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Distribution of halogens in an Antarctic ordinary chondrite, Y-74014 (H6)

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Abstract: One of the striking features in Antarctic meteorites is overabundances of halogens, especially iodine. In order to investigate how these halogens are distributed in constituent mineral phases of Antarctic chondrites, the outer portion of Yamato (Y)-74014 H6 chondrite (Y-74014,101) was subjected to fractional dissolution using several solutions with different chemical properties. Pulverized meteorite sample was successively leached by acetone, (hot) water, EDTA and nitric acid, and individual leachates as well as the acid residue were analyzed for halogens by neutron activation analysis. About 10% of iodine was recovered in acetone whereas only less than 2% of Cl and Br are leached, suggesting that overabundant iodine is partly present in the form of acetone-soluble, possibly organic compound. Dissolution patterns of Cl and I with water are similar to each other. This implies that contaminated Cl and I both reside in a common phase, presumably in akaganéite, a corrosion product of Fe-Ni alloy with chlorine attracted from the environment. Either iodine was involved in this mineral when corrosion reaction occurred or iodine was later migrated into the mineral by exchanging with Cl^- and/or OH^- . For the chronological studies using long-lived nuclides such as ^{36}Cl and ^{129}I , it is essential to use indigenous halogens in meteorites. For such purposes, the acid-residual fraction can be used even for Antarctic meteorites having overabundant halogens. In addition, Cl, Br and I contents in bulk Allende and Bruderheim chondrites are also obtained in this study and their abundances are briefly discussed.

1. Introduction

Chemical properties of halogens have been extensively studied and are known to vary largely from element to element. In contrast, cosmochemical properties of halogens are poorly understood. Cosmochemically, halogens are classified into moderately volatile elements and are believed to behave accordingly during condensation in the early solar system (Fegley and Lewis, 1980). However, condensation behaviors of halogens, especially of Br and I, have not been fully described. One of the best approaches to figure out the cosmochemistry of halogens in the early solar system is to determine the precise abundance and the distribution of halogens in meteorites.

The bulk abundances of halogens in meteorites (mostly chondrites) were once

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extensively determined in 60's. Neutron activation analysis was mainly applied for the determination of Cl, Br and I. Even with these data being included, however, the number of halogen data for meteorites is still very small compared with those for other trace elements. Solar (and chondritic) abundances of these three halogens decrease with increasing the atomic number (Wasson and Kallemeyn, 1988). The reliability of halogen data for chondritic meteorites seems to follow this trend. Although a great development in analytical methods and instruments has been achieved in past several decades, neutron activation analysis is still the only method reliably applied for the determination of Cl, Br and I in meteorite samples even at present. Radiochemical separation is generally needed in neutron activation for the determination of Cl, Br and I in meteorite samples. Only Br can be determined non-destructively for some cases.

One of the striking features in halogen abundances in meteorites is their anomalous overabundances in Antarctic meteorites. This was first observed in eucrites (Dreibus and Wänke, 1983) and later confirmed in other types of Antarctic meteorites including chondrites (Dreibus *et al.*, 1986). Among halogens, iodine shows especially high concentration and an apparent but smaller excess was observed for chlorine. The later observations that degree of overabundance decreases with depth from the surface (Ebihara *et al.*, 1990; Heumann *et al.*, 1990; Langenauer and Krähenbühl, 1993a, b) and that iodine overabundance is correlated with the degree of oxidation of iron (Shinonaga *et al.*, 1994b) suggest that I and Cl overabundances were caused by the addition of halogen-containing contaminants to the surface of meteorites on Antarctica.

In this study, we investigate the distribution of halogens (Cl, Br and I) in an Antarctic H6 ordinary chondrite, Yamato (hereafter, Y)-74014 by using neutron activation analysis. We selected the outer portion of this meteorite (Y-74014,101), which has an apparent overabundance of I and Cl. For this purpose, fractional dissolution by several solutions with different chemical properties was applied. Based on the data obtained, we figure out how much of halogens (especially overabundant halogens) are distributed in constituent mineral phases of Y-74014,101 and discuss the geochemical behaviors of halogens in the surface layer of chondrites on Antarctica. We further consider if it is possible to separate the indigenous halogens from overabundant, bulk halogens in connection with cosmochronology using long-lived halogen nuclides such as ^{36}Cl and ^{129}I . Along with the dissolution experiment, bulk abundances of Cl, Br and I were determined for Allende, Bruderheim as well as Y-74014,101 and their abundances are briefly discussed.

