

Short communication

Chlorine isotope vapor–liquid fractionation during experimental fluid-phase separation at 400 °C/23 MPa to 450 °C/42 MPa

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Abstract

We measured experimentally the chlorine isotope fractionation between coexisting vapor and liquid in the system H₂O–NaCl. Experiments were performed between 23 and 28 MPa along the 400 °C isotherm and between 38 and 42 MPa along the 450 °C isotherm. Calculated chlorine isotope fractionation $\Delta^{37}\text{Cl}_{\text{vapor-liquid}} = \delta^{37}\text{Cl}_{\text{vapor}} - \delta^{37}\text{Cl}_{\text{liquid}}$ ($1\sigma = \pm 0.17\text{‰}$) between coexisting vapor and liquid are generally within 0.2‰ of 0, although there is a trend at both 400 °C and 450 °C in which the $\Delta^{37}\text{Cl}_{\text{vapor-liquid}}$ values change with pressure beyond statistical uncertainty as follows:

$P_{\text{critical}} - P$ [MPa]	$\Delta^{37}\text{Cl}_{\text{vapor-liquid}}$
0	0.0
1.0 to 1.5	+0.2
2.5 to 3.0	-0.2
3.5 to 4.0	+0.2
>4.5	0.0

This trend is supported by earlier work of Magenheim [A.J. Magenheim, 1995. Oceanic borehole fluid chemistry and analysis of chlorine stable isotopes in silicate rocks. PhD Thesis, University of California, San Diego, 184]. While the fractionation trend is interesting from a theoretical viewpoint, the near-zero $\Delta^{37}\text{Cl}_{\text{vapor-liquid}}$ values suggest that evolved vapor–liquid samples, such as volcanic fumarolic gases and degassed glasses should faithfully preserve the $\delta^{37}\text{Cl}$ value of the fluid responsible for magma production at depth. Even extensive Rayleigh fractionation could not change the chlorine isotope composition of a fluid by more than 0.5‰ from its original degassed value.

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1. Introduction

Chlorine is the predominant anion in most crustal fluids of magmatic, hydrothermal or meteoric origin thereby making chlorine stable isotopes a powerful

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tracer that may be used to identify Cl-sources in volcanic gases and hydrothermal vent fluids, shed light on Cl behavior in subduction processes, and evaluate the global Cl budget. Chlorine is also the main ligand for many metals in hydrothermal ore forming fluids (Seyfried and Ding, 1993). Determining the source of chlorine in crustal fluids is therefore not only of geochemical but also of economic importance (Butterfield et al., 1990). For this purpose it is necessary to discriminate the chlorine inputs from the different fluid reservoirs. The two stable chlorine isotopes ^{37}Cl and ^{35}Cl have natural relative abundances of $\sim 24\%$ and 76% , respectively and a relative mass difference of 5.7% . They provide a potentially powerful geochemical tool for discriminating different fluid reservoirs once the $\delta^{37}\text{Cl}$ signature of each reservoir and the geochemical behavior of chlorine isotope fractionation during fluid mediated or fluid dominated processes are known.

The chlorine isotope composition of fluids may not only change by mixing of fluids from different reservoirs and/or by fluid–rock interaction, but also by fluid phase separation, which provides an efficient mechanism to not only fractionate dissolved elements but also isotopes (e.g., Shmulovich et al., 1999; Liebscher et al., 2005). In water–salt systems, the vapor–liquid two-phase field expands to notably higher temperature and pressure than in the pure H_2O -system (Bischoff and Pitzer, 1989). Because high- T /low- P conditions favor fluid phase separation, un-mixing of seawater into low salinity vapor and high salinity brine is rather the rule than the exception in submarine hydrothermal systems (Bischoff and Pitzer, 1989; Massoth et al., 1989; Butterfield et al., 1990, 1994). Here phase separation can explain most of the chlorine concentration variability documented in hydrothermal fluids venting at the seafloor (You et al., 1994; Von Damm et al., 2003); however, the effect of fluid phase separation on chlorine isotopes remains controversial.

