**HIGH TEMPERATURE COMPONENTS OF MAGMA-
RELATED GEOTHERMAL SYSTEMS: AN
EXPERIMENTAL AND THEORETICAL APPROACH**

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Summary

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SECTION I: Executive Summary

This summarizes select components of a multi-faceted study of high temperature magmatic fluid behavior in shallow, silicic, volcano-plutonic geothermal systems. This work built on a foundation provided by DOE-supported advances made in our lab in understanding the physics and chemistry of the addition of HCl and other chlorides into the high temperature regions of geothermal systems. The emphasis of this project was to produce a model of the volatile contributions from felsic magmatic systems to geothermal systems.

The proposed research included work on HCl- and H₂SO₄ -bearing brine alteration of silicates at 500 °C and 500 bars (e.g. Hall, 1999; Frank et al., 1998) and work on the relationship between melt aluminosity and HCl in the magmatic volatile phase (e.g. Piccoli et al., 1999; Williams et al., 1997).

Successful integration of laboratory and theoretical approaches is critical to the prediction of magmatic-hydrothermal effects in geothermal systems, particularly with respect to how magmatic/high-temperature input to geothermal systems can affect the sulfate and chloride-associated acidity. This work will be performed at The University of Maryland at College Park primarily by Drs. Philip Candela (Professor of Geology) and Philip Piccoli (Assistant Research Scientist), and by graduate students under our direction.

SECTION II: Experimental Studies of Brine ∨ Solid ∨ Melt Systems

Over the past several years, we have characterized critical parameters related to the chloride acidity of magmatic contributions to geothermal systems. Given that a significant proportion of the acidity in magmatic hydrothermal systems is sulfur-acidity, we explored the chemical properties of sulfate in vapor undersaturated brines, including their reaction with assemblages of rock-forming minerals, likely to be found associated with geothermal reservoirs. We studied brine interactions with amphibole and biotite-bearing assemblages in the system KCl- NaCl- H₂O- HCl- (SO₄Cl₂) near vapor saturation. We employed high ratios of brine to minerals, as in the study of Frank et al. (1998) to map out mineral stability. Our experiments were performed at salinities near the vapor-saturated boundary, and were conducted in Pt capsules. We utilized an Ar pressure medium with hematite as a H₂ "getter" to maintain sulfate stability.

In our experiments, we have mapped out regions of amphibole (tremolite) reactivity in H/K and SO₄=Cl- space. We evaluated the composition of brines in the equilibrium:

We also mapped out the stability of k-feldspar-muscovite-andalusite-quartz as a function of brine composition in synthetic geothermal systems at temperatures of 400-550°C, and pressures of 25-60 MPa.

We also performed experiments at 800 °C and 100 MPa on the relationship between the molar Al/(K+Na+2Ca) ratio in melts and the composition of vapor-undersaturated brines. Some of the aluminosity (ASI= .93 to 1.00) is due to chlorine incorporated into the melt as NaCl. These

experiments have been run with molar K-Na ratios of the brine equal to unity, and melt compositions defined by the 100 MPa granite minimum. Under these conditions, melts remain peralkaline even at high concentrations of HCl in the brine.

We have applied these systematics to igneous intrusions in the Sierra Nevada batholith. Our calculations show that aqueous magmatic fluids evolved from the Billy Lake-Rush Creek magma had a concentration of HCl in the vapor phase of 0.02 molal.

Select Milestones:

Reactions between a sulfate-bearing, vapor-undersaturated brine and the mineral assemblage potassium feldspar-albite-quartz-tremolite-apatite at 500°C and 50 MPa.

Hall, M.

