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Articles

Accurate determination of three halogen elements (Cl, Br, and I) in U.S. Geological Survey geochemical reference materials by radiochemical neutron activation analysis and an exhaustive comparison with literature data: a review

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Since trace amounts of three halogens (chlorine, bromine, and iodine) in 17 U.S. Geological Survey (USGS) geochemical reference materials were recently determined using radiochemical neutron activation analysis (RNAA) by the authors, the RNAA data of the three halogens were exhaustively compared with corresponding literature data and some inconsistencies were found. Those inconsistencies can be explained by the loss of iodine in pretreatment of the solution that is subjected to inductively coupled plasma mass spectrometry (ICPMS), incomplete quantitative collection of chlorine in pyrohydrolysis preconcentration for ICPMS, and overestimation due to the interference in the ICP double focusing sector field MS (ICPSFMS) instrument. Using the relative standard deviation (RSD) that accompanies the mean value in each USGS material, homogeneity of halogens in the USGS materials has been discussed.

1. Introduction

When determining the elemental composition of geochemical and cosmochemical samples, it is usual to search for any scientific implications related to those samples by consulting chemical, geochemical and cosmochemical properties of the elements of interest. For halogens, their chemical properties have been extensively studied and are known to vary from element to element. However, geochemical and cosmochemical properties of halogens are poorly understood because accurate and reliable data for halogen abundance have been rarely reported for samples such as crustal rock, mantle material and meteorites. Iodine, among the halogens, is the most informative element in discussion of the geochemical circulation of crustal material because geochemists often discuss the geochemical circulation of iodine in the earth's surface, oceanic crust, continental crust, and mantle.[1] Iodine is also of high importance and of particular interest for cosmochemists when they discuss the cosmochemical behavior of its extinct nuclide ^{129}I (half-life of 15.7 million years) in the early solar system. Since halogens differ in volatility from element to element, their content and relative abundance are highly informative when discussing the petrogenesis of samples.[2] Thus the scarcity of reliable data for geochemical and cosmochemical samples hinders the geochemical and cosmochemical discussion of halogens.

There are few accurate and reliable data of halogens in terrestrial rock samples, as can be witnessed in the data library for geological rock samples prepared by United States Geological Survey (USGS) (at http://crustal.usgs.gov/geochemical_reference_standards/powdered_RM.html). Various kinds of rocks within the database are recorded with only information values or a few recommended values for halogen concentration, but for most of the rocks no values are listed. This deficit is probably related to difficulties in determining trace amounts of halogens within these samples. Recently we have improved the radiochemical neutron activation analysis (RNAA) procedure for trace amounts of halogens (chlorine, bromine and iodine) and have demonstrated that our RNAA data for Br and I are more reliable and accurate than the data obtained by inductively coupled plasma mass spectrometry (ICPMS) coupled with pyrohydrolysis preconcentration.[3] Then, our RNAA procedure was applied to 17 USGS geochemical reference materials and trace concentrations of three halogens (chlorine, bromine and iodine) were determined.[4] As some of the 17 reference materials have literature values for halogens, our RNAA values were exhaustively compared with those literature values. From the comparison, the consistency of the two data sets was evaluated and the causes of inconsistency between them were investigated. In addition, the homogeneity of each reference material was discussed, based on the relative standard deviation (RSD) that accompanies the mean value in each reference material.

2. Procedure of RNAA

2.1. Sample preparation. The 17 USGS geochemical reference materials are listed in Table 1, together with additional information. The materials were all obtained commercially. All the materials were in powder and were not subjected to any additional treatment such as drying. About 20-300 mg of each powder sample was weighed, inserted into a clean, small plastic vial that was sealed and then re-sealed inside a clean polyethylene bag. Chemical standard solutions of the three halogens of interest were prepared for use in the quantification by RNAA. An appropriate amount of each halogen solution (containing 90 µg of chlorine, 50 µg of bromine, and 10 µg of iodine) was dropped onto a paper disk (17 mm diameter, ADVANTEC, Filter Paper No.7), weighed, dried under a heat lamp and doubly sealed into polyethylene bags. Extreme care was taken to prevent loss of iodine when preparing the iodine reference sample.[5,6] Halogen standard solutions were prepared by dissolution of KCl (99.9% Wako Pure Chemical Industries, Ltd., hereafter Wako Chemical), KBr (99.9% Wako Chemical), and KI (reagent special grade Wako Chemical) for Cl, Br, and I respectively.

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TABLE 1: USGS geochemical reference materials analyzed by RNAA

Sample code	sample type	sampling location
BHVO-2	basalt	pahoehoe lava, the Halemaumau crater, Hawaii, USA
BCR-2	basalt	Bridal Veil Flow Quarry, Oregon, USA
BIR-1a	basalt	interglacial lava flows, Reykjavik, Iceland
W-2a	diabase	the Bull Run quarry, Centreville, Virginia, USA
AGV-2	andesite	eastern side of Guano Valley, Lake County, Oregon, USA
DNC-1a	dolerite	Braggtown quarry, North Carolina, USA
GSP-2	granodiorite	Silver Plume quarry, Colorado, USA
DTS-2b	dunite	Twin Sisters Range, Washington, USA
QLO-1a	quartz latite	Lake County, Oregon, USA
COQ-1	carbonatite	Oka complex, Montreal, Canada
CLB-1	coal	Lower Bakerstown coal bed, Maryland, USA
SDC-1	mica schist	Washington D.C. area, USA
Nod-P-1	manganese nodule	Pacific Ocean (14° 50' N, 124° 28' W)
Nod-A-1	manganese nodule	Atlantic Ocean (31° 02' N, 78° 22' W)
SBC-1	marine shale	Westmoreland County, Pennsylvania, USA
SGR-1b	shale rock	Green River, Wyoming, USA
DGPM-1	disseminated gold ore	Pinson mine, Nevada, USA

