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Determination of hydrogen in rock samples by neutron-induced prompt gamma-ray analysis

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Prompt gamma-ray analysis was applied to determine hydrogen in geological samples. In order to obtain accurate values, blank values were estimated and subtracted. Samples were dried to constant weight in an oven. Helium gas was introduced into the sample box to purge the air containing moisture during the measurement. Hydrogen contents in some geochemical standard samples were determined and highly reproducible values were obtained.

Introduction

Hydrogen is the lightest element in the periodic table. It is mostly distributed as water on the Earth's surface. Water is also present in the Earth's crust and its behavior affects the volcanic activity. Hence, it is important to determine water contents in rocks which are generally very low (for example, water contents in igneous rocks and sedimentary rocks are 0.2%–2.4%[1] and 0.15%–6.4%,[2] respectively). A typical and traditional quantitative analytical method to determine water in rock samples is gravimetry,[3] in which water is evaporated from the rock samples at high temperature and weighed. In this method, large amount of sample is needed for weighing water accurately. Rock samples used for gravimetry deformed by heating, which may somewhat change its chemical form by oxidization and/or reduce volatile elements. Therefore, this method is not suitable for precious samples like meteorites. Infrared spectrometry is also often used for the determination of the water content. For this method, highly hygroscopic reagent (KBr) must be used to prepare a sample for IR measurement. It is not suitable to determine water content in rock samples, either.

Neutron-induced prompt gamma-ray analysis (PGA) is a non-destructive method and suitable for such samples as meteorites[4] and archeological samples.[5] Hydrogen is one of the elements having high sensitivity in PGA. In this study, we aimed to apply PGA to determine hydrogen in rock samples. For achieving this purpose, we evaluated background and blank levels of hydrogen in order to obtain its accurate contents.

Experimental

Irradiation and measurement

Samples were sealed in fluorinated ethylene polyethylene (FEP) film which was washed and then dried in advance. Neutron irradiation was performed by using the PGA system at the JRR-3 reactor of Japan Atomic Energy Research Institute (JAERI). The size of an FEP film bag was smaller than the neutron beam size (2×2 cm^2). The bag was fixed with Teflon string to a sample holder, which was set at an angle of 45° to the neutron beam. After setting, the sample was irradiated with thermal neutron (neutron flux: $1.6\cdot10^8$ n·cm^{-2}·s^{-1}) and prompt gamma-rays were detected by a Ge-detector coupled with 16k channel MCA.

Background level of hydrogen in a sample box

In PGA system at JRR-3, irradiation is usually performed in a sample box in the helium atmosphere to reduce prompt gamma-rays from atmospheric nitrogen.[6] For hydrogen analysis, it is important that hydrogen content in the sample box is kept constant and as low as possible. Thus, we examined hydrogen contents in the sample box by changing the helium flow rate at 500 and 1000 ml/min.

Blank level of hydrogen introduced by FEP film

The moisture adsorbed on FEP film used to cover rock samples may positively contribute in determining hydrogen in rock samples. Therefore, blank level of hydrogen introduced by FEP film was measured repeatedly by changing the number of sheets of FEP film to find any relationship between the blank level of hydrogen and the number of FEP sheets.

Calibration line of hydrogen

The calibration line of hydrogen was drawn by using primary chemical standard, potassium hydrogen phthalate (PHP) of 0.6 mg to 342.8 mg. After the mass of PHP was kept constant, PHP was sealed in FEP film bags. We examined a linearity of calibration line and the detection limit of hydrogen.

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Determination of hydrogen in rock samples by PGA

To control the analytical procedure for the determination of hydrogen in rock samples, we used powdered geochemical reference standard samples issued by the Geological Survey of Japan (GSJ). We selected four samples; JB-3, JSO-2, JP-1 and JLk-1. JB-3 (Basalt) has the lowest value of H_2O^+ in GSJ geochemical standard rocks,[1] while JSO-2 (Soil) has the highest H_2O^+.[7] JP-1 (Peridtite) has the highest concentration of H_2O^+ among igneous rock reference samples issued by GSJ.[1] JLk-1 (Lake Sediment) was chosen as a geochemical sample with high water content.[2] Potassium hydrogen phthalate was used as a reference chemical standard.

