Review

Screening of organic halogens and identification of chlorinated benzoic acids in carbonaceous meteorites

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Abstract

The occurrence of halogenated organic compounds measured as a sum parameter and the evidence of chlorinated benzoic acids in four carbonaceous meteorites (Cold Bokkeveld, Murray, Murchison and Orgueil) from four independent fall events is reported. After AOX (Adsorbable organic halogen) and EOX (Extractable organic halogen) screening to quantify organically bound halogens, chlorinated organic compounds were analyzed by gas chromatography. AOX concentrations varying from 124 to 209 µg Cl/g d.w. were observed in carbonaceous meteorites. Ion chromatographic analysis of the distribution of organically bound halogens performed on the Cold Bokkeveld meteorite revealed that chlorinated and brominated organic compounds were extractable, up to 70%, whereas only trace amounts of organofluorines could be extracted. Chlorinated benzoic acids have been identified in carbonaceous meteorite extracts. Their presence and concentrations raise the question concerning the origin of halogenated, especially chlorinated, organic compounds in primitive planetary matter.
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Keywords: Carbonaceous chondrite; Chlorobenzoic acids; AOX; EOX

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Aqueous extracts of the Murchison meteorite, a CM2 chondrite, contain numerous organic acids such as monocarboxylic acids (Yuen and Kvenvolden, 1973; Lawless and Yuen, 1979), dicarboxylic acids (Lawless et al., 1974) hydroxyo-carboxylic acids (Peltzer and Bada, 1978), phosphonic and sulfonic acids (Cooper et al., 1992), and amino acids (Kvenvolden et al., 1970; Pizzarello et al., 1994). Polycyclic aromatic hydrocarbons have been found in various other meteorites (Hayes, 1967; Sephton et al., 1992). A comprehensive review on organic constituents in meteorites is given by Sephton (2002). In addition to qualitative and quantitative analyses, organic compounds found in meteorites have been investigated isotopically in order to establish their origin. Evidence from isotopic abundance of hydrogen and carbon indicates that meteorite carbonaceous phases are derived from interstellar sources (Clayton et al., 1973; Engel et al., 1990; Krishnamurty et al., 1992). For most organic compounds isotopic anomalies, comparing to terrestrial sources, have been observed (Epstein et al., 1987; Pizzarello et al., 1994).

To date, the chemistry of the organic matter in the Cold Bokkeveld, Murchison and Orgueil meteorites have been well investigated. Several mechanisms of formation of hydrocarbons and their derivatives such as Fischer-Tropsch-like reactions in the solar nebula (Cronin and Pizzarello, 1990; Fomenkova et al., 1994; Sephton et al., 2001) or Miller–Urey and Strecker synthesis on a meteorite parent body, have been proposed (Cronin et al., 1993) as well as concerted cycloaddition reactions controlled by the Woodward-Hoffmann rules (Mimura, 1995).

The solvent extractable organic compounds of the Murchison meteorites were estimated to be less than 10% of the total carbon content (Cronin et al., 1993). The present study was undertaken to assess the occurrence and abundance of organohalogenes in carbonaceous chondrites. Through element screening, halogenes have been analyzed previously in carbonaceous chondrites (Dreibus et al., 1979), but a balance between organic and inorganic halogenes or an identification of halogenated organic molecules in meteorites is only poorly documented. The first investigation on halogenated organic compounds was performed by Mueller (1953) on Cold Bokkeveld, a C-2 type carbonaceous chondrite (Wiik, 1956). This meteorite is known to contain 2.2% organic carbon. The amount of extractable organic material with organic solvents was determined to be 11.1 mg/g d.w. Mueller's analysis indicated 5.89% halogenes (chlorine assumed to be the dominant element of the halogen group) in the organic extract and termed it 'chlorobitumens', no halogenes have been recorded from any of the terrestrial bitumens. This extraordinary chlorine content has been considered as an important fact, but numerous authors did not exclude the possibility that this chlorine content could probably be attributed to the solvent trichloromethane used as extractant.