Experimental data on chlorine isotope fractionation due to phase separation are restricted to two unpublished theses, both indicating only negligible chlorine isotope fractionation between coexisting vapor and brine (Magenheim, 1995; Phillips, 1999). Unfortunately, two out of six vapor samples studied by Magenheim (1995) may have been contaminated by coexisting brine; and, Phillips (1999) sampled and analyzed only the vapor and not the conjugate brine due to the conditions of the experimental set-up. Nevertheless, weak to negligible vapor–liquid fractionation of chlorine isotopes is in accord with theoretical estimates by Schauble et al. (2003), which show that ^{37}Cl should only have a very weak preference for the vapor compared to coexisting

brine. Multiple chlorine isotope studies on mid-ocean ridge vent fluids also support a weak to negligible vapor–liquid isotope fractionation (Von Damm et al., 1997; Bach et al., 2002; Bonifacie et al., 2004, 2005). On the other hand, Lüders et al. (2002) and Germann et al. (2003) found notable chlorine isotope fractionation in sphalerite-hosted fluid inclusions from the JADE field and the North Fiji basin and in quartz-hosted fluid inclusions from Mina Nerón, Iberian Pyrite Belt, respectively. Based on correlations between chlorine concentration, Cl/Br ratios, and $\delta^{37}\text{Cl}$ values in the fluid inclusions, these authors convincingly showed that the observed chlorine isotope fractionation should be indeed due to fluid phase separation. In contradiction to the theoretical estimates by Schauble et al. (2003), their data indicate preferential fractionation of ^{37}Cl into the brine.

In order to address the conflicting results from the different studies, we present new experimental results on the vapor–liquid fractionation of chlorine isotopes. Experiments were performed at $400\text{ }^\circ\text{C}/23$ to 28 MPa and $450\text{ }^\circ\text{C}/38$ to 42 MPa , i.e. at conditions relevant to submarine hydrothermal systems and sometimes referred to as sub- and supercritical fluid phase separation with respect to a hydrothermal fluid with seawater salinity of $\sim 3.2\text{ wt.}\%$ NaCl.

2. Experimental and analytical techniques

2.1. Experimental technique

The samples of this study are identical to those studied by Liebscher et al. (2005). A detailed description of the experimental set-up is given there and in Liebscher et al. (2006) and will be summarized here only briefly. Experiments were performed in a rockable, large-volume Ti-autoclave (550 cm^3) with sampling lines for liquid and vapor on opposite sides. It is externally heated with an overall temperature accuracy of $\pm 2\text{ }^\circ\text{C}$. The internal temperature gradient is $< 1\text{ }^\circ\text{C}$. Pressure is recorded online with an accuracy of $\pm 0.1\text{ MPa}$. Liquid and vapor are sampled in an upright position of the autoclave, which puts the denser liquid at the bottom and the less-dense vapor at the top. The pressure drop during sampling is less than 0.1 MPa resulting in quasi-isobaric sampling of coexisting vapor–liquid pairs. The experiments were performed at constant temperatures along the $400\text{ }^\circ\text{C}$ isotherm from 27.9 to 23.4 MPa and the $450\text{ }^\circ\text{C}$ isotherm from 41.8 to 38.6 MPa (Table 1). The sampling pressure is adjusted by extraction of vapor through the vapor line, which decreases the bulk density and thus the pressure. Before

Table 1

NaCl concentrations and $\delta^{37}\text{Cl}$ values in coexisting vapor and liquid samples and calculated vapor–liquid fractionation $\Delta^{37}\text{Cl}_{\text{vapor-liquid}}$ of the chlorine isotopes