Rock samples (0.5–1 g) were heated at 110 °C for 1 hour in an oven to remove the moisture adsorbed on the surface of samples and cooled at room temperature in a desiccator for 30 minutes. A cycle of heating and cooling was repeated several times until the mass of the sample became constant. When the mass of the sample became constant, 100–300 mg of the sample was sealed in an FEP film bag.

Results and discussion

Background level of hydrogen in a sample box

Count rates of 2223 keV prompt gamma-rays from hydrogen in the sample box are summarized in Table 1. As expected, the count rate was decreased with increasing helium flow rate. At a flow rate of 1000 ml/min, the count rate became the lowest (0.00441±0.00099 cps) which corresponds to 0.0059 mg of hydrogen. By flowing helium gas, not only the background peak of hydrogen due to the atmospheric moisture, but also the background due to nitrogen was reduced. In the later experiment, helium flow was 1000 ml/min into the sample box during the measurement.

Blank level of hydrogen introduced by FEP film

The hydrogen blank was determined at each irradiation run with changing the number of sheets of FEP film (Fig. 1). The hydrogen mass shown in Fig. 1 covers both background hydrogen in the sample box and hydrogen blank introduced by the FEP film. The blank level of hydrogen was found to be nearly constant regardless of the number of the FEP films. An average value of the blank hydrogen was 0.0167±0.0021 (1σ) mg. The net contribution of hydrogen introduced by the FEP films was calculated to be 0.0108±0.0025 (1σ) mg. Considering that the value was nearly constant and was independent on the number of FEP sheets, the hydrogen blank introduced by the FEP film was not originated from the moisture adsorbed on the surface of the FEP film and/or hydrogen impurities in them. If there is any hydrogen in and/or on materials of the sample box, it could contribute to the background by the scattering neutron irradiation. Even if this is the case, the background hydrogen would be dependent on the number of FEP films. Although conclusive explanation can not be presented for the blank introduced by the FEP film, an average value of 0.0167 mg was practically used for the blank correction of hydrogen in this study.

Calibration line of hydrogen in PHP

The intensity of hydrogen prompt gamma-ray was measured by changing the mass of PHP. The calibration line is shown in Fig. 2. Closed and open circles show count rates of hydrogen with and without blank correction, respectively. Closed circles shown an excellent linearity suggesting that our blank correction seems to work practically. Judging from the linearity shown in Fig. 2, it is concluded that hydrogen of down to 0.015 mg can be determined by our present PGA procedure. Thus, we expected that hydrogen could be determined for 100 mg of JB-3 whose recommended value of H_2O^+ is the lowest among geological reference standard rock samples issued by GSJ.[1]

Determination of hydrogen in rock samples

Four GSJ geochemical standard samples were analyzed repeatedly from 3 to 5 times. Data are shown in Fig. 3, where average hydrogen concentrations are given with errors of absolute and relative standard deviation in percents (1σ). Though samples analyzed in this study have various hydrogen contents (0.03% to 1.4%), highly reproducible values were obtained for each sample, with relative standard deviations varying from 1.1% for JP-1 to 11% for JB-3.

Table 1. Background level of hydrogen in the sample box

He flow rate, ml/min	Count rate,* cps
0	0.0417 ± 0.0032
500	0.00553 ± 0.00126
1000	0.00441 ± 0.00099

* For 2223 keV γ-ray.

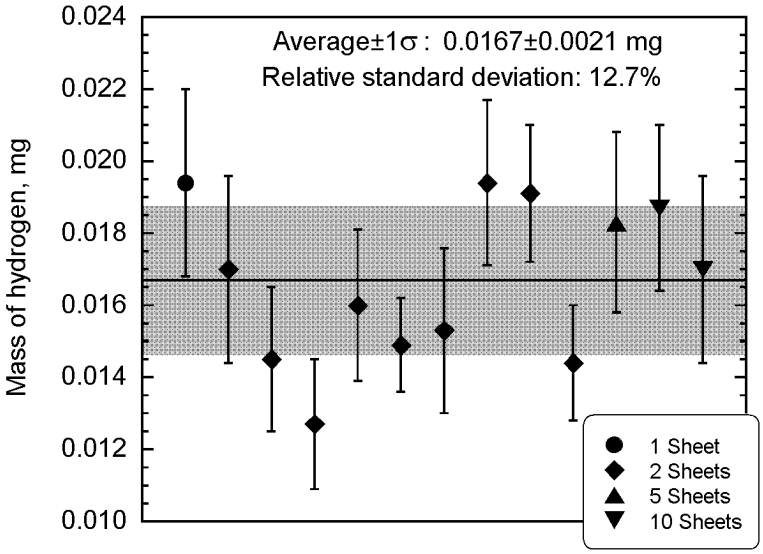

Fig. 1. Blank level of hydrogen introduced by FEP film. A horizontal line and a dark belt correspond to an average of 13 individual values and their standard deviation (1σ), respectively