Studier et al. (1965) reported the occurrence of volatile chlorinated organic compounds in carbonaceous meteorites: alkyl chlorides (C12 to C18) were detected in both the Cold Bokkeveld and Orgueil meteorites whereas dichlorobenzene was restricted to the Cold Bokkeveld and monochlorobenzene to the Orgueil meteorite, respectively. Further chlorinated benzenes and chlorinated alkanes have been also found in the Murray meteorite (Hayes and Biemann, 1968; Studier et al., 1968). The observation that meteorite extracts had no measurable optical activity and a comparatively high oxygen content led to the suggestion that these compounds were of nonbiological origin (Hayes, 1967; Cronin et al., 1988). The low temperature of decomposition of the extract further suggested that the carbonaceous complexes from the meteorite were formed at low temperature and pressure or were from terrestrial contamination.

The present work was conducted in order to supplement our investigations on naturally produced organohalogenes and their abiotic formation mechanisms (Müller et al., 1996; Niedan and Schöler, 1997; Keppler et al., 2000; Schöler and Keppler, 2003).
graphy, and gas chromatography. AOX and EOX were used to screen for bulk and extractable organohalogens. The characterization and distribution of organic halogens were performed after combustion by means of ion chromatography. Chlorinated organic compounds were identified by means of gas chromatography with two different detectors (Atomic Emission Detector and Mass Spectrometry).

2.1. Samples

The samples of the Murchison meteorite (3.9 g, USNM-5452) and the Murray meteorite (2 pieces, 2.9 g and 1.0 g, USMN-1769, respectively #99 and #100), both C2 chondrites, were obtained from the Smithsonian Institution, Washington (DC). The sample, Orgueil (3.93 g, No. 235), was obtained from the French National Museum of Natural History. The sample of the Cold Bokkeveld meteorite (21.9 g, 2 pieces) was provided by the Institute of Mineralogy of the University of Tübingen/Germany.

A fragment of each meteorite was powdered in a mortar and used as described below. As the Cold Bokkeveld was abundantly available all analyses were carried out on it, while other specimens were analyzed for AOX and of extracts by gas chromatography.

2.2. Extraction, fractionation of the sample and derivatization

Three grams of the sample was extracted with hexane (50 ml) in a Soxhlet apparatus for 24 h. The organic extract was separated, dried on Na$_2$SO$_4$ (3 g), then reduced to 5 ml in a rotary evaporator and afterwards by a gentle stream of nitrogen to 1.5 ml. This extract is called fraction 1 (F1). The remaining residue was processed as above, but with ethyl acetate (50 ml) to obtain fraction 2 (F2).

After changing the pH value to 12 by addition of NaOH pellets, the sample was extracted with 50 ml bidistilled water on a horizontal shaker. The sample was centrifuged, the aqueous supernatant separated and then adjusted to pH 2 by dropwise addition of conc. H$_2$SO$_4$. The aqueous extract was saturated with ammonium sulfate and extracted with ethyl acetate (3 x 20 ml) for the polar compounds. The whole procedure was repeated twice. The combined organic extracts were dried on Na$_2$SO$_4$, then reduced to 5 ml in a rotary evaporator and afterwards by a gentle stream of nitrogen to 1.5 ml to constitute the polar fraction 3 (F3). The fraction F3 was obtained according to a modified standard humic acids extraction method (Michaelis et al., 1995; Niedan and Schöler, 1997). The remaining residue was washed with water and dried (Remainder).

The polar compounds of F3 were methylated by reaction with diazomethane. A diethylether solution (100 µl) of diazomethane (0.1 M) was added to F3. The reaction ran at room temperature for 1 h. The remaining diazomethane was removed with a gentle stream of purified nitrogen.

3. Analytical procedures

3.1. Adsorbable organic halogens (AOX)

Twenty grams of sample was disaggregated by a freeze-thaw technique according to Nkusi and Müller (1995). The sample was mixed with 20 mg activated carbon and 10 ml 0.2 M NaNO$_3$ (pH 0.5) in a 250 ml beaker and shaken at 200 rpm for 1 h. The sample suspension was suction filtered through a polycarbonate filter (25 mm, 0.4 mm pore size). Inorganic halides were removed by washing with 30 ml 0.01 M NaNO$_3$ solution (pH 3). Analyses were made with a Euroglas AOX-analyzer. The filter with the activated carbon was incinerated at 1000 °C in a stream of oxygen and the liberated halides were micro-coulometrically titrated with silver ions. To determine blank values, 20 mg activated carbon was determined likewise. Each sample was analyzed twice and the results are expressed in mg/kg d.w. chlorine equivalent.

