

An Analysis of the Chemical Compositions of Groundwaters Utilizing a Leaching Technique. An Application to the Rokko Mountains and Their Surroundings

YUZO TAMARI,* YUKIHARU INOUE, HARUO TSUJI, and YUZURU KUSAKA
Department of Chemistry, Faculty of Science, Konan University, Higashinada-ku, Kobe 658
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The chemical composition of groundwaters from granitic alluvial plains is different from that from the clayey "Kobe-group" strata surrounding the Rokko mountains. The former groundwaters are dominantly rich in Ca and HCO_3^- , while the latter are rich in Na and HCO_3^- . In order to investigate the difference in the groundwater compositions, a chemical leaching technique was applied to samples of soils, well-sediments, and rocks collected from the Rokko mountains and their surroundings. Three leaching solutions used were as follows. CO_2 -saturated water to investigate the effect of chemical weathering; a 0.1 M HNO_3 solution to remove hydroxide, sulfide, and colloidal matters; and a 1 M $\text{CH}_3\text{COONH}_4$ solution to leach exchangeable ions from the samples. In the leaching, leachable amounts of Na, K, Ca, and Mg as the major species and Fe and Mn as the minor species in groundwaters were determined. From the results of leaching and adsorption experiments for cations, and from a comparison of the analytical values of the cations in groundwaters with the data of the leaching experiments on the key diagram, the association of the chemical species dissolved in groundwaters with the geological characters was analysed.

The Rokko mountains are located north of Osaka Bay, behind the port of Kobe. The mountains essentially consist of granitic rocks characterized by biotite, and they are covered with granitic detritus called "Masatsuchi." The detritus forms alluvial plains and terrace deposits in the southern part of the Rokko mountains, and the detrital layers form a well aquifer because of the poorly coagulating layers. In the northern or north-western side of the mountains, the Neogene strata (*ca.* 15 million years old), called argillaceous "Kobe group" strata, which are composed of such detritus as silt mudstone, sandstone, and conglomerates and of volcanoclastic materials containing large amounts of tuff, are widely distributed.¹⁾

It has been generally recognized that the chemical species dissolved in groundwaters are mainly Na^+ , Ca^{2+} , Mg^{2+} , K^+ , HCO_3^- , Cl^- , SO_4^{2-} , and soluble SiO_2 , and that these species make up more than 95% of the total dissolved solids.²⁾ The chemical compositions of groundwaters in the Rokko mountains and their surroundings

have been studied, and the concentrations of major and trace species have been reported by some of the present authors.^{3,4)} Table 1 shows some of the analytical results in their reports. This table shows that the groundwaters from the alluvial plains are dominantly rich in Ca and HCO_3^- , whereas the groundwaters from the Kobe-group area are rich in Na and HCO_3^- . The difference in the chemical compositions of groundwaters in these two areas is explained by the following reactions of major chemical species: the chemical actions controlling the dissolution of the major species are weathering by CO_2 for granitiform soils in the alluvial plains, while the cation-exchange reactions by clay minerals are dominant in the Kobe-group area. In order to analyse the difference in the chemical compositions of groundwaters between the alluvial plains and the Kobe-group area, and in order to elucidate the association of geological strata with the chemical compositions, a chemical leaching technique was applied in this work.

Chemical leaching techniques are generally utilized

TABLE 1. MEAN CHEMICAL COMPOSITIONS OF GROUNDWATERS

| Chemical species | Alluvial plains | | Kobe-group strata | | | |
|------------------|-------------------------|------------|-------------------------|------------|----------------------|------------|
| | 34 Shallow groundwaters | | 38 Shallow groundwaters | | 15 Deep groundwaters | |
| | ppm | epm | ppm | epm | ppm | epm |
| | Av. \pm S.D. | (% of epm) | Av. \pm S.D. | (% of epm) | Av. \pm S.D. | (% of epm) |
| Ca | 42 \pm 15 | 2.1 (57) | 12 \pm 9.2 | 0.60 (26) | 1.6 \pm 1.3 | 0.08 (2) |
| Mg | 5.7 \pm 2.3 | 0.47 (13) | 2.3 \pm 1.7 | 0.19 (8) | 0.2 \pm 0.2 | 0.02 (0.4) |
| Na | 21 \pm 8.2 | 0.91 (25) | 32 \pm 20 | 1.4 (62) | 99 \pm 21 | 4.3 (97) |
| K | 6.9 \pm 3.5 | 0.18 (5) | 3.1 \pm 3.1 | 0.08 (4) | 0.9 \pm 1 | 0.02 (0.6) |
| Cations | | 3.66 (100) | | 2.27 (100) | | 4.42 (100) |
| HCO_3^- | 92 \pm 26 | 1.5 (51) | 63 \pm 51 | 1.0 (47) | 260 \pm 67 | 4.3 (89) |
| Cl | 26 \pm 15 | 0.73 (25) | 23 \pm 16 | 0.65 (30) | 9.2 \pm 7.1 | 0.26 (5) |
| SO_4 | 33 \pm 14 | 0.69 (24) | 23 \pm 9 | 0.48 (23) | 14 \pm 12 | 0.29 (6) |
| SiO_2 | 21 \pm 6.1 | | 29 \pm 10 | | 33 \pm 10 | |
| Anions | | 2.92 (100) | | 2.13 (100) | | 4.85 (100) |

