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Chloromethane release from carbonaceous meteorite affords new insight into Mars lander findings

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Controversy continues as to whether chloromethane (CH₃Cl) detected during pyrolysis of Martian soils by the Viking and Curiosity Mars landers is indicative of organic matter indigenous to Mars. Here we demonstrate CH₃Cl release (up to 8 µg/g) during low temperature (150–400 °C) pyrolysis of the carbonaceous chondrite Murchison with chloride or perchlorate as chlorine source and confirm unequivocally by stable isotope analysis the extraterrestrial origin of the methyl group (δ²H +800 to +1100‰, δ¹³C –19.2 to +10‰). In the terrestrial environment CH₃Cl released during pyrolysis of organic matter derives from the methoxyl pool. The methoxyl pool in Murchison is consistent both in magnitude (0.044%) and isotope signature (δ²H +1054 ± 626‰, δ¹³C +43.2 ± 38.8‰) with that of the CH₃Cl released on pyrolysis. Thus CH₃Cl emissions recorded by Mars lander experiments may be attributed to methoxyl groups in ungraded organic matter in meteoritic debris reaching the Martian surface being converted to CH₃Cl with perchlorate or chloride in Martian soil. However we cannot discount emissions arising additionally from organic matter of indigenous origin. The stable isotope signatures of CH₃Cl detected on Mars could potentially be utilized to determine its origin by distinguishing between terrestrial contamination, meteoritic infall and indigenous Martian sources.

Controversy has persisted regarding the interpretation of data from Mars lander experiments designed to detect organic material in Martian soil. The Viking 1 Mars Lander thermal volatilization experiment showed release of chloromethane (CH₃Cl) at 200 °C (30 pmol from 100 mg soil)¹. In a second experiment by Viking 2, CH₃Cl was not detected but dichloromethane (CH₂Cl₂) was present (0.05–47 pmol/100 mg soil)². These results were initially dismissed as terrestrial contamination although chlorinated compounds were not detected in blank analytical runs. Whilst the presence of CH₂Cl₂ could possibly be attributed to such contamination it is difficult to envisage CH₃Cl as a contaminant at the concentration observed. Later discovery of perchlorate (ClO₄⁻) in Martian Arctic soil by the Phoenix Lander³ prompted the suggestion by Navarro-González et al.⁴ that the heating of ClO₄⁻ with indigenous organic material in Martian soil could lead to oxidation of most organic matter to CO₂ and H₂O but with formation of trace amounts of CH₃Cl and CH₂Cl₂ by chlorination of organic matter with Cl₂ and possibly HCl produced during decomposition of perchlorate. CH₃Cl and CH₂Cl₂ formation was demonstrated on heating Mars-like soils from terrestrial hyper-arid environments with 1% magnesium perchlorate at 500 °C^{4,5}. The recent Mars Science Laboratory (MSL) mission, Curiosity, again noted CH₃Cl on pyrolysis of soil from Rocknest at 144–533 °C (1.4 nmol/100 mg soil) and at 98–425 °C (2.3 nmol/100 mg soil)^{6,7}. Both CH₂Cl₂ (0.8–1.2 nmol/100 mg soil) and traces of chloroform (CHCl₃, 0.02–0.04 nmol/100 mg soil) were also observed on pyrolysis at lower temperatures. Again the results were largely attributed to contamination by volatiles thermally released from the soil samples, in this case by reaction of a derivatization reagent from the wet chemistry experiment with perchlorate^{6,7}. However the relative molar abundances of the total C1/C4 chlorinated hydrocarbons were much higher and more variable than those found in laboratory analogue experiments with the derivatization reagent⁷. Hence, even though considered less likely, other sources for the organic carbon, such as Martian surface matter were not ruled out.

Thus although CH₃Cl has been detected on two separate Mars Lander missions, its presence has been in general discounted as a contaminant, not least because it was considered unlikely that such a compound could be a major

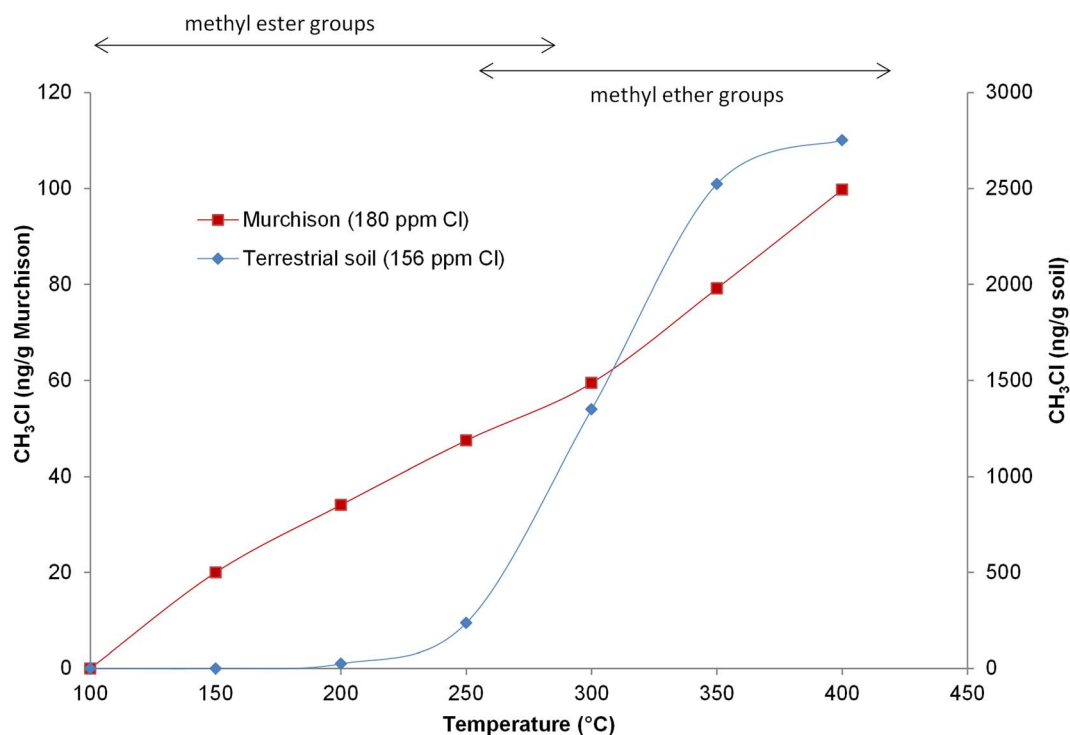


Figure 1 | Cumulative CH₃Cl production from Murchison and terrestrial soil. The sample was heated in a glass vessel (under N₂) for 15 min at 150°C then heating was programmed to increase at 50°C min⁻¹ to 200°C, at which temperature the sample was held for 15 min. This programming in 50°C increments continued to a maximum temperature of 400°C. The amount of CH₃Cl was measured at the end of the hold period at each temperature by gas chromatography–mass spectrometry¹⁰. After this the vessel was opened and flushed with N₂ before resealing for the next heating step. The arrows indicate the temperature ranges where methyl ester and ether groups are converted to CH₃Cl.

product of thermal conversion of organic matter. Hence Biemann and coworkers^{1,2,8} concluded that organic matter, if present in the samples analysed by Viking 1 and 2, was at extremely low levels, a view however strongly challenged in recent years^{4,6,7,9}. In addition, a very recent report suggested that indigenous martian or meteoritic organic carbon sources may be preserved in the mudstone at Yellowknife Bay. However it was not positively established that the carbon source of the chlorinated hydrocarbons released during its pyrolysis was of Martian origin¹⁰.

