GEOCHEMISTRY

The Effect of CO_2 on the Solubility of Aqueous Chloride Fluid in Dacite, Phonolite, and Rhyolite Melts

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Abstract—The solubility of H_2O-CO_2-Cl-containing fluids of various concentrations (0, 3, 10, and 23 wt % of HCl and from 0 to ~8−15 wt % of CO_2) in dacite, phonolite, and rhyolite melts at 1000ºC and 200 MPa was studied in experiments. It was shown that the Cl concentration in the melt increased substantially from rhyolite to phonolite and dacite (up to 0.25, 0.85, and 1.2 wt %, respectively). The introduction of CO_2 into the system resulted in an increase in the Cl content in the melt composition by 20−25%. One may suppose that Cl reactivity in a fluid increases in the presence of CO_2 to cause growth of the Cl content in the melt. The introduction of CO_2 into the system considerably affects the content of H_2O in aluminosilicate melts as well. Thus, the addition of CO_2 decreases the H_2O content in the melt by ~0.5−1.0 wt %. The decrease in the H_2O content in an aluminosilicate melt is probably caused by fluid dilution with CO_2 resulting in a decrease in the H_2O mole fraction and fugacity in the fluid.

Volatile components (H_2O, CO_2, and Cl) are among the most characteristic in various magmatic processes. The separation of volatile matter from a magma melt is usually caused by a pressure fall and melt crystallization during the rising of magma from the deep Earth's crust, as well as by magma eruptions. The separation as such of volatile matter may be a motive force of the mentioned processes. Carbon dioxide and other carbon compounds, both raised with magma and formed from the assimilation of carbonate rocks by silicates, may have a considerable influence on the variation of the total solubility of other volatile components (e.g., of Cl) in magma [1, 2]. At present, the processes as such have been poorly studied.

Only a few publications are available on the influence of individual volatile components on the solubility of H_2O-Cl-containing fluid in magma melts. Thus, the addition of fluorine increases the chlorine content in a phonolite melt from 0.5 to 0.7 wt % at $T = 850°C$ and $P = 200$ MPa [3, 4]. At the same time, the

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addition of sulfur at equal $P-T$ conditions decreases the chlorine content in the rhyodacite melt from ~0.8 to ~0.7 wt % [5]. The latter effect is caused by a decrease in the Fe content in the melt owing to binding with sulfur.

According to published data, dacite melts are characterized by higher CO_2 solubility owing to the presence of both molecular CO_2 and carbonate complexes compared to rhyolite or basalt melts of the prevailing molecular CO_2 or carbonate forms, respectively [6−8]. An increase in the water content in the melt composition results in a sufficient decrease in the molecular CO_2−carbonate ion ratio in the quenched glass [9−11].

The authors have studied experimentally the solubility of H_2O-CO_2-Cl-containing fluids of different concentrations (0, 3, 10, and 23 wt % of HCl and from 0 to ~8−15 wt % of CO_2) in synthesized dacite, phonolite, and rhyolite melts (table) at $T = 1000°C$, $P = 200$ MPa, $\log f_{O_2} \sim$ (Ni−NiO) + 3.5 by [12], and an experiment duration of five days. Chlorine and CO_2 were added initially as HCl aqueous solutions and oxalic acid $H_2C_2O_4 \cdot 2H_2O$, respectively. About 5 mg of HCl solution, ~1.0−1.5 mg of oxalic acid, and ~50 mg of powdered previously synthesized aluminosilicate glass were placed into a platinum capsule. The

Table 1. Compositions of the initial aluminosilicate melts (normalized for 100%)

Melt	SiO_2	TiO_2	Al_2O_3	FeO_{tot}	MgO	CaO	Na_2O	K_2O	A/CNK[a]
Dacite	66.7	0.8	16.7	4.1	1.4	3.6	4.0	2.7	1.05
Phonolite	57.5	–	21.8	2.2	0.2	3.0	5.7	9.6	0.87
Rhyolite	76.2	0.1	12.8	0.8	–	0.7	4.6	4.8	0.91
Andesite [8]	57.44	1.06	17.53	7.20	4.31	7.42	3.32	1.61	0.85

[a] A/CNK is the $Al_2O_3/(CaO + Na_2O + K_2O)$ mole ratio in the melt.

experiments were carried out in internally heated high-pressure vessels.

After the experiment, the content of gaseous CO_2 in a capsule was determined by weight losses. The capsule was weighed, frozen in liquid nitrogen, punctured with a needle, and weighed anew after reaching room temperature. The amount of quenching aqueous chloride solution in the capsule was determined in a similar mode. The punctured capsule was weighed, then exposed for 3 min at 110°C, and weighed anew after cooling to room temperature. The glass composition and Cl content were determined using an EDX system and wave spectrometer combined with CamScan MV2300 electron microscope. No visible crystallization of aluminosilicate glass was detected. The water content in the glass was determined by Karl Fischer titration. The possible CO_2 content in the glasses was evaluated by published data [2]. One may suppose that the total CO_2 content was small (below 0.1 wt %). Since the experiments considered were carried out under conditions of water saturation, the water content in melts amounted to 4.5–6 wt %. The mole frac-

tions of H_2O, CO_2, and Cl in fluids were calculated in view of the mass balances. The procedure of experiments as such, along with the conditions of analyzing the obtained quenching phases, is described in more detail in [3].

