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Chlorine isotope fractionation between chloride (Cl^-) and dichlorine (Cl_2)

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Abstract

The use of chlorine stable isotopes (^{35}Cl and ^{37}Cl) can help to constrain natural processes that involve chlorine species with different oxidation states. Theoretical studies based on thermodynamic and quantum mechanical approaches predict large isotope fractionation during redox reactions but to date, these reactions have not been studied experimentally.

Here, we explore the chlorine isotope fractionation during the oxidation of hydrated Cl^- (redox state of -I) to Cl_2 (redox state of 0) at 25°C and at 0°C . Our apparatus consists of a sealed glass reactor where liquid HCl is mixed with liquid H_2O_2 , a strong oxidant. Following complex reaction pathways, this mixture ultimately leads to the oxidation of Cl^- and to the formation of Cl_2 gas. As long as it is degassing, the Cl_2 gas is flushed out of solution using N_2 as a vector-gas from the glass-reactor to a potassium hydroxide (KOH) solution (pH 14) where it disproportionates into soluble species: Cl^- and ClO^- . After each experiment, the chlorine isotopic composition was measured in the recovered KOH -trap solution, as well as in the residual HCl solution. Consistent with

theoretical predictions, the produced Cl₂ gas is always enriched in the heavier ³⁷Cl as compared to the initial Cl-reservoir.

The following isotope fractionation factors are obtained:

-at 0°C the isotopic fractionation $1000\ln\alpha_{(Cl_2-Cl)}$ is 4.51 (+1.65/-0.49) ‰

-at 25°C the isotopic fractionation $1000\ln\alpha_{(Cl_2-Cl)}$ is 3.94 (+0.69/-0.18) ‰

From the obtained data it is suggested that the production of Cl₂ gas in our experiments is best described by a closed-system distillation. Our results are in agreement with published theoretical ab initio calculations.

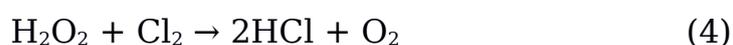
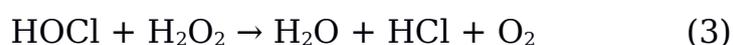
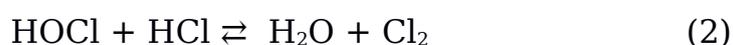
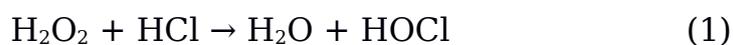
1. Introduction

The electron configuration of halogens is characterized by an outer electron shell that is only one electron short to reach a noble gas configuration. This results in the reduced form -I as the dominant oxidation state for halogens. At the earth's surface, chlorine is overwhelmingly found as chloride (Cl⁻) in aqueous phases and is usually considered as chemically non-reactive. Recent studies are pointing out the role and the potential importance of other, more oxidized, chlorine species in various natural environments or in biologically controlled reactions. For example, it was recently discovered that salt marshes are major sources for CH₃Cl emissions with potentially large implications for ozone depletion (Rhew et al., 2000; Keppler et al., 2005; Blei et al., 2010). Likewise, the occurrence of perchlorate salts in hyperarid regions (Dasgupta et al., 2005; Kounaves et al., 2010) questions the fate of marine aerosols in the high atmosphere. On Mars, recent data from orbiters and landers have confirmed the persistence of highly oxidized chlorine species such as chlorate and perchlorate (Keller et al., 2006; Hecht et al., 2009; Hanley et al., 2012; Farley et al., 2016), providing potential constraints on Mars' past hydrogeology. In addition, major concerns were raised on the environmental presence of persistent organo-chlorine compounds of anthropogenic origin with serious health risks for the human population (Wolff et al., 1993; Simonich and Hites, 1995; Blais et al., 1998).

The study of chlorine stable isotopes (³⁵Cl and ³⁷Cl) is highly relevant in many of these environments (e.g. Sturchio et al., 2011; Bernstein et al., 2011).

Classic thermodynamic laws and quantum mechanics predict different isotopic partitioning between substances in chemical equilibrium. Except for a few studies on specific molecules such as HCl or perchlorate (Hoering and Parker, 1961; Ader et al., 2008; Sharp et al., 2010), experimental determination of isotope partitioning are lacking for most Cl-bearing molecules. As a consequence, in most cases, only theoretical investigations (Urey and Greif, 1935; Urey, 1947; Richet et al., 1977; Schauble et al., 2003; Czarnacki and Hałas, 2012) can be used to estimate the fractionation factor between two chlorinated compounds. The most complete work was published by Schauble et al. (2003). Based on *ab-initio* calculations of vibrational frequencies, they predicted reduced partition function ratios (or β -factors) for numerous Cl-bearing minerals and gases, and pointed out strong correlations between oxidation state and isotope partition function (with the β -factor being positively correlated to the oxidation state). In their study however, the β -factor for hydrated chloride (Cl^-), which is the dominant chlorine species, was not predicted, likely due to poor understanding of the role of the hydration shell on isotope partitioning. Recently, Czarnacki and Hałas (2012) explored the role of the hydration shell on Cl^- , Br^- and S^{2-} . Their *ab-initio* calculations were less sophisticated than the ones used by Schauble et al. (2003), but their predictions at different temperatures for the equilibrium of the $\text{Cl}_{\text{aq}} - \text{HCl}_{\text{gas}}$ system are at first order in good agreement with experimental results obtained by Sharp et al. (2010).

