PIXE法による地学系試料化学分析の特徴

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要旨

　　0.5～1 mgのごく少量の地学系試料の化学組成を測定するために、ポリカーボネート製濾紙にトラップされた地質調査所の標準岩石の粉体試料の化学分析がPIXE法により行われた。岩石粉体試料については、0.2 μm、0.6 μm、0.8 μmの濾紙に比較して、0.4 μmの濾紙の変動が少なく、鉱石粉体試料については、0.4 μm、0.6 μm、0.8 μmの濾紙に比較して、0.2 μmの濾紙の変動が少なかった。PIXE法による標準岩石の測定値は、X線の自己吸収のために公表値とは若干異なっていた。測定値と推奨値を基にして補正係数が得られた、これらの補正係数を使うことで、岩石と鉱石のごく少量の粉体試料の化学組成を正確に測定できる可能性がある。

Characteristics of chemical analysis of geological samples by PIXE

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Abstract

Chemical analysis of fine-grained power samples from the Geological Survey of Japan trapped on a polycarbonate filter were carried out by PIXE to measure the chemical compositions of geological samples having small volumes (1 to 0.5mg). The variability of results obtained by using a filter with a pore size of 0.4 µm was smaller than the variability of results obtained by using filters with pore sizes of 0.2, 0.6 and 0.8 µm for rock samples. The results obtained by using filter with a pore size of 0.2 µm were better than the results obtained by using filters with pore sizes of 0.4, 0.6 and 0.8 µm for ore samples. Results of chemical analysis of powder samples of Japanese rock standards by PIXE were slightly different from certified values by the Geological Survey of Japan because of self-absorption of characteristic X-rays in measurements. Calibration factors were calculated on the basis of the measured values and certified values. The use of these calibration factors enables accurate results to be obtained for small amounts of powder samples of rocks and ores.

1 Introduction

Natural geological samples are generally heterogeneous and often contain low concentrations of trace elements. There are various methods, such as PIXE, XRF and ICP-MS, for chemical analysis of geological samples (Goodall et al., 2005; Vaggellia et al., 2003; Zhang et al., 2011; Giulia et al., 2008; Sila et al., 2010; Zhang et al., 2010). Kano et al. (1983) developed a method of quantitative analysis making use of the continuous background, Koyama and Ito (1991) developed a standard-free method that makes use of the ratio of peak yield to yield of continuous X-rays, and Sera et al. (1996; 1999; 2002; 2006; 2009) developed a standard-free method for quantitative

analysis of bio-samples and a powdered internal-standard method for quantitative analysis of soil, ash, sediment, deposit, tailings, powder sample of rock, etc. The aim of this study was to develop a method for chemical analysis determined by PIXE for small amounts of powder samples of rock and ore samples trapped on polycarbonate filters with pore size of 0.2 μm, 0.4 μm, 0.6 μm and 0.8 μm.

2 Experiment

2.1. Samples

In this experiment, fifteen samples as standard reference samples from the Geological Survey of Japan were used for chemical analysis of concentrations of major, minor and trace elements using PIXE. The samples included JB-1a, JB-2, JB-3, JP-1, JGb-1, JA-1, JA-2, JA-3, JG-1a, JG-2, JG-3, JR-1, JR-2, JZn-1 and JCu-1. Detailed information about sample collection and handling can be found on the homepage of GSJ.

2.2. Sample preparation

The membrane filters used in this study were made of polycarbonate with characteristics of low non-specific binding and optically translucent, extremely uniform, cylindrical pores, excellent chemical resistance, good thermal stability, non-hygroscopic and extremely weight-stable. Membrane filters with pore sizes of 0.2 μm, 0.4 μm, 0.6 μm and 0.8 μm were chosen as the target filters for characteristic X-ray and continuous X-ray background measurement to determine the concentrations of major and trace elements in order to find the most suitable target filter.

A schematic flowchart of the procedure for preparing a powder sample is shown in Fig. 1. The target filter was prepared as follows: 1) the powder was weighed for ore samples (2.0 mg powder) and rock samples (1.0 mg powder), 2) the powder was dispersed in distilled water, 3) the solution was vibrated by an ultrasonic cleaner for about 3 minutes to completely disperse the power, 4) the membrane filter was set on the filter holder, 5) the solution was transferred into the funnel of a vacuum filtration system, 6) the internal wall of the beaker was rinsed with distilled water, 7) the solution was filtrated by a vacuum filtration system, 8) the filter was placed on the slide as a target, 9) the slide was kept in a polypropylene bottle for PIXE analysis.