Sulfate-bearing hydrothermal fluids can be observed at the surface of the earth (i.e. volcanic aerosols and hot springs); however, little is understood about deep, high-temperature (~500°C), sulfate-bearing brines. Potassically altered mineral assemblages containing hydrothermal "shreddy" biotite are commonly observed in porphyry copper deposits, and are associated with brine-bearing fluid inclusions. In many systems the alteration occurs near the magnetite-hematite oxygen fugacity buffer, and the brines clearly contained dissolved sulfur. In order to constrain the concentration of sulfate in the brine phase responsible for this type of alteration, we performed experiments between minerals and brine with variable sulfate to chloride ratios. We examined the equilibrium: $4\text{H}_2\text{O} + 5\text{KMg}_3\text{Si}_3\text{AlO}_{10}(\text{OH})_2 + 24\text{SiO}_2 + 6\text{CaSO}_4 = 3\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2 + 5\text{KAlSi}_3\text{O}_8 + 6\text{H}_2\text{SO}_4$, at 500°C and 50 MPa. The brine consisted of NaCl, KCl, H₂SO₄, and Na₂SO₄, and the salinity of the brine was held constant at 42 wt.% NaCl equivalent (on an equal anion mole basis). The sulfate concentration and the acidity of each experiment were systematically changed by varying SO₄/Cl and H/K, respectively, of the

brine. Phlogopite nucleation was not detected in any of the experimental runs; however, runs seeded with phlogopite showed no obvious signs of phlogopite destruction. Furthermore, in all the runs with $H/K < 0.09 \pm 0.01$ no mineral alteration was observed. Conversely, in all the runs with the ratio of $H/K > 0.09 \pm 0.01$, talc was observed to have nucleated on tremolite. We hypothesize that talc may be a metastable, pre-phlogopite phase that nucleates preferentially to phlogopite.

K-feldspar-muscovite-andalusite-quartz-brine phase equilibria: an experimental study at 25 to 60 MPa and 400 to 550°C

Frank, M.R., Candela, P.A., and Piccoli, P.M.

Felsic magmas may evolve one or more water or chlorine-rich fluid phases which can transport heat and solutes into associated hydrothermal systems and can contribute to alteration and ore deposition. To understand the role of a high-salinity aqueous phase in the magmatic hydrothermal environment, the composition of a subcritical, vapor-undersaturated high-salinity liquid phase (brine) in equilibrium with K-feldspar-muscovite-quartz and muscovite-andalusite-quartz was determined for pressures and temperatures ranging from 25 MPa and 400°C to 60 MPa and 550°C, with total Cl (NaCl + KCl + HCl) concentrations ranging from 3.42 to 8.56 (moles of solute/kg solution). Values of $\log_{10} (KCl/HCl)$ have been obtained for the equilibria: $1.5 \text{ K-feldspar} + HCl = 0.5 \text{ muscovite} + 3 \text{ quartz} + KCl$ and $\text{muscovite} + HCl = 1.5 \text{ andalusite} + 1.5 \text{ quartz} + 1.5 \text{ H}_2\text{O} + KCl$. For the K-feldspar-muscovite-quartz-brine equilibrium, $\log_{10} (KCl/HCl) = 1.6 \pm 0.1, 0.81 \pm 0.06, 0.54 \pm 0.04$ and 0.42 ± 0.08 at 25 MPa and 400°C, 40 MPa and 450°C, 50 MPa and 500°C, and 60 MPa and 550°C (pressures and temperatures of the experiments), respectively. For the muscovite-andalusite-quartz-brine equilibrium, $\log_{10} (KCl/HCl) = 0.63 \pm 0.1, -0.063 \pm 0.06, 0.17 \pm 0.05$, and 0.25 ± 0.08 at the pressures and temperatures of the experiments, respectively. Comparison of our results with previous studies conducted at higher pressures and with lower-salinity aqueous phases show that the mineral

stability fields in the K-feldspar-muscovite-andalusite-quartz system shift to lower KCl/HCl values with increasing salinity and decreasing pressure.

Alkali exchange equilibria between a silicate melt and coexisting magmatic volatile phase: an experimental study at 800°C and 100 MPa

Frank, M.R., Candela, P.A., and Piccoli, P.M.