In the present study, we report for the first time the chlorine isotope fractionation associated with oxidation of dissolved Cl^- to Cl_2 gas at 25°C and at 0°C. We generated oxidized chlorine species by mixing hydrochloric acid solution (12N) with hydrogen peroxide (30% and 50% for two independent experiments). The reaction between these two compounds leads to the formation of Cl_2 gas following a complex pattern of reactions:



These equations were proposed by [Skudaev et al. \(2008\)](#). Equation (2) indicates the formation of Cl_2 , but Equations (3) and (4) suggest that an excess of H_2O_2 may inhibit the formation of Cl_2 to the benefit of O_2 . Reactions (3) and (4) prevent a complete oxidation of Cl^- in the initial HCl solution.

Here we experimentally constrain the isotope fractionation between dissolved Cl^- and Cl_2 . We also explore the kinetics of the Cl_2 generation, as well as the evolution with time of its isotope composition. We discuss the notion of isotope equilibrium in the context of our experiments, and evaluate whether the isotope fractionation between Cl^- and Cl_2 is consistent with the β -factors proposed by [Schauble et al. \(2003\)](#) and [Czarnacki and Hałas \(2012\)](#).

2. Apparatus and chemical procedure

Our apparatus consists of a sealed glass-reactor that is closed by a septum, in order to inject the two reagents (HCl and H_2O_2) in an O_2 -free atmosphere (see Figure 1). The glass-reactor is open at the top and connected to a N_2 -gas tank (that will serve as vector-gas) and is also connected in series to the bottom of two glass tubes (traps) that are filled with a KOH solution (4M). The first trap is sealed and directly connected to the second one that is open to the fume hood.

2.1. Principles

The N_2 gas flux is set to 2 mL/min and bubbles through the two glass tubes filled with KOH solution. After 30 minutes the entire system is considered as completely devoid of air and the HCl liquid solution is introduced with a syringe through the septum in the glass-reactor. Thereafter, the H_2O_2 liquid solution is injected. The mixture colours yellow almost instantaneously and bubbles start to form within less than one minute. Any exsolved Cl_2 from the solution is removed from the glass-reactor and flushed to the first KOH solution trap by the vector-gas. When interacting with the high pH (=14)

solution, Cl_2 gas disproportionates in two soluble chlorine species: chloride and hypochlorite, according to the following equation:



In order to evaluate the quantitative dissolution of Cl_2 in the first KOH trap, a second KOH trap was installed after the first one, and its chlorine content was monitored as well.

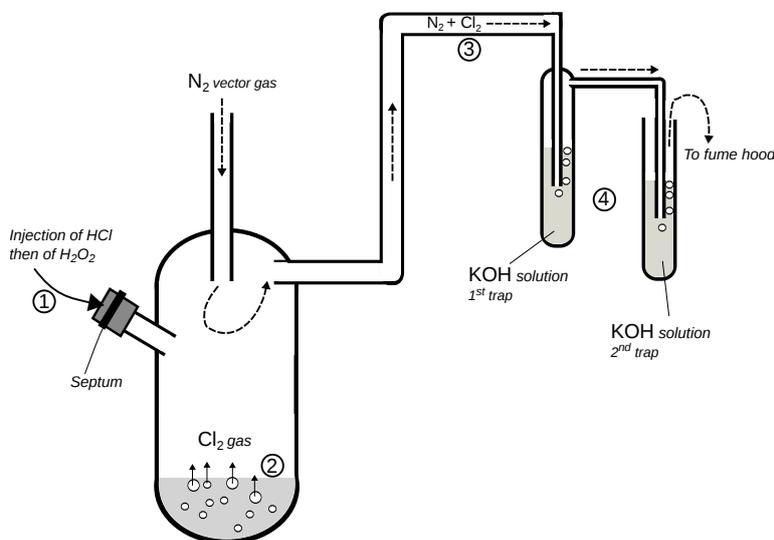


Figure 1: Drawing of our apparatus and the most important phases of the experiment. (1) First the liquid HCl solution is added and second the liquid H₂O₂ solution is added through the septum in the glass-reactor. In (2) the Cl₂ is leaving the solution and is carried over in (3) by the N₂ vector-gas. In 4) the gas composed of N₂ and Cl₂ bubbles through the first KOH trap and Cl₂ disproportionates in Cl⁻ and ClO⁻. The second KOH trap is a safety trap in case not all Cl₂ was trapped in the first trap.

