

Development and utilization of geochemical reference materials

— Reliability improvement in the analysis of geological materials —

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The Geological Survey of Japan has issued about 50 reference materials over the past 50 years. They have been used all over the world to improve the reliability in chemical analysis of geological materials. Geological samples of rocks, ores, minerals, soils, sediments, etc. generally contain various elements at high concentration levels. For accurate chemical analysis, it is necessary to use geochemical reference materials that contain major components at similar levels to the samples to be analyzed and predetermined concentration of target elements. In this paper, scenarios to develop geochemical reference materials for Japan and the rest of the world are described. Methods for selecting and grinding sample materials, the determination of reference values, and data sharing are also reported.

Keywords : reference material, geochemistry, chemical analysis, geological materials, sample grinding

1 Introduction (what are geochemical reference materials?)

The chemical analysis of elements, a part of the geological survey activities of the Geological Survey of Japan (GSJ), is an essential technique for examining geological characteristics and geologic history. For example, chemical analysis is essential in the utilization of mineral resources for exploration and formation analysis of ore deposits, the evaluation of their feasibility as resources, among others. As such, accurate chemical analyses are desired in the trading of actually mined ores. In addition, chemical analysis is necessary for environmental assessments, such as those considering contamination by specific elements and the ways these elements migrate. The geological materials that are the targets of a geological survey, such as rocks, ores, minerals, soils, and sediments, contain various elements in high concentration. For example, there are as many as 10 elements of relatively high contents that are referred to as major components of rock samples such as silicon, aluminum, iron, etc. These components of high concentration affect each other in chemical analysis; therefore, to chemically analyze specific elements accurately, the effects from other elements must be identified accurately. Therefore, for accurate chemical analysis, it is effective to use reference materials with similar major component contents (similar effects from high-content elements) and with the target element concentration determined. These reference materials for accurate chemical analysis of geological materials are called “geochemical reference materials,” and they are used

as reference materials essential for the chemical analysis of geological materials around the world, such as for the development of methods of chemical analysis for geological materials, accuracy management for day-to-day analysis, and preparation of calibration curves to gauge instrumental analysis.

Generally, when analyzing the chemistry of geological materials, massive samples are ground into powders by using various crushers. Because natural rocks are aggregates of various minerals, from the perspective of the representativeness of the sample, a certain amount (hundreds of grams to several kilograms) of the sample is ground and homogenized, and a portion of these powders is sampled and analyzed for chemistry. Fundamentally, geochemical reference materials are obtained by grinding source rocks into powders and then storing these powders in bottles or other containers (Fig. 1).

The history of the development of geochemical reference materials began in 1949 when the U.S. Geological Survey (USGS) issued the G-1 (granite) and W-1 (diabase) reference materials. In Japan, the Geological Survey of Japan (GSJ) began developmental studies in 1964, and the first reference material, JG-1 (granodiorite), was issued in 1967. Thereafter, the responsibility was passed to the Research Institute of Geology and Geoinformation of GSJ, and about 50 types of reference materials have been prepared in the subsequent 50 years (Table 1). More than 10,000 units of these GSJ geochemical reference materials have been distributed

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Table 1. Geochemical reference materials published by GSJ

Volcanic rocks		Sedimentary rocks	
JA-1	Andesite (1982)	JLs-1	Limestone (1987)
JA-1a	Andesite (2002)	JCp-1	Coral (1999)
JA-2	Andesite (1985)	JCT-1	Giant Clam (2002)
JA-2a	Andesite (2013)	JDo-1	Dolomite (1987)
JA-3	Andesite (1986)	JSI-1	Slate (1988)
JB-1	Basalt (1968)	JSI-2	Slate (1989)
JB-1a	Basalt (1984)	JCh-1	Chert (1989)
JB-1b	Basalt (1996)		
JB-2	Basalt (1982)	Sediments	
JB-2a	Basalt (2004)	JLk-1	Lake sediment (1987)
JB-3	Basalt (1983)	JSD-1	Stream sediment (1988)
JB-3a	Basalt (2003)	JSD-2	Stream sediment (1989)
JF-1	Feldspar (1985)	JSD-3	Stream sediment (1989)
JF-2	Feldspar (1986)	JSD-4	Stream sediment (2005)
JG-1	Granodiorite (1967)	JSD-5	Stream sediment (2006)
JG-1a	Granodiorite (1984)	JMS-1	Marine sediment (1999)
JG-2	Granite (1985)	JMS-2	Marine sediment (2000)
JG-2a	Granite (2015)	JMS-3	Marine sediment (2007)
JG-3	Granodiorite (1986)		
JGb-1	Gabbro (1983)	Coal fly ash and soil	
JGb-2	Gabbro (1991)	JCFA-1	Coal fly ash (1995)
JH-1	Hornblende (1992)	JSO-1	Soil (1997)
JP-1	Dunite (1984)	JSO-3	Soil (2009)
JP-2	Dunite (2011)		
JR-1	Rhyolite (1982)	Ores and minerals	
JR-2	Rhyolite (1983)	JMn-1	Manganese nodule (1994)
JR-3	Rhyolite (1990)	JZn-1	Zinc ore (2000)
JSy-1	Syenite (1993)	JZn-2	Zinc ore (2008)
		JCu-1	Copper ore (2001)

around the world and are contributing globally to improve the reliability of chemical analyses.

2 Background and history of development

2.1 Technological background and history of development during the 1940s

In traditional chemical analysis of geological materials, the wet method is used to separate elements (components) chemically, and gravimetric, volumetric, and colorimetric methods are used for quantification. This method is extremely accurate when such analysis is appropriate, but complex operations are required to separate and quantify elements; thus, the method requires experience and a large investment of time. Under such



Fig. 1 Geochemical reference materials published by GSJ
From left: JA-1a, JB-2a, JB-3a, JZn-1, and JCu-1
Powdered samples are packed in bottles and distributed.

conditions, a method for the analysis of the major components of silicate rocks through spectroscopic analysis (emission analysis) using a DC arc was developed, and the era of instrumental analysis began. Compared to the traditional wet method, which requires experience and a large amount of time, instrumental analysis increased the efficiency of chemical analysis significantly. However, instrumental analysis is fundamentally a comparative analysis of physical quantities such as intensity or absorption of light, and it requires criteria. In addition, for samples with complex elemental compositions, such as geological materials, the effects of existing forms of elements and interference by other elements are significant, which caused some problems. To solve these problems, it is useful to create criteria from natural rocks having the same composition as the samples. Based on this idea, Fairbairn at the Massachusetts Institute of Technology (MIT) led the preparation of reference materials from volcanic rocks, and in 1949, the USGS published two references: G-1(Granite) as the representative reference for acidic rocks with high silicon dioxide content and W-1(Diabase) as the representative for basic rocks with less silicon dioxide.^[1]

2.2 The world's first collaborative analysis and evaluation

These two samples were distributed to research institutions, including notable universities and geological surveys (GS) around the world, and collaborative analysis was conducted to decide the standard values for the reference. This was an important effort in the sense that it was the first international collaborative analysis of geological materials using common samples. The results of the collaborative analysis, which were reported by Fairbairn *et al.* in 1951,^[2] were shocking. Despite the fact that those who participated in the collaborative analysis were top analysts with first-class techniques from the various countries, the results were not as consistent as predicted. The analytical results for silicon dioxide in G-1 and W-1 are shown in Fig. 2. The differences among the reported results were too large, so a standard value for instrumental analysis could not be decided. The cause for these large differences was that differences among analytical methods were too significant, which thus resulted in a new challenge: the improvement of analytical methods. Subsequently, studies to improve analytical methods were conducted around the world, and finally, in the early 1960s, the desired standard value (recommended value) was reported.^{[3][4][5]} In addition to improvements in analytical methods for major components using the same samples, the development of analytical methods for trace components was actively pursued. The analysis of trace components is strongly affected by major components; however, because collaborative analysis had accurately determined the values of the major components, these samples became ideal materials for examination of trace component analysis worldwide. Furthermore, to establish a standard, many reported analytical values must be compiled. Statistical

examinations of geological materials analysis have also been conducted, and these have contributed significantly to the chemical analysis of geological materials.

