Investigation of the distribution of elements of the whole of Japan and their applications

— Geochemical map of land and sea of Japan —

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A geochemical map of the whole of Japan has been drawn for the first time by surveying the distribution of elements in land and sea throughout Japan. This map revealed the natural background of the elements distribution and allows us to know the continuous flow of elements from land to sea. The samples used in this work are 3024 riverbed sediments and 4905 seabed sediments, and 53 elements including toxic elements of As, Hg, Cd, etc. have been analyzed. In this research, a new survey method has been established for a certain district at first and then it has been applied to the whole of Japan with modification taking realistic operability into consideration, and the object has been extended from land, sea to soil. The geochemical map is also used for evaluating the pollution of soils and marine sediments resulting from human and industrial activities. The results have been made public through publication and website and have had various social impacts. In this paper, the research scenario adopted to compose the geochemical map of Japan is first described, then a series of research processes are described starting from material sampling and treatment chemical analysis, measurement of element concentration, composition of geochemical map to data release.

Keywords : Geochemical map, distribution of elements, toxic elements, environmental pollution

1 Introduction

What elements exist in our surroundings and what are the concentrations of those elements? Such basic knowledge has not been understood until recently. And such knowledge has not been readily accessible. A geochemical map enables anyone to understand this valuable information visually at one view. For example, when discussing soil and marine pollution, which have become severe problems, such a tool will become a key to infer the distribution of toxic elements such as arsenic, mercury, and cadmium. This paper describes how the nationwide geochemical map in Japan was first planned, and then how it was actually made and used.

2 Background and purpose of the geochemical map

2.1 What is a geochemical map?

A geochemical map is a distribution map of elemental concentrations on the surface of Earth (surface of the Earth's crust). Figure 1 depicts what factors determine the distributions of elements. The most important of them is what kinds of rock and sediment are distributed in the region. This is a natural background. Additionally, influences from industrial, agricultural and urban life activities are important influences. The actual distributions of the elements constitute the sum of these various factors. In other words, for pollution, we should consider these factors in comparison with the natural background.

2.2 Purpose

The purposes of the geochemical map are mainly classifiable as two (Fig. 1). The first is to provide basic geochemical information about the land of Japan. Information about the distribution and movement of elements in the surface of the earth are basic data supporting all discussions related to earth science such as the origin of rock or the formation of the Japanese islands. That information is the basis for the research of earth sciences, which are undertaken to study what elements exist and where they are distributed. It is also important to know the regional elemental concentration or the average chemical composition of a larger area. For example, the average chemical composition of Japan is the most basic information, showing what elements make up the Japanese islands. Another example is the natural radiation dose, as estimated from the concentrations of uranium and thorium on the Earth's surface. As a scientific application, the geochemical map is used to estimate the natural background radiation dose using a liquid scintillation device (KamLAND) for neutrino measurements at Kamioka in Gifu Prefecture. Here, the dose is inferred from the concentrations of the uranium and thorium on the Earth's surface, as obtained from the geochemical map[1].

The second purpose is to address environmental problems. The geochemical map provides the key to clarification of the soil and marine pollution by industrial or factory wastes. To evaluate such pollution, it is important to obtain the natural background, which is then used as a baseline of pollution and the distribution of toxic elements. However, such an investigation has remained limited to small regions.

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No detailed or comprehensive investigation has yet been performed for the entire country of Japan. In this study, the distribution of 53 elements and their background concentrations including toxic trace elements (As, Be, Cd, Hg, Mo, Sb, etc.) in the land and sea of Japan were obtained through production of a geochemical map. We also investigated the geochemical behavior of elements and the origin of elements in the environment[2][3]. The geochemical map shows the nationwide distribution of elements and provides basic data to clarify the origin and the circulation mechanism of elements. It also offers basic data for the evaluation of the anthropogenic pollution in the environment, for the prevention of the spread of contamination, and for remediation planning.

3 Flow of geochemical mapping

Figure 2 depicts the scheme of the geochemical map. There are four steps that must be taken to produce the geochemical map: sample collection, sample treatment, chemical analysis to measure the concentrations of the elements, and map drawing using a geographic information system (GIS). First, the sampling position was determined by reference to existing geographical, geological, and soil maps in the laboratory. Then the samples were collected at selected points in the field. Samples were stream sediments, marine sediments, and soils collected from all over the country. After bringing the samples back to the laboratory, they were dried and sieved in the laboratory. If necessary, the magnetic minerals were separated or powdered. Then, the samples were decomposed with the mixed acids, and the concentrations of elements were measured using the ICP–AES, ICP–MS, and atomic absorption spectrometry. The geochemical map was drawn using GIS from the obtained elemental concentrations of respective samples. Photographs of sampling, the collected samples, the sample treatment, and the geochemical map for the stream sediments and the marine sediments are also portrayed in the figure. Regarding stream sediments, sampling was easy: one could go to the river and collect the samples. However, sample preparation required separation of the magnetic minerals after sieving and drying. For the collection of marine sediments, use of a ship was necessary. Samples were obtained by dropping the sampler to the sea floor. Collected samples were dried and powdered. Chemical analyses and map drawing were conducted similarly for all samples.

4 Development of research of geochemical mapping

The geochemical map was made to explore the mineral deposits to find local high concentration anomalies of heavy metals on the surface. However, in developed countries, few undiscovered deposits exist. The geochemical map is now of great interest from another perspective, as an illustration of environmental problems, because the map shows where and how toxic elements are distributed. In this respect, the British group of Webb in Imperial College formed a nationwide geochemical map for the first time in the world[4]. They produced a nationwide geochemical map by collecting about 50,000 samples gathered throughout the United Kingdom (about 151,000 km^2). It was designated as a Geochemical Atlas. At present, the geochemical map has been extended to encompass all European countries[5]. Please refer to references cited herein for more information about foreign and domestic geochemical maps[6]-[9].