Sample	Pressure (MPa)	NaCl (wt.%) ^a	$\delta^{37}\text{Cl}$ (‰)	$\Delta^{37}\text{Cl}_{\text{vapor-liquid}}$ (‰) ^b
<i>450 °C isotherm</i>				
Initial		8.80 (5)	+0.39	
V19	41.8	7.38 (4)	−0.01	
L19	41.7	20.29 (12)	+0.05	−0.06
V20	41.6	4.03 (4)	+0.22	
L20	41.5	21.8 (2)	+0.01	+0.21
V21	40.9	2.84 (2)	+0.35	
L21	40.7	22.9 (1)	+0.24	+0.11
V22	39.9	1.773 (7)	−0.25	
L22	39.8	24.9 (1)	+0.12	−0.37
V23	38.7	1.117 (7)	+0.37	
L23	38.6	26.2 (2)	+0.23/+0.10 ^c	+0.14/+0.27
<i>400 °C isotherm</i>				
Initial		2.35 (1)	+0.39	
V25	27.9	2.22 (3)	+0.21	
L25	27.9	4.60 (5)	+0.13	+0.08
V26	27.6	1.210 (3)	+0.35	
L26	27.6	11.17 (3)	+0.30	+0.05
V27	26.8	0.413 (5)	+0.38	
L27	26.8	13.74 (8)	+0.06	+0.32
V28	25.5	0.168 (3)	−0.08	
L28	25.4	17.67 (8)	+0.08	−0.16
V29	24.6	0.100 (3)	+0.50	
L29	24.5	20.9 (1)	+0.29	+0.21
V30	23.6	0.064 (3)	+0.07	
L30	23.4	23.6 (2)	0.00	+0.07

Errors (1σ) in parentheses refer to last digits; analytical error (1σ) of $\delta^{37}\text{Cl}$ is $\pm 0.12\text{‰}$, total analytical error (1σ) of $\Delta^{37}\text{Cl}$ is $\pm 0.17\text{‰}$.

^a Taken from Liebscher et al. (2005).

^b Calculated as $\Delta^{37}\text{Cl}_{\text{vapor-liquid}} = \delta^{37}\text{Cl}_{\text{vapor}} - \delta^{37}\text{Cl}_{\text{liquid}}$.

^c Determined in duplicate.

sampling a vapor–liquid pair, the system is allowed to equilibrate for at least 24 h. The initial NaCl concentrations were 2.35 wt.% NaCl at 400 °C and 8.80 wt.% NaCl at 450 °C, corresponding to the NaCl concentrations at the critical point of the respective isotherms (8.8 wt.% NaCl at 450 °C and 2.22 wt.% NaCl at 400 °C; data from Bischoff and Pitzer, 1989). The initial $\delta^{37}\text{Cl}$ value was $+0.39 \pm 0.12\text{‰}$. As the experiments were originally designed to study the vapor–liquid fractionation of boron and its isotopes (Liebscher et al., 2005) the starting solutions also contained about 200 ppm of boron.

Our experimental technique with pressure adjustment by extraction of NaCl poor vapor preferentially removes H_2O from the system. It stepwise increases the bulk NaCl concentration during subsequent isothermal sampling of vapor–liquid pairs to lower pressures along the vapor–liquid two-phase field boundaries and also

potentially alters the bulk chlorine isotope composition. The bulk composition in the autoclave therefore changes when stepping from one vapor–liquid pair to the next. As long as the system remains two-phase, this change in bulk composition does not affect the vapor–liquid fractionation of the chlorine isotopes. It does, however, preclude a mass-balance calculation for coexisting vapor–liquid pairs to check for internal consistency because we cannot quantify the shift in bulk composition. We therefore test equilibrium of coexisting vapor–liquid pairs by comparing the measured NaCl concentrations with the well-known P – T – X_{NaCl} phase relations in the H_2O –NaCl system (e.g., Bischoff and Pitzer, 1989).

2.2. Analytical techniques

Na^+ concentrations were measured using ICP-AES with an accuracy of better than 3% rel. NaCl concentrations were then calculated assuming all Na^+ being present as NaCl. Concentrations were density corrected using the conversion tables of Wolf et al. (1982). Chlorine isotope ratios for both vapor and liquid phases were determined using methyl chloride as an analyte (Kaufmann et al., 1984). Chloride was precipitated as AgCl , converted to CH_3Cl by reaction with CH_3I at 80 °C and purified in a gas chromatographic column prior to analysis using dual inlet mode on a Finnigan MAT Delta XL Plus mass spectrometer at the University of New Mexico. The isotope compositions are expressed in per mil vs. SMOC, where

$$\delta^{37}\text{Cl} = \left(\frac{\left(\frac{^{37}\text{Cl}}{^{35}\text{Cl}} \right)_{\text{sample}}}{\left(\frac{^{37}\text{Cl}}{^{35}\text{Cl}} \right)_{\text{standard}}} - 1 \right) \times 1000. \quad (1)$$

Standard Mean Ocean Chloride (SMOC) has a defined $\delta^{37}\text{Cl}$ value of 0‰ (Kaufmann et al., 1984). The error on each analysis is $\pm 0.12\text{‰}$ based on long-term reproducibility of 3 separate internal laboratory standards. Details of the procedure can be found in Barnes and Sharp (2006). Chlorine isotope vapor–liquid fractionation is reported in terms of $\Delta^{37}\text{Cl}_{\text{vapor-liquid}}$ defined as $\delta^{37}\text{Cl}_{\text{vapor}} - \delta^{37}\text{Cl}_{\text{liquid}}$.