2.3. Analysis

Chemical compositions of the samples were determined by PIXE at Nishina Memorial Cyclotron Center (NMCC), Japan Radioisotope Association, using 2.9 MeV protons from a baby cyclotron. Beam currents, accumulated charge and typical measurement time were 20-40 nA, 11-19 μC and 5-10 min, respectively. X-ray spectra were analyzed using the SAPIX program. Quantitative data were obtained by the combination of data determined by PIXE and certified values of the standard reference samples from GSJ.
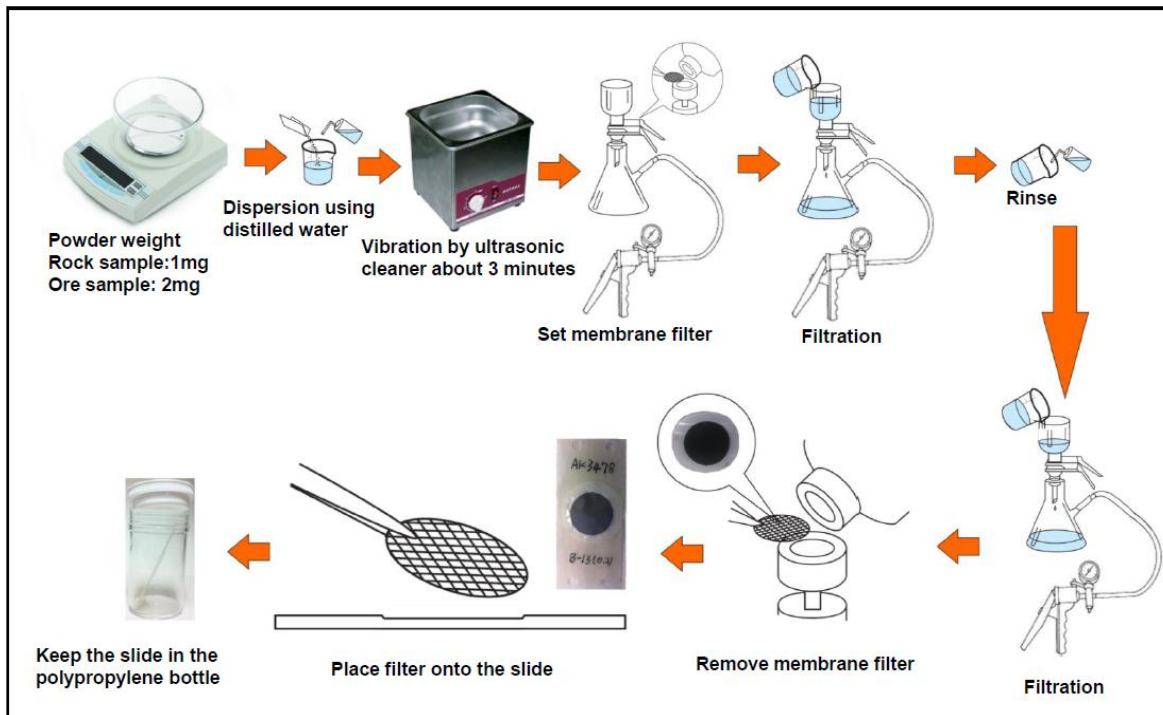
Fig.1. Schematic flowchart of the procedure for preparing a powder sample for analysis by PIXE in the geoscience field.

3 Result and discussion

The relations between values measured by PIXE and certified values by GSJ for the contents of SiO_2, TiO_2, Al_2O_3, MnO, MgO, CaO, Na_2O and K_2O for rock samples are shown in Fig. 2. Data for P_2O_5 were not examined because the amount of P_2O_5 was very small in the reference sample and the amount was lower than the detection limit of PIXE. The results for values determined by PIXE and certified values of JZn-1 and JCu-1 were shown for contents of Cu, Zn, Pb, Sr, Cd, As and S in Fig. 3. The results show an overall good correlation between concentrations measured by PIXE and the certified concentrations except for JP-1, JB-3 and JA-1.