2.3 Early development of global reference materials

Various examinations and research development occurred as a result of work on these first two samples. As a result, to samples that were considered simply as standards for instrumental analysis, a new utility value, the development and evaluation of analytical methods and techniques (precision, accuracy, and level of expertise), was born. Thus, the necessity and utility of reference materials became widely acknowledged. The fact that the initial analytical values did not agree led to utility values of the reference materials. However, the first two samples were nearly exhausted because they had been used for ten years or more worldwide. Foreseeing this problem, in the 1960s, the USGS prepared six types of new samples, including G-2 (granite) to replace G-1, and reference materials were also being actively developed in many other countries. The list of the main countries (organizations) includes the USA (National Bureau of Standards, NBS), the UK (Bureau of Analyzed Samples, BAS), France (Centre de Recherches Petrographique et Geochimiques, CRPG), Canada (Nonmetallic Standards Committee Canadian Association for Applied Spectroscopy, CAAS), East Germany (Zentrales Geologisches Institut, ZGI), and Japan (GSJ) (names of organizations are as of the 1960s). The commonality among all of these organizations is that each used geological materials from its own country. Based on the list of reference materials related to geochemistry provided by Ando (1967),^[1] reference materials that were issued at that time in the countries (by the organizations) listed above are summarized in Table 2. The table reveals the intentions of the various countries and organizations by the types of geological materials that were used as reference materials. The USGS focused on volcanic rocks, which are common in the bedrock of the USA, but NBS focused on materials that could be raw materials and

Table 2. International geochemical reference materials in 1967

Excerpt from Ando (1967)^[1] for samples published from major organization

Country	Organization	Samples
USA	USGS	andesite, basalt, diabase, dunite, granite, granodiorite, nepheline syenite, peridotite (in preparation)
	NBS	basalt, bauxite, refractory bricks, cement (five types), iron ore (two types), limestone, manganese ore, magnesite, petalite, phosphate ore, silica sand, tin ore, spodumene, zinc ore
UK	BAS	refractory bricks (two types), iron ore, manganese ore, slag (three types)
France	CRPG	basalt, biotite, granite (three types)
East Germany	ZGI	basalt, clay shale, granite, limestone
Canada	CAAS	syenite, sulfide ore
Japan	GSJ	granodiorite, basalt (in preparation)

products of the mining and manufacturing industries. Like the USGS, GSJ began their efforts with volcanic rocks.

3 Developmental scenario of GSJ

3.1 Basic concepts at the outset

3.1.1 Background and significance of creating reference materials in Japan

The most important significance of developing geochemical materials in Japan is “elucidating the chemical compositions of domestically produced rocks at the global research level.”^[6] In the 1960s, when such studies began, instrumental analysis was not common, and the wet method was mainly used. It took time to obtain chemical data, and a single analytical value was extremely important and valuable. Despite this

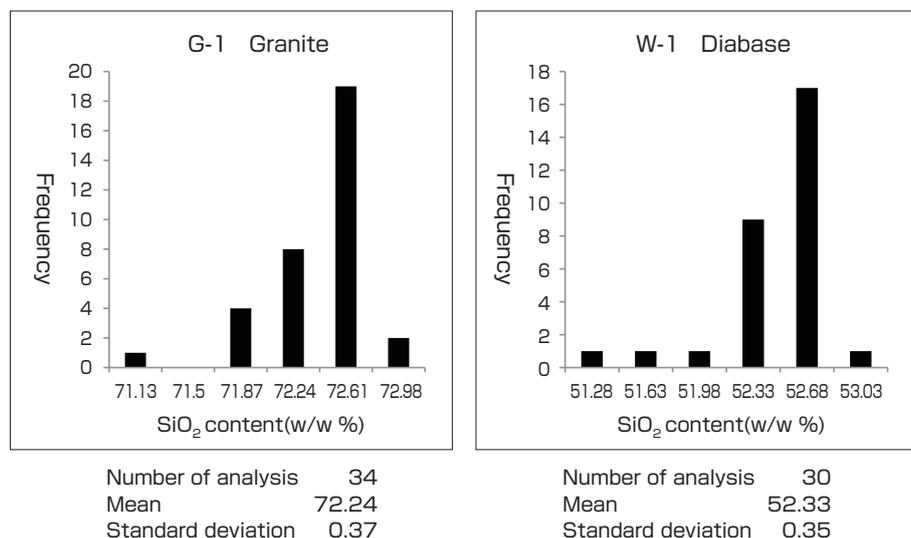


Fig. 2 F Silicon dioxide contents and histograms for G-1 and W-1 as reported in 1951 (prepared from Fairbairn et al. (1951)^[2])
Peaks occur in areas greater than the mean value, showing scattering.

situation, the first samples, G-1 and W-1, were analyzed globally and a large amount of data was collected. The values were determined at a global research level. In addition, the number of geochemical reference materials was small at that time, and these materials were analyzed globally immediately after issuance. In other words, during that time, a large number of global-level analytical values could be obtained from reference materials based on rocks in Japan that were released to the research community. Based on the thinking of current reference material development, this may seem strange. However, in the initial stage, sample preparation and the assigning of values had large research and developmental importance, and these goals were established as the main target. In addition, the rocks that constitute a country (types and chemical compositions) are different for each country, and the necessity and priority of each rock type were also different; therefore, to prioritize the preparation of samples necessary for research and development domestically, it was desirable to make the samples in Japan. It was much easier to obtain materials produced within the country rather than having to import materials from foreign countries, and it was meaningful to promote their use in Japan and raise the standard of analytical techniques.

3.1.2 Basic concept

The first problem to be considered was the rock types for which reference materials should be prepared. The intentions of the manufacturing organization are normally reflected strongly in this selection. In reference to the preceding significance, the basic concept determined was that the first rock types to be prepared should be “rocks that represent Japan.” This decision also had practical significance because the rocks that represent Japan were well represented in geological research documents (petrological descriptions, geological ages, chemical analyses, etc.) and many studies and analyses had been conducted. Consequently, these materials had many opportunities to be used for research, and the prepared reference materials would be used frequently;

thus, good analytical values could be collected more easily and the use of the reference materials would be widespread.