To inform this debate we wish to draw attention to the fact that CH₃Cl production from organic matter in the presence of Cl⁻ in the terrestrial environment is a ubiquitous and well-documented phenomenon^{11–13}. The compound is generated mainly from the methoxyl groups of the biopolymers pectin and lignin and, in the case of the former, the reaction can occur at ambient temperatures at physiological pH. Indeed the plant methoxyl pool is the predominant source of CH₃Cl present as a trace gas in the terrestrial atmosphere^{13,14}. Both ester and ether methoxyl groups in organic matter are subject to attack by Cl⁻ on pyrolysis under aerobic or anaerobic conditions. This solid state reaction requires intimate mixing of a chloride salt and organic material. Methyl ester pyrolysis to CH₃Cl occurs at low temperatures and in high yield between 150 to 250°C^{11,12}, whilst methyl ether conversion predominantly takes place between 300 and 400°C^{11,15}. It is possible that the production of CH₃Cl reported from organic matter in the presence of ClO₄⁻ is largely due to the formation of Cl⁻ during decomposition of ClO₄⁻ rather than reaction of Cl₂ or HCl with organic matter as previously postulated⁴.

In this study we investigate the potential for production of CH₃Cl from meteoritic matter. We present data obtained from the pyrolysis (150 to 400°C) of samples of the Murchison meteorite (a well investigated carbonaceous chondrite of type CM2 that fell in Australia in 1969) both with and without Cl⁻ and ClO₄⁻ supplementation which

clearly demonstrate formation of CH₃Cl from organic matter of extraterrestrial origin. The Murchison meteorite has an organic carbon and total chlorine content (TCl) of around 2% and 0.018%, respectively^{16,17}, and contains substantial amounts of hematite and serpentine-like minerals¹⁶, rendering it a suitable analogue for the bulk of infalling meteoritic material on Mars^{18,19}. For comparison we studied a terrestrial soil sample (an oxisol from Maui Island, Hawaii) with an organic carbon and TCl content of around 7% and 0.016%, respectively. The Hawaiian soil also contained large amounts of iron oxides and silicates and might be considered similar to Martian soil analogues recently employed in experiments⁹. We report that methoxyl groups of the intact organic matter reaching the Martian surface can be converted to CH₃Cl by pyrolysis with perchlorate or chloride in Martian soil. These observations are consistent with the well-documented release of CH₃Cl in the terrestrial environment from the methoxyl pool of organic matter in the presence of chloride^{11–13}. Our data offers a simple explanation for the CH₃Cl observed during in-situ thermal analyses of Martian samples by previous Mars landers. We further show that the stable carbon and hydrogen isotope signatures of CH₃Cl could potentially be utilized to determine the origin of CH₃Cl detected on Mars by distinguishing between terrestrial contamination, meteoritic infall and indigenous Martian sources. For future planetary missions we suggest that CH₃Cl could be an important target compound for constraining the origin of any organics found.

Results

Firstly we examined ground samples of Murchison and Hawaiian soil for their potential to form CH₃Cl during thermal conversion at low temperatures. Significant CH₃Cl release from Murchison was observed at temperatures between 200 and 400°C (Fig. 1). However the Hawaiian soil sample showed 28 fold greater CH₃Cl release over the heating cycle. The much lower emissions from

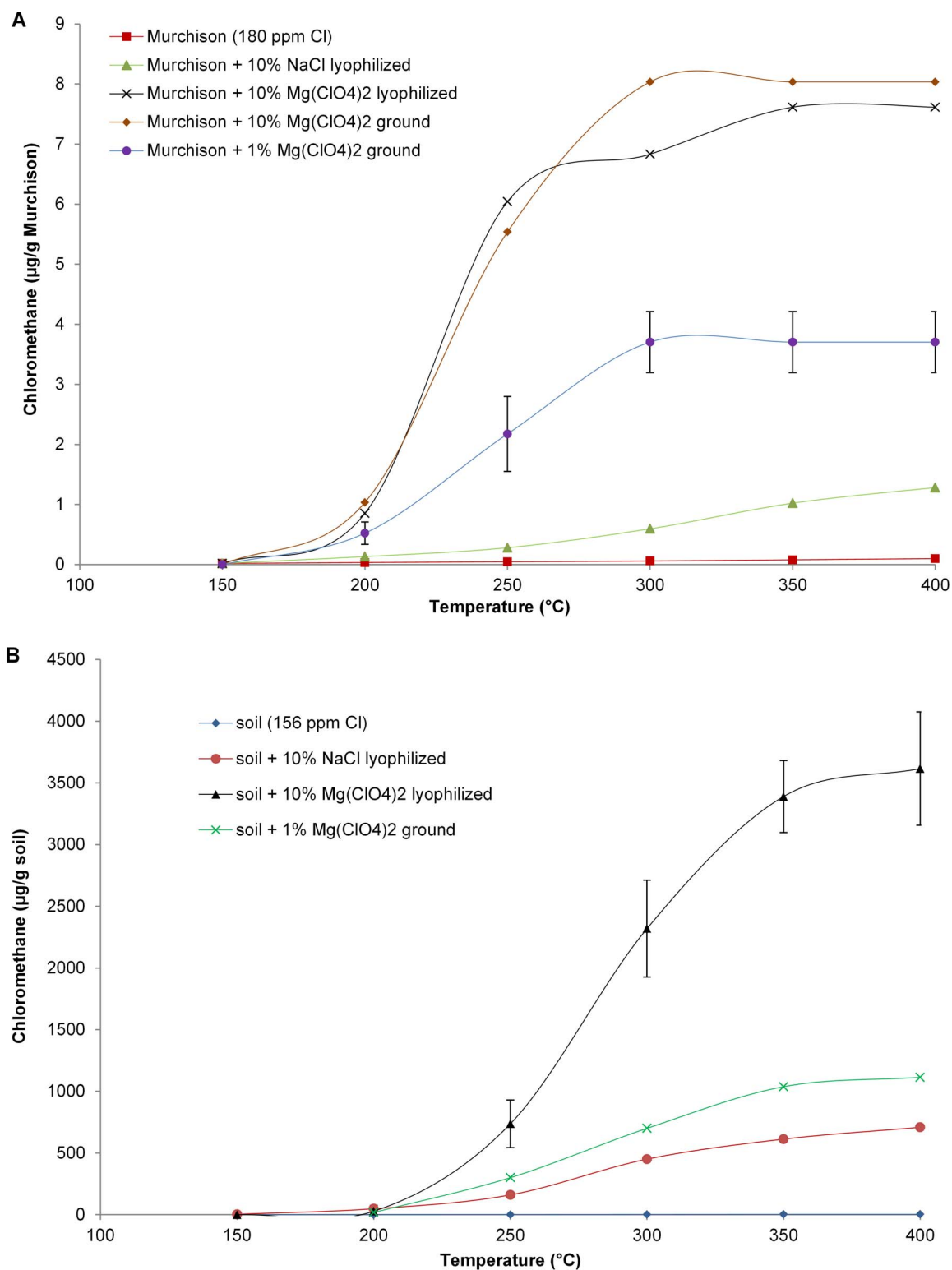


Figure 2 | Cumulative CH₃Cl production when supplemented with NaCl or Mg(ClO₄)₂. (A) Murchison and (B) terrestrial soil; both non-supplemented and when supplemented with sodium chloride or magnesium perchlorate. Experimental protocol is given in Fig. 1 and text. Error bars indicate SD of mean values from independent samples (n = 3–4).