4.1 Research scenarios at the National Institute of Advanced Industrial Science and Technology (AIST)

Figure 3 depicts the scenario for making and opening to

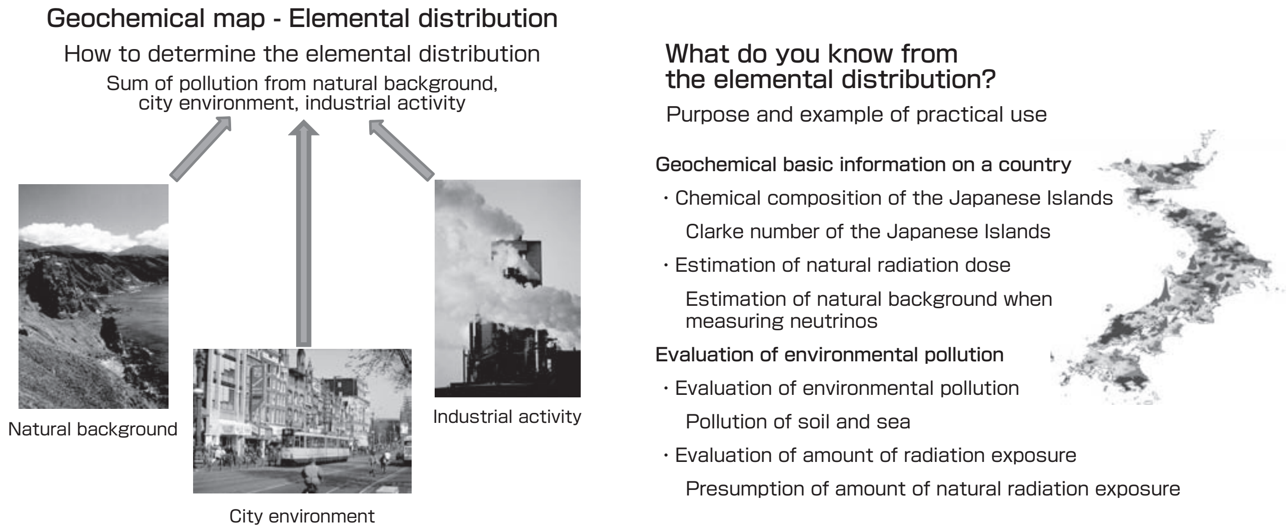

Fig. 1 Factors of elemental distributions in the geochemical map and an example of its practical use
The sum of the natural background and pollution of industrial activities and the city environment yields an element distribution. A geochemical map is used as basic geochemical information related to a country and for the evaluation of environmental pollution.

the public of the geochemical map of Japan. As factors affecting the production of a geochemical map, elemental distribution, elemental abundance, crust surface, kind of element, kind and collection density of sample, land or sea, representativeness of samples, processing of sample, chemical analysis, media to the public, drawing and standardization of data, system of research and analysis, standardization of method were considered, as shown in the figure. These basic factors for fabricating a geochemical map can be unified further as five components: basic characteristics, completeness, reliability, user convenience, and operability. Each of these components becomes a basis for the geochemical map. The final goal is the formation and public presentation of a geochemical map of all Japan, in which the sea and land maps are unified.

Figure 4 depicts the history of the geochemical map in AIST. It was the first time for us to produce a geochemical map systematically for the northern Kanto region, although the geochemical exploration to find mineral deposits had been conducted in AIST for a long time up to that time. The purpose of the project was the construction of techniques and methodology as a first step to our assessment of chemicals throughout the whole country. Then, the geochemical map of Sendai and Yamagata, and the coast of Sea of Japan (from Hokuriku to Akita) were made in respective projects. Subsequently, the geochemical map of land of the whole country was completed. As the next step, a nationwide geochemical map of the sea was fabricated as an extension of the land map. Then the nationwide geochemical map of land and sea was completed. At present, a nationwide geochemical map of soils is being developed as an additional resource.

4.1.1 Geochemical map of northern Kanto (Seeking to build and develop the methodology)

The Geological Survey of Japan (GSJ) compiled a geochemical map of the northern Kanto region from Mito to Iwaki in 1991, as described above[10][11]. The motivation for starting the project was the completion of the British geochemical map of the U.K., which was published and which subsequently caused a huge impact on studies there and abroad. The simplicity and strong impression of the map are noteworthy: any map user can survey the elemental distribution of the entire U.K. easily by color. The technique was geochemical exploration seeking ore deposits, which was the same goal as that pursued by the geochemistry group of GSJ up to that time. The project of geochemical map started as a large project with high expectations; all groups related to geochemistry cooperated to produce maps jointly at that time.

In the geochemical map of the northern Kanto region, 3850 stream sediment samples were collected from the area of about 4000 km^2 (the sampling density was one sample to about 1 km × 1 km). At the project's outset, it was an important problem that this huge number of samples had to be collected. Eventually, 7–8 researchers and more than 20 assistants (students) formed several teams. The samples were collected during the first two weeks of the summer

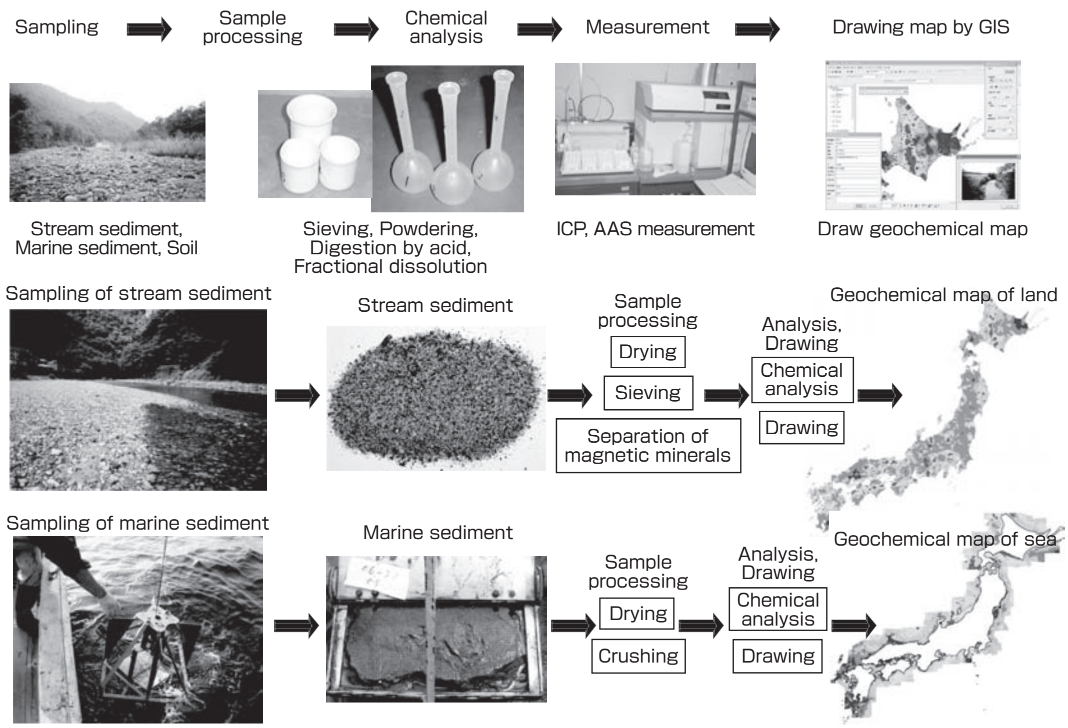

Fig. 2 Scheme of making the geochemical map

The figure shows the workflow from sampling to drawing the geochemical map by GIS, samples used for this study, stream sediments and marine sediments, sample treatments, chemical analysis, and drawing the geochemical map.