3. Results

Experimental and analytical results are summarized in Table 1. Within experimental and analytical uncertainties, the measured NaCl concentrations in the conjugate vapor–liquid pairs fit the Bischoff and Pitzer (1989) vapor–liquid two-phase field data for the H_2O –

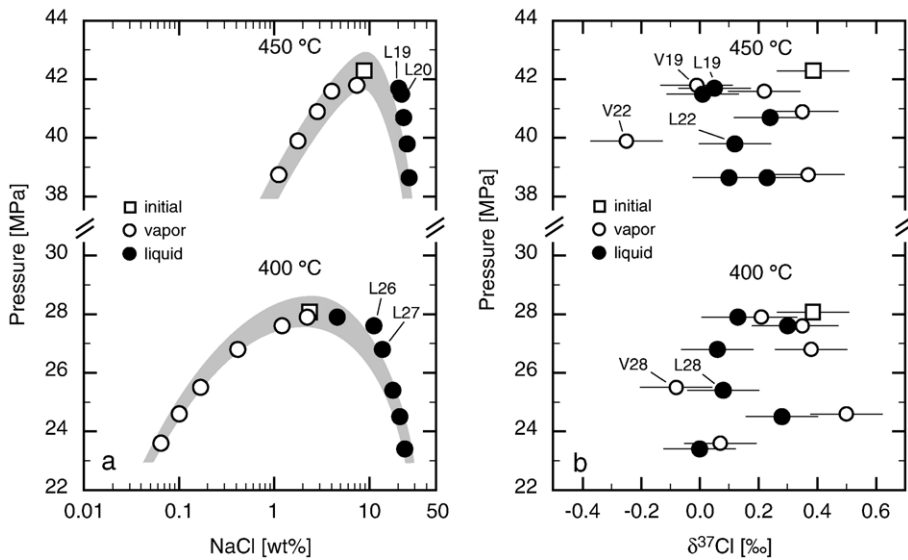


Fig. 1. NaCl concentrations (a) and chlorine isotope compositions (b) in coexisting vapor–liquid pairs along the 450 and 400 °C isotherms. (a) NaCl concentrations are calculated from measured Na^+ concentrations. The NaCl concentrations reproduce the vapor–liquid two-phase field data of Bischoff and Pitzer (1989) for the H_2O –NaCl system (shaded areas, accounting for the temperature uncertainty of ± 2 °C in our experimental runs). Only liquid samples L19 and L20 at 450 °C and L26 and L27 at 400 °C have higher NaCl concentrations than predicted by the Bischoff and Pitzer (1989) data (adopted and modified from Liebscher et al., 2005). (b) $\delta^{37}\text{Cl}$ values of vapor (open circles), liquid (filled circles) and initial (open squares). Only vapor–liquid pairs V19/L19, V22/L22 and V28/L28 have $\delta^{37}\text{Cl}_{\text{vapor}} < \delta^{37}\text{Cl}_{\text{liquid}}$. The data suggest $\delta^{37}\text{Cl}_{\text{initial}} > \delta^{37}\text{Cl}_{\text{bulk}}$ at all run conditions along both isotherms.

NaCl system at 400 and 450 °C (Fig. 1a). Only four liquid samples, L19 and L20 at 450 °C and L26 and L27 at 400 °C, have calculated NaCl concentrations that are above those predicted by Bischoff and Pitzer (1989).