3.1. Relation between measured values and the pore sizes of membrane filters for rock samples

The concentrations of oxides of Japanese rock standards detected by PIXE were estimated with reference to known concentrations of elements in the rock standard. The elements were Fe for JB-1a, JB-1, JB-3, JP-1, JGB-1, JA-1, JA-2 and JA-3 and K for JG-1a, JG-2, JG-3, JR-1 and JR-2. The recalculated concentrations of SiO_2 and
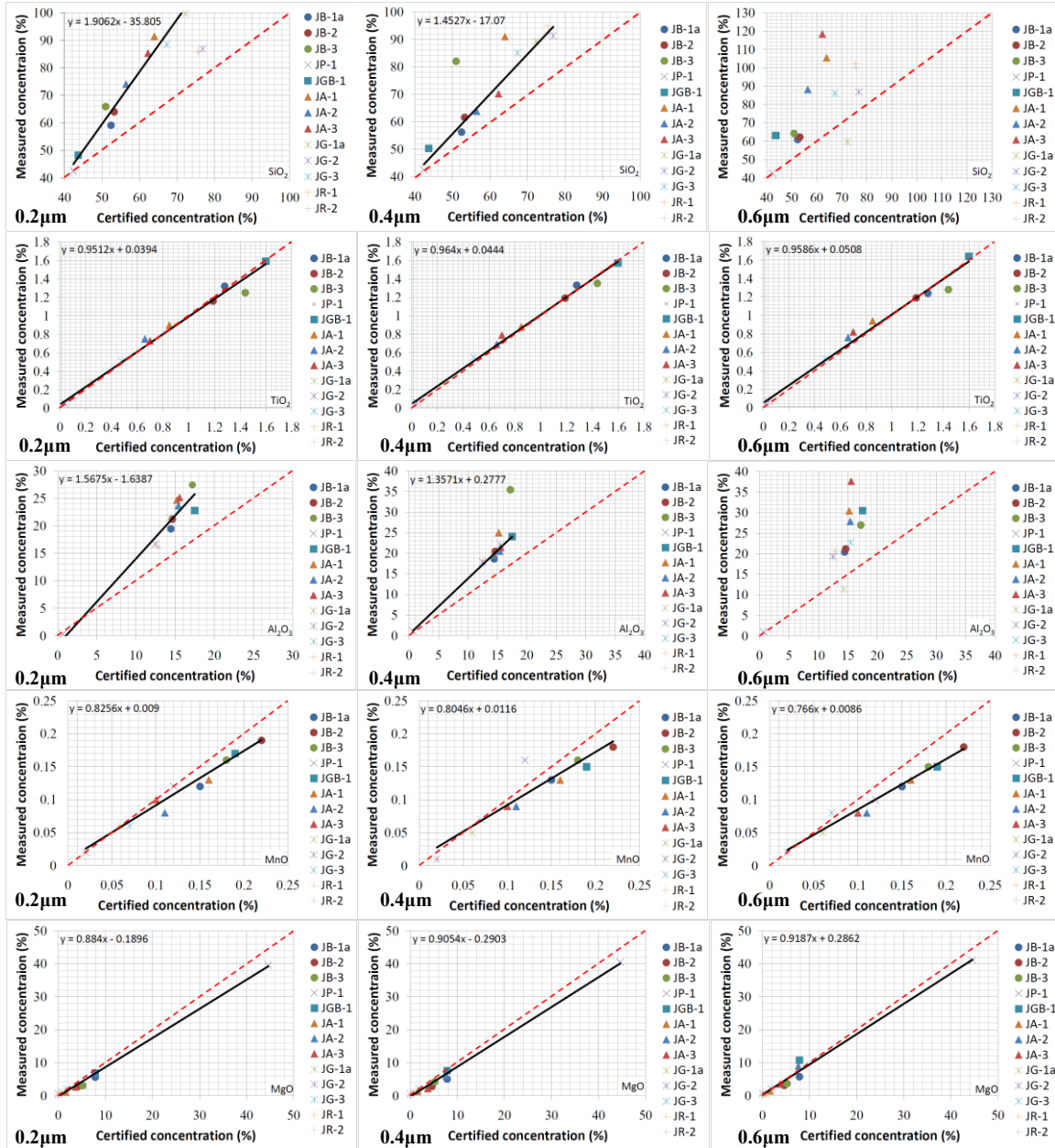
Fig.2. Scatter plots and calibration lines of measured concentrations of oxides against certified concentrations when pore sizes of filter target were 0.2 μm, 0.4 μm and 0.6 μm. The red dashed line is the 'y=x' line, and the black solid line is the calibration line.