2.2. First experiment

The first experiment was conducted at 25°C. We used 5 mL liquid HCl solution (12N) which corresponds to an amount of approximately 60 mmol of Cl⁻, to which we added 1 mL H₂O₂ solution (30%), which corresponds to an amount of 10 mmol. This experiment lasted 1 hour. In order to follow the evolution of Cl₂ production with time as well as its isotopic composition, the two KOH traps were replaced with fresh ones at time t=5, t=15, t=30, t=45 and t=60 minutes. By definition time t=0 corresponds to the injection of the H₂O₂ solution in the glass-reactor.

2.3. Second experiment

The second experiment was conducted at 0°C by immersing the glass-reactor in ice-water. We used 3 mL of liquid HCl solution (12N) which corresponds to an amount of approximately 36 mmol of Cl⁻, to which we added 0.6 mL of liquid H₂O₂ (50%), corresponding to an amount of about 10.5 mmole of H₂O₂. This experiment lasted for 2 hours and traps 1 and 2 were not replaced during that time interval.

3. Determination of δ³⁷Cl and Cl⁻ amount

The chlorine stable isotope composition (³⁵Cl and ³⁷Cl) is usually reported with the δ³⁷Cl notation, in permil variations relative to Standard Mean Ocean Chlorine (SMOC) defined as:

$$\delta^{37}\text{Cl} = [({}^{37}\text{Cl}/{}^{35}\text{Cl})_{\text{sample}}/({}^{37}\text{Cl}/{}^{35}\text{Cl})_{\text{SMOC}} - 1] \times 1000 \quad (6)$$

We measure the δ³⁷Cl on CH₃Cl-gas in a dual-inlet gas-source mass-spectrometer (Delta plus XP, ThermoFisher), following the classic method described by [Kaufmann et al. \(1984\)](#); [Long et al. \(1993\)](#) and [Eggenkamp \(1994\)](#). With this protocol, chlorine must be in the form of Cl⁻ and dissolved in acidified water to be precipitated as silver chloride salt (AgCl). The AgCl salt is then reacted with CH₃I to quantitatively produce CH₃Cl-gas. The CH₃Cl gas is purified from excess CH₃I by preparative gas-chromatography (using two Porapak-Q filled columns) and quantified with a Baratron pressure-gauge in a calibrated volume before it is introduced into the mass-spectrometer. The δ³⁷Cl is then calculated from the signal intensities of m/z 52 (CH₃³⁷Cl) and m/z 50 (CH₃³⁵Cl). One measurement consists of a series of 10 individual comparisons of the 52/50 ratio in the sample CH₃Cl to that of the 52/50 ratio of the CH₃Cl gas used as a laboratory standard. The reference gas is compared with a CH₃Cl gas prepared from seawater chloride at least twice a day, and typically following every 5 to 6 samples. In our laboratory, the external reproducibility on an international standard seawater is usually better than ±0.04 ‰ (1σ, n=25 in the course of this study).

In a solution of known volume, the quantification of the Cl-amount is usually achieved from the measurement of the Cl⁻ concentration with High Performance Liquid Chromatography (HPLC). However, this technique is reliable only if chlorine exists as dissolved Cl⁻.

To understand these experiments, we must constrain the isotopic composition as well as the Cl amount of: 1) the initial Cl-reservoir (that is the initial HCl solution), 2) the residual Cl-reservoir (that is the final HCl solution after reacting with H₂O₂), and 3) the Cl₂ products at different times in the case of the Experiment 1 or at the end of the experiment in the case of the Experiment 2. However, while $\delta^{37}\text{Cl}$ and Cl-amount determinations are relatively straightforward when chlorine is only present as Cl⁻, it becomes more complex when chlorine also exists in the form of other species. In this study, for the solutions where other oxidized forms of chlorine were expected, we needed at first to quantitatively reduce these species to Cl⁻ in order to perform precise $\delta^{37}\text{Cl}$ measurements and Cl-amount quantifications of the bulk chlorine. In the next section we describe in detail how we proceed for each sample that was recovered from our experiments.

3.1. The initial Cl-reservoir

The initial volume of HCl solution introduced in the glass-reactor is known. Therefore, the quantification of the initial Cl-amount can be calculated from the Cl-concentration given by the manufacturer, the concentration measured in HPLC (since chlorine only exists as Cl⁻), or the concentration estimated from the amount of CH₃Cl produced for the $\delta^{37}\text{Cl}$ analysis. With chlorine being exclusively present as Cl⁻, measuring the $\delta^{37}\text{Cl}$ of the initial HCl solution is also straightforward by following the classic method described above.