vacation over five years. At this time, the sample treatment was planned to be completed to the greatest extent possible in the field. The most important consideration was to finish the sieving and drying in the field. Fine-grained sands were separated by sieving them with river water. Then chemical analyses were conducted using ICP emission spectrometry. Thereafter, automated neutron activation-analysis was used to analyze many elements simultaneously. The analyzed elements were 26 elements such as cobalt, chromium, copper, nickel, phosphorus, lead, uranium, and zinc. This research

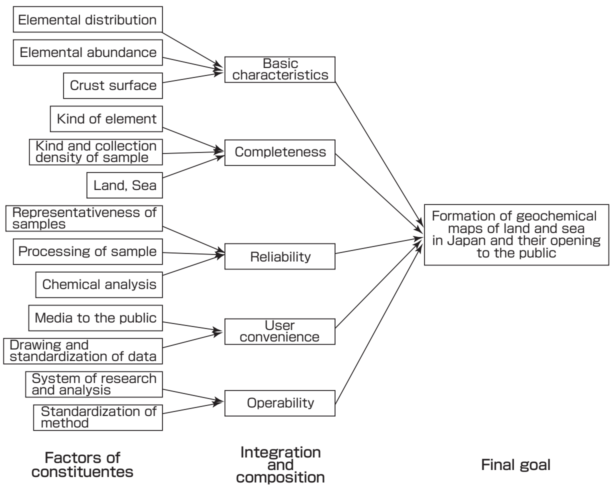

Fig. 3 Formation of the geochemical map of Japan and a scenario for opening access to the public
Components and key basic elements to support the geochemical map and the final goal

project was extremely important because the geochemical mapping of large areas was done for the first time in Japan. However, because it required a huge amount of work from sampling to analysis, it was important to allocate individual roles and to work appropriately.

4.1.2 Geochemical map of Japan (Development by converting the mode of thinking)

After the project of mapping the northern Kanto region, we sought to extend the area of the geochemical map to the whole country. However, because the same method in the northern Kanto region would have to be applied similarly, we were unable to continue the project. Because the area of Japan is about 380,000 km^2, the necessary number of samples would become 380,000 as 1×1 km mesh. Because such a huge amount of time and cost were deemed necessary to achieve the project, nobody would take the group's appeals seriously, even when proposed. Meanwhile, the work to produce the geochemical map around Sendai[12] and Yamagata City[13] was continued, although the area was quite small. As the sea area, the geochemical map was also formed in the coastal area from the Noto Peninsula to the seas off Akita[14].

The major turning point came from a discussion on the topic of whether a nationwide geochemical map was truly impossible. Although it seemed infeasible because the project needed funding and staff on an enormous scale, it was suggested that the mode of thinking should be reversed. First

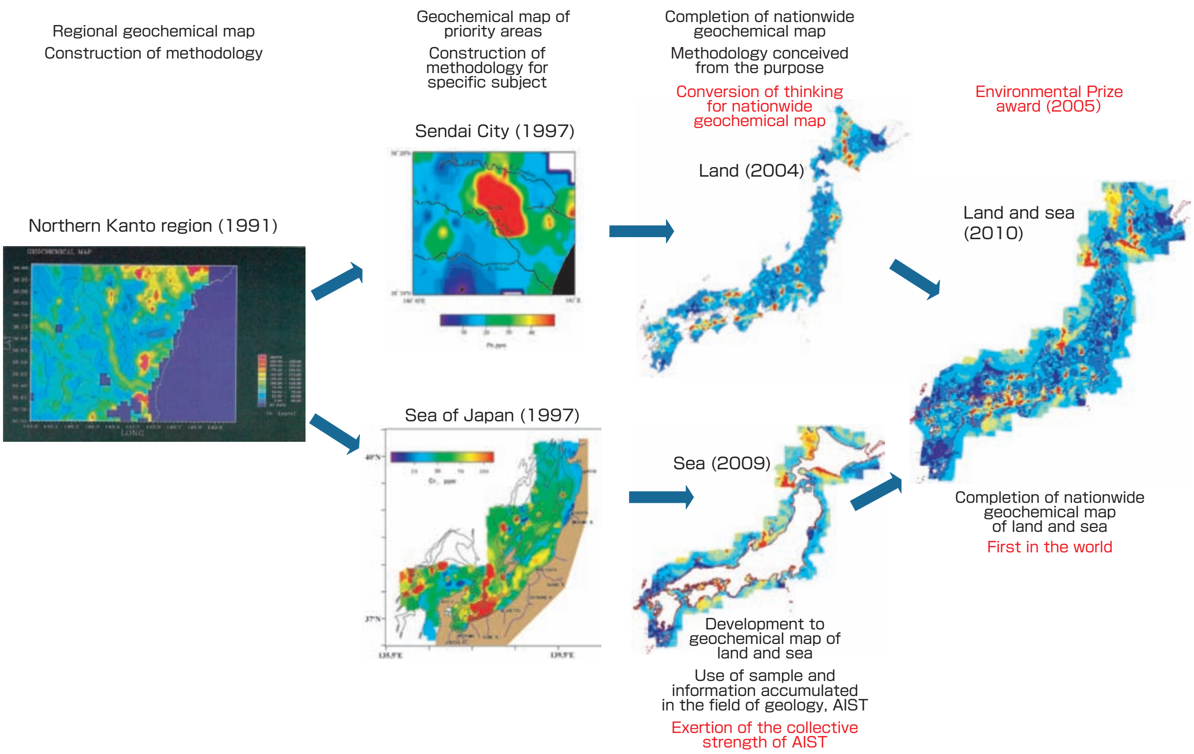

Fig. 4 Development of research in producing a geochemical map
From the geochemical map of the northern Kanto region (1991) to a geochemical map of the land and sea

such costs and staff should be estimated as necessary from a realistic viewpoint to compile such a nationwide geochemical map. At that time, the sample collection density of 1 km mesh was thought to be primarily important, and a coarser density was not meaningful. However, if the coarser mesh were adopted, then a possible plan could be formulated in terms of cost, the number of workers, and the period needed for the project. The period of the plan of the project was set as five years, and the number of samples was suppressed to about 3000 by setting the mesh to 10 km. Consequently, the nationwide geochemical map plan became a feasible one by adoption of the sample number and mesh.