3.1.3 Examination of underlying technologies and strengths of GSJ

The necessary technologies underlying the preparation of reference materials are roughly divided into sample selection, grinding methods, and standard value determination methods (described in Chapter 4). The advantages of GSJ for these underlying technologies and the development of reference materials are shown in Fig. 3. Understanding the need is the most important aspect for selecting samples, and reference materials are prepared by geochemical researchers who need them the most. In addition, because there were notable researchers in each field regarding various types of geological materials, an environment for making the best choices was established, and this included the perspective of using rocks that represent Japan. Because GSJ is the geological survey organization representing Japan, it was able to secure a variety of types of samples domestically. Rocks that represent Japan exist in significant abundance, so there was no problem securing necessary amounts of samples. In addition, the chemical analysis technology of GSJ that existed at the time was highly appraised worldwide, therefore, the initial analytical value (analyzed by GSJ) when reference materials were prepared and distributed was highly reliable and believed to contribute to the further utilization of reference materials.

3.2 Evaluation and development of reference materials

3.2.1 Japan's first geochemical reference materials

With the basic concept and the advantages of GSJ described above, the development of geochemical reference materials began in Japan in 1964 (research topic: “study of geochemical reference material”), and the first two reference materials, JG-1 (1967, granodiorite, Sori, Gunma Prefecture) and JB-1 (1968, basalt, Sasebo, Nagasaki Prefecture), were prepared.

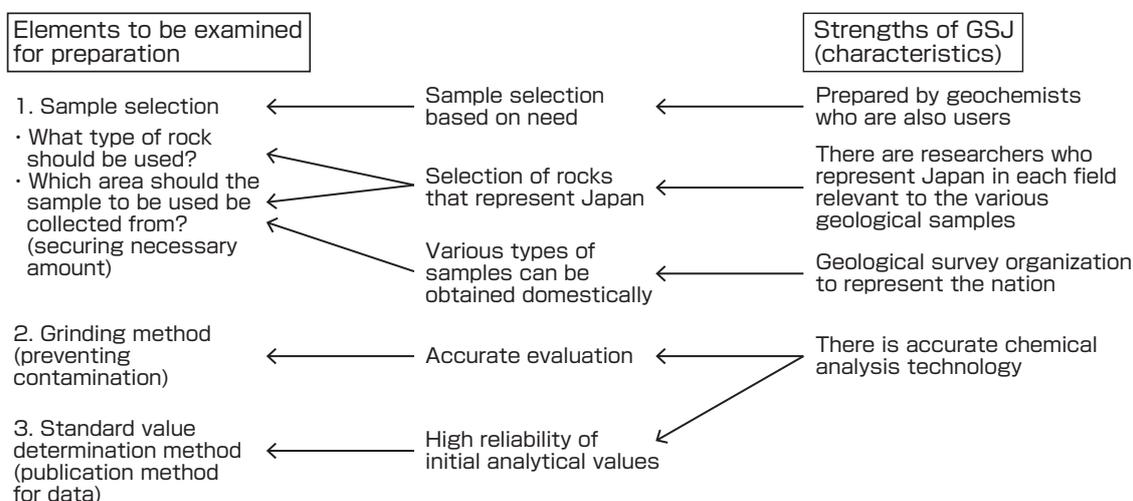


Fig. 3 Underlying technology for geochemical reference materials and strengths of GSJ

The most notable characteristic of these two samples is that contamination was strictly prevented. Geochemical reference materials are fundamentally prepared by grinding massive rocks into powders; therefore, a certain amount of contamination from the crusher cannot be avoided. The details are discussed in Chapter 4. The mixing in of iron, etc., from the steel crushers that were generally used in the 1960s was tolerated, and for those who were actually conducting chemical analyses, as long as the mixing was uniform and did not impact the decomposition of samples, it did not interfere with the utilization of the reference materials. However, from the perspective of elucidating the chemical composition of rocks that represent Japan, contamination needed to be minimized as much as possible; thus, sample rocks were crushed with mortar and pestle made of the same rock (“tomozuri” method). This process took a large amount of time and effort, but because of sufficient care, Japan attained the utmost trust in its reference materials from international organizations as the following comment shows: “The reference materials of Japan are prepared with extreme care and reflect the composition of original rocks directly.” As a result, in addition to normal chemical analysis values, isotopic ratios and ages of rocks were reported, and physical constants such as elastic wave velocity and breaking strength^[7] were reported from rock fragments. At the time, there was no other example of reporting on the physical constant of the reference materials for chemical analysis, and these results were highly appraised globally. By virtue of being globally utilized as such, the stock of both samples was exhausted and distribution was discontinued in the early 1980s. Therefore, in 1984, as re-prepared samples of JG-1 and JB-1, JG-1a and JB-1a were newly prepared by using the same source rock. It is impossible to make reference materials of identical elemental contents even when the same source rocks are used. Therefore, newer batches of reference materials were given subscripts, a, b, c, etc., to differentiate them.

3.2.2 High evaluation leads to project status

The success of the first two types of reference materials led to a significant change in the atmosphere of geochemical reference material development. The research effort for initial development in 1964 was part of basic research and its budget was limited. However, because of the high praise the work received, it became a project—special research “study of rock reference material preparation” of the Geological Survey—in 1981. After it became a special project, the rate of preparation increased, and in 1982, the third reference material, JA-1 (andesite, Mount Hakone), was prepared. Since then, two to three types of new reference materials have been prepared each year, and around 1990, 17 types of the first volcanic rock series (two of these are the re-prepared types mentioned above) were prepared, and these were followed by nine types of the sedimentary rock series. Thus, the goal of “rocks that represent Japan” was mostly completed. This achievement

was highly praised as seen in the following comment: “GSJ’s reference materials represent the most representative rocks of Japan, and their compositions are the same as the chemical compositions of the Japanese Islands.” Appended figures and tables in the “*New Cyclopedia of Earth Sciences*,” published in October 1996, presented the recommended values (standard values) of the main components of the 15 types of the volcanic rock series (excluding two types that were discontinued) and the nine types of the sedimentary rock series as the “major chemical composition of rock reference samples of the geological survey.”^[8] In this manner, the significance of reference material preparation at GSJ was acknowledged widely. In addition, the advanced analytical technology at GSJ contributed greatly to its success. At the time, reference materials were distributed with initial analytical values analyzed by GSJ that was the issuing organization. Subsequently, analytical data were collected to determine the standard values. With this method, it took some time for the standard values to be decided. As the reliability of the initial analytical values analyzed by GSJ was high, these initial values were used as standard values in many general analytical labs.

By 1990, the geochemical reference materials were distributed widely, and these materials were used regularly not only by initial research organizations but also by general analytical labs. Additionally, reference materials had been issued for many types of rocks. The list of geological reference materials summarized by Abbey in 1977^[9] included 75 types issued by 16 organizations. In the list summarized by Potts in 1992,^[10] the number of types had increased to 493 by 35 organizations, and new development for the project was being contemplated by GSJ.

3.3 Changes in distribution of reference materials and instrumental analysis

3.3.1 Changes in needs

In the early stage of reference material development, users were mostly universities and research organizations, which not only used reference materials but also participated in the decision on the values of reference materials. To present more accurate and precise standard values, they joined forces with the development organizations to prepare reference materials. However, as the development of reference materials became widespread and utilization by general analytical labs and researchers with less expertise in chemical analysis increased, most users simply used the pre-valued samples as reference materials rather than participating in value determination. The goal of developing analytical methods for research purposes did not change, but the original use of reference materials for accuracy management of analyses and preparation of calibration curves, etc., became mainstream. This was a natural progression of reference material development as it moved away from its initial

stage and reached its mature stage leading to changes in the sample selection, standard value determination methods, and distribution methods.