TABLE 2: Nuclear data of radioactive nuclides concerned in RNAA

Element	Target nuclides	Isotopic abundance (%)	Cross section[a] (barn)	Produced nuclide[b]	Half life	γ-ray energy[c] (keV)
$_{17}$Cl	^{37}Cl	24.24	0.43	^{38}Cl	37.18 m	1642, 2168
$_{35}$Br	^{81}Br	49.31	2.64	^{82}Br	35.34 h	776, 554
$_{53}$I	^{127}I	100	6.2	^{128}I	25.0 m	443

[a] Neutron capture cross-section for thermal neutrons.
[b] Produced by neutron capture reaction.
[c] Used in gamma-ray spectrometry for quantification of elements.

2.2. Neutron irradiation. Two USGS materials, together with a set of three reference halogen samples, were irradiated for 10 min with a thermal neutron flux of 3.3×10^{12} cm^{-2} s^{-1} at Kyoto University Research Reactor Institute (KURRI), with the exception that a 1 min irradiation was used in the one experimental run for the Manganese Nodule sample (Nod-P-1). When a high flux reactor is used, samples need to be cooled to prevent iodine loss,[7] however no such cooling was required with the neutron flux used in our previous study.[4] After irradiation, the USGS materials were held for a few minutes to enable the decay of ^{28}Al, and were then subjected to radiochemical separation of neutron-activated halogen radionuclides (^{38}Cl, ^{82}Br, and ^{128}I).

2.3. Radiochemical purification procedure, gamma ray measurement and yield determination in RNAA. The procedure of radiochemical purification for halogens, gamma-ray measurement and yield determination was essentially the same as that described in our previous work[3] and is briefly outlined here. An irradiated reference material is transferred to the nickel crucible, which contains a known amount of each halogen carrier and a manganese carrier, and is fused with NaOH. The fused cake is digested in water and the hydroxide precipitate is separated from the supernatant. A few mg of sodium sulfite (solid) is then added to the supernatant solution containing the halogens in order to prevent the loss of iodine and facilitate the neutralization of the supernatant in the next step. From the supernatant, which is made slightly acidic by adding 6M HNO_3, an initial precipitate of PdI_2 is formed by adding $Pd(NO_3)_2$ solution. Then a mixture of AgCl+AgBr precipitates is formed by adding $AgNO_3$ solution to the supernatant containing chlorine and bromine. The PdI_2 and the mixture of AgCl+AgBr precipitates are washed with a sufficient amount of 0.2M HNO_3. Those precipitates are subjected to gamma-ray counting with a Ge semiconductor detector (ORTEC GEM-50195). The use of the manganese carrier, the addition of sodium sulfite as a solid and the washing by 0.2M HNO_3 improve the analytical sensitivity in this RNAA procedure and the effects are described elsewhere in detail.[3] The reagents used here were of reagent special grade (Wako Chemical).

For the determination of iodine and chlorine, the radioactivity of ^{128}I and ^{38}Cl was measured by using a Ge detector for 300–1,000 s and 500–1,000 s, respectively. For bromine, ^{82}Br was measured for 50,000–100,000 s on the following few days after the radiochemical procedure. The three halogen reference samples were measured individually after the completion of the measurements, for for 200-500 s for Cl and I, and 1,000–2,000 s for Br.

Chemical yields of the three halogens were determined by the reactivation method. After the completion of all gamma-ray measurements, a set of 4-6 samples (either of PdI_2 or AgBr+AgCl mixture), along with reference samples for the corresponding halogens, were irradiated for 10 sec at the same irradiation facility as used earlier. The radioactivity of ^{38}Cl, ^{82}Br, and ^{128}I was measured for 100 s for each nuclide. The nuclear data related to the NAA of the halogens are summarized in Table 2.

3. Results and Discussion

3.1. Cl, Br, and I contents in USGS reference materials. Each material was analyzed two to four times (individual values are tabulated in Appendix). For seven USGS materials which were analyzed twice, the two analytical values for the three halogens are in agreement within uncertainties, and mean values between those two analytical values are summarized in Table 3. An uncertainty quoted for each mean value between two analytical values is just the value calculated from two individual uncertainty values accompanied by the two analytical values. Since ten USGS materials besides the seven described above have three or four analytical values for the three halogens, mean values with one sigma of standard deviation for those ten materials are also summarized in Table 3, with the exception that the bromine value in BCR-2 is the mean of two analytical values. The chlorine and bromine contents vary from 5.64 mg kg^{-1} for BIR-1a (basalt) to 4,410 mg kg^{-1} for Nod-A-1 (manganese nodule), and from 0.039 mg kg^{-1} for BIR-1a (basalt) to 52.1 mg kg^{-1} for CLB-1 (coal), respectively. The iodine content varies from 0.041 mg kg^{-1} for BIR-1a (basalt) to 599 mg kg^{-1} for CLB-1 (coal). The variation is thus over two, three and four orders of magnitude for chlorine, bromine and iodine, respectively, confirming that the RNAA procedure applied in our previous study[4] has a much larger dynamic range in determining the three halogens in geochemical powder materials.