Al_2O_3 were overestimated compared to the certified values. The recalculated concentrations of MgO and MnO were underestimated compared to the certified values. For SiO_2, the slope of the calibration line (Fig. 2) was used as the calibration coefficient to evaluate effect of pore size of the filter. If the slope of the calibration line was close to that of the line of 'y=x', the result of the concentration of oxide component determined by PIXE is accurate. The slopes of filters with pore sizes of 0.2 μm and 0.4 μm are 1.91 and 1.45, respectively. The filter with a pore size 0.6 μm, the calibration points were scattered on the plot, and the calibration slope was therefore not obtained. The results suggest the filter with a pore size of 0.4 μm gives better calibration than do other
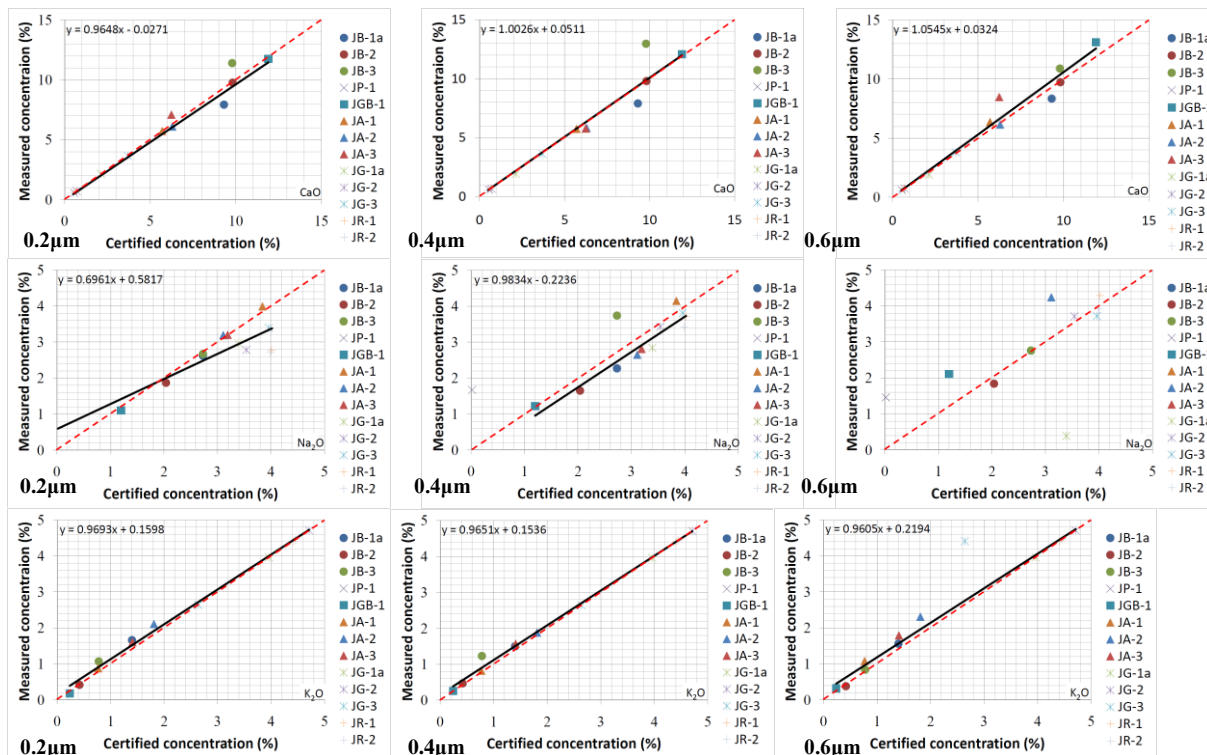
Fig.2. Continued.

filters. There was a large deviation relative to the calibration line for SiO_2 in the samples of JB-3 and JA-3 compared with other reference samples. The reason is thought to be related to the sample itself or systematic error from the process for preparation of the filter target. A similar tendency was observed for Al_2O_3 and Na_2O: a pore size of 0.4 μm was also better for obtaining an accurate concentration. For MnO and MgO, all of the calibration lines were regressed on the right side of the line of 'y=x', and the measured concentrations were significantly lower than their certified values. The slopes of the calibration lines of 0.2 μm, 0.4 μm and 0.6 μm were 0.83, 0.80 and 0.77, respectively, for MnO and 0.88, 0.91 and 0.92, respectively, for MgO. The filter with a pore size of 0.4 μm was better for analysis of MnO and MgO. For TiO_2, CaO and K_2O, all of the calibration lines were almost the same as the line of 'y=x', and the measured concentrations were almost equal to the certified values. The slopes of calibration lines of 0.2 μm, 0.4 μm and 0.6 μm were close to 1: 0.95, 0.96, and 0.96, respectively, for TiO_2; 0.96, 1.00, and 1.05, respectively, for CaO; and 0.97, 0.97, and 0.96, respectively for K_2O. The filter with a pore size of 0.4 μm was also better as a target for these oxides. The degree of linearity of data obtained from the measured values and certified values was much better for the filter with a pore size of 0.4 μm than for the filters with pore sizes of 0.2 μm and 0.6 μm.