The measured chlorine isotope composition of vapor covers a small range of -0.25‰ to $+0.37\text{‰}$ at 450 °C and -0.08‰ to $+0.50\text{‰}$ at 400 °C. The $\delta^{37}\text{Cl}$ values of the coexisting liquids range from $+0.01\text{‰}$ to $+0.24\text{‰}$ at 450 °C and 0.00‰ to $+0.30\text{‰}$ at 400 °C (Fig. 1b; Table 1). The $\delta^{37}\text{Cl}$ values of vapor and liquid, except for V29, are both generally lower than the $\delta^{37}\text{Cl}$ value of the starting material. This indicates a shift in bulk isotopic composition before sampling the first vapor–liquid pair. Vapor–liquid pairs V19/L19 and V22/L22 at 450 °C and V28/L28 at 400 °C have $\delta^{37}\text{Cl}_{\text{vapor}} < \delta^{37}\text{Cl}_{\text{liquid}}$, all other vapor–liquid pairs have $\delta^{37}\text{Cl}_{\text{vapor}} > \delta^{37}\text{Cl}_{\text{liquid}}$. The calculated $\Delta^{37}\text{Cl}_{\text{vapor-liquid}}$ values as function of the distance to the critical pressure $P_{\text{crit}} - P$ of the respective isotherm are shown in Fig. 2. Using the relationship for the sum of errors $1\sigma_{\text{total}} = \sqrt{\sigma_{\text{vapor}}^2 + \sigma_{\text{liquid}}^2}$, which accounts for the individual analytical sigmas of vapor and liquid, results in a total analytical error for the difference between the two values of $\pm 0.17\text{‰}$ (1σ). Samples at $P_{\text{crit}} - P$ near 1 MPa, 2.5 MPa and 3.5 MPa plot at values that are statistically different from $\Delta^{37}\text{Cl}_{\text{vapor-liquid}} = 0$. A hand-drawn fit to the data suggest that there is a slight positive $\Delta^{37}\text{Cl}_{\text{vapor-liquid}}$ value at 1 MPa, which

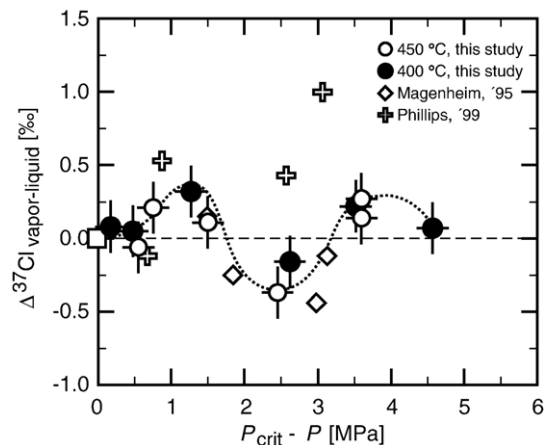


Fig. 2. Chlorine isotope fractionation $\Delta^{37}\text{Cl}_{\text{vapor-liquid}} = \delta^{37}\text{Cl}_{\text{vapor}} - \delta^{37}\text{Cl}_{\text{liquid}}$ between coexisting vapor and liquid at 400 °C (black circles) and 450 °C (open circles) as function of the pressure difference (ΔP) to the critical curve at 400 and 450 °C. Thin dashed line refers to $\Delta^{37}\text{Cl}_{\text{vapor-liquid}} = 0$, i.e. no chlorine isotope fractionation. At the critical curve $\Delta P = 0$ and per definition $\Delta^{37}\text{Cl}_{\text{vapor-liquid}} = 0$ (open rectangle). The $\Delta^{37}\text{Cl}_{\text{vapor-liquid}}$ values are positive at $\Delta P \sim 1$ MPa, negative at $\Delta P \sim 2.5$ MPa and positive at $\Delta P \sim 3.5$ MPa, although the difference from $\Delta^{37}\text{Cl}_{\text{vapor-liquid}} = 0\text{‰}$ is not much larger than the total error of measurement. The fact that this trend is seen for both 400 and 450 °C, is in agreement with data from Magenheim (1995) (open diamonds) and passes through $\Delta^{37}\text{Cl}_{\text{vapor-liquid}} = 0$ at $P_{\text{crit}} - P = 0$ strengthens the conclusion that the trend is real. The data from Phillips (1999) (open crosses) show a larger spread and do not agree well with those of Magenheim (1995) and the present study.

decreases to a slight negative value at 2.5 MPa and back to a positive value at ~ 3.5 MPa. This trend is seen for both 400 and 450 °C and in earlier experiments by Magenheimer (1995).