When the two shale samples (SBC-1 and SGR-1b) were fused with NaOH in radiochemical purification for halogens, a flame was sometimes found in nickel crucible. Since those shale materials have organic form of carbon, the flame must have been derived by the combustion of organic compounds included in those shale materials. The two samples were repeatedly analyzed (3 and 2 times for SBC-1 and SGR-1a, respectively) and reasonable agreements were confirmed among duplicate data for individual halogens. Probably, the samples ignited after being melted with NaOH and the equilibrium between neutron-capturing radioactive nuclides and stable nuclides was established among individual halogens. Nevertheless, since a possibility of loss of stable halogens before isotopic equilibration cannot be denied, it may be safe to regard our data as lower limits.

The drying instructions for the manganese nodule samples (Nod-P-1 and Nod-A-1), indicate that they can absorb up to 10% by weight of moisture when exposed to air overnight. As already mentioned, those samples were not dried before

TABLE 3: Cl, Br and I Content in USGS Geochemical Reference Materials Analyzed by RNAA[a] and from the Literature

Sample		Cl (mg kg^{-1})	Br (mg kg^{-1})	I (mg kg^{-1})
DTS-2b	**RNAA (n = 3)**	**10.7 ± 0.3**	**0.093 ± 0.002**	**0.789 ± 0.148**
COQ-1	**RNAA (n = 2)**	**27.5 ± 1.1**	**0.071 ± 0.006**	**0.331 ± 0.094**
CLB-1	**RNAA (n = 4)**	**1190 ± 150**	**52.1 ± 6.8**	**599 ± 52**
SBC-1	**RNAA (n = 3)**	**24.9 ± 2.4** [b]	**0.355 ± 0.005** [b]	**5.07 ± 0.19** [b]
DGPM-1	**RNAA (n = 2)**	**315 ± 12**	**0.843 ± 0.033**	**3.55 ± 0.13**
W-2a	**RNAA (n = 4)**	**220 ± 22**	**0.309 ± 0.040**	**0.405 ± 0.071**
	Certificate of Analysis	190 [c]	- [d]	- [d]
SGR-1b	**RNAA (n = 2)**	**22.0 ± 1.0** [b]	**0.409 ± 0.020** [b]	**2.16 ± 0.15** [b]
	Certificate of Analysis	32 [c]	- [d]	- [d]
DNC-1a	**RNAA (n = 4)**	**18.1 ± 3.2**	**0.063 ± 0.013**	**0.102 ± 0.018**
DNC-1	INAA[10]	- [d]	<0.5	- [d]
	Compiled[8]	37 [e]	- [d]	- [d]
	Certificate of Analysis	60 [c]	- [d]	- [d]
	XRF[9]	60 ± 4	- [d]	- [d]
QLO-1a	**RNAA (n = 3)**	**244 ± 16**	**1.03 ± 0.05**	**0.741 ± 0.088**
	Compiled[8]	219[e]	2.07 [c]	- [d]
	Certificate of Analysis	220 ± 18[e]	2.1 [c]	- [d]
	INAA[10]	- [d]	1.08 ± 0.11	- [d]
SDC-1	**RNAA (n = 2)**	**30.0 ± 1.4**	**0.111 ± 0.011**	**0.187 ± 0.034**
	Compiled[8]	32 [e]	0.097 [c]	- [d]
	INAA[10]	- [d]	<0.5	- [d]
	Certificate of Analysis	32 [c]	- [d]	- [d]
GSP-2	**RNAA (n = 3)**	**363 ± 29**	**0.117 ± 0.020**	**0.075 ± 0.018**
	Noble gas[18]	381 ± 29	0.077 ± 0.023	0.020 ± 0.006
	various methods[11]	400 ± 10	- [d]	- [d]
BHVO-2	**RNAA (n = 2)**	**104 ± 4**	**0.240 ± 0.013**	**0.307 ± 0.050**
	IC[12]	150 ± 21	- [d]	- [d]
	ICPMS[12]	- [d]	0.269, 0.277	0.016 ± 0.002
	IC[13]	81 ± 11	- [d]	- [d]
	ICPMS[13]	- [d]	0.29 ± 0.10	0.020 ± 0.012
	IC[14]	89 ± 7	- [d]	- [d]
	IC[17]	84 ± 5	- [d]	- [d]
	Noble gas[18]	102 ± 1	0.259 ± 0.005	0.070 ± 0.004

TABLE 3: Cl, Br and I Content in USGS Geochemical Reference Materials Analyzed by RNAA[a] and from the Literature (Continued)

Sample		Cl (mg kg^{-1})	Br (mg kg^{-1})	I (mg kg^{-1})
BCR-2	**RNAA (n = 3)**	**112 ± 1**	**0.144 ± 0.008**[f]	**0.082 ± 0.022**
	IC[12]	98 ± 8	-[d]	-[d]
	ICPMS[12]	-[d]	0.157, 0.175	0.017 ± 0.004
	IC[14]	89 ± 6	-[d]	-[d]
	IC[17]	94 ± 4	-[d]	-[d]
	XRF[15]	101	-[d]	-[d]
	Noble gas[18]	106.4 ± 0.3	0.192 ± 0.022	0.058 ± 0.002
BIR-1a	**RNAA (n = 4)**	**5.64 ± 0.43**	**0.039 ± 0.012**	**0.041 ± 0.009**
	Noble gas[18]	11	0.037	0.007
BIR-1	IC[12]	44	-[d]	-[d]
	IC[17]	5.7 ± 0.3	-[d]	-[d]
	ICPMS[12]	-[d]	0.065 ± 0.026	0.014 ± 0.002
	INAA[10]	-[d]	<2	-[d]
	Compiled[8]	26[g]	-[d]	-[d]
	Certificate of Analysis	26[c]	-[d]	-[d]
AGV-2	**RNAA (n = 2)**	**72.8 ± 2.7**	**0.101 ± 0.007**	**0.197 ± 0.038**
	IC[12]	75 ± 3	-[d]	-[d]
	ICPMS[12]	-[d]	0.107, 0.145	0.007 ± 0.001
	IC[14]	61 ± 3	-[d]	-[d]
	Noble gas[18]	83	0.244	0.080
Nod-P-1	**RNAA (n = 4)**	**1380 ± 140**	**5.93 ± 0.76**	**157 ± 17**
	ICPSFMS[16]	-[d]	30.3 ± 2.2	31.4 ± 0.3
Nod-A-1	**RNAA (n = 2)**	**4410 ± 160**	**14.8 ± 0.5**	**367 ± 9**
	ICPSFMS[16]	-[d]	40.9 ± 0.7	47.7 ± 3.2