For confirming the reliability of the results obtained, data for concentrations determined by PIXE was examined statistically by a statistical program (SPSS17.0). Univariate analysis of a general linear model (GLM) was performed on the measured concentration data. The GLM univariate procedure provides regression analysis and analysis of variance for one dependent variable by one or interactions with factors can be included. The profile plot
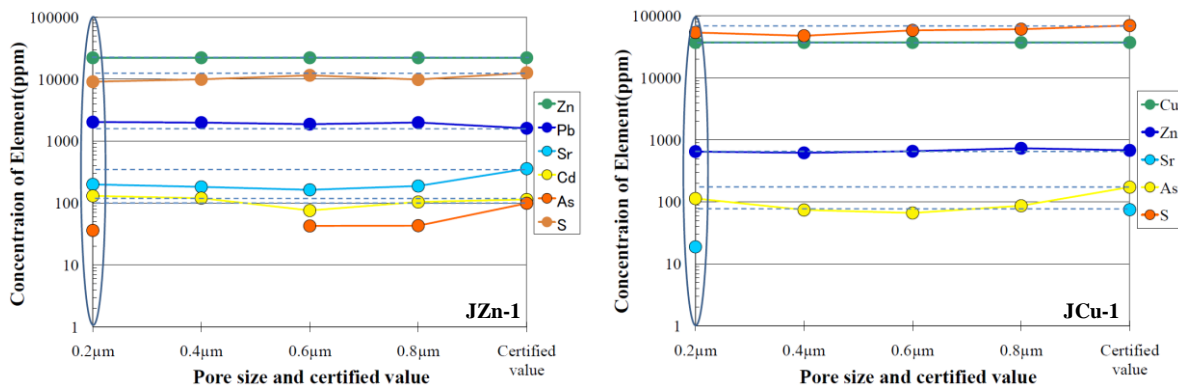
Fig.3. Comparison of the measured concentrations of trace elements obtained by PIXE with the certified concentrations of JZn-1 and JCu-1. The pore sizes of the filter target were 0.2 μm, 0.4 μm, 0.6 μm and 0.8 μm. The dashed lines represent the lines of certified values determined by GSJ. If the measured concentration of the element is in agreement with the corresponding certified concentration, the plotted point of the element is either on the dashed line or adjacent to the dashed line.