3.2. The residual Cl-reservoir

At the end of the experiment, chlorine may occur not only in the reduced Cl⁻ form in residual Cl-reservoir. According to Equations (1) and (2), chlorine might also be present in oxidized forms such as HClO or dissolved Cl₂, species

that cannot be measured by HPLC. Hence, we increased the pH of the residual solution to approximately 14 through the addition of solid KOH, so that the possible remaining Cl_2 could disproportionate to Cl^- and ClO^- . The residual solution is then heated to 80°C and zinc powder (Zn^0) is added in excess to reduce ClO^- to Cl^- , similarly to the method proposed by [Ader et al., 2001](#) for the reduction of perchlorate. Then, nitric acid (HNO_3 , 16N) is slowly added to the solution in order to oxidize and dissolve the remaining excess of Zn^0 . At this step, the residual solution is acidic and chlorine only occurs as dissolved Cl^- . Therefore, conditions are met for the $\delta^{37}\text{Cl}$ determination with the classic method as described above.

Extreme chemistry of the reduced-residual solution, together with elevated Cl concentrations do not allow a reliable quantification of Cl-content with HPLC without introducing uncertainties associated with dilutions by several orders of magnitude. A preliminary attempt to quantify the remaining chloride in the reservoir through CH_3Cl quantification before $\delta^{37}\text{Cl}$ analysis, was inconclusive because of the large uncertainties on the solution volumes used for CH_3Cl production.

3.3. The Cl_2 products

While it bubbles through the KOH solution, the Cl_2 gas disproportionates into Cl^- and ClO^- , two soluble species. The recovered solutions are already under alkaline conditions because of the excess of OH^- and Zn^0 powder is therefore directly added in excess after heating the solution to 80°C . Finally, as for the residual Cl-reservoir, nitric acid (16N) is added to oxidize and dissolve the excess of Zn^0 . Once the trap is acidified and free from Zn^0 , the solution is ready for the precipitation of Cl^- as AgCl for subsequent $\delta^{37}\text{Cl}$ determination. Again, as for the residual Cl-reservoir, the bulk-amount of chlorine present in the trap is calculated from the precise quantification of the CH_3Cl gas formed and introduced in the mass-spectrometer.

3.4. The efficiency of the ClO⁻-reduction step

In the case of the residual Cl-reservoir or in Cl₂, it is possible to precipitate only the Cl⁻ form as AgCl. Recovered AgCl was quantified and compared to the amount of recovered chlorine when the reduction approach (Zn addition) was used on aliquots of a given solution. We observed that the amount of recovered chlorine when Zn was added was exactly twice the amount produced without Zn. This illustrates that the Cl₂ disproportionates quantitatively in a 1:1 ratio to Cl⁻ and ClO⁻.

4. Results

4.1. Cl₂ production rate and isotopic fractionation: Exp. 1

During the course of Experiment 1, we changed the KOH-traps at different time intervals: 5, 15, 30, 45 and 60 minutes. After one hour, the solution in the glass-reactor was not degassing anymore and we assumed that the reaction was finished. The safety traps (or second traps) were at all time intervals free of chlorine, indicating that all Cl₂ formed during the experiment disproportionated quantitatively in the first KOH-trap. All first trap solutions (taken at the varying times) were processed through the reduction step as described above, and their bulk Cl-amount was determined by measuring the CH₃Cl gas pressure before δ³⁷Cl analyses.

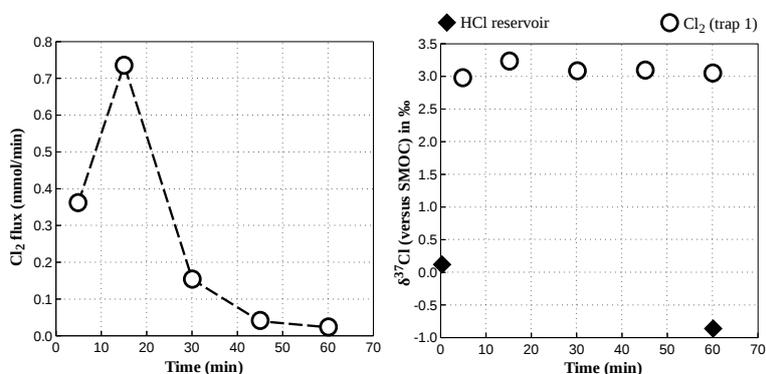


Figure 2: Evolution of the chlorine flux and the chlorine isotope composition in the KOH traps of experiment 1. a) The flux of Cl₂ expressed in mmol/min versus the time of the experiment. b) The δ³⁷Cl of the produced Cl₂ at different times (round circles) and the δ³⁷Cl of the initial and final HCl reservoir (black diamond). Error bars are smaller than symbols.