Many experimental studies have been performed to evaluate the composition of coexisting silicate melts and magmatic volatile phases (MVP). However, few studies have attempted to define the relationship between melt chemistry and the acidity of a chloride-bearing fluid. Here we report data on melt composition as a function of the HCl concentration of coexisting brines. We performed 35 experimental runs with a NaCl-KCl-HCl-H₂O brine (70 wt% NaCl [equivalent])-silicate melt (starting composition of Qtz_{0.38}Ab_{0.33}Or_{0.29}, anhydrous) assemblage at 800°C and 100 MPa. We determined an apparent equilibrium constant

$$K'_{\text{meas}}(\text{K}, \text{Na}) = (C_{\text{Na}}^{\text{m}} \times C_{\text{KCl}}^{\text{b}}) / (C_{\text{NaCl}}^{\text{b}} \times C_{\text{K}}^{\text{m}})$$

for the equilibrium

as a function of the HCl concentration in the brine ($C_{\text{HCl}}^{\text{b}}$). Although $K'_{\text{meas}}(\text{K}, \text{Na})$ was not affected by variations in KCl/NaCl of the brine, it did vary inversely with $C_{\text{HCl}}^{\text{b}}$. The relationship is given by

$$K'_{\text{meas}}(\text{K}, \text{Na}) = K'_{\text{ex}}(\text{K}, \text{Na}) + \frac{a}{C_{\text{HCl}}^{\text{b}}}$$

[where C_{HCl}^b is in wt% and $a = 0.03$; $K'_{\text{ex}}(\text{K}, \text{Na}) = 0.40 \pm 0.03$ (1σ) and represents the exchange of model sodium and potassium between chloride components in the brine and the aluminate components (NaAlO_2 and KAlO_2) in the melt. This empirical result will be discussed in light of a structural hypothesis; however, validation of the model awaits determinations based on spectroscopy or transport properties—thermodynamic relations alone cannot be used as evidence of structure. The form of this equation is consistent with a model wherein sodium is present in the melt as both sodium aluminate and sodium hydroxide components, and HCl reacts with the NaOH component in the melt to produce NaCl and H_2O .

The correlation between fugacity of H_2O ($f_{\text{H}_2\text{Osys}}$), model $\text{NaOH}^m/\Sigma\text{Na}^m$, aluminum saturation index (ASI), and the ratio $(\text{HCl}/\text{NaCl})^b$ of an exsolving MVP is complex. $f_{\text{H}_2\text{Osys}}$ and the ASI are the main controls on model $\text{NaOH}^m/\Sigma\text{Na}^m$ in the system, with model $\text{NaOH}^m/\Sigma\text{Na}^m$ increasing with increasing $f_{\text{H}_2\text{Osys}}$. This relationship can be used to estimate the C_{HCl}^b in subaluminous systems, an improvement over previous models. Data for metal partitioning between a volatile phase and melt are commonly presented in the literature as metal–sodium exchange equilibria (i.e., $K_{\text{Cu,Na}}$ for the exchange of copper and sodium). However, the variation in $K'_{\text{meas}}(\text{K}, \text{Na})$ observed in this study implies that the treatment of metal partitioning between a volatile phase and melt as metal–alkali exchange equilibria is complex because alkali partitioning is not constant and suggests that experimental partitioning studies need to carefully control the HCl/NaCl in experimental vapors and brines. This effect may explain discrepancies in metal–alkali exchange equilibria presented in the literature. Therefore, metal–alkali exchange cannot be described fully by a single metal–alkali equilibrium but must be examined by multiple equilibria.

Hydrogen-alkali exchange between silicate melts and two-phase aqueous mixtures: an experimental investigation

Williams, T.J., Candela, P.A. and Piccoli, P.M.

