GEOCHEMISTRY

Experimental Study of Chlorine and Fluorine Partitioning between Fluid and Subalkaline Basaltic Melt

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The study of solubility of volatile components in natural magmatic melts of different compositions and their partitioning between the fluid and the melt are of significant interest for modeling the magma degassing of volcanoes, understanding the transportation and deposition of ore components, and constructing models of ore deposit formation. We have studied experimentally for the first time the simultaneous distribution of chlorine and fluorine between Cl- and F-bearing aqueous fluids and the basaltic melt. We have established the anomalous behavior of volatile components in the studied system, resulting in the enhanced concentration of Cl and F in the silicate melt and aqueous fluid, respectively.

According to experimental data [1–5], the solubility (highest content) of Cl in the basaltic melt is higher than in other magmatic melts and can reach 1.8–5.9 wt %. The fluid/melt partition coefficient of Cl ($D_{Cl}^{fluid/melt}$) is close to unity. It was established that the composition of the melt, especially the contents of Fe, Ca, and Mg, strongly affects the chlorine solubility. In addition to melt composition, the Cl behavior is also controlled by pressure [2, 4]: the Cl content is minimal at 5 kbar and maximal at 1 kbar. The study of Cl and F behavior in the apatite–basaltic (norite) melt–fluid system [5] showed that the model reduced basaltic melts are 3 to 30 times enriched in Cl as compared to F. The fluorine solubility in melts, unlike the chlorine solubility, depends little on their composition, except for the Ca content. The weight percentage ratio of the Cl content in the fluid and the melt (coefficient $D_{Cl}^{fluid/melt}$) varies within 0.3–4.4.

The starting material in our work was represented by a subalkaline basalt (etnaite [6]) sample from Etna

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Volcano with the following composition (normalized to 100%, in wt %): 48.0 SiO_2, 1.9 TiO_2, 16.6 Al_2O_3, 9.3 FeO_{tot}, 0.22 MnO, 6.1 MgO, 11.5 CaO, 3.5 Na_2O, 2.1 K_2O, 0.59 P_2O_5, 0.11 Cl, 0.05 F, and 0.12 H_2O (mol Al_2O_3/(CaO + Na_2O + K_2O) = 0.57). Glasses obtained by melting were treated with HCl, HF, and (HCl + HF) with concentrations ranging from 1 to 7 m for each acid (table). The starting material (5–6 mg solution and approximately 50 mg basaltic glass with the solution/glass powder ratio of 0.09–0.14) was loaded in Au–Pd capsules (with 20% Pd), which were preliminarily saturated in Fe at oxygen fugacity f_{O_2} corresponding to the Ni–NiO buffer. Experiments were conducted at $T = 1200 \pm 5°C$, $P = 200 \pm 1$ MPa, and f_{O_2} of Ni–NiO in an internally heated pressure vessel (IHPV) equipped with rapid quench and the facility for specification and control of the hydrogen (oxygen) fugacity during the experiment. The f_{H_2} value was given by a mixture of Ar and H_2 gases in a calculated proportion. The P_{H_2} value during experiment was determined with a Pt sensor membrane located near the capsules with the samples [7]. Experiments lasted for 3–3.6 days.

Run products consisted of basaltic glass without visible crystals. The chemical composition of quenched glasses was determined using a Cameca SX-100 electron microprobe. The Cl, F, and H_2O contents in the fluid equilibrated with the basaltic melt were calculated by the mass balance technique. Calculations were performed for each run using the known (accurate to $n \times 10^{-5}$ g) weights of starting components, precise initial concentrations of starting solutions, and compositions of quenched basaltic glasses. We used this calculation technique because the amount of the quenched fluid is insufficient for its direct determination. The method of calculations is described in detail in [8]. Based on the standard coulometric Karl–Fischer titration method [9], the content of water in quenched glasses is 4.81–5.46 wt %. Knowledge of the Cl, F, and H_2O contents in the fluid and the melt allowed us to determine the

Starting composition of the solution; contents of Cl, F, and H_2O; atomic Cl/F ratios in the basaltic glass and solution (fluid) after run; and atomic fluid/melt partition coefficients of Cl and F