2. Experimental

2.1. Samples

For this study, we requested NIPR for the outer portion of Y-74014. About 0.8 g of the allocated specimen (Y-74014,101) was ground and homogenized in an agate mortar. This homogenized sample was divided into several portions and was

used for dissolution experiments as well as bulk analysis for halogens. In addition to Y-74014, Allende and Bruderheim were analyzed for bulk abundances of three halogens (Cl, Br and I). For Allende, the Smithsonian reference powder sample (split 11, position 11) prepared by E. Jarosewich was used. For Bruderheim, about 10 g (in total) of several lumps were ground and homogenized in a clear agate mortar.

2.2. Radiochemical neutron activation analysis (RNAA) for the determination of three halogens (Cl, Br and I) in rock samples

We followed the RNAA procedure by Shinonaga *et al.* (1994a) and Ebihara *et al.* (1997) for the determination of Cl, Br and I. In short, about 100–200 mg of each powdered rock sample (meteorite, geological standard, etc.) is taken in a clean polyethylene vial (5 mm ϕ \times 20 mm). Two samples along with reference standards prepared from chemical reagents are placed in a Cd can with 1 mm thickness and are irradiated in an F-core ($n_{\text{th}} = 1.5 \times 10^{12}$ n/cm² s; $\text{Cd}_{\text{Au}} \sim 5$) for 10–30 min in the TRIGA-II reactor at the Institute for Atomic Energy, St. Paul's (Rikkyo) University. After the irradiation, radiochemical separation of halogens is immediately performed. Rock samples are fused with NaOH. The fused cake is dissolved in water and the hydroxide precipitate is separated by centrifugation. To the supernatant, Na₂SO₃ is added to keep iodine as I⁻, followed by nitric acid to make the solution slightly acidic. Then, Pd(NO₃)₂ is added to the solution to precipitate I⁻ as PdI₂, which is collected on a filter paper for gamma-ray counting of ¹²⁸I. AgNO₃ is added to the supernatant solution, precipitating Cl⁻ and Br⁻ as AgCl and AgBr, respectively. These precipitates are collected together on a filter paper for gamma-ray counting of ³⁸Cl and ⁸²Br. Chemical yields of individual halogens were determined by reactivation.

2.3. Leaching experiment of Y-74014,101

Successive leaching was performed for fractional dissolution of constituent mineral phases of Y-74014,101. The sample was firstly leached by acetone in order to know how much of halogens are present in the acetone-soluble, possible organic form. This step was introduced in consideration that iodine is heavily overabundant in some Antarctic meteorites (*e.g.*, Dreibus and Wänke, 1983) and that iodine was suggested to be transported in the form of organic form from the sea (*e.g.*, Heumann *et al.*, 1987). The second leaching was conducted by water, considering that halogens are generally leached by water to considerable extent in non-Antarctic chondrites. Some halide compounds could be leached in this step. Lawrencite (FeCl₃) was once proposed as one of such compounds but is now questioned as discussed later. The third leaching was done by ammoniacal EDTA (0.1 M; pH 9), which can dissolve Ca-phosphates (Cl-apatite and whitlockite (merrillite)) (Ebihara and Honda, 1984). Cl-apatite must be a host phase of chlorine and could also be the case for other halogens in chondrites. After EDTA-leaching, the sample was leached by nitric acid (6 M), which dissolves Fe-Ni metal, Fe sulfide (troilite) and olivine. The acid-resistant phases consist of pyroxene and plagioclase for most part.

Table 1. Leaching conditions applied to Y-74014,101.

Solution	Leaching conditions ^a (5 min each)	Minerals expected to be dissolved
Acetone	r. t.; const. stir.	—
Water	80°C; occ. stir.	(lawrencite) ^b
0.1 M EDTA (ammoniacal; pH. 9)	80°C; occ. stir.	Ca-phosphates
6 M nitric acid	80°C; occ. stir.	Fe-sulfide, Fe-Ni alloy, olivine
	(alkaline fusion)	pyroxene, plagioclase, chromite, spinel

^a r. t. = room temperature; const. stir. = constantly stirring; occ. stir. = occasionally stirring.

^b The presence of lawrencite is questionable. Probably, Cl-containing akaganéite is dissolved by water. See text for details.

The chemical property of leaching solution becomes strong at later steps (with leaching steps proceeding). The volume of each solution (2 ml) and the contact time (5 min) were fixed in any leaching procedure. The separation in chemical dissolution is not always clear-cut; mineral phases to be dissolved at a certain step may remain partly undissolved and be recovered in the following steps, especially in this experiment because the contact time is too short. Only the acid-dissolution can be a clear-cut separation. If an element becomes colloidal, it is not recovered correctly in the solution; silica may occur when the concentration of Si is high in mineral acids of high concentration. No such colloidal materials were observed to form in this study. Leaching conditions and mineral phases to be leached in individual steps are summarized in Table 1.