† 1 M = 1 mol dm⁻³, 1 ml = 1 cm³.

TABLE 2. SAMPLING DESCRIPTIONS

| Sample | Location | Geology |
|---------------------|---------------------------------------|-------------------|
| Soil No. 1 | Konan University #9 | Alluvial plains |
| Well-sediment No. 1 | Konan University #18 | Alluvial plains |
| Well-sediment No. 2 | Ohgo-cho, Kita-ku, Kobe | Kobe-group strata |
| Well-sediment No. 3 | Yokawa-cho, Kita-ku Kobe | Kobe-group strata |
| Well-sediment No. 4 | Yokawa-cho, Kita-ku Kobe | Kobe-group strata |
| Well-sediment No. 5 | Ohzo-cho, Kita-ku, Kobe | Kobe-group strata |
| Montmollironite | Mississippi, U.S.A. | |
| Bentonite | Gunma prefecture | |
| Kaolinite | Georgia, U.S.A. | |
| Mt. Rokko Granite | Okamoto, Kobe | |
| JB-1 | Japanese basalt, G.S.J. ^{a)} | |

a) Detailed locations are described by Ando.¹¹⁾

to separate different minerals, such as ferro-manganese and carbonate, or trace elements adsorbed on minerals to solutions by means of chemical reactions.⁵⁻⁷⁾ This technique is also used for the state analysis of Se in sediments.⁸⁾ In this work, a chemical leaching method was applied to powdered samples of rocks, soils, and well-sediments collected from Mt. Rokko and its surroundings, using leaching solutions of 0.1 M HNO₃, 1 M CH₃COONH₄, and CO₂-saturated water. From the results of 1) the X-ray diffraction patterns of the samples, 2) leaching experiments in which amounts of Na, K, Ca, Mg, Fe, and Mn removed from the samples by the leaching solutions were determined, 3) adsorption experiments using commercially available clay minerals and the samples, and 4) the analysis of key diagrams on which the leaching and analytical results of groundwaters had been plotted, it has been concluded that the chemical composition of each groundwater from the alluvial plains and the Kobe-group area depends on their geological strata, and that the leaching method is significant in analysing the influence of the geological strata on the chemical species dissolved in groundwaters.

Experimental

Samples, Reagents, and Apparatus. The sampling descriptions of the well-sediments, rocks, soils, and clay minerals used for these experiments are given in Table 2. The sediment samples were collected from the bottom to a depth of about 5 cm in relatively shallow wells, using a mud-sampler (Rigo Co., Ltd., model No. 2007).

The solutions of 0.1 M HCl, 0.1 M HNO₃, and 0.1 M CH₃COOH were prepared by diluting each reagent of an analytical-reagent grade with distilled water. The pH 7 solution of 1 M CH₃COONH₄ was also prepared by dissolving 77.09 g of CH₃COONH₄ with water to a 1000 ml volume and by adjusting the pH to 7.0 with a small quantities of CH₃COOH and NH₄OH solutions.

The following pieces of apparatus were employed; a flame photometer (Hiranuma-sangyo Co., Ltd., model FPF-2A), a spectrophotometer (Hitachi, Ltd., model 100-10), an atomic absorption spectrophotometer (Hitachi, Ltd., model 207), an X-ray diffractometer (Rigaku-denki Co., Ltd., model MJ-200-DH), and a washer-bath with irradiation by ultrasonic waves (Shimada Physical and Chemical Industrial Instruments Co., Ltd., model CF-16-2B, 200 W 28 kHz, and Branson Instruments Co., Ltd., model Bransonic 12,80 W 60 Hz).

