Sensitivity Variation for H, B, Si, Cl, Ca and Cd in Solid Materials by Prompt Gamma-ray Analysis with a Special Emphasis on the Presence of Hydrogen

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The effects of neutron scattering by matrix hydrogen in geological samples were examined in order to accurately determine their chemical compositions by neutron-induced prompt gamma-ray analysis (PGA). Three different matrix materials including basaltic reference rock sample (JB-2) mixed with chemical reagents including H-containing ones were analyzed by using thermal and/or cold neutron-guided beams of JRR-3 at Japan Atomic Energy Agency. The sensitivity change of elements with the variation of the H concentrations was evaluated for disk and spherical target geometries. The results show that the analytical sensitivities of B, Cl and Cd in disk samples seem to increase with increasing the matrix H concentrations by the irradiation of both thermal and cold-neutron beams. The sensitivity enhancement of B for disk-shaped JB-2 mixed with up to 2% mass H is within the analytical uncertainty associated with PGA with a thermal-neutron beam.

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Introduction

Non-destructive analysis is highly desired for solid materials, including meteorites. Neutron-induced prompt gamma-ray analysis (PGA) can be one of the most advantageous analytical tools for solid materials, especially for their bulk analyses. When bulky solid samples are analyzed by PGA, neutron absorption, neutron scattering and gamma-ray attenuation triggered in the sample have to be considered and corrected, if necessary. Among such elements as scattering neutrons effectively, hydrogen (H) is the most concerned, because it has a high thermal scattering cross section of 80 barns, and it can be present in some geological and cosmochemical samples with high contents.

The neutron-scattering effect caused by matrix H on the elemental analytical sensitivity (count rates per unit mass) has been studied for PGA with both thermal and cold neutrons.¹⁻³ Although the sensitivity enhancement in thermal neutron-induced prompt gamma-ray analysis (TNPGA) was observed, contradicting interpretations were proposed; either it can be quantitatively accounted for by elastic neutron scattering,⁴ or it can be attributed to inelastic neutron scattering.⁵ To make the situation more complicated, the element sensitivity was observed to decrease with the H content and the target thickness in cold neutron-induced prompt gamma-ray analysis (CNPGA), which was explained partly in terms of increasing of the average neutron energy.⁶

The effect of neutron scattering on the analytical sensitivity

depends upon the neutron spectrum characteristics of the beam. TNPGA measurements at the National Institute of Standards and Technology (NIST), USA were performed on the roof of the reactor using neutron beam directed from the reactor core, yielding a relatively high proportion of fast neutrons as well as background gamma-rays, which originated in the reactor core or the beam tube.⁷ In the PGA system at JRR-3 of Japan Atomic Energy Agency (JAEA), the cold and thermal neutrons are guided out from the reactor core by using super mirror tubes of various curvatures, which considerably reduces the proportion of first neutrons and background gamma-rays. In this study, in order to determine the elemental compositions of hydrogenous geological and cosmochemical samples as accurately as possible by PGA, the neutron-scattering effect caused by the matrix H in such samples was evaluated through analyses of the chemical reagents and geological reference materials for both TNPGA and CNPGA by using cold and thermal-neutron guided beams of JRR-3, respectively.

Experimental

Experimental outlines and sample preparation

The experiments were designed to characterize the effect of neutron scattering by matrix H on the elemental sensitivity in both geological and cosmochemical samples using the PGA method. We studied the sensitivity changes for some elements as a function of the H concentration and the dependence of the elemental sensitivity on the target shape. A summary of the experiments is presented in Table 1. Each experiment is briefly described as follows.

Experiment 1: The sensitivity variation with the H concentration

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Table 1 Summary of the experiments performed in this study

