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Determination of chlorine, bromine and iodine in rock samples by radiochemical neutron activation analysis

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Chlorine, bromine and iodine (hereafter, halogens) were determined for rock samples by radiochemical neutron activation analysis. The powdered samples and reference standards prepared from chemical reagents were simultaneously irradiated for 10 to 30 minutes with or without a cadmium filter in a TRIGA-II reactor at the Institute for Atomic Energy, Rikkyo University. The samples were subjected to radiochemical procedures of halogens immediately after the irradiation. Iodine was firstly precipitated as PdI_2, and chlorine and bromine were successively precipitated as Ag-halides at the same time. In this study, geological standard rocks, sedimentary rocks and meteorites were analyzed for trace halogens. In some Antarctic meteorites, iodine contents were observed to be anomalously high. Chlorine contents also are somewhat high. The overabundance of iodine and chlorine must be caused by terrestrial contamination on the Antarctica.

Introduction

Halogens are widely distributed in geological materials. The average abundances of Cl, Br and I in the earth crust were estimated by MASON[1] to be 130, 2.5 and 0.5 ppm, respectively. BOWEN[2] also estimated the crustal abundances of Br and I to be 0.37 and 0.14 ppm, which are 6.8 and 3.6 times lower than the estimates by MASON,[1] respectively. These values are largely dependent on the halogen data for the major crustal rocks used for their estimation. It may be noted that there are large scatterings in the halogen data reported for these geological materials. Such large scatterings may indicate that trace halogens, especially Br and I, are difficult to be accurately determined for geological samples. On the other hand, the CI estimates of MASON[1] and BOWEN[2] for the crust abundance are coincidentally the same (130 ppm). In CI chondrites, whose elemental abundances are mostly adopted for the solar system abundances, halogen abundances were obtained to be 704 ppm for Cl, 3.57 ppm for Br and 0,433 ppm for I.[3] It may be also noticed that the Cl contents in CI chondrites reported are narrowly spread from 720 to 840 ppm whereas those for Br and I are widely spread from 3.3 to 5.1 ppm and from 0.23 to 1.21 ppm, respectively. As CI chondrites must be much uniform in chemical composition than terrestrial (crustal) rocks, these large scatterings, especially for Br and I, must be artificial, possibly due to analytical problems, rather than indigenous.

For the determination of Cl, Br and I in geological samples, the following analytical methods have been applied; instrumental and radiochemical neutron activation analysis (INAA and RNAA), mass spectrometric isotope dilution analysis (MSIDA), ion-selective electrode, ion chromatography and X-ray fluorescence. Among these methods, RNAA has several advantages: (1) Cl, Br and I can be determined, (2) their data are highly accurate and reliable and (3) analytical sensitivities are high for all three halogens. INAA can be applied only if the halogen contents are high enough compared with those for the matrix elements. Among halogens, iodine has the lowest abundance in geological samples and could be reliably determined only by RNAA. For this reason, the RNAA procedure for I has been extensively examined and developed. EBIHARA et al.[4,5] examined in detail the RNAA procedure for I, which was later used for the analysis of Antarctic meteorites.[6] SHINONAGA et al.[7] presented Cl, Br and I data for several igneous standard rocks obtained by RNAA and MSIDA. In RNAA, three halogens were determined separately using different aliquants of individual samples. Their RNAA procedures are satisfactory for well homogenized and large samples. However, if the sample size is too small to be analyzed separately for Cl, Br and I, the RNAA procedure used by SHINONAGA et al.[7] cannot be applied. Such a requirement is often encountered when meteorite samples and rare geological samples such as mantle xenoliths and mineral separates are to be analyzed. For these cases, it is required that all three halogens are determined for a small, single specimen. If three halogens are determined for a single specimen, we can explicitly discuss the fractionation among halogens. This must be very significant, because halogens could be heterogeneously distributed within geological samples.

In this work, we describe the RNAA procedure for trace Cl, Br and I in geological samples. In this procedure, these three halogens are aimed to be determined for a small, single sample. The analytical procedure was first applied to geological standard rock samples in order to appraise the

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procedure. Sedimentary rocks and meteorite samples also were analyzed using this procedure. The analytical results for these samples are shown and some related discussions are made.