At the first step, the geochemical map was to cover the whole country first, even with coarse sampling density. Thereafter, as necessary, the density was expected to be raised separately for specific areas of interest. In this way, both demands of covering the whole country and scientific significance would eventually be fulfilled. The budget was obtained from the Environment Agency, and the project was begun in 1999. The first geochemical map of the whole country of Japan was therefore completed in 2004[2]. Several features of elemental distribution in the Japanese archipelago were clarified for the first time in spite of the coarse mesh of 10 km that was chosen. Results show that it is not necessary to worry about the overly coarse sample collection density to understand anything. Fortunately, the nationwide geochemical map of Japan has attracted much social and scientific interest because of its ease of visual comprehension. It has been used in various fields. The project team won the “Environmental Prize” in 2005[15].

4.1.3 Geochemical map of the sea (Progress to the next stage)

Several ideas of how to advance the research of geochemical map to the next step were then raised. Another possible project was the elemental distribution for land extending into the sea. Geochemical mapping of sea areas off the coast of Hokuriku to Akita had been done before. The GSJ has studied the sea around Japan for many years, and many previously collected sea bottom sediments have been analyzed. For the geochemical map of the sea of the whole country, we can use those prior collected samples accumulated by GSJ. In our project, the bottom sea sediments were newly collected in the sea where no samples had existed before (about 30 percent of the whole country). Consequently, all marine sediments in the sea of the whole country could be collected. The total old and new samples were 4905. The geochemical map of the land and sea of the whole country was completed using these samples in 2010[3]. The nationwide geochemical map of both land and sea was the first of its kind in the world. The elemental distributions between land and sea were thus connected, which enabled us to elucidate the movement of elements from land to sea. A soil geochemical map of the whole country is being made at present as development of further study by collecting about 3000 soil samples throughout the country.

5 Factors of technology to produce a geochemical map (Development of technologies for objectives)

Factors of technology that are useful for producing a geochemical map include sample collection, chemical analysis, and map drawing. To achieve the objectives, the actual techniques to produce geochemical map are described to notify users of differences from the conventional method. For a detailed description of the procedures, refer to the past reports of the literature[2][3]. The important considerations are the automation of handling vastly numerous samples and the standardization of processes for all samples using a single technique. Because the geochemical maps had been made using different techniques in various regions, it was difficult to compare them quickly. However, by adopting standardized techniques, data of the whole country can now be analyzed systematically in a unified manner.

5.1 Sample collection

5.1.1 Geochemical map of the northern Kanto region[11]

In making the geochemical map of a large area, how we collect numerous samples is the most important consideration. The initial method used for collection of stream sediments in this study was how to reduce the sample processing time after sampling. Therefore, we tried to finish the necessary work such as sieving to the greatest degree possible in the field. Actually, one researcher and 2–3 assistants (students) constituted one team, which moved to the sampling position by car in checking 1/25,000 or 1/50,000 geographical maps. It was necessary to move to small rivers for sampling in cases of the geochemical map of 1 km mesh. If unable to reach it by car, it was necessary to walk to the sampling area. The sampling position was determined principally as the end of the branch of a river (the most downstream reaches of the watershed). The sampling point was determined beforehand in the laboratory, and how we could reach the area quickly was important.

After arriving at the sites, the teams separated stream sediments finer than 80 mesh (about 0.17 mm) by sieving. Stream sediments were put on the sieve of 80 mesh, and the sand and mud of 80 mesh or less which passed through the sieve were separated using filter paper by pouring the river water. However, some samples took a very long time for filtration because the filter paper became clogged, or it took much time in searching the sands of minute grains because we were sometimes unable to find them where the flow of the river was fast. If the required amount of the sample was not taken, then the filtration was repeated, which took much more time. After that painstaking process, often only several samples were collected in a day. The samples were brought to a hotel by the team and laid out to dry. They almost always dried completely overnight. In this way, about 60–100 samples per person were collected during trips conducted over two weeks, and 600–800 samples were collected overall.

5.1.2 Geochemical map of the whole country[2]

When the geochemical map of the whole country was being made, reducing the human load for work in handling vastly numerous samples was the most important problem, as we had learned when producing the geochemical map of the northern Kanto region. If all the sampling work were outsourced, then the necessary time and effort for us would have decreased. However, the cost would become too enormous to realize it as a normal research project. To save costs, the samples were to be collected by ourselves to the greatest extent possible. It was also important that the time-consuming sampling process be simplified. For that reason, work such as filtering was not performed in the field and no other work than collecting the sample was conducted. In this way, the costs were reduced, even if the work was outsourced. Consequently, the drying and sieving were not conducted in the field as in the case of the northern Kanto region map compilation. Fine-grained sand of about 2 kg was sampled using a shovel or bottom sampler. Moreover, the sampling point was set to the place where a large river intersected a large road: a location that could be reached easily. However, it took much time to move to the next sampling site because the sampling density was coarse and the distance separating sampling points was great. Especially for deep valleys in mountainous areas, even if it was apparently possible to collect a sample easily when viewed on a map, the actual river was often far under a cliff. Even in such cases, there was usually a small path running down to the river for use by sport anglers. Nevertheless, the sampling was sometimes impossible depending on the circumstances of the field. Eventually, about half of the total of 3024 samples were collected by ourselves. Otherwise, samples were taken by outsourcing. In all cases, dryness and sieving were done separately in a laboratory. However, the sample processing was efficient because the process allowed preparation of many samples at one time.

5.1.3 Sampling of sea-bottom sediments[3]

The most daunting problem was sampling to produce the geochemical map of the sea. The marine sediments were necessarily collected using a ship. Therefore, it was much too difficult to do ourselves, unlike the sample collection that was conducted on land. Especially, when the depth was more than several hundreds of meters, sample collection was impossible without a large specialized ship. It also entailed huge costs. We were able to reduce the costs greatly using marine sediment samples that the GSJ had collected in the past. In the survey, a marine research vessel of more than 2000 t was used for the surrounding seas of Japan whose depth was up to about 3000 m. For this study, the samples were newly collected in the sea for which we had no sample. Because the project had tight budget limitations, the depth of the seas in which we could collect the samples was at most 100–200 m. However, the areas with seas less than 200 m deep were sufficiently wide to constitute a good sampling area, especially in the west of Japan, where the continental shelf is developed well. There we were able to cover the large area of the sea easily. The marine sediment samples were collected using a glove bottom sampler (Smith–Macintyre type bottom sampler) that was installed on the survey ship. Sample processing was done fundamentally in the same way as for the samples from the land. The marine samples were 4905. Figure 2 depicts how the collected samples were raised from the sea bottom.