Exp. No.	Neutron beam	Shape	Sample mass/g	H content, %	H-containing reagent	Matrix	Other elements added	Elemental data shown
1	Thermal & cold	Disk 13 mm ϕ	Fixed 0.14 – 0.20	Varied 0.21 – 5.02	Benzoic acid	Graphite	B, Cd, Cl	B, Cd, Cl, H
2	Thermal & cold	Sphere 13 mm ϕ	Fixed 1.0	Varied 0.42 – 6.72	Urea	Deuterourea	B, Cd, Cl	B, Cd, Cl, H
3	Thermal	Disk 13 mm ϕ	Fixed 0.15	Varied 0.03 – 1.9	w & w/o oxalic acid	JB-2	—	B
4	Thermal	Disk 10 mm ϕ	Varied 0.2 – 1.0	Fixed 3.57	Oxalic acid	JB-2	—	B, Ca, Si

in disk samples was studied for both thermal and cold-neutron beams; disks of constant dimension (13 mm ϕ $\times$ 1 mm thickness) were prepared with different H concentrations by mixing of powdered chemical standards H₃BO₃, NH₄Cl and CdCO₃ with graphite (JAERI-G1) and/or benzoic acid. Seven different mixtures were prepared by grinding in an agate mortar with various combinations of the substances; and the disks were made by using a tablet molding device. Each disk weighed about 140 – 200 mg. Hydrogen concentrations in the disks ranged from 0.21 to 5.02%.

Experiment 2: The sensitivity variation with the H concentration was studied for spherical samples with fixed diameter (13 mm), which were prepared with different H concentrations (0.42 to 6.72% H) by the mixing of H₃BO₃, NH₄Cl and CdCO₃ with deuterourea (98% atom)/urea using a molding machine. The sample mass of each sphere was fixed to be about 1 g. Both thermal and cold-neutron beams were applied.

Experiment 3: The matrix H effect on elemental analysis by TNPGA was studied using JB-2 (0.028% H), a basaltic reference rock powder prepared by Geological Survey of Japan (GSJ), and JB-2 mixed with oxalic acid (H concentration of up to 1.9%) in disk-shaped samples (13 mm ϕ $\times$ ~1 mm thickness). Hydrogen contents were varied from 0.028% (no oxalic acid added) to 1.9%, which is close to the H contents in CI chondrites, as explained later. The sample mass was fixed to be about 150 mg. Only a thermal-neutron beam was applied in this experiment.

Experiment 4: The sensitivity change with increasing the sample mass was studied. For such a purpose, five disk samples, each of which had the same dimensions (10 mm ϕ $\times$ ~1 mm thickness) and the same mass (about 200 mg) with a constant H concentration (3.57%), were prepared by mixing JB-2 with oxalic acid in the same way as that for Experiment 3. For increasing the sample mass, disk samples were stacked, with the thickness being increased up to 5 mm. Only a thermal-neutron beam was applied.

Irradiation and counting

The disk and sphere samples were sealed into thin FEP (fluorinated ethylene propylene) film bags for neutron irradiation. Each sample was irradiated for about 2 – 10 h by thermal neutrons (flux: 2.4×10^7 n cm⁻² s⁻¹) and/or cold neutrons (flux: 1.4×10^8 n cm⁻² s⁻¹), which were guided out of the research reactor JRR-3 at JAEA. The cold and thermal-neutron beam energies were distributed over the peak energy of 3.0 and 15 meV, respectively. The neutron beam was collimated to a size of 20 $\times$ 20 mm at the entrance of a sample box, in which He gas was introduced to purge the atmospheric gas. Prompt gamma-rays were detected by a Ge detector coupled with a 16-k channel pulse-height analyzer. The Ge detector was surrounded by a bismuth germanium oxide (BGO) detector so that gamma-rays due to Compton scattering of high-energy prompt gamma-rays would be effectively suppressed by measuring the coincident signals from Ge and BGO detectors.⁸ To monitor the change in the neutron flux throughout the course

of the experiments, a Ti foil was irradiated, and its prompt gamma-rays were counted at regular intervals. Prompt gamma-ray intensities measured on different days were normalized to the average count-rate of the 341.7 and 1381.7 keV gamma-rays of Ti measured with each system of TNPGA and CNPGA. Corrections were also made to account for the presence of H in the background. The gamma-ray intensities of 477.6 keV for B, 558.3 keV for Cd, (786.3 + 788.4) keV for Cl, 2223 keV for H, 3539 keV for Si, and 1942 keV for Ca were used for sensitivity determination. A blank FEP film was measured for background correction.