We have performed two types of dissolution experiments (Experiments A and B) as follows;

[Experiment A] About 200 mg of the Y-74014,101 powdered specimen is taken into a polyethylene vial and irradiated with reference standards of three halogens under the same condition as used for the bulk analysis. No Cd can was used, intending not to reduce the analytical sensitivity of chlorine. After the irradiation, the meteorite sample was transferred into a glass vial and was leached successively with different solutions. The acid residual phase was separately prepared by using an aliquot of the powdered Y-74014,101 and was irradiated so that its halogen (especially, iodine) abundances can be determined precisely. The acid-soluble and residual fractions were analyzed for halogens by using the same RNAA procedures as applied to bulk meteorite samples (described in Section 2.2). The acetone, water and EDTA leachates were measured with a Ge detector without radiochemical purification of halogens. Chemical yields for solution samples were assumed to be 100%. For this purpose, standard solutions were pipetted into vials, irradiated without drying and measured.

[Experiment B] In order to figure out how halogens are leached in individual solvents, another powdered sample of Y-74014,101 was irradiated and successively leached three times with each solvent of acetone, water and EDTA. The experimental condition of this experiment was the same as that for Exp. A. Each leachate was

measured for halogens without their radiochemical purification.

3. Results and discussion

3.1. Halogen abundances in bulk meteorite samples

Table 2 summarizes the analytical results of halogens in bulk meteorite samples. Allende and Bruderheim were analyzed twice. One set of halogen data for Allende, Bruderheim and Y-74014,101 were already reported by Ebihara *et al.* (1997), but were not discussed. Therefore, these data are included in this table and will be discussed together with another set of data for Allende and Bruderheim in the following.

Allende For Allende, a large scattering in halogen data is not observed not only between our two sets of data but also among all data including literature values. This is probably because not only our data but also most of literature values listed in Table 2 are obtained for the Smithsonian reference sample, which was prepared by homogenizing 4 kg of Allende bulk specimen (Jarosewich *et al.*, 1987). One of our chlorine values seems to be suspiciously high. Similarly high values were obtained for some geological standard rocks analyzed at the same time. We suspect that an analytical error occurred in the experimental run for these samples. Our Br values (1.60 and 1.56 ppm) show an excellent agreement with the two RNAA values (1.54 and 1.52 ppm) by Müller (cited by Jarosewich *et al.*, 1987) and with INAA values (not cited in Table 2) (1.5–1.7 ppm; mean 1.6 ppm) by Kallemeyn and Wasson (1981) and Kallemeyn *et al.* (1989). Bromine abundances in most carbonaceous chondrites are high enough to be determined by INAA as shown by Kallemeyn and Wasson (1981). Our two values of iodine show a good consistency, but are slightly higher than literature values. The literature values by Dreibus *et al.* (1979) are generally low; they did not use the Smithsonian reference sample.

Bruderheim Among meteorites, Bruderheim has been the most extensively

Table 2. Analytical results of Cl, Br and I in bulk chondritic meteorites^a.

Samples	Cl, ppm	Br, ppm	I, ppb
Allende (CV3)	320 (9.3), [400] ^b	1.60 (18), 1.56 (15)	210 (14), 200 (18)
<i>Lit.</i> ^c	<u>316</u> ¹ , 265 ¹ , 237 ²	<u>1.54</u> ¹ , 1.52 ¹ , 0.79 ²	<u>160</u> ²
Bruderheim (L6)	137 (10), 91 (13)	1.35 (12), 0.84 (16)	24 (58), 32 (36)
<i>Lit.</i> ^c	<u>2.5-130</u> ³ , 100 ²	<u>0.026-1.56</u> ³ , 0.20 ²	<u>6-450</u> ³ , 40 ²
Y-74014,101 ^d (H6)	753 (5.6)	0.77 (12)	2260 (2.7)
<i>Mean</i> ^e	<u>80</u>	0.5	68

^a Figures in parentheses correspond to relative errors (in % for 1 σ) due to counting statistics. Underlined values were already reported in Ebihara *et al.* (1997).

^b Suspiciously high.

^c Literature values: (1) Jarosewich *et al.* (ed.), 1987; (2) Dreibus *et al.*, 1979; (3) Goles and Anders, 1962; Reed and Allen, 1966; Goles *et al.*, 1967; Clark *et al.*, 1967 (see text for details).

^d Outer portion.