Experimental

Samples

Geological standard rock, sedimentary rocks and meteorite samples were analyzed in this work. Some descriptions for these samples are summarized in Table 1. The standard rock samples used were prepared and issued by the Geological Survey of Japan (GSJ). These samples were already powdered and were not subjected to further pulverization. For sedimentary rocks, we used an aliquant of the same samples as analyzed by EBIHARA et al.[4,5] Y-74014 belongs to so-called Antarctic meteorites which were collected on Antarctica and was loaned by the National Institute of Polar Research. Both Y-74014 and Bruderheim were originally received in chips, some of which (about several hundreds mg) were powdered in a clean agate mortar in our lab. For Allende, we used the reference sample (in powder) prepared by the Smithsonian Institution. About 100 mg of each powdered sample was weighed in a small plastic vial, which had been already washed in HNO_3, ethanol and deionized/distilled water. The vial was tightly closed with a lid and then sealed in a clean polyethylene bag.

Table 1. Brief descriptions for samples analyzed in this work

Name	Petrology/mineralogy	Sampling location
Standard rocks		
JB-1	Alkali basalt	Sasebo, Nagasaki, Japan
JR-1	Rhyolite	Wada, Nagano, Japan
JR-2	Rhyolite	Shimosuwa, Nagano, Japan
Sedimentary rocks		
D-41-7	Siltstone	Tomioka, Gunma, Japan
D-41-9	Siltstone	Tomioka, Gunma, Japan
Meteorites		
Allende	Carbonaceous chondrite	Chihuahua, Mexico
Bruderheim	Hypersthene chondrite	Alberta, Canada
Y-74014	Bronzite chondrite	Yamato Mountains, Antarctica

Reference standard, samples and carrier solutions

Reference standard samples were prepared just before each analytical run from the standard solutions which also were newly prepared at each time. We basically followed the preparation method described by SHINONAGA et al.[7] with an appropriate modification. In preparing the reference standard samples, special care was taken for iodine because iodine, which was initially present in form of I^- in the standard solution, could be easily oxidized into I_2 and eventually lost. This was investigated by EBIHARA et al.[8] in detail. Carrier solutions of Cl, Br and I were also prepared using the same reagents as used for the preparation of the standard samples.

Irradiation

Usually, two rock/meteorite samples were irradiated at each run. These samples along with a set of reference standard samples of Cl, Br and I were placed in a polyethylene capsule and irradiated for 10 to 30 minutes in the F-21 or F-24 irradiation site (nominal thermal and fast neutron fluxes: $1.5 \cdot 10^{12}$ and $5 \cdot 10^{11}$ $n \cdot cm^{-2} \cdot s^{-1}$, respectively) of the TRIGA-II reactor at the Institute for Atomic Energy, Rikkyo University. A Cd filter (thickness: 1 mm) was often used in irradiating the samples. Some nuclear data concerned in this study are summarized in Table 2.

Radiochemical separation procedure

We aimed to design a continuous chemical procedure applicable for the determination of Cl, Br and I in a single sample. The chemical procedures for individual halogens[7] were introduced in our procedure. The outline of the chemical scheme is shown in Fig. 1 and described briefly below. The details should be referred to SHINONAGA et al.[7]

After the irradiation, the samples were cooled for a few minutes and the chemical separation immediately started.

Table 2. Nuclear and other related data concerned in this study

Element	Target nuclide	Isotopic abundance, %	Produced nuclide	Cross section,[a] %	Half-life	Main γ-ray energy,[b] keV
$_{17}$Cl	^{37}Cl	24.23	^{38}Cl	0.38/0.32	37.2 min	1642, 2168
$_{35}$Br	^{81}Br	49.31	^{82}Br	2.6/51	353. h	554, 619, 777
$_{53}$I	^{127}I	100	^{128}I	6.2/150	25.0 min	443

[a] Thermal neutron cross sections, followed by resonance integrals.

[b] Underlined γ-rays were used for the determination of corresponding halogens.