The data obtained in the experiments on H_2O–CO_2–Cl fluids were compared to those of similar experiments on H_2O–Cl fluids and to published data for the andesite melt [8, 13] (table; Fig. 1).

It is shown that the Cl content in the melt increases considerably from the rhyolite, phonolite, dacite, and andesite compositions (up to 0.25, 0.85, 1.2, and 2.8 wt %), which is primarily caused by growth of the concentration of Ca and, probably, of Mg and Fe in the melt composition [4]. The authors found previously that the growth in the concentration of bivalent alkaline-earth elements (especially of Ca) in the melt composition caused the greatest increase in the Cl content in the melt [14]. A likely mechanism of Cl introduction into the structure of the granodiorite melt was proposed [15].

The addition of CO_2 to the system results in an increase in the Cl content in all the melts treated (Fig. 1). With small amounts of Cl in the experiments, CO_2 increases the Cl content in the melt by 5–10%. This growth is enhanced by the increase in the total Cl content in the fluid. Thus, at a Cl mole fraction in the fluid over 0.10, the Cl concentrations in the melt increase in the CO_2-containing system by even 20–25% relative to the data of experiments without CO_2. One may assume that the presence of CO_2 increases the Cl reactivity in the fluid to cause a growth in the Cl content in the melt.

The introduction of CO_2 into the system affects the H_2O content in aluminosilicate melts as well (Fig. 2). Thus, the addition of CO_2 decreases the H_2O content in the melt by ~0.5–1.0 wt %. The decrease in the H_2O content in the aluminosilicate melt under the addition of CO_2 is probably caused by fluid dilution with carbon dioxide resulting in a decrease in the H_2O mole fraction and fugacity in a fluid.

One must note that CO_2 solubility in the phases of a system and, quite possibly, the effect of CO_2 on the behavior of other volatile components might be considerably modified, probably towards the growth, in
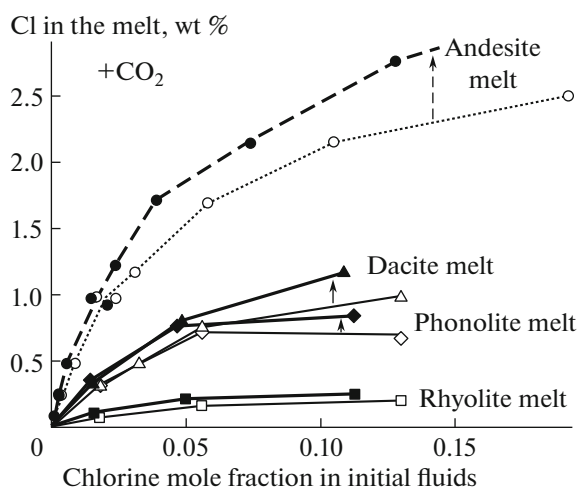

Fig. 1. The influence of CO_2 and the melt composition on the chlorine content in the melt. The authors' data for dacite, phonolite, and rhyolite compositions; the andesite melt by [8]. See Fig. 2 for signs of different melt and fluid compositions. The thick and thin lines show the experiments on CO_2–H_2O–Cl- and H_2O–Cl-fluids, respectively.
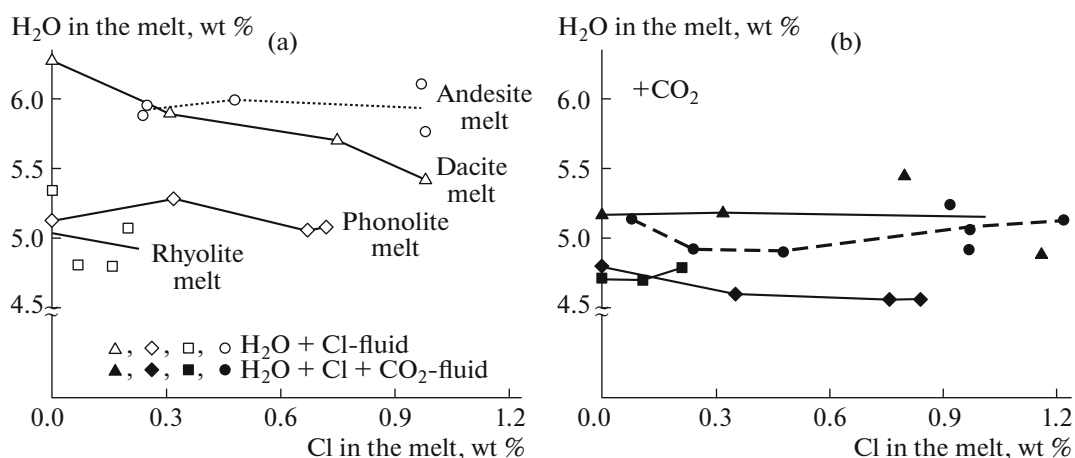
Fig. 2. The influence of CO_2 and the melt composition on the H_2O content in the melt. (a) Experiments on H_2O-Cl-fluids and (b) experiments on CO_2-H_2O-Cl-fluids. See Fig. 1 for other notations.

the case of a lower H_2O content in the system and in the melts undersaturated with aqueous fluid.

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