^e Mean values for H chondrites (Wasson and Kallemeyn, 1988).

analyzed for halogens. There can be seen a large discrepancy in literature data of Cl, Br and I. For Cl, the following values were reported; 66–130 ppm (Goles *et al.*, 1967), 100 ppm (Dreibus *et al.*, 1979) and 2.5–50.0 ppm (Reed and Allen, 1966). Our values (91, 137 ppm) are in a range of the former two report. For Br, there is a large variation of more than two orders of magnitudes in literature values; 0.97 and 1.56 ppm (Wyttenbach *et al.*, 1965), 0.20 ppm (Dreibus *et al.*, 1979), 0.12–0.18 ppm (Goles *et al.*, 1967), 0.05–0.12 ppm (Reed and Allen, 1966), and 0.026 and 0.030 ppm (Lieberman and Ehmann, 1967). Our values (1.35, 0.84 ppm) are consistent with the highest values reported. Considering this and an excellent agreement for Allende between our values and literature ones, Br content in Bruderheim must be larger than most of reported values. It may be noted that most literature values are smaller than our values and that literature values are not largely variable in individual studies. This hints that there could have happened an experimental problem in some of the previous works. Once, Ebihara *et al.* (1982) pointed that there appeared a systematic variation in neutron activation data of Br for CI chondrites. Such a systematic variation may occur either by volatilization of Br in meteorite and/or reference standard samples irradiated in a high flux reactor or by improper radiochemical separation of Br after neutron irradiation. In this study, we used a low flux and low power reactor, where no volatilization loss was confirmed even for I, which is more easily lost than Br in neutron activation.

There is also a large discrepancy in literature values of I; 450 and < 74 ppb (Reed and Allen, 1966), 40 ppb (Dreibus *et al.*, 1979), 18 and 27 ppb (Clark *et al.*, 1967), 5–27 ppb (Goles and Anders, 1962), and 6 and 7 ppb (Goles *et al.*, 1967). Our values (32 and 24 ppb) are consistent with each other and further with most literature values except an anomalously high value of 450 ppb. Please note that a detection limit of our procedure is ~ 10 ppb and thus a fairly large error is accompanied with our RNAA values of several 10s ppb. Some values smaller than 10 ppb in literatures may reflect either loss of iodine from meteorite samples during experiments or heterogeneous distribution of iodine in Bruderheim. An average value of iodine for Bruderheim seems to be smaller than an estimated mean for L chondrites (53 ppb; Wasson and Kallemeyn, 1988).

Y-74014,101 Comparing with the mean values of halogens in H chondrites (Wasson and Kallemeyn, 1988), an apparent overabundance can be seen for I and Cl in Y-74014,101, as expected. Indeed, I and Cl contents in Y-74014,101 are 2 orders of magnitudes and five times higher than those in Bruderheim, respectively. On the other hand, a Br content in Y-74014,101 seems to be normal. Among Antarctic meteorites having an apparent overabundance of halogens, Shinonaga *et al.* (1994b) observed a correlation between Cl and I contents. Langenauer and Krähenbühl (1993b) observed an enrichment of Br only in the outermost thin layers of Antarctic chondrites. All these data suggest that Antarctic meteorites are the least contaminated with Br among three halogens discussed here. Considering that an iodine content larger than 2 ppm is an extreme value and that a chlorine content of 500 ppm is among the highest values for Antarctic H chondrites (Shinonaga *et al.*, 1994b), the specimen of Y-74014,101 used in this study is one of the most

heavily contaminated meteoritic materials with halogens (Cl and I in this case).

3.2. Fractional dissolution of halogens in Y-74014,101

In the first experiment (Exp. A), the activated meteorite sample was successively leached by 4 different solvents (acetone, water, EDTA and nitric acid). For this experiment, leaching was not repeated for each solvent. Halogen contents in individual leachates and the acid residual fraction were determined. The results of Exp. A are summarized in Table 3, where contents (in ppm) and relative fractions (in%) of recovered halogens in each step are given. In this table, summed contents of halogens in four leaching steps and in the acid-residual fraction are compared with the RNAA values from the bulk analysis. A fairly good agreement can be seen between two sets of data for three halogens, especially for Br and I. A difference in two Cl values is somewhat larger than a combined error of counting statistical errors for two values. Overall analytical errors, however, are generally larger than statistical errors, especially for values in Exp. A and are conservatively estimated to be about 10% (1σ). Thus, it can be concluded that individual halogens were quantitatively collected in fractional dissolution steps in Exp. A.

In the second experiment (Exp. B), leaching was repeated three times with each of acetone, water and EDTA and dissolution patterns in these three solutions were compared for each halogen. The results of Exp. B are summarized in Table 4. Only upper limit values can be obtained for Br with acetone- and EDTA-leaching and I with EDTA-leaching. Values in Table 4 are given in ppm (μg of dissolved halogens divided by a mass in g of the initial meteorite sample used). Values in parentheses indicate counting statistics (% for 1σ). When this value exceeds 33%, an upper

Table 3. Contents (in ppm; upper values) and fraction (in %; lower and italicized values) of halogens recovered in each solvent by successive dissolution [Exp. A]^a.