of estimated marginal means in the SPSS GLM is a line plot for the mean concentration of each oxide and shows an interaction between the pore size and reference sample (Fig. 4). For example, the shapes of lines of 0.2 μm, 0.4 μm, 0.6 μm and certified value for SiO_2 content are similar and parallel to each other. That suggests that there is no interaction, but the line of 0.4 μm is more adjacent to the line of the certified value relative to the lines of 0.2 μm and 0.6 μm, though the measured average concentrations of 0.2 μm, 0.4 μm and 0.6 μm for SiO_2 are larger than that of the certified value. That means that pore size of 0.4 μm is better as a filter target for analysis by PIXE. For other oxide including of TiO_2, Al_2O_3, MnO, MgO, CaO, Na_2O and K_2O, the filter with a pore size of 0.4 μm is better for determining the concentrations in rock samples. The small table inserted in each diagram shows results of post hoc tests of pore size. The results are listed in order according to their mean value for the dependent variable with the pore size groups. Here, for SiO_2, the certified value group is shown first as this group has the lowest mean concentration and the 0.6 μm group is shown last as this group has the highest mean concentration. The subsets show the mean concentration from each group listed in different columns. If the means for two groups are shown in different subsets, this indicates that there is a statistically significant difference between these two groups. Conversely, if the means for two groups are shown in the same subset, this indicates that there is no statistically significant difference between these two groups. For example, the mean concentration of the certified value for SiO_2 is shown in a subset indexed as No. 1, whereas the mean concentrations determined by PIXE using filters with pore sizes of 0.2 μm, 0.4 μm and 0.6 μm are separated into another subset indexed as No. 2. The results indicate that the mean concentration of the certified value is significantly different from the mean concentration of three other filters with pore sizes of 0.2 μm, 0.4 μm and 0.6 μm. However, the mean concentration using the filter with a pore size of 0.4 μm is closer to the mean concentration of the certified values than are the mean concentrations using filters with pore sizes of 0.2 μm and 0.6 μm, suggesting that the filter with a pore size of 0.4 μm is better for measurement of SiO_2 content. Another example is for TiO_2: the mean concentration of all four groups is clustered in one subset marked as No. 1, suggesting that there is no significant difference among the four groups. Each of the pore sizes can
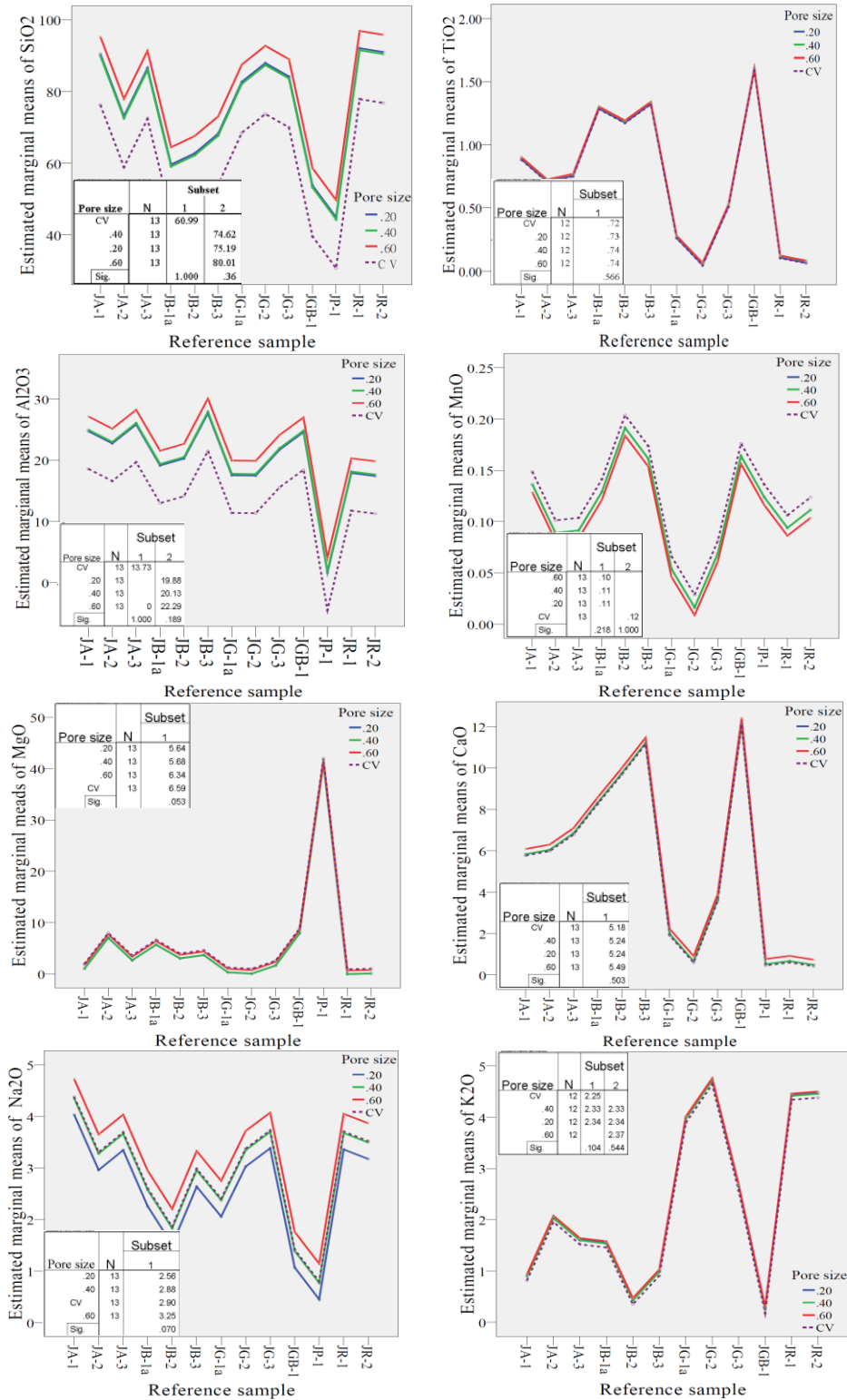
Fig.4. Profile plot of estimated marginal means of oxides derived from statistical calculation through carrying out SPSS. The small table inserted for each shows results of post hoc tests of pore size. The dashed line represents the certified value of GSJ rock standard, and the solid lines show the measured concentration of oxides using the filters with pore sizes of 0.2 μm, 0.4 μm and 0.6 μm.

be a good filter target, but considering other oxides and the order of the mean concentration, the filter with a pore size of 0.4 μm is thought to be a better filter target in this experiment.