[a] Mean values followed by standard deviations (1σ) (n=3, 4). Mean values followed by an uncertainty which is simply the value calculated from two individual uncertainty values (n=2).

[b] It may be safe to regard RNAA data as lower limits (see text for details).

[c] Information values.

[d] Not reported.

[e] Recommended values

[f] n=2.

[g] Proposed values.

RNAA because they are usually stored in a desiccator. If those samples absorbed up to 10% by weight of moisture prior to RNAA, it would be safe to enhance our concentration data by a factor of 1.1 to compensate for moisture.

In Table 3, our data are compared with the values in the literature,[8-18] although the data usable for the comparison of our data are still limited in number, as is evident in Table 3. Literature values for chlorine include the data obtained by ion chromatography (IC) or x-ray fluorescence analysis (XRF) and compiled data such as information, recommended and proposed values, whereas those for bromine include the data obtained by ICPMS or instrumental neutron activation analysis (INAA) and compiled data as information values. The compiled data for chlorine and bromine were reported by Reference[8] and in the certificates of analysis for individual USGS materials. Literature values for iodine were obtained by ICPMS. In the cases where IC or ICPMS were used, pyrohydrolysis concentration for halogen or the other chemical treatment was performed. Additionally, halogen concentration measurements by the noble gas method are reported,[18] and these results are also included in Table 3. A comparison of our data with the literature data is discussed in the following sections.

3.2. Comparison of RNAA data with literature data for USGS reference materials other than basalt, andesite and manganese nodule materials. Eleven USGS materials other than basalts (BHVO-2, BCR-2, BIR-1a), andesite (AGV-2), and manganese nodules (Nod-P-1 and Nod-A-1) are presented in this section. Five USGS materials out of 11 have no literature values for halogens: DTS-2b (dunite), COQ-1 (carbonatite), CLB-1 (coal), SBC-1 (marine shale) and DGPM-1 (disseminated gold ore). Two USGS materials out of 11 have only information values for chlorine, W-2a (diabase) and SGR-1b (shale rock), where RNAA values are consistent with the information values within uncertainties of 30%. Three USGS materials, DNC-1a (dolerite), QLO-1a (quartz latite) and SDC-1 (mica schist), have some kind of literature values, and RNAA values are approximately consistent with those literature values, except for chlorine in DNC-1a and the compiled bromine values in QLO-1a. Since DNC-1a is a second bottling of the original DNC-1 material, the chemical composition of DNC-1 can be used in the comparisons with DNC-1a. For chlorine in DNC-1a (DNC-1), the literature values are two to three times higher than the RNAA value, which is a mean value of replicate analysis results. In our RNAA results, the chlorine value for DNC-1a has relatively larger uncertainty than those for BIR-1a and DTS-2b which have chlorine contents lower than that of DNC-1a. In general, a larger uncertainty is to be obtained from a measured value with poorer counting statistics, corresponding to a lower elemental content. In this case, however, variation of the four measured values in DNC-1a (shown in Appendix) causes the larger uncertainty in the chlorine value for DNC-1a, suggesting heterogeneity of the halogen distribution in DNC-1a (and/or DNC-1). The heterogeneity of halogen in the USGS materials analyzed in our previous study[4] is discussed in detail in the last section before the conclusion. Such heterogeneity may be responsible for inconsistency in the chlorine values between RNAA and the literature data, although the quality of XRF data in DNC-1[9] is doubtful. For DNC-1a and SDC-1, the bromine values obtained by RNAA are consistent with their upper limit values obtained by INAA,[10] and for QLO-1a, the bromine value obtained by RNAA is in good agreement with that by INAA.[10] This may suggest that the data quality of two values from RNAA and INAA for QLO-1a is better than that of the two information values, and it is entirely reasonable that RNAA data have higher sensitivity and accuracy than INAA data. For the final material, GSP-2, data obtained by RNAA and noble gas method agree within uncertainties for both chlorine and bromine, whereas for iodine the value of the noble gas method is lower than the RNAA value. This inconsistency for iodine between the noble gas method and RNAA is also found in the basalt and andesite samples as shown in the next section. To elucidate the tendency of the noble gas method giving lower values than the RNAA method, further studies along this line are in progress. Regarding GSP-2, the RNAA value is consistent with the literature value of chlorine obtained by various methods[11] within uncertainties. Since we have demonstrated that the RNAA procedure applied in our previous study[4] is effective in determining halogens in geological rock samples, we envisage that our RNAA data will be reflected in any future compilation in the establishment of a database of USGS geochemical reference materials.

