3 | 0.03 | 1.3 | 0.03 | 1.5 | 0.04 | 1.4 | 0.04 | 1.3 | 0.03 |
| Ca | (mg/l) | (me/ <i>l</i>) | 7.6 | 0.38 | 7.9 | 0.39 | 9.0 | 0.45 | 8.0 | 0.40 | 7.4 | 0.37 | 8.2 | 0.41 | 8.3 | 0.41 | 10.8 | 0.54 |
| Mg | (mg/l) | (me/ <i>l</i>) | 1.7 | 0.14 | 2.4 | 0.28 | 3.3 | 0.27 | 3.4 | 0.28 | 2.8 | 0.23 | 2.7 | 0.22 | 2.6 | 0.21 | 3.5 | 0.29 |
| TOt. C | ations | (me/ <i>l</i>) | | 0.83 | | 1.05 | | 0.98 | | 0.95 | | 0.94 | | 0.99 | | 0.99 | | 1.33 |
| Dis. O ₂ | (mg/l) | | 7.89 | | 7.66 | | 8.29 | | 7.90 | | 8.00 | | 9.60 | | 8.73 | | 7.29 | |
| Free CO | $O_2 (mg/l)$ | | 0.54 | | 1.83 | | 0.54 | | 0.31 | | 0.47 | | 0.35 | | 0.39 | | 1.53 | |
| NO_2^- | (mg/l) | | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | |
| NH_4^+ | (mg/l) | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.1 | | 0.1 | | 0.1 | | 0.1 | |
| Fe ²⁺ | (mg/l) | | 0.15 | | 0.08 | | 0.10 | | 0.08 | | 0.08 | | 0.08 | | 0.05 | | 0.01 | |
| TOt. Fe | ΓΟt. Fe (mg/l) 0.20 0.10 | | | | 0.25 | | 0.10 | | 0.09 | | 0.1 | | 0.09 | | 0.03 | | | |
| Mn | Mn (mg/ <i>l</i>) | | 0.00 | | 0.00 | | 0.00 | Į. | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | |
| PO_4^{3-} | D_4^{3-} (mg/l) 0.07 0.21 | | | | | | 0.00 | | 0.00 | | 0.07 | | 0.00 | | 0.00 | | 0.10 | |
| SiO ₂ | SiO_2 (mg/l) (m mol) | | 34.1 | 0.57 | 40.0 | 0.67 | 33.5 | 0.56 | 37.5 | 0.62 | 38.0 | 0.63 | 33.5 | 0.56 | 36.8 | 0.61 | 34.2 | 0.57 |

- 351 -

Chemical evolution of groundwater quality (K. Ikeda)

| Old F | uji aquite | er | | | | | | | | | | | | | | | |
|---|-----------------------|-----------------|------|------|------|------|-----------|------|-------|------|-------|------|------|------|---------|------|--|
| Well No |). | | 0 | F-1 | 0 | F4 | 0 | F-6 | 0 | F-9 | OF | -12 | OI | r–14 | OI | F-16 | |
| Depth o Screen | f (m) | | 178 | -250 | 210 | -250 | 190 | -230 | 173 | -200 | 145 | -195 | 150 | ⊢170 | 150-200 | | |
| Total D | epth (m) |) | 25 | 0 | 25 | 0 | 23 | 0 | 20 | 200 | | 200 | | 180 | | 200 | |
| Temp. | (C) | | 1 | .3.9 | 1 | .3.2 | 1 | 3.0 | 13.5 | | 13.6 | | 14.3 | | 1 | 4.4 | |
| EC (S. 2 | 25C) | | 13 | 0 | 157 | | 18 | 7 | 21 | 7 | 19 | 0 | 15 | 2 | 14 | 2 | |
| pH | | 8.1 | | 7.9 | | | 8.1 | | 8.0 | | 7.7 | | 7.5 | | 7.5 | | |
| RpH | | | 8.1 | | 8.1 | | | | | | 8.0 | | | | 7.9 | | |
| HCO ₃ | (mg/ <i>l</i>) | (me/ <i>l</i>) | 50.0 | 0.82 | 73.2 | 1.20 | 88.5 1.45 | | 114.1 | 1.87 | 106.8 | 1.75 | 87.2 | 1.43 | 71.4 | 1.17 | |
| Cl- | (mg/ <i>l</i>) | (me/ <i>l</i>) | 2.2 | 0.06 | 4.1 | 0.12 | 4.6 | 0.13 | 8.9 | 0.25 | 2.9 | 0.08 | 3.0 | 0.09 | 3.4 | 0.10 | |
| SO_4^{2-} | (mg/l) | (me/l) | 8.8 | 0.18 | 16.5 | 0.34 | 16.3 | 0.34 | 13.5 | 0.28 | 14.7 | 0.31 | 15.2 | 0.32 | 11.6 | 0.24 | |
| $NO_{\overline{3}}$ | (mg/l) | (me/ <i>l</i>) | 0.0 | 0.00 | 1.1 | 0.02 | 1.5 | 0.02 | 1.1 | 0.02 | 0.1 | 0.00 | 0.7 | 0.01 | 1.5 | 0.02 | |
| TOt. Ar | ions | (me/ <i>l</i>) | | 1.06 | | 1.68 | | 1.94 | | 2.42 | | 2.14 | | 1.85 | | 1.53 | |
| Na | (mg/l) | (me/ <i>l</i>) | 7.6 | 0.33 | 12.5 | 0.54 | 13.5 | 0.59 | 20.0 | 0.87 | 18.6 | 0.81 | 18.0 | 0.78 | 11.1 | 0.48 | |
| K | (mg/l) | (me/ <i>l</i>) | 1.7 | 0.04 | 1.0 | 0.03 | 1.8 | 0.05 | 2.9 | 0.07 | 3.4 | 0.09 | 2.2 | 0.06 | 1.4 | 0.04 | |
| Ca | (mg/l) | (me/ <i>l</i>) | 9.3 | 0.46 | 14.5 | 0.72 | 15.4 | 0.77 | 19.4 | 0.97 | 17.8 | 0.89 | 12.0 | 0.60 | 10.2 | 0.51 | |
| Mg | (mg/l) | (me/ <i>l</i>) | 3.0 | 0.25 | 5.4 | 0.44 | 5.9 | 0.49 | 6.8 | 0.56 | 6.0 | 0.49 | 5.0 | 0.41 | 5.5 | 0.45 | |
| TOt. Ca | tions | (me/ <i>l</i>) | | 1.08 | | 1.73 | | 1.90 | | 2.47 | | 2.28 | | 1.85 | | 1.48 | |
| Dis. O ₂ | (mg/ <i>l</i>) | | 8.20 | | 6.09 | | 5.81 | | 1.58 | | 4.86 | | | | 8.01 | | |
| Free CO | $l_2 (mg/l)$ | | 0.65 | | 1.46 | | 1.15 | | 1.83 | | 3.42 | | 5.49 | | 3.57 | | |
| NO_2^- | (mg/l) | | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | | |
| NH_4^+ | (mg/l) | | 0.05 | | 0.1 | | 0.1 | | 0.0 | | 0.1 | | 0.0 | | 0.2 | | |
| Fe ²⁺ | (mg/l) | | 0.05 | | 0.06 | | 0.10 | | 0.03 | | 0.08 | | 0.02 | | 0.02 | | |
| TOt. Fe | TOt. Fe (mg/l) 0.06 | | | 0.19 | | 0.13 | | 0.04 | | 0.13 | | 0.02 | | 0.02 | | | |
| Mn | (mg/ <i>l</i>) | | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.04 | | 0.00 | | 0.00 | | |
| PO_4^{3-} | (mg/l) | | 0.08 | | 0.10 | | 0.01 | | 0.20 | | 0.19 | | 0.16 | | 0.09 | | |
| $\begin{array}{c c} PO_4^{3-} & (mg/l) \\ SiO_2 & (mg/l) (m \text{ mol}) \end{array}$ | | 33.5 | 0.56 | 31.7 | 0.53 | 32.7 | 0.55 | 33.5 | 0.56 | 36.7 | 0.61 | 35.4 | 0.59 | 36.1 | 0.60 | | |

- 352 --

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Bulletin of the Geological Survey of Japan, Vol. 40, No. 7

| Table 6 | (continued) |
|---------|-------------|
|---------|-------------|

| Foot s | lope of N | At. Fuji (| chiefly Old | Fuji aquife | r) · | | | | omennuou) | | | | | | | |
|---------------------|-----------------|-----------------|-------------|-------------|------|--------------|------|------|-----------|------|------|------|------|------|------|------|
| Well No |). | | F | s–2 | Fs | s – 3 | Fs | s5 | Fs | s–9 | Fs | -11 | Fs | -13 | Fs | -14 |
| Depth o Screen | f (m) | | 47- | -115 | 80.5 | -130 | 70- | -114 | 100 | -120 | 93- | 114 | 101 | -200 | 79- | -130 |
| Total D | epth (m) | 1 | 11 | .5 | 13 | 0 | 12 | 0 | 13 | 0 | 12 | 0 | 20 | 0 | 13 | 0 |
| Temp. | (C) | | 1 | 6.1 | 1 | 3.5 | 1 | 3.8 | 1 | 4.9 | 1 | 5.0 | 1 | 6.9 | 15.1 | |
| EC (S. 2 | 25C) | | 10 | 5 | 8 | 5 | 10 | 0 | 9 | 8 | 9 | 8 | 7 | 2 | 8 | 7 |
| pH | | | | 7.3 | | 7.8 | | 7.5 | | 7.7 | | 7.3 | | 6.6 | | 7.2 |
| RpH | | | | 7.7 | | 8.0 | | 7.7 | | 7.8 | | 7.7 | | 7.8 | | 7.6 |
| HCO ₃ | (mg/l) | (me/ <i>l</i>) | 30.5 | 0.50 | 48.2 | 0.79 | 40.9 | 0.67 | 42.7 | 0.70 | 41.5 | 0.68 | 39.7 | 0.65 | 37.8 | 0.62 |
| Cl- | (mg/l) | (me/ <i>l</i>) | 5.3 | 0.15 | 1.8 | 0.05 | 2.1 | 0.06 | 3.9 | 0.11 | 3.4 | 0.10 | 3.5 | 0.10 | 3.1 | 0.09 |
| SO_4^{2-} | (mg/l) | (me/ <i>l</i>) | 7.2 | 0.15 | 4.4 | 0.09 | 4.0 | 0.08 | 4.0 | 0.08 | 5.2 | 0.11 | 3.5 | 0.07 | 5.7 | 0.12 |
| NO_{3} | (mg/l) | (me/ <i>l</i>) | 13.0 | 0.21 | 0.04 | 0.00 | | | 6.5 | 0.10 | 6.3 | 0.10 | 0.11 | 0.00 | 7.4 | 0.12 |
| TOt. Ar | nions | (me/l) | | 1.01 | | 0.93 | | 0.81 | | 0.99 | | 0.99 | | 0.82 | | 0.95 |
| Na | (mg/l) | (me/ <i>l</i>) | 3.7 | 0.16 | 5.7 | 0.25 | 6.1 | 0.27 | 6.9 | 0.30 | 6.4 | 0.28 | 4.1 | 0.18 | 5.8 | 0.25 |
| K | (mg/l) | (me/ <i>l</i>) | 2.1 | 0.05 | 1.0 | 0.03 | 1.0 | 0.03 | 1.5 | 0.04 | 1.5 | 0.04 | 2.0 | 0.05 | 1.4 | 0.04 |
| Ca | (mg/l) | (me/ <i>l</i>) | 13.0 | 0.65 | 7.6 | 0.38 | 7.5 | 0.37 | 7.5 | 0.37 | 8.5 | 0.42 | 7.3 | 0.36 | 8.2 | 0.41 |
| Mg | (mg/l) | (me/ <i>l</i>) | 3.0 | 0.25 | 2.8 | 0.23 | 2.6 | 0.21 | 2.5 | 0.21 | 2.8 | 0.23 | 2.5 | 0.21 | 3.0 | 0.25 |
| TOt. Ca | tions | (me/ <i>l</i>) | | 1.11 | | 0.89 | | 0.88 | | 0.92 | | 0.97 | | 0.80 | | 0.95 |
| Dis. O ₂ | (mg/ <i>l</i>) | | 9.14 | | 9.56 | | 9.27 | | 8.66 | | 8.54 | | 8.64 | | 8.70 | |
| Free CO | $O_2 (mg/l)$ | | 2.30 | | 1.93 | | 2.05 | | 1.47 | | 3.32 | | 15.8 | | 3.78 | |
| NO_2^- | (mg/l) | | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | |
| $\rm NH_4^+$ | (mg/l) | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| Fe ²⁺ | (mg/l) | | 0.31 | | 0.02 | | 0.02 | | 0.02 | | 0.03 | | 0.04 | | 0.03 | |
| TOt. Fe | (mg/l) | | 0.68 | | 0.03 | | 0.13 | | 0.05 | | 0.05 | | 0.64 | | 0.00 | |
| Mn | (mg/l) | | 0.00 | | 0.00 | | 0.02 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | |
| PO_4^{3-} | (mg/l) | | | | | | 0.10 | | 0.14 | | 0.13 | | 0.09 | | 0.10 | |
| SiO ₂ | (mg/ <i>l</i>) | (m mol) | 45.2 | 0.75 | 30.8 | 0.51 | 34.2 | 0.57 | 38.8 | 0.65 | 41.5 | 0.65 | 54.5 | 0.91 | 44.2 | 0.74 |

Chemical evolution of groundwater quality (K. Ikeda)