3.2. Relation between measured values and pore sizes of membrane filters for ore samples

Similar to major elements of the rock, when analyzing the concentrations of trace elements of ore in a specified deposit by PIXE, consideration should be given to which pore size of the membrane filter is most appropriate as a target after filtration for crushed powder. In this experiment, Japanese standard samples for ore JZn-1 and JCu-1 were examined. The results are shown in Fig. 3. If the measured concentration of a trace element is in agreement with the corresponding certified value, the plotted point of the trace element is projected either on the dashed line or adjacent to the dashed line.

The concentrations of Pb, S and Zn for JZn-1 (zinc-rich ore sample) determined by PIXE using filters with pore sizes 0.2 μm, 0.4 μm, 0.6 μm and 0.8 μm are similar to concentrations of the certified values. However, for Cd, As and Sr, the measured concentrations using the filter with a pore size of 0.2 μm are closer to the certified values than are the measured concentrations using other filters with different pore sizes. Thus, the filter with a pore size of 0.2 μm is thought to be a suitable filter for PIXE measurement in JZn-1. For JCu-1(copper-rich ore sample), the same analytical procedure was applied to determine a suitable filter. The filter with a pore size of 0.2 μm was shown to be suitable for chemical analysis by PIXE.

3.3. Calibration factor

As shown above, a pore size of 0.4 μm is better for measurement of major element in rock samples by PIXE, whereas a pore size of 0.2 μm is better for other ore samples. However, the values measured by PIXE are slightly different from the certified values by GSJ owing to self-absorption of characteristic X-rays in measurements. Thus, the factor should be estimated to calibrate the difference between the measured and certified values. In this experiment, the ratio of the measured value divided by the certified value was calculated and the calibration factor (C.F.) was obtained by calculating the average of the ratio to the corresponding element, which is given by the following equation:

$$(C.F.)_j = \sum_{i=1}^{n} M_{i,sa} \Big/ n C_{i,st}$$

where $M_{i,sa}$ and $C_{i,st}$ are the measured and certified concentrations of element j to the ith reference standard sample in GSJ; j is a specified element such as Si (herein converted to SiO_2); and i is a reference standard sample such as JB-1a. The results of calculation are summarized in Tables 1 and 2 and Fig. 6. The horizontal lines in the box chart denote the 25th, 50th, and 75th percentile values (Fig. 5). The error bars denote the 5th and 95th percentile values. The red dashed line is an equivalent line between the measured value and the certified value. The samples of JA-1, JB-3
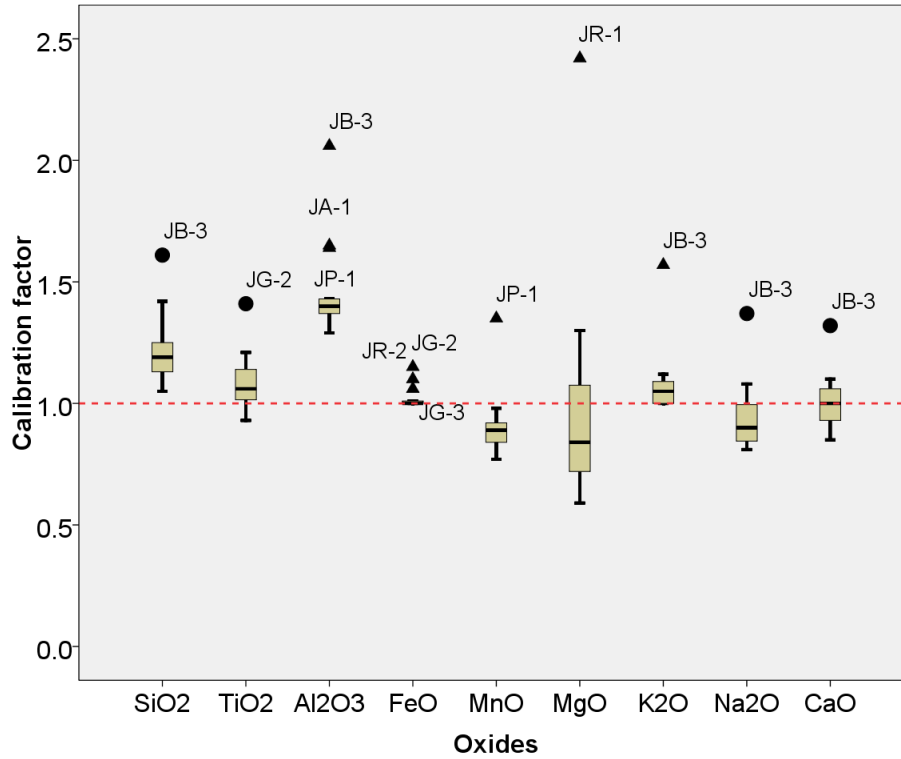
Fig.5. Box chart of the ratio of measured values to certified values for the oxides determined by PIXE to the standard sample of GSJ.