Murchison are explained not only by the lower organic matter content but also more importantly by the much reduced methoxyl content of the Murchison organic matter. Methoxyl content of Hawaiian soil organic matter determined using hydrogen iodide (HI)²⁰ was $1.55 \pm 0.66\%$. Determination of the methoxyl content of the organic component in Murchison proved more difficult presumably because

the physical nature of the meteoritic material rendered the methoxyl groups less accessible. Successive treatments with HI yielded a methoxyl content of $0.044 \pm 0.025\%$. Release of CH₃Cl from Hawaiian soil organic matter attains a maximum at 300–350°C as would be predicted since it contains a substantial proportion of methyl ether groups (lignin type)^{11,15} whereas the temperature profile of



Table 1 | Amounts of CH_3Cl , CH_2Cl_2 and CHCl_3 formed during low temperature thermal decomposition over various temperature ranges of Murchison and soil samples when supplemented with $\text{Mg}(\text{ClO}_4)_2$ at two different concentrations. Data were collected separately from Figure 2

Sample	$\text{Mg}(\text{ClO}_4)_2$ %	Temperature range °C	CH_3Cl	CH_2Cl_2 ng g ⁻¹	CHCl_3	Ratio $\text{CH}_3\text{Cl}/\text{CH}_2\text{Cl}_2$	Ratio $\text{CH}_3\text{Cl}/\text{CHCl}_3$
Murchison	1	150–200	309	traces [#]	traces*	-	-
Murchison	1	200–250	969	7.1	traces*	137	-
Murchison	10	150–200	900	traces [#]	traces*	-	-
Murchison	10	200–250	4100	1205	160	3.4	26
soil	1	150–200	17800	traces [#]	traces*	-	-
soil	1	300–350	380000	128	12	2970	31700
soil	10	150–200	61600	traces [#]	traces*	-	-
soil	10	300–350	1040000	2370	30	438	34700

[#]below quantification limit of 0.6 ng per 100 mg sample,

*below quantification limit of 0.9 ng per 100 mg sample.

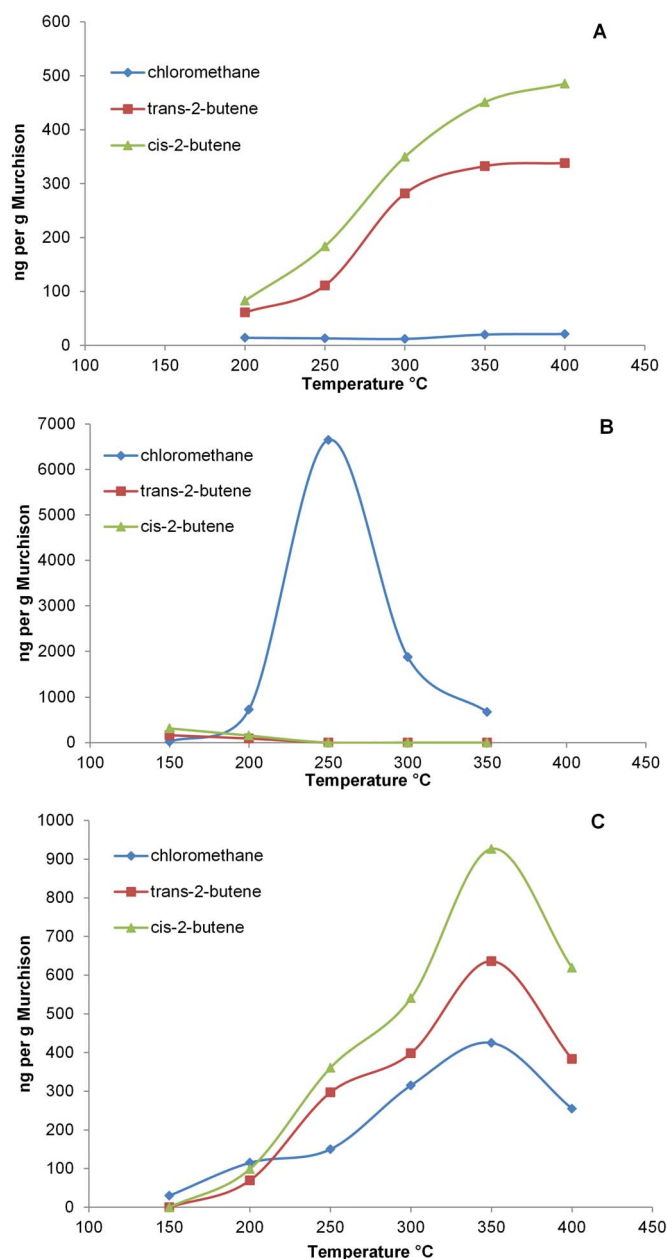


Figure 3 | Release of chloromethane, *trans*-2-butene and *cis*-2-butene from Murchison. (A) Murchison without supplementation, (B) with added $\text{Mg}(\text{ClO}_4)_2$ (10%) and (C) with added with NaCl (10%) over the temperature range 150 to 400°C (50°C steps); amounts produced at each temperature step.

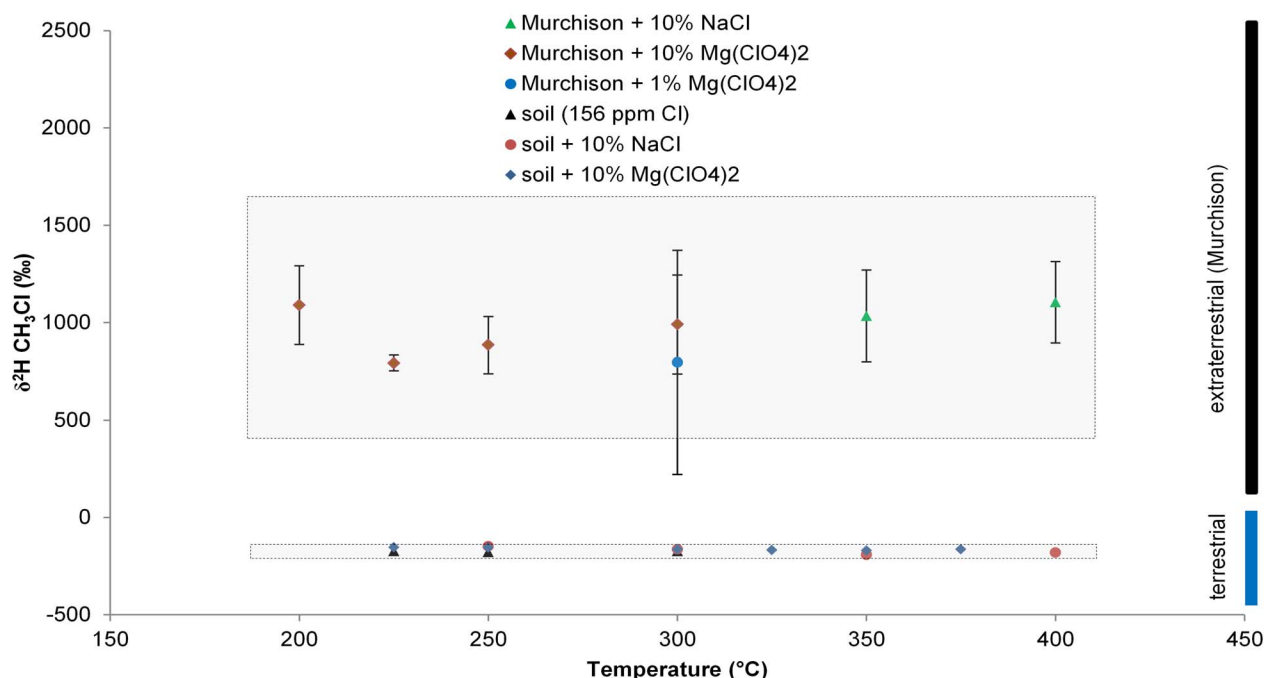


Figure 4 | Stable hydrogen isotope composition of chloromethane. $\delta^2\text{H}$ values of CH_3Cl released during pyrolysis of Murchison and terrestrial soil. Grey shaded areas indicate the $\delta^2\text{H}$ of the organic matter methoxyl pool (mean \pm SD, $n = 5-10$). The black and blue vertical bars indicate the ranges of $\delta^2\text{H}$ for extracted organic matter and volatiles from Murchison^{24,34,35} and terrestrial organic matter³⁶, respectively. Error bars indicate SD of mean values from independent samples ($n = 3-4$). SDs for soil sample were in the range of 1 to 30‰ and thus too small to be displayed.

Murchison emissions is more linear indicating that methyl ester groups, which release CH_3Cl at lower temperatures, may also be of significance.