5.2 Chemical analysis

In this study, because it was necessary to analyze numerous samples, sample processing and analysis were automated and standardized as much as possible. In the geochemical map of the northern Kanto region, 26 elements were analyzed using ICP emission spectrometry and neutron activation analysis. For the geochemical map of the whole country, 53 elements were measured using ICP mass spectrometry and atomic absorption spectrometry. In both cases, an auto-sampler and automated measurement systems were used to the greatest extent possible. To simplify the sample treatment, stream sediments of less than 80 mesh were analyzed without powdering. In most cases, the analytical results obtained for samples that had not been powdered were the same as those obtained for powdered samples. Moreover, the stream sediment was analyzed after extracting magnetic minerals such as iron sands using a magnet. Heavy minerals are sometimes concentrated by the fractionation of river water. The purpose of extracting magnetic minerals is to avoid letting the map become an unnatural geochemical map. Especially in regions where many iron sands exist, the geochemical map becomes an *iron sand map*. Samples were decomposed using mixed acids of nitric acid, perchloric acid, hydrofluoric acid, and 0.1N hydrochloric acid.

5.3 Drawing of the geochemical map

In drawing a continuous geochemical map from geographically discrete sampling points, it is necessary to interpolate in areas for which data do not exist. The watershed analysis was made by GIS to determine the upper watershed area for each sampling point of stream sediment. The elemental concentration for each area is assumed to be the same. To simplify the calculation, the watershed area was converted to square mesh and the concentration data were allocated as the same value to each mesh. Then the geochemical map was drawn by interpolating the mesh data. In this study, the geochemical map was made without consideration of the movement of the marine sediment by seawater or the oceanic current because a more realistic portrayal quickly became too complicated to calculate.

6 Geochemical map of Japan and its implications (Behaviors of elements in nature and in human activities)

This study produced geochemical maps showing distributions of 53 elements in sea and land areas. It is necessary to interpret each elemental behavior according to its circumstances because its behaviors in nature and in human activities might differ from those of other elements. Here, we describe geochemical maps of chromium and mercury, which have characteristic features in terms of their respective distributions. Please refer to individual reports in the literature for details related to other elements and features of elemental distribution in respective regions[16]-[20].

6.1 Geochemical map of chromium (Cr)

Figure 5-1 shows the geochemical map for chromium. The two red lines in Hokkaido and Shikoku (areas of high Cr concentration) in this figure are noticeable first. A remarkable high-Cr concentration region of more than 200 ppm exists along the median tectonic line. The tectonic line crosses from west to east of the Shikoku and Kinki regions, reaches the Tokai and Kanto regions and another crosses the center part from north to south in Hokkaido. This prevalence is thought to result from the green rocks and ultra-basic rocks distributed along these regions that contain chromium and nickel in very high concentrations. The red area of high concentration in the sea is apparent in the coastal areas of off southern Hokkaido and Hokuriku. The most remarkable area is along the Hime River in Itoigawa, where the northern end of the Fossa Magna in Hokuriku District is located. The high concentration region of chromium on land extends to the sea. A high concentration region of chromium along the Hime River on land continues to the deep sea valley. Therefore, the detritus of the serpentine, which contains chromium in high concentration moves from the Hime River to the Toyama deep sea valley in the sea. This figure also portrays the topography of the seabed in this region. It is readily apparent that a deep sea valley exists in the north of Hime River and that the sediment flows from the Hime River along this valley to the sea.

6.2 Geochemical map of mercury (Hg)

Figure 5-2 shows the geochemical map of mercury. The mercury concentration is remarkably high in the region where large-scale mercury deposits such as Itomuka mine in Hokkaido and Yamato mine on the Kii Peninsula exist. Furthermore, the concentration of mercury is high around big cities such as Tokyo and Osaka on the land, and concentrations are high in Tokyo Bay, Ise Bay, and Osaka Bay. This prevalence is affected by anthropogenic influences from cities with large populations. This figure also shows geochemical maps of Kyushu, Hokuriku, and Kinki regions. The high concentrations of mercury off the coast of Niigata and in the Yatsushiro Sea and western Kyushu are visible in the figure. It is possible that the influence of the past mercury pollution remains in these high-concentration regions. The high concentration of mercury in the northern sea around Sado is considered to reflect the influence of the Sado gold mine in the past. The high concentrations of mercury in Ise Bay and Osaka Bay in the Kinki region are thought to be influenced by large-scale Yamato mercury deposits in the Kii

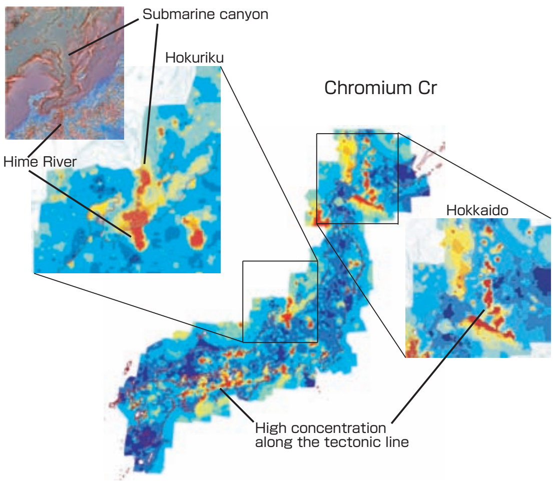

Fig. 5-1 Geochemical map of chromium (Cr) of Japan, Hokuriku and Hokkaido regions

A high Cr concentration region is apparent along the median tectonic line and the tectonic line in the center of Hokkaido. The high concentration region extends from Hime River to the sea.