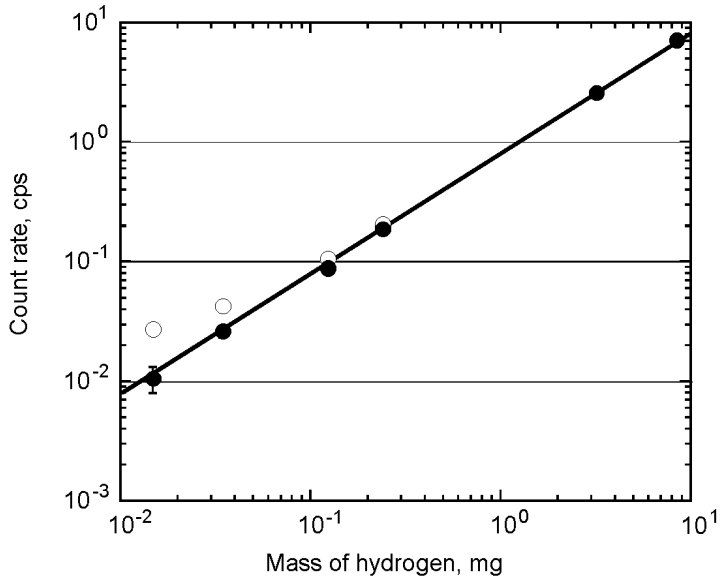

Fig. 2. Calibration line between hydrogen content and its prompt gamma-ray intensity. Closed and open circles show count rates of hydrogen prompt gamma-ray with and without correction of blank, respectively. 0.015 mg of hydrogen contained in 0.6 mg of PHP is corresponding to the blank level. Relative statistic errors for 0.6 mg PHP and the other PHP samples were 24% and lower than 15% (1σ) after blank correction, respectively

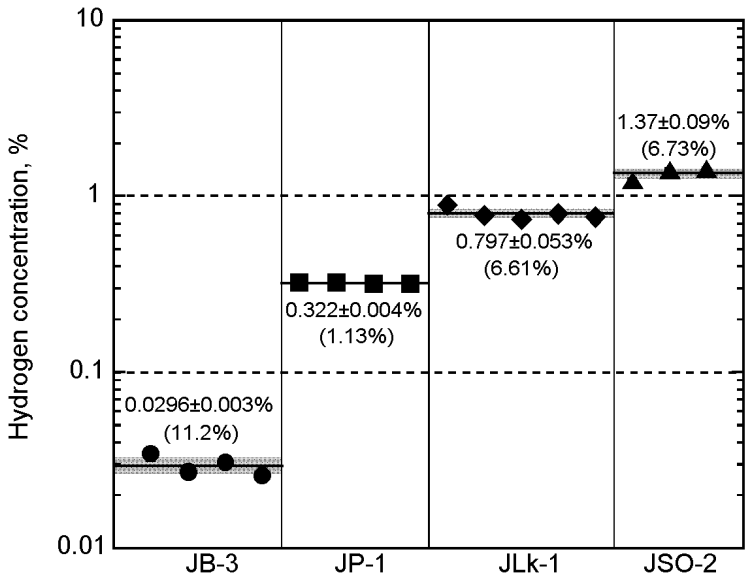

Fig. 3. Hydrogen concentrations in four geochemical standard samples. A horizontal line and dark belt correspond to an average of values analyzed repeatedly from 3 to 5 for each sample and their standard deviation (1σ), respectively. Numerical figures in each column express average values and their standard deviations, with their relative standard deviations (%) in parenthesis

