HALOGEN CONTENTS IN METEORITES (1) CARBONACEOUS CHONDRITES. M. Ebihara[1] and S. Sekimoto[2], [1]Department of Earth Sciences, Waseda University (1-6-1 Nishi-waseda, Shinjuku-ku, Tokyo 169-8050, Japan; ebiharamitsuru@aoni.waseda.jp), [2]Institute for Integrated Radiation and Nuclear Sciences, Kyoto University (2 Asashiro-nichi, Kumatori, Osaka 590-0494, Japan; sekimoto@rri.kyoto-u.ac.jp)

Introduction: Halogen elements are among the least characterized elements in cosmochemical behaviors. A major reason is due to luck of their accurate data, especially for bromine (Br) and iodine (I). Chlorine (Cl), Br and I contents in bulk samples of meteorites were extensively determined in 1960's by using neutron activation analysis (NAA). Although great innovation in analytical instruments and techniques has been achieved in past several decades, meager situation concerning the meteoritic halogen data has not been really improved. Among several analytical methods applicable to bulk solid samples for determining their Cl, Br and I contents, NAA may be still the best choice at present. Especially, radiochemical NAA (RNAA) can yield very accurate content data for these three halogens in solid samples, as recently demonstrated by the presentation of a large number of analytical data for geochemical reference samples issued by Geological Survey of Japan [1] and United State Geological Survey [2].

Recently, a large set of data for three halogens (Cl, Br and I) in chondritic meteorites were reported [3]. In comparing their data for the Allende CV meteorite with our previously published data [4,5], there noticed a large difference in analytical data for the three halogens, with the newly reported data [3] being systematically smaller by factors of 4 (for Cl and Br) and 6 (for I). Similar scattering including anomalously low content data of halogens can be seen in 1960's data. For elucidating a reason for making such a discrepancy and for better understanding the cosmochemical characteristics of halogens, we performed the determination of halogen contents (for Cl, Br and I) in carbonaceous chondrites by means of RNAA. A total of 19 chondrites (2 CIs, 5 CMs, 5 COs and 7 CVs) were analyzed.

Experimental: The RNAA procedure for determining the three halogens is essentially the same as applied to geochemical reference samples [1,2]. About 50 to 100 mg and 20 to 40 mg powder samples were used for COs and CVs, and CIs and CMs, respectively. Two powder samples were simultaneously irradiated with neutrons at the Kyoto University reactor (KUR) (thermal neutron flux: 1.5×10^{12} n $cm^{-2}s^{-1}$) for 10 min along with reference standards of Cl, Br and I prepared from chemical reagents. After the irradiation, each sample was fused with NaOH together with known amounts of halogen carriers in a Ni crucible for about 10 min. Fusion cakes were dissolved in water and three halogens were successively and radiochemically purified as forms of palladium halide for I and silver halides for Cl and Br. As soon as these precipitates were prepared, gamma-ray counting started for ^{128}I, followed by ^{38}Cl. ^{82}Br was measured on the following day. Chemical yields were determined by means of reactivation method, where the same precipitates were neutron-activated for a short time (5 to 10 sec).

Results and Discussion: Murchison, Allende, Leoville and Vigarano were analyzed multiple times. For Allende, analysis was repeated five times for three differently prepared powders; the Smithsonian Institution (SI) reference powder [6] and two in-house powders. Reasonable consistencies can be seen for the three halogens, especially for Cl. Our data for the SI powder sample are in good agreement with literature data except the recently reported values [3]. Large differences can be seen between our data and the literature data [3] for the three halogens not only for Allende but also for Orgueil (CI), Murchison (CM) and Efremovka (CV), with the newly published values [3] being considerably (more than an order of magnitude for some cases) smaller than our values. Considering the reliability of halogen content data for geochemical reference samples [1,2] and the consistency in the Allende data, we incline to conclude that the recently published data [3] were erroneously determined.