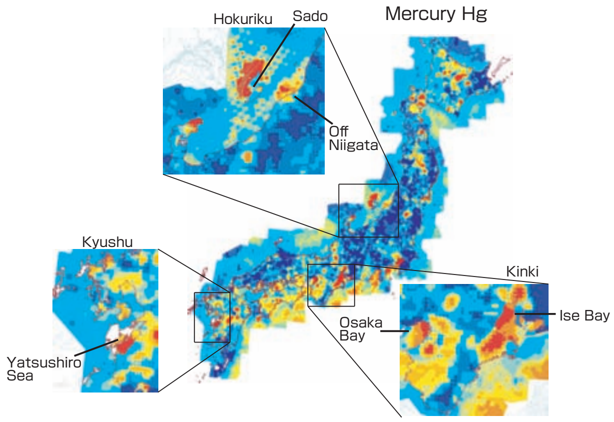

Fig. 5-2 Geochemical map of mercury (Hg) of Japan, Kyushu, Hokuriku, Kinki regions

High Hg concentrations off the coast of Niigata and in the Yatsushiro Sea reflect the influence of past mercury pollution. That in the sea off northern Sado reflects the influence from gold mines in the past. The high concentrations in Tokyo Bay, Ise Bay, and Osaka Bay are attributable to anthropogenic influences from the nearby large cities.

Fig. 5 Elucidating elemental behavior in nature and human activities using a geochemical map

Peninsula, in addition to anthropogenic influences from the large cities nearby.

7 Disclosing data to the public (Providing information to society as a public good)

A geochemical map homepage was made, presenting data of the geochemical map which had been accumulated. It was then made available to the public for easy access and reference on the web. Figure 6 shows the geochemical map homepage. The geochemical map of land and sea of the whole country is visible here, as are the regional geochemical maps and detailed information of each elemental concentration for all 3024 stream sediments and 4905 marine sediments. All of that information can be accessed easily on the network. Moreover, a photograph of the sampling point and the sample are displayed for all stream sediments. Photographs of the samples are available for some bottom sea sediments. Especially, a photograph of stream sediment can be enlarged by clicking, and the kind of rock and sediment distributed in the region can be investigated. In addition, the elemental concentration and the latitude and longitude of all the samples, the geochemical map of the whole country and regional map (the raster map / GIS shape file), and related information are downloadable from the website.

8 Practical use of a geochemical map (Various uses of the basic information of the nation)

The geochemical map presents the elemental distribution on the surface of the earth's crust for land and sea areas. The data are important as basic information of the entire nation. In addition, because stream sediments were collected from throughout the country and because the individual stream sediments represent their local watersheds, the average concentration of all the samples can be considered as an average chemical composition of Japan. The average chemical composition of Japan (Clarke number of the Japanese archipelago)[21], as calculated from a distribution ratio and the composition of typical 166 rock samples distributed in Japan is desired. This is considered to be a theoretical value, although the mean value of 3024 stream sediments in the geochemical map is a value that was actually measured in the field. It was clarified in this study that both values agree very well.

A geochemical map can also be used for evaluation of natural radiation doses, as determined by the sum of the natural radiations from surrounding rocks and sediments and the cosmic rays. The former is calculable roughly from the contents of potassium, uranium, and thorium in rocks and sediments obtained from the geochemical map. For instance, the natural radiation dose is known to be large in west Japan, where granite that contains much potassium, uranium, and thorium is widely distributed. The contamination levels of radioactivity from nuclear facilities in various regions can be evaluated through comparison with the natural background level.

For social purposes, the geochemical map is used as basic data for the evaluation of soil pollution. The concentration of elements is readily apparent from the map in the

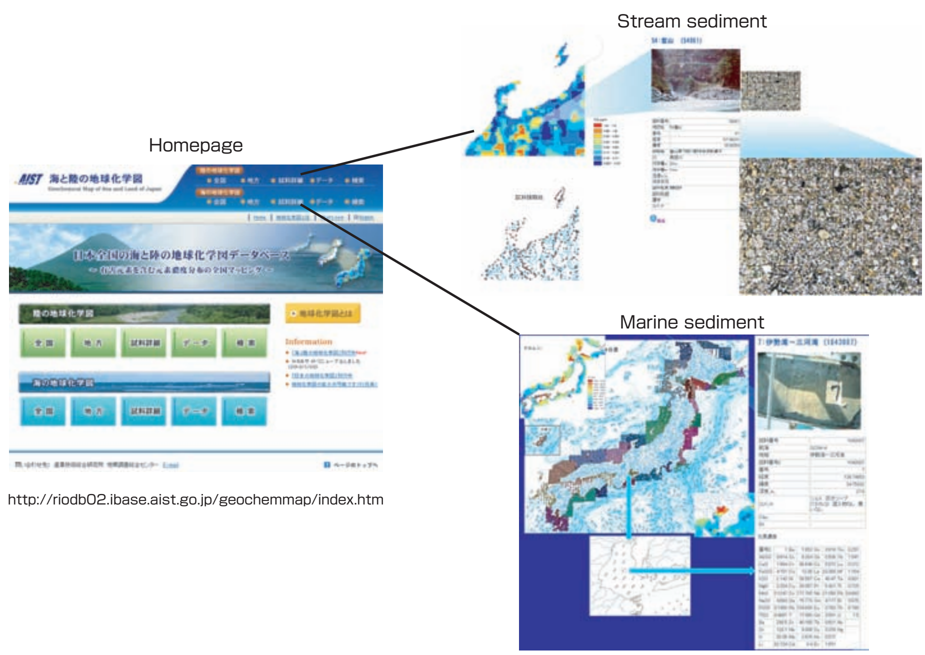

Fig. 6 Homepage of geochemical map
The homepage of the geochemical map (http://riodb02.ibase.aist.go.jp/geochemmap/index.htm) and detailed information of individual stream and marine sediments are shown. Photographs of sampling points and samples of stream sediment and marine sediment, the elemental concentration and the latitude and longitude of all the samples are shown.

facilities of municipalities and plants of companies. It is very effective as a preliminary check for additional detailed surveys of pollution. As described previously in 2.1, it is important to compare the measured concentrations with natural background levels. Then the environmental base line level can be known when the soil pollution is examined. If there are mineral deposits or hot springs in surrounding areas which have high natural background levels of elements, then it is necessary to distinguish anthropogenic pollution from these natural factors. Because the geochemical map represents the natural background level, the environmental pollution can be evaluated through comparison with the map as background. Such data are useful as base data to prevent the spread of pollution locally and nationally, and to produce appropriate policies of pollution control and remediation. A risk assessment of the location of a factory using a geochemical map enables us to reduce soil pollution assessment costs.

As described above, because all data of the geochemical map are fundamentally open to the public, various users propose different uses that we had not considered. For example, a joint research project with the Institute of Police Science was made to study the possibility of identifying the sources of soil using the database of the geochemical map of the whole country at present. We also hope that the data of the geochemical map will be useful for other socially beneficial tasks in the future.