Preparation of Samples. Wet sediment samples collected from wells were centrifuged, and the solid parts of the samples were dried for 5 h at 110 °C. After cooling, the samples were crushed in an agate mill and then powdered so as to pass through a 100-mesh-size sieve. Finely powdered dry samples were prepared by quartering them four times after the samples had been mixed in an agate mill for 10 min. Samples of rocks and clay minerals were also prepared in the same manner. In this sample preparation, about 95% of the homogeneities for trace elements in sediment samples and more than ca. 90% of the homogeneities for major constituents in artificial samples were estimated.^{9,10)}

Leaching Solutions. The solutions used for the chemical leaching experiments were as follows. 1) CO₂-saturated water to investigate the effect of chemical species being dissolved in groundwaters by chemical weathering by CO₂; 2) a 1 M CH₃COONH₄ solution to remove the exchangeable ions sorbed by clay minerals; 3) a 0.1 M HCl solution to leach the metal sulfides and hydroxides and loosely adsorbed metal ions that were originally present in overlying water as fine-grained suspended phases;⁶⁾ and 4) 0.1 M HNO₃ and 0.1 M CH₃COOH solutions to compare the effects of the leaching.

Recommended Leaching Procedure. Figure 1 shows the recommended procedure for the leaching method as established from the experimental results of investigating the effect of the reaction temperatures of leaching solutions, the effect of the intensity of ultrasonic waves irradiated during the leaching, and the effect of the irradiation time of ultrasonic waves on the leachable amounts of Na, K, Ca, Mg, Fe, and Mn.

One gram of a powdered sample was placed in a stoppered centrifugal tube (Vol. 50 ml), and a 25-ml portion of a leaching solution was added to the tube. The tube was set in a water-bath filled with hot water (40 °C) and irradiated by ultrasonic waves with an electric current of 3 A and for an irradiation time of 20 min. The tube was centrifuged for 10 min at 2500 rpm; then the supernatant solution was filtered (filter pore-size: 0.45 μ) and transferred to a 50-ml measuring flask (Fraction No. 1). A 25-ml portion of the same fresh leaching solution was added to the residue in the tube; the mixture was irradiated for 20 min and then centrifuged. The solutions from Fractions No. 2 to No. 5 were prepared in the same way.

In the leaching with CO₂-saturated water, CO₂ gas was introduced into a mixture of 1 g of the sample and 25 ml of H₂O in a centrifugal tube under the same reaction conditions as are shown in Fig. 1.

Procedure of Adsorption Experiments. A solid-residue sample, after treatment by the leaching procedure with the 1 M CH₃COONH₄ solution, was used for the experiments. The sample was washed with water and then centrifuged.

TABLE 3. CHEMICAL COMPOSITIONS OF SAMPLES

| Sample | Na(%) | K(%) | Ca(%) | Mg(%) | Fe(%) | Mn(ppm) |
|---------------------|-------|-------|-------|-------|-------|---------|
| Soil No. 1 | 1.78 | 3.45 | 1.09 | 0.397 | 2.78 | 1790 |
| Well-sediment No. 1 | 1.32 | 2.12 | 0.735 | 0.358 | 3.12 | 931 |
| Well-sediment No. 2 | 1.17 | 1.93 | 0.435 | 0.427 | 3.35 | 577 |
| Well-sediment No. 3 | 1.03 | 1.27 | 0.418 | 0.336 | 6.74 | 2460 |
| Well-sediment No. 4 | 1.44 | 2.11 | 0.541 | 0.273 | 1.81 | 349 |
| Montmollironite | 0.258 | 0.623 | 0.431 | 1.48 | 3.25 | 147 |
| Bentonite | 2.69 | 1.56 | 0.258 | 0.325 | 0.129 | 87 |
| Kaolinite | 0.045 | 0.279 | ND | 0.062 | 0.502 | ND |
| Mt. Rokko Granite | 2.60 | 3.29 | 0.303 | 0.041 | 1.10 | 384 |
| JB-1 ^{a)} | 2.08 | 1.19 | 6.63 | 4.66 | 6.30 | 1200 |

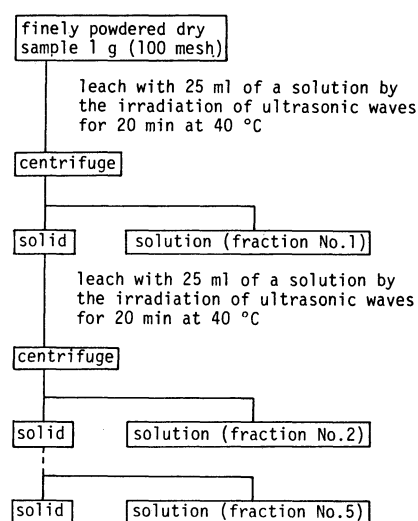
a) Certified values.¹¹⁾

Fig. 1. The flow diagram of the leaching procedure.