Run no.	Starting composition of solution	N	Cl in fluid	F in fluid	H_2O in fluid, mol % (wt %)	Cl in melt	F in melt	H_2O in the melt, wt %*	Cl/F in the fluid	Cl/F in the melt	$D_{Cl}^{fluid/melt}$	$D_{F}^{fluid/melt}$
			at % (wt %)			at % (wt %)						
PG-31	H_2O	18	0.00 (0.01)	0.01 (0.01)	99.99 (99.99)	0.17 (0.11)	0.15 (0.05)	4.81 ± 0.07	0.38	1.15	0.02	0.05
PG-37	1.1 mHCl	15	0.21 (0.42)	0.02 (0.02)	99.76 (99.56)	0.73 (0.46)	0.14 (0.05)	5.13 ± 0.14	9.44	5.09	0.29	0.16
PG-33	3.5 mHCl	19	0.91 (1.77)	0.06 (0.06)	99.03 (98.17)	1.61 (1.01)	0.14 (0.05)	5.04 ± 0.07	14.6	11.5	0.56	0.44
PG-20	8.5 mHCl	16	4.21 (7.96)	0.08 (0.08)	95.71 (91.96)	3.53 (2.26)	0.13 (0.05)	5.46 ± 0.07	50.7	26.3	1.19	0.62
PG-38	1.0 mHF	15	0.00 (0.00)	1.70 (1.80)	98.30 (98.20)	0.17 (0.11)	0.45 (0.15)	5.13 ± 0.14	0.00	0.37	0.00	3.78
PG-34	3.1 mHF	3	0.00 (0.00)	4.84 (5.09)	95.16 (94.91)	0.17 (0.11)	1.10 (0.37)	5.13 ± 0.14	0.00	0.15	0.01	4.40
PG-22	7.5 mHF	19	0.00 (0.01)	15.74 (16.46)	84.25 (83.53)	0.17 (0.10)	1.82 (0.62)	5.21 ± 0.09	0.00	0.09	0.02	8.65
PG-36	1.1 mHCl + 3.1 mHF	15	0.26 (0.50)	5.52 (5.79)	94.23 (93.71)	0.73 (0.46)	1.08 (0.36)	5.13 ± 0.14	0.05	0.68	0.35	5.12
PG-30	1.1 mHCl + 7.5 mHF	18	0.30 (0.58)	17.27 (17.99)	82.43 (81.43)	0.68 (0.43)	1.76 (0.59)	5.03 ± 0.05	0.02	0.39	0.43	9.84
PG-35	3.5 mHCl + 1.0 mHF	16	1.07 (2.07)	2.21 (2.31)	96.72 (95.62)	1.77 (1.12)	0.45 (0.15)	5.13 ± 0.14	0.48	3.93	0.60	4.92
PG-32	3.4 mHCl + 3.1 mHF	18	0.53 (1.03)	8.79 (9.18)	90.68 (89.79)	1.65 (1.04)	0.87 (0.30)	5.04 ± 0.07	0.06	1.89	0.32	10.05
PG-21	3.4 mHCl + 7.6 mHF	15	1.57 (3.02)	15.13 (15.59)	83.30 (81.38)	2.03 (1.30)	2.31 (0.79)	5.31 ± 0.06	0.10	0.88	0.77	6.55
PG-29	8.5 mHCl + 1.0 mHF	18	3.39 (6.45)	3.90 (3.97)	92.71 (89.58)	3.35 (2.12)	0.41 (0.14)	5.16 ± 0.07	0.87	8.15	1.01	9.49
PG-19	8.3 mHCl + 3.3 mHF	18	3.74 (7.07)	8.36 (8.47)	87.90 (84.46)	4.16 (2.67)	1.22 (0.42)	5.28 ± 0.14	0.45	3.40	0.90	6.83

Notes: (m) Molality of solution, i.e., number of gram-moles of the present dissolved acid material divided by 1000 g (water + second dissolved matter); (N) number of microprobe analyses in this run.

* Karl–Fischer titration method.

fluid/basaltic melt partitioning coefficients of Cl and F, $D_{Cl(F)}^{fluid/melt}$ (table).

The Cl content in the basaltic melt is as much as 4.16 at % (2.67 wt %). It was established that the Cl solubility in the basaltic melt positively correlates with the Cl content in the fluid. The dependence is close to linear (Fig. 1), with a steeper slope at a low (no more than 0.3 at %) Cl content in the fluid. The position of isolines of Cl contents in the melt and fluid (D_{Cl} = 1) emphasizes enrichment of the melt in Cl with respect to the fluid. Data points with low (0.01–1.7 at %) and elevated (2.2–17.3 at %) F contents in the fluid define a single trend, indicating a lack of appreciable influence of the F influx in the system on Cl solubility.