- 353 -

| Bulletin | of | the | Geological | Survey | of | Japan, | Vol. | 40, | No. | 7 |
|----------|----|-----|------------|--------|----|--------|------|-----|-----|---|
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|--|---|--|--|--|---|
| Allu | FL | OF | AU | AL | Fs(OF) |
| $17.1 {\pm} 0.7$ $16.1 {\sim} 18.1$ | $15.9 {\pm} 1.0 \\ 14.6 {\sim} 18.0$ | 13.7 ± 0.7 $13.0 {\sim} 15.9$ | $^{15.7\pm1.1}_{13.7\sim17.3}$ | 15.2 ± 1.0 $13.3 \sim 17.6$ | $14.9 \pm 1.0 \\ 13.5 {\sim} 16.9$ |
| $7.1 {\pm} 0.2 \\ 6.9 {\sim} 7.4$ | $7.2 {\pm} 0.4 \\ 6.5 {\sim} 7.5$ | $7.8 {\pm} 0.3 \\ 7.4 {\sim} 8.2$ | $7.5 \pm 0.3 \\ 7.0 {\sim} 7.9$ | $_{7.4 \sim 8.4}^{8.1 \pm 0.2}$ | $7.4 \pm 0.3 \\ 6.6 {\sim} 7.8$ |
| $3.80 \pm 2.98 \\ 0.05 {\sim} 7.06$ | $8.19 \pm 1.10 \\ 5.80 \sim 9.50$ | ${}^{6.17\pm1.93}_{1.58\sim9.21}$ | $7.33 \pm 2.89 \\ 0.46 \sim 9.08$ | $\substack{7.87 \pm 0.94 \\ 4.67 \sim 9.60}$ | $8.70 \pm 0.75 \\ 6.84 \sim 9.70$ |
| $\substack{109.2\pm27.0\\85.4{\sim}155.9}$ | $63.9 \pm 18.0 \\ 38.4 \sim 83.0$ | $87.4 {\pm} 19.1 \\ 50.0 {\sim} 118.3$ | $47.7 {\pm} 16.8 \\ 25.3 {\sim} 60.4$ | $51.2 \pm 6.9 \\ 39.0 \sim 72.6$ | $\begin{array}{c} 45.7 \pm 9.3 \\ 30.5 {\sim} 66.5 \end{array}$ |
| $^{13.2\pm8.9}_{7.7\sim32.2}$ | $5.6 {\pm} 1.6 \\ 3.7 {\sim} 8.1$ | $5.9{\pm}7.7$ $1.9{\sim}34.1$ | $_{2.0\sim 6.3}^{3.8\pm 1.2}$ | $_{2.4\sim7.5}^{3.2\pm1.0}$ | $_{1.8\sim 6.7}^{3.1\pm 1.1}$ |
| ${}^{30.3\pm13.3}_{4.0\sim46.5}$ | $^{13.7\pm5.0}_{5.1\sim20.0}$ | $13.9 \pm 3.3 \\ 7.8 {\sim} 20.0$ | $_{1.3\sim23.7}^{6.7\pm6.3}$ | $5.5 {\pm} 3.8 \\ 2.2 {\sim} 16.2$ | $_{2.5\sim15.5}^{5.2\pm2.3}$ |
| $_{0.0\sim 8.7}^{3.2\pm 3.3}$ | $5.8 \pm 5.2 \\ 2.2 \sim 9.6$ | $_{0.9\pm0.9\ 0.0\sim34.1}^{0.9\pm0.9}$ | $_{0.0 \sim 13.2}^{2.0 \pm 4.2}$ | $_{0.0 \pm 0.4}^{0.5 \pm 0.4}$ | $_{1.0 \sim 13.0}^{3.0 \pm 3.8}$ |
| ${}^{12.9\pm10.6}_{7.0\sim36.7}$ | $_{6.9\sim19.0}^{9.5\pm3.1}$ | $^{15.8\pm4.9}_{7.6\sim29.0}$ | $7.2 \pm 3.0 \\ 5.4 {\sim} 7.7$ | $_{5.2 \sim 15.2}^{7.0 \pm 2.1}$ | 6.2 ± 1.5 $3.7 \sim 9.5$ |
| $_{1.8 \sim 3.4}^{2.3 \pm 0.6}$ | $_{1.4\sim 3.0}^{2.2\pm 0.6}$ | $_{1.0\sim 3.4}^{2.1\pm 0.7}$ | $_{0.8\sim2.2}^{1.8\pm1.1}$ | $_{1.4\pm0.4}^{1.4\pm0.4}_{1.0\sim6.7}$ | $_{1.4\pm0.4}^{1.4\pm0.4}_{1.0\sim6.9}$ |
| ${}^{32.9\pm6.3}_{25.1\sim41.6}$ | $14.2 {\pm} 2.9 \\ 10.0 {\sim} 18.4$ | $^{14.1\pm3.3}_{7.5\sim19.7}$ | $7.9{\pm}2.9 \\ 1.6{\sim}13.2$ | ${}^{8.6\pm1.2}_{5.6\sim11.7}$ | ${}^{8.8\pm2.2}_{5.8\sim13.0}$ |
| $7.1 \pm 1.8 \\ 5.2 \sim 9.0$ | $5.1{\pm}1.1\ 3.5{\sim}6.9$ | $5.4 {\pm} 1.2 \\ 2.6 {\sim} 7.4$ | $_{0.8\sim 4.3}^{3.3\pm 1.1}$ | $_{1.7\sim5.3}^{3.1\pm0.7}$ | $_{2.1\sim5.1}^{3.1\pm0.9}$ |
| $27.6 {\pm} 9.5 \\ 16.7 {\sim} 42.3$ | $41.6 {\pm} 5.7$ $39.8 {\sim} 49.1$ | ${}^{34.4\pm1.9}_{30.4\sim38.3}$ | $35.1 \pm 11.5 \\ 33.1 \sim 45.1$ | ${}^{34.8\pm7.0}_{28.0\sim40.5}$ | 39.2 ± 5.8 $30.8 \sim 54.5$ |
| | Allu 17.1 ± 0.7 $16.1 \sim 18.1$ 7.1 ± 0.2 $6.9 \sim 7.4$ 3.80 ± 2.98 $0.05 \sim 7.06$ 109.2 ± 27.0 $85.4 \sim 155.9$ 13.2 ± 8.9 $7.7 \sim 32.2$ 30.3 ± 13.3 $4.0 \sim 46.5$ 3.2 ± 3.3 $0.0 \sim 8.7$ 12.9 ± 10.6 $7.0 \sim 36.7$ 2.3 ± 0.6 $1.8 \sim 3.4$ 32.9 ± 6.3 $25.1 \sim 41.6$ 7.1 ± 1.8 $5.2 \sim 9.0$ 27.6 ± 9.5 $16.7 \sim 42.3$ | $\begin{array}{c c c c c c c c c c c c c c c c c c c $ | $\begin{array}{c c c c c c c c c c c c c c c c c c c $ | $\begin{array}{c c c c c c c c c c c c c c c c c c c $ | $\begin{array}{c c c c c c c c c c c c c c c c c c c $ |

Table 7Maximum, minimum, and mean values of the chemical analyses and their standard deviations of fresh
groundwater in various volcanic layers.

Above values are average and standard deviation; below values are minimum-maximum range.

this area contains little iron and manganese, reflecting this environment.

Table 7 shows the mean value, range and standard deviation for each of the physical and chemical characteristics of the groundwater in each aquifer in this area. The water quality of groundwater varies from one aquifer to another. The characteristics and distribution of the water quality of groundwater in each aquifer are as follows. Groundwater in the New Fuji Lava Layer

The groundwater in this layer has been salinized since 1960, starting near the harbour of Tagonoura. Figure 9 shows the water quality map obtained as a result of the groundwater analyses in this layer which has not been salinized. The value of pH is about 7. The water temperature is about 15°C. The concentration of SO_4^{2-} is 14 mg/l in average. Bicarbonate accounts for more than 60% of the total quantity of dissolved matter (equivalent).

Groundwater in the Ashitaka Volcanic Sand and Gravel Upper Layer

Aquifer of the Ashitaka volcanic sand and gravel upper layer underlies in the area at the east side of the Wada River where the Fuji lava layer is absent. In this layer, groundwater also has been increasingly salinized after the salinization of the Fuji lava layer groundwater. Figure 9 shows the water quality map which is based on the analyses of the groundwater in this layer which has not been salinized. The mean values for the concentration of HCO_3^- , Cl^- , and SO_4^{2-} in the groundwater are 43.9, 3.9 and 7.1 mg/l. All of them are lower than those of the groundwater in the New Fuji lava layer. The value for SO_4/Cl (weight ratio) is 1.8, which is in contrast to 2.2 for the groundwater in the Fuji lava layer. This seems to reflect the different sulfide contents of the volcanic ejecta of Mt. Fuji and Mt. Ashitaka.

Groundwater in the Old Fuji Agglomeratic Mud Flow

This mud flow layer lies beneath the New Fuji lava layer which is distributed at

Chemical evolution of groundwater quality (K. Ikeda)



Fig. 9 Water quality map in the alluvium, New Fuji lava and Ashitaka upper part of volcanic gravel.

the foot of Mt. Fuji and in the lowland. Near the harbour of Tagonoura it still continues at a depth of 250 meters. It is clear that it has a thickness of more than 150 meters. Usually samples of groundwater in this layer are collected from a screen laid at a depth of 150 to 200 meters. The water temperature is 13.7° C on the average, which is the lowest of all types of volcanic ejecta layer groundwaters in the study area. Its pH value is 7.8.

The average concentrations of HCO_3^- , Cl^- , SO_4^{2-} and SiO_2 are 86.0, 5.7, 14.4 and 34.4 mg/l, respectively. It should be noted that, while Cl^- and SO_4^{2-} have the same concentrations as in the lava layer aquifer, the concentration of HCO_3^- is a little higher and that of SiO_2 is a little lower than in the case of the New Fuji lava layer. Figure 10 shows the water quality map for the ground-

water in this layer. Characteristic feature of this figure is that the concentrations of dissolved constituents in groundwater are the highest near the middle point between the Fuji River and the harbour of Tagonoura.

Groundwater in the Ashitaka Volcanic Ejecta Lower Layer

The groundwater in this layer occurs in the lower part of the Ashitaka volcanic ejecta layer located to the east of the Wada River and is separated from the upper layer by a weathered yellowish brown loam layer. The loam layer lies at a depth of 50 meters near the boundary between the foot of Mt. Ashitaka and the lowland. It inclines to the southwest. The gradient is approximately 3–4/100 and the depth near the coast is more than 175 meters.

Samples of the groundwater in this layer



Bulletin of the Geological Survey of Japan, Vol. 40, No. 7

Fig. 10 Water quality map of the Old-Fuji and the Ashitaka lower part of volcanic gravel aquifers.

were collected from a screen laid at 150-200 m. That is almost the same depth as the groundwater in the Old Fuji agglomeratic mud flow layer. But the quality of this groundwater is different from that of the groundwater in the Old Fuji agglomeratic mud flow layer. The water temperature is 13.3 to 17.6°C, showing a relatively wide variation. The average water temperature is 15.2°C, which is apparently higher than in the groundwater of the Old Fuji agglomeratic mud flow layer. Its pH value is 8.1 on the average, and is the highest of all types of groundwater in this area. The mean value of the concentration of HCO_3^- is 51.2 mg/l, which is lower by 40% than that in the Old Fuji agglomeratic mud flow layer. The mean for SO_4^{2-} is 5.3 mg/l, which is less than half the concentration of the Old Fuji agglomeratic mud flow layer.

As is clearly seen from the water quality map in Fig. 10, the boundary between the groundwater in this layer and that in the Old Fuji groundwater is clearly seen by means of the difference in quantity of the dissolved constituents.

Groundwater in the Area at the Foot of Mt. Fuji

Sixteen groundwater samples from the gently sloping area at the southern foot of Mt. Fuji, whose altitude ranges from 30 to 500 meters were collected. From the wells which have screens at depths of 50 to 120 meters, 14 samples were collected. The other two are samples from the wells which have screens at depths of 50 to 70 meters. At the foot of Mt. Fuji, the lava layer has a thickness of 50 to 100 meters from the ground surface. Most of the groundwater samples therefore are collected from both, the New Fuji lava layer and the Old Fuji ag-

glomeratic mud flow layer.

The water temperatures range from 13.9 to 16.9°C. There is no significant correlation between the water temperature and the altitude. The water temperature tends to remain at the same level in the longitudinal direction along the slope. In a zone which runs through Kubo, Godo and east of Ishizaka the water temperature of the groundwater is low, always remaining at the 13°C level. The water temperatures range from 15 to 16°C in the area closer to Fujinomiya.

As shown in Fig. 10, the concentrations of the dissolved constituents in the ground-water in the mountain foot area are the lowest. The mean values for the concentrations of HCO_3^- , Cl^- and SO_4^{2-} are 43.9, 3.2 and 5.3 mg/l, respectively.

3.2 Relation between Rocks and Chemical Properties of Groundwater

The aquifer composing rocks in this area are roughly divided into three types: the New Fuji lava, the Old Fuji agglomeratic mud flow and the Ashitaka volcanic sand and gravel.

The New Fuji lava is the older lava of New Fuji, and it forms the main aquifer for the groundwater in the area at the southern foot of Mt. Fuji. It commonly is olivine basalt consisting mainly of plagioclase, olivine, augite, and magnetite (SAWAMURA, 1955). The chemical composition of the New Fuji after TSUYA (1971) is shown in Table 8.

The Old Fuji agglomeratic mud flow consists of volcanic mud flow, volcanic sand and gravel, breccia layer and so on. All these constituents are basaltic (TSUYA, 1971). Its main constituent minerals are plagioclase, augite and olivine.

According to FUJII and YUI (1985), the volcanic ejecta of Mt. Ashitaka are divided into the older, middle, younger and youngest ejecta. The older ejecta consist

 Table 8
 Chemical composition of New Fuji lava rocks.

| | | | | (weigh | it %) |
|------------------|-------|-------|-------|--------|-------|
| No. | 1 | 2 | 3 | 4 | 5 |
| SiO_2 | 49.18 | 50.12 | 49.60 | 50.08 | 50.87 |
| TiO ₂ | 1.03 | 1.91 | 1.97 | 1.97 | 1.70 |
| Al_2O_3 | 16.74 | 16.26 | 16.14 | 15.83 | 17.44 |
| Fe_2O_3 | 4.00 | 3.05 | 3.67 | 4.89 | 3.68 |
| FeO | 8.48 | 10.10 | 9.90 | 9.04 | 7.55 |
| MnO | 0.15 | 0.23 | 0.23 | 0.23 | 0.21 |
| MgO | 5.28 | 4.67 | 4.79 | 4.67 | 4.12 |
| CaO | 10.42 | 8.60 | 8.80 | 8.77 | 8.86 |
| Na_2O | 2.42 | 2.78 | 2.90 | 2.87 | 3.16 |
| K_2O | 1.16 | 0.96 | 0.93 | 0.99 | 0.97 |
| P_2O_5 | 0.54 | 0.29 | 0.31 | 0.38 | 0.31 |
| H_2O^+ | 0.17 | 0.44 | 0.55 | 0.11 | 0.47 |
| H_2O^- | 0.19 | 0.20 | 0.14 | 0.24 | 0.20 |
| Others | | | | | _ |
| Total | 99.76 | 99.61 | 99.93 | 100.12 | 99.54 |

No. 1 Mishima lava No. 2 Hataoka lava No. 3 and No. 4 Katsura lava No. 5 Otawa lava (after TSUYA, 1971)

mainly of basalt and basaltic andesite and the middle ejecta of a large quantity of basaltic tuff breccia. The younger ejecta consist of olivine and two-pyroxene andesite. The youngest ejecta consist of dacite lava which contains amphibole.

FUJII and YUI also reported that the chemical composition of the volcanic ejecta of Mt. Ashitaka is similar to that of Fuji rocks in MgO, SiO₂ and Na₂O contents, but lower in FeO, K₂O and TiO₂ contents and K₂O/Na₂O ratio (mol ratio). While the mean value for K₂O/Na₂O ratio is 0.21 (calculation based on Table 8) for the Fuji lava, it is approximately 0.17 for the Ashitaka lava (calculation based on the diagram worked out by FUJII and YUI (1985)).

The chemical constituents of the groundwater in these volcanic ejecta include those of rain and snow, which fell on Mt. Fuji and Mt. Ashitaka, and those dissolved from the rocks as a result of the contact of the groundwater with the rock.

| | of water from the summit of Mt. Fuji. |
|---------|---------------------------------------|
| | |
| | water in Japan, and chemical analyses |
| Table 9 | Average chemical composition of ram- |

| | Concentration (mg/l) | | | | | |
|------------------|----------------------|-------------------------------------|-----------------------|--|--|--|
| Constituent | Rainwater | Summit of Mt. Fuji (IKEDA, 1964) | | | | |
| | (SUGAWARA, 1967) | Kinmeisui Spring | Kusushidake Spring | | | |
| HCO ₃ | | 3.1 | 3.2 | | | |
| C1- | 1.1 | 0.1 | 1.1 | | | |
| SO_4^{2-} | 4.5 | 2.0 | 0.4 | | | |
| Na | 1.1 | 0.4 | 1.1 | | | |
| K | 0.26 | 0.1 | 0.3 | | | |
| Ca | 0.94 | 0.81 | 0.32 | | | |
| Mg | 0.36 | 0.48 | 0.29 | | | |
| Fe | 0.23 | 0.02 | 0.02 | | | |
| SiO_2 | 1.78 | 3.6 | 2.9 | | | |
| pH | | 6.2 | 6.3 | | | |

The average concentrations of dissolved constituents in rainwater in Japan were calculated by SUGAWARA and HANYA (1964). Also, the results of analyses of samples of the spring water (Kimmeisui and Kusushigadake spring water) collected at the summit of Mt. Fuji are available. Table 9 shows the water quality of rainwater and of the spring water.

The quantity of the chemical constituents in rainwater is very small compared with that in groundwater. SO_4^{2-} , Cl^- and Na⁺ are prevalent in rainwater, while there is very little HCO₃⁻. The first rainwater coming into contact with the rock at the summit of Mt. Fuji contains a small quantity of HCO₃⁻ and SiO₂.

The key diagram of Fig. 11 shows the chemical composition of the volcanic ejecta distributed in the area. The groundwater in each aquifer consists of 60 to 90% HCO₃⁻ and 55 to 80% of Ca²⁺+Mg²⁺. The water quality type is of Ca-HCO₃. It is possible to divide the chemical characteristics of groundwater into several groups by the key diagram.