3.3.2 Progress in analytical methods

Figure 4 shows the changes in the analytical methods that were used in the chemical analysis of geological materials. The initial instrumental analyses required large instruments, had high cost, and the analytical accuracy was insufficient. Therefore, except for trace elements with which quantitative analysis with the wet method is difficult, the most common method employed was the wet method. However, analytical equipment evolved rapidly with development in X-ray fluorescence analysis and atomic absorption spectrometry, and in the 1970s, instrumental analysis quickly became widespread. With the development in the 1980s of atomic emission spectrometry and mass spectrometry using inductively coupled plasma (ICP), the majority of chemical analyses were conducted through instrumental analysis. The wet method, which achieved high accuracy, remained as the official method of JIS and other organizations, but the main analysis methods had shifted toward instrumental analysis. The development and distribution of reference materials are strongly associated with the distribution of such general-purpose methods of instrumental analysis. For example, X-ray fluorescence analysis combines several geochemical reference materials to prepare a calibration curve for quantitative analysis, thus accurate quantitative analysis is impossible without geochemical reference materials. In the atomic absorption spectrometry and the ICP method, the use of the geochemical reference materials

is essential for evaluating the effects from matrix and coexisting components and managing analytical accuracy. The development and progress of analytical instruments and the development and distribution of reference materials have evolved together.

4 Underlying technology for reference material development

4.1 Sample selection

4.1.1 Initial sample selection (rocks that represent Japan)

Based on the basic concept of rocks that represent Japan, volcanic rocks (silicate rocks) that constitute the Japanese Islands were prepared first. As the first two types of reference materials, JG-1 (J for Japan and G for Granite), which is a granitic rock with high silicon dioxide content, and JB-1 (B for Basalt), which is a mafic basalt (high iron and magnesium) with relatively low silicon dioxide content, were selected. The next question was from which area the samples should be collected, and based on ample geological research materials, granodiorite from Sori, Gunma Prefecture, was chosen for JG-1, and alkaline basalt from Sasebo, Nagasaki Prefecture, was chosen for JB-1. For the actual sample collection, because rocks exposed at the surface are affected by weathering and pollution, fresh samples that had not been exposed to the atmosphere were sampled from quarries and rock pits (Fig. 5). For the preparation of reference materials, about 200 kg of a sample is needed. Specifically, for the first two types, about 400 kg of the source rock was sampled,

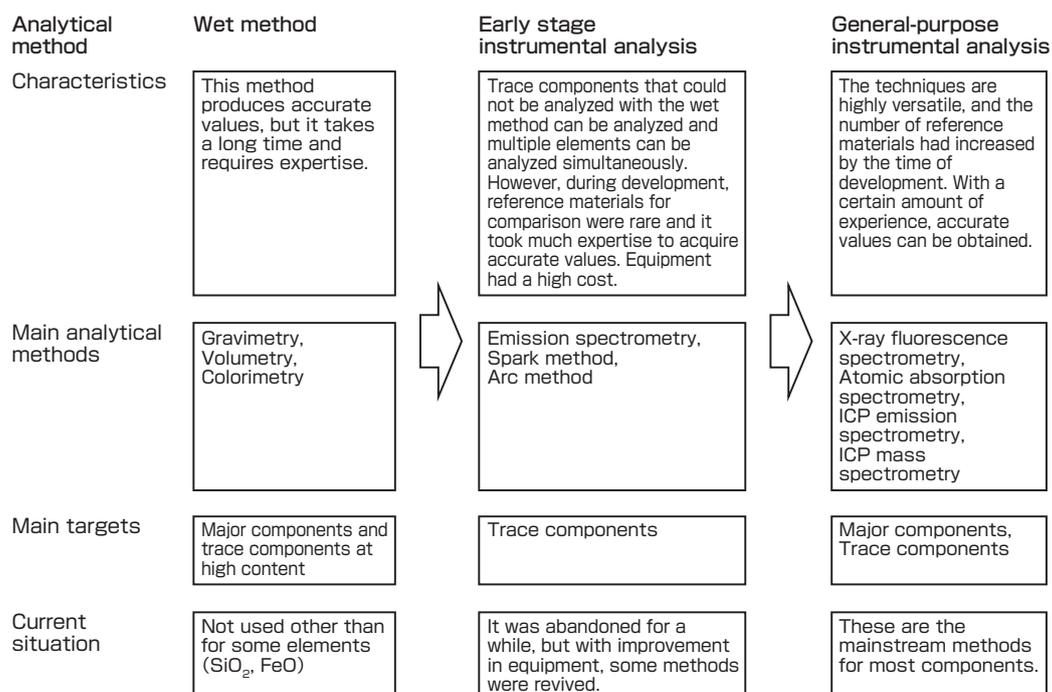


Fig. 4 Main chemical analysis techniques for geological materials and changes through time
Temporal changes in analytical methods are shown from left to right.

including some for future research. Such an amount of rock could be secured with relative ease at the selected locations.

As mentioned earlier, these two types of reference materials were highly praised and led to the creation of a project status for the work. Subsequently, representative rock types of Japan were prepared in the volcanic and sedimentary series, and for the very important granite (G), basalt (B), and andesite (A), three kinds of samples were prepared for each rock type, as shown in Table 1. Because each rock type is subdivided according to various characteristics even within the same general rock type, the whole geology was observed and reference materials were prepared from important sections. Using basalt as an example, the basalt produced in Japan can be divided roughly into three types according to the mineral and chemical compositions: alkaline basalt rich in sodium and potassium but poor in iron, tholeiitic basalt rich in calcium and iron but poor in sodium and calcium, and high-alumina basalt that falls between the previous two and is rich in aluminum. For each division, JB-1 (Sasebo, Nagasaki Prefecture), JB-2 (Izu Oshima Island), and JB-3 (Mount Fuji) were prepared, respectively.

4.1.2 Sample selection suitable for instrumental analysis and environmental analysis

Once the volcanic and sedimentary series were completed in the 1980s, sample selection based on geological classification changed to selection based on analytical chemistry. Specifically, as appropriate concentration in samples was desired in order to prepare calibration curves for instrumental analysis, such as atomic absorption spectrometry and ICP atomic emission spectrometry, by ranking previously

prepared samples in their order of concentration of each component, samples were selected to fill the gaps, and the instrumental analysis series was prepared. A specific example is JSy-1 (syenite), which is rich in aluminum, sodium, and potassium. As there was no appropriate sample in Japan, a reference material was prepared by purchasing a source rock from Canada.

Around that time, environmental research became active globally, and the need to analyze environmental samples such as soils and sediments increased significantly. At laboratories that prepared geochemical reference materials, the “Geochemical Map” project—the mapping of elemental concentration—progressed simultaneously, and as reference materials for the river and marine sediments used to make geochemical maps were desired, preparation of the environmental analysis series began. A characteristic example is JCp-1 (coral). To reconstruct environmental information of the marine environment from the present to several hundreds of years ago, various elements in coral samples were analyzed at many laboratories. However, there was a problem in the reliability of the analytical results. Therefore, in response to requests from related projects, a coral reference material for general chemical analysis was prepared for the first time in the world.^[11] It was used worldwide to improve analytical accuracy (improved reconstruction accuracy of environmental change) and for comparison of analytical results between laboratories (securing of reliability of analysis).