4. Discussion

The good agreement of the measured NaCl concentrations in the conjugate vapor–liquid pairs with the Bischoff and Pitzer (1989) vapor–liquid two-phase field data indicates overall chemical equilibrium conditions during sampling. The data give no hints to any significant contamination of the samples although the higher than predicted NaCl concentrations in L19, L20, L26, and L27 might reflect some salt precipitates in the sampling line. The internal consistency of the $\delta^{37}\text{Cl}$ data, however, indicates that these potential salt precipitates have no effect on the measured $\delta^{37}\text{Cl}$ values. We have no explanation for the observed shift in bulk isotopic composition. Extraction through the vapor line within the one-phase field above the critical point, i.e. before sampling the first vapor–liquid pairs, should not change the bulk isotopic composition. The observed shift may reflect some sampling effects that we cannot quantify. However, a shift in bulk isotopic composition has no effect on the calculated $\Delta^{37}\text{Cl}_{\text{vapor-liquid}}$ values. The initial solutions contained about 200 ppm boron because the experiments were originally designed to study the boron fractionation. But there is no reason to believe that this has any measurable effect on chlorine isotope fractionation. Altogether, we conclude that the derived $\Delta^{37}\text{Cl}_{\text{vapor-liquid}}$ values represent equilibrium values. Our data clearly show that chlorine isotope fractionation between vapor and liquid is $<0.2\text{‰}$ at 400 to 450 °C/23.5 to 41.8 MPa. There appears to be a pressure-dependent fractionation at both 400 and 450 °C, which is seen both in our data set and that of Magenheimer (1995). Although the effect is only slightly larger than the total error of the $\Delta^{37}\text{Cl}_{\text{vapor-liquid}}$ measurement, the fact that it is observed in two independent studies strengthens the conclusion. The results of Phillips (1999) show a larger spread that does not agree well with those of Magenheimer (1995) and the present study. The discrepancy may be due to the fact that only vapor was measured in Phillips (1999). Given that all physicochemical parameters of vapor and liquid (e.g., composition and density) change in a monotonous way along the vapor–liquid two-phase field boundaries with decreasing pressure we have no explanation why $\Delta^{37}\text{Cl}_{\text{vapor-liquid}}$ should change sign in a regular way as a function of pressure. However, pressure effects have been seen in other isotopic systems (e.g., Horita et al., 2002).

Regardless whether the observed change in sign of $\Delta^{37}\text{Cl}_{\text{vapor-liquid}}$ is real or some experimental or analytical artefact, the results of this study suggest that chlorine isotope vapor–liquid fractionation above 400 °C/23 MPa is non-zero, but nevertheless small, and that vapor phase separation should not have a significant effect on the measured isotope composition of either the vapor or the liquid. This is in accordance with results from chlorine isotope studies on mid-ocean ridge vent fluids (e.g., Bonifacie et al., 2005). Even in an extreme case of Rayleigh fractionation, where 90% of the fluid is lost to a vapor phase, the $\delta^{37}\text{Cl}$ value of the remaining fluid would change by only 0.5‰, given a $\Delta^{37}\text{Cl}_{\text{vapor-liquid}}$ value of 0.2‰. Therefore, it is safe to assume that samples of volcanic gases or extensively degassed fluids should preserve the $\delta^{37}\text{Cl}$ values of the original single phase fluid and sampling either fluid or vapor will give the $\delta^{37}\text{Cl}$ values of the original Cl-bearing fluid. This picture may, however, change for P – T conditions notable below those of the present study as indicated by the studies of Lüders et al. (2002) and Germann et al. (2003). Here, estimated P – T conditions for fluid-phase separation are, e.g., 350 ± 50 °C/ 17 ± 5 MPa for the JADE Field (Lüders et al., 2002) and 250 ± 50 °C/ 6 ± 2 MPa for Mina Nerón, Iberian Pyrite Belt (Germann et al., 2003). Clearly, further experiments are needed to address the question of chlorine isotope vapor–liquid fractionation at such low P – T conditions.

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