After washing with water twice, a 25-ml portion of the solution adjusted to pH 7 and containing definite amounts of the chloride of each Na, K, Ca, and Mg was added to the sample. The mixture was irradiated by ultrasonic waves for 100 min (20 min \times 5) at 40 °C. Then, after the centrifugation, the amounts of Na, K, Ca, and Mg in the supernatant liquid were determined.

Determination of Elements. To each solution from Fractions No. 1 to No. 5, 1 ml of a 10% La solution and 1 ml of a 5 M HNO₃ solution were added, and the mixture was diluted with water to 50 ml. In the solution, the Na and K were determined by flame photometry, and the Ca, Mg, Fe, and Mn, by atomic-absorption spectrophotometry.

For the determination of the Na, K, Ca, Mg, Fe, and Mn content of the samples given in Table 2, the samples were wet-ashed by general HF-HClO₄-HNO₃ treatments; these elements were then determined by the analytical procedure described above.

Results and Discussion

Analytical Data of Samples. Table 3 lists the Na, K, Ca, Mg, Fe, and Mn content of the samples. As shown in this table, the content of each element in the Mt. Rokko granite sample is fairly close to that of one reported by Kasama.¹⁾ However, it is difficult to find the geological differences between samples from the chemical compositions shown in this table.

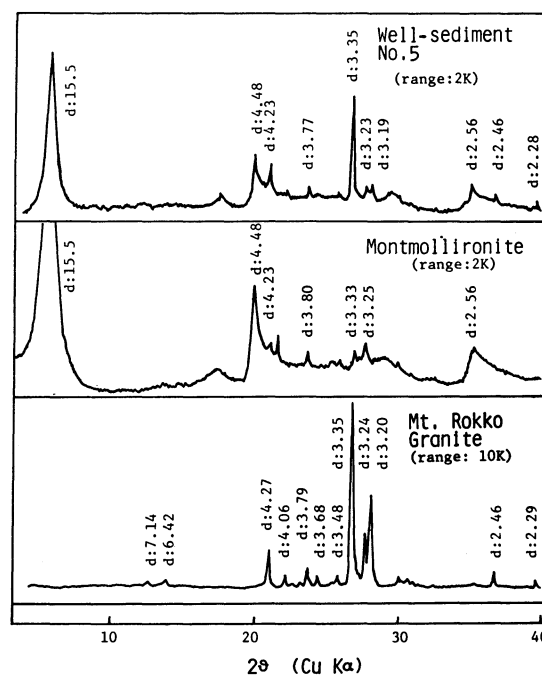


Fig. 2. X-Ray diffraction spectra of samples.

Figure 2 shows some typical X-ray diffraction patterns of the samples. The diffraction patterns of the soil No. 1 and the well-sediment No. 1 from the alluvial plains were identical with that of the Mt. Rokko granite, in which peaks corresponding to quartz (d: 4.26, 3.35, 2.46, 2.24, and 2.13) were found. In the well-sediments No. 2—No. 5 from the Kobe-group area, the peaks of montmollironite and quartz were detected.

Reproducibility of the Leaching Method. Table 4 shows the reproducibility of the leaching method, repeated four times by the recommended procedure given in Fig. 1. In this experiment, the soil No. 1 and a 0.1 M HNO₃ solution were used as the sample and the leaching solution respectively. For each element, in the sum of five fractions, a coefficient of variation of 0.99—4.5%, which was approximately within the limits of analytical error, was obtained.