3.2. Extractable organic halogens (EOX)

A 100 µl aliquot of the extracted fraction was carefully injected into a combustion oven at 850 °C. The titration of the halogens as chlorine equivalent was performed according to the AOX-method described above.

3.3. Ion chromatography analysis

Ion chromatography was used to determine the distribution of organic halogens in different samples. Aliquots of about 10 mg solid sample were prepared for incineration according to the AOX method and 50 µl of the different fractions were incinerated according to the EOX method and used for further analysis. The liberated halides were trapped in a NaOH solution (0.001 M) and then processed for IC analyses.

3.4. IC parameters

A Dionex ion chromatograph 4000 equipped with a conductivity and a UV–Vis detector, automated injected volume was 20 µl. Eluent: 10 mM sodium hydroxide; pre-column: AGA4-SC (50 x 2 mm ID); separation column: ionpac AS4A-SC (250 x 4 mm ID); flow rate: 2 ml/min; detection: suppressed conductivity 3.5 µS; pressure: 9660 kPa.
3.5. Gas chromatographic analysis

Fraction F3 was derivatized prior to analysis and was analyzed by gas chromatography combined with mass spectrometry (GC/MS) or with an atomic emission spectrometer (GC/AED). All analyses were compared with external standards to identify and quantify compounds.

A Varian gas chromatograph combined with a Finnigan 5100 EI (70 eV) mass spectrometer with a quadrupole mass separator was used; split/splitless injector: 270 °C; manually injected volume: 1 μl; splitless time: 1 min; pre-column: 1.5 m × 0.32 mm ID Phenyl-Sil deactivated; separation column: DB 5 (30 m × 0.32 mm ID); thickness: 0.25 μm; carrier gas: helium 2.5 ml/min; temperature program: 45 °C for 1 min, 10 °C/min to 150 °C, 5 °C/min to 250 °C.

A Hewlett-Packard 5890 gas chromatograph combined with an AED detector HP 5921A was also used; split/splitless injector: 250 °C; automatically injected volume: 1 μl; splitless time: 1 min; pre-column: 2 m × 0.32 mm ID Phenyl-Sil deactivated; separation column: HP 5 (30 m × 0.25 mm ID); thickness: 0.25 μm; carrier gas: helium 1.2 ml/min; temperature program: 45 °C for 1 min, 10 °C/min to 150 °C, 5 °C/min to 250 °C.

4. Results and discussions

4.1. AOX

AOX measurements, expressed as chlorine equivalents, of meteorite samples showed concentrations ranging from 124 to 209 ng/g d.w. (Table 1). The measurements were carried out after quantitative removal of inorganic halides as described above.

Assuming that in carbonaceous meteorites most of the carbon is in the form of organic material, no correlation was found between measured AOX concentrations and the carbon contents examined by Wiik (1956). The Orgueil meteorite, for example, with a distinctly higher carbon content than Murray exhibited almost the same AOX concentrations.

Another approach to verify the removal of inorganic halogens is the examination of the halogen contents of organic extracts of the sample. As the Cold Bokkeveld meteorite was abundantly available, the EOX and the distribution of halogen species in different fractions were investigated on this sample. AOX measurements were carried out on the bulk of the sample (A1) and after the extractions (Remainder) (Table 2). Fractions F1, F2, and F3 were analyzed for their EOX contents. The results show that only about 25% of the bulk AOX (A1) could be extracted with organic solvents of different polarity. This corroborates the results reported by Hayes (1967) concerning the extraction of organic carbon in C1 and C2 chondrites. About a 4% loss of organic halogens was observed after extraction, when the remainder was compared with the extracted amount.

Assuming that inorganic halides (even those trapped in macromolecules) are quantitatively removed, it should be noted that the largest fraction of the organo-

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>AOX</th>
<th>2-CBA</th>
<th>4-CBA</th>
<th>2,4-CBA</th>
<th>2,5-CBA</th>
<th>2,6-CBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Murray</td>
<td>131</td>
<td>n.d.</td>
<td>n.d.</td>
<td>7.4</td>
<td>n.d.</td>
<td>0.3</td>
</tr>
<tr>
<td>Cold Bokkeveld</td>
<td>209</td>
<td>n.d.</td>
<td>8.4</td>
<td>10.3</td>
<td>n.d.</td>
<td>0.2</td>
</tr>
<tr>
<td>Orgueil</td>
<td>124</td>
<td>n.d.</td>
<td>6.9</td>
<td>9.4</td>
<td>n.d.</td>
<td>1.7</td>
</tr>
</tbody>
</table>

n.d. not detected (detection limit: 0.1 μg/g).