In Figure 2a we show the flux of Cl-degassing (in mmol Cl/min), calculated from the Cl-amount in the traps at different times. The maximum degassing occurs at about 15 min (Figure 2a). In the trap recovered at 60 min, the calculated flux is less than 0.03 mmol/min indicating that the reaction was nearly complete. By summing the Cl-amounts measured in all recovered traps, we calculate that after the 60-minutes experiment 12.6 ± 0.4 mmol of chlorine (or 6.3 mmol of Cl₂) was degassed from the aqueous solution in the glass-reactor. Compared to 61 ± 1 mmol chlorine initially present in the Cl-reservoir (as Cl⁻), this corresponds to chlorine oxidation yield of 21 ± 1 %.

In Figure 2b we report $\delta^{37}\text{Cl}$ values for each of the recovered KOH-traps as well as $\delta^{37}\text{Cl}$ values of the Cl-reservoir at the start and the end of the experiment. $\delta^{37}\text{Cl}$ of the residual Cl-reservoir was measured with and without the reduction step and no significant differences in the $\delta^{37}\text{Cl}$ were observed (neither on the total Cl-amount). This observation suggests that concentrations of other species than Cl⁻ are undetectable with our experimental setup. With $\delta^{37}\text{Cl} = 0.18 \pm 0.03\text{‰}$ in the initial Cl-reservoir, the $\delta^{37}\text{Cl}$ value of the Cl₂ gas produced shows a high and relatively constant enrichment in ³⁷Cl with an average $\delta^{37}\text{Cl}$ value of $3.1 \pm 0.1 \text{‰}$ (1 σ). In detail, two distinct values are measured at $t = 5$ min with $\delta^{37}\text{Cl} = 2.99 \pm 0.05 \text{‰}$ and at $t = 15$ min with $\delta^{37}\text{Cl} = 3.24 \pm 0.04 \text{‰}$. They may both reflect a kinetic process occurring at the beginning of degassing. Consistent with the enrichment measured in the Cl₂ gas at the end of the experiment, the residual Cl-reservoir is depleted in the heavier isotope relative to the initial reservoir ($\delta^{37}\text{Cl} = 0.18 \pm 0.03\text{‰}$) and shows a negative $\delta^{37}\text{Cl} = -0.78 \pm 0.05 \text{‰}$ at the end of the experiment.

4.2. Rayleigh distillation versus Batch equilibrium model: Exp.1 and 2

We considered two possible distillation models to describe our experiments. 1) The Rayleigh (open-system) distillation: the Cl-amount in the initial reservoir is known and as soon as the product (Cl₂) forms, it is constantly removed from the original reservoir with a constant isotopic fractionation. Therefore, the

KOH-trap solutions are sampling the cumulated products at various time. 2) Batch (closed-system) equilibrium: The initial Cl-amount in the reservoir is known and the Cl₂ is instantaneously formed with a given isotopic fractionation when H₂O₂ is added, but remains in solution. Then the Cl₂ slowly escapes from the solution with no isotopic fractionation and is carried over to the KOH-traps.