Effect of Leaching Solutions. Table 5 gives the experimental results of the leaching with different solutions from the samples. It may be found from the table that the amounts of each of six elements leached

TABLE 4. REPRODUCIBILITY OF THE LEACHING METHOD

| Run No. | Sample | Fraction | Na | K | Ca | Mg | Fe | Mn |
|--------------|------------|----------|----------|----------|-----------|----------|-----------|----------|
| 1 | Soil No. 1 | 1 | 185 | 195 | 8270 | 398 | 536 | 257 |
| | | 2 | 20 | 60 | 617 | 82 | 352 | 69 |
| | | 3 | 10 | 35 | 190 | 55 | 278 | 55 |
| | | 4 | 15 | 35 | 79 | 34 | 214 | 32 |
| | | 5 | 8 | 18 | 45 | 23 | 158 | 18 |
| | | Sum | 238 | 343 | 9201 | 592 | 1538 | 431 |
| 2 | Soil No. 1 | 1 | 195 | 190 | 8300 | 378 | 513 | 250 |
| | | 2 | 20 | 60 | 657 | 89 | 335 | 66 |
| | | 3 | 10 | 35 | 193 | 54 | 262 | 45 |
| | | 4 | 15 | 28 | 85 | 34 | 212 | 29 |
| | | 5 | 9 | 18 | 52 | 23 | 152 | 19 |
| | | Sum | 249 | 331 | 9287 | 587 | 1474 | 409 |
| 3 | Soil No. 1 | 1 | 185 | 180 | 8300 | 393 | 543 | 257 |
| | | 2 | 23 | 58 | 661 | 84 | 328 | 61 |
| | | 3 | 19 | 40 | 151 | 47 | 257 | 40 |
| | | 4 | 9 | 28 | 88 | 34 | 199 | 30 |
| | | 5 | 9 | 28 | 70 | 30 | 194 | 29 |
| | | Sum | 245 | 334 | 9270 | 588 | 1521 | 417 |
| 4 | Soil No. 1 | 1 | 185 | 185 | 8450 | 376 | 525 | 244 |
| | | 2 | 13 | 30 | 446 | 55 | 180 | 39 |
| | | 3 | 13 | 48 | 367 | 75 | 308 | 58 |
| | | 4 | 9 | 28 | 91 | 34 | 188 | 30 |
| | | 5 | 8 | 28 | 67 | 30 | 188 | 28 |
| | | Sum | 288 | 319 | 9421 | 570 | 1389 | 399 |
| Average±S.D. | | Sum | 240±9.20 | 332±9.91 | 9295±92.0 | 584±9.74 | 1481±66.7 | 414±13.5 |
| C.V. (%) | | | 3.83 | 2.98 | 0.99 | 1.67 | 4.50 | 3.26 |

Values: $\mu\text{g/g}$ (microgram amounts of an element leached from a 1-g sample).

TABLE 5. EFFECTS OF LEACHING SOLUTIONS

| Sample | Leaching soln | Na($\mu\text{g/g}$) | K($\mu\text{g/g}$) | Ca(g/g) | Mg($\mu\text{g/g}$) | Fe($\mu\text{g/g}$) | Mn($\mu\text{g/g}$) |
|---------------------|--|-----------------------|----------------------|---------|-----------------------|-----------------------|-----------------------|
| Soil No. 1 | CO ₂ -saturated water | 327 | 288 | 5815 | 251 | ND | 57 |
| | 0.1 M HCl | 234 | 288 | 8720 | 558 | 2000 | 467 |
| | 0.1 M HNO ₃ | 240 | 332 | 9300 | 584 | 1480 | 414 |
| | 0.1 M CH ₃ COOH | 230 | 245 | 8460 | 335 | 24 | 255 |
| | 1 M CH ₃ COONH ₄ | 148 | 186 | 7400 | 146 | ND | 293 |
| Well-sediment No. 2 | CO ₂ -saturated water | 544 | 666 | 549 | 177 | ND | 15.0 |
| | 0.1 M HCl | 533 | 1482 | 4080 | 1640 | 6406 | 83.6 |
| | 0.1 M HNO ₃ | 547 | 1652 | 3550 | 1670 | 6488 | 84.1 |
| | 0.1 M CH ₃ COOH | 513 | 969 | 1410 | 564 | 4904 | 29.4 |
| | 1 M CH ₃ COONH ₄ | 580 | 1565 | 2750 | 455 | ND | 42.7 |

Values: μg amounts of an element leached in the sum of 5 fractions from 1 g of a sample.

with the 0.1 M HCl solution was nearly equal to that leached with the 0.1 M HNO₃ solution, but was larger than that leached with the 0.1 M CH₃COOH and 1 M CH₃COONH₄ solutions. In the leaching with the CO₂-saturated water, the dissolved amounts of the elements tended to agree with that of the 0.1 M HCl or 0.1 M HNO₃ solution from the soil No. 1 and not with that from the well-sediment No. 2. This difference between the two samples probably depends on the characteristics of their samples, *i.e.*, the fact that montmollironite was contained in the well-sediment No.2, while quartz was found in the soil No. 1.