Currently, we are compiling a soil geochemical map using about 3000 soil samples collected from throughout the country. We will apply a geochemical map to elucidate the distribution and the diffusion processes of elements in crust's surface, and will develop an evaluation system of toxic elements for environmental pollution that incorporates land, river, and sea areas. We also want to integrate various data such as those related to geology, geography, pollution, and social data to investigate environmental pollution in the future.

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Author

Noboru Imai

Completed the doctoral course in Chemistry at the Graduate School of Science, The University of Tokyo in 1980, earning a Ph.D. (Science). Joined the Geological Survey of Japan, Agency of Industrial Science and Technology (current AIST) in 1981. Became the group leader of the Geochemistry Group, Institute of Geology and Geoinformation. Engaged in research of the geochemistry of rocks and sediments, ESR dating, geochemical map, and geochemical standard reference materials. For this study, was in charge of the geochemical map of the land and sea in Japan. Awarded the Environmental Prize for the geochemical map in 2005, and a Prize of the Minister of Education, Culture, Sports, Science and Technology for a certified reference material in 2010.

Discussions with Reviewers

1 General comments

Comment (Shigeko Togashi, Evaluation Department, AIST)

This paper is meaningful for the methodology to complete the geochemical map of land and coast of Japan as one of the basic geological information of the country. By converting the conception, the geochemical map covered the whole country by acquiring external budget although it started from the regional map of small areas. Especially, it is noted that an Environmental Prize was awarded for the widely used geochemical map in society. This paper therefore is suitable for publication in *Synthesiology*.

As described in this paper, it is better to show first what the geochemical map is and how it is used for the reader by using figures which are easy to understand. Please indicate the keywords of some concrete examples also from the practical use of the later chapter. In addition, for the history of geochemical mapping in AIST the description of the methodology should be more generalized as a method of synthesiology. Although the original manuscript was "just explanation", the manuscript which was reconstructed by generalizing the approach of research and the methodology of the social contribution has been much improved by corresponding to the above-mentioned primary comment.

Answer (Noboru Imai)

According to the reviewer's comment, the structure of the text was changed to clarify the thrust of the discussion. The geochemical map is explained in "2.1 Background of the geochemical map", and the scheme of the geochemical map is described in "3. Flow of geochemical mapping". The configuration of the entire text was modified.

2 Similarity of research scenarios

Comment (Akira Ono, AIST)

The target of this research is making the geochemical map of Japan which covers both the sea and land. The result is not only original but also excellent as the *Type 2 Basic Research* and *Product Realization Research* using the integration and synthetic methods.

Making the geochemical map is considered to be comparable with making a large-scale database. I have an experience to build a database of physical properties, and think that the setting a scenario seems to be analogous to that of geochemical map.

Fundamental qualities of the database are composed of the characteristics of data, coverage and reliability of data, convenience in the use, and operability in making and using the database. I think these qualities of the database are also common to the geochemical map. If you agree with this, please draw an analogous scenario for the geochemical map, which I think will make it easier for the reader to understand.

Answer (Noboru Imai)

Thank you for reviewing the manuscript so carefully and thoughtfully. I also very much appreciate your suggesting a figure of the concrete scenario. The figure is intelligible in allowing a purview of the whole work. Several terms were corrected based on this suggestion; the scenario is depicted in Fig. 3. The viewpoint outside of this specialty has been particularly helpful for me to understand the work more comprehensively.

3 Motivation at an early stage of the research

Question (Akira Ono)

As described in this paper, the origin of a geochemical map of Japan goes back to that of the northern Kanto region developed in 1991. After that it took 20 years to publish the geochemical map of Japan. I think that the methodology which was developed in making the geochemical map of the northern Kanto region led to today's success.

In that sense, I think that it was a very important point that you decided to start the work of the geochemical map of the northern Kanto region. What was the motivation that made you decide to start it then? Did you start it because you were inspired by the British geochemical map research in advance, or because of your own academic interest?

Answer (Noboru Imai)

It was a very important point that the geochemical map of the northern Kanto region was first launched as you pointed out. I think that there were several purposes for starting the geochemical map project at that time. The geochemical map of the northern Kanto region was completed in March 1991. The five-year project was started on April 1, 1985. Therefore, we had actually prepared the project from 1984 because the budget had passed in the prior year. At that time, because I had just started my career as a researcher, I did not know all the circumstances surrounding the start-up of the project. However, I think it occurred as follows.

The first motivation of the start-up of the project was the British geochemical map, which made a big impression on many people, as you pointed out. The ease of understanding the distribution of elements in the UK at a glance gave us a strong impression. Moreover, the used methodology was exactly the same as that for geochemical exploration to find mineral deposits, which was the method used by the geochemistry group in GSJ. Therefore, it seemed to us that we could undertake the project without delay.

The research groups involved in the geochemical map then were doing basic research in geochemistry and doing chemical analyses of geological materials. They had been working somehow far from the main stream of making "the geological map" in GSJ. The geochemical map work started as a big project necessitating the cooperation of several geochemistry groups to produce the map collaboratively. Therefore, we harbored great expectations for its progress as a first project for the geochemistry groups. A unique scientific interest was also involved: to know the distribution and the movement of elements in the earth's crust. However, the promotion of geochemical study by introduction of large-scale equipment such as neutron activation analysis and ICP emission analysis was another major purpose. I think everyone certainly appreciated the project after the nationwide geochemical map was completed.

4 Similarity of the methodology between field research and laboratory experiment

Question (Akira Ono)

In viewpoint of the amount of data, the sampling points at a finer interval and the coverage of a wider area are in tradeoff. Which you should give priority to and how you harmonize them may be hard problems. In this work, it may have been an important point for you to assume first that even coarse sampling was scientifically meaningful if the coverage was wide enough, (which was excellently revealed later).

Suppose a laboratory experiment where we measure a physical property of a sample changing the sample temperature in a range. It is recommended that measurements are made firstly over the whole range of temperature at a coarse temperature interval to see quickly the overall trend. Then measurements follow at a finer temperature interval in selected ranges of interest. I think that the technique of understanding the whole image first and proceeding toward detailed parts is a common approach, which is very effective even if the field of research is different. Unlike the laboratory experiment, because the field research cannot be repeated easily, such a technique is thought to be more important.

Answer (Noboru Imai)

I think that the technique of understanding the whole image first and proceeding toward detailed parts is important, as you have pointed out. As for the question about why we did not notice that point earlier, because similar research projects including those of foreign countries had adopted the mesh size of 1 km, we did not consider trying a more coarse mesh to cover the whole country. Considering that there are various types of mountains, valleys and plains, a mesh size of 10 km seemed to be too coarse to obtain useful data from geographical and geological viewpoints. I did not realize at that time that excellent geochemical maps could be obtained with such a coarse mesh size.