As is clearly seen from the key diagram,

 $\rm HCO_3^-$ and $\rm Ca^{2+} + Mg^{2+}$ account for the most part of the increment of chemical constituents in rainwater as a result of its contact with volcanic ejecta.

The relationship between total dissolved solids and HCO_3^- (Fig. 12) shows that the quantity of bicarbonate is heavily dependent on the total dissolved solids. The increase in quantity of SiO₂ is also closely related to the increase in total dissolved solids resulted from the water-rock contact (Fig. 13). The only exception to this is the groundwater in the Old Fuji aquifer, in which the quantity of SiO₂ tends to level off even if the total dissolved solids increase.

Another difference between the groundwater in the Old Fuji aquifer and that in other volcanic ejecta is seen in the relationship between the quantity of SiO_2 and that of Na⁺. While SiO_2 :Na ratio (mol ratio) is approximately 2:1 for the groundwater in the Fuji lava and that in the Ashitaka volcanic ejecta layer, it is approximately 1:1 for the groundwater in the Old Fuji aquifer (Fig. 14).

As stated above, the difference between the groundwater in the Old Fuji aquifer and that in the other volcanic ejecta is conspicuous concering the relationship between SiO_2 and the other dissolved constituents.

In the case of the groundwater in the Fuji lava and that in the Ashitaka volcanic ejecta layer, the mol ratios of SiO₂ to each of Na⁺ and HCO₃⁻ are approximately 2:1 and 1:1.4 respectively. Although these two types of groundwater, in the Fuji lava layer and in the Ashitaka volcanic layer, are not distinguishable by these mol ratios, they can be distinguished by larger total dissolved solids (Fig. 9), higher SO₄²⁻ concentration (Table 7) and a higher K/Na (mol ratio) for the groundwater in the New Fuji lava layer than for that in the Ashitaka volcanic layer.

As stated formerly, these characteristics of the groundwater quality were formed





Groundwater from the upper aquifers above a depth of 150 meters. Allu: Alluvial deposits, FL: New Fuji lava, AU: Ashitaka, volcanic sand and gravel upper.



Groundwater from the lower aquifers below a depth of 150 memters: AL: Ashitaka volcanic sand and gravel lower, OF: Old Fuji, agglomeratic mud flow.

Fig. 11 Key diagram showing the chemical character of groundwater in the study area.



Bulletin of the Geological Survey of Japan, Vol. 40, No. 7

Fig. 12 The relationship between dissolved solids and bicarbonate contents in groundwater from volcanic aquifers in the study area.



Fig. 13 The relationship between dissolved solids and silica contents in groundwaters.



Fig. 14 The relationship between silica and sodium in groundwater of Old-Fuji and other volcanic aquifers.



Fig. 15 Classification of groundwater by some selected constituents ratios.

Bulletin of the Geological Survey of Japan, Vol. 40, No. 7

through the water-rock interaction in each layer. Most characteristic feature of the water quality is the relation between dissolved SiO_2 and other cationic constituents in the water. In Figure 15, the groundwaters in the volcanic ejecta of Old Fuji, New Fuji and Ashitaka are classified on the basis of the mol ratio of SiO_2 to total cation. The characteristics of the groundwater in each layer are expressed by the mol ratios of Mg to Ca, and K to Na.

The mol ratios of K to Na in the groundwater in the Fuji lava and that in the Ashitaka ejecta are 0.17 and 0.12 on the average. The difference in mol ratios reflects the difference in K/Na in the rock as referred by FUJII and YUI (1985).

3.3 Changes in Groundwater Quality in a Groundwater Flow System

The chemical evolution of the water which has come into contact to the rock, eroding the rock and increasing the quantity of the dissolved constituents in it is explained by the behaviour of H^+ in the water entering the grids of minerals and displacing the cations in the minerals (FREDRECKSON, 1951). Generally, H^+ in natural water is produced by the chemical reaction between water and CO₂ gas, expressed by the following equation.

 $CO_2+H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3 \quad (3-1)$ In rare cases, H^+ exists as a free in-

In rare cases, H^+ exists as a free inorganic acid in natural waters, but no free inorganic acid in the water of this area could be observed. H^+ is produced mainly as a result of the chemical reaction of CO₂ gas. The chemical reaction between the water and CO₂ gas begins between rainwater and the atmosphere. The concentration of CO₂ in the atmosphere is 0.03% and rainwater has approximately 1 mg/l of dissolved CO₂. The rainwater which contains CO₂ precipitates and infiltrates into the soil. At this stage rainwater contains the maximum quantity of CO₂.

Table 10 shows the result of measurements of the concentration of CO_2

| bow one one one property of allowing allowing the | | | | | | | | |
|---|---------------------|-----|---------------------|--|--|--|--|--|
| No. | CO ₂ (%) | No. | CO ₂ (%) | | | | | |
| 1 | 0.060 | 6 | 0.092 | | | | | |
| 2 | 0.24 | 7 | 0.067 | | | | | |
| 3 | 0.130 | 8 | 0.062 | | | | | |
| 4 | 0.105 | 9 | 0.054 | | | | | |
| 5 | 0.172 | 10 | 0.049 | | | | | |
| | N=10 | Av. | 0.103 | | | | | |

in the soil gas, conducted in the Iwamoto district of Fuji City, which is located at the foot of Mt. Fuji. The concentration of CO_2 collected at 10 points at a depth of 1 meter and alined at 10 meters intervals ranges from 0.06 to 0.24%. The values are 2–8 times as high as that in the atmosphere.

On the other hand, the groundwater in the volcanic ejecta in this area shows a high degree of saturation of dissolved oxygen, which suggests that there are few organic materials in these aquifers which consume oxygen. CO_2 originating from decomposition of organic substances is minor. Thus, these aquifers are considered to be closed systems as far as CO_2 is concerned.

It is assumed that CO_2 charged water, while percolating the soil zone, consumes CO_2 by the weathering reactions of the rocks in the water-bearing layer. While the concentration of the bicarbonates of Ca^{2+} , Mg^{2+} , Na^+ , and K^+ increases, the CO_2 decreases by means of the water-rock interaction. As groundwater moves along its flow paths in the aquifer, increases of those chemical constituents which reflect the aquifer rock quality occur. As can be seen from Fig. 12, the quantity of HCO_3^- in the water increases in proportion to the degree of the weathering reaction of CO₂, which means that the quantity of HCO3- is closely correlated with the total dissolved solids.

In this area there exist successive layers of volcanic ejecta which are considered to be closed systems concerning CO₂. Furthermore, the lithological properties of each

-362-

aquifer are considered relatively homogeneous. Therefore, the groundwater moving in each aquifer comes into contact with the same rock and the same waterrock interaction occurs continuously. The chemical reaction of the moving groundwater is thought to undergo the same process as that of the weathering reaction of a static water-rock system.

The most important rock-forming mineral in the volcanic ejecta in this area is plagioclase, which accounts for about 40%of the normative minerals calculated for the chemical composition of the New Fuji lava. If it is assumed that the water-rock interaction in this area is a water-plagioclase reaction, then the water-plagioclase reaction in the New Fuji lava can be explained by the following expression. In it Na:Ca (0.35:0.65, mol ratio) is based on the mean value for chemical constituents in the New Fuii lava (Table 8).

 $2Na_{0.35}Ca_{0.65}Al_{1.65}Si_{2.35}O_8 + 3.3CO_2 +$

 $7.75H_2O \rightarrow 0.7Na^+ + 1.3Ca^{2+} +$

 $3.3HCO_{3}^{-} + 1.4H_{4}SiO_{4} +$

 $\begin{array}{cc} 1.65Al_2Si_2O_5(OH)_4 & (3\text{--}2)\\ \text{The chemical equation } (3\text{--}2) \text{ shows the} \end{array}$

chemical reaction in which kaolinite is formed. The change in chemical composition of the moving groundwater will be characterized by increase in the quantity of Na⁺, Ca²⁺, HCO₃⁻ and dissolved SiO₂(H₄ SiO₄) with the mol ratio of 0.7:1.3:3.3:1.4.

For the groundwater both in the New Fuji lavas and in the upper part of the Ashitaka volcanic sand and gravel layer, pH values indicate that the groundwater is neutral and SiO₂:Na (mol ratio) is 2:1 even at their coastal ends, which suggests that kaolinite is formed in these layers. Furthermore, in the groundwater of the Old Fuji agglomeratic mud flow layer underlying the New Fuji lava layer in the lowland, as shown in Figs. 12 and 13, the concentration of HCO₃ increases as the increase in total dissolved solids, while the concentration of SiO₂ remains constant at about 38 mg/l, and pH is higher with relatively high quantity of Na⁺ than that of other volcanic aquifers in this area.

In order to explain the difference in water quality between groundwaters in the Old Fuji and the New Fuji, it is necessary to take into account the water-rock interaction in these aquifers.

Differences in water-rock interaction have been noted previously in literatures. For example, KOVDA and SAMOILOVA (1969) presented a diagram showing how kaolinite tends to accumulate in uplands area and montmorillonite in lowlands as a consequence of groundwater flow.

GARRELS (1967), WALLICK (1981) and ICHIKUNI *et al.* (1982) assumed the formation of montmorillonite by a reaction of the following type:

The chemical equation (3-3) shows that in this stage Ca²⁺ and SiO₂ in the groundwater are lost or their quantity decreases.

3.4 Groundwater Flow Pattern Revealed by Bicarbonate Concentration

It is assumed that in the groundwater moving in a continuous and lithologically homogeneous aquifer the quantity of bicarbonate continues to increase until it reaches the saturation point. Under this assumption, there might be a correlation between the reaction time and the concentration of HCO_3^- as a reaction product.

When the groundwater moves between two points, the higher the velocity, the shorter the reaction time is and the smaller the increment of the concentration of HCO_{3}^{-} is.

In view of the fact that in the studied area there exist in volcanic ejecta layers, it is hypothesized that the spatial distribution of HCO_3^- concentration indicates the direction of groundwater movement.

Figure 16-1 shows the distribution of







 HCO_3^- concentrations and the estimated flow direction of the shallow groundwater. Near the point where the Akabuchi River flowing along the boundary between Mt. Fuji and Mt. Ashitaka runs out to the lowland and near the point where the Taki River flowing at the foot of Mt. Fuji runs out to the lowland, are areas with low con-

Bulletin of the Geological Survey of Japan, Vol. 40, No. 7



Chemical evolution of groundwater quality (K. Ikeda)

Fig. 17 Distribution of the potentiometric surface and specific yield of wells of groundwater in the slope of Mt. Fuji area.

centrations of HCO_3^- and HCO_3^- concentration increases in the direction of southwest.

Figure 16–2 shows the distribution of HCO_3^- in the Old Fuji agglomerative mud flow layer at depths of more than 150 meters and the Ashitaka volcanic ejecta lower layer and the estimated direction of groundwater movement in both aquifers. The distribution of HCO_3^- concentrations is characterized by the equi-concentration contours in an extremely narrow range along the Wada River and a sudden change in concentration. Groundwater of which the bicarbonate content has a range of 70 to 110 mg/l is distributed to the west of the Wada River, and groundwater of which the bicarbonate content has a range of 42 to 65 mg/l to the east of the Wada River. Along the Wada River, the groundwater in this aquifers qualitatively becomes divided into two types.

The groundwater in the agglomeratic mud flow layer at the western side shows increase in HCO_3^- concentration toward the coast and forms a semicircle area of more than 100 mg/l at the western side of the harbour of Tagonoura. Groundwater seems to become stagnant near this area.

At the eastern side of the harbour of Tagonoura, equiconcentration lines show higher concentration from the southern foot of Mt. Ashitaka toward the harbour of Tagonoura. It seems that the groundwater recharged at the foot of Mt. Ashitaka moves southwestward along the gradient of the Ashitaka volcanic ejecta layer.

At the foot of Mt. Fuji HCO_3^- concentration is the lowest in this area which range 30 to 66 mg/l. HCO_3^- concentration increases as altitude decreases and groundwater flow generally paralles to the lay of the land. HCO_3^- concentration is relatively low near the Okubo-Godo-Funakubo area where the groundwater temperature is low, which suggests that there is significant groundwater movement near this area.

On the other hand, Fig. 17 shows the distribution of hydraulic heads and specific capacity values. Data on static water level, running water level and pumpage are those available from Fuji City Waterworks department (unpublished data, 1986). The direction of groundwater flow, which is suggested by the distribution of HCO_3^- concentrations, makes clear that there is a high hydraulic head point, as well as a very high specific capacity point. This hydrological data suggest that points of high groundwater flow—these points are valleys—correspond well to the distribution of HCO_3^- concentration.

3.5 Discussion on the Chemical Evolution of Groundwater

It is assumed that the chemical composition of the groundwater in the volcanic ejecta in this area results from the interaction between rainwater, CO_2 and volcanic rock in an oxidizing environment, with HCO_3^- as anion and Na⁺, K⁺, Ca²⁺, Mg²⁺ as cations and water-soluble SiO₂(H₄SiO₄) dissolved in groundwater. SiO₂:Na (mol ratio) in the groundwater in the New Fuji lava layer and the Ashitaka volcanic ejecta layer is 2:1, the ratio is nearly equal to that obtained from the chemical equation (3–2) in which kaolinite is produced as a result of the weathering reaction between the feldspar in rocks and water containing CO_2 . This mol ratio seems to corroborate the above assumption. It is then necessary to examine whether it is possible to explain all dissolved constituents by a chemical reaction of the kaolinite production from minerals composing the lava.

If it is assumed that minerals which compose the New Fuji lava are plagioclase, olivine, augite and magnetite (SAWAMURA, 1955), the weathering reaction in which these minerals produce kaolinite can be explained as follows. The expressions for the reaction were worked out on the basis of those formulated by GARRELS (1967).

The expression for plagioclase is the same as the chemical equation (3-2) shown in 3.3.

The chemical equation for pyroxene (general name for augite, etc.) is as follows, if it is assumed that it contains equal quantities of Mg and Fe:

 $\begin{array}{l} 2Mg_{0.5}Fe_{0.5}SiO_3 + 4CO_2 + 6H_2O \\ \rightarrow Mg^{2+} + Fe^{2+} + 2H_4SiO_4 + 4HCO_3^{-} \end{array} \right.$

In an oxidizing environment, Fe^{2+} is

(3-6)

precipitated immediately.

 $Fe^{2+}\!+\!2HCO_3\!+\!1/2H_2O\!+\!1/4O_2$

 $\rightarrow 1/2Fe_2O_3 + 2CO_2 + 3/2H_2O$ (3-5) Chemical equation (3-6) is obtained from (3-4) and (3-5).

 $2Mg_{0.5}Fe_{0.5}SiO_3 + 4CO_2 + 6H_2O$

 \rightarrow Mg²⁺+2HCO₃+2H₄SiO₄

Although olivine is thought to be a solid solution with a formulation of $(Mg, Fe)_2$ SiO_4 -Mg₂SiO₄-Fe₂SiO₄, it is considered to be Mg₂SiO₄ here for the sake of simplification.

 $Mg_2SiO_4 + 4CO_2 + 4H_2O$

 $\rightarrow 2Mg^{2+} + 4HCO_3^- + H_4SiO_4$ (3-7)

Though existence of orthoclase of other K-bearing minerals was never mentioned in previous studies of the New Fuji lava (TSUYA, 1971; SAWAMURA, 1955), the chemical composition of the lava indicates that K is present. Although K is thought to
be contained in late stage minerals as sodic plagioclase or glass, it is assumed here that it is produced as a result of the weathering reaction of orthoclase.