The effect of supplementation of Murchison and Hawaiian soil samples with Cl^- or ClO_4^- was then investigated. An intimate mixture of supplement and sample was achieved by addition as an aqueous solution followed by lyophilization. When the Murchison sample with 10% NaCl (6.1% Cl^-) was heated to 400°C, CH_3Cl emissions were some 13 fold higher than those of the non-supplemented sample (Fig. 2A). No other chlorinated compounds such as CH_2Cl_2 and CHCl_3 were detected. In view of the suggestion that heating of Martian soil with ClO_4^- could lead to formation of CH_3Cl ^{4,5} supplementation of Murchison at 1 and 10% magnesium perchlorate (0.32 and 3.2% on a Cl basis, respectively) was examined. At the 1% supplementation level CH_3Cl emissions were approximately 40 fold higher than for the non-supplemented material and increased a further 2 fold at the 10% level. No significant difference was noted on overall emissions whether powdered magnesium perchlorate was ground with the sample or added as an aqueous solution and lyophilized prior to pyrolysis. Interestingly, CH_2Cl_2 and traces of CHCl_3 were detected at the 1% supplementation level although total emissions of CH_2Cl_2 were over two orders of magnitudes less than those of CH_3Cl , but increased markedly at higher perchlorate concentrations (Table 1). The Hawaiian soil sample displayed similar CH_3Cl release patterns to those of Murchison when either Cl^- or ClO_4^- was added (Fig. 2B). Chloromethane release increased by factors of approximately 250 and 1300 on supplementation with Cl^- or ClO_4^- , respectively. As with Murchison when supplemented with ClO_4^- , CH_3Cl release ceased at 400°C. The greatly increased emissions observed from the fortified Hawaiian soil relative to the fortified Murchison sample can as with the non-supplemented samples be attributed to the much higher methoxyl content. Again maximum CH_3Cl emissions occurred at temperatures above 250°C in contrast with Murchison where emissions mainly occurred between 200 and 300°C with maximum release at 250°C. Maximum conversion of

methoxyl groups to CH_3Cl from Murchison and Hawaiian soil samples were ~25 and 60%, respectively when 10% magnesium perchlorate were added. These conversion rates are in line with those previously reported for terrestrial biological material under similar temperatures regimes^{11,12,15}. The lower conversion rates observed for Murchison is presumably due to its more complex mineralogical composition. No CH_2Cl_2 or CHCl_3 emissions were detected from Cl^- supplemented soil samples but ClO_4^- supplementation again resulted in release of traces of these compounds (Table 1).

Non-chlorinated volatile organic compounds (VOCs) were also observed during thermal treatment of Murchison and Hawaiian soil samples. Interestingly the formation and release of the VOCs were very different from those for CH_3Cl . Figure 3 shows the release of CH_3Cl and two non-chlorinated compounds, *trans*-2-butene and *cis*-2-butene, from Murchison with and without ClO_4^- supplementation. When Murchison was heated without ClO_4^- , the non-chlorinated compounds were much more abundant than CH_3Cl (Fig. 3A, Supplementary Table 2). However, upon addition of ClO_4^- the non-chlorinated VOCs were only observed at temperatures below 200°C (Fig. 3B, Supplementary Table 2) whereas maximum CH_3Cl formation was at 250°C. Moreover CH_3Cl release dramatically increased, by two to three orders of magnitude, upon supplementation. This might indicate that during decomposition of ClO_4^- the organic matter giving rise to the VOCs was effectively oxidized and thus explains why they are not formed at measureable levels. However because CH_3Cl is preferentially formed, when chlorine is available, from methoxyl groups which are not as prone to such oxidation processes at lower temperatures its formation is enhanced. In addition other chlorinated methanes, such as CH_2Cl_2 and CHCl_3 , which were not detected in Murchison and soil without added ClO_4^- , were clearly identified in the samples that contained ClO_4^- . These chlorinated compounds were not observed when chloride (NaCl) was added to Murchison. Thus, after low temperature pyrolysis (150 to 300°C) of Murchison in the presence of ClO_4^- , chlorohydrocarbons were by far the most abundant

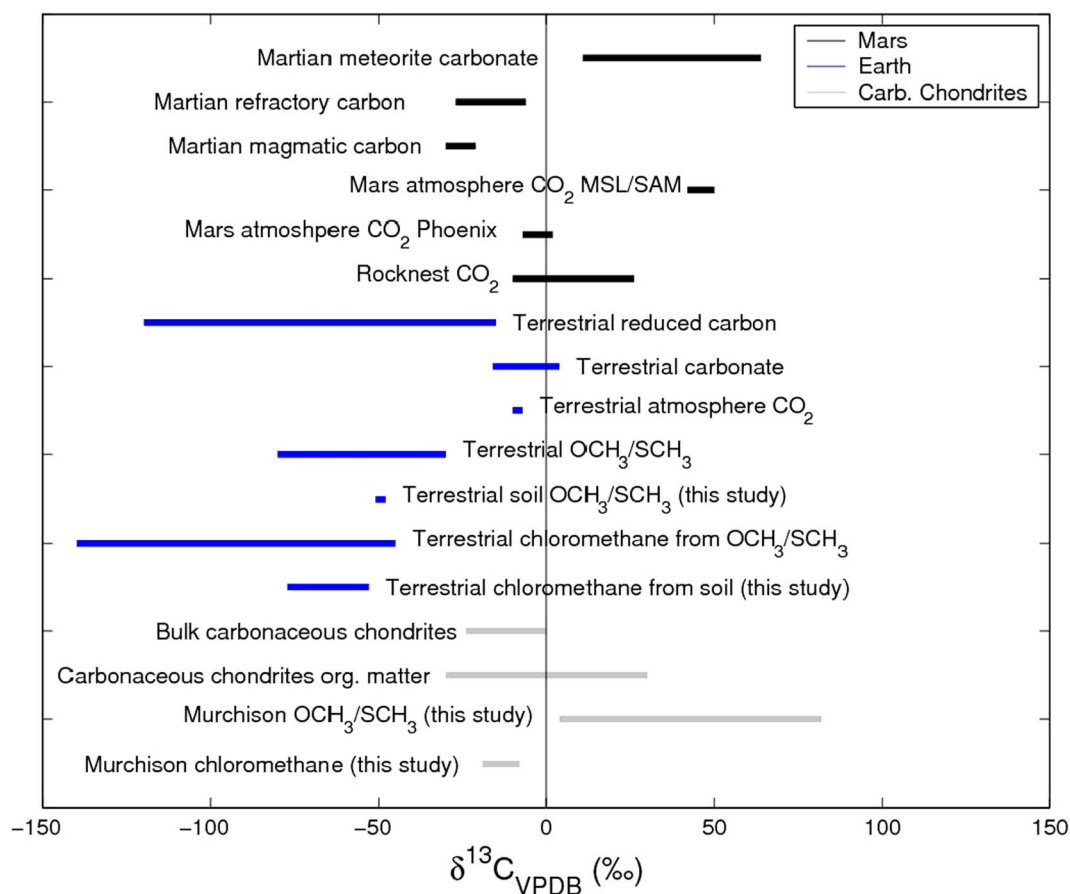


Figure 5 | $\delta^{13}\text{C}$ values on Earth and in relevant solar system reservoirs. Carbon isotopic composition of materials from Mars^{7,48–50}, Earth⁴⁵ and carbonaceous chondrites^{27,51–53} (modified Leshin *et al.*⁷). For comparison $\delta^{13}\text{C}$ values of CH_3Cl and precursor methoxyl groups measured during this study and from previous studies^{12,13,23}.

organic compounds detected by the analytical procedures employed in this study. Interestingly the temperature profile for CH_3Cl release from Murchison with added ClO_4^- showing maximum formation at around 250°C (Fig. 3B) is remarkably similar to that recently reported for CH_3Cl release from heated samples of Martian fines at Rocknest⁶ and a mudstone at Yellowknife Bay¹⁰ whereas Murchison without supplementation or with added NaCl showed a different pattern of CH_3Cl formation over this temperature range (Fig. 3C).