Leaching solution	Cl	Br	I
Acetone	7.3 (10)	0.011 (27)	0.181 (2.9)
	<i>1.2</i>	<i>1.5</i>	<i>8.3</i>
Water	297 (1.6)	0.511 (2.1)	1.000 (1.5)
	<i>48</i>	<i>69</i>	<i>46</i>
0.1 M EDTA (pH 9)	103 (3.6)	0.075 (6.9)	0.748 (2.3)
	<i>17</i>	<i>10</i>	<i>34</i>
6 M Nitric acid	174 (4.9)	0.133 (9.2)	0.165 (11)
	<i>28</i>	<i>18</i>	<i>7.5</i>
(Residue)	41 (12)	0.014 (13)	0.092 (24)
	<i>6.7</i>	<i>2.0</i>	<i>4.2</i>
Total ^b , ppm	620 (2.0)	0.75 (2.3)	2.2 (1.7)
Whole rock ^c , ppm	750 (5.6)	0.77 (12)	2.3 (2.7)

^a Values in ppm denote halogen contents (in μg) divided by an initial amount (in g) of chondrite. Figures in parentheses correspond to relative errors (in % for 1σ) due to counting statistics.

^b Total of five fractions including residual fraction.

^c Values of whole sample analysis (cited in Table 2).

Table 4. Halogens (in ppm) in each step during stepwise dissolution [Exp. B]^a.

Leaching solution	Step	Cl	Br	I
Acetone	1	13 (29)	< 0.10 ^b	0.21 (7.7)
	2	< 12	< 0.08	0.16 (18)
	3	< 0.62	< 0.04	0.069 (26)
Water	1	280 (4.1)	0.54 (6.2)	0.82 (3.6)
	2	62 (8.8)	0.05 (30)	0.22 (12)
	3	33 (15)	< 0.04	0.12 (30)
EDTA	1	56 (21)	< 0.07	< 0.35
	2	< 19	< 0.05	< 0.23
	3	< 37	< 0.07	< 0.48
Total ^c		440–520	0.59–1.04	1.56–2.7
Estimated ^d		500	0.62	2.0

^a Halogens contents (in μg) recovered in each step divided by an initial amount (in g) of chondrite. Figures in parentheses correspond to relative errors (in % for 1σ) due to counting statistics.

^b An upper limit value is shown if an error exceeds 33%.

^c Total of nine fractions (three for each acetone, water and EDTA). A real value should be in the range shown. See text for details.

^d Estimated from total fractions recovered in three solutions (acetone, water, EDTA) in Exp. A and whole rock contents (Table 2).

limit is given in Table 4. “Total” values in Table 4 show summed halogens recovered in a total of 9 dissolution steps; a minimum value is a sum of positively determined values only and a maximum content is a sum of a minimum value and all upper limit values if any. An actual value should fall in-between. “Estimated” values in Table 4 are calculated from total dissolved fractions in acetone, water and EDTA (Table 3) and bulk halogen contents in Y-74014,101 (Table 2). Since “Estimated” values are in the range of “Total” values, the results of Exp. B are judged to be reliable.

Recovered fractions of three halogens in four solvents and in the acid-residue are shown in Fig. 1. Dissolution modes are obviously different among Cl, Br and I. About 10% of iodine is dissolved in acetone whereas only less than 2% of Cl and Br are recovered. As already discussed, Y-74014,101 has a large overabundance of iodine and such an overabundant iodine was suggested to be carried in the form of methyl iodide (Heumann *et al.*, 1987, 1990). A relatively high recovery of iodine by acetone seems to be consistent with this suggestion, considering that methyl iodide can be easily dissolved in an organic solvent like acetone. However, a much higher recovery of iodine in water and EDTA (80% in total) weakens this argument. Presumably, iodine was transferred in the form of methyl iodide as suggested and was adhered on the surface of meteorites on Antarctica. Iodine was then gradually migrated into the inside of meteorites, possibly through cracks, with methyl iodide being decomposed and with more stable, water-soluble iodine compound forming.

It is well known that Cl and Br in non-Antarctic ordinary chondrites are leached by water (or hot water) to some extent and that Br is more easily leached