 $\begin{array}{ll} 2KA1Si_{3}O_{8}+2CO_{2}+11H_{2}O\\ \rightarrow 2K^{+}+2HCO_{3}^{-}+4H_{4}SiO_{4}+\\ Al_{2}Si_{2}O_{5}(OH)_{4} \end{array} \hspace{2cm} (3-8) \\ \end{array}$

Expressions for magnetite in an oxidizing environment are:

 $\begin{array}{l} 2Fe_{3}O_{4}+2CO_{2}+H_{2}O\\ \rightarrow Fe^{2+}+2HCO_{3}^{-}+Fe_{2}O_{3} & (3-9)\\ Fe^{2+}+2HCO_{3}^{-}+1/4O_{2} \rightarrow Fe_{2}O_{3}+H_{2}O & (3-10) \end{array}$

Magnetite does not contribute to the formation of chemical composition of water through (3-9) and (3-10).

Generally the groundwater in the volcanic ejecta in this area contains extremely small quantities of Fe^{2+} and Mn^{2+} . This means that the rock hardly can contribute to the formation of Fe^{2+} and Mn^{2+} in the groundwater.

The Ashitaka volcanic ejecta are lower in concentration of FeO, K_2O and TiO_2 than rocks of the New Fuji lava layer, but they are similar in terms of constituent minerals. So the same expression for weathering reaction as that for the New Fuji lava can be assumed.

On the other hand, the Old Fuji agglomeratic mud flow layer in generally basaltic. The rocks in the mud flow are generally olivine basalt, augite and olivine basalt. The constituent minerals are plagioclase, pyroxene and olivine (TSUYA, 1971). In view of the fact that SiO_2 :Na (mol ratio) in the groundwater in this area is 1:1 and pH value is about 7.8 (alkaline), it is assumed that a chemical reaction in which montmorillonite is formed as explained by the equation (3–3) occurs, as reported by GARRELS (1967), WALLICK (1981) and ICHIKUNI (1982).

Equilibrium constant k in this reaction is expressed by the following equation.

$$k = \frac{\lfloor Ca^{2+} \rfloor \lfloor SiO_2 \rfloor^8}{[H^+]^2}$$
(3-11)

The logarithmic equation for the above is $\log k = \log Ca^{2+} + 2 pH + 8 \log SiO_2$

(3-12)

If the value of log k obtained from the equation (3-12) on the basis of molarity for Ca²⁺, pH and SiO₂ remains the same, regardless of the increase of other constituents, this suggests that the equation (3-3) is in equilibrium.

Figure 18 shows the relation between Na⁺ and log k plotted for the water quality of the groundwater in this area. The log k for the groundwater in the Old Fuji agglomeratic mud flow remains at the same level 13.7 ± 0.3 on the average, which suggests that the equation (3–3) for the kaolinite-montmorillonite system is almost in equilibrium.

Judging from the groundwater quality in the Old Fuji system, it is necessary to assume a weathering reaction to produce kaolinite and montmorillonite. There is a report by TSUYA (1971) on the chemical composition of the Old Fuji volcanic rock. According to the report, Ca:Na (mol ratio) is 0.66:0.33, which is nearly equal to the mean value for the New Fuji lava. The weathering reaction of the Old Fuji volcanic rock in which kaolinite is produced seems to go through processes as explained by weathering reaction equations (3–2), (3–6), (3–7) and (3–8) and then a process as explained by equation (3–3).

Table 11 shows the chemical equations for the weathering reaction in which rockforming minerals produce kaolinite and montmorillonite. Table 12 shows the stoichiometric relation between them, expressed by means of mol ratios.

Table 13 shows the results of calculations carried out under the assumption that the chemical composition of the groundwater in the volcanic ejecta in this area is formed as a result of the weathering reaction. The calculation is based on the Tables 11 and 12 and existence of rainwater as well as water-soluble NaCl and CaSO₄



Bulletin of the Geological Survey of Japan, Vol. 40, No. 7

Fig. 18 Sodium concentration versus log $([Ca^{2+}]/[H^+]^2) + 8 \log SiO_2$ for groundwater in volcanic aquifers.

Table 11 Chemical reactions for weathering of silicate minerals to kaolinite, smectite and soluble cations.

 $\begin{array}{ll} 2Na_{0.35}Ca_{0.65}Al_{1.65}Si_{2.35}O_8+3.3CO_2+7.75H_2O=0.7Na^++1.3Ca^{2+}+3.3HCO_3^-+1.4H_4SiO_4+1.65Al_2Si_2O_5(OH)_4\\ Plagioclase (Na 0.35:Ca 0.65) Kaolinite\\ 2KAlSi_3O_8+2CO_2+11H_2O=2K^++2HCO_3^-+4H_4SiO_4+Al_2Si_2O_5(OH)_4\\ Orthoclase (K-feldspar) Kaolinite\\ Pyroxene (Mg 0.5: Fe 0.5) MgSiO_3+2CO_2+3H_2O=Mg^{2+}+H_4SiO_4+2HCO_3^-\\ FeSiO_3+2CO_2+3H_2O=Fe^{2+}+H_4SiO_4+2HCO_3^-\dots(Step 1)\\ Fe^{2+}+2HCO_3^-+1/2H_2O+1/4O_2=1/2Fe_2O_3+2CO_2+3/2H_2O\dots(Step 2)\\ (Step 1+Step 2) 2Mg_{0.5}Fe_{0.5}SiO_3+4CO_2+6H_2O=Mg^{2+}+2HCO_3^-+2H_4SiO_4\\ Olivine Mg_2SiO_4+4CO_2+4H_2O=2Mg^{2+}+4HCO_3^-+H_4SiO_4\\ 7Al_2Si_2O_5(OH)_4+Ca^{2+}+8H_4SiO_4=6Ca_{0.17}Al_{2.34}Si_{3.66}O_{10}(OH)_2+8H_2O+2H^+\\ Kaolinite \\ Macl=Na^++Cl^-\\ CaSO_4=Ca^{2+}+SO_4^-\\ Base exchange \\ 2Na-clay+Ca^{2+}=Ca-clay+2Na^+\\ \end{array}$

* Smectite is the name of the montmorillonite group.

originating from the rock. Of the chemical constituents in the groundwater, Na^+ , Ca^{2+} , K^+ , HCO_3^- and SiO_2 are produced as a result of the weathering reaction of

plagioclase and orthoclase and Mg^{2+} , HCO_3^- , SiO_2 and so on as a result of the weathering reaction of olivine.

If it is not assumed that the chemical con-

Chemical evolution of groundwater quality (K. Ikeda)

| | | | Weathering product (mole) | | | | | | | | | |
|---------------------------------|------|------------------|---------------------------|-------------|--------------|----|------------------|------------------|------------|-----------|----------|--|
| Original minerals | mole | | | | TZ - 1' - '' | C | | | | | | |
| | | HCO ₃ | C1- | SO_4^{2-} | Na+ | K+ | Ca ²⁺ | Mg ²⁺ | H_4SiO_4 | Kaolinite | Smectite | |
| Plagioclase (Na0.35: Ca0.65) | 2 | 3.3 | | | 0.7 | | 1.3 | | 1.4 | 1.65 | | |
| K-feldspar | 2 | 2 | | | | 2 | | | 4 | 1 | | |
| Pyroxene (Mg1: Fe1) | 2 | 2 | | | | | | 1 | 2 | | | |
| Mg-olivine | 1 | 4 | | | | | | 2 | 1 | | | |
| Kaolinite | 7 | | | | | | -1 | | -8 | | 6 | |

Table 12 Mole ratios of weathering products (from the equations of Table 11).

Table 13 Dissolved constituents in groundwater and reconstruction of water quality by combination of weathering reactions from actual silicate minerals, 13–1 FL, AL, and AU groundwaters 13–2 OF groundwater.

| Ashitaka-lower | volcanic: | AL | ground | lwater |
|----------------|-----------|----|--------|--------|
|----------------|-----------|----|--------|--------|

| Weathering reactions | | | | Concentrati | ion (10^{-3}) | M) | | |
|--|------------------|------|-------------|-------------|-----------------|------------------|-----------|---------------------------------|
| *Dissolved | HCO ₃ | Cl- | SO_4^{2-} | Na+ | K+ | Ca ²⁺ | Mg^{2+} | H ₄ SiO ₄ |
| in water | 0.84 | 0.09 | 0.06 | 0.30 | 0.03 | 0.21 | 0.13 | 0.56 |
| Plagioclase (Na 0.35: Ca 0.65) → Kaolinite | 0.54 | | | 0.11 | | 0.21 | | 0.24 |
| K-feldspar — Kaolinite | 0.03 | | | | 0.03 | | | 0.06 |
| Pyroxene | 0.26 | | | | | | 0.13 | 0.26 |
| Mg-olivine | 0 | | | | | | 0 | 0 |
| NaCl | | 0.09 | | 0.09 | | | | |
| CaSO ₄ | | | 0.06 | | | 0.06 | | |
| Base exchange | | | | +0.10 | | -0.05 | | |
| Sum of reactions | 0.84 | 0.09 | 0.06 | 0.30 | 0.03 | 0.22 | 0.13 | 0.56 |

Ashitaka-upper volcanic: AU groundwater

| Weathering reactions | | | | Concentrati | ion (10^{-3}) | M) | | |
|--|------------------|------|-------------|-------------|-----------------|------------------|-----------|------------|
| *Dissolved | HCO ₃ | Cl- | SO_4^{2-} | Na+ | K + | Ca ²⁺ | Mg^{2+} | H_4SiO_4 |
| in water | 0.78 | 0.11 | 0.07 | 0.31 | 0.04 | 0.20 | 0.14 | 0.56 |
| Plagioclase (Na 0.35: Ca 0.65) → Kaolinite | 0.45 | | | 0.10 | | 0.18 | | 0.20 |
| K-feldspar — Kaolinite | 0.04 | | | | 0.04 | | | 0.08 |
| Pyroxene | 0.28 | | | | | | 0.14 | 0.28 |
| Mg-olivine | 0 | | | | | | 0 | 0 |
| NaCl | | 0.11 | | 0.11 | | | | |
| CaSO ₄ | | | 0.07 | | | 0.07 | | |
| Base exchange | | | | +0.10 | | -0.05 | | |
| Sum of reactions | 0.78 | 0.11 | 0.07 | 0.31 | 0.05 | 0.20 | 0.14 | 0.56 |

| Fuji lava: FL ground | water | | | | | | | | | | | |
|--|------------------|-------|-------------|-------------|-----------------------------|------------------|---------------------|------------------|-----------|------------|--|--|
| Weathering reactions | | | | | Concentration $(10^{-3} M)$ | | | | | | | |
| *Dissolved | HCC |)_ | Cl- | SO_4^{2-} | Na | a+ | K+ | Ca ²⁺ | Mg^{2+} | H_4SiO_4 | | |
| in water | 1.1 | 0 | 0.17 | 0.15 | 0 | .41 | 0.05 | 0.35 | 0.22 | 0.67 | | |
| Plagioclase (Na 0.35: Ca 0.65) \rightarrow Kaolinite | 0.6 | 1 | | | 0 | .13 | | 0.25 | | 0.26 | | |
| K-feldspar — Kaolinite | 0.0 | 6 | | | | 1 | 0.06 | | | 0.12 | | |
| Pyroxene | 0.2 | 4 | | | | | | | 0.12 | 0.24 | | |
| Mg-olivine | 0.2 | 0 | | | | | | | 0.10 | 0.05 | | |
| NaCl | | | 0.17 | | 0 | .17 | | | | | | |
| CaSO ₄ | | | | 0.15 | | | | 0.15 | | | | |
| Base exchange | | | | | +0 | .10 | | -0.05 | | | | |
| Sum of reactions | 1.1 | 0 | 0.17 | 0.15 | 0 | .40 | 0.06 | 0.35 | 0.22 | 0.67 | | |
| Old-Fuji volcanic: Ol | F ground | water | | | | | | | | | | |
| Weathering reactions | | | | | Conce | ntration | (10 ⁻³ M |) | s. | | | |
| *Dissolved | HCO ₃ | C1- | SO_4^{2-} | Na+ | K^+ | Ca ²⁺ | Mg^{2+} | H_4SiO_4 | Kaolinite | Smectite | | |
| in water | 1.43 | 0.17 | 0.15 | 0.69 | 0.05 | 0.32 | 0.22 | 0.57 | | | | |
| Plagioclase (Na 0.35: Ca 0.65) \rightarrow Kaolinite | 0.94 | | | 0.20 | | 0.37 | | 0.40 | 0.47 | | | |
| K-feldspar \rightarrow Kaolinite | 0.05 | | | | 0.05 | | | 0.10 | 0.05 | | | |
| Pvroxene | 0.26 | | | | | | 0.13 | 0.26 | | | | |
| Mg-olivin | 0.18 | | | | | | 0.09 | 0.05 | | | | |
| NaCl | | 0.17 | | 0.17 | | | | | | | | |
| CaSO ₄ | | | 0.15 | | | 0.15 | | | | | | |
| Kaolinite \rightarrow Smectite | | | | | | -0.03 | | -0.24 | -0.20 | +0.18 | | |
| Base exchange | | | | +0.32 | | -0.16 | | | | | | |
| Sum of reactions | 1.43 | 0.17 | 0.15 | 0.69 | 0.05 | 0.33 | 0.22 | 0.57 | 0.32 | +0.18 | | |

Bulletin of the Geological Survey of Japan, Vol. 40, No. 7

Table 13 (continued)

* Dissolved constituents in water data from the average values of the chemical analyses in Table 7.

stituents in the groundwater in the Fuji lava and the Ashitaka volcanic ejecta reflect the weathering reaction in which rock-forming minerals produce kaolinite and that some part of the Ca^{2+} is produced as a result of this reaction through cation exchange with Na⁺ in the aquifer, there will be no mass balance between the mineral system and the water quality system. Similarly, if it is not assumed that the chemical constituents in the groundwater in the Old Fuji volcanic rock go through processes of production of montmorillonite and cation exchange, there will be no mass balance between the mineral system and the water quality system.

However, there is a strong opinion by clay mineralogists that kaolinite does not change to montmorillonite under a condition of normal groundwater temperature in Japan. As stated earlier, the tendency for constancy of log k in Fig. 18 at higher Na⁺ concentrations suggests equilibrium between kaolinite and montmorillonite. Therefore, if kaolinite does not changes to montmorillonite, production of montmorillonite from rock-forming minerals has to be considered. Experimental verification of the assumption that kaolinite changes to montmorillonite stated by GARRELS (1967) is a future task.

It is generally thought that it takes an extremely long time before the water-rock interaction reaches equilibrium. Thus the groundwater in the Old Fuji mud flow seems to be one with a long residence time. OCHIAI (1967) reported that the groundwater in the Old Fuji mud flow is at least 50 vears old based on their measurement on tritium concentration in it. They also measured tritium concentration in the groundwater in the New Fuji lava and reported that the groundwater in it is relatively new. It seems therefore that the water quality of the groundwater in the New Fuji lava differs from that of the groundwater in the Old Fuji mud flow in terms of duration of the water-rock interaction.

4. Mixing of the Fresh Groundwater and Intruded Sea Water

In the studied area salinization has been observed since 1960. Figure 8 shows the scope of salinization and locations of salinized groundwater samples as of 1970. Salinization occurred after а sharp drawdown of groundwater level which had been observed for several years and the salinized area expanded from near the coastline to the inland. In view of these hydrological phenomenon, sea water intrusion must be assumed. The chemical composition of the salinized groundwater, however, is quite different from that of the fresh groundwater mixed with sea water. This raises two important questions. The first question is: How to identify the origin of salt water which has caused salinization? The origin of salt water can be sea water, fossil salt water or pore water (interstitial water).

The second question is: If it is assumed that salt water originated in sea water, why has such an extreme change in water quality resulted after the mixing of fresh groundwater and sea water? This phenomenon cannot be explained by mere mixing of two types of water with different water quality. So it seemed obvious that this can be explained by a water-rock/sediment interaction. In other words, it was necessary to take the rocks and sediments in the aquifer into account in explaining this phenomenon.