4.2 Grinding of samples

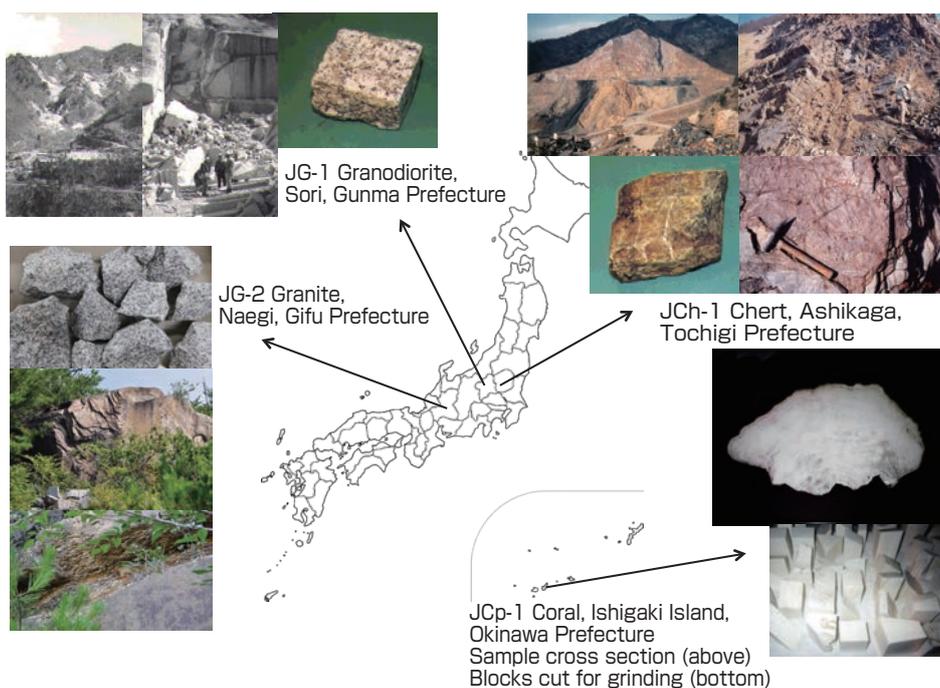


Fig. 5 Examples of sampled source rocks and sampling sites

4.2.1 Examination of grinding methods without contamination

The most important issue in grinding samples is contamination that may come from grinding equipment. Details of the examination process for grinding were summarized by Ando (1984),^[6] so only an outline is provided here. During the development stage at GSJ, the biggest issue was contamination from the steel crushers. If the whole process was conducted with steel equipment, trace components such as manganese and nickel (contained in iron materials) in addition to iron would be likely contaminants, and in a grinding experiment at GSJ using silica stone, the contamination of iron could not be avoided. However, considering that samples are ground in units of 100s of kg, the use of a steel crusher is extremely efficient. When the USGS prepared G-1, a steel jaw crusher was used and the contamination of some iron was unavoidable. The South African metallurgical laboratory (National Institute for Metallurgy, NIM), which began development at the same time as Japan, has removed iron contamination from the steel jaw crusher using a magnet (magnetic separator) to prevent contamination. The disadvantage of this method is that it also removes magnetic minerals included in the original samples, such as magnetite, along with the iron contamination. As mentioned earlier, considering that the USGS method and the NIM method use the chemical analysis of elements as the standard, this problem is actually not a big issue. However, focusing on the basic concept of development at GSJ, because a method that contains contamination and removes specific substances can potentially change the original characteristics of samples and because it was deemed desirable to prepare reference materials retaining as much of the original

characteristics as possible, a method that was not impacted by contamination was searched. The results led to “tomozuri,” in which samples are ground in a crusher made of the same material as the sample. An outline of this grinding process is shown in Fig. 6. For JG-1 and JB-1, a mortar and pestle was prepared using granite and basalt, respectively. Samples were first ground roughly in these mortars and pestles and then ground and mixed in a ceramic pot mill. Because samples are ground by hand using mortar and pestle, despite the lack of contamination, a large amount of effort and time is required. However, at the time, no other reference materials in the world were prepared with the care and attention given to this grinding process. Because of the extreme care used in the preparation of these samples, high praise was received, as mentioned earlier, and it contributed strongly to subsequent development of reference materials.

4.2.2 Efficient grinding method

In the 1980s, the preparation of reference materials received project status, and reference materials were prepared each year. At this point, it became difficult to expend the effort that was put into the first reference materials, and it became necessary to examine the efficiency of grinding. For the third reference material, JA-1 (andesite, Mount Hakone), coarse grinding was conducted using a mortar and pestle made of the same rock as JB-1 and pulverization was done using a ball mill with an alumina lining.^[6] This method allowed the processing of much larger amounts of samples compared to using a pot mill, and as the alumina used as the lining is contained in rock samples at high concentration, it did not affect the samples easily by contamination. In addition, another effort was made: the ball used for

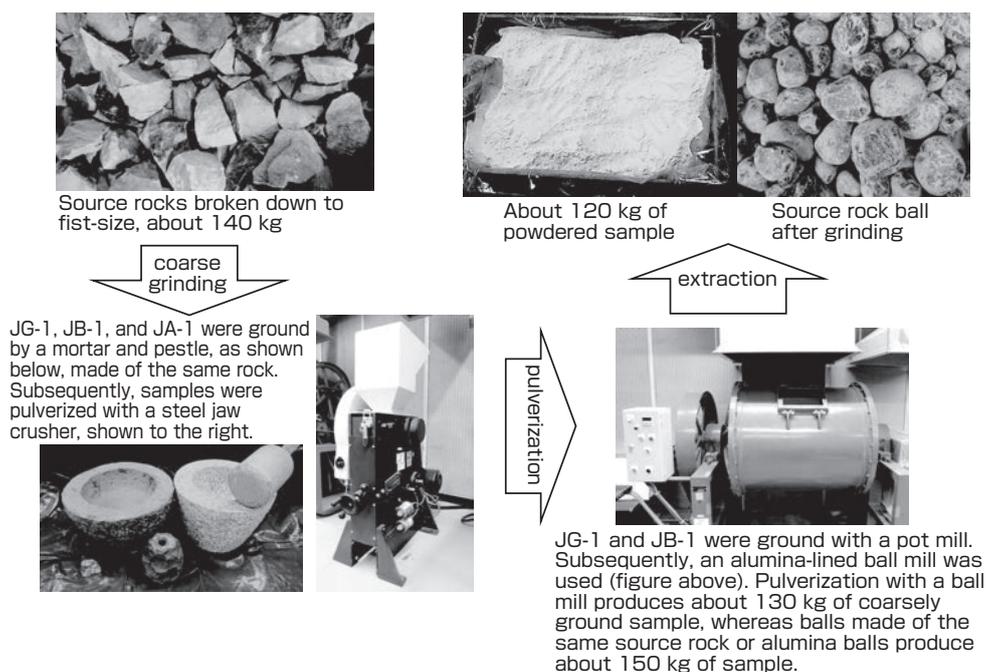


Fig. 6 Schematics of sample grinding process
Guideline to place 100 g and prepare 1,000 samples

Table 3. The major component contents of the JB-1 sample and the re-prepared sample

	JB-1 (1968) recommended values	JB-1a (1984) recommended values	JB-1b (1996) initial analytical values
(w/w %)			
SiO ₂	52.37	52.41	51.11
Al ₂ O ₃	14.53	14.45	14.38
T-Fe ₂ O ₃	8.99	9.05	9.02
MnO	0.153	0.148	0.147
(μg/g)			
Co	38.2	38.6	40.3
Cr	425	392	439
Cu	55.1	56.7	55.5
Ni	133	139	148