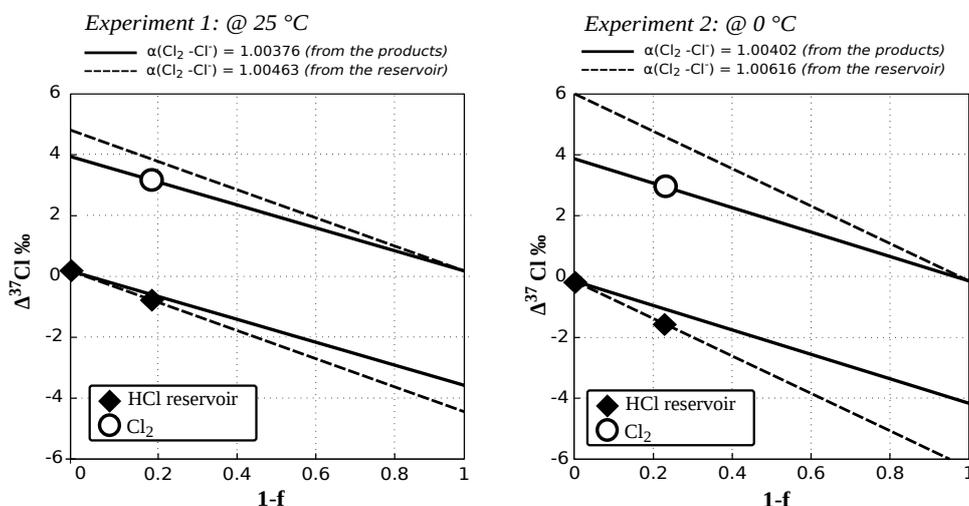


Figure 3: Evolution of the isotopic composition of the products and of the Cl-reservoir as function of 1-f (where f is the remaining fraction of the initial Cl-reservoir), modelled for Experiment 1 (a) and for Experiment 2 (b). In both figures, the isotopic composition of the Cl₂-products and of the residual reservoir are expressed as $\Delta^{37}\text{Cl}$ (in ‰), which is defined as the difference between the measured $\delta^{37}\text{Cl}$ and the $\delta^{37}\text{Cl}$ of the initial Cl-reservoir ($\Delta^{37}\text{Cl} = \delta^{37}\text{Cl} - \delta^{37}\text{Cl}_{\text{ini}}$). The evolution of the Cl-reservoir ($\delta^{37}\text{Cl}_{\text{Res}}$) and Cl₂-product ($\delta^{37}\text{Cl}_{\text{Prod}}$) are modelled by using α fractionation factor calculated either from the residual Cl-reservoir (dashed-line) or from the Cl₂-products (plain line), using the following relations (derived from Eq. 7 and 8): $\delta^{37}\text{Cl}_{\text{Res}} = \delta^{37}\text{Cl}_{\text{ini}} + (f - 1) * 1000 \ln \alpha_{(\text{Cl}_2 - \text{Cl}')}$ and $\delta^{37}\text{Cl}_{\text{Prod}} = \delta^{37}\text{Cl}_{\text{ini}} + f * 1000 \ln \alpha_{(\text{Cl}_2 - \text{Cl}')}$. From the latter equation it follows that the y-intercept for $f=1$ holds: $\delta^{37}\text{Cl}_{\text{Prod}} = \delta^{37}\text{Cl}_{\text{ini}} + 1000 \ln \alpha_{(\text{Cl}_2 - \text{Cl}')}$.

Based on the chlorine isotopic composition in the trap solutions from Experiment 1, it is most likely that the latter has taken place in our experiment. The Cl₂ produced in Experiment 1 has a nearly constant $\delta^{37}\text{Cl}$ over time step suggesting that the oxidation reaction was virtually instantaneous in a batch-like mode. Hence we calculate the fractionation factors in our system following the batch model, a closed-system equilibrium. The fractionation factor $\alpha_{(\text{Cl}_2 - \text{Cl}')}$ can independently be calculated either from the isotopic composition of the products ($\delta^{37}\text{Cl}_{\text{Prod}}$), either from the isotopic composition of the residual Cl-reservoir ($\delta^{37}\text{Cl}_{\text{Prod}}$), following the classic equations:

$$\ln \alpha_{(\text{Cl}_2\text{-Cl})} = (\delta^{37}\text{Cl}_{\text{Res}} - \delta^{37}\text{Cl}_{\text{Ini}}) / [(f-1) * 1000] \quad (7)$$

or

$$\ln \alpha_{(\text{Cl}_2\text{-Cl})} = (\delta^{37}\text{Cl}_{\text{Prod}} - \delta^{37}\text{Cl}_{\text{Ini}}) / f * 1000 \quad (8)$$

where $\delta^{37}\text{Cl}_{\text{Ini}}$ the chlorine isotope composition of the initial Cl-reservoir (HCl) and f is the remaining fraction of the initial reservoir.

4.2.1. *Experiment 1*: In Figure 3 we modelled the evolution of the $\delta^{37}\text{Cl}$ of the cumulated products and of the Cl-reservoir in function of $1-f$ and the fraction of the initial Cl-reservoir that degassed as Cl_2 . In this Figure these parameters are modeled with $\alpha_{(\text{Cl}_2\text{-Cl})}$ values calculated from the product (plain line) or from the residual Cl-reservoir (dashed-line). Note that in this model, since Cl_2 is likely formed instantly in the glass-reactor, there is only one value for the $\delta^{37}\text{Cl}$ of the product which corresponds to an average value (weighted by concentrations) of all the recovered traps. The calculated fractionation factors are different depending on whether they are calculated with the product's $\delta^{37}\text{Cl}$ or with the residual reservoir's $\delta^{37}\text{Cl}$ values. Using the cumulated products an $\alpha_{(\text{Cl}_2\text{-Cl})} = 1.00376$, corresponding to a fractionation of about 3.76‰ is calculated, while with the residual reservoir an $\alpha_{(\text{Cl}_2\text{-Cl})} = 1.00463$ is calculated, corresponding to a fractionation of about 4.63‰.