4.1 Salinization of Groundwater in the Coastal Area

Salinization in this area began near the mouth of the Numa River in 1960. Salt water intrusion began near the boundary between two areas of the New Fuji lava laver and the Ashitaka volcanic sand and gravel layer, which are the two major layers in this area, and then expanded northward along the Wada River where the boundary mesh distributes. In 1961 the salt water intruded into the lava layer aquifer near the western coast of the harbour of Tagonoura and then the groundwater in the New Fuji lava layer in the inland area was salinized rapidly. On the other hand, the rate of salinization of the groundwater in the Ashitaka volcanic sand and gravel laver at the eastern side of the Wada River was slow but expanded steadily. Figure 19 shows how salinization expanded from its initial stage until 1966. Figure 20 shows the vertical distribution of salinized groundwater as of 1970 for geological sections A-A' and B-B' in Fig. 2. At that point of time none of the alluvial layer, the Old Fuji agglomerative mud flow layer and the Ashitaka volcanic sand and gravel lower layer was salinized. Thus salinization in this area appears to be limited to the major



Bulletin of the Geological Survey of Japan, Vol. 40, No. 7

Fig. 19 Advance of sea water intrusion into groundwater. Dotted line shows the boundary between the New Fuji lava distributed area (western side) and the Ashitaka volcanic sand and gravel layer (eastern side).

aquifers in the lava layer and the Ashitaka volcanic sand and gravel upper layer.

Salinization of the groundwater in the New Fuji lava layer in this area is closely related to the change in groundwater level. Figure 6 shows that there was a sharp drawdown of lava groundwater level from 1960 to 1963. At the well b which is 2.7 km away from the coast the groundwater level dropped by as much as 4 meters during that period. Figure 21 shows the relation between Cl⁻ concentration and groundwater level at point FY-2 since 1965. As can be seen from this diagram, Cl⁻ concentration increases or decreases as groundwater level drops or rises. As this diagram shows, it is clear that the groundwater in the lava layer in this area was salinized as a







Fig. 21 Secular changes of groundwater level and chloride concentration in New Fuji lava aquifer, 1961–1970, and 1970–1983.

result of drawdown of groundwater level. The change in Cl^- concentration since 1970 is that observed at the observation well G–3. There has been a sharp decrease in Cl^- concentration since 1972. This decrease in Cl^- concentration is related to the rise of groundwater level by about 3 meters since 1972 at the well G–3, as shown in Fig. 6. These data are very important, because they suggest that the salinized aquifer can be recovered into fresh groundwater aquifer by raising groundwater level.

4.2 Origin of Salt Water

Salinization of the groundwater in the

New Fuji lava layer and the Ashitaka volcanic sand and gravel layer is monitored by the observation of Cl⁻ concentration which was conducted once a month (based on data available from Shizuoka Prefecture) and chemical analysis of all species of 50 samples was conducted twice a year. Of these samples, 7 samples (FY 1–7) collected from the groundwater in the New Fuji lava layer and 5 samples (FG 1–5) collected from the groundwater in the Ashitaka volcanic sand and gravel layer were selected as the representative samples from low to high levels of salinization of groundwater (see Fig. 2). Then,

measurement of the isotopic composition of oxygen and hydrogen of water was conducted using these representative samples (ANDO and IKEDA, 1980).

show the relation of δ^{18} O and δ D values to material is negligible, it is assumed that, salinization of groundwater was caused by coefficients of the Cl⁻ to the δ D, to the δ^{18} closer to the SMOW point. The correlation with higher Cl⁻ concentration are plotted point of SMOW (Standard Mean Ocean gravel layer along a line connecting the lava and the Ashitaka volcanic sand and for the salinized water in both the New Fuji $\delta D = 8 \delta^{18}O + 10$ parallel to the global meteoric water line fresh groundwater are plotted on a ed groundwater, δ^{18} O and δ D values for the groundwater, and the 11 samples of saliniz-<u>_</u> and hydrogen of water. Figures 22 and 23 values of isotopic composition of oxygen result of mixing can be expressed by the when sea water mixes with fresh water, the and hydrogen of water tween the isotopic composition of oxygen measurements. Since the interaction besea water intrusion. respectively. O, and the δD to the $\delta^{18}O$ were above 0.9, Water) and the fresh groundwater. Table 14 shows the results of these concentration of a sample of fresh These (Craig, data 1961) and those and the aquifer suggest . Those that line

4.3 Water-Rock/Sediment Interaction in Salinized Groundwater

The water quality of the groundwater in the lava layer and Ashitaka volcanic sand and gravel upper layer in this area before salinization was characterized by singledigit Cl⁻ concentration (HIRUKAWA *et al.*, 1957; IKEDA, 1967), which was close to the mean value for the water quality of the groundwater in both layers and it was of Ca-HCO₃ type.

If it is assumed that the groundwater was salinized as a result of sea water intrusion, most of the Cl⁻, Na⁺, Ca²⁺, Mg²⁺ and $SO_4^{2^-}$ content-excluding HCO₃⁻ and SiO₂,

| Table 14 | Chemical and isotopi | c compositions of | of salinized | groundwaters | from the l | New Fuji lava | a aquifer and the | Ashitaka-upper aquifer |
|----------|----------------------|-------------------|--------------|--------------|------------|---------------|-------------------|------------------------|
|----------|----------------------|-------------------|--------------|--------------|------------|---------------|-------------------|------------------------|

| Loc. No. | Depth m | δD_{SMOW} | $\delta^{18}O_{\mathrm{SMOW}}$ | Tw °C | pН | M–Alk me/l | Cl- mg/l | $rac{\mathrm{SO}_4^{2-}}{\mathrm{mg}/l}$ | $\frac{NO_{\overline{3}}}{mg/l}$ | Na mg/ <i>l</i> | K mg/l | Ca mg/l | Mg mg/ <i>l</i> | Fe mg/l | SiO_2 mg/l |
|-------------|------------|-------------------|--------------------------------|----------|-----|---------------|-------------|---|----------------------------------|--------------------|-----------|------------|--------------------|------------|-----------------|
| FY-1 | 150 | -50.5 | -7.55 | 15.6 | 7.2 | 0.78 | 5.1 | 5.0 | 7.5 | 6.0 | 2.4 | 12.0 | 4.3 | 0.02 | 45.0 |
| FY-2 | 100 | -49.9 | -7.46 | 16.7 | 6.6 | 0.73 | 1414.0 | 229.6 | 3.3 | 500.0 | 19.7 | 280.8 | 110.8 | 0.01 | 41.0 |
| FY–3 | 70 | -36.1 | -6.4 | 14.3 | 6.5 | 0.76 | 6156.0 | 872.4 | 1.5 | 2910.0 | 62.6 | 525.7 | 445.1 | 0.04 | 31.4 |
| FY-4 | 107 | - 4.24 | -0.36 | 15.1 | 6.8 | 1.53 | 17641.0 | 2315.0 | | 9150.0 | 335.0 | 435.3 | 1148.0 | 0.36 | 26.0 |
| FY-5 | 107 | -46.7 | -7.13 | 15.9 | 7.0 | 1.30 | 2344.0 | 327.0 | | 1350.0 | 62.5 | 70.0 | 129.3 | | |
| FY-6 | 107 | -11.7 | -1.69 | 14.9 | 7.0 | 1.46 | 14807.0 | 2088.0 | | 8096.0 | 301.0 | 408.2 | 1009.5 | 0.56 | 21.8 |
| FY–7 | 100 | - 1.36 | -0.24 | 14.8 | 7.1 | 1.58 | 18281.0 | 2535.0 | | 10200.0 | 508.0 | 417.1 | 1244.8 | 1.44 | 20.1 |
| FG-1 | 135 | -46.7 | -6.7 | 15.5 | 7.5 | 6.39 | 497.5 | 63.5 | | 51.8 | 6.5 | 184.5 | 62.9 | 0.13 | 39.2 |
| FG-2 | 100 | -45.2 | -6.7 | 15.8 | 7.7 | 0.87 | 1448.1 | 194.1 | | 243.0 | 19.0 | 457.0 | 148.1 | 0.03 | 35.5 |
| FG-3 | 90 | -46.6 | -7.7 | 13.7 | 7.4 | 0.74 | 1996.5 | 255.1 | | 636.0 | 17.7 | 453.3 | 149.2 | 0.66 | 32.7 |
| FG-4 | 84 | -35.1 | -4.8 | 17.6 | 7.5 | 1.18 | 7089.0 | 870.2 | | 2170.0 | 61.1 | 1598.9 | 598.8 | 0.55 | 28.3 |
| FG-5 | 90 | -37.7 | -5.5 | 15.8 | 7.2 | 0.78 | 4708.5 | 626.9 | | 1340.0 | 48.7 | 1105.5 | 427.0 | 0.24 | 33.3 |
| | | | | | | | | | | | | | | | |

 $M-Alk(me/l) \times 61.0 = HCO_3 (mg/l)$

- 375 -



Bulletin of the Geological Survey of Japan, Vol. 40, No. 7

Oxygen-18 and deuterium contents in fresh and salinized groundwater. Fig. 22



Correlation of isotopic composition to chloride concentration of the salinized groundwater. Fig. 23



Fig. 24 The relationship between chloride concentration and selected constituents in salinized groundwater.

the two major components of the fresh groundwater-originated in sea water and the ratio of each of these components to Cl^- should be close to that observed in sea water. Figure 24 shows the relation between the Cl^- content and the Na⁺, K⁺, Ca²⁺, Mg²⁺, Br⁻ and I⁻ content of the salinized groundwater.

In the salinized groundwater Ca/Cl is by

far higher and Na/Cl and K/Cl are lower than in sea water, from which it is obvious that the relation between these cation components and Cl^- cannot be explained by mere mixing of fresh groundwater and sea water.

As regards anions in the salinized groundwater, SO_4/Cl is a little higher, and I/Cl is a little lower in the salinized groundwater

— 377 —



Fig. 25 Key diagram showing chemical character changes by salinized groundwater.

than in sea water. Br/Cl in the salinized groundwater is the same as in sea water.

The change in chemical composition when fresh groundwater is salinized is shown in the key diagram in Fig. 25. The salinized groundwater is very Ca^{2+} rich in comparison with the mixing line in the case of mere mixing of fresh groundwater and sea water. It belongs to the water quality type of Ca–Cl in the key diagram classification. As shown in the same diagram, however, the anion composition is similar to that of "fresh water+sea water" as the triangular coordinate system of Cl⁻, SO₄²⁻ and HCO₃⁻ + CO₃²⁻ indicates.

The above-mentioned isotopic composition of oxygen and hydrogen of water and anion composition suggests that the groundwater in this area was salinized as a result of sea water intrusion. On the other hand, the cation composition shows a very different chemical characteristics. Based on these facts, it can be assumed that the groundwater in this area was salinized as a result of a water-rock/sediment interaction-mainly a cation exchange reaction-between the intruding sea water and the geological materials, which are the clay/ silt layers distributed on and beneath the aquifer. In this area in particular, it appears that the interaction between the intruded sea water and the clay/silt layers distributed on and beneath the lava and the Ashitaka volcanic sand and gravel upper layer was involved in the salinization of the groundwater.

According to the result of identification of non-clay and clay minerals by X-ray diffraction (Fig. 26), these samples of the clay/silt layers contain non-clay minerals such as quartz and plagioclase and clay minerals such as chlorite and illite.

It can thefore be assumed that the sea water which had intruded into the aquifer came into contact with these clay/silt layers acting as confining layers for the groundwater and was then changed in quality mainly as a result of its cation exchange with clay minerals.

— 378 —



Fig. 26 X-ray diffraction analyses of core samples.

5. Laboratory Experiments Regarding Water-Rock Interaction

As stated in Chapter 3, formation of the chemical composition of the groundwater

in this area is characterized by an increase in chemical constituents in the moving groundwater and a change in water quality, which suggest that it is possible to estimate the direction of the groundwater flow and

Bulletin of the Geological Survey of Japan, Vol. 40, No. 7

classify aquifer on the basis of the characteristic chemical composition. In this chapter, the mechanism of water quality formation through the water-rock interaction between aquifer materials and rainwater, which is the base of the above, is studied.

For this purpose, samples of the New Fuji lava and the Ashitaka volcanic rocks, both of which are the major aquifer materials in this area, were collected and then the interaction between them and pure water was observed in the laboratory. This laboratory experiment is advantageous in that it makes it possible to observe a natural phenomenon in its simplified form in the laboratory and trace the change in water quality over time.

Also laboratory experiment on salinization of groundwater was conducted for the purpose of identifying the geological materials which interact with the intruded sea water and clarifying such underground reactions as solution, deposition and cation exchange reaction in the laboratory.

- 5.1 Types and Methods of Experiments
- (1) Experiment on Solution of Powdered Rock Samples in Water

Leaching experiments on samples of the New Fuji and Ashitaka volcanic ejecta, collected from 11 points in this area were carried out. Figure 8 shows the locations of rock sampling and Table 15 the types of rock samples.

The rock samples were crushed into powder of less than 100 mesh (0.147 mm)and 2.5 g of it was put into a 250 ml polyethylene bottle together with 250 ml of distilled water. Then each bottle was sealed completely and stored in a dark place at room temperature. After a given period of time, the water in each bottle was analyzed to determine the dissolved constituents in it. The periods of storage of bottle were 7, 14, 23, 247, 380, 660 and 870 days, respec-

| Rock sample No. | Sample rock name | Sample site |
|--------------------|--------------------------------------|---------------------------------------|
| R- 1 | New Fuji volcano Fuji lower lavas | Outcrop |
| R- 2 | Fuji basal lavas | Outcrop |
| R- 3 | Fuji lower lavas | Outcrop |
| R- 4 | Fuji lower lavas | Outcrop |
| R- 5 | Fuji middle lavas | Outcrop |
| R- 6 | Fuji lower lavas | Boring core $(-5 \sim -17 \text{ m})$ |
| R- 7 | Ashitaka middle (tuff breccia) | Outcrop |
| R- 8 | Ashitaka lower (basalts) | Outcrop |
| R- 9 | Ashitaka middle (tuff breccia) | Outcrop |
| R-10 | Ashitaka lower (basalts) | Outcrop |
| R–11 | Ashitaka lower (basalts) | Outcrop |

Table 15 Lithology of the sampled rocks.

tively. Each bottle remained sealed for each period of storage, sometimes being shaken to accelerate mixing of constituents. The chemical constituents analyzed were pH, HCO_3^- , Cl^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} , Na⁺, K⁺, and SiO₂.

(2) Experiment on Interaction between Geological Test Samples and Sea Water

Three samples of clay layers (1-1, 1-2, 2-2) were collected at wells G-1, G-2 (Fig. 2) and the lava sample (2-3) was collected at depths as shown in Fig. 27. Silt and clay were prepared from clay layer samples by the elutriation method and were then airdried. And samples of these air-dried silt and clay were used in the experiment. Two kinds of experiments were carried out:

1) Leaching Experiment on Geological Test Samples with Sea Water

In this experiment a separating funnel and the leaching tube were used as leaching device (see Fig. 28). The leaching tube was filled with a mixture of quartz sand and sample (2:1 or 4:1); quartz sand was prepared to be mashed with warm dilute hydrochloric acid and then with pure water, onto which sea water was dropped



Fig. 27 Geological column at G-1 and G-2 and sampling depth of the test material.

from the separating funnel. Then the eluate was divided into several fractional solutions and the chemical composition of each fractional solution was analyzed.

2) Cation Exchangeable Capacity (CEC) and Exchangeable Cation Analysis

The improved method (WATANABE, 1961) of the analytical method of CEC developed by Schollenberger and SIMON (1945) was used for this analysis. 1N solution of CH₃COONH₄, used as leaching solution, was dropped onto the sample and then NH₄⁺ absorbed into the sample was extracted with NaCl solution for estimation. The absorption of NH₄⁺ was defined as cation exchangeable capacity (CEC).

 Na^+ , K^+ , Ca^{2+} , Mg^{2+} and other cations

Chemical evolution of groundwater quality (K. Ikeda)



Fig. 28 Apparatus of experiment.

which were dissolved in the leaching solution as a result of displacement by NH_4^+ were analyzed. These cations were defined as exchangeable cations.

In the experiment, the leaching solution was washed in ethyl alcohol solution because the divalent ion/monovalent ion ratio increases, if it is washed in pure water (SAYLES and MANGELSDORF, 1977).