Leaching of Elements from Samples. Table 6 lists the amounts of elements leached from different samples. From the table, the following characteristics of the leaching could be recognized.

In the alluvial soil No. 1, the considerably large amount of Ca was more easily dissolved with the CO₂-saturated water than in the Kobe-group samples. In the well-sediments from the Kobe-group strata, the percentages of Na and K leached with the CH₃COONH₄ solution were remarkably higher than that from the alluvial samples, and the amounts of Na, K, Ca, and Mg leached by the HNO₃ solution were almost equal to that by the CH₃COONH₄ solution. Similar results of the leaching were found in the clay minerals, montmollironite and kaolinite. This similarity is considered to be due to the presence of montmollironite in all the Kobe-group samples.

Adsorption of Cations on Samples. Adsorption experiments were carried out in order to investigate the chemical state of the elements in these samples;

TABLE 6. ANALYTICAL RESULTS OF ELEMENTS IN THE LEACHING EXPERIMENT

| Sample | Leaching soln | Na($\mu\text{g/g}$) | K($\mu\text{g/g}$) | Ca($\mu\text{g/g}$) | Mg($\mu\text{g/g}$) | Fe($\mu\text{g/g}$) | Mn($\mu\text{g/g}$) |
|---------------------|---------------------------------|-----------------------|----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| Soil No. 1 | 0.1 M HNO_3 | 240(1.35) | 332(0.962) | 9295(85.3) | 584(14.7) | 1481(5.33) | 414(23.1) |
| | 1 M $\text{CH}_3\text{COONH}_4$ | 184(1.03) | 186(0.539) | 7397(67.9) | 146(3.68) | ND | 294(16.4) |
| | CO_2 -saturated water | 226(1.27) | 241(0.699) | 5508(50.5) | 157(2.95) | ND | 57(3.2) |
| Well-sediment No. 1 | 0.1 M HNO_3 | 151(1.14) | 411(1.94) | 2978(40.5) | 552(15.4) | 4611(14.8) | 414(44.5) |
| | 1 M $\text{CH}_3\text{COONH}_4$ | 92(0.70) | 242(1.14) | 1406(19.1) | 158(4.41) | ND | 161(17.3) |
| | CO_2 -saturated water | 342(2.59) | 635(3.00) | 1349(18.4) | 270(7.54) | ND | ND |
| Well-sediment No. 2 | 0.1 M HNO_3 | 547(4.68) | 1562(8.09) | 3543(81.5) | 1668(39.1) | 6488(19.4) | 84(15) |
| | 1 M $\text{CH}_3\text{COONH}_4$ | 580(4.96) | 1565(8.11) | 2760(63.5) | 455(10.7) | ND | 43(7.4) |
| | CO_2 -saturated water | 544(4.65) | 666(3.45) | 549(12.6) | 177(4.15) | ND | 15(2.6) |
| Well-sediment No. 3 | 0.1 M HNO_3 | 2758(26.8) | 1633(12.9) | 3051(73.0) | 243(7.23) | 29660(44.0) | 1312(53.3) |
| | 1 M $\text{CH}_3\text{COONH}_4$ | 2683(26.1) | 2038(16.1) | 3368(80.6) | 212(6.31) | 114(0.17) | 764(31.1) |
| | CO_2 -saturated water | 703(4.88) | 639(3.03) | 1912(35.3) | 389(14.2) | 1858(10.3) | 133(38.1) |
| Well-sediment No. 4 | 0.1 M HNO_3 | 718(4.99) | 711(3.37) | 2098(38.8) | 303(11.1) | 20(0.11) | 113(32.4) |
| | 1 M $\text{CH}_3\text{COONH}_4$ | 1059(7.35) | 387(1.83) | 849(15.7) | 173(6.34) | ND | ND |
| | CO_2 -saturated water | 65(2.5) | 399(6.31) | 3805(88.3) | 2991(20.2) | 200(0.62) | 56(38) |
| Montmoll-ironite | 0.1 M HNO_3 | 63(2.4) | 348(5.51) | 4532(105) | 3313(22.4) | ND | 51(35) |
| | 1 M $\text{CH}_3\text{COONH}_4$ | 83(3.2) | 403(6.38) | 200(4.64) | 119(0.80) | ND | ND |
| | CO_2 -saturated water | 6862(25.5) | 484(3.10) | 676(26.3) | 379(11.7) | 116(9.00) | 13(15) |
| Bentonite | 0.1 M HNO_3 | 10262(38.2) | 1006(6.47) | 2422(94.0) | 572(17.6) | ND | ND |
| | 1 M $\text{CH}_3\text{COONH}_4$ | 10(2.2) | 13(0.47) | ND | 284(45.8) | 4(0.08) | ND |
| | CO_2 -saturated water | 18(4.0) | 30(1.1) | ND | 281(45.3) | ND | ND |
| Kaolinite | 0.1 M HNO_3 | 146(0.56) | 470(1.43) | 303(10.0) | 66(16) | 1523(13.8) | 110(28.6) |
| | 1 M $\text{CH}_3\text{COONH}_4$ | 84(0.32) | 116(0.35) | 218(7.19) | 15(3.7) | ND | 30(7.8) |
| | CO_2 -saturated water | 362(1.39) | 388(1.18) | 323(10.7) | 30(7.3) | ND | ND |
| Mt. Rokko Granite | 0.1 M HNO_3 | 388(1.87) | 276(2.34) | 4377(6.65) | 7918(17.1) | 4889(7.74) | 177(14.3) |
| | 1 M $\text{CH}_3\text{COONH}_4$ | 96(0.46) | 169(1.43) | 1439(2.19) | 786(1.70) | ND | 50(4.0) |
| | CO_2 -saturated water | 73(0.31) | 99(1.7) | 1243(1.89) | 998(2.16) | ND | 62(5.0) |