We first thought that regional geochemical maps made by the local governments and universities in individual prefectures should be connected to cover the whole country. However, this did not progress very easily, and small-scale geochemical maps are now being made at a university to which the proposer of the first project moved, and at other universities which have an interest in compiling and contributing local geochemical maps.

5 Representativeness of samples

Question (Akira Ono)

In this research, the stream sediment at the root of a branch of a river is assumed to represent the area of watersheds of the branch. I think this is a very good idea. However, how did you check the assumption that the stream sediment fully represents the watersheds? Please tell us of any other thoughts concerning representativeness of analytical results, for example other conditions that might be needed.

As you mentioned about the element distribution in soil in your manuscript, what is the difference of the definition between surface of the crust and soil? I imagine as an amateur that soil is mixed in the stream sediment at the root of a branch of a river. Is the mixing of soil in the sediment negligible?

Although the element distribution in soil is not the main subject in this paper, can you tell us where you should sample the soil so that the sampled soil represents a certain area?

Answer (Noboru Imai)

It was confirmed in several places that the stream sediment at locations in the watersheds of the rivers represent its whole watershed. The examples of zinc and phosphorus concentrations in Sendai City are shown as follows. In Fig. a, the 39th sample, which is taken at the root of the Hirose River, is thought to be a representative point in the entire watershed of the Hirose River. Figure b shows that the averages of the concentrations of both zinc and phosphorus for all samples in the watershed agree well with the concentration of the 39th sample. Therefore, in this case, the entire watershed of the Hirose River is well represented by sample No. 39.

To improve the representativeness, the sampling site is carefully selected to facilitate collection of samples that are as fine as possible. In addition, samples which are thought to be influenced by human activities such as industrial wastewater or enrichment of heavy minerals such as of iron sand should be avoided carefully.

Regarding the difference of the definition between the earth's crust surface and the soil, the thickness of the earth's crust is several kilometers on land and several tens of kilometers in the sea. The definition of the word "surface crust" is ambiguous. Nevertheless, I think the thickness is within 1 km, from several tens to hundreds of meters. The soils are composed from the surface organic layer to A, B, C horizons in sequence proceeding to greater depths. The thickness is from a few centimeters to several tens of centimeters (several meters). The ratios of the soil in stream sediments differ greatly from place to place, but the ratio is not so large because the soil thickness is sufficiently small compared with the surface crust, although the surface materials are mainly incorporated into stream sediment. After all, because the soil is fundamentally the product of the surrounding rocks and sediments by erosion, the chemical composition of the soil does not differ much from that of rocks and sediments, although there are various additional anthropogenic influences from external contamination.

Regarding the sampling method, the sampling point density is determined from the number of samples and the area. In this

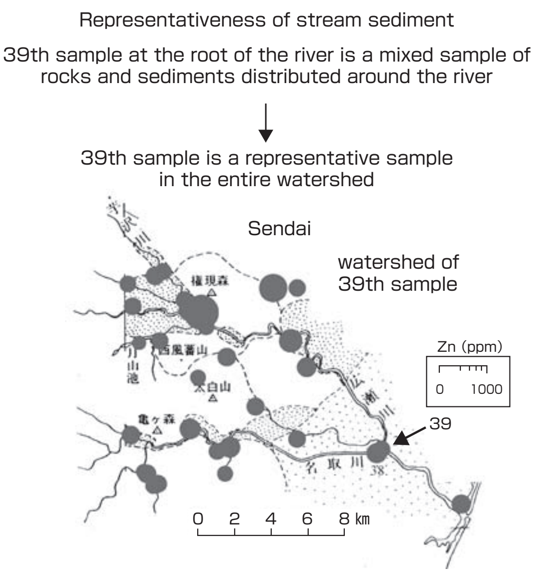

Fig. a Zinc and phosphorus concentrations in Sendai City

study, it was about 10 km mesh. Therefore, one sample was collected from every 10 × 10 km area. The sampling density was so coarse that the sampling points were determined carefully, and they should represent a wide area in producing a nationwide map. Actually, while we referred to and compared the geological and the soil maps, the sampling points were determined so that the points represent the geological and soil divisions of each area. Results show that the geochemical map using the stream sediments agrees well with that using the soil. However, when we can take a higher sampling density, the soil is basically collected in an exact grid.

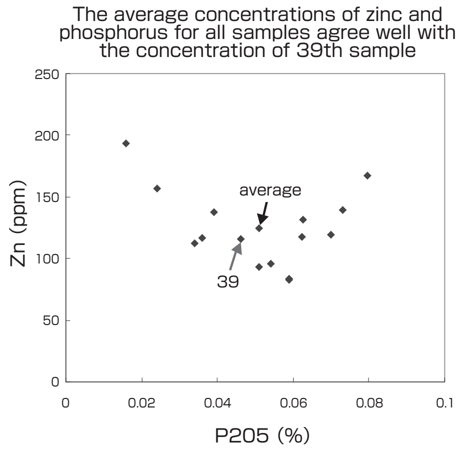

Fig. b Scatter plot

6 Sample storage and future study

Question (Akira Ono)

In the investigation of marine sediments, it is written that the samples collected by AIST in the past were used for the chemical analysis in this study. This indicates satisfactorily the continuity, integrity, and mutual availability of research which reflect the excellent function and system of the AIST organization.

Are the samples as well as those newly collected in your project in land and sea stored in Geological Museum for the use in which more detailed analysis will be needed in the future?

Answer (Noboru Imai)

The researchers and persons in charge of the GSJ project of collecting bottom sea sediment in the marginal sea in Japan also joined our project of the geochemical map for the collection of the marine sediment. Therefore, we were able to use a huge number of sediment samples collected in the past, and in this study by collecting the new samples in areas for which there were no samples, we were able to obtain a full set of sediments for areas throughout Japan. Therefore, we were also able to contribute much to their project of marginal sea mapping and assessment.

About 3,000 stream sediments, 5,000 bottom sea sediments, and 3,000 soils collected in the geochemical map project are stored and classified to be used anytime. That inventory is extremely valuable property for which the samples whose chemical composition is known are kept to be used as a set for the whole country. The samples have been used by outside researchers to date for making a national soil database of the Institute of Police Science and for producing a national map of a strontium isotopic ratio at Nagoya University. Principally, the geological samples were kept in the Geological Museum. The samples collected through the geochemical map project are also kept in the Geological Museum, as you have pointed out.