3.3. Comparison of RNAA data with literature data for BHVO-2, BCR-2, BIR-1a and AGV-2.

The three basalts (BHVO-2, BCR-2 and BIR-1a) and the andesite (AGV-2) analyzed using RNAA in our previous study[4] were also analyzed using IC[12-14,17] for chlorine, ICPMS[12, 13] for bromine and iodine, and the noble gas method[18] for the three halogens. First, our RNAA data are compared with the IC and ICPMS data. As the pretreatment of IC and ICPMS, the three halogens were preconcentrated using pyrohydrolysis, in which the rock materials are heated with vanadium pentoxide under an oxygen flow in an electric furnace and the expelled halogens are then trapped into an alkaline solution. Each experimental condition of the pyrohydrolysis is described in the literature.[12-14, 17] In terrestrial rock materials, halogens are expected to be present in the form of a monovalent anion, such as F^-, Cl^-, Br^-, and I^-. In pyrohydrolysis, some halogens (at least, chlorine, bromine and iodine) are expected to be mostly oxidized to gaseous halogen molecules (dimer) like Cl_2, Br_2 and I_2,[19, 20] which are trapped in alkaline solution, where they are probably in the form of a monovalent anion. The solution is then introduced into the IC and ICPMS instruments. In the analytical procedure of Reference[12], the solutions obtained from pyrohydrolysis are slowly evaporated in order to concentrate the solution by a factor of around ten. Reference[13] used the same analytical procedure as Reference[12].

As already mentioned, the USGS materials were each analyzed two to four times in our previous study[4] and the values obtained[4] were reasonably consistent with one another for each halogen. Our RNAA data for BHVO-2, BCR-2, BIR-1a and AGV-2 are mostly consistent with the literature data for chlorine and bromine, but not for iodine. As for bromine in BHVO-2, BCR-2 and AGV-2, where two ICPMS values were reported by Reference[12]. The RNAA values are consistent with one of those two values within uncertainties of 10%. For bromine in BIR-1a, using the chemical composition of BIR-1 for the comparison in the same way that DNC-1 was used to represent DNC-1a, our RNAA value is also in agreement with the ICPMS value reported by Reference[12] within uncertainties. The bromine content of this material is lowest among the 17 USGS materials analyzed in our previous study[4]. As for iodine in BHVO-2, BCR-2, BIR-1a and AGV-2, however, the RNAA values are not consistent with ICPMS values reported by Reference[12] and Reference[13]. The RNAA values vary from 0.041 mg kg^{-1} for BIR-1a to 0.307 mg kg^{-1} for BHVO-2, whereas the ICPMS values are much lower. The ICPMS values were also very similar, spanning a much smaller range, especially in BHVO-2, BCR-2 and BIR-1, where they varied from 0.014 mg kg^{-1} to 0.020 mg kg^{-1}. Such an inconsistency between RNAA values and ICPMS values may be due to a loss of iodine during the preconcentration in the analytical procedure.

Presumably the loss of iodine could have occurred in the procedure used by Reference[12] and by Reference[13], where the solutions obtained from pyrohydrolysis were slowly evaporated in order to concentrate the solution by a factor of around ten. Bulk iodine could be lost in the solutions during the concentration by evaporation, such that the amount of residual iodine in the concentrated solutions could be very similar. This suggests that the concentration of the solution after pyrohydrolysis by evaporation should not be used for the determination of iodine.

To discuss the chlorine content, our RNAA values were compared to the IC values of References[12-14, 17] for BHVO-2, BCR-2, BIR-1a and AGV-2 in Table 4. The ratios of IC values to RNAA values given in the table are plotted in Figure 1. In calculating the mean ratio, a value for BHVO-2 reported by Reference[12] was ruled out using the outlier test under the 2σ-criterion. An uncertainty quoted for each ratio is simply the value calculated from two individual uncertainty values accompanied by RNAA and IC data. Although the IC values are very consistent with the RNAA values for BIR-1a (BIR-1) and AGV-2 reported by Reference[17] and Reference[12], respectively, it can be seen that the IC data show systematically lower values than the RNAA data by a factor of 0.87±0.09. It is presumed that the quantitative collection of chlorine cannot always have been achieved in the pyrohydrolysis procedure used by References[12-14, 17]. A similar situation for bromine and iodine in sedimentary rock reference samples has been pointed

TABLE 4: Ratio of IC Value to RNAA Value

sample	IC/ RNAA [a]
BHVO-2(Michel and Villemant)	1.44 ± 0.21
BHVO-2(Balcone-Boissard et al)	0.78 ± 0.11
BHVO-2(Wang et al)	0.85 ± 0.08
BHVO-2(Shimizu et al)	0.81 ± 0.06
BCR-2(Michel and Villemant)	0.88 ± 0.07
BCR-2(Wang et al)	0.80 ± 0.06
BCR-2(Shimizu et al)	0.84 ± 0.04
BIR-1a / BIR-1(Shimizu et al)	1.01 ± 0.09
AGV-2(Michel and Villemant)	1.03 ± 0.06
AGV-2(Wang et al)	0.84 ± 0.05
Arithmetic mean	0.87 ± 0.09 [b]

[a] RNAA and IC values from Table 3.

[b] A ratio for BHVO-2 (Michel and Villemant) is ruled out (see text for details). An uncertainty means a standard deviation (1σ).