Values: microgram amounts of an element leached in the sum of 5 fractions from a 1-g sample,

Values in parentheses: $\frac{\text{microgram amounts of an element leached in the sum of 5 fractions from a 1-g sample}}{\text{total microgram amounts of an element in a 1-g sample}} \times 100 (\%)$.

TABLE 7. ANALYTICAL RESULTS OF CATIONS IN THE ADSORPTION EXPERIMENT

| Sample ^{a)} | Cation | Added (μg) | Adsorbed (μg) | Leached ^{b)} (μg) | Ratio of adsorbed to leached |
|---------------------------|--------|-------------------------|----------------------------|---|------------------------------|
| Montmollironite (1 g) | Na | 4980 | 1730 | 63 | 27 |
| | K | 5130 | 1880 | 348 | 5 |
| | Ca | 4980 | 2480 | 4532 | 0.5 |
| | Mg | 4880 | 2430 | 3313 | 1 |
| Bentonite (1 g) | Na | 4980 | 720 | 10262 | 0.07 |
| | K | 5130 | 1130 | 1006 | 1 |
| | Ca | 4980 | 4730 | 2422 | 2 |
| | Mg | 4880 | 1380 | 572 | 2 |
| Kaolinite (1 g) | Na | 4980 | 1130 | 18 | 63 |
| | K | 5130 | 325 | 30 | 11 |
| | Ca | 4980 | 350 | ND | ND |
| | Mg | 4880 | 225 | 281 | 0.8 |
| Soil No. 1 (1 g) | Na | 1130 | 100 | 184 | 0.5 |
| | K | 1800 | 110 | 186 | 0.6 |
| | Ca | 9690 | 560 | 7397 | 0.08 |
| | Mg | 2000 | 110 | 146 | 0.8 |
| Well-sediment No. 2 (1 g) | Na | 900 | 100 | 580 | 0.2 |
| | K | 1440 | 440 | 1565 | 0.3 |
| | Ca | 7750 | 1480 | 2760 | 0.5 |
| | Mg | 1600 | 219 | 455 | 0.5 |

a) Samples treated by leaching with the 1 M $\text{CH}_3\text{COONH}_4$ solution. b) Amounts of cations leached with the 1 M $\text{CH}_3\text{COONH}_4$ solution (see Table 6).