T-: total, JB-1&JB-1a: Imai *et al.* (1995)^[12],
JB-1b: Terashima *et al.* (1998)^[13]

grinding was a fist-sized to egg-sized mass of the same rock (source rock ball). By grinding through “tomozuri,” contamination was minimized. Afterwards, the mortar and pestle was considered too inefficient, and a steel jaw crusher became the mainstream tool for grinding (blade is made from manganese steel). Around this time, as a certain amount of iron and manganese were contained in samples and equipment was improved, the contamination from the jaw crusher ceased to be a problem. Currently, as shown in Fig. 6, after grinding with a steel jaw crusher, samples are pulverized in an alumina-lined ball mill with an alumina or source rock ball. When JG-1 and JB-1 were exhausted, the re-prepared samples JG-1a and JB-1a were prepared from the remaining samples collected at the time of initial reference preparation; they were ground by the current method. As JB-1b is a re-re-prepared sample of JB-1, the analytical values of major components in three samples of JB-1, 1a, and 1b were compared as an example (Table 3), and there was no sign of effects from the crusher.

4.3 Standard value determination method and publication of data

4.3.1 Standard value determination and publication of data during free distribution

Prepared samples were analyzed first by GSJ and then distributed worldwide with these initial analytical values, while additional analytical data were gathered. Basically, it was notified publicly through reviews of academic societies etc. that the samples had been prepared,^{[14][15]} requests for distribution were gathered, and under the condition to send back analytical data of the sample, reference materials were distributed free of charge. There were two methods of distributing reference materials. One of these methods was used by GSJ: in return for free distribution, the reporting of analytical values was required, and the standard values were decided from the collected analytical values. The

other method was to sell the reference materials with standard values assigned. Currently, the latter method is the mainstream method; however, at the time, only NBS (present-day NIST) and BAS used the latter method, and a majority of the organizations distributed reference materials via the first method. Only the latter fits the original definition of reference materials, and the former should be called a common analysis sample for research. However, based on the USGS's experience with G-1 and W-1, analytical values may change according to evolution of analytical methods. Although a majority of the elements are targets of analysis (research) of geological materials, it is difficult to assign a definite value to many of the elements from the beginning. Therefore, to collect analytical values of various elements in response to evolving analytical methods, the former method was more effective.

Reported analytical results were summarized and published in a journal for the first time in 1971.^[16] At that point, all analytical values (24 for JG-1 and 17 for JB-1, including analytical methods and the name of the analysts), the overall mean, standard deviation, and the mean except value that exceeds $\pm 2\sigma$ from the mean were published. Subsequently, after a certain amount of analytical values had been collected, the reported analytical values were calculated statistically to obtain the standard value, and this standard value was published. However, as the number of analytical values increased, not all of the results could be published, and reports were limited to the mean value for each analytical method and the range of analytical values. In short, although it is called “standard value,” its name also has changed through time. In the early stage, it was called “Consensus Mean (Value),” but afterwards, results with a sufficient number of analytical values and high reliability were called “Recommended Value.” Results with a limited number of analytical values and low reliability were initially called “preferable data,” but were later changed to “Reference Value.” In addition, because of the nature of the method by which the standard value was decided based on collected analytical values after distribution, the standard value had the potential to change. Table 4 shows changes in the major component values of the JG-1 sample, which actually changed little.

4.3.2 Change in the distribution method and certified reference materials

Once geochemical reference materials became widely used, free distribution with the requirement of reporting of analytical values became difficult for general users, and the demand for the sale of reference materials without a requirement for reporting increased. In addition, global standardization by ISO started to affect geochemical reference materials in the late 1990s, and the production of certified reference materials, which are distributed with certified values (determined

Table 4. Changes in major component standard values for the JG-1 sample

Year	1971	1974	1988	1994
Name of standard value	consensus mean	consensus mean	consensus value	recommended value
(w/w %)				
SiO ₂	72.24	72.28	72.30	72.30
TiO ₂	0.26	0.27	0.26	0.26
Al ₂ O ₃	14.21	14.23	14.20	14.20
T-Fe ₂ O ₃	2.21	2.17	2.14	2.18
MnO	0.06	0.061	0.063	0.063
MgO	0.73	0.73	0.74	0.74
CaO	2.18	2.17	2.18	2.20
Na ₂ O	3.39	3.38	3.39	3.38
K ₂ O	3.96	3.96	3.97	3.98
P ₂ O ₅	0.10	0.098	0.097	0.099

1971 : Ando *et al.* (1971)^[16], 1974 : Ando *et al.* (1974)^[17],
 1988 : Ando *et al.* (1989)^[18], 1994 : Imai *et al.* (1995)^[12]

by a method with its accuracy verified), was considered. Under these circumstances, GSJ became an independent administrative agency from the national research institution in April of 2000, and, fundamentally, reference materials became available only by sale. In addition, based on its track record, GSJ was acknowledged globally as a main issuing (producing) organization of geochemical reference materials, and it also bore social responsibility to a certain degree. Therefore, for the sale of GSJ reference materials, it was determined that it would be best to follow the regulations of ISO and provide certified reference materials. Thus, GSJ initiated a

completely opposite method of selling reference materials with a certificate. ISO certification as a reference material producer was acquired in 2007 through the ASNITE program of the International Accreditation Japan (IA Japan), the National Institute of Technology and Evaluation (NITE).^[19] Currently, all newly prepared reference materials are certified reference materials (Fig. 7), and GSJ was awarded a Prize of the Minister of Education, Culture, Sports, Science and Technology (Department of Development) for the “Development of Certified Geochemical Reference Materials” in 2010.

4.3.3 Publication via database

In the beginning, the whole data of reported analytical values was published in academic journals and some other sources. However, as the number of analytical values increased, it became difficult to publish the whole data in paper format. Consequently, as the Internet became well established, a program of publishing research results widely in the form of a database (RIO-DB project) was begun at the former Agency of Industrial Science and Technology. Analytical data of geochemical reference materials could be processed statistically, and information such as samples, components (elements), analytical values, analytical methods, analysts, and literature (the date of publication) were digitized as a set. Thus, the database could be created with relative ease. For this reason, it was proposed as one of the first contents to be summarized under the RIO-DB project. This was an ideal method for GSJ because it was searching for a method by which as many analytical values as possible could be published. The database allows for publication of the whole

Contents of a certificate

- Producer (issuer)
- Sample name
- Main usage
- Certified value and reference value
- Analytical method (measurement method)
- Pretreatment of sample (decomposition method)
- Determination method for certified value
- Sample preparation method (preparation method)
- Notes on usage and storage
- Confirmation of homogeneity
- Cooperation organizations
- Issuing date and person in charge
- Contact information
- Etc.



Fig. 7 An example of a certificate

List of described items and a part of the certificate for JB-2a: Izu Oshima basalt

body of data and it can be utilized widely. The “Rock Reference Samples DataBase,” developed in this manner, was extremely popular, and it improved the convenience of using the reference materials, contributing to further distribution and development of RIO-DB. Currently, it is published as the “Geochemical Reference Samples DataBase” of the GSJ Database Collection (Gbank) (Fig. 8). GSJ is the only organization in the world that is publishing all reported data.