and JP-1 can be regarded as anomalous samples for analysis on Al_2O_3 content because the calibration factors of these samples have a large error over the 95th percentile (Fig. 5). The ratio on the 50th percentile can be regarded as the calibration factor (C.F.). The calibration factors of oxides of rock samples were calculated using the equation and the results are summarized in Table 1. The calibration factor of trace elements of ore samples and the ratio in GSJ standard samples are summarized in Table 2.

Table1. Calibration factor calculated from concentrations of oxides by PIXE / Certified value to filter with a pore size of 0.4 μm for rock samples.

	JB-1a	JB-2	JB-3	JP-1	JGB-1	JA-1	JA-2	JA-3	JG-1a	JG-2	JG-3	JR-1	JR-2	C.F.	Max	Min
SiO_2	1.07	1.16	1.61	1.05	1.15	1.42	1.13	1.13	1.23	1.19	1.26	1.25	1.22	1.22	1.61	1.05
TiO_2	1.04	1.00	0.93		0.98	1.03	1.05	1.13	1.07	1.41	1.14	1.14	1.21	1.09	1.41	0.93
Al_2O_3	1.29	1.40	2.06	1.65	1.38	1.64	1.33	1.37	1.36	1.43	1.43	1.43	1.37	1.47	2.06	1.29
FeO	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.01	1.15	1.06	1.01	1.10	1.03	1.15	1.00
MnO	0.89	0.83	0.91	1.35	0.77	0.85	0.83	0.84	0.89	0.88	0.92	0.98	0.96	0.92	1.29	0.77
MgO	0.64	0.60	0.81	0.95	0.97	0.84	0.80	0.59	1.30		1.18	2.42		1.01	2.42	0.59
CaO	0.85	1.00	1.32	1.06	1.01	1.01	0.93	0.93	0.90	0.96	0.98	1.06	1.10	1.01	1.32	0.85
Na_2O	0.83	0.81	1.37		1.02	1.08	0.85	0.88	0.84	0.97	0.96	0.92	0.86	0.95	1.37	0.81
K_2O	1.07	1.12	1.57		1.06	1.07	1.04	1.11	1.00	1.00	1.00	1.00	1.00	1.09	1.57	1.00

5 Conclusions

A relatively simple sample preparation method was developed for PIXE analysis of geological powder samples using a membrane filter. Fifteen standard samples that were previously analyzed by GSJ were used for evaluating the accuracy of different membrane filters with pore sizes of 0.2 μm, 0.4 μm, 0.6 μm and 0.8 μm. The results suggest that the filter with a pore size of 0.4 μm is better for the chemical analysis of rock samples, whereas the filter with a pore size of 0.2 μm is better for ore samples. A calibration method was developed for calibrating the difference between the measured concentration and the certified value determined by GSJ. On the basis of this method, we calculated the calibration factors for the rock samples and ore samples.

Table2. Calibration factor calculated from concentrations of elements by PIXE /Certified value to filter with a pore size of 0.2 μm for ore samples.

	JZn-1	JCu-1	C.F.
Cu	BDL	1.00	**1.00**
Zn	1.00	0.95	0.75
Pb	1.26	BDL	1.26
Sr	0.56	0.25	0.40
Cd	1.14	BDL	1.14
As	0.36	0.66	0.51
S	0.72	0.77	0.74

BDL: below detection limit.

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