The F content in the basaltic melt is as high as 2.31 at % (0.79 wt %). The F solubility in the basaltic melt also shows an almost linear positive correlation with the F content in the fluid (Fig. 2), with a slightly steeper slope for low F content and the subsequent weak flattening. The position of isopleths of F contents in the melt and fluid (D_F = 1) emphasizes enrichment of the fluid in F relative to the melt. Runs with low (0.001–1.6 at %) and elevated (3.4–4.2 at %) Cl contents in the fluid showed no significant influence of the Cl content on the F solubility in the melt. This is possibly related to an insufficient number of runs. The enrichment of the silicate melt and aqueous fluid in Cl and F, respectively, is well illustrated, for instance, by run PG-32; the starting solution has equal contents of Cl and F (3 mHCl + 3 mHF), while the quenched glass contains 1.65 at % Cl and 0.87 at % F (table).

A proportional increase of Cl and F solubility in the melt with increasing content of these volatiles in the
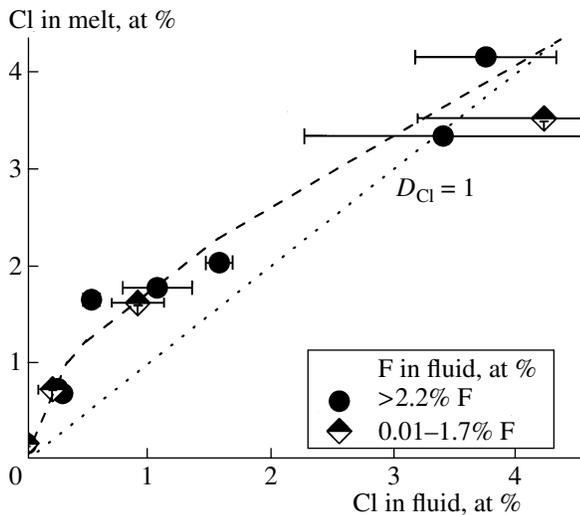
Cl in melt, at %

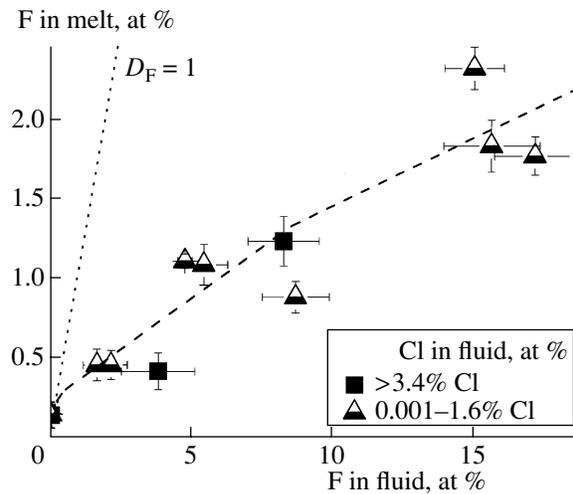**Fig. 1.** Variations of the Cl content in the basaltic melt vs. the Cl content in the coexisting H_2O–Cl–F-bearing fluid at $T = 1200°C$, $P = 200$ MPa, and f_{O_2} of Ni–NiO. Dashed line ($D_{Cl} = 1$) shows equal Cl contents in the melt and fluid.

F in melt, at %

Fig. 2. Variations of the F content in the basaltic melt vs. the F content in the coexisting H_2O–Cl–F-bearing fluid at $T = 1200°C$, $P = 200$ MPa, and f_{O_2} of Ni–NiO. Dashed line ($D_F = 1$) shows equal F contents in the melt and fluid.

fluid (almost linear dependences in Figs. 1 and 2) may indicate a homogeneous (single-phase) state of the fluid coexisting with the basaltic melt at given parameters. According to [8, 10, and others], the behavior of Cl solubility in the water-saturated aluminosilicate melts strongly varies depending on the phase state of the coexisting chlorine fluid. In particular, when the total Cl content in the fluid increases, the Cl solubility in the melt will increase proportionally in the case of equilibrium with the single-phase fluid and will remain constant in the case of equilibrium with the two-phase fluid (aqueous vapor phase + brine).

Under the conditions studied, the atomic fluid/melt partitioning coefficient of Cl ($D_{Cl}^{fluid/melt}$) is 0.3–1.2 (Fig. 3). If the Cl content in fluid is less than 3 at % (6 wt %), this coefficient is significantly lower than unity; i.e., Cl can concentrate in the melt. The atomic fluid/melt partitioning coefficient of F ($D_F^{fluid/melt}$) is significantly higher (3.8–10) if the F content in fluid is 1.7–17 at % (Fig. 4). Thus, the F content is significantly lower in the melt of the studied subalkaline basalts relative to the fluid; i.e., F is accumulated in fluid in the studied system. If we omit runs with an extremely low F content in the fluid, the Cl/F ratio in experiments with the basaltic melt varies from 0.1 to 8.2 (table); i.e., the ratio is always higher than in the fluid (0–0.87), except for opposite relationship observed at an extremely low F content in the fluid (<0.1 at %), when the Cl/F ratio in the fluid is more than in the melt.