<table>
<thead>
<tr>
<th>Fraction</th>
<th>AOX</th>
<th>EOX</th>
<th>Fluorine</th>
<th>Chlorine</th>
<th>Bromine</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1 (Bulk)</td>
<td>209</td>
<td>–</td>
<td>65.9</td>
<td>136</td>
<td>22.8</td>
</tr>
<tr>
<td>F1</td>
<td>–</td>
<td>12.6</td>
<td>n.d.</td>
<td>31.6</td>
<td>6.1</td>
</tr>
<tr>
<td>F2</td>
<td>–</td>
<td>9.8</td>
<td>n.d.</td>
<td>35.4</td>
<td>5.4</td>
</tr>
<tr>
<td>F3</td>
<td>–</td>
<td>28.6</td>
<td>4.2</td>
<td>40.2</td>
<td>6.3</td>
</tr>
<tr>
<td>Remainder</td>
<td>150</td>
<td>–</td>
<td>61.7</td>
<td>28.8</td>
<td>5.0</td>
</tr>
</tbody>
</table>

n.d., not detected (detection limit: 1 μg/g).

–, not measurable with the applied method.
halogens was not easily extractable. The remainder represents about 75% of the bulk AOX concentration. We presume, as previously reported for soil samples, that the largest fraction of these compounds are high molecular or polymerically bound.

Comparing the different extraction steps, it should be concluded that the alkaline hydrolysis was more effective than the non-polar extractants. For example, it was possible to extract up to 13% of the organic halogens with water by changing the pH value as described above. Only about 10% of the total organic halogen was extracted by the non-polar extractants hexane and ethylacetate.

4.3. The distribution of organically bound halogens

The distribution of organic halogens in different fractions of the Cold Bokkeveld meteorite and in the bulk sample is listed in Table 2. The data are the mean of three measurements based on a new method which couples the AOX method with ion chromatography. Iodine could not be determined because the concentration was below the detection limit (10 μg/g). The data obtained for fluorine and chlorine analyses in the bulk sample are comparable with the data from previous measurements of the total halogen contents in meteorites (Dreibus et al., 1979). All extractable organofluorines (about 6%) were found in the polar fraction F3.

However, no reasonable agreement could be found with the data for bromine. About 80% of chlorine and 75% of bromine organically bound in the meteorite sample are extractable. A comparison between the organic halogen distribution and the group parameters AOX and EOX is not conclusive, since fluorine is not microcoulometrically detectable.

Fig. 1. (a) Total ion chromatogram of the methylated compounds of the aqueous fraction F3 from the Cold Bokkeveld meteorite. 4-chlorobenzoic acid and 2,4-dichlorobenzoic acid are present. (b) Single ion chromatogram (m/z 173) of the same sample showing the abundance of 2,4- and 2,6-dichlorobenzoic acid.
The abundance ratio of organic halogens deduced from our measurements strongly suggests that chlorine is the main element in extraterrestrial halogen chemistry.

4.4. Chlorinated benzoic acids

Quantitative screening of CBA in fraction F3 of different meteorites is shown in Table 1. The results of the gas chromatographic analyses are depicted in Figs. 1 and 2. On the basis of retention times and comparison with external standards, 4-chlorobenzoic acid, 2,4- and 2,6-dichlorobenzoic acids could be identified (Table 1 and Fig. 1). A special study of the three isomers of dichlorinated benzoic acid indicated that the concentrations of the 2,4-isomer were generally higher than that of the 2,6-isomer. The 2,5-dichlorobenzoic acid could not be detected in all samples. We found up to 1.7 μg/g d.w. 2,6-dichlorobenzoic acid, whereas

Fig. 2. GC/AED chromatograms of methylated compounds of the aqueous fraction F3 from the Cold Bokkeveld meteorite; (a) chlorine channel (479 nm), (b) bromine channel (478 nm).