Two processes could account for the apparent discrepancy between calculated $\alpha_{(\text{Cl}_2\text{-Cl})}$. The first involves the occurrence of a yet unconstrained chlorine speciation in the residual Cl-reservoir. For example, a fraction of the reservoir chlorine could have oxidized into HOCl as driven by reaction 1. Such speciation would not be precipitated as AgCl, and therefore would not be taken into account in the measurement of the bulk $\delta^{37}\text{Cl}$ of the residual Cl-reservoir. Note that since the $\delta^{37}\text{Cl}$ of the residual Cl-reservoir was similar whether it was measured with or without the reduction step, this unconstrained Cl-species must therefore have been refractory to reduction in the residual reservoir. Alternatively, the lower value calculated from the residual Cl-reservoir could indicate that the reaction was not complete at the

moment the experiment was stopped. Although the degassing was no longer visible after an hour, the completion of the gas loss while stored could have caused a loss of heavy chlorine isotope as monitored during the experiment, accounting for the isotope discrepancy. Finally, we used both $\alpha_{(\text{Cl}_2-\text{Cl}^-)}$ from the residual Cl-reservoir and from the products to calculate to calculate an optimal $\alpha_{(\text{Cl}_2-\text{Cl}^-)}$ value and uncertainties (see 5. Discussion).

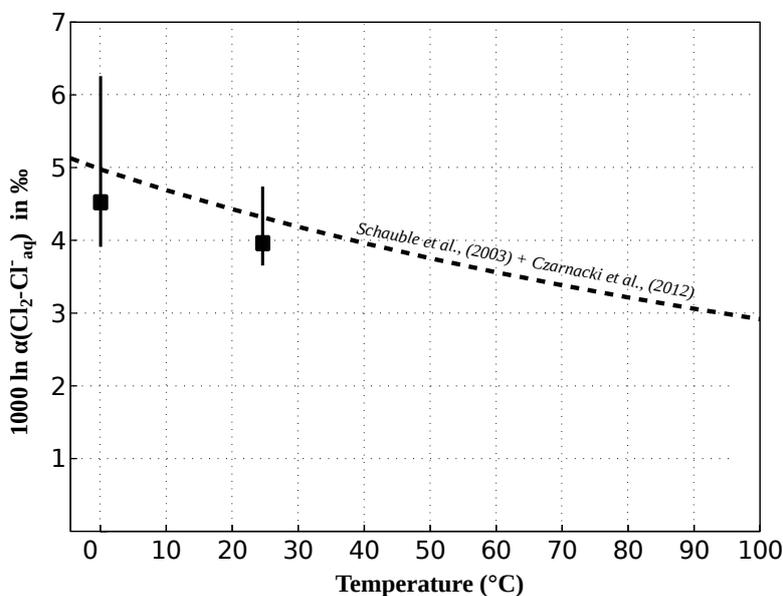


Figure 4: Measured Cl isotope fractionation compared to the theoretical fractionation as calculated by Schauble et al. (2003) and Czarnacki and Hałas (2012). The $1000\ln\alpha_{(\text{Cl}_2-\text{Cl}^-)}$ values (black square) are calculated such that the difference between the batch-equilibrium model and both measured values in the product and the residual Cl-reservoir are minimized. Error bars then correspond to maximum or minimum $1000\ln\alpha_{(\text{Cl}_2-\text{Cl}^-)}$ values determined either from the reservoir or from the product.

4.2.2 Experiment 2: The second experiment was conducted at 0°C. In this experiment, the hydrogen peroxide solution used was more concentrated (50%) than the one used in the first experiment (30%). This more concentrated solution resulted in a slightly increased production of Cl_2 gas relatively to the initial Cl reservoir as compared to Experiment 1. The evolution of the isotopic compositions of the products and reservoirs along with the fraction of the initial Cl-reservoir removed is represented in Figure 4. Unlike Experiment 1 the fractionation factors are almost identical if calculated from the product or from the residual Cl-reservoir. The fractionation factor $\alpha_{(\text{Cl}_2-\text{Cl}^-)} = 1.00402$ when calculated from the product and $\alpha_{(\text{Cl}_2-\text{Cl}^-)} = 1.00616$ when calculated from the residual Cl-reservoir. Like in Experiment 1, an unconstrained Cl-chemistry may have occurred in the Cl-reservoir, leading to

the observed discrepancy. Note that while the difference between $\alpha_{(\text{Cl}_2-\text{Cl}^-)}$ calculated from the product and from the residual Cl-reservoir is larger than in Experiment 1, both of them are higher than the one calculated in Experiment 1, which is likely resulting from the relation between temperature and equilibrium isotopic exchange under isotopic equilibrium (Bigeleisen and Mayer 1947).