5 Summary and the future of geochemical reference materials

5.1 Summary of GSJ geochemical reference materials

To summarize the development of geochemical reference materials by GSJ, the goal of “elucidating the chemical compositions of domestically produced rocks at the global research level,” which was the initial intent, was sufficiently achieved by the preparation of the volcanic and sedimentary series and their evaluation. In addition, the development of reference materials came with responsibilities that change according to the age and the environment such as social responsibility as a producer of global reference materials, supplying reference materials needed by the age, and promoting widespread utilization and user services of reference materials. To these responsibilities, GSJ has responded accordingly through the following means: distribution of certified reference materials that follow the regulations of ISO, distribution of suitable reference materials for instrumental analysis and environmental analysis, and implementation of user support through the webpage

(database). There were some imperfections, but GSJ fulfilled its role sufficiently. From the beginning of their development, GSJ geochemical reference materials have been used worldwide. About half of the present customers are in foreign countries. As an issuing organization representing Japan, it is a pride of GSJ to have developed reference materials that are used globally. In addition, as stated previously, reference materials have changed with the age. In the future, flexible responses to various types of changes will likely lead to success.

5.2 Geochemical reference materials in the future

How will geochemical reference materials change in the future? It is easy to predict expanding utilization and increasing importance of reference materials. In addition, it should be possible to predict some changes in the surrounding environment. First, the analysis of environmental samples will likely increase and so will demand for quality standards. Second, the number of analysts who can perform analysis using the wet method will decrease dramatically, and the number of technicians who work much like operators of instrumental analytical equipment will increase. Additionally, many analyses will be performed by automatic analysis and flow analysis, in which untreated raw samples are set in a device, the device automatically performs various processes with a push of a button, and analytical results are received as output. Analysis for existing forms of elements in samples also will likely increase.

As a result, the development of reference materials to satisfy

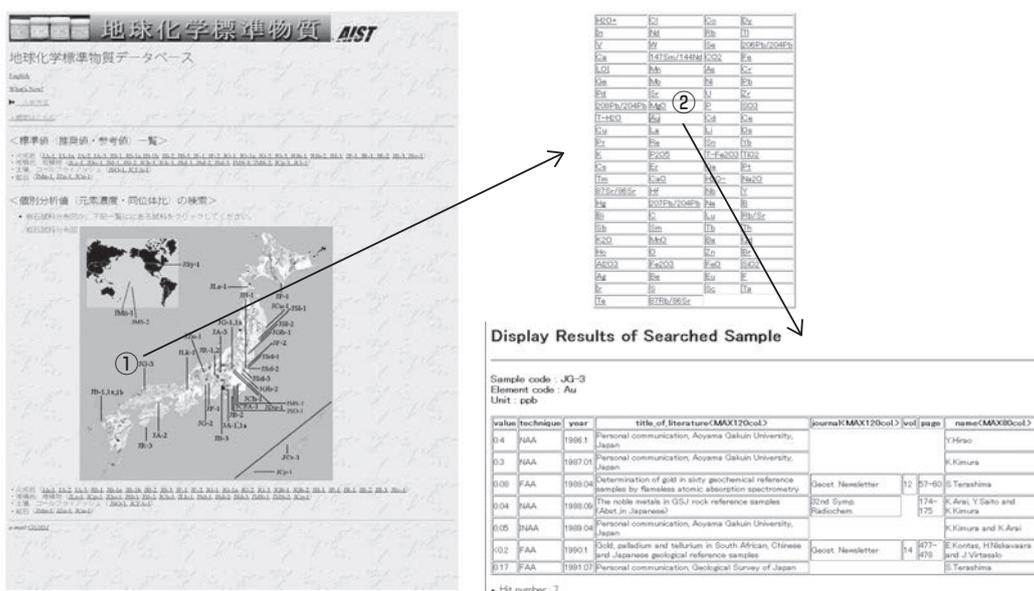


Fig. 8 Publication of geochemical reference materials database

Geochemical reference materials homepage

(<https://gbank.gsj.jp/geostandards/welcome.html>)

- ① When one clicks on the sample name for which he/she would like to see analytical data, the list of analytical components is displayed.
- ② When one clicks on the component name, the list of all reported analytical data is displayed.

the needs of environmental and morphological analysis will be desired. The largest problem with the development of such reference materials is the stability of the sample. This paper did not address stability, which is an important factor for reference materials. The reason for this omission is that rock samples are fundamentally stable and can be used almost indefinitely. JG-1 and JB-1 samples can still be used as reference materials from data analyzed more than 40 years ago. However, for samples suitable for environmental and morphological analysis, even if suitable reference materials were developed, the duration of their usage would be highly limited. For example, for the analysis of hexavalent chromium in contaminated soil samples (includes certain organics and water), much of hexavalent chromium would change to trivalent chromium after a certain period of time after grinding and packaging in a bottle. Thus, even if reference materials for analysis of hexavalent chromium could be prepared, their effective duration would be extremely short. In addition, the matrix of reference materials that will be demanded in environmental analysis is diverse, and the target components will also likely be diverse. Hence, in order to perform accurate analysis with the automatic analysis methods described earlier, it is necessary to develop reference materials suitable to this more diverse matrix in the shortest amount of time possible. The GSJ reference materials are prepared by grinding natural samples, and at least several years are required from conceptualization of development to supply. Hence, as the supply needed in the future would be impossible with such a short cycle and timeframe, the development of reference materials for which the necessary matrix and components are industrially synthesized is desired. It will be difficult to respond to this need by GSJ alone, and this technological development is extremely important not only for geochemistry but also for overall reference materials. Therefore, with the leadership of the National Metrology Institute of Japan (NMIJ), knowledge and technology in each area of the National Institute of Advanced Industrial Science and Technology (AIST) should be combined to more effectively address this issue.

5.3 Future plans for GSJ geochemical reference materials

The importance of the currently prepared geochemical reference materials will not change in the future. As mentioned earlier, because these references can be used indefinitely, mutual evaluation of analytical results 40 or more years old and current results is possible, and their supply as foundational reference materials needs to be maintained. Currently, samples prepared in the initial series are being exhausted; thus, there is a focused effort on re-preparation of samples in order to maintain the supply of reference materials. In addition, through recent research developments, elemental analyses of individual trace minerals that constitute the boundary of minerals are being attempted through localized analysis using lasers and ion

probes. Reference materials vitrified by the melting of rocks (homogenized through vitrification) that can respond to such localized analysis are desired. Currently, only the USGS is able to provide the reference materials vitrified through the melting of rocks. It is necessary to closely examine this topic, including cooperation with the USGS.

Finally, in the development of reference materials, the most important concern in any situation is to maintain analytical technology that can provide accurate values (standard values). In the future, a variety of reference materials will be prepared, but the necessity of assigning an accurate value will not change. As mentioned earlier, as the number of experienced technicians decreases and the number of technicians who work as operators of instrumental analysis equipment increases, this is the most important issue for GSJ and AIST as research organizations that represent the nation.

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interesting that during the 50 years of research and development, scenarios have been flexibly reviewed according to the user's needs for reference materials, which have been reflected in the subsequent research plans. It is also noteworthy that the geological reference materials, including the ideas unique to Japan, are being used worldwide.

This paper is structured in such a manner that it is easy to grasp for readers unfamiliar with this field, and will likely be used as a reference by many. I believe this is a paper well suited for publication in *Synthesiology*.