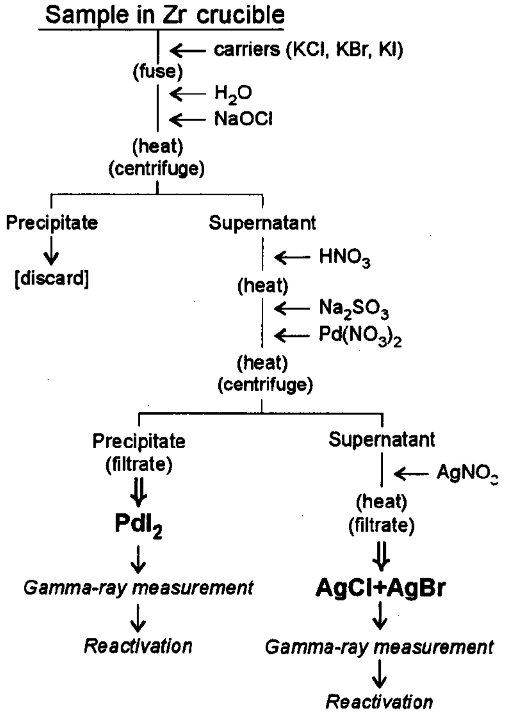

Fig. 1. Scheme for radiochemical separation of Cl, Br and I

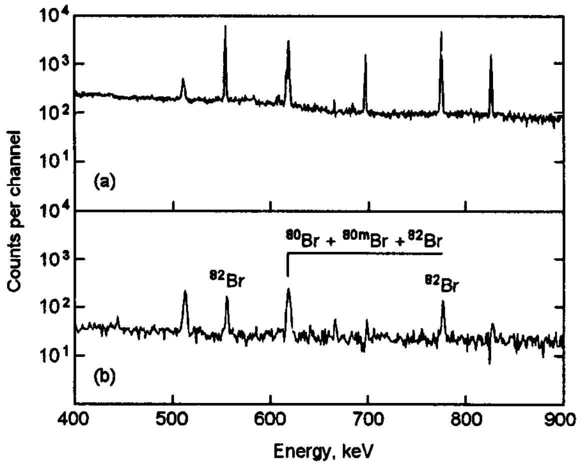

Fig. 2. Gamma-ray spectra of AgCl–AgBr precipitate separated from the sedimentary rock, D-41-7; (a) measured with cooling of half a day after irradiation; (b) measured in 1-2 hours after irradiation

The samples were transferred into Zr crucibles, in which known amounts (by volume) of halogen carrier solutions had been taken and heated to dryness on a hot plate. The samples were fused with NaOH or KOH. After the fusion, the chemical procedure for iodine was initiated. Iodine was finally precipitated as PdI_2 and collected on a filter paper for γ-ray counting. The supernatant was saved for the chemical separation of Cl and Br, which were finally precipitated as AgCl and AgBr, respectively, and collected together on a single filter paper for γ-ray counting. Two samples were usually processed in parallel. Once the chemical separation of iodine was over (normally within an hour), those for Br and Cl began and were completed in next half an hour.

Gamma-ray counting

The γ-ray measurement of ^{128}I started as soon as the PdI_2 samples were prepared. The measurement of the iodine standard sample normally preceeded these measurements. After the measurements of ^{128}I, those for ^{38}Cl followed. These measurements took place at the reactor facility. In this study, bromine was determined by using ^{82}Br rather than a shorter half-lived nuclide ^{80}Br ($T_{1/2}$ = 17.6 min). The AgCl–AgBr precipitates were brought to the Radioisotope Research Laboratory of Tokyo Metropolitan University and were measured. One sample was normally counted for 4–8 hours depending on the acivity of ^{82}Br. As a result, sufficient counts were accumulated as shown in Fig. 2a where a γ-ray spectrum for D-41-7 is shown. If ^{80}Br is used, rather complicated

Table 3. Analytical results for Cl, Br and I contents in GSJ standard rocks[a]

Sample	Cl, ppm	Br, ppb	I, ppb
JB-1	210 ± 20[b]	490 ± 70	36 ± 6
Lit.[c]	175 ± 17[d]	600 ± 30	38 ± 7
JR-1	1180 ± 80	2280 ± 210	80 ± 7
Lit.[c]	990 ± 90	2300 ± 100	75 ± 13
JR-2	990 ± 80	1640 ± 140	69 ± 1
Lit.[c]	1000 ± 10	2200 ± 300	72 ± 7

[a] A Cd-filter was used in irradiating the samples.
[b] Error due to counting statistics (1σ).
[c] Literature values from Reference 7.
[d] Standard deviation (1σ).

Table 4. Analytical results (in ppm) for Cl, Br and I in sedimentary rocks

Sample	Cd filter[a]	HCl	Br	I
D-41-7	with Cd	320 ± 30[b]	2.4 ± 0.2	1.07 ± 0.03
D-41-7	with Cd	320 ± 30	2.4 ± 0.1	1.04 ± 0.04
D-41-7	without Cd	200 ± 20	2.2 ± 0.2	1.07 ± 0.04
Lit.[c]			2.5	0.94
D-41-9	with Cd	340 ± 30	3.40 ± 0.5	1.27 ± 0.04
D-41-9	without Cd	220 ± 20	2.90 ± 0.3	1.15 ± 0.03
Lit.[c]			2.9	1.20

[a] Neutron irradiation with or without using a Cd filter.
[b] Error due to counting statistics (1σ).
[c] Literature values from reference 9 for Br and from reference 4 for I.

procedure for data reduction is needed.[7] Furthermore, as shown in Fig. 2b, a peak at 616 keV emitted by ^{80}Br was not large enough to yield good statistics when the AgCl–AgBr precipitate was measured in our procedure.