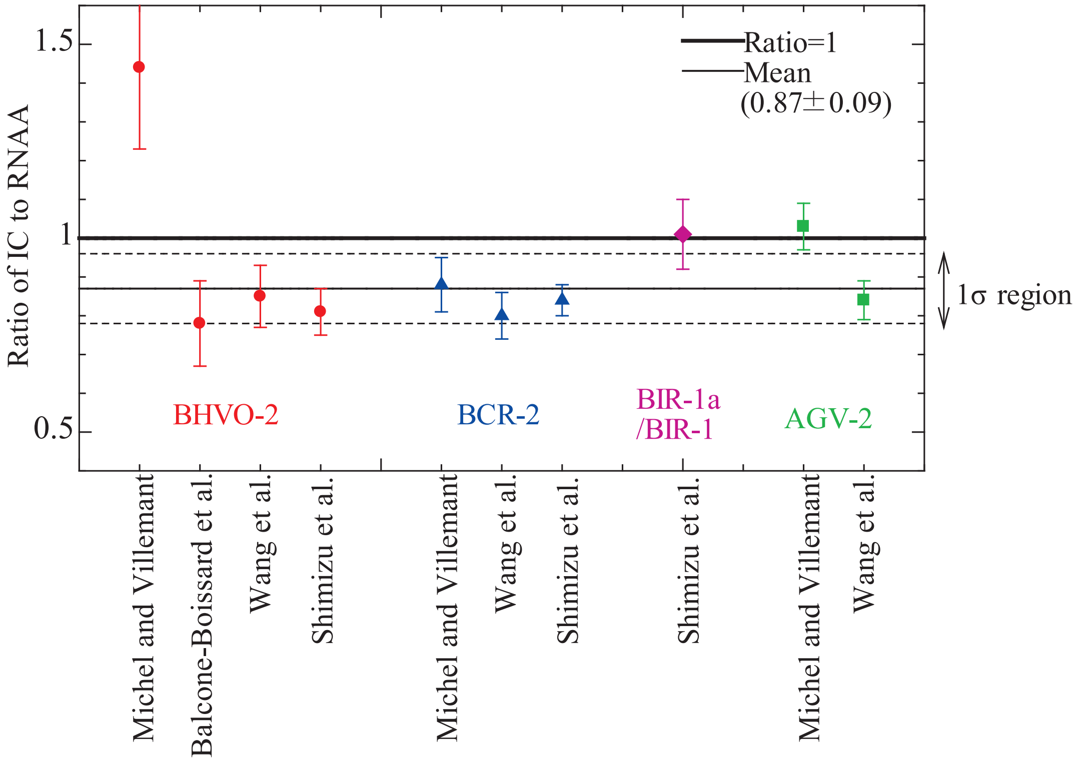

Figure 1. Chlorine concentration ratio, IC value over RNAA value.

out in our previous work.[3] This suggests a limitation of the pyrohydrolysis procedure in the determination of halogens (especially chlorine) by IC. It may be noted, however, that RNAA and IC data agree within 15% for chlorine, as shown by the mean value of individual ratios, and further that IC coupled with pyrohydrolysis can work well for such studies where only rough abundances of halogens are required and for materials with chlorine content varying from 5 mg kg^{-1} (BIR-1a) to around 100 mg kg^{-1} (such as in BHVO-2 and BCR-2). An advantage of choosing RNAA for halogen analysis is noted elsewhere.[3]

Comparing the values of the noble gas method with the RNAA values in BHVO-2 and BCR-2, the former values are consistent with the latter ones within uncertainties of 3σ for chlorine and bromine in BHVO-2 and for bromine and iodine in BCR-2. As for chlorine in BCR-2 both of the two values agree within 10%, although that of the noble gas method is lower than that of the RNAA considering uncertainties of 3σ. Regarding iodine in BHVO-2, the noble gas method value is apparently lower than that of the RNAA. Since uncertainties are not evaluated in values of the noble gas method for BIR-1a and AGV-2, the RNAA values for these two materials cannot be compared with values of the noble gas method in detail. For the four materials of interest in this section and GSP-2, for iodine, the values of the noble gas method tend to be lower than the RNAA values. As already mentioned in the previous section, this inconsistency is under investigation. Considering the data quality of our RNAA values as discussed above and elsewhere,[3] our RNAA data for the four USGS materials considered in this section would contribute to any future compilation in the establishment of a database of USGS geochemical reference materials.

3.4. Comparison of RNAA data with literature data for manganese nodule materials. The two manganese nodules (Nod-P-1 and Nod-A-1) analyzed using RNAA in our previous study[4] were also analyzed using inductively coupled plasma double focusing sector field mass spectrometry (ICPSFMS)[16] for bromine and iodine. Before analysis by ICPSFMS, the nodule materials were subjected to an acid digestion procedure, in which the nodule materials are heated with a mixture of concentrated nitric, hydrochloric and hydrofluoric acids by using microwave. The digestion solution was diluted appropriately and then introduced into the ICPSFMS instrument.