Assuming that hydrogen is present only as water in the samples, we calculated water contents based on our hydrogen values. Calculated values of water concentration were shown in Fig. 4, where an average value for each sample is normalized to its recommended value. Ranges of individual analytical data announced by GSJ on its website[8] are also shown. Our estimated water contents are systematically higher than the recommended[1,2] or reference[7] values, ranging from 12% for JLk-1 to 47% for JB-3. Recommended and reference values were mostly determined by gravimetric method.[8] Among four samples analyzed in this study, JB-3 have the lowest contents of hydrogen and the largest scatter in the reported values, implying that it is hard to determine water content in this sample precisely by gravimetry. JLk-1 and JSO-2, which are lake sediments and soil, respectively, seem to contain considerable amounts of hydrocarbons in consideration of their high carbon contents (1.5%[2] and 4.06%,[7] respectively), and therefore, contain considerable amounts of hydrogen composing hydrocarbons. Apparently, such hydrogen results in high estimation of water concentration for JLk-1 and JSO-2. In contrast, hydrocarbons are scarcely present in JB-3 and JP-1 (both igneous rocks), considering that carbon contents are reported to be 120 and 764 ppm,[1] respectively.

A possible cause for our systematically high water contents even in igneous rock samples, JP-1 and JB-3, is moisture adsorbed on samples during the preparation after drying. In fact, an increase of 0.4% and 0.05% was observed in 10 minutes after drying for JP-1 and JB-3, respectively. After 10 minutes, the mass hardly changed. Although such increments were small, it corresponds to about 20% and 25% of each recommended value[1] of H_2O^+ for JP-1 and JB-3, respectively. A value of 20% for JP-1 is exactly the same as an increment of our data from its literature value,[1] as noticed in Fig. 4. Therefore, the adsorption of moisture during the sample preparation can explain our higher hydrogen data for JP-1 and JB-3. Such an increment could be adsorbed for two others samples, JLk-1 and JSO-2, which showed 0.8% and 0.7% increases in 10 minutes after drying, respectively. These increments correspond to about 12% and 8% of recommended[2] or reference[7] value of H_2O^+ of JLk-1 and JSO-2, respectively. In the case of JSO-2, an excess of the calculated water content is dominated by hydrocarbons rather than moisture adsorbed during the sample preparation for PGA. From these experiences, it can be concluded that it is highly essential to prepare samples in dry atmosphere for accurately determining H_2O^+ contents in powdered rock samples by PGA.

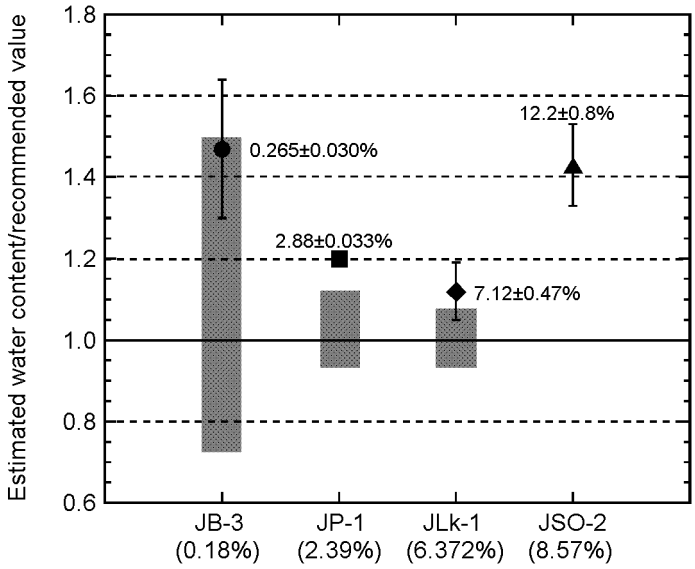

Fig. 4. Calculated water concentrations normalized to recommended values for four geochemical reference samples. Water concentrations are calculated from our hydrogen data assuming that hydrogen is present only as water in the samples. Dark rectangles designate ranges of individual analytical data announced by GSJ on its web site.[8] Numerical figures within the figure frame express our calculated water concentrations, while those in parenthesis are recommended values of H_2O^+

Conclusions

Neutron-induced prompt gamma-ray analysis was applied to determine hydrogen in geochemical reference standard samples. After correction for blank contributions, highly reproducible values were obtained. It is thus concluded that the PGA procedure developed in this study is highly reliable for determining hydrogen contents in geochemical samples. Our water concentrations calculated from hydrogen concentrations are systematically higher than the literature values because of hydrocarbons and/or moisture adsorbed during preparation.

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