Comment (Chikao Kurimoto, AIST)

The Geological Survey of Japan (GSJ) and the Research Institute of Geology and Geoinformation of GSJ have published over 50 types of reliable reference materials during the past 50 years. The paper summarizes the significance, process, and results of studies by GSJ on the global trends in standard materials for geochemical reference and the development of these standard materials. In addition, the changes and future outlook of the standard materials with the advancement of analytical instruments have also been discussed. As such, this paper reviews the advances in geochemical reference materials in the last 50 years, and proposes future developments; and thus, I believe this paper is suitable for publication in *Synthesiology*.

2 Importance of the wet method

Question (Akira Ono)

Can I assume the following based on this paper? “The advantage of instrumental analysis is that it does not require labor and skills; however, analytical results are relative. Therefore, to calibrate the instruments, reference materials with absolute value for elemental concentration are necessary. In contrast, although the wet method requires labor and skills, its analytical results provide absolute value of elemental concentration. Therefore, the reference values of elemental concentration for reference materials are determined using the wet method.”

If the above understanding is correct, in order to guarantee the reliability of analytical values (absolute value), the GSJ researchers also need to make technological advancement for the wet method to provide absolute value. What is your opinion on this issue? Is AIST still focusing on the wet method?

Answer (Takashi Okai)

In the early days of developing geochemical reference materials, values were determined using the wet method, as you have pointed out. However, now, as shown in Fig. 4, the values for silicon dioxide (SiO₂) and ferrous oxide (FeO) are determined using the wet method (gravimetric method for SiO₂ and titration method for FeO), and the values for other major components are obtained through general instrumental analyses, such as atomic absorption spectrometry and inductively coupled plasma atomic emission spectrometry. Studies have been conducted for the improvement of instruments and the assessment of the effect of other elements (such as interference). The precision of the quantitative analysis by these instrumental analyses has increased. With the adoption of official methods such as JIS, and the efforts of the NMIJ, the standard materials for each element have been prepared. The standard solution can now be prepared for the calibration curve with the certified reference materials for traceability. Furthermore, the values for standards are determined by collaborative analyses. However, sufficient precision in the wet method requires skills, and only a few institutions provide such skilled analyses.

Currently, no new wet method is being developed for geochemical reference materials, but the wet method has been used for chemical analysis of geological samples for a long time, and there have been many improvements. Therefore, it is a well-

Discussions with Reviewers

1 General

Comment (Akira Ono, Special Emeritus Advisor AIST)

The Geological Survey of Japan has been researching and developing geochemical reference materials for about 50 years. This paper clearly describes the scenarios of developing and providing geochemical reference materials in order to support highly reliable chemical analysis of geological samples. It is quite

developed method. In the wet method, expertise, which is difficult to express in the procedure of an analytical method, can lead to differences. AIST has abundant expertise and is focusing on maintaining the technology for accurate wet method analysis. Specifically, in addition to passing on the skills to the younger generations, given the current situation where there are few institutions that are able to perform the wet method analysis, it would be important to share the information externally in order to sustain the use of the technology.

3 Relationship where the analytical methods and target materials compete in terms of accuracy

Comment (Akira Ono)

I thought it was interesting that in the early stages of development of the geochemical reference materials described in Subchapter 2.2, when common samples were collaboratively analyzed by major institutions around the world, the variability in data was much larger than expected. As a result, it led to a higher precision of the analytical method. The reviewer has the following proposition on this issue. What is the authors' opinion?

Analysis consists of methods and target materials. If a certain target material is analyzed with multiple analytical methods and the results vary, there are two possible causes for such variability. One is the variability existing in the analytical methods, including the reproducibility of the measurements. The other is the variability existing in the target material itself, which can be attributed to the heterogeneity in a sample or temporal changes in its characteristics. These two types of variability are observed together, and usually cannot be separated. However, if one type of variability is assumed to be significantly less than the other, the more significant cause for the variability can be clearly identified, and a clear way to reduce such variability can thus be conceived.

As discussed in Subchapter 2.2, the cause of variability in the analytical results could not be attributed to the variability of the targets, but was because of the variability of the analytical methods. This inference led to the beginning of new studies.

In contrast, to evaluate the variability of target materials, a much more stable analytical method must be used. We assume that instrumental analysis has a better resolution and stability compared to the wet method. As such, the analytical method and target compete with each other as far as accuracy is concerned. If one makes progress, the other follows until it surpasses its counterpart. In this manner, both make progress. The present case was an example of such a situation, which I found interesting.

I also feel that those taking part in the collaborative analysis without fear of varying results in a stage where the results were unpredictable (not being afraid of his/her own result being different from others) are worthy of praise for their courage and determination. This effort is considered to be of universal value till date.

Answer (Takashi Okai)

Regarding the variability of the results, I was amazed by the high technological level back then. In a collaborative analysis, when evaluating the variability of analytical methods and target materials that you commented on, little variation in the skills of the participating analysts needs to be ensured. When multiple analysts perform the same analytical method, if there is variability of analytical skills (or if overall skill level is

low), the results will show variability beyond the fundamental variability expected in that analytical method. In such a case, if multiple analytical methods are compared, the variability of each analytical method becomes larger than the variability between the analytical methods, and the difference between each analytical method is masked. In the present study, the difference observed for silicon dioxide, as shown in Fig. 2, was due to a few procedure differences in the gravimetric methods rather than differences in the analytical methods. For such a minor difference in procedure to be identified as a difference caused by the analytical methods, each analyst had to have performed their analyses with extremely high precision. Therefore, it reaffirmed the extremely high level of analytical skills exhibited by institutions that took part in the collaborative study back then.

The competition between the analytical methods and the target materials was also inferred. In the response to discussion 2, I stated that these days the values for standard materials are mainly determined through instrumental analysis. Indeed, the development in instrumental analysis and standard materials impacted on each other, and in both cases, progress was made owing to the competition.

Participating in a collaborative study is a serious challenge; however, I think that pride as a skilled analyst was an important motivation (the possibility that one's own data may be the only outlier can put great pressure on an analyst). I believe it is important to guide the next generation until they attain such pride as analysts.

4 Underlying technologies and strengths of GSJ

Comment (Chikao Kurimoto)

In Section 3.1.3, the elemental technologies and strengths of GSJ have been discussed. Figure 3 shows their relationship. The content is correct, but if Fig. 3 could illustrate the relationship of the two and their impacts, their relationship would become clearer. It could clearly indicate the significance of this study and the elemental technologies and strengths of GSJ.

Answer (Takashi Okai)

As you have pointed out, the elemental technologies and strengths of GSJ have merely been listed. Therefore, along with the content of Section 3.1.3, I have inserted the impacts of strengths of GSJ on the examination of the elemental technologies between the two, and have connected these relationships using arrows. Thus, the findings of our study and the elemental technologies and strengths of GSJ were integrated.

5 GSJ geochemical reference materials

Comment (Chikao Kurimoto)

Subchapter 5.3, titled "Future plans for GSJ geochemical reference materials," is quite interesting. This paper summarizes the long-term progress in geochemical reference materials, which is a valuable indication of the future prospects. Therefore, comments on the fundamental policy and future plans of GSJ would have been beneficial for the readers. In future, I hope that there will be further discussions within GSJ based on this paper.

Answer (Takashi Okai)

At present, these are simply ideas that I have, and hence, I refer to them as "future plans." However, I hope to utilize them for future discussions.