EXPERIMENTAL STUDY OF Cl, F and H$_2$O SOLUBILITIES IN PHONOLITIC MELT

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Solubility study of volatiles in natural magmatic melts of different composition and research of their partitioning between fluid and melt are of fundamental importance for modeling of magma degassing processes of volcanoes, for the understanding of processes of transport and sedimentation of ore components and for the construction of models of formation of ore deposits. Experimental investigation of fluid-magmatic systems with complex H$_2$O-Cl-F-bearing fluid was not regularly carried out, as distinct from systems with simpler Cl-or F-containing fluids.

The synthetic analogue of K-rich natural phonolit was used as starting glass. The aqueous solutions of HCl, HF and mixed solutions HCl+HF of various concentrations were applied as starting solutions. The initial solution / silicate glass ratio was 0.10–0.15 by weight. Experiments were carried out using Au and Au-Pd capsules in conventional horizontal externally heated cold seal pressure vessels and in internally heated pressure vessels. The conditions of experiments were: P =200 MPa; T ~850°C with f_{O2} = Ni/NiO and T =1000°C with f_{O2} ~QFM+4; the duration of runs was 6-8.5 days.

At T ~850°C the run products were composed of glass and small amount mineral phases (below 10 vol.%) among which mica prevailed. The chemical composition of mica is close to biotite composition. At T =1000°C the run products were composed only of quenched glass. Chemical compositions of quenched products were determined by an electron microprobe analyses. The water contents of quenched glasses in several runs were measured by "Karl-Fischer titration method". The Cl, F, and H$_2$O contents of the fluid phase, which was in equilibrium with the silicate melt, were calculated by the mass balance method. Using these data the partition coefficients of Cl and F between fluid and melt were calculated.

The obtained at 850-865°C, 200 MPa and f_{O2} ~NNO results on solubilities of Cl and F in phonolitic melt, and also on Cl/F ratios in the melt and on the partition coefficients of Cl and F between fluid and melt ($D_{Cl(F)*}$) are submitted in Fig. 1-5. The Cl solubility in phonolitic melt comes up to 0.72 wt. % (1.20 mol. %, at 850°C) and 0.82 wt. % (at 1000°C), and the F solubility in the melt comes up to 0.87 wt. % (2.66 mol. %, at 850°C) and 0.44 wt. % (at 1000°C). The chlorine solubility in phonolitic melt is two times more, than in rhyolitic melt [1].
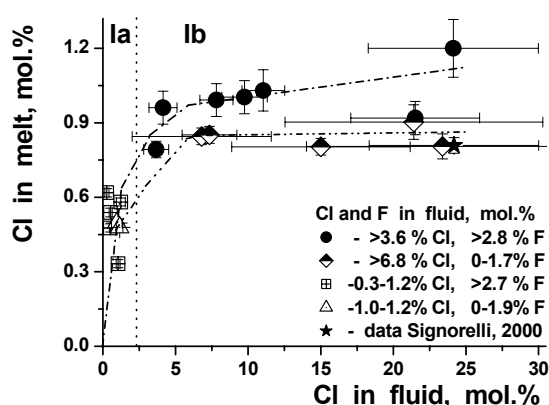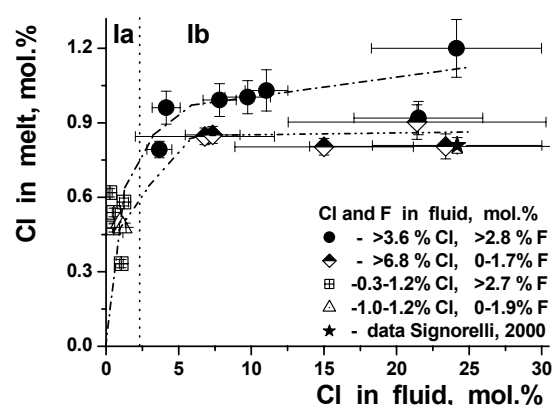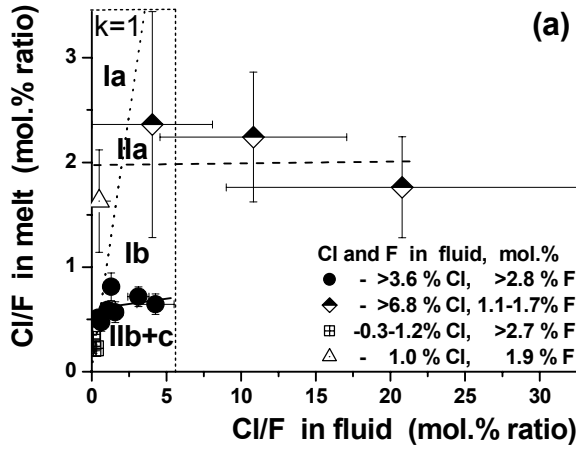

Fig. 1.