Yield determination

Chemical yields were determined by a reactivation method. After the γ-ray measurements were completed, the PdI_2 and AgCl–AgBr precipitates were again irradiated for a few seconds in the RSR irradiation site of the same reactor used for the initial irradiation. The same amounts of the carrier solutions as used for the chemical separation were taken onto the filter papers, dried under a heat lamp and heat-sealed in polyethylene bags. These monitor samples also were irradiated simultaneously along with the chemically separated samples. The same nuclides and γ-rays in the measurements were used to determine the chemical yields, which were found to be ~90%, ~80% and ~60% in average for Cl, Br and I, respectively.

Results and discussion

Evaluation of the proposed analytical procedure

In order to appraise the analytical procedure described in the previous section, several GSJ standard rock samples, for which the Cl, Br and I contents had been reported, were analyzed. The analytical results were given in Table 3, where the literature values[7] are compared. The standard rock samples were all irradiated with a Cd-filter.

The analytical values obtained in this work are mostly consistent with the literature values for Cl, Br and I. It is rather surprising to see that the I values are the most consistent between two sets of data. Our data for Br are systematically lower than the literature values, which were obtained using ^{80}Br instead of ^{82}Br. As already described, the data reduction is rather complicated if ^{80}Br is used; even so it cannot be concluded that systematically high values in the literature[7] are due to this factor. Considering that such a difference is small and Cl and, especially, I values are highly consistent between our data and literature values, we can conclude that the analytical procedure developed in this work is highly effective for the determination of trace Cl, Br and I in a single geological sample.

The effectiveness of a Cd filter in irradiating geological samples

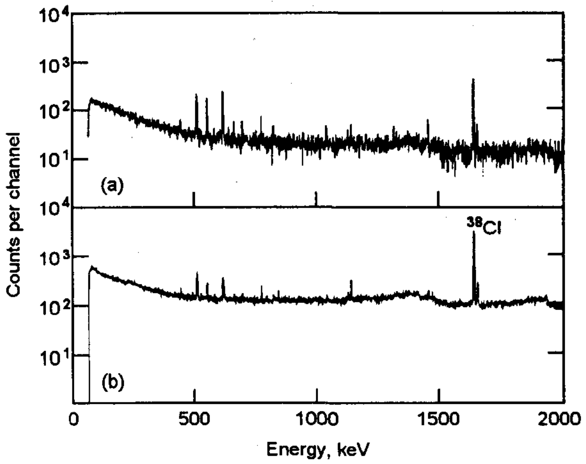

Fig. 3. Gamma-ray spectra of AgCl–AgBr precipitate separated from D-41-7, measured in 1-2 hours after irradiation; (a) irradiated with a Cd filter, (b) irradiated without a Cd filter

The sedimentary rock samples were irradiated in two different ways; with and without a Cd filter. The analytical results are compared in Table 4. Since Cd has a large cross section for thermal neutron, a Cd filter is effective to suppress the production of unwanted radioisotopes such as ^{24}Na and ^{56}Mn. Among the target nuclides of Cl, Br and I (listed in Table 2), ^{127}I has the highest ratio of resonance integral to thermal neutron cross section whereas ^{37}Cl has the lowest ratio, which is similar to those for ^{55}Mn and ^{23}Na. This suggests that the analytical sensitivity of Cl is reduced while those for Br and I are relatively enhanced when a Cd filter is used. In Fig. 3, two γ-ray spectra of the AgCl and AgBr precipitates for D-41-7 irradiated with and without a Cd filter were compared. It is apparent that overall the activities for the sample irradiated with a Cd filter (Fig. 3a) are considerably lower than those for the sample irradiated without a Cd filter (Fig. 3b). As expected, γ-ray peaks emitted by ^{38}Cl are reduced in Fig. 3a compared with those in Fig. 3b. However, two main peaks at 1642 and 2168 keV (not shown) are prominent in both spectra in Fig. 3. This sample contains almost 200 ppm of Cl, which is almost comparable to Cl contents for crustal rocks and major chondritic meteorites, suggesting that Cl can be sensitively determined even using a Cd filter in irradiating the samples.