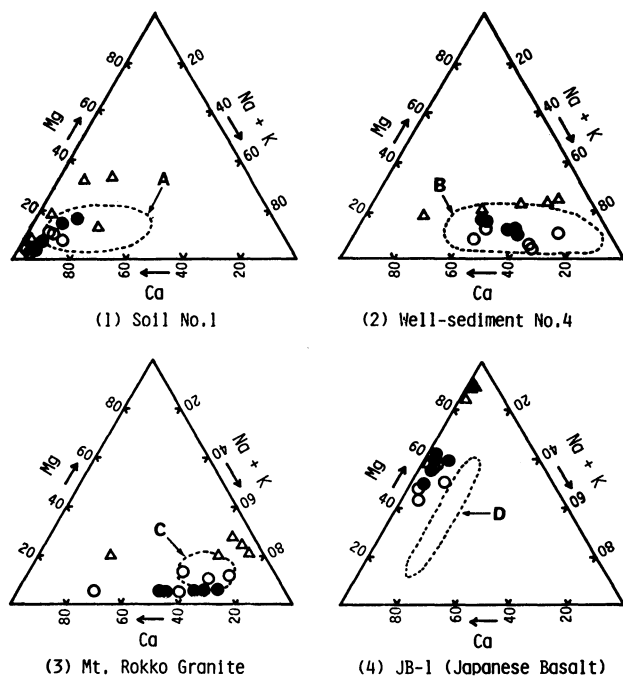


Fig. 3. Key diagram of relative percentages of milligram equivalents.

●: Leaching by CO_2 -saturated water, ○: 1 M $\text{CH}_3\text{COONH}_4$ leaching, △: 0.1 M HNO_3 leaching, A: 34 Groundwaters from the alluvial plains, B: 38 Groundwaters from the Kobe-group strata, C: 7 Stream waters from topmost Mt. Rokko, D: 8 groundwaters from the worldwide 8 basaltic regions.

the soil No. 1 from the alluvial plains, the well-sediment No. 2 from the Kobe-group strata, and the clay minerals. Table 7 shows the results of the experiments. In this table, the amounts of elements leached from the original sample (see Table 6) are also listed.

In the montmollironite and bentonite, the amounts of divalent Ca adsorbed was higher than that of monovalent Na and K. The adsorptive behavior of the cations was observed also in the soil No. 1 and the well-sediment No. 2. However, from the fact that the ratio of the amounts adsorbed to those leached is 0.08 for Ca in the soil, it can be seen that scarcely no exchangeable Ca existed in the soil from the alluvial plains. In contrast, from the relatively high ratio of 0.5 for Ca in the well-sediment No. 2, it seems that much Ca was present as exchangeable ions in the sediment from the Kobe-group strata.

Association of the Chemical Species Dissolved in Groundwaters with Their Surrounding Geology. Figure 3 gives the key diagram of the relative percentages of milligram equivalents for Na+K, Ca, and Mg leached from the four samples.

In Fig. 3-(1) for the soil No. 1, it is indicated that the plots of cations leached from the soil agree almost entirely with the A area, the plots of the 34 shallow groundwaters from the alluvial plains

(see Table 1). A similar agreement is also found in the well-sediment No. 1 from the same alluvium.

In Fig. 3-(2) for the well-sediment No. 4 from the Kobe-group strata, the plots of leached cations, especially with the $\text{CH}_3\text{COONH}_4$ solution or the CO_2 -saturated water, overlap well with the analytical results of the 38 shallow groundwaters (B) from the Kobe-group strata.^{3,4)} This agreement is also found in the well-sediment No. 3 from the same strata.

The leaching data of the Mt. Rokko granite, plotted in Fig. 3-(3), are somewhat scattered, but those with the CO_2 -saturated water tend to overlap with the results of the 7 stream waters located at the top of Mt. Rokko (C).¹²⁾ From this tendency, it can be pointed out that the chemical composition of stream waters is determined by the leaching of constituents in the granitic rocks by chemical weathering with CO_2 .

In Fig. 3-(4) for JB-1, it is shown that the plots of cations leached with the CO_2 -saturated water or the $\text{CH}_3\text{COONH}_4$ solution fall close to the analytical data of the 8 groundwaters in the 8 basaltic regions worldwide (D).¹³⁾

In conclusion, it can be analysed that the chemical compositions of groundwaters are considerably influenced by the geological strata through which the groundwaters pass, and that they can be estimated by utilizing the proposed leaching experiments for the solid samples around the groundwater area. In the leaching, the CO_2 -saturated water is effective for investigating the influence of rocks on groundwaters, whereas the 1 M $\text{CH}_3\text{COONH}_4$ solution is useful for the samples containing clay minerals.

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