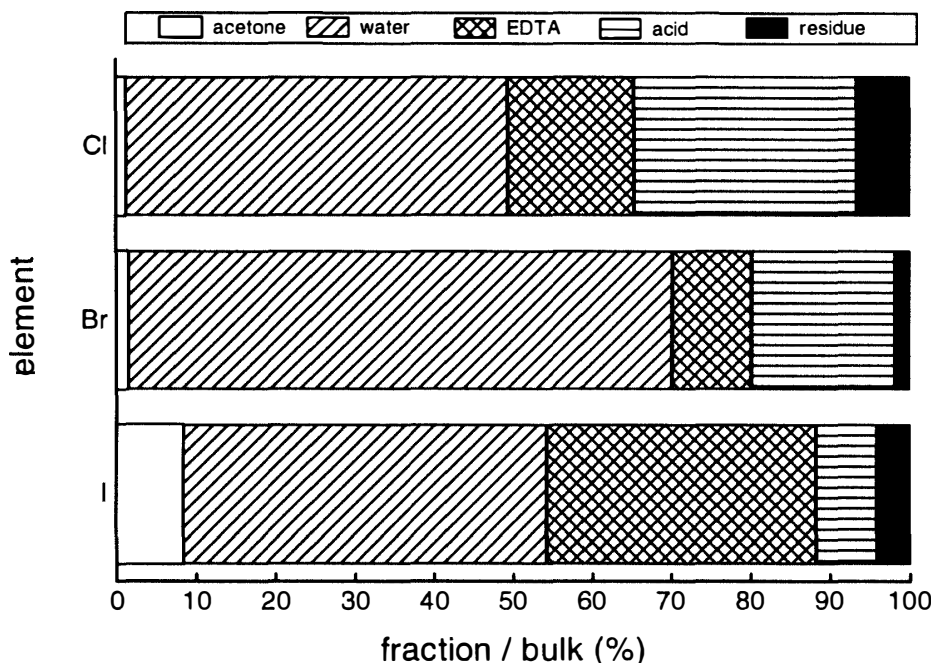


Fig. 1. Recovered fractions (in % relative to bulk contents) of Cl, Br and I in acetone, water, EDTA and nitric acid leachates and the acid-residual fraction.

than Cl in a relative sense (Reed and Allen, 1966). Iodine was also observed to be leached by water for non-Antarctic meteorites (Goles and Anders, 1962; Reed and Allen, 1966). For Y-74014,101, about 70% of the total Br was recovered in H₂O. Significant but slightly smaller amounts (~50%) of Cl and I were also recovered in water. Considering that the iodine content in Y-74014,101 is two orders of magnitude higher than that in Bruderheim, the water-soluble iodine for Y-74014,101 is mostly due to contaminant adhering onto the meteorite surface on Antarctica rather than to indigenous minerals containing iodine in meteorites. Water-soluble chlorine is also attributable to contaminant for most part, considering an anomalously high content of chlorine in Y-74014,101 and a large recovery of chlorine in water. A parallel dissolution of Cl and I in successive leaching by water (Fig. 2) suggests that contaminated Cl and I both reside in a common phase in Y-74014,101. Different contaminants have been proposed for Cl and I; airborne sea spray for Cl and methyl iodide for I (Heumann *et al.*, 1987, 1990; Langenauer and Krähenbühl, 1993a, b).

Buchwald and Clarke (1989) examined metal phases in Antarctic iron and stony meteorites and observed that akaganéite (with up to 5 wt% Cl) and goethite as the major corrosion products. They concluded that akaganéite containing chlorine was formed by the corrosion of Fe-Ni alloy with chlorine which was attracted from the environment and reached to metals through cracks. When the corrosion reaction occurs with Fe-Ni alloy and chlorine (possibly Cl⁻ ion), some iodine may be involved in this reaction, being incorporated into akaganéite. Alternatively, iodine may migrate into akaganéite later by replacing Cl⁻ and OH⁻ sites in akaganéite with I⁻. Presumably, most Cl and I leached by water can be