Results and Discussion

Element sensitivities as a function of matrix hydrogen concentration

For solid disk geometry: The results of the element sensitivity variation with increasing of matrix H concentration in disk samples (Experiment 1) are shown in Figs. 1a and 1b for a thermal-neutron beam and a cold-neutron beam, respectively. In these figures, the sensitivity is expressed by the relative sensitivity by normalizing each sensitivity to that with 0% H, which was obtained by extrapolating the sensitivity trend for each element to 0% mass H on the assumption that the sensitivity varies linearly in the range of 0 to 5% H mass. An average sensitivity of different samples (two to four samples) with an accompanied uncertainty (standard deviation; 1 σ) is plotted for each element at each set of seven different H compositions. Indicated uncertainty due to the reproducibility of replicate measurements is within the normal range of routine measurements of the PGA system at JRR-3 of JAEA (less than 10% for 1 σ).⁹ Here, the uncertainty involved in the extrapolated sensitivity for 0% mass is not included. Although the data scatter is large in Figs. 1a and 1b, the relative count rates (analytical sensitivities of elements) seem to increase with increasing the matrix H concentrations for both thermal and cold-neutron beams. In addition, it can be seen that the increasing rate of the sensitivity varies among the elements concerned with an order of Cd > Cl > B $\approx$ H.

Paul *et al.*⁶ performed a similar experiment using solid urea/graphite/KBr disks of constant thickness by TNPGA, and found that the sensitivities for K and Br increase linearly with the optical thickness (macroscopic total cross section multiplied by the disk thickness), or as a function of the H concentration (over 0 to 5.88%). When the H concentration becomes greater than 0.5%, the macroscopic total cross section becomes dominated by the scattering cross section of H. Obviously, our results concerning the TNPGA sensitivity variation with the H concentration for disk samples shown in Fig. 1a are consistent with the findings of Paul *et al.*⁶ The TNPGA sensitivity enhancement of elements in the disk sample seems to be largely due to the elastic scattering of neutrons, which changes the mean free path of neutrons within the target, and therefore

Fig. 1 Analytical sensitivities change for B (◆), Cd (△), Cl (○) and H (×) in disk samples in (a) thermal-neutron beam PGA and (b) cold-neutron PGA. Uncertainties are the standard deviations (1σ) of the measurements of two to four samples with the same H content.

increases the probability of neutron absorption.

In CNPGA of disk samples, the elemental sensitivity also tends to increase with increasing of the matrix H content (Fig. 1b). Commonly, the CNPGA sensitivity is expected to decrease with increasing of both the H mass fraction and the target thickness. In fact, Mackey *et al.*³ reported that the interaction of cold neutrons with a warm target results in an increase in the average energy of the neutron beam, which in turn decreases the analytical sensitivity. With a thin-disk (~ 1 mm) sample, however, such an effect could not become obvious.⁶ For thin-disk samples, it is probable that inelastic scattering, which is effective in increasing the neutron energy (temperature), cannot be significant. In this work, the same situation as that for TNPGA must have occurred; the elastic scattering leads to a change in the mean-free path of a neutron, increasing the sensitivity with increasing H concentration.

For solid sphere geometry: The sensitivity variation of H, B, Cl and Cd with the matrix H concentration for a solid-sphere geometry is shown in Figs. 2a and 2b for TNPGA and CNPGA, respectively. Measurements were made at 9 different steps having different H contents. Each sample was measured

Fig. 2 Analytical sensitivities change for B (◆), Cd (△), Cl (○) and H (×) in solid sphere samples in (a) thermal-neutron beam PGA and (b) cold-neutron PGA. The uncertainties are the standard deviations (1σ) of the two to three replicate measurements.

repeatedly (two to three times), and the reproducibility is shown as uncertainty (1σ). As shown in Fig. 2a for TNPGA, the element sensitivity seems to stay constant, except for H. The H sensitivity apparently decreases with increasing H concentration. In CNPGA, the analytical sensitivity clearly decreases with increasing matrix H concentration. Although large scatterings are accompanied, there appears to be a difference in the elemental sensitivities among the elements of concern. A similar experiment was performed by Mackey *et al.*² They found no apparent effect on the H sensitivity for various substances having different H contents from 5.57% (SRM 1570) to about 15% (paraffin). At present, we have no reasonable explanation for this contradiction.