Clay minerals in the silt/clay samples were identified with an X-ray diffraction instrument (manufactured by Rigaku Denki K.K.). The powdered samples were suspended in a small quantity of water and then put on a glass slide and dried. The clay films thus prepared were used as samples and their measurement was conducted under the testing conditions shown in Fig. 26.

- 5.2 Result of Analysis
- (1) Leaching Experiment on Formation of Water Quality



Bulletin of the Geological Survey of Japan, Vol. 40, No. 7

Fig. 29 Dissolution of chemical constituents in the water-rock reaction experiment.

Figure 29 shows the change over time of the chemical constituents which were dissolved from the powdered rock samples in the leaching experiment mentioned in 5.1 (1). The result of this experiment can be summarized as follows:

1) The concentration of dissolved chemical constituents increases in proportion to the logarithm of the time of contact.

2) The composition of dissolved chemical constituents changes over time. The composition of the major chemical constituents after a lapse of 660 days was 50–75 equivalent % of $Ca^{2+}+Mg^{2+}$ in cation and 85–90 equivalent % of HCO_3^- in anion.

3) A very small quantity of Cl^- dissolves from the rock. Dissolution of Cl^- stops before the end of the first month. The quantity of Cl^- dissolution hardly increases

thereafter.

4) SO_4^{2-} dissolves little by little from the rock and it seems that sulfur compounds in it are oxidized little by little in the course of weathering.

5) After a lapse of 380 days white precipitate was found on the surface of the powdered rock sample. As a result of X-ray diffraction it was found that this precipitate is amorphous. Its major chemical constituents are SiO_2 , Al_2O_3 and Fe_2O_3 . The other chemical constituents include TiO_2 and CaO.

6) After a lapse of 660 days a decrease of Ca^{2+} and a rapid increase of Na^+ was observed in the dissolved chemical constituents.

7) The pH value changed from "slightly acidic" to "slightly alkaline." Chemical evolution of groundwater quality (K. Ikeda)



Fig. 30 Key diagram showing chemical character for water-rock interaction experiment.

8) SO_4/Cl ratio in the composition of dissolved chemical constituents in the case of samples of the New Fuji lava was higher than in the case of samples of the Ashitaka volcanic rock.

As shown in Fig. 29, in the chemical reaction observed in the above-mentioned experiment the dissolution rate gradually became lower and the pH value increased over time. This phenomenon seems to occur because CO_2 in water is involved in the water-rock interaction, gradually decreasing and thus decelerating the interaction.

As shown in the key diagram of Fig. 30, the composition of dissolved chemical constituents after a lapse of 660 days is, excepting the relatively low Cl^- and SO_4^{2-} content and the low concentration of dissolved chemical constituents, quite similar to that seen in the groundwater in the New Fuji laval and the Ashitaka volcanic sand and gravel layer. It is quite natural that the $Cl^$ and SO_4^{2-} content is relatively low because the sample contains no Cl^- and SO_4^{2-} originating in rainwater. The low concentration of dissolved chemical constituents can be explained by the experimenting condition under which the ratio of water to the rock sample is 100:1.

Figure 31 shows the change over time of the composition of dissolved chemical constituents. Na/Ca, K/Na, Mg/Ca and SiO₂/ total cations (mol ratio each) were used as chemical indices. For the purpose of comparison of these chemical indices for the original rock, the experimental eluate water and the groundwater, the mean value for chemical constituents in the original rock and that for each of the groundwater in the New Fuji lava layer and the groundwater in the Ashitaka volcanic sand and gravel layer are shown in Tables 4 and 3, respectively.

Na/Ca (mol ratio) is higher in the case of the experimental eluate water and the groundwater than in the case of the original

Bulletin of the Geological Survey of Japan, Vol. 40, No. 7



Fig. 31 Changes of sodium to calcium ratio, potassium to sodium ratio and magnesium to calcium ratio, during the experiments.

31–1 New Fuji lava rock samples

rock, which means that Na⁺ is more soluble than Ca²⁺. The fact that the first experimental eluate water after a lapse of 7 days showed the highest Na/Ca means that Na⁺ is most soluble. After a lapse of more than 7 days Na/Ca decreases as a result of an increase in the quantity of dissolved Ca²⁺, coming close to that for the original rock. After a lapse of 660 days, however, the Ca²⁺ content decreases and the Na⁺ content increases despite the increase in the total quantity of dissolved chemical constituents, which suggests that some cation exchange reaction occurred in the experiment system.

As stated earlier, K/Na (mol ratio) is higher in the case of the original rock and the groundwater in the Fuji lava than in the case of the original rock and the groundwater in the Ashitake volcanic sand and gravel layer. The same phenomenon was observed with the experimental eluate water. Excepting the eluate water with one sample of the New Fuji lava (0.10–0.13) and that with one sample of the Ashitaka volcanic sand and gravel layer (0.13), all the other 5 samples showed mol ratios of 0.06-0.09.

There was no significant difference in Mg/Ca among the original rock, the experimental eluate water and the ground-water. There was little change over time in Mg/Ca for the experimental effluent.

In the comparison of the experimental eluate water and the groundwater in the New Fuji lava and the Ashitaka volcanic rock in terms of SiO₂/total cations (total cations are represented as total milliequivalents per liter for Ca²⁺ + Mg²⁺ + Na⁺ + K⁺ and SiO₂ as millimol per liter), the range for the eluate water contact with the New Fuji lava rock were 0.5–0.7, that for the groundwater in New Fuji lava layer and in the Ashitaka volcanic layer were 0.5–0.6. Thus the experimental and the groudwater are harmonious with each other.

 SiO_2 :Na for the experimental eluate water (after a lapse of 660 days) was 1.8:1

^{31–2} Ashitaka volcanic rock samples

Table 16 Water quality by water-rock experiment (660 days) and calculated composition by weathering reactions (Table 11, 12).

| Weathering reactions | | | | Concentrati | ion (10^{-4}) | M) | | |
|--|------------------|------------|-------------|-------------|-------------------------|------------------|------------------|---------------------------------|
| Dissolved | HCO ₃ | C1- | SO_4^{2-} | Na+ | K + | Ca ²⁺ | Mg^{2+} | H ₄ SiO ₄ |
| in water | 3.29 | 0.16 | 0.23 | 1.37 | 0.16 | 0.68 | 0.49 | 2.20 |
| Plagioclase (Na 0.35: Ca 0.65) \rightarrow Kaolinite | 2.15 | | | 0.45 | | 0.84 | | 0.90 |
| K-feldspar → Kaolinite | 0.16 | | | | 0.16 | | | 0.32 |
| Pyroxene | 0.98 | | | | | | 0.49 | 0.98 |
| Mg-olivine | 0 | | | | | | 0 | 0 |
| NaCl | | 0.16 | | 0.16 | | | | |
| $CaSO_4$ | | | 0.23 | | | 0.23 | | |
| Base exchange | | | | +0.78 | | -0.39 | | |
| Sum of reactions | 3.29 | 0.16 | 0.23 | 1.39 | 0.16 | 0.68 | 0.49 | 2.20 |
| | | r | Water-rock | experiment | t | | | |
| | The water c | ontact wit | h Ashitaka | volcanic ro | ock sample | es (average) | 1 | |
| Weathering reactions | | | | Concentrat | ion (10 ⁻⁴) | M) | | |
| Dissolved | HCO ₃ | C1- | SO_4^{2-} | Na+ | K+ | Ca ²⁺ | Mg ²⁺ | H_4SiO_4 |
| in water | 3.34 | 0.13 | 0.12 | 1.27 | 0.12 | 0.68 | 0.47 | 2.14 |
| Plagioclase (Na 0.35: Ca 0.65) \rightarrow Kaolinite | 2.28 | | | 0.48 | | 0.89 | | 0.96 |
| K-feldspar → Kaolinite | 0.12 | | | | 0.12 | | | 0.24 |
| Pyroxene | 0.94 | | | | | | 0.47 | 0.94 |
| Mg-olivine | 0 | | | | | | 0 | 0 |
| NaCl | | 0.13 | | 0.13 | | | | |
| CaSO ₄ | | | 0.12 | | | 0.12 | | |
| Base exchange | | | | +0.66 | | -0.33 | | |

Water-rock experiment The water contact with Fuji lava rock samples (average)

for the effluent of the Fuji lava and 2:1 for the effluent of the Ashitaka volcanic rock, which suggests occurrence of a weathering reaction in which plagioclase changes into kaolinite.

3.34

0.13

0.12

1.27

0.12

Sum of reactions

Calculation was done on the assumption that the dissolved chemical constituents in the experimental eluate water were produced as a result of a weathering reaction, based on the equations of Tables 11 and 12. Table 16 shows the mass balances of chemical constituents, under each of which each mineral produces each ion. In this table of mass balances, which was prepared on the assumption that silicate minerals in the rock samples have gone through a weathering reaction, the balance is not kept unless it is also assumed that there were some cation exchange reactions. This assumption is necessary because the Ca and Mg content of cation in water is smaller than that in the original

0.68

0.47

2.14



Triangular diagram of Ca:Mg:Na+K composition

- Rock sample of Fuji lavas
- Rock sample of Ashitaka volcanic rocks
- Water from W-R interaction experiment
- O Groundwater in FL(mean value)
- \triangle Groundwater in AL (mean value)
- 🛦 Groundwater in OF (mean value)
- Fig. 32 Composition in mol-percentage of Ca, Mg, and Na+K in host volcanic rocks, water from water-rock experiments and groundwaters.

rock and the converse is true of the Na content. According to Fig. 29 which shows the result of a laboratory experiment, with the experimental eluate water of all of the samples RW 1-11, the experimental value for Ca²⁺ decreases and that for Na⁺ increases rapidly after a lapse of 660 days, despite the fact that experimental values for all the other ions continue to increase over time. This means that there was a cation exchange reaction even in the sealed system of pure water and the rock sample alone. Thus the table of mass balances, including cation exchange reactions, shown in Table 16 seems to reflect accurately the result of the laboratory experiments on the water-rock interaction.

Figure 32 shows a comparison of the chemical constituents in the original rock,

the experimental eluate water and the groundwater in this area on triangular coordinates of the three constituent system of Ca, Mg and Na+K. The experimental eluate water from the original rock is Na+K rich in comparison with the original rock. The values for the groundwater and those for the experimental eluate water are harmonious with each other.

These results indicate that the chemical constituents in the original rock are not necessarily identical with those in dissolved ions. They also seem to indicate that there are many aspects of the process of water quality formation which cannot be interpreted correctly without taking into account the cation exchange reaction between Na⁺ and Ca²⁺.

As stated earlier, the table of mass balances, as shown in Table 13, which relates the formation of the groundwater in this area is invalid unless it presupposes a cation exchange reaction. These experiment results seem to suggest that this thinking is right. These experiment results also suggest that an argument about the chemical constituents in the plagioclase in the original rock which is merely based on the result of analysis of water quality may lead to a wrong interpretation about it.

Figure 33 shows the process of water quality formation in the dissolution experiment plotted in the diagram which BRICKER and GARRELS (1967) prepared using the equilibrium constant for mineral phase and chemical constituents in water. As can be seen from this diagram, mineral phase in equilibrium with water varies with the time. In the initial stage of the water-rock interaction the experimental eluate water is seen to evolve as it moves toward the gibbsite area, then to the kaolinite area and finally to the boundary between the kaolinite area and Ca-montmorillonite area. In actuality, the groundwater is located far beyond in the direction of the evolution of the experimental eluate water. The ground-



Fig. 33 Evolution of water quality of water from water-rock experiments on the activity diagram. Arrow shows the change of the quality with the lapse of time.

water in the Fuji lava and the Ashitaka volcanic sand and gravel upper layer is plotted in the kaolinite area, the groundwater in Ashitaka volcanic sand and gravel lower layer near the boundary between the kaolinite area and the Ca-montmorillonite area and the groundwater in the Old Fuji mud flow in the Ca-montmorillonite area.

These experimental results also suggest that types of minerals which are produced as by-products (weathering products) of formation of the water quality of the groundwater in the volcanic rocks vary with the time.

Another process of water quality evolution clarified as a result of the dissolution experiment can be studied in terms of the relation between Na⁺ and log (Ca²⁺/H²) +8 log SiO₂—i.e. log k. As shown in Fig. 18, in this relation the composition of dissolved constituents in the experimental eluate water on the lava sample R–3 is characterized by increase of Na⁺ and decrease of log k. In other words, the composition of dissolved constituents changes as they move toward the area indicated by the groundwater in the lava. Accordingly, in this diagram the process of change in water quality, from the very beginning of the water-rock interaction to a state nearly equal to that of equilibrium, is drawn in the direction of the arrow. It seems that Figs. 33 and 18 will serve as important indicators of the evolution of the water quality of the groundwater in volcanic rock areas.

(2) Experiment on Sea Water-Sediments Interaction

Figure 34 shows the result of a laboratory experiment of leaching geological core samples with sea water. G 2–3 sample is the New Fuji lava salinized by sea water and G 2–2 sample is the confin-



Bulletin of the Geological Survey of Japan, Vol. 40, No. 7

Fig. 34 Chemical change of percolated sea water on the experiment of sea water-sediments interaction.

ing layer of the salinized aquifer.

The experiment result shows that the New Fuji lava (G 2–3) itself, which has become an aquifer, hardly changes the chemical composition of sea water.

In an experiment with the clay/silt sample G 2–2, the chemical composition of the leaching solution (sea water) changed remarkably, which means that sea water apparently underwent a change in quality. The leaching solution showed more increase of Ca^{2+} and SO_4^{2-} in comparison with sea water. Mg^{2+} concentration is almost same between the two. As can be seen from Table 17 which shows increase or decrease of each of the chemical constituents in sea water, decrease of Na⁺ and K⁺ is not consistent with increase of Ca^{2+} and Mg^{2+} . Part of the increment of Ca^{2+} dissolves from the clay/silt sample in the form of sulfate.

Dissolution of sulfate from the clay/silt sample was also observed in the case of pure water leaching. When the dissolution of the sulfate in the clay/silt sample is corrected, decrease of $Na^+ + K^+$ becomes almost consistent with increase of $Ca^{2+} +$ Mg^{2+} , which means that there was a cation exchange reaction between the alkaline earth metal ion in the sample and the alkali metal ion in sea water.

In this experiment, change in the quality of the first fraction solution was most remarkable. The other fraction solutions are almost in equilibrium with sea water, excepting the fact that they contain larger quantities of SO_4^{2-} and Ca^{2+} than sea water. This experiment was conducted under normal atmospheric pressure and at normal room temperature. The whole ex-

| | HCO ₃ | | HCO ₃ | | Cl- | | SO_4^{2-} | | Anion total | Na ⁺ | | K + | | Ca ²⁺ | | Mg^{2+} | | Cation total |
|---|------------------|------|------------------|--------|-----------------|-------|-------------|------|----------------|-----------------|------|------------|-------|------------------|-------|-----------|--|-----------------|
| | mg/l | me/l | mg/l | me/l | mg/l | me/l | me/l | mg/l | me/l | mg/l | me/l | mg/l | me/l | mg/l | me/l | me/l | | |
| Original sea water sample | 122.6 | 2.01 | 15618 | 440.43 | 2175 | 45.24 | 478.68 | 8670 | 376.28 | 312 | 7.98 | 340 | 17.00 | 1060 | 87.24 | 488.50 | | |
| 1st leaching sea water (6 m <i>l</i>) | 113.5 | 1.86 | 15618 | 440.43 | 2403 | 49.98 | 492.24 | 8580 | 372.37 | 275 | 7.04 | 557 | 27.85 | 1063 | 87.40 | 494.66 | | |
| 2nd leaching sea water (7 m <i>l</i>) | 113.5 | 1.86 | 15618 | 440.43 | 2267 | 47.15 | 489.25 | 8660 | 375.84 | 288 | 7.37 | 384 | 19.20 | 1066 | 87.74 | 490.15 | | |

Table 17 Chemical changes of sea water composition after leaching of the silt-clay samples.