Measurements of the stable hydrogen and carbon isotope values ($\delta^2\text{H}$, $\delta^{13}\text{C}$) of CH_3Cl using an automated purification and pre-concentration procedure²¹ were conducted where concentrations permitted at various stages during pyrolysis of the Murchison and Hawaiian soil samples (Fig. 3). Mean $\delta^2\text{H}$ of CH_3Cl emissions from Murchison ranged from roughly $+800$ to $+1100$ per mil (‰) and unequivocally confirm the extraterrestrial origin of the methyl group. The values are in the same range as those measured for the methoxyl pool ($+1054 \pm 626$ ‰) in Murchison and are quite different from those of hydrogen in organic matter on Earth. They are within the range of values reported for various types of organic compounds in Murchison ($+188$ to $+2980$ ‰) thus excluding terrestrial contamination as the methoxyl source (Fig. 4). In contrast mean $\delta^2\text{H}$ for CH_3Cl from -192 to -149 ‰ for emissions by terrestrial soil are within the expected range for terrestrial organic matter and similar to those measured for the methoxyl pool (-184 ± 10 ‰) of such matter. These values are also consistent with the predicted values of CH_3Cl when derived from ether and ester methoxyl groups^{21,22} of organic matter derived from vegetation in Hawaii which indicate a mean

isotope fractionation of -178 ± 34 ‰ relative to the modelled precipitation values of Hawaii. Thus thermal treatment of Murchison and Hawaiian soil samples causes no significant fractionation between the precursor methyl group and the CH_3Cl emitted, a finding in accord with previous observations of CH_3Cl release from terrestrial samples during thermal conversion^{21–23}.

The mean $\delta^{13}\text{C}$ value for the terrestrial methoxyl pool (-49.2 ± 1.2 ‰) was quite different from that for Murchison ($+43.2 \pm 38.8$). The organic carbon in Murchison has been reported to be isotopically very heterogeneous²⁴ and this might explain the much larger variations for $\delta^{13}\text{C}$ values found for the methoxyl groups of Murchison. Similarly, mean $\delta^{13}\text{C}$ values of CH_3Cl emissions from terrestrial soil (ranging from -74 to -54 ‰) and Murchison (ranging from -19.2 to $+10$ ‰) on pyrolysis between 200 and 350°C were distinct from one another, (Fig. 5, Supplementary Table 1). Figure 6 shows a two-dimensional plot of the $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values of CH_3Cl emissions from the terrestrial environment and Murchison. Also shown are the predicted values for CH_3Cl emissions from a biological Martian origin (for details of assumptions made see discussion). From this figure it is clear that isotopic signatures would be a powerful tool in constraining the origin of the organic matter precursor of CH_3Cl derived from Martian soil.

Discussion

In light of our results and in view of the relatively high meteoritic debris content expected in Martian soil (2 – 40 %)^{18,25,26}, CH_3Cl emissions on pyrolysis of such soils should be anticipated if Cl^- or ClO_4^- are present even in low concentrations, provided all organic matter

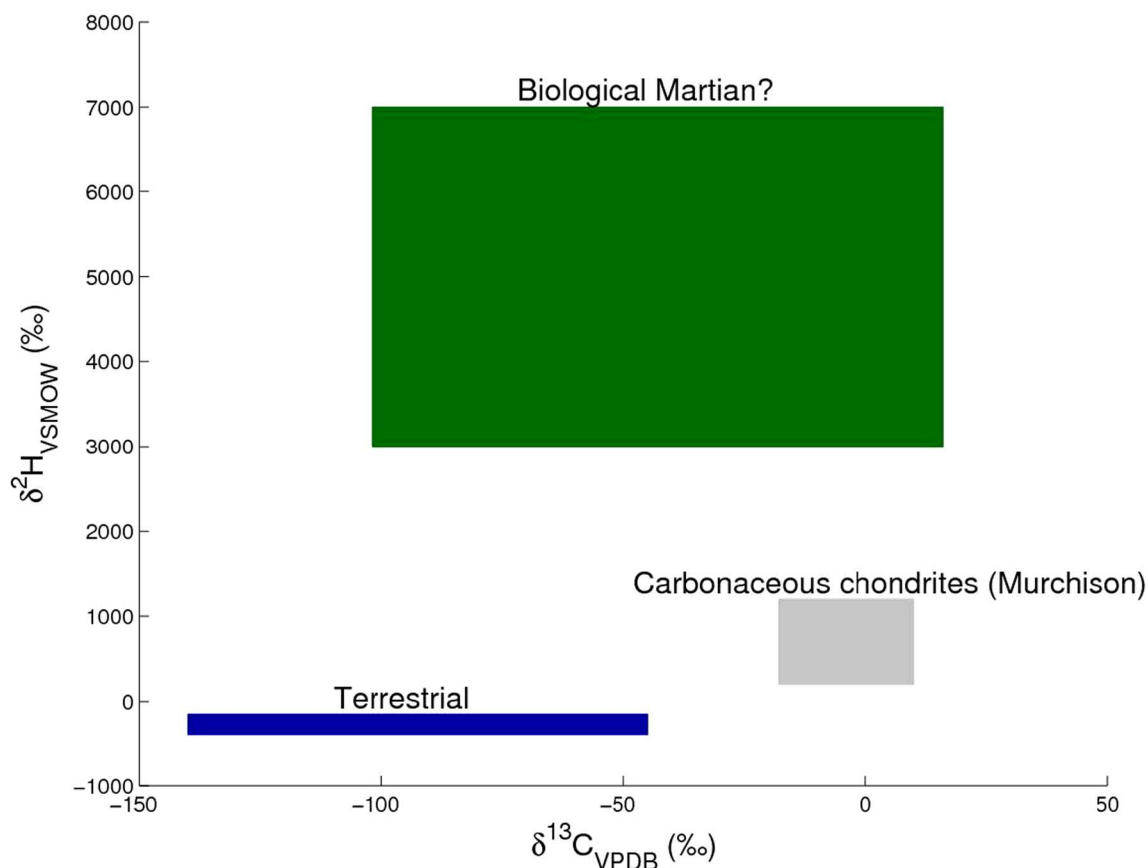


Figure 6 | Isotopic composition of CH_3Cl of terrestrial and extraterrestrial organic matter. Stable carbon and hydrogen isotope composition of CH_3Cl released during low temperature pyrolysis of terrestrial and extraterrestrial organic matter. The green box indicates hypothetical biological Martian signatures based on assumptions provided in the discussion section, the most important of which is that we assumed that life forms on Mars would have evolved in a similar way to those on earth.

has not been destroyed by short-wave UV radiation^{27–30} or oxidants such as hydrogen peroxide and perchlorate³¹. Perchlorate should normally be chemically stable at Martian temperatures, but can release reactive species on gamma irradiation³². Total Cl at the Viking sites averaged 0.73% at Chryse Planitia and 0.44% at Utopia Planitia³³ and 0.06 to 0.68% at Meridiani Planum (by Opportunity rover)³⁴ but the speciation was not determined. The Wet Chemistry Laboratory on Phoenix Mars Lander found 0.4 to 0.6% soluble ClO_4^- and 0.01 to 0.04% soluble Cl^- in Martian Arctic soil whilst Mars Odyssey showed total Cl averaging 0.49% (0.1–1%) from equator to mid latitudes³⁵. Making the assumption that the Martian soil contained 2–40% carbonaceous meteoritic debris then based on emissions from the Murchison meteorite, the anticipated CH_3Cl yield from 100 mg of Martian soil could range from 0.2 to 52 ng (4 to 1030 pmol) if Cl is present entirely as Cl^- at concentrations between 0.018 and 6%. If a significant proportion of Cl is present as ClO_4^- , CH_3Cl yields could be substantially higher. Thus a soil ClO_4^- content of 0.9% (0.3% on a Cl basis) would increase the upper limit of the range to 148 ng/100 mg soil (see calculation of CH_3Cl release rates from Martian soils in Methods section). The range is entirely consistent with CH_3Cl release from the Viking 1 soil sample at Chryse Planitia and also those observed at Rocknest by the Curiosity mission. Whilst the postulated yield in surface soil may be diminished if UV radiation and oxidation are significant degradative pathways for organic matter, such processes will be much less relevant in sub-surface samples. Although our calculations are based on the probable CH_3Cl flux from organic matter of meteoritic origin, it is not inconceivable that a proportion of CH_3Cl emissions from Martian soils arises from organic matter associated with an

indigenous biological source with Cl^- or ClO_4^- as Cl donor. The emission of small quantities of CH_2Cl_2 on pyrolysis of an intimate mixture of Murchison and perchlorate may imply that the detection of this compound in vapors from heated Martian soil may not be entirely attributable to terrestrial contamination.