Fig. 3. GC/AED chromatograms of methylated compounds of the aqueous fraction F3 from the Cold Bokkeveld meteorite; from top to bottom: chlorine channel (479 nm), carbon channel (496 nm), hydrogen channel (486 nm), oxygen channel (777 nm). Compounds a and b denote the methyl esters of 2,4-dichlorobenzoic acid and 4-chlorobenzoic acid.
4-chlorobenzoic acid is the only detectable monochlorinated CBA in carbonaceous chondrites (up to 8.4 μg/g d.w.). The 2,4-dichlorobenzoic acid, with concentrations up to 10.3 μg/g d.w., has been detected as the major CBA in carbonaceous chondrites. No CBAs were detectable in the Murchison meteorite, but their concentrations were likely below the detection limits (0.1 μg/kg).

The GC-AED analyses (Fig. 2) confirmed the presence of chlorinated and brominated compounds. Neither fluorinated nor iodinated compounds were detected (Figures not shown). The chromatogram of the chlorine channel (479 nm) of the AED detector (Fig. 2a) shows the presence of many chlorinated compounds, whereas only one major brominated compound (Fig. 2b) is present in the bromine channel (478 nm). By using full scan GC-MS and comparing the GC-MS chromatogram with the GC-AED chromatogram, it was possible to identify a number of halogenated organic compounds.

The results of the attribution of chlorinated compounds of the AED chromatogram of carbon channel (496 nm), hydrogen channel (486 nm), and oxygen channel (777 nm), depicted in Fig. 3, indicate that chlorinated compounds are significant constituents of the C, H, O pools in the meteorite sample. The identification of 2,4-dichlorobenzoic acid and 4-chlorobenzoic acid on the chlorine-channel of the AED chromatogram (Fig. 3) revealed elsewhere that the identified compounds are the major chlorinated organics in the analyzed sample.

5. Contamination

Contamination of meteorite samples with organic compounds is a serious problem and must be addressed. Assuming that laboratory contamination was kept at a very low level, the measured high concentrations of AOX and EOX provide clear evidence of halogenated organic compounds.

The 4-chlorobenzoic acid has been formerly used as preservative in food industry whereas the different dichlorinated benzoic acids have been exclusively used as intermediates for the synthesis of pesticides. Elsewhere the physico-chemical properties of CBA minimize the possibility of high atmospheric contamination.

Since the CBA have not been extensively spread into the environment as pesticide or for other purposes (Frear, 1975), the abundance and the isomeric distribution of chlorinated benzoic acids in the alkaline hydrolysis fraction of carbonaceous meteorites suggest that these compounds are indigenous and not a result of terrestrial contamination.

A de-novo formation of dichlorobenzoic acids during Earth entry might be conceivable, because these compounds are produced at elevated temperatures in the flue gas of waste incinerators (Mowrer and Nordin, 1987), but those meteorites never exceeded temperatures above 400 °C (Sephton, 2002).

In addition, the distribution of the dichlorinated isomers in natural and contaminated terrestrial samples is different from that in the investigated meteorite samples. In all terrestrial samples, only the 2,4- and the 2,5-isomers have been found in significant concentrations while the enzymatic chlorination of benzoic acid with chloroperoxidase solely yielded the 2,5-isomer (Flanagan and May, 1993; Michaelis et al., 1995; Niedan and Schöler, 1997). The absence of the 2,5-isomer in carbonaceous meteorites obviously reduces the possibility of an enzymatic contamination while the presence of the 2,6-isomer in meteorite samples supports the hypothesis of an extraterrestrial origin.

6. Conclusions

The high AOX and EOX contents and the detection and the isomeric distribution of CBAs in carbonaceous chondrites provide persuasive evidence that halogenated organic compounds are present in the investigated meteorites. A part of these compounds is relatively labile and can be separated by extraction, while the larger part appears to be polymerically linked.

The detection of chlorinated organic compounds in extraterrestrial samples provides new evidence of natural abiotic halogenation. Even though biological halogenation catalyzed by haloperoxidase enzymes has been demonstrated as a major route for natural organohalogen production (Geckeler and Eberhardt, 1995), abiotic pathways appear to occur in the case of extraterrestrial production as reported for other organic compounds.

Our knowledge concerning possible abiotic pathways of forming chlorinated organic compounds is limited. Terrestrial considerations point to a low temperature and pressure controlled abiotic halogenation in meteorites. Although contamination is unlikely, isotopic analyses of halogenated organic compounds are needed to conclusively determine their extraterrestrial origin.

References