- 389 -

| | | Table | e 18 M | ineralogy o | f the silt-clay | samples. | | | | | | | |
|------------|-----------------------|-----------|-------------------------|--------------|---------------------|----------|----------|---------|--------|--|--|--|--|
| | | | Constituent of minerals | | | | | | | | | | |
| Sample No. | Sampling depth (m) | | Clay pa | $(-2 \mu m)$ |) | | | | | | | | |
| | , | Kaolinite | Illite | Chlorite | Montmori llonite | Quartz | Feldspar | Calcite | Gypsum | | | | |
| G 1–1 | 51 | II | II | II | _ | ## | ₩ | + | + | | | | |
| G 2–2 | 97 | II | II | II | _ | +++ | # | ± | ± | | | | |

 $-\colon Not$ detected; I: 0–9%; II: 10–19%; III: 20–29% (wt.%)

+: Detected; #: minor; #: major

perimenting process, from the first drip of sea water until the last stage, took about 6 hours. The result of this experiment implies that the interaction between sea water and the chemical constituents in a layer is rather quick.

In this experiment, as the SO_4^{2-} content of the leaching solution increased, pH value decreased, HCO_3^- concentration decreased and free CO_2 concentration increased. This phenomenon shows that sulfides in the clay/silt sample were oxidized and dissolved in the leaching sea water. It seems that chemical reactions represented by the following equations occurred.

| $2O_2 + HS^- \rightarrow SO_4^{2-} + H^+$ | (5-1) |
|---|-------|
| $HCO_3^- + H^+ \rightarrow H_2O + CO_2$ | (5–2) |

Table 18 shows the result of X-ray diffraction of the chemical constituents in the clay/silt samples (1–1 and 2–2) used in the leaching experiment with sea water. These samples consist of clay minerals containing mainly chlorite, illite and kaolinite and nonclay minerals containing mainly quartz and plagioclase. The sample G 2–2 has a CEC of 8.3 milliequivalents per 100 g (Table 19). It seems that there was a cation exchange reaction between sea water and clay minerals in the clay/silt layer which becomes the confining layer for the ground-water.

The composition of the exchangeable cations in the sample G 2-2 was measured before and after leaching in the leaching experiment. Table 19 shows the result of this leaching experiment. The composition of the exchangeable cations before the sample comes into contact with sea water is characterized by abundance of Ca²⁺, while after leaching it is characterized by abundance of Na⁺. This change indicates that there were cation exchange reactions in which exchangeable Ca²⁺ was discharged into sea water and Na⁺ and K⁺ in sea water were absorbed in the calv sample as exchangeable cations. Figure 35 illustrates these cation exchange reactions.

Table 20 shows the result of calculation of the quantity discharged or absorbed of

| Table 20 | Changes in exchangeable cations of | | | | | | |
|----------|---------------------------------------|--|--|--|--|--|--|
| | the silt-clay sample through reaction | | | | | | |
| | with sea water. | | | | | | |
| | | | | | | | |

| Sample | Na+ | K+ | Ca ²⁺ | Mg ²⁺ |
|--------|-------|-------------|------------------|------------------|
| | (me | /100 g of s | silt-clay sam | ple) |
| G 2–2 | -2.58 | -0.49 | +3.00 | +0.07 |

Table 19Exchangeable coations of the silt-clay samples under original conditions and after equilibration to the
sea water.

| Sample Depth (m) | | Exchangeable cation composition (Original) | | | Σ Cations | CEC (NH ₄ Ac) | Exchangeable cation composition (Equilibrium with sea water) | | | | |
|------------------|----|--|------|------|------------------|-----------------------------|--|------|------|------|------|
| | | ×Na | ×K | ×Ca | $\times Mg$ | me/100 g | me/100 g | ×Na | ×K | ×Ca | ×Мg |
| G 2–2 | 97 | 0.06 | 0.02 | 0.64 | 0.28 | 7.20 | 8.31 | 0.37 | 0.08 | 0.28 | 0.27 |

 $\times Na \ \times K \ \times Ca$ and $\ \times Mg:$ equivalent fraction

Fig. 35 Cation exchange reaction between silt-clay sample G 2-2 and sea water.



Fig. 36 Change of exchangeable cations after the reaction between the core sample (G 2–2) and sea water, compared with the difference of cation composition of a salinized water sample (FY–2) from that estimated on the basis of simple mixing.

each of the exchangeable cations Na⁺, K⁺, Ca²⁺, and Mg²⁺. It is obvious that the sample G 2–2, which was collected from right above a salinized lava layer, absorbed 2.5 milliequivalents/100 g of Na⁺ and 0.49 milliequivalents/100 g of K⁺ from sea water and discharged 3.00 milliequivalents/100 g of Ca²⁺ and 0.07 millliequivalents/100 g of Mg²⁺.

The above-mentioned experimental results can illustrate the phenomenon of salinization of the groundwater in this area. The water quality of the salinized groundwater is characterized by abundance of Ca²⁺, which seems to be attributable mainly to a cation exchange reaction between it and clay minerals in the clay/silt layer which acts as a confining layer. This may be explained by the fact that, as shown in Fig. 36, the ratio of the difference between the concentration of each of Ca^{2+} , Mg^{2+} , Na⁺ and K⁺ in the actual salinized groundwater and "fresh water+sea water" is relatively consistent with the result of calculation of the quantity discharged or absorbed of each of Ca^{2+} , Mg^{2+} , Na^+ and K^+ .

On the other hand, there is no significant difference between the concentration of SO_4^{2-} in the salinized groundwater and the calculated value for the simple mixing of sea water and fresh groundwater. But in the case of the salinized groundwater $SO_4/$ Cl is a little higher and HCO_3/Cl is a little lower than in the case of "fresh water+sea water". This phenomenon may be explained by the fact, as was observed in the experiment leaching the geological test samples with sea water, sulfide compounds were oxidized and dissolved in sea water as a result of the intruded sea water's contact with the clay/silt layer in an oxidizing environment. It seems that H⁺ produced as a result of this oxidization reaction decomposed HCO_3^- , thereby lowering pH value.

6. Interpretation of the Hydrological Phenomenon of Salinization of Groundwater Based on the Study of Cl⁻ Concentration

As stated in chapters 4 and 5, it is obvious that salinization of the groundwater

- 391 -



Bulletin of the Geological Survey of Japan, Vol. 40, No. 7

Fig. 37 Flowing interval at the well B and the calculated water level by Ghyben-Herzberg principle.



Fig. 38 The relationship of fresh water-salt water interface in coastal aquifer by Ghyben-Herzberg principle (after Harder et al., 1966).

in this area was caused by sea water intrusion. Thus the concentration of Cl^- in groundwater can be used as an element indicative of sea water intrusion. In this chapter the mechanism of sea water intrusion in the initial stage of salinization of groundwater is studied through the relation between the concentration of Cl^- in groundwater and groundwater level.

6.1 Relation between Cl⁻ Concentration and Ghyben-Herzberg's Wedge of Salt Water

In the following a description of the

changes in the concentration of Cl^- in the groundwater in the intermittently flowing well in the Tago district on the western side of the harbour of Tagonoura based on the result of a survey of the concentration of Cl^- contained in the artesian groundwater in the Fuji lava aquifer is given.

The well B is located 570 meters away from the coastline. Figure 37 shows Cl⁻ concentration values, flowing intervals and the result of conversion of values for tide level at the harbour of Shimizu (Japan Meteorological Agency, 1961) into Tokyo Bay Medium Tide Level values (T.P.). The Cl⁻ concentration changes from 90, 106 mg/l at low tide to 144,155 mg/l at high tide, which evidences the effect of tidal change on Cl⁻ concentration. At the high tide, the groundwater flows for 4 hours and stops flowing at the low tide. Thus groundwater level varies with the phase of tidal change.

The head of the well B, 114.5 meters deep, is 2.493 meters above sea level. The New Fuji lava layer distributes 103.7-114.5 meters in depth. Its screen is as deep as the depth of the lava layer. Until 1959 the well used to flow continuously and Cl⁻ concentration used to be about 3 mg/l. This means that the groundwater could be salinized even when groundwater level was above sea level. This phenomenon suggests that it is related to Ghyben-Herzberg's principle.

As shown in Fig. 38 (HARDER *et al.*, 1953), the wedge of salt water intrudes into the inland as a result of the difference in density between sea water and fresh water near the coast. In actuality there appears a mixing area between salt water and fresh water. But here it is assumed that there appears a clear salt water/fresh water interface between them. The well B with increasing Cl⁻ concentration is thought to be located at the tip of the intruding wedge of salt water. It can be said that the well B came into contact with the salt water/fresh water interface at a depth of 114.5 meters.

Figure 37 shows, in broken lines, the result of calculation using Ghyben-Herzberg's principle.

$$\mathbf{h} = (\boldsymbol{\rho}\mathbf{s} - 1)\mathbf{H} \tag{6-1}$$

- where h: fresh water level above sea level ρ s: density of sea water (1.025, g/cm³)
 - H: depth of salt water/fresh water interface (from sea level)

Given the sea level which varies with tidal change as base

- at low tide: $h_{min} = (\rho s-1) H_{min}$ (6-2)
- at high tide: $h_{max} = (\rho s 1) H_{max}$ (6-3)

The intermittent flowing of groundwater from the well B is well consistent with the result of the above calculation, which means that salinization of the intermittently flowing well B can be explained by the intrusion into the inland of Ghyben-Herzberg's wedge of salt water. The fact that this phenomenon can be explained by Ghyben-Herzberg's principle seems to mean that the New Fuji lava aquifer has a structure which opens toward the sea.

Based on Ghyben-Herzberg's principle, HARDER *et al.* (1953) represented the relation between the length of the wedge of salt water in the artesian groundwater layer in a coastal area (L) and the flux of the fresh water which passes through the unit cross section of the artesian groundwater layer (q) as follows:

$$q = \frac{K}{2} (\rho s - 1) \frac{M^2}{L}$$
 (6-4)

Were K: hydraulic conductivity of aquifer, cm/sec

M: thickness of aquifer

The equation (6–4) indicates that, if the aquifer is homogeneous and fresh water flows steadily, there is a correlation between the wedge of salt water and the flux of fresh water.

As a result of calculation done on the assumption that L is 570 meters, thickness of aquifer is 10 meters and hydraulic conductivity of lava aquifer (K) is 1.7×10^{-1} cm/sec (Table 2). The flux of fresh water (q) is given with 2.24×10^{-4} m/min. Thus, it can be assumed theoretically that if the value for the flux of fresh water is smaller than this value, even though groundwater level higher than sea level, L will be longer than that of the well B and the scope of salinization will be expanded. The reverse may be true if the value for the flux of fresh water is larger than this value.

6.2 Sea Water Intrusion as a Result of Reversal of Hydraulic Gradient

Here the result of survey of water level



Bulletin of the Geological Survey of Japan, Vol. 40, No. 7

Fig. 39 Comparison of groundwater levels and fresh water-salt water interface in January 1961 and March 1966.

of and Cl⁻ concentration in the New Fuji lava aquifer and the Ashitaka volcanic sand and gravel aquifer conducted in March 1966 will be analyzed.

The groundwater level, which was above sea level in January 1961, fell below sea level and Cl⁻ concentration increased remarkably in March 1966. Figure 39 shows the water levels of and Cl⁻ concentrations in the New Fuji lava aquifer measured at the geological section C–C' extending from the coast to inland on the western side of the harbour of Tagonoura in January 1961 and March 1966. The tip of the wedge of salt water, which had reached the well B located 570 meters away from the coast in January 1961, reached the well C', located 2,500 meters away from the coast in 1966, while at the well C, located 1,000 meters away from the coast, Cl⁻ concentration in the groundwater was 19,000 mg/l which almost the same as that in sea water.

This seems to express that most of the groundwater in the New Fuji lava aquifer extending toward the coast from the well C was replaced with sea water. At this point of time the groundwater level fell as low as 5.0 meters below sea level. This means that despite the New Fuji lava aquifer dip toward the sea as shown in Fig. 39, the hydraulic head inclined toward the inland.

Since Ghyben-Herzberg's principle presupposes the static goundwater level



Fig. 40 Groundwater levels in New Fuji lava along the C–C' line and Ashitaka upper aquifer along the D–D' line in March 1966.

- 395 -

which is always above sea level, the abovementioned situation where the hydraulic gradient is below sea level causes sea water to flow into the inland.

The sea water intrusion toward inland can be calculated using Darcy's formula.

 $q=K \times dh/dl$ (6-5) Where q: flux, K: hydraulic conductivity of aquifer and dh/dl: hydraulic gradient

The equation (6-5) indicates that the flux of sea water intruding into the aquifer in the direction of the sea to inland is in proportion to the drawdown of the ground-water level in the inland.

Figure 40 shows the hydraulic head of the New Fuji lava aquifer extending along the line C-C' in Fig. 2 and that of the

Ashitaka volcanic sand and gravel upper aquifer extending along the line D-D' in Fig. 2 as measured in March 1966. The hydraulic head of each of the New Fuji lava aquifer and the Ashitaka volcanic sand and gravel upper aguifer is shaped like the letter "V". The gradient between the hydraulic head of the coastal side and the lowest hydraulic head on the inland side is reversed. The gradient of that of the groundwater in the New Fuji lava is $3.2 \times$ 10^{-3} and that in the Ashitaka volcanic sand and gravel upper aquifer is 3.8×10^{-3} . The hydraulic conductivity of the New Fuji lava laver ranges from 2.5×10^{-2} to 1.13 cm/ sec and that of the Ashitaka volcanic sand and gravel upper layer from 1.1×10^{-2} to

| Dunenn of the Geological Survey of Jupan, Vol. 40, 110. 7 | Bulletin | of the | Geological | Survey | of Japan, | Vol. | 40, | No. | 7 |
|---|----------|--------|------------|--------|-----------|------|-----|-----|---|
|---|----------|--------|------------|--------|-----------|------|-----|-----|---|

| the basis of | nydrological cal | culation and | the velocity of s | ea water int | rusion. | |
|---|------------------------------------|-----------------------|-------------------------------|---|---|--|
| | Hydraulic conductivity K | Hydraulic gradient | Flux q | Effective porosity ne | Actual velocity | Actual velocity by Cl ⁻ tracer |
| | $10^{-2} {\rm cm} { m sec}^{-1}$ | | $10^{-4}\mathrm{cm~sec^{-1}}$ | % | $10^{-4} \mathrm{cm}^{4} \mathrm{sec}^{-1}$ | $10^{-4}\mathrm{cm~sec^{-1}}$ |
| New Fuji lava | | | | | | |
| in the study area | 2.5 - 113 | $3.2 \cdot 10^{-3}$ | 0.8-36.2 | $\begin{array}{c} 10 \\ 20 \end{array}$ | $\begin{array}{c} 8-362 \\ 4-181 \end{array}$ | 127 |
| at the H well | 36.5 | $3.2 \cdot 10^{-3}$ | 11.7 | 10-20 | 58-117 | 127 |
| Ashitaka volcanic sand and gravel upper part | 1.1 - 1.4 | $3.8 \cdot 10^{-3}$ | 0.4–0.5 | | — | 39 |

Table 21 Comparison of actual velocity values for the New Fuji lava aquifer and the Ashitaka-upper aquifer on and of hydrological cal vilation and the valuat

 1.4×10^{-2} cm/sec. If these values are applied to Darcy's formula, the fluxes of intruding sea water (q) for both aquifers are:

New Fuji lava layer:

 $q = (0.8 - 35.2) \times 10^{-4} \text{ cm/sec}$

Ashitaka volcanic sand and gravel upper laver:

 $q = (4.8 - 5.3) \times 10^{-5} \text{ cm/sec.}$

The flux (q) thus obtained represents the rate of flow per unit cross section. The value for the actual velocity of sea water intruding into the aquifer can be obtained as average interstitial velocity (v_a) . And the average interstitial velocity (v_a) is the amount of q divided by effective porosity (ne, the ratio of pores to the quantity of water involved in groundwater flow, Kayane, 1980).

 $v_a = q/ne$

(6-6)OCHIAI (1965), who measured porosity of the New Fuji lava layer by the use of the gamma-gamma ray logging method at Takaoka in Fuji City, reports that porosity of the compact lava is less than 10% and that of the vesicular lava is 20%.