Fig. 2.
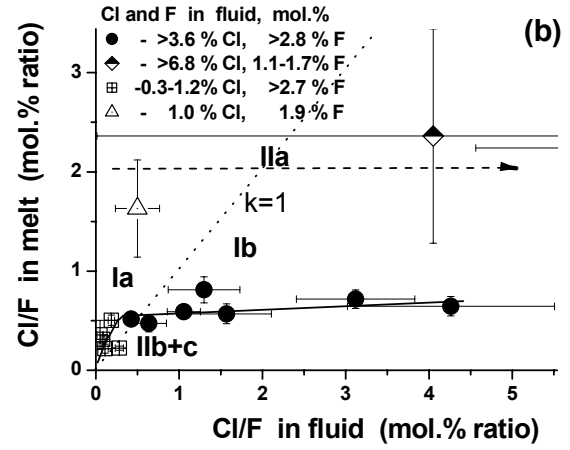
Fig. 3a.

Fig. 3b. The central fragment of fig. 3a.

Fig. 4.

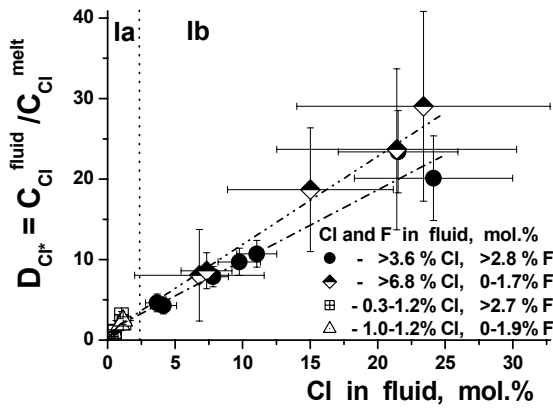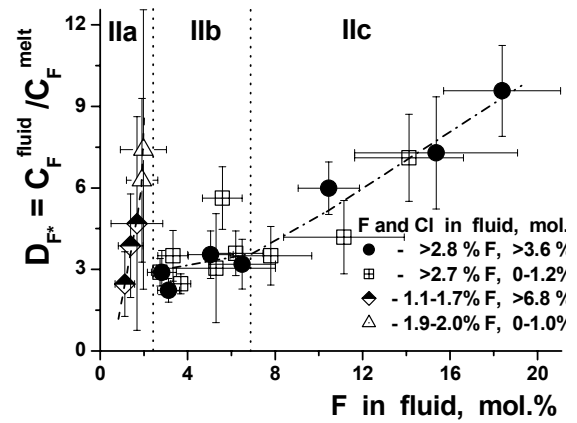**Fig. 5.**

This fact shows that the volatiles solubility in magmatic melt is influenced by the melt composition. Our data are in good agreement with [1] on solubility of chlorine in similar phonolitic melt for F-free system. Addition of F to chlorine-containing system with Cl enriched fluid ($\geq$3.6 mol. %, area Ib in fig. 1) increases the Cl solubility in the melt on 20-30 relative % and does not influence on the Cl solubility in the melt at Cl-poor fluid ($\leq$1.2 mol. %, area Ia in fig. 1). The temperature increase from 850 up to 1000°C has not appreciable effect on the Cl solubility in the melt. Although the analytical error of fluorine determination in the melt is high, the F solubility in phonolitic melt shows nonlinear positive dependence on F content in coexisting fluid (fig. 2). At F-poor fluid (1.1-2.0 mol. % F, area IIa on fig. 2) the F solubility in the melt increases on 50-70 relative % at significant growth of Cl content in the fluid (from 0 up to 23.4 mol. %). At F-rich fluid ($\geq$2.7 mol. %, area IIb-IIc on fig. 2) the addition of Cl does not practically influence the F solubility in the melt. Solubility of fluorine in phonolitic melt decreases twice (from 0.87 to 0.44 wt. %) with temperature growth from 850 up to 1000°C and with f_{O2} increase from NNO up to ~QFM+4.

The Cl/F ratios in phonolitic melt vary in rather small range between 0.2 and 2.4 at change of Cl/F ratios in the fluid from 0.04 up to ~21. They form two groups of values: 0.2-0.7 (at 850°C), 0.5-1.0 (at 1000°C) at F-rich fluid ($\geq$2.7 mol. %, area IIb+c in fig. 3a-3б) and 1.6-2.4 at F-poor fluid ($\leq$2.5 mol. %, area IIa in fig. 3a-3б). The values of Cl/F ratios in the melt change enough weakly with increase of Cl/F ratios in the fluid more than 0.5. This relative constancy of Cl/F ratios in the melt at significant

change of Cl/F ratios in the fluid is, probably, connected with fluid immiscibility (namely, vapor + salt brine). The mole partition coefficient of Cl between the fluid and the melt grows from 0.4 up to 29 at $850^{\circ}C$ (fig. 4) and from 0.4 up to 37 at $1000^{\circ}C$ with Cl increase in the fluid. The mole partition coefficient of F between the fluid and the melt is ~2 - 9.5 at $850^{\circ}C$ (fig. 5) and ~5 - 40 at $1000^{\circ}C$.

Reference

1. *Signorelli S., Carroll M.R.* Solubility and fluid-melt partitioning of Cl in hydrous phonolitic melts // Geochim. Cosmochim. Acta. 2000. V. 64. N. 16. PP. 2851-2862.