5. Discussion

When the calculated *ab-initio* reduced partition functions, or β -factors, of the Cl_2 gas molecule proposed by [Schauble et al. \(2003\)](#) and the reduced partition function of hydrated Cl^- calculated by [Czarnacki and Hałas \(2012\)](#) are combined, it is possible to determine the theoretical equilibrium fractionation factor (equal to the ratio of the β -factors) between Cl_2 and hydrated Cl^- at different temperatures. In Figure 5 we show the $1000\ln\alpha_{(\text{Cl}_2-\text{Cl}^-)}$ in ‰ as function of the temperature (in °C) calculated after β -factors from [Schauble et al. \(2003\)](#); [Czarnacki and Hałas \(2012\)](#), as well as the experimental $1000\ln\alpha_{(\text{Cl}_2-\text{Cl}^-)}$ we determined at 25 °C (Experiment 1) and at 0 °C (Experiment 2). For each of these experiments we calculated the $\alpha_{(\text{Cl}_2-\text{Cl}^-)}$ value that was minimizing the difference between the batch-equilibrium model and the measured values in both the product and the residual Cl-reservoir (black square in Figure 4).

This leads to an isotope fractionation $1000\ln\alpha_{(\text{Cl}_2-\text{Cl}^-)} = 4.51 (+1.65/-0.49)$ ‰ at 0 °C and an isotope fractionation $1000\ln\alpha_{(\text{Cl}_2-\text{Cl}^-)} = 3.94 (+0.69/-0.18)$ ‰ at 25 °C.

Our experimental α -factors determined at 0 °C and 25 °C are in close agreement with the theoretical calculations of isotopic equilibrium between Cl_2 gas and hydrated Cl^- .

6. Conclusions

In this study, we explored the chlorine isotope fractionation associated with the oxidation of hydrated Cl^- (redox state of -I) into Cl_2 gas (redox state of 0).

The Cl₂ gas is produced through a complex reaction mechanism after mixing a liquid HCl solution (12N) with a liquid hydrogen peroxide solution (either 33% or 50%). We measured the $\delta^{37}\text{Cl}$ of the Cl₂ formed as well as the $\delta^{37}\text{Cl}$ of the remaining residual HCl-solution. The Cl₂ gas formed was strongly enriched in the heavier isotope ³⁷Cl (high $\delta^{37}\text{Cl}$ values) relative to the residual solution (low $\delta^{37}\text{Cl}$ values), consistent with theoretical expectations that in equilibrium fractionation the more oxidized forms are enriched in the heavier isotope.

$\delta^{37}\text{Cl}$ data from the produced Cl₂ in Experiment 1 suggested that the chlorine gas was formed in a closed-system (Batch). The fractionation factors that were determined are absolutely consistent with the equilibrium fractionation factors calculated by [Schauble et al. \(2003\)](#) and [Czarnacki and Hałas \(2012\)](#), indicating that the Cl₂ generation is likely to occur at thermodynamic equilibrium.

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Experiment 1: @ 22°C, 5ml HCl (12M) ~ 60 mmol-Cl + 1ml H2O2 (30%) ~ 10 mmol-H2O2

Trap (min)	Cl conc. (mmol/L)	Volume (mL)	Cl content (mmol)	Cumul. Product (mmol)	Flux/Producti on (mmol/min)	$\delta^{37}\text{Cl}$ (vs SMOC) ‰	Remaining fraction <i>f</i>
0							
5	183.1	10	1.8	1.8	0.37	2.99	
15	734.9	10	7.3	9.2	0.73	3.24	
30	234.3	10	2.3	11.5	0.16	3.08	
45	67.6	10	0.7	12.2	0.05	3.11	
60	39.4	10	0.4	12.6	0.03	3.05	
Cumul. Prod				12.6		3.16	0.79*
	11749**	5	58.7			0.18	
	12489**	5	62.4			0.19	
HCl res. Average	12119		60.6			0.18	
Residual Cl	n.m	6	n.m			-0.78	

Trap	Cl conc. (mmol/L)	Volume (mL)	Cl content (mmol)	Cumul. Product (mmol)	Flux/Producti on (mmol/min)	$\delta^{37}\text{Cl}$ (vs SMOC) ‰	Remaining fraction <i>f</i>
T1	574.16	13.2	7.6	7.6	n.m	2.94	
T2	65.93	11	0.7	8.3	n.m	3.04	
Cumul. Prod				8.3		2.95	0.77*
	12614**	3	37.8			-0.16	
	12282**	3	36.8			-0.13	
HCl res. Average	12448		37.3			-0.15	
Residual Cl	n.m	3.6	n.m			-1.56	

* The remaining fraction of the initial reservoir *f*, is calculated based on the Cl-content in the cumulated product and the Cl-content in the initial reservoir

n.m: non measured

Table 1: Results for Experiment 1 (conducted at 22°C) and Experiment 2 (conducted at 0°C).