Matrix H effect on geological and cosmochemical samples

Most geological and cosmochemical samples are “dry”, having H concentrations of less than 1%. Among meteorites, Ivuna-type carbonaceous chondrites (hereafter, CI chondrites or CI) are known to have the highest contents (about 2% in mass) of H,¹⁰ most of which is known to be present as OH in hydrous minerals. This group of meteorites is of special importance because they have not experienced any thermal event so far, and have essentially the same chemical composition as that of the Sun, except for a few extremely volatile elements, such as H, C, N and O as well as noble gases.¹¹ It is well-acknowledged that

Fig. 3 Thermal-neutron PGA sensitivity enhancements for B measured in the disk of JB-2 and JB-2 mixed with oxalic acid. The uncertainties (1σ) are due to the counting statistics only.

the solar system abundances of the elements are one of the most fundamental numbers, and that these numbers are mostly derived from meteorites, especially CI chondrites by their chemical analyses. As discussed in the previous sections, the elemental sensitivity can be affected by the presence of H in the matrix either in disk shape or in spherical shape for both CNPGA and TNPGA; therefore, it is essential to correctly evaluate such an effect for accurate determinations of the elemental compositions of CI chondrites (and other similarly hydrous materials) by PGA. For this purpose, we performed Experiment 3, where a geological reference sample JB-2 (basaltic rock powder) as a meteorite-analogue was used and oxalic acid was mixed with different H contents up to 1.9 mass%. The result is shown in Fig. 3, where the relative sensitivities of B are plotted at different H mass contents by normalizing to the sensitivity with 0% of H mass. A value of 0% H was obtained by extrapolating the sensitivity trend to 0% mass H on an assumption of the linear trend. Note that JB-2 contains 0.028% mass H,¹² and its average sensitivity with 1σ standard deviation of three-times measurements is shown in Fig. 3. For other samples (mixture of JB-2 and oxalic acid), the sensitivities obtained from one measurement are plotted along with the counting statistics (1σ). As can be seen in Fig. 3, the sensitivity of B apparently increases with increasing the H content. With about 2% of H, the sensitivity was enhanced by about 8%. These results are mostly consistent with those of Experiment 1, which are shown in Fig. 1a. In Experiment 1, graphite was used as a matrix material, whereas a basaltic reference sample, JB-2, was used in Experiment 3. Although additional experiments are needed for further consideration on the effect due to the matrix material, it may be worth pointing out that the sensitivity enhancement with the presence of H is confirmed with the matrix of either graphite or silicate.

For the TNPGA at JRR-3 of JAEA, the sample was suspended with Teflon string in a Teflon frame. At each measurement, the sample was replaced by hand and installed into the sample holder. With repeated measurements, it was confirmed that the reproducibility of prompt gamma-ray count rates increased to about 7–10% (1σ),⁹ even for such peaks of the relatively high count rates, whose counting statistics were much less than 7%. The reproducibility in the PGA measurement seems to be

Fig. 4 Thermal-neutron PGA sensitivities (relative to 0.2 g disk sensitivity) measured in the disk of JB-2 with fixed 3.57% H for Si (○), Ca (△) and B (◆). The uncertainties (1σ) are due to counting statistics.

somewhat higher than the reproducibility involved in INAA. Considering such a reproducibility in PGA, an enhancement of 8% with 2 mass% of H for CI chondrites can be regarded to be within the marginal range for correction. For most geological and cosmochemical samples, including meteorites other than CI chondrites, the H contents are less than 2 mass%. Therefore, the correction for the sensitivity enhancement due to the matrix H in TNPGA can be ignored for most silicate rock samples.

Sensitivity variation with sample thickness

The sensitivity variation with mass (thickness) of a disk-shaped sample in TNPGA was evaluated for the practical analysis of geological and cosmochemical samples in Experiment 4. In this experiment, disk samples of JB-2 mixed with oxalic acid (having constant H mass of 3.57%) were prepared with a total mass ranging from 0.2 to 1.05 g. The relative sensitivities of B, Si and Ca are shown in Fig. 4, where the sensitivities for the minimum mass (0.2 g) are used for the normalization standard. As shown in Fig. 4, the relative sensitivities for the three elements decrease with increasing the sample mass, although each count has a relatively large counting uncertainty. Among the three elements, the relative sensitivity of Si stayed rather constant over the mass range concerned, whereas those of B and Ca apparently decreased with increasing the mass. If the reproducibility of PGA measurements (7–10% for 1σ) is taken into consideration, it may be concluded that the sensitivity change can be ignored for the mass range up to 0.4 g for the sample matrix examined in Experiment 4.