Two γ-ray spectra for the PdI_2 precipitates prepared from D-41-7 are shown in Fig. 4, where the spectra for the sample irradiated with a Cd filter (Fig. 4a) and without a Cd filter (Fig. 4b) are compared. It is noticeable that a peak at 443 keV emitted by ^{128}I is more prominent in Fig. 4a than that in Fig. 4b. It can be also pointed out that a large peak appears at 1642 keV emitted by ^{38}Cl as shown in Fig. 4b. Apparently, some Cl would be precipitated with PdI_2. Since ^{38}Cl emits two prominent γ-rays having much higher energy than ^{128}I, the presence of ^{38}Cl increases the background level in the low energy region where a peak from ^{128}I emerges and, in tern, decreases the analytical sensitivity of iodine. Igneous rocks are relatively depleted in iodine compared with sedimentary rocks (see Tables 3 and 4). Thus, the irradiation using a Cd filter is highly advantageous to those samples where iodine is relatively depleted compared with chlorine.

In Table 4, there seems to be an apparent difference in the Cl data between two groups of the samples irradiated with and without a Cd filter; Cl values for the samples irradiated with a Cd filter are systematically higher than those for the samples irradiated without a Cd filter. As Cd absorbs thermal neutron, high energy neutron-induced reaction [such as (n,p) and (n,α) reactions] rather than a neutron/capture reaction [(n,γ) reaction] could be responsible for such a systematic difference. A possible reaction is $^{41}K(n,\alpha)^{38}Cl$. The contribution of this reaction to the Cl data was once evaluated;[7] 1 g K corresponds to 64 μg Cl at Cd/Au ratio of 3.5. Such a contribution is elevated if samples are irradiated with a Cd filter. Although fairly large errors are introduced, there also seems to be a systematic difference in the Cl data for JB-1 and JR-1 between our data and literature values which were obtained without a Cd filter. The degree of the contribution due to $^{41}K(n,\alpha)^{38}Cl$ reaction depends on the K/Cl ratio for the corresponding sample. Potassium contents in the sedimentary rocks were determined by INAA; 3.4% for D-41-7 and 3.0% for D-41-9. The K/Cl ratios for D-41-7 and D-41-9 (170 and 136, respectively) are higher than those for JB-1 and JR-1 (68 and 37, respectively), suggesting that the contribution of $^{41}K(n,\alpha)^{38}Cl$ reaction becomes more significant for the sedimentary rocks than that for the standard rocks. Assuming that the difference in Cl contents of D-41-7 and D-41-9 between two groups (with and without a Cd filter) are due to the $^{41}K(n,\alpha)^{38}Cl$ reaction, we obtain that 1 g K corresponds to 3.75 mg Cl for the irradiation with a Cd filter at the F-21 or F-24 site. Using this value, Cl contents for the standard rocks are recalculated and found to be 165 ppm for JB-1, 1040 ppm for JR-1 and 850 ppm for JR-2. The corrected values for JB-1 and JR-1 are more consistent with the literature values than the uncorrected values. The corrected value for JR-2, however, is lower than the literature value. Thus, the contribution of $^{41}K(n,\alpha)^{38}Cl$ seems to be highly responsible for the systematic increment of Cl values for the samples irradiated with a Cd filter. This problem is not completely resolved yet and, therefore, needs to be investigated.

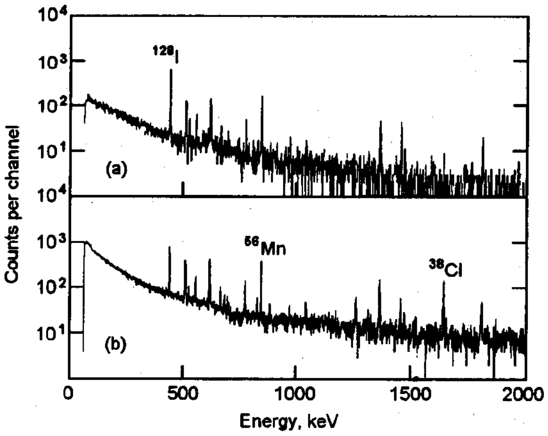

Fig. 4. Gamma-ray spectra of PdI_2 precipitate separated from D-41-7, measured in an hour after irradiation; (a) irradiated with a Cd filter, (b) irradiated without a Cd filter

Table 5. Analytical results for Cl Br, and I contents in chondritic meteorites[a]

Sample	Classification[b]	Cl, ppm	Br, ppb	I, ppb
Allende	C3, fall	320 ± 30[c]	1620 ± 290	212 ± 30
Lit.[d]		316, 265	1540, 1520	160
Bruderheim	L6, fall	137 ± 14	1350 ± 160	24 ± 14
Lit.[e]		27–212	120–390	30–76
Y-74014	H6, find	750 ± 40	770 ± 90	2260 ± 60
Lit.[e]		7–210	140–780	67–120

[a] A Cd-filter was used in irradiation of samples.