Although Martian organic matter was not definitively confirmed in the recent MSL^{6,7}, the presence of materials that produce substantial amounts of oxygen upon heating suggests that its detection in Martian soils will be difficult using pyrolysis techniques. Perchlorates decompose most organics to CO_2 when heated, but clearly not methoxyl groups (as we have shown in both Murchison and terrestrial soil), because these organic moieties specifically form CH_3Cl at relatively low temperatures when chlorine is available. Thus CH_3Cl is one of the few compounds formed in substantial quantities from organic matter during pyrolysis that survive the strong oxidation processes occurring during decomposition of perchlorate. In light of this study we suggest that CH_3Cl production during low temperature pyrolysis of Martian soils could be an important indicator of organic matter on Mars. Pyrolysis temperatures in the range of 200 to 250°C are considered of most potential since CH_3Cl emissions are at a maximum. Furthermore, the nature and quantities of the chlorinated methanes and their homologues detected may provide an indication of the perchlorate content of Martian soils as was recently postulated^{4,6,7,36}. Particularly with supplementation at higher perchlorate concentrations the ratios of $\text{CH}_3\text{Cl}/\text{CH}_2\text{Cl}_2$ and $\text{CH}_3\text{Cl}/\text{CHCl}_3$ were greatly reduced (Table 1) and in a similar range than those previously reported by the MSL at Rocknest⁶.

We further propose that measurement of the stable isotope signature of CH_3Cl emissions would define its origin by distinguishing



between terrestrial, meteoritic infall and indigenous Martian sources (Fig. 6). Ranges of $\delta^{13}\text{C}$ (-140 to -47%) and $\delta^2\text{H}$ (-400 to -150%) values of CH_3Cl emissions from terrestrial matter during low temperature pyrolysis are based on the results reported and assumptions made by Keppler *et al.*^{12,27}, Greule^{20,21,37} and Komatsu *et al.*³⁸. Ranges of $\delta^2\text{H}$ and $\delta^{13}\text{C}$ values from Murchison are results from this study. We here assume that the range might be also representative of other carbonaceous chondrites.

The hypothetical biological Martian isotope signatures are based on the following assumptions: life forms evolved in a similar way to those on earth including uptake of carbon and hydrogen (using water and inorganic carbon CO_2) with isotopic fractionations similar to those on earth. On Mars $\delta^2\text{H}$ values of atmospheric water and water in sediments/rocks have been reported to be in the range of $\sim +3000$ and $+7000\%$ ^{7,39} (and references therein). On earth $\delta^2\text{H}$ values of bulk biological organic matter usually reflect $\delta^2\text{H}$ values of precipitation⁴⁰. Hydrogen isotope fractionations between source water and biologically produced organic compounds, in the range of -100 to -200% , have been observed for lipids or methoxyl groups^{41–43}. Thus we would assume a range of $\sim +3000$ to $+7000\%$ for $\delta^2\text{H}$ values of CH_3Cl released from hypothetical biological Martian organic matter because no obvious fractionation (between methoxyl groups and CH_3Cl) was observed in this study for the release of CH_3Cl during low temperature pyrolysis of soil and Murchison samples. It is also important to note that methoxyl groups are considered to be chemically stable in that the hydrogen atoms of the methoxyl moiety do not exchange with those of surrounding water during ongoing degradation processes²². Furthermore the reaction pathway for conversion of halides to halomethanes^{11,12,15} at low temperatures (up to 400°C) has been shown to cause no substantial hydrogen isotope fractionation between the precursor methyl group and the halomethane^{20,21}.

In contrast to hydrogen fractionation we assume several significant fractionation steps for the biological formation of organic carbon compounds on Mars similar to processes known on Earth⁴⁴. For precursor carbon we consider CO_2 in the Martian atmosphere (measured range -22 to $+50\%$)³⁹ as the potential carbon source (Fig. 5) available for metabolism of ancient Martian life forms and hence use these $\delta^{13}\text{C}$ values for our hypothesis. On Earth carbon isotope fractionation for heterotrophic and autotrophic organisms (e.g. plants and animals)^{42,45} relative to inorganic carbon (CO_2 , carbonate) is well described⁴⁴. Plants and other autotrophs fix CO_2 . Enzymatic isotope effects and overall fractionations associated with fixation of inorganic carbon during autotrophic growth are known to be in the range of -2 to -36% ⁴⁴. Animals and other heterotrophs utilize organic compounds and usually they reflect the $\delta^{13}\text{C}$ values of their diet. However, if the assimilated carbon is a small molecule (like CO_2 , CH_4 , or acetate), as e.g. for methanogens, significant isotopic fractionation is likely to accompany fixation or assimilation⁴⁴. Additional carbon isotope fractionation in C1 metabolism relative to bulk organic matter has also been described^{12,46}. For example in plants carboxyl groups in pectin are esterified by the enzyme pectin O-methyltransferase (PMT) using S-adenosylmethionine (SAM) as methyl donor. Work on purine alkaloids in several plant species has suggested that the methyl pool in SAM is significantly depleted relative to the carbohydrate pool⁴⁶. Moreover, enzymic transmethylation involving SAM can entail a substantial kinetic isotope effect (KIE). A similar KIE in the enzymic methylation of pectin by PMT utilizing ^{13}C -depleted SAM as the methyl donor could account for the magnitude of the ^{13}C depletion observed in the pectin methoxyl pool. To date, carbon fractionation of biological OCH_3 relative to the inorganic carbon sources ($\Delta \sim 10$ to -33%) has been reported^{12,23}. A further stable carbon isotope fractionation can be expected when CH_3Cl is released at temperatures between 200 and 300°C from OCH_3 groups as previously reported¹³ and noted during this study ($\Delta \sim -10$ to -30%). The summed fractionation (i. inorganic carbon fixation, ii: C1 metabolism, and iii. CH_3Cl release) from initial

inorganic precursor CO_2 on Mars to the final release of CH_3Cl is then hypothesized to be in the range of -30 to -80% . Given the measured $\delta^{13}\text{C}$ values of -22 to $+46\%$ for inorganic carbon available for biosynthesis on Mars (Fig. 5) we would therefore expect possible $\delta^{13}\text{C}$ values for CH_3Cl released during low temperature pyrolysis of biological Martian methoxyl groups likely to be in the range of -102 to $+16\%$.

Thus, as can be easily seen in Figure 6, based on our current data and the isotopic constraints regarding biological Martian organic matter, all three recently discussed possible sources for CH_3Cl observed during pyrolysis of Martian fines^{4,6,7,10}, including terrestrial contamination, meteoritic infall or biological Martian origin would be clearly distinguishable if the isotopic composition of the emitted CH_3Cl was known.