Mackey *et al.*² examined the thermal-neutron sensitivity change of several elements in SRM 1632a (Bituminous Coal), which has 3.85 mass% of H with increasing thickness (or sample mass) with a fixed diameter (12.7 mm). They observed that the B and H sensitivities increase with increasing the disk thickness over the range of 0 to 2 mm and that, beyond 2 mm, the sensitivities then decrease with increasing the disk thickness thereafter. However, they found no clear sensitivity changes of other elements (Si, K, Cl, Sm, Gd) over the entire range of thickness (1 to 12 mm). In Experiment 4 of this study, each 200 mg disk corresponds to 1 mm thickness. As can be seen in

Fig. 4, no enhancement of the sensitivities for any element was observed for the disk mass range of 400 mg to 1 g (corresponding thickness of 2 to 5 mm). Using Monte-Carlo simulation calculations, Copley and Stone¹³ showed that the mean path length of monoenergetic neutrons in the target depends on the size and shape of the target. Upon scattering with the target material (sample), neutrons are either absorbed in the target sample or scattered out of the sample, depending upon its shape and size. The scattering rate depends on the elemental composition and its density in the sample. Regardless of the neutron scattering efficiency, the neutron flux can be decreased in thick samples due to the absorption of neutrons. If the target material has a well-defined chemical composition and geometry, the correction factor for such a neutron self-shielding effect can be easily calculated using general formulas.¹⁴ For real samples, like geological reference rocks and chondritic meteorites, however, it seems to be less practical to apply such calculation protocols for obtaining a correction factor of the neutron scattering and absorption.

Conclusions

The effects of neutron scattering by matrix H in geological and cosmochemical samples were examined in order to accurately determine their chemical compositions by neutron-induced prompt gamma-ray analysis (PGA). The analytical sensitivities of the elements in disk samples seem to be increased with increasing the matrix H content for both thermal and cold-neutron beams. Since the sensitivity enhancement due to the matrix H up to 2 mass% in silicate rock samples is within the marginal range of uncertainty due to the reproducibility in TNPGA, its correction can be ignored for both geological and cosmochemical samples. When the reproducibility of PGA measurements is taken into consideration, the sensitivity change can be ignored for disk-shaped samples with a mass range up to 0.4 g.

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References

1. E. A. Mackey, G. E. Gordon, R. M. Lindstrom, and D. L. Anderson, *Anal. Chem.*, **1991**, 63, 288.
2. E. A. Mackey, G. E. Gordon, R. M. Lindstrom, and D. L. Anderson, *Anal. Chem.*, **1992**, 64, 2366.
3. E. A. Mackey, *Biol. Trace Elem. Res.*, **1994**, 43 – 45, 103.
4. E. A. Mackey and J. R. D. Copley, *J. Radioanal. Nucl. Chem.*, **1993**, 167, 127.
5. R. Trubert, G. Duplatre, and J. C. H. Abbe, *Appl. Radiat. Isot.*, **1991**, 42, 699.
6. R. L. Paul and E. A. Mackey, *J. Radioanal. Nucl. Chem.*, **1994**, 181, 321.
7. D. L. Anderson, M. P. Failey, W. H. Zoller, W. B. Walters, G. E. Gordon, and R. M. Lindstrom, *J. Radioanal. Nucl. Chem.*, **1981**, 63, 97.
8. C. Yonezawa, A. K. H. Wood, M. Hoshi, Y. Ito, and E. Tachikawa, *Nucl. Instrum. Methods Phys. Res., Sect. A*, **1993**, 329, 207.
9. N. Shirai and M. Ebihara, Manuscript under preparation, August 30, 2011.
10. B. Mason, *Space Sci. Rev.*, **1962**, 1, 621.
11. K. Lodders, “*Astrophysics and Space Science Proceedings*”, ed. B. Eswar Reddy, **2010**, Springer-Verlag Berlin, Heidelberg, 379 – 417.
12. N. Imai, S. Terashima, S. Itoh, and A. Ando, *Geochem. J.*, **1995**, 29, 91.
13. J. R. D. Copley and C. A. Stone, *Nucl. Instrum. Methods Phys. Res., Sect. A*, **1989**, 281, 593.
14. R. F. Fleming, *Int. J. Appl. Radiat. Isot.*, **1982**, 33, 1263.