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Quantitative Modeling of Magmatic Volatile Phase Exsolution

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Water-rich fluids in many ore-generative and geothermal systems include magmatic water as well as other constituents of magmatic origin. The volatile phases exsolved from felsic melts in the earth's upper crust can range from gas-like (~250kg/m^3) to more liquid-like densities under magmatic conditions. The magmatic volatile phases may comprise H_2O, CO_2, H_2S, SO_2, HCl, etc., plus metal chlorides and other compounds (e.g., H_2MoO_4). The critical curve for the appropriate compositions, at least in the simpler salt-water subsystems, passes through the P-T space characteristic of shallow felsic magmatism; therefore, we might expect to find that vapors, brines or supercritical fluids can exist in these systems.

One of our challenges is to predict the composition of the magmatic volatile phases based on magma composition, pressure and temperature, and determine how hypotheses, e.g. for the origin of ore deposits, may then be evaluated. The equilibrium constraints are complex in themselves; however, shallow-level (epizonal) magmatic processes of devolatilization may occur at significant deviations from equilibrium during the upward emplacement of magma. With regard to equilibrium constraints, we must consider the relationship among melt structure, composition and thermodynamics.

Our experimental results on rhyolite/brine partitioning at 800°C and 100 MPa suggest that the total chloride concentration in a "100 MPa ternary minimum" melt in equilibrium with a 70 wt.% NaCl (equivalent) vapor-undersaturated brine (of constant chloride concentration) increases with increasing HCl/(NaCl+KCl+HCl), i.e. HCl in the volatile phase reacts with NaOH in the melt to produce molecular H_2O and NaCl in the melt. This is consistent with the model of Kohn et al. (1989), wherein water reacts with NaAl complexes in the melt to produce NaOH and HAl complexes. We suggest the hypothesis, based on our experimental data, that the addition of HCl results in a replacement of melt OH by Cl, analogous to neutralization reactions in aqueous solutions at ambient laboratory conditions. Further, our data show that the KNa_{-1} (volatile phase/melt) exchange constant decreases with increasing HCl concentration in the volatile phase:

$$K(K,Na) = 0.4 + 240/(HCl, ppm).$$

These data are consistent with a model wherein Na is distributed over $NaAlO_2$ and NaOH complexes in the melt; K may play a similar role, but our data are consistent with a high proportion of K (relative to Na) remaining in a charge balancing position. Other equilibria involving HCl include:

$$0.5\ H_2O + 0.5\ Al_2O_3^{m} + NaCl^{v} = HCl^{v} + NaAlO_2^{m}$$

(where $Al_2O_3^m$ indicates Al not charged balanced by alkalis in the melt, and the superscripts m and v indicate melt and volatile phase, respectively), and,

$AuO_{0.5}{}^{m} + HCl^{v} = AuCl^{v} + H_2O$ (with similar relations for other Cl-complexed metals).

Equilibrium and non-equilibrium mass transfer effects on the composition of magmatic volatile phases include both progressive crystallization and devolatilization. Simple chemical models belie the physical complexity of magmatic systems; yet, some general principles, such as the relative effects of the crystallization of pyrrhotite and iss on the composition of the MVP can be evaluated. In accord with the results of Lynton et al. (1993) and Jugo et al. (1999), some ores that show evidence of near-solidus pyrrhotite saturation in associated melts do not have significant Cu, whereas magmas that are oxidized are commonly associated with ores that contain significant Cu. In some cases, volatile exsolution occurs far from equilibrium; in such cases, rates of diffusion may limit the ability of a volatile phase to remove ore metals from the melt. Cu and Mo diffusion coefficients in melts suggest that Cu diffuses faster in felsic melts than Mo. Slower diffusing species would not be incorporated into bubbles of the magmatic volatile phase during rapid volatile exsolution. Volatiles may therefore remove Cu, but leave Mo (and W?) in the glass or later-formed crystalline phases.

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