Methods

Sample preparation. The Murchison meteorite fell near the town of Murchison (Victoria, Australia) on September 28, 1969 and a total recovered mass of ~ 100 kg was collected that year. In recent years it is the largest primitive type CM meteorite to fall on Earth and is composed mainly of silicates, Fe-oxides and sulphides and a substantial amount of organic matter. Approximately 15 g of the Murchison meteorite was available for the investigations conducted in this study (see Supplementary Fig. 1). The material was ground in a ceramic mortar to a particle size distribution peaking around 100 μm , similar to the dominant size of unmelted micrometeorite infall¹⁸. The organic carbon and total chlorine content of Murchison were determined at 2% ¹⁶ and 180 ppm¹⁷, respectively.

Hawaiian soil Ah (oxisol) was collected from Maui Island, ground to a powder and lyophilized. A large fraction of this material also consisted of silicates and Fe-oxides. The organic carbon and total chlorine content of the soil were measured at 7% and 156 ppm, respectively.

Supplementation of chlorine to Murchison and soil sample. Sodium chloride (NaCl) and magnesium perchlorate $\text{Mg}(\text{ClO}_4)_2$ (CAS number: 10034-81-8) were purchased from SIGMA. Aqueous solution (1 ml) containing either 100 mg NaCl or 10 mg $\text{Mg}(\text{ClO}_4)_2$ was added to ground Murchison or terrestrial soil sample. The mixture was homogenized and samples were then lyophilized. In some experiments $\text{Mg}(\text{ClO}_4)_2$ was added in solid form to ground Murchison or terrestrial soil sample and then homogenized in a ceramic mortar.

Thermal treatment of samples. Experiments were conducted with 100 to 1000 mg meteorite or 5 to 250 mg soil samples. The sample was placed inside a leak-tight glass pyrolysis tube (2.8 cm outer diameter and 18.5 cm length (total gas volume ~ 74 ml), flushed with dry nitrogen (99.999%) or helium (99.999%) and then placed into a GC oven (see Supplementary Fig. 2) where the temperature could be increased up to 400°C .

Analytical procedures. Identification and quantitation of chlorinated compounds. Samples of the headspace from the pyrolysis reactor were removed and transferred to a cryogenic pre-concentration unit (in-house preparation) which was connected to a gas chromatograph mass spectrometer (HP 6890 Series Gas Chromatograph/HP 5973 Mass Selective Detector, Agilent Technologies, Palo Alto, USA). The gas chromatograph was fitted with a GasPro column (60 m \times 0.32 mm i.d.; Agilent Technologies, Palo Alto, USA) and the temperature was isothermally held either at 70 or 150°C . For identification of analytes, the mass spectrometer was operated in the total ion mode measuring ion currents between 10 and 200 amu. For analyte quantification the mass spectrometer was employed in the selected ion mode (SIM) measuring ion currents at m/z 49, 50, 51, 52, 83, 84, 85, 86. For example CH_3Cl was identified both by its retention time and mass spectrum and quantification was performed using SIM measuring ion currents at m/z 50 and 52 amu (Supplementary Fig. 3). To quantify the peak area for ion m/z 50 at the expected retention time of CH_3Cl was compared to a standard response curve. Its detection limit was 0.6 ng. Control samples were prepared and treated in an identical fashion to that of the samples except that no meteoritic material or soil was added to the pyrolysis tube.

During thermal treatment of NaCl supplemented and non-supplemented Murchison and soil samples CH_3Cl was the only chlorinated organic volatile detected by the analytical technique employed for this study. However when these samples were supplemented with perchlorate dichloromethane (CH_2Cl_2) and chloroform (CHCl_3) were also observed.

Formation of CH_2Cl_2 and CHCl_3 from samples supplemented with ClO_4^- . CH_2Cl_2 and CHCl_3 emissions were dependent on both the amount of added ClO_4^- and pyrolysis temperature (Supplementary Table 1). Both compounds were identified from their retention time and mass spectrum and for quantification the mass spectrometer was operated in the selected ion mode (Supplementary Fig. 4).

Cryogenic pre-concentration unit for stable hydrogen isotope measurements. A cryogenic pre-concentration unit with several purification and concentration stages was designed and built in-house (Supplementary Fig. 5). A detailed description of the system is provided in Greule *et al.*²¹. In brief: following evacuation of a sample loop



(100 ml), a gas sample was allowed to enter the sample loop after passing through an Ascarite II and iodine pentoxide chemical trap for removal of CO₂ and unsaturated hydrocarbons, respectively. (Note the iodine pentoxide chemical trap was not used for isotopic measurements of CH₃I). Following equilibration, the sample was flushed into two physical traps. The temperature of the first trap (empty 1/8" stainless steel tube) was set at -30°C to remove water. The second trap (1/8" stainless steel tube filled with glass beads) was cooled to -170°C, a temperature sufficient to trap CH₃Cl quantitatively. After 10 min this trap was rapidly heated to 150°C and CH₃Cl was flushed to a focus trap (50 cm × 0.25 mm i.d. deactivated fused silica capillary placed in liquid nitrogen, at -196°C). After 15 min, the focus trap was removed from liquid nitrogen to enable transfer of CH₃Cl via a heated transfer line (90°C) to the gas chromatograph - thermal conversion - stable isotope ratio mass spectrometry (GC-TC-IRMS) unit.

Measurement of stable hydrogen isotope values of CH₃Cl using GC-TC-IRMS analysis. Hydrogen isotope ratios of CH₃Cl (δ²H-CH₃Cl) were measured by compound specific high-temperature conversion isotope ratio mass spectrometry analysis (GC-TC-IRMS) (Supplementary Fig. 6). The cryogenic pre-concentration unit (described above) was directly coupled to a Hewlett Packard HP6890 gas chromatograph (Agilent Technologies, Palo Alto, USA) which was interfaced with an Isoprime IRMS via a 1050°C GCV high-temperature conversion reactor (Isoprime, Manchester, UK). The GC was equipped with a GasPro column (60 m × 0.32 mm i.d.; Agilent Technologies, Palo Alto, USA) and was held isothermal either at 70 or 150°C. The pyrolysis reactor contained a 0.65 mm i.d. quartz tube packed with chromium pellets (Isoprime, Manchester, UK). The helium flow from the pre-concentration unit was set to 1.0 ml/min.

A tank of ultrahigh-purity hydrogen (Hydrogen 5.0, Air Liquide, Düsseldorf, Germany) with a certified δ²H V-SMOW value of -172 ± 2‰ (certified by Air Liquide) was used as the working reference gas. The H3⁺ factor, determined daily during this investigation (3 month period), was in the range 4.79–5.00 ppm/nA.

The conventional 'delta' notation, which expresses the isotopic composition of a material relative to that of a standard on a per mil (‰) deviation basis, was used: values of δ²H (‰) relative to that for V-SMOW are defined by the equation

$$\delta^2\text{H} = \left(\left(\frac{{}^2\text{H}}{1\text{H}} \right)_{\text{sample}} / \left(\frac{{}^2\text{H}}{1\text{H}} \right)_{\text{standard}} \right) - 1$$

All sample results were corrected for area and day-to-day drift in the system using a local CH₃Cl reference that was measured several times daily (for calibration refer to Greule *et al.*²¹). The stable hydrogen isotope values for the local CH₃Cl reference was -117.1‰. The method allows determination of isotopic values of samples ranging from -100 to -300‰ with typical standard deviations better than ±3‰ for δ²H-CH₃Cl values²¹. It is important to note that as the range of δ²H values spanned by the reference materials was quite narrow, the scale calibration was thus not ideal and this could have affected the uncertainty range of the very positive δ²H-CH₃Cl values (+400 to +1600‰) from the Murchison samples.

Chloromethane emission rates from Murchison samples without chloride or perchlorate supplementation were too low to enable reliable isotopic measurements. Furthermore emission rates of CH₂Cl₂ and CHCl₃ from Murchison supplemented with ClO₄⁻ were also too low to enable reliable stable hydrogen isotope measurements.