[b] C3, L6 and H3 according to Reference 10; fall – observed fall; find – unobserved fall.

[c] Error due to counting statistics (1σ).

[d] Literature values from Reference 11 for Cl, Br and from Reference 4 for I.

[e] Literature values (ranges for corresponding groups of meteorites) from Reference 12.

Application of the analytical procedure to meteorite samples

The RNAA procedure for the determination of Cl, Br and I was applied to several meteorite samples. As meteorite samples are precious in general, it is advisable to used small portions in the chemical analysis. For such a concern, the present method can be a great advantage. The results are shown in Table 5. Even at present, the cosmochemistry of halogens are poorly understood, mainly because halogens have been scarcely determined with great care. We may compare our data with the literature values obtained for Allende; our values for Cl, Br and I are mostly consistent with the literature values. For the other two meteorite samples, only ranges of the reported values for corresponding groups (L and H) are shown. It can be noted that the reported values are spread over wide ranges for all halogens. It is not certain whether these wide ranges are indigenous or artificial (due to contamination or analytical errors). Considering that similar scatterings observed for Br and, especially, for I in CI chondrites seem to be superficial, possibly due to analytical problem, it may be safe not to emphasize the cosmochemical significance for such large discrepancies.

Some of our data are apparently out of the ranges namely the Br value for Bruderheim and Cl and I values for Y-74014. No explanation can be thought of for the former. An upper limit (390 ppb) for the corresponding group (L group) is significantly lower than those for the other ordinary chondrite groups (780 ppb for H group and 870 ppb for LL group).[12] As our value of 1350 ppb is still higher than these upper limits, contamination and/or analytical problem could be a possible explanation. On the other hand, Cl and I values for Y-74014 are 3.6 and 19 times higher than their limits for H chondrites, respectively. Y-74014 is an Antarctic meteorite, recovered on Antarctica. It is now well acknowledged that Antarctic meteorites suffer from contamination on Antarctica to some extent. The surface must be contaminated most seriously but some contaminants can migrate into the interior portion. Iodine was observed to be overabundant in some Antarctic meteorites.[13,14] Chlorine contents were also confirmed to be systematically high in Antarctic meteorites, but the degree of enrichment for Cl is lower than that for iodine.[6] Apparently, high abundances of I and Cl in Y-74014 were caused by the terrestrial contamination on Antarctica after the meteorite fell.

Conclusions

A chemical scheme for RNAA of Cl, Br and I applicable to rock samples, such as igneous silicates, sedimentary rocks and meteorites were suggested. In this scheme, Cl, Br and I are determined using neutron-captured radionuclides, ^{38}Cl, ^{82}Br and ^{128}I, respectively. The RNAA scheme was applied to some geological standard rocks. The analytical results of Cl, Br and I were in good agreement with their literature values, suggesting that the procedure presented is highly effective in determining trace Cl, Br and I in geological materials. In the proposed scheme, a Cd filter is used in irradiating the rock samples. This leads to the decrease in the production of unwanted radionuclides, mainly ^{24}Na and ^{56}Mn, and, as a result, the increase in the relative analytical sensitivities for Br and, especially, for I. Although the production of ^{38}Cl is suppressed, Cl can be sensitively determined by this scheme because Cl is relatively abundant compared with Br and I. If samples contain high K compared with Cl, the contribution of ^{38}Cl produced by the reaction ^{41}K(n,α)^{38}Cl becomes significant and should be corrected. Meteorite samples also were analyzed for Cl, Br and I using the RNAA procedure described in this work. It was confirmed that an Antarctic ordinary chondrite (Y-74014) had anomalously high iodine content. The abundancy of Cl is also higher than the (normal) range for the corresponding group of meteorites. Both I and Cl must have deposited onto the meteorite surface on Antarctica and then migrated into the interior portion over a long period of time.

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