Experimental study and thermodynamic model for chlorine solubility in polymerized aluminosilicate melts

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Chlorine is the most important halogen in aqueous fluids ranging from sea water in subduction zones to magmatic and hydrothermal environments in diverse geodynamic settings. In order to characterize the geochemical cycle of chlorine, the pressure and temperature dependence of chlorine solubility in silicate melts must be understood. We have experimentally measured the chlorine solubility at 1100-1600 ^{o}C and up to 20 kbar using five anhydrous aluminosilicate melts: in the Na_2O-Al_2O_3-SiO_2 system. All starting glasses were doped with 5 wt. % of pure NaCl as a chlorine source so that all runs were saturated with molten salt, forming an immiscible phase. In all melt compositions, the chlorine solubility appears to be independent of temperature but it significantly increases with pressure. The absence of temperature dependence implies that the dissolution of NaCl into the silicate network is entropic and is not associated with a change in enthalpy. The pressure dependence is described by molar volume of dissolution in the silicate melt, $\Delta_r V$ = -2.8 to -1.7 J.bar^{-1}, which is strongly composition-dependent and by isothermal compressibility of NaCl, β = 8-14·10^{-5} bar^{-1}. In the SiO_2-$NaAlO_2$ binary, the solubility of chlorine rises by 2.5 mole Cl/mole Al at 1 atm and by 5.7 mole Cl/mole Al at 20 kbar. In the peralkaline melts the solubility increases by 0.07 mole Cl/mole Na^{exc} whereas in the peraluminous compositions it increases by 0.22 mole Al^{exc} at 1 atm. The ratio of solubility gradients is equal to the charge ratio of the two network modifiers and it is used to formulate a unified thermodynamic description of chlorine solubility from peralkaline to peraluminous compositions applicable at 0.001-20 kbar. The dramatic increase in chlorine solubility with the pressure and the amount of network modifiers implies

that (1) decompression increases chloride activity in the melt and promotes the halide saturation during magma ascent, (2) natural magmas may have lost portion of their chlorine budget during rise, and (3) variations in the alumina saturation index during magma differentiation have substantial effect on chlorine solubility, i.e., the partitioning coefficient of chlorine, $D^{fl/melt}$, and the fluid salinity are predicted to increase as subaluminous compositions are approached. Our results highlight the need for better understanding of halogen behavior in high-pressure melts in order to unravel the fluid-melt partitioning in subduction zones or the origin of brines in the source regions of kimberlite magmas.