Stable hydrogen isotope values of bulk methoxyl groups. Hydrogen isotope signatures of the bulk methoxyl pool (Supplementary Fig. 7), including esterified and ether bonded methyl groups (also methyl thioesters), of the meteorite and soil samples were measured as CH₃I released upon treatment of the samples with HI. The procedure employed was that of Greule *et al.*²⁰ except that larger samples of headspace were withdrawn and pre-concentrated using the above described cryogenic pre-concentration unit. Hydroiodic acid (HI, 0.5 ml, 55–58%) was added to the sample (5 to 1000 mg) in a glass vial (5 ml). The vials were sealed with caps containing PTFE lined butyl rubber septa and incubated for 30 min at 130°C. After heating, the vials were allowed to equilibrate at room temperature (22 ± 0.5°C, air conditioned room) for at least 30 min before a sample of headspace was transferred to cryogenic pre-concentration unit and the GC-TC-IRMS system.

The primary reference working standard for reporting on the VSMOW scale was CH₃I with a measured value of -179.0 ± 2.9‰ (n = 15, 1σ). The δ²H value of this standard (δ²H-CH₃I) was calibrated against international reference substances (IAEA-CH-7 [δ²H_{VSMOW}: -100.3‰], NBS-22 [δ²H_{VSMOW}: -118.5‰]) and a tertiary standard (IA-R002, purchased from Iso-Analytical Ltd, Sandbach, UK [δ²H_{VSMOW}: -111.2‰]) using an EA-IRMS system configured for δ²H measurements (elemental analyser-isotopic ratio mass spectrometer, Iso-Analytical Ltd, Sandbach, UK). As the range of δ²H values spanned by the reference materials was quite narrow, the scale calibration was thus not ideal and this could have affected the uncertainty range of the very positive δ²H-CH₃I values (+800 to +1100‰) measured for the Murchison samples.

Measurement of stable carbon isotope values of CH₃Cl using GC-C-IRMS analysis. Carbon isotope ratios of CH₃Cl (δ¹³C-CH₃Cl) were measured by compound specific combustion isotope ratio mass spectrometry analysis (GC-C-IRMS) (Supplementary Fig. 8). The cryogenic pre-concentration unit (described above) was directly coupled to a Hewlett Packard HP6890 gas chromatograph (Agilent Technologies, Palo Alto, USA) which was interfaced with an Isoprime IRMS via a 850°C GC5 combustion

reactor (Isoprime, Manchester, UK). The GC was equipped with a GasPro column (60 m × 0.32 mm i.d.; Agilent Technologies, Palo Alto, USA) and was held isothermal at 75 or 140°C. The combustion reactor contained a 0.65 mm i.d. quartz tube filled with copper(II) oxide (CuO) rods. The helium flow from the pre-concentration unit was set to 1.3 ml/min.

A tank of ultrahigh-purity carbon dioxide (CRYSTAL mixture ISO-TOP, Air Liquide, Düsseldorf, Germany) was used as the working reference gas. The conventional 'delta' notation, which expresses the isotopic composition of a material relative to that of a standard on a per mil (‰) deviation basis, is used: values of δ¹³C (‰) relative to that for V-PDB are defined by the equation

$$\delta^{13}\text{C} = \left(\left(\frac{{}^{13}\text{C}}{12\text{C}} \right)_{\text{sample}} / \left(\frac{{}^{13}\text{C}}{12\text{C}} \right)_{\text{standard}} \right) - 1$$

All sample results were corrected for day-to-day drift in the system using a local CH₃Cl reference that was measured several times daily. The stable carbon isotope value for the local CH₃Cl reference was -30.34‰.

Stable carbon isotope values of bulk methoxyl groups. Carbon isotope signatures of the bulk methoxyl pool (Supplementary Fig. 9), including esterified and ether bonded methyl groups (also methyl thioesters), of the meteorite and soil samples were measured as CH₃I released upon treatment of the samples with HI by the procedure of Greule *et al.*²⁷ except that larger samples of headspace were withdrawn and pre-concentrated using the above described cryogenic pre-concentration unit. The procedure employed is identical to that described above for the analysis of stable hydrogen values of bulk methoxyl groups except that the sample size was 100 mg and 2 mg for meteorite and soil, respectively.

The primary reference working standard for reporting on the VPDB scale was CH₃I with a measured value of -69.27 ± 0.05‰ (n = 15, 1σ). The δ¹³C value of this standard (δ¹³C-CH₃I) was calibrated against international reference substances (IAEA-CH-6 [δ¹³C_{VPDB}: -10.43‰], IAEA-CH-7 [δ¹³C_{VPDB}: -31.83‰] and NBS-22 [δ¹³C_{VPDB}: -29.81‰]) using an EA-IRMS system configured for δ¹³C measurements (elemental analyser-isotopic ratio mass spectrometer, Iso-Analytical Ltd, Sandbach, UK). The range of δ¹³C values spanned by the reference materials was quite narrow, the scale calibration was thus not ideal and this could have affected the uncertainty range of the more positive δ¹³C-CH₃I values measured for the Murchison samples.

Measurements of non-chlorinated volatile organic compounds (VOCs). For the analysis of VOCs with a m/z > 47 amu a Varian gas chromatograph GC 3400 linked to a Varian Saturn 4D with electron impact ionization and ion trap mass spectrometer was used. The GC was equipped with a capillary column DB-5 (60 m; 0.32 mm i.d.; 1 μm film thickness; Agilent Technologies, Palo Alto, USA). Dynamic injection and preconcentration was performed by a customized purge and trap system⁴⁷. The mass spectrometer was operated in the total ion mode measuring ion currents between m/z 47 and 200 amu and compounds were identified by spectral comparison with a NIST mass spectral library.

Detection of C1 to C4 hydrocarbons by gas chromatography - flame ionization detection. Headspace from the reaction chamber was sampled using a 10 ml Hamilton gas tight syringe and analysed by gas chromatography (HP-AL/S column, 30 m length × 0.535 mm i.d. × 15μ film thickness Al₂O₃, Agilent Technologies, Palo Alto, USA) with flame ionization detection. Volatile organic compounds (C1 to C4) such as methane, ethane, ethene, propane, propene, butenes and butane were monitored from Murchison and soil with and without added ClO₄⁻ when heated at 250°C (Supplementary Table S2). A reference gas including several hydrocarbons was used for quantification.

Calculation of chloromethane release rates from Martian soils. The cumulative amounts of CH₃Cl produced from Murchison with and without added chlorine species (chloride and perchlorate) at temperatures from 200 to 400°C are shown in Figs. 1 and 2. The amounts range from 100 ng g⁻¹ (no supplementation) up to 1300 ng g⁻¹ with 6% chloride added and 3700 ng g⁻¹ with ClO₄⁻ content of 0.9% (0.3% on a Cl basis). Assuming that Martian soil consists of 2 to 40% meteoritic debris^{18,25,26} all of which is carbonaceous chondritic in composition, and that the fluxes determined on Murchison in the laboratory are representative of thermal volatilization experiments with Martian soils then we calculate the CH₃Cl yield from 100 mg of Martian soil could range from 0.2 to 52 ng (4 to 1030 pmol) (100 ng g⁻¹ × 0.02 g × 0.1 lower range and 1300 ng g⁻¹ × 0.4 g × 0.1 upper range) if Cl is present entirely as Cl⁻ at concentrations between 0.018 and 6%. If a significant proportion of Cl is present as ClO₄⁻, CH₃Cl yields could be substantially higher. A soil ClO₄⁻ content of 0.9% would increase the upper limit of the range to 148 ng/100 mg (3700 ng g⁻¹ × 0.4 g × 0.1). A higher ClO₄⁻ concentration would increase the CH₃Cl yield and also markedly increase the formation of other chlorinated compounds such as CH₂Cl₂ and CHCl₃.

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Author contributions

F.K., J.T.G.H. and D.B.H. conceived the study. F.K., T.S. and M.G. carried out the experiments. F.K., J.T.G.H., D.B.H., U.O. and H.F.S. worked on the scientific interpretation and wrote the manuscript.

Additional information

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>



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