Within limitation of the number of data for CIs, general trends in halogen abundances in the four groups of carbonaceous chondrites can be confirmed. Among the three halogens, Cl shows the smallest variation in its contents in individual groups. Mean contents of Cl decrease from CIs to CMs and then to COs-CVs with relative ratios of 1:0.59:0.38-0.40. Depletion degrees of the Cl contents in CMs and COs-CVs relative to those of CIs are similar to those for moderately volatile elements such as Se, Te and Cs. 50% condensation temperature of Cl from the gas of solar composition at 10^{-4} atm was proposed to be 863K [7] and 948K [8], which seems to be a bit too high. There appears no difference in Cl contents between COs and CVs. It is recognized that cosmochemically volatile elements like Zn and In are systematically depleted in COs compared with those in CVs, but that less volatile elements like Sb and Ge are inversely depleted in CVs rather than in COs [9]. Chlorine stands between these two groups, along with Sn and, probably, Se-Te, which also suggests lower condensation temperature of Cl than proposed. In contrast to the case of Cl, Br and I contents vary considerably, especially in CMs. It seems to be less meaningful to calculate the average for Br and I contents in carbonaceous chondrites unless the number of analyses is statistically meaningful. With such a reservation, it may be pointed that both Br and I are apparently depleted in CMs and COs-CVs compared with those in CIs, being consistent with an understanding of their behaviors in terms of element condensation. However, with examining in detail, there seems to be a contrast between Br and I; Br contents of CMs are similar to or even lower than those of COs-CVs, while I contents of CMs are higher than those of COs-CVs as expected.

Anomalous contents of Br and I can be noticed in both inter- and intra- meteorite comparisons. In CMs, high contents of Br and I were observed in Bells: and Boriskino. In CVs, Vigarano shows similarly high but less abundant Br and I contents. In these meteorites, not only Br and I but also Cl has a little high contents, with I being relatively the most abundant. For Allen-de, three data for the SI powder sample yielded excel-lent reproducibility for the three halogens. This is because the SI powder sample was prepared by grind-ing and homogenizing chunk specimens weighing 4 kg [6]. Two in-house powder samples have slightly different contents of Br and I from those of the SI sample. Similar intra-meteorite variations can be con-firmed in Leoville and Vigarano. These anomalously large variations of Br and I contents in intra- and in-ter-meteorite samples can be best explained in terms of aqueous transportation of these elements on mete-orite parent bodies. Such an aqueous alteration, how-ever, may have scarcely affected Cl, suggesting that Br and I do not largely reside in chlorapatite in CMs and

CI chondrites still hold the status as the solar system standard for elemental abundances. Two CIs (Orgueil and Ivuna) were analyzed in this study and their Cl, Br and I content data were compared with literature values. Even in CIs, Br and I contents seem to vary just like those in CMs and CVs. A systematic variation of Br contents among three CIs (Orgueil, Ivuna and Alais) was once clearly demonstrated [10], spreading over a factor of two from 5.05 ppm for Ivuna down to 2.26 ppm for Alais with Orgueil in-between. Interestingly, such a variation of Br contents was observed to be positively correlated with Au contents in the three CIs, concluding that both elements were transported in the form of Au-Br complex by hydrothermal alteration on the parent body of CIs [10]. The same order between Orgueil and Ivuna can be seen not only for Br data but also for I values obtained in this study, although Cl contents do not similarly vary. Judging from several viewpoints, among the three CIs practically usable for chemical analysis, Orgueil was suggested to have undergone little transport of Br (and I) during the hydrothermal alteration stage on the parent body [10]. If so, Br and I contents of Orgueil obtained in this study may be adopted as representative values for CIs, considering that our Br value is consistent with literature values. For Cl, a mean value of its contents of Orgueil and Ivuna can be used for a representative value of Cl content of CIs. Based on these halogen contents of CIs, solar system abundances of Cl, Br and I can be calculated and summarize in Table 1, along with literature values. Our new estimates are similar to the literature values for Cl and Br, but about 50% to 70% larger for I. In the past, the solar abundance of I has been commonly estimated based on abundance values of several neighboring elements (Sb, Te, Xe, Cs and Ba) because of insufficient analytical data. At this moment, we have no reasonable explanation for the difference for I. The sampling bias is likely.

Table 1. Solar system abundances of Cl, Br and I ($Si=10^6$)

Cl	Br	I	literature
5600	12.0	1.57	*this work*
5340	11.8	0.90	[11]
5240	11.8	0.90	[12]
5237	11.32	0.998	[8]
5170	10.7	1.10	[13]
5170	10.7	1.05	[14]
850[a]	0.67[a]	0.118[a]	[3]

[a]Calculated from the Orgueil data [3].

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