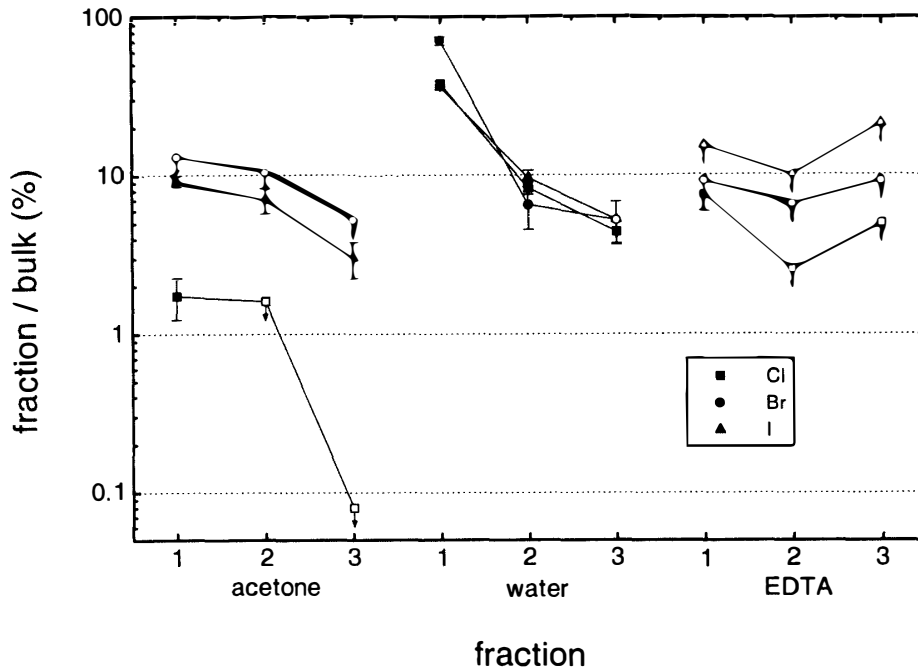


Fig. 2. Dissolution patterns of Cl, Br and I in acetone, water and nitric acid leaching. Leaching was repeated successively three times for each solvent. Open symbols denote upper limit values. It is obvious that three halogens are easily leached with water. A parallel dissolution of Cl and I in successive leaching by water suggests that contaminated Cl and I reside in a common phase in Y-74014,101.

attributed to the corrosion product, akaganéite. It may be noted in Fig. 2 that Br also is similarly leached along with Cl and I. Among three halogens, Br is least contaminated in Y-74014,101, suggesting that Br leached by water is mostly indigenous. As there is no observation concerning the host phase for water-soluble Br in (non-Antarctic) chondrites, it can be concluded either that Br is also highly concentrated in akaganéite or that Br is allocated in mineral phases with a similar solubility against water to that of akaganéite. If the former is the case (and seems to be more likely), indigenous Br was largely remobilized with moisture penetrating through cracks from the surface and redistributed into akaganéite. It should be noted that the linkage of akaganéite and overabundant halogens (especially Cl and I) is probable only for metal-containing meteorites (chondrites and possibly iron meteorites). Iron-free meteorites such as eucrites must have different distribution of overabundant halogens, which is to be studied in future for better understanding of geo- and cosmochemistry of halogens.

The initial mass reduces up to 40% by the dissolution with nitric acid. The acid-residual fraction mainly consists of pyroxene and plagioclase. Some minor oxide minerals such as spinel and chromite are also included. It is likely that any halogen contaminant adhering on the surface of Antarctic meteorites can be removed through acid leaching. It is worth pointing out that 4.2% of the total iodine remains in the acid residual fraction of Y-74014,101, suggesting that the initial iodine is quantitatively allocated in the acid residual fraction if the indigenous

content of iodine in Y-74014,101 is similar to a mean value of H chondrites (68 ppb). Crab and Anders (1982) observed a large excess of ^{129}Xe (due to decay of ^{129}I) in HCl and HNO_3 -resistant phase, most probably pyroxene (enstatite) in enstatite chondrites. The present study suggests a similar distribution of iodine even in ordinary chondrites. This is somewhat puzzling because Y-74014,101 is an equilibrated ordinary chondrites and the acid residual fraction contains no low temperature mineral phases in which moderately volatile halogens are supposed to condense. Either iodine does not behave like volatile elements under reducing condition at the early solar system or iodine migrates into high temperature minerals such as pyroxene during metamorphism. Even for the latter case, the migration must have taken place at the early stage of the solar system since ^{129}Xe from the decay of ^{129}I was observed to be present in pyroxene of enstatite chondrites.

3.3. Separation of indigenous halogens and contaminated halogens in Antarctic meteorites by using selective dissolution method

The degree of overabundance of halogens in Antarctic meteorites vary from element to element; iodine shows the largest anomaly, followed by Cl and F, with a small anomaly of Br (Shinonaga *et al.*, 1994b; Langenauer and Krähenbühl, 1993b). The results obtained in this study support these observations (except for F). As