According to [11 and others], the fluid-saturated magmatic systems under conditions of geological interest show the following trend: Cl is concentrated in the aqueous solution rather than in the aluminosilicate melt, whereas F is preferentially concentrated in the melt. We obtained the opposite (anomalous) results. During Cl and F partitioning between aqueous Cl- and F-bearing fluid and the subalkaline basaltic melt under the P–T–f_{O_2} conditions studied, Cl and F are concentrated in the melt and aqueous fluid, respectively. One can suggest that natural subalkaline basic melts under certain conditions can also accumulate Cl owing to fluid-magmatic interaction.
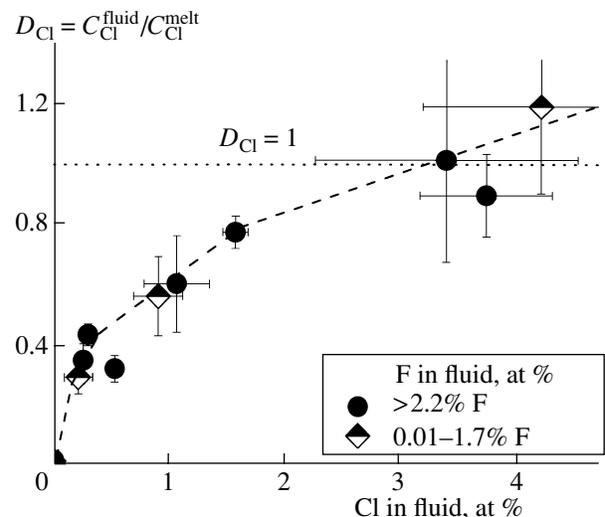
$D_{Cl} = C_{Cl}^{fluid}/C_{Cl}^{melt}$

Fig. 3. The Cl partitioning between the fluid and the melt vs. the Cl content in the coexisting fluid during the experiment. Dashed line ($D_{Cl} = 1$) emphasizes that the partitioning coefficient of Cl is less than unity in most samples.
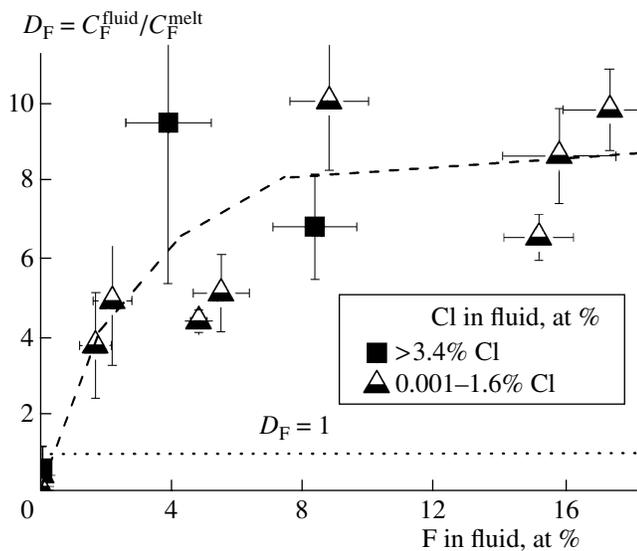
$D_F = C_F^{fluid}/C_F^{melt}$

Fig. 4. The F partitioning between the fluid and the melt depending on the F content in the coexisting fluid during the experiment. Dashed line ($D_F = 1$) emphasizes that the partitioning coefficient of F is more than unity in most samples.

Based on melt inclusion data in basalts, the F content is typically higher than the Cl content (0.03–0.04 wt % Cl, 0.07–0.17 wt % F, and Cl/F ratio is 0.2–0.5) [12–14]. Following [2], we assume that such low Cl contents can be caused by its loss during the subsurface magma degassing. The melt presumably retains F better than Cl, and the F loss during degassing is significantly lower.

According to [15], gas samples from fumaroles of Etna Volcano during the period 1992–1995 showed a steady Cl/F ratio (5–14). Comparison of these data with experimental data suggests the following conclusion. Given that the analyzed fumarole gases were in equilibrium with the basaltic melt in the deep-seated chamber under the studied *P–T* parameters, Cl must sharply predominate over F in the basaltic melt composition.

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