Chlorine in fluid-magmatic systems: Experimental data

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A most important part played by volatile components in magmatic, metamorphic, and hydrothermal processes is well-established. Of the other volatiles, chlorine has a special place because for the largest number of elements the presence of chlorine is the main condition for their extraction by water fluids from magmatic melts due to complex formation. The geochemical data on the chlorine concentration in the continental crust are much versatile, this being much lower against the chlorine concentrations in melts yielded from thermobarogeochemical studies. This fact is due to three principal factors, viz: losses upon crystallization, chlorine losses upon magma eruption on the Earth's surface, losses upon the interaction with fluids. Taking into account the impossibility of quantitative estimation of chlorine losses in the process of evolution of the fluid-magmatic systems and hence the impossibility of estimating original chlorine concentrations in magmas of various compositions, the experimental modelling of the fluid-melt equilibrium seems most correct. The experimental studies of chlorine solubility in melts of various compositions and its partitioning between the phases were conducted in high-pressure cells of three types, viz: horizontal two-chamber bomb, gas bomb, and cylinder-piston apparatus at temperatures 800–1200°C and pressures to 15 kb. Natural and model systems of from basaltic to granitic compositions were studied in equilibrium with water-chloride fluids of various concentrations.

In this work we have summarized our own experimental and published data on chlorine solubility in melts of various compositions. Maximum chlorine concentrations were found in basalts and granodiorites (1.0–1.3 wt.%) at a pressure of 2 kb and experimental temperatures 1200 and 1000°C, respectively. As the pressure was increased to 4 kb the solubility of chlorine in the melts was decreased by 1.5–2 times. In the acidic melt–1m NaCl equilibria the solubility of chlorine at 800–900°C and 1.5 kbar increases in the series Ab, Ab-Qz, Ab-Ort-Qz, Ab-Ne and natural granite from 0.08 to 0.33 wt.%. We have found the positive correlation of chlorine solubility with the concentra-

tion in a melt of alkalies, calcium, and iron, and negative correlations with the concentration of silicon and possibly, magnesium. The solubility of chlorine grows with the fluid concentration, being higher in the systems with HCl-containing fluid. The composition (structure) of the melt largely determines the way by which chlorine dissolves in the melt, and its concentration. This is confirmed by the experimental studies of the system Ab-Qz-1m NaCl with different Na/Al ratio in the melt. The minimal chlorine solubility is observed at the molar Na/Al ratio being unity. The obtained results suggest the mechanism of the chlorine dissolution both as molecular forms (NaCl, KCl, HCl) and via complex formation of ionic chlorine with excessive aluminium or sodium in the melt.

The experimental data have been first obtained for the chlorine solubility in an alumosilicate melt Ab-Ort-Qz in the pressure range to 15 kbar and T = 850°C (Fig. 1). A complex behaviour has been established for the pressure dependence with a maximal chlorine concentration in the melt at 7–7.5 kbar. Possibly, this fact can be explained by the change of the coordination number of aluminium (from 4 to 6) in this pressure range which also evidences for the existence of chlorine-aluminium complexes. The experimental data on the coefficients of partitioning of chlorine between the fluid and the melt depending on various factors suggest the idea of creating a model of the behaviour of chlorine in the magmatic process. The concentration of chlorine in natural samples is largely determined by saturation of the original magmas with water. If the water-saturation proceeds at early stages then chlorine goes to the fluid and at eruption small amounts of it get to the atmosphere. If the magmas get water-saturated upon eruption and no biotite, apatite, and amphiboles crystallize there with, then chlorine goes to the atmosphere. At the transition of chlorine into the fluid the effectiveness of the extraction of ore and other elements depends on the water/chlorine concentration. At high chlorine in the original melt the first portions of the fluid phase contain little chlorides. If the melt had a small original water
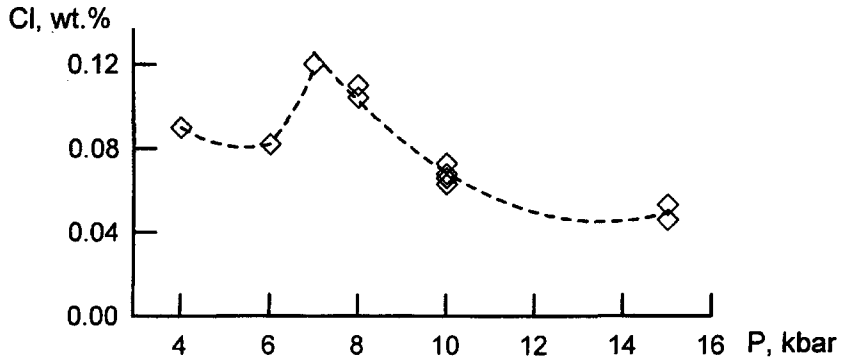
FIG. 1. Pressure dependence of chlorine solubility in the system Ab-Ort-Qz-1m NaCl at 500°C.

concentration and fractionation is proceeding for a long time with the chlorine content of 2000–3000 ppm in the melt the first fluid portions will contain to 50% alkali halogenides which is confirmed by the fluid inclusions data.