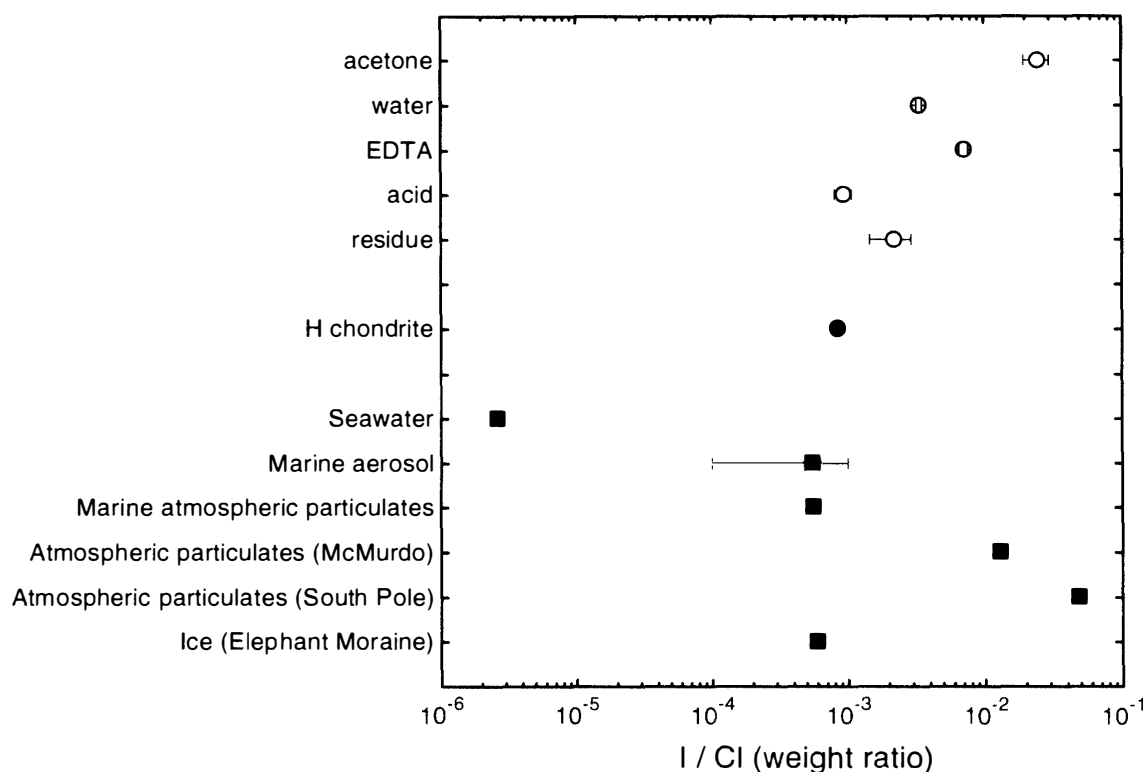


Fig. 3. I/Cl ratios in individual leachates and the acid-residual fraction of Y-74014, compared with those for seawater, marine aerosol, Antarctic ice and dust particles collected on marine and Antarctica. The I/Cl ratio of acetone leachate is close to that of dust particles collected in inland on Antarctica, suggesting that iodine is selectively long-transported in the form of organic material, possibly methyl iodide.

already noted, the overabundant halogens were contributed by several contaminants such as airborne sea spray and methyl iodide, possibly originated in the sea. These contaminants are adhered on the surface of Antarctic meteorites located on bare ice fields of Antarctica. Figure 3 compares the I/Cl ratios in individual leachates and the acid residual fraction of Y-74014,101 with those for seawater, marine aerosol, Antarctic ice and dust particles collected on marine surface and Antarctica (Dreibus *et al.*, 1986; individual data therein). The relative abundance of iodine over chlorine in the dust particles increases with increasing the distance from the coast. The I/Cl ratio of acetone leachate is close to that of dust particles collected in inland of Antarctica. This ratio decreases with the lapse of leaching. I/Cl ratios of acid-soluble and acid-residual phases are still slightly higher than but similar to the ratio indigenous to chondrites. This does not mean that Cl and I recovered in these fractions are indigenous, because total amounts of Cl and I in these fractions are about 3 times and 4 times higher than their bulk mean contents in H chondrites, respectively. Additionally, it is not guaranteed that indigenous Cl and I are not fractionated in acid-soluble and acid-residual fractions of H chondrites. Indeed, I/Cl ratio in the acid-residual fraction of Y-74014,101 is 2–3 times higher than the H chondrite mean ratio although Cl and I in this fraction are least-contaminated.

For the chronological study of Antarctic meteorites using long half-life nuclides of halogens, it is very essential to distinguish indigenous halogens from overabundant, contamination-dominant ones. For the study of cosmic-ray produced nuclide ^{36}Cl , it is not adequate to use bulk sample since the chlorine leached with water is a mixture of indigenous and contaminated chlorine. The chlorine recovered by EDTA-leaching could be indigenous as EDTA selectively dissolves Ca-phosphates, but it may be safe not to use this chlorine because the water-soluble, Cl-containing phase can not always be dissolved with water quantitatively. The acid-leachable chlorine may be mostly indigenous, but can still be contributed from contaminant. It is likely that some akaganéite is closely located with Fe-Ni metal alloy, which is not affected with water and EDTA but totally dissolved with acid. Thus, the acid-residual fraction must be the only material suitable for ^{36}Cl study although the chlorine content in this fraction is reduced largely compared with the (indigenous) chlorine in bulk sample. For the study of extinct nuclide ^{129}I , the acid residual fraction must also be the only choice. If iodine contents in the acid residual phase are as high as those in the bulk chondrites, as suggested in this study, the acid residual fraction of chondrites can be very promising for I-Xe chronological study. Further studies are needed for understanding how promising the acid residual phases of non-Antarctic and Antarctic chondrites are for chronological studies using long-lived halogen nuclides and why and where these nuclides are located in these phases.

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