Our RNAA data for Nod-P-1 and Nod-A-1 are not consistent with the literature data obtained by ICPSFMS for either bromine or iodine. In the case of iodine the ICPSFMS values are lower than the RNAA values. Such an inconsistency between RNAA values and ICPSFMS values also may be derived from the loss of iodine in the acid digestion procedure involving heating by microwave.[21] To prevent the loss of iodine, nitric acid should not be used for an acid digestion in principle, and heating of the digestion solution must be achieved with extreme care. Regarding bromine, on the other hand, the ICPSFMS values are higher than the RNAA values by a factor of about three to five. Such an inconsistency between RNAA values and ICPSFMS values may be due to the interference effect of this ICPSFMS instrument.[22] Bromine is determined by ICPSFMS and/or ICPMS using the isotopes ^{79}Br and ^{81}Br. The mass of those two bromine isotopes is very close to the biatomic $(^{40}Ar^{40}Ar)^+$ molecule of mass 80. Since argon is so abundant in the plasma of the ICPSFMS and/or ICPMS, the combination of two ^{40}Ar ions causes a large peak at mass 80 whose peak tail could interfere with either stable isotope of bromine. Additionally, there are several potential interferences on ^{79}Br and ^{81}Br: $(^{40}Ar^{39}K)^+$, $(^{63}Cu^{16}O)^+$ and $(^{40}Ar^{38}Ar^{1}H)^+$ interference with ^{79}Br; and $(^{40}Ar^{41}K)^+$, $(^{65}Cu^{16}O)^+$ interference with ^{81}Br signals.[22] To quantify ^{79}Br successfully without interference from $(^{40}Ar^{39}K)^+$, $(^{63}Cu^{16}O)^+$, or $(^{40}Ar^{38}Ar^{1}H)^+$, the ICPSFMS instrument should be operated in resolution (m/δm) of >10,200, >12,800, or >5,400, respectively. (The required resolution for successful quantification of ^{79}Br is explained in Appendix.) In case of the literature values for bromine, however, the ICPSFMS instrument was operated in medium resolution mode (m/δm=4,500) for ^{79}Br, so interference from $(^{40}Ar^{39}K)^+$ and $(^{63}Cu^{16}O)^+$ could not have been removed from the ^{79}Br signal. Thus a possible explanation for higher bromine values in ICPSFMS than in RNAA could be an overestimation due to the interference at mass 79 in the ICPSFMS instrument. Since ICPSFMS operation in high res-

TABLE 5: RSD values with each halogen mean value for USGS materials

Sample code	Chlorine		Bromine		Iodine	
	RSD (1σ: %)	Contents (mg kg^{-1})	RSD (%)	Contents (mg kg^{-1})	RSD (%)	Contents (mg kg^{-1})
BCR-2	1.1	112 ± 1	-[a]	0.144 ± 0.008	27.0	0.082 ± 0.022
BIR-1a	7.6	5.64 ± 0.43	32.4	0.039 ± 0.012	20.7	0.041 ± 0.009
Nod-P-1	10.4	1380 ± 144	12.9	5.93 ± 0.76	11.1	157 ± 17
DTS-2b	2.4	10.7 ± 0.3	2.1	0.093 ± 0.002	18.8	0.789 ± 0.148
CLB-1	12.8	1190 ± 152	13.0	52.1 ± 6.8	8.6	599 ± 52
SBC-1	9.6	24.9 ± 2.4	1.3	0.355 ± 0.005	3.8	5.07 ± 0.19
W-2a	10.2	220 ± 22	13.0	0.309 ± 0.040	17.6	0.405 ± 0.071
DNC-1a	17.9	18.1 ± 3.2	20.2	0.063 ± 0.013	18.1	0.102 ± 0.018
QLO-1a	6.7	244 ± 16	5.0	1.03 ± 0.05	11.9	0.741 ± 0.088
GSP-2	8.1	363 ± 29	17.0	0.117 ± 0.020	23.3	0.075 ± 0.018

[a] Not given (see text for details).

olution mode (HRM) is generally at a resolution (m/δm) of 10,000, it is fundamentally difficult to quantify ^{79}Br successfully without interference of $(^{40}Ar^{39}K)^+$ and $(^{63}Cu^{16}O)^+$ even using the HRM. This suggests that bromine separation as a pretreatment of samples is essential for bromine determination using ICPSFMS and/or ICPMS.

3.5. Heterogeneity of halogen in USGS materials. Although reference materials are expected to be homogeneous in elemental content, some materials, such as sedimentary materials, have been reported to be inhomogeneous due to heterogeneities in their constituent minerals.[23] Here we discuss heterogeneities of halogens in the ten USGS materials for which we have determined three or four analytical values using RNAA.[4] The discussion of homogeneity or heterogeneity of a material generally involves sample mass, that is, a material may be homogeneous for an element in 1 g of sample but may be inhomogeneous in 100 mg of sample. Since about 20-300 mg of USGS materials were treated in RNAA,[4] homogeneity or heterogeneity for the ten USGS materials can be discussed in restricted sample mass. It is meaningful to make such discussion even in restricted sample mass, because a few tens or hundreds mg of those reference materials are usually used for chemical analysis using ICPMS, NAA, *etc.*

As already mentioned, each uncertainty value for those ten USGS materials is one sigma of standard deviation in the individual (three or four) analytical values for the corresponding materials. The relative standard deviation (RSD) values are shown in Table 5. The RSD for bromine in BCR-2 is not given because the bromine value in BCR-2 is the mean of just two analytical values. These RSD values are controlled by the variance among three or four analytical values. The variance depends on incidental uncertainty in our RNAA. Consequently, the RSD values obtained in our RNAA are affected by incidental uncertainty. The incidental uncertainty may occur in gamma-ray counting and in weighing out powder samples and chemical standard solutions for quantification, and heterogeneity in powder samples maybe also a factor of the incidental uncertainty. In USGS materials containing higher halogen contents, generally, the RSD values tend to become lower. The RSD values shown in Table 5 are plotted against the chlorine, bromine, and iodine contents in Figure 2(a-c), respectively. The RSD values against the halogen contents in 12 reference materials prepared by Geological Survey of Japan (GSJ) are also shown in this figure. Their values and contents are obtained by RNAA in our previous study[3] and tabulated in Appendix. For bromine and iodine, it can be seen that the RSD values tend to be lower in USGS and GSJ materials with higher halogen contents as described above. However, Nod-P-1 and CLB-1 have relatively high RSD values in bromine, although their bromine contents are high. A similar situation can be seen for chlorine.