Table 21 shows the actual velocity of intrusion of sea water into the Fuji lava layer for the effective velocity of 10% and 20%.

The result of calculation based on the values for the hydraulic head of the New Fuji lava layer groundwater measured in March 1966 shows that the actual velocity of intrusion of sea water into this aquifer may be 0.35-15.65 meters/day when the effective porosity is 20% and 0.7-31.3 meters/day when it is 10%. As shown in Table 21, the actual velocity calculated on the basis of the hydraulic conductivity of the lava aguifer at the well H located on the line C-C' is 5.0-10.1 meters/day for the effective porosity range of 10 to 20%.

6.3 Velocity of Sea Water Intrusion Calculated by the Cl⁻ Concentration

Here a method of calculating the velocity of intrusion of sea water as it moves inland from a point near the coast in the initial stage of salinization of groundwater and the result of the calculation are examined. In this method, the velocity of intrusion of sea water is calculated on the basis of the relation between the distance from the coast and the point of time when Cl- concentration begins to increase, under the assumption that the point of time when Clconcentration in the groundwater in the same aquifer measured at points located at different distance from the coast begins to increase is the point of time when the tip of the wedge of salt water reaches the point where Cl- concentration begins to increase.

Figure 41 shows the distribution of wells of groundwater in the New Fuji lava aquifer located on the western side of the harbour of Tagonoura. The wells B, C, D, H, K and L are located 570 to 1,100 meters away from the coastline. This means that Cl⁻ concentration in the groundwater of each of these wells began to increase from



Chemical evolution of groundwater quality (K. Ikeda)

Fig. 41 Rate of sea water intrusion into New Fuji lava aquifer from sea shore to inland near Tagonoura harbour, in January 1961.

January 1961 to February 1961. The longer the distance between a well and the coastline, the later is the point of time when Cl⁻ concentration begins to increase. This means that sea water moved to the inland from the coast. Velocity of intrusion of sea water, which was calculated on the basis of the time that has elapsed since when Cl⁻ concentration in groundwater of each well reached 250 mg/l, and the distance between each well and the coastline, was 11 meters/day.

Figure 42 shows the result of calculation of the velocity of intrusion of sea water into the Ashitaka volcanic sand and gravel upper aquifer using Cl^- concentration as an indicator. The velocity of intrusion of sea water thus calculated was 3.3 meters/day.

Since salt water originated in sea water at stated earlier, Cl^- concentration can be regarded as a tracer of sea water intrusion. The above-mentioned data, which were obtained as a result of field survey in this area, are thought to represent the velocity of sea water intrusion as proved by increase in Cl^- concentration.

Comparisons of the values for actual velocity of sea water intrusion into the New Fuji lava layer calculated with this method and those obtained as a result of hydrological calculation conducted on the basis of hydraulic conductivity, hydraulic

Bulletin of the Geological Survey of Japan, Vol. 40, No. 7



Fig. 42 Rate of sea water intrusion into Ashitaka-upper aquifer along the D-D' line.

gradient and effective porosity, indicate that both are almost conformable to each other as far as the New Fuji lava aquifer is concerned (see Table 21). Comparison of two sets of values for the Ashitaka volcanic sand and gravel aquifer was impossible because there are no data on the effective porosity for this aguifer available. But the fact that actual velocity of sea water intrusion into this aguifer of 39.4×10^{-4} cm/sec was obtained as a result of calculation done on the basis of the flux of this aquifer of $(0.42-0.53) \times 10^{-4} \text{ cm/sec}$ and by the use of Cl- concentration as an indicator implies that the effective porosity of this aquifer must be 1.1-1.3%. But this value is too small for a sand and gravel layer. If the actual velocity calculated by the use of Cl⁻ as an indicator is correct, it is necessary to reexamine the hydraulic gradient or the hydraulic conductivity applied to Darcy's formula.

The following can be taken into account in considering the hydraulic gradient. In an area where groundwater is salinized it often happens that groundwater users stop pumping up the groundwater which was salinized and therefore deteriorated and bore wells one after another increasingly inland-ward from the coast in search of a source of non-salinized water. It is possible therefore that there appeared a locally larger hydraulic gradient near the boundary between salinized groundwater and fresh groundwater. If it is assumed that the effective porosity of the Ashitaka volcanic sand and gravel layer is 10%, the layer may have had a hydraulic gradient of 3.6/100. Thus the hydraulic gradient of the line D– D' in Fig. 40 must be modified as indicated with the dotted line.

Considering the local condition relative to the hydraulic gradient, the facts about velocity of sea water intrusion which were clarified as a result of survey of the phenomenon of salinization in this area seem to indicate that the mechanism of groundwater flow in an aquifer is almost conformable to the hydrological interpretation based on Darcy's formula.

7. Conclusion

This study was conducted for the pur-

-398-

pose of analyzing the groundwater quality in the area at the southern foot of Mt. Fuji on the assumption that the formation and evolution of the groundwater quality in a groundwater flow system is closely related to the chemical reactions between the groundwater and geological materials which result from groundwater flow.

In the studied area, a three-dimensional water quality distribution applicable to each of the Old Fuji layer, the New Fuji layer and the alluvial layer is observed on the western side of the geological boundary between the Fuji lava and the Ashitaka volcanic sand and gravel located at depths of 50 to 100 meters. A three-dimensional water quality distribution applicable to each of the Ashitaka volcanic sand and gravel upper/lower layers and the alluvial layer is also observed on the eastern side. The groundwater quality in each of these layers can be classified rather distinctly by the use of HCO_3^- concentration and the SO_4 /Cl, K/Na and SiO₂:Na ratios. This seems to indicate the result of a water-rock interaction which reflects the chemical and physical properties of the aquifer materials.

The water-rock interaction in the volcanic ejecta layers in this area seems to be a weathering reaction between the groundwater containing CO_2 gas and the minerals composing the volcanic ejecta. In this study, a model of the water quality formation through this weathering reaction was constructed and the process of formation of the groundwater quality in the volcanic ejecta was studied. Conclusions of this study are as follows.

 SiO_2 :Na in the groundwater in the volcanic ejecta layers except for in the Old Fuji layer was 2:1, which suggests a weathering reaction in which the plagioclase composing the New Fuji lava changes into kaolinite. Na/Ca is larger than the chemical composition of the New Fuji lava, which suggests that the lava's Na⁺ is

given priority over its Ca^{2+} in dissolving in groundwater. As one of the causes, it was confirmed in the leaching experiment using powdered rock samples with pure water that dissolved Ca^{2+} was absorbed in solid facies through a cation exchange reaction. Values for SiO₂:Na ratio and Na/Ca in the leaching water were almost the same as those for the groundwater, which means that the chemical constituents in the volcanic ejecta layer were produced as a result of a weathering reaction between rainwater and rocks.

SiO₂:Na in the groundwater in the Old Fuji agglomerative mud flow layer is approximately 1:1, which differs from SiO₂:Na values for the groundwater in other layers.

The tendency for constancy of log k at 13.7 ± 0.3 in log k–Na⁺ diagram at higher Na⁺ concentrations suggests equilibrium between kaolinite and montmorillonite in the Old Fuji agglomeratic mud flow layer. Long residence time of groundwater in the Old Fuji aquifer supports the above conclusion.

The above-mentioned water-rock interaction in a groundwater flow system results in an increase of bicarbonate with groundwater flow. Accordingly, the distribution of HCO_3^- concentration in the groundwater in the same continuous aquifer can indicate the direction of groundwater flow.

The direction of groundwater flow suggested by the distribution of HCO_3^- concentration is described as follows. The groundwater recharged on the slope of Mt. Fuji flows to the foot of the mountain as groundwaters in the New Fuji lava and the Old Fuji agglomeratic mud flow layer. Then it moves through these layers which are distributed continuously in the area extending from the foot of the mountain to the lowland. At the coastal area, the groundwater in the New Fuji lava layer flows toward the coast line. The groundwater in the Old Fuji layer forms a stagnation area near the middle point between the mouth of the Fuji River and the harbour of Tagonoura.

The groundwater in the Ashitaka volcanic sand and gravel layer flows along the direction of the inclination of the volcanic ejecta layer which extends beneath the alluvial layer south and southwest of the foot of Mt. Ashitaka. Then it flows to southwest, and comes into contact with the groundwater in the Old Fuji at a south-to-north line along the Wada River.

The above-mentioned facts indicate the possibility of interpreting such hydrological phenomena as distribution, continuity and flow of groundwater by using water quality.

The following has been clarified concearning the phenomenon of salinization of groundwater.

The groundwater in the New Fuji lava and the volcanic sand and gravel, both of which are the major aquifers in this area, was salinized caused by a rapid drawdown of groundwater level. The distribution of Cl^- concentration in these aquifers suggests sea water intrusion into the inland from the coast.

The water quality of the salinized groundwater is of Ca–Na–Cl type which is quite different from that of "fresh water+sea water".

The isotopic compositions of oxygen and hydrogen of the salinized groundwater are distributed on a line connecting the fresh groundwater and the SMOW (Standard Mean Ocean Water) datum point on the $\delta^{18}O-\delta D$ diagram.

The result of a leaching experiment by drilled core samples collected in the salinized area has proved that the sea water which has come into contact with the clay/ silt layer overlying the New Fuji lava layer undergoes a change in quality into the same water quality as the salinized groundwater. This change in water quality can be explained by the change in the composition of exchangeable cations of the clay/silt. The water quality of the salinized groundwater suggests that there occurred a cation exchange reaction and to a little extent a dissolution of sulfide in the clay/silt as sulfate both of which are caused by a contact between the intruding sea water and the clay/silt layer which acts as confining layer of the New Fuji lava groundwater. In this case, the exchangeable cation composition of the clay/silt layer has a dominant effect on the formation of the water quality of the salinized groundwater.

Acknowledgments: The author expresses his deep gratitude to his adviser, Dr. I. KAYANE, Professor of Institute of Geoscience, the University of Tsukuba, for his unfailing guidance throughout the completion of this work. Special thanks are extended to professor Dr. S. TAKAYAMA, Professor Dr. S. SHIMODA, Institute of Geoscience, the University of Tsukuba, and Professor Dr. S. SHINDOH, Department of Earth Sciences, the Faculty of Science, Chiba University, for their suggetions and guidance.

The author is grateful to Dr. T. KAKIMI, the former Director General, Geological Survey of Japan, for his encouragements during this work, and to Dr. K. ONO, Director, Environmental Geology Department, Dr. N. ANDO, Dr. Y. TAGUTSCHI of Environmental Geology Department, and Dr. N. TONO, Director, Geochemistry Department, Geological Survey of Japan, Dr. T. MURASHITA, for many helpful suggestions and discussions relating to this work, and Dr. M. YOSHII of Geological Survey of Japan, for making the computer programs available for his work.

Thanks are also extended to Shizuoka Prefectural Government, and Fuji City for the permission to use the data of groundwater in the Fuji region. Finally, the author thanks to factories and their persons concerned with his field survey or sampling work in Fuji region.

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-401-

Bulletin of the Geological Survey of Japan, Vol. 40, No. 7

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LIST OF SYMBOLS

| Symbol | | Definition |
|-----------------------------|---|---|
| Et | : | Evapotranspiration $[LT^{-1}]$ |
| Η | : | Depth from sea level (T.P.) to fresh groundwater-salt water interface |
| | | level [L] |
| $\mathrm{H}_{\mathrm{max}}$ | : | H at high tide [L] |
| $\mathrm{H}_{\mathrm{min}}$ | : | H at low tide [L] |
| Κ | : | Hydraulic conductivity [LT ⁻¹] |
| L | : | Wedge of salt water [L] |
| М | : | Thickness of the aquifer [L] |
| Р | : | Precipitation [LT ⁻¹] |
| hos | : | Density of sea water $[ML^{-3}]$ |
| h | : | Head of fresh groundwater above sea level (T.P.) [L] |
| h_{max} | : | h at high tide [L] |
| \mathbf{h}_{\min} | : | h at low tide [L] |
| k | : | Equilibrium constant [Dimensionless] |
| ne | : | Effective porosity [Dimensionless] |
| q | : | Specific flux $[LT^{-1}]$ |
| 1 | : | Distance [L] |
| t | : | Time [T] |
| va | : | Actual velocity $[LT^{-1}]$ |
| | | dimension: |
| | | |

富士山南麓地域における地下水水質の進化

池田喜代治

要 旨

本研究は火山地域における地下水中の化学成分と帯水層の岩質との関係,および帯水層中の地下水の 流動と地下水中の化学成分組成・濃度進化との関係の解明を主目的としている.研究対象地域は富士山 南麓の緩傾斜地から駿河湾沿いの海岸低地である.本地域には富士山系の古富士,新富士の火山噴出物, 愛鷹火山噴出物が分布し,海岸低地ではこれらの地層の上を富士川系の河川堆積物が覆っている.これ らの地層中の地下水を103試料採取して水質分析を行い,また,帯水層を構成する富士および愛鷹火山 噴出物11試料を採取して純水一岩石粉末試料系の密封試料をつくり常温・常圧下の水一岩石相互作用に関 する室内実験を行った.

水質調査の結果,各地層中の地下水は Ca^{2+} , Mg^{2+} , Na^+ , K^+ の炭酸水素塩および SiO_2 を主成分とした $Ca-HCO_3$ 型の水質であること, HCO_3 濃度,K/Na比, Na/SiO_2 比, SO_4/Cl 比などが帯水層ごとに異なる特徴があり,これらの化学的指標によって帯水層の三次元的区分が可能であることが判明した.これらの水質の形成機構を解明するために行った水一岩石実験の結果は,新富士溶岩および愛鷹火山岩試料から水に溶出する化学成分が,それぞれの岩石を帯水層とする地下水の化学組成と同様の組成をもち,K/Na比, Na/SiO_2 比もほぼ同じ値をとることを示した.

Bulletin of the Geological Survey of Japan, Vol. 40, No. 7

本地域の火山噴出物の地下水の水質についてのもう一つの特徴は SiO₂: Na の関係においてみられる. 古富士を除く火山噴出物中の地下水は2:1を示し,火山岩中の主要造岩鉱物である斜長石が風化してカオリナイトになるときに水中に生ずる SiO₂: Na と同じ比を示し,これらの地下水の水質が,雨水による帯水層岩石のカオリナイトへの風化反応の過程で生じていることを示唆した.

一方,海岸低地の古富士泥流中の地下水のSiO₂:Naの比は約1:1で,pH は7.8以上を示し,他の 火山噴出物中の地下水とは異なっている.本地下水はカオリナイトとモンモリロナイトが平衡状態にあ るときに示す平衡定数の値が一定となる傾向があり,これは地下水の滞留時間が非常に長いためと解釈 された.

富士山体の勾配に沿って海岸低地下に連続する新富士溶岩,古富士泥流層中の地下水は,地下水の流動に伴って HCO₃ の増加がみられる.本地域の地下水の水頭分布図,比湧出量分布図と HCO₃ の濃度 分布図の結果は調和的で, HCO₃ 分布が地下水の流動方向を示すことが明らかになった.

本地域ではまた海岸低地下の火山噴出物中の淡水地下水の塩水化現象がみられる.塩水化は地下水開 発に伴う急激な地下水位の低下によって生じた.代表的な塩水化地下水12試料について,酸素・水素同 位体組成の測定を行った結果は,淡水地下水と海水の混合水としての同位体組成を示した.しかし採取 した塩水化地下水は例外なく両者の混合水よりも著しく Ca²⁺に富んだ Ca-Na-Cl 型を示した.塩水化 地域の試錐試料を用いた水-岩石実験の結果,溶岩層上位の粘性土層と接触した海水は塩水化地下水と 同じ水質に変化することが明らかになった.以上の結果から,本地域の塩水化地下水の水質進化は侵入 海水と加圧層を構成する粘性土層との接触によって,主として陽イオン交換反応,一部は粘性土中の硫 化物の溶解によるものと結論された.

(受付:1989年3月2日;受理:1989年5月30日)