Experiments were performed in the three-phase system high-silica rhyolite melt + low-salinity aqueous vapor + hydrosaline brine, to investigate the exchange equilibria for hydrogen,

potassium, and sodium in magmatic-hydrothermal systems at 800 °C and 100 MPa, and 850 °C and 50 MPa. The $K^{\text{aqm/melt}}_{\text{H,Na}}$ and $K^{\text{aqm/melt}}_{\text{H,K}}$ for hydrogen-sodium exchange between a vapor + brine mixture and a silicate melt are inversely proportional to the total chloride concentration (ΣCl) in the vapor + brine mixture indicating that HCl/NaCl and HCl/KCl are higher in the low-salinity aqueous vapor relative to high-salinity brine. The equilibrium constants for vapor/melt and brine/melt exchange were extracted from regressions of $K^{\text{aqm/melt}}_{\text{H,Na}}$ and $K^{\text{aqm/melt}}_{\text{H,K}}$ versus the proportion of aqueous vapor relative to brine in the aqueous mixture (F^{aqv}) at P and T, expressed as a function of ΣCl . No significant pressure effect on the empirically determined exchange constants was observed for the range of pressures investigated. Model equilibrium constants are: $K^{\text{aqv/melt}}_{\text{H,Na}}(\text{vapor/melt})=26(-1.3)$ at 100 MPa (800 °C), and 19(- 7.0) at 50 MPa (850 °C); $K^{\text{aqv/melt}}_{\text{H,K}}=14(-1.1)$ at 100 MPa (800 °C), and 24(-12) at 50 MPa (850 °C); $K^{\text{aqb/melt}}_{\text{H,b}}(\text{brine/melt})= 1.6(-0.7)$ at 100 MPa (800 °C), and 3.9(-2.3) at 50 MPa (850 °C); and $K^{\text{aqb/melt}}_{\text{H,K}}=2.7(-1.2)$ at 100 MPa (800 °C) and 3.8(-2.3) at 50 MPa (850 °C). Values for $K^{\text{aqv/melt}}_{\text{H,K}}$ and $K^{\text{aqb/melt}}_{\text{H,K}}$ were used to calculate KCl/HCl in the aqueous vapor and brine as a function of melt aluminum saturation index (ASI: molar $\text{Al}_2\text{O}_3/(\text{K}_2\text{O}+\text{Na}_2\text{O}+\text{CaO})$) and pressure. The model log KCl/HCl values show that a change in melt ASI from peraluminous (ASI = 1.04) to moderately metaluminous (ASI = 1.01) shifts the cooling pathway (in temperature-log KCl/HCl space) of the aqueous vapor toward the andalusite+muscovite+K-feldspar reaction point.

Estimation of aqueous HCl and Cl concentrations in felsic systems

Piccoli, P.M., Candela, P.A. and Williams, T.J.

Two models are presented which can be used to make order of magnitude estimates of the concentration of HCl and Cl in the magmatic volatile phase (MVP). One model is based primarily upon aplite chemistry, and the other is based primarily on apatite chemistry; the models are not entirely independent, and additional information can be gained by using the models in conjunction with one another. Combining both methods allows for the calculation of a model

bulk Cl concentration of magmatic vapor. Both models are applied to a natural system: the Billy Lake granite and Rush Creek quartz–monzodiorite in the Sierra Nevada Batholith of eastern California. The bulk composition of aplite and other granitic rocks of (vapor-saturated) near-minimum melt compositions can be used to estimate maximum HCl/total Cl for the magmatic vapor phase. The composition of the aplites in the Billy Lake–Rush Creek (BLRC) system has been used to determine model HCl/KCl and HCl/NaCl for the vapor in equilibrium with the aplite melts; both ratios are on the order of unity (1.1). These values suggest that the maximum $\text{HCl/Cl} \sim 1/3$, corresponding to a concentration of HCl in the magmatic vapor of ~ 0.02 molal if the magmatic system was saturated with a brine phase. Apatite compositions can be used to estimate the HCl concentration in the magmatic vapor as a function of temperature. Based on the P_2O_5 and SiO_2 concentrations in the aplites, and the solubility of apatite in silicate melts, apatite began to crystallize at 820°C in the aplites, which also yields an estimate of 0.02 molal for the concentration of HCl for the BLRC system by the apatite method. Within error, both models produce the same result.

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