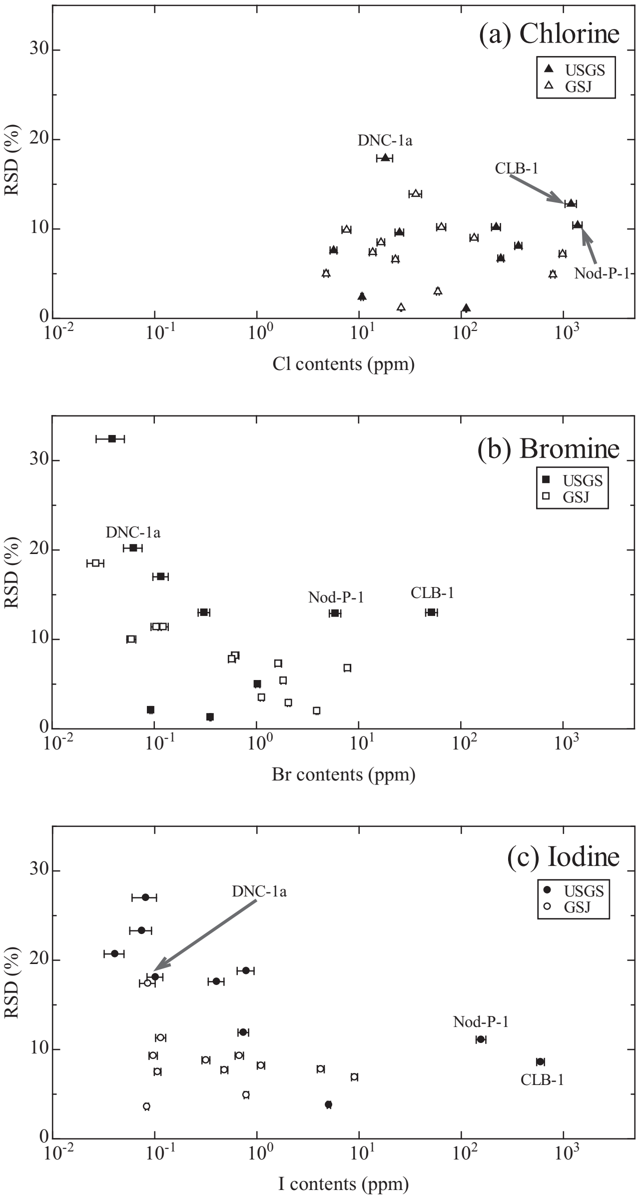

Figure 2. RSD values versus Cl, Br and I contents for the USGS and GSJ materials. (a) Cl, (b) Br, and (c) I.

Considering that both the 10 USGS and the 12 GSJ materials are analyzed by RNAA in the same way, the incidental uncertainty which raises those two RSD values may be likely to derive from heterogeneity in powder samples rather than an accident in experimental procedure. At the present stage, however, we are not able to conclude that CLB-1 and Nod-P-1 can be inhomogeneous in halogens, because sample mass of CLB-1 and Nod-P-1 used in RNAA was sometimes smaller (20-50 mg) than the masses of the other materials analyzed. (Sample mass used in each analytical run is shown in Appendix.) Heterogeneity of halogen distribution in DNC-1a was also suggested above in Results and Discussion, section 2. To investigate the heterogeneity of halogens in those two materials as well as the other materials in detail, several aliquots of materials with different weights should be studied by RNAA.

4. Conclusions

Through an exhaustive comparison of our halogen data determined by RNAA with the corresponding data in literature, the following findings have been made in relation to the individual reference materials.

For DTS-2b (dunite), COQ-1 (carbonatite), CLB-1 (coal), SBC-1 (marine shale) and DGPM-1 (disseminated gold ore), there are no literature values for halogens. Chlorine, bromine, and iodine values for those five reference materials are first reported by using RNAA.

For W-2a (diabase) and SGR-1b (shale rock), our RNAA values for chlorine are consistent with the literature (information) values within uncertainties of 30%. Bromine and iodine values for those two reference materials are first reported by using RNAA.

For DNC-1a (dolerite), QLO-1a (quartz latite) and SDC-1 (mica schist), our RNAA values for chlorine and bromine are approximately consistent with the literature values, except for chlorine in DNC-1a. The iodine values for these three reference materials are first reported by using RNAA.

For GSP-2 (granodiorite), our RNAA values for chlorine and bromine are consistent with the literature values, whereas the literature value for iodine is lower than the RNAA value.

For BHVO-2, BCR-2, BIR-1a (basalts), and AGV-2 (andesite), our RNAA values for bromine are consistent with the corresponding literature values, whereas the literature values for iodine are lower than the RNAA values. Such an inconsistency between RNAA values and literature values obtained by ICPMS can be explained by a loss of iodine in pretreatment for ICPMS, where the solutions obtained from pyrohydrolysis were slowly evaporated in order to concentrate the solution. The literature values for chlorine are systematically lower than the RNAA values by a factor of 0.87±0.09, suggesting that chlorine cannot be quantitatively extracted from basalt and andesite materials.

For Nod-P-1 and Nod-A-1 (manganese nodules), the literature values for iodine are lower than the corresponding RNAA values. Such an inconsistency between RNAA values and literature values can also be explained by the loss of iodine in pretreatment for ICPSFMS, where powder samples are subjected to an acid digestion procedure with using nitric acid and heating by microwave. The bromine values obtained by ICPSFMS (literature values) are higher than the RNAA values by a factor of about three to five. A possible explanation for an overestimation by ICPSFMS could be an interference at mass 79 which is used for bromine determination.

Finally, the heterogeneity of halogens in USGS materials was assessed by using their RSD values and contents. To investigate the heterogeneity of halogens in CLB-1 and Nod-P-1 in detail, several aliquots of materials with different weights should be studied by RNAA.

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