**EXPERIMENTAL AND THEORETICAL INVESTIGATION OF
THE PRODUCTION OF HCl AND SOME METAL CHLORIDES
IN MAGMATIC/HYDROTHERMAL SYSTEMS**

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Progress Report No. 10 (1Q/93)

DOE Progress Report for the project entitled "Experimental and Theoretical Investigation of the Production of HCl and Some Metal Chlorides in Magmatic/Hydrothermal Systems", Project No. DEFG07-90ID13025 for Budget Year 9/28/92-9/27/93. This report (Progress Report #10) is to cover the period of January through March, 1993 (1Q/93).

It is well documented that Cl and F concentrations in magmatic-hydrothermal systems are important in determining whether a particular source has the potential to produce an 'ore-forming' fluid in some environments. Inability to sample these fluids directly in inactive systems has led to a variety of techniques which have the potential to be used to obtain information about the chemistry and timing of exsolution of these ore-forming fluids. To this end, we have formulated and documented a model in which the halogen (Cl and F) concentration in the mineral apatite in mid-crustal silicic plutonic systems can be used to make estimates of magmatic Cl and F concentrations at the time apatite was crystallizing (*e.g.* Piccoli and Candela, 1992; 1993a). This original model was limited for a variety of reasons: 1) the model relied heavily on published experimental data that were confined to metaluminous and peralkaline compositions, and 2) the model was derived to simulate mid-crustal level plutonic systems (~ 6 km) which are sometimes thought to exsolve a magmatic fluid after significant crystallization has occurred. The formulation and application of this model has been described in previous Department of Energy Progress Reports, and in a variety of other forums (*e.g.* Piccoli, 1992; Piccoli and Candela, 1992; 1993a; 1993b).

Application of the model to shallow systems (emplaced at depths of 1-2 km), for example the Billy Lake-Rush Creek Volcano-Plutonic Complex, requires modification of the original model by the incorporation of additional solubility and partitioning experimental data, and

extrapolation of the working range of calculations to lower temperatures. Furthermore, additional problems arise in the simulation and interpretation when modelling shallow systems that were not present or not as prevalent in deeper systems. The solubility of water is lower in shallower systems and melts saturate with respect to a magmatic fluid earlier in their evolution which often leads to extensive hydrothermal proliferation which requires the model to be operable at sub-solidus temperatures. Extrapolation of the model to lower temperatures allows the potential for additional information to be obtained. Shallow plutonic systems lend themselves to additional problems, especially interaction with meteoric water for extended periods of time. We are currently attempting to deal with these problems.

Effort is also being exerted in distinguishing between magmatic and hydrothermal signatures in apatite chemistry. Preliminary calculations are being performed, using the data from the Billy Lake-Rush Creek apatites, to determine if the halogen concentrations in these apatites represent a magmatic, hydrothermal, combined, or possibly a signature that can't be distinguished. These calculations are difficult as they are modelling a process which is constantly changing. For example, changing partitioning systematics with changing temperature, changing melt composition, changing composition of the fluids, changing apatite solubility systematics, *etc.*, all have to be accounted for as apatite continues to grow in a magmatic-hydrothermal environment. We are in the process of making these calculations and determining how the composition of magmatic and hydrothermal apatites would differ, and whether these effects could be determined using electron probe, or if spatial constraints within apatite inhibit this.

We are also in preliminary stages of expanding the compositional range of which these calculations can be performed. Recently, apatite solubility experiments have been performed in

silicic melts which are peraluminous in nature (Pichavant and others, 1992); as aqueous phase/melt partitioning experiments, HCl/total Cl experiments and experiments on melt composition as a function of crystallization have been published, this allows for the potential for the 'working compositional range' of the model to be extended. We are currently incorporating this new apatite solubility data from experiments in peraluminous systems. Upon completion, this will have the potential to model highly evolved silicic systems.

The extrapolation of the model to both lower temperatures, and an expanded compositional working range should lead to the potential for important information about the magmatic-hydrothermal transition.

References

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- Piccoli, P.M. and Candela, P.A., 1993b, Magmatic-Hydrothermal Volatile History of the Billy Lake-Rush Creek Volcano-plutonic Complex, Ritter Range, Sierra Nevada Batholith, California. EOS-Transactions of the American Geophysical Union, v. 74, p. 333.
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- Pichavant, M., Montel, J.M., and Richard, L.R., 1992, Apatite solubility in peraluminous liquids: Experimental data and an extension of the Harrison-Watson model: *Geochimica et Cosmochimica Acta*, v. 56, p. 3855-3861.

Additional work that has been completed under this contract during this reporting period are the completion of revisions, and subsequent acceptance of the manuscript Apatite in felsic rocks: a model for the estimation of initial halogen contents in the Bishop Tuff (Long Valley) and Tuolumne Intrusive Suite (Sierra Nevada Batholith) Magmas, which has been accepted for publication in the American Journal of Science, and an abstract which will be presented in May at the Spring meeting of the American Geophysical Union (which is reproduced below).

Magmatic-Hydrothermal Volatile History of the Billy Lake-Rush Creek Volcano-plutonic Complex, Ritter Range, California

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The Billy Lake granite (BL) and Rush Creek quartz-monzodiorite (RC) comprise a small volume, texturally and compositionally zoned composite suite of rocks. Field observations suggest that the Billy Lake-Rush Creek Complex (BLRC) was emplaced at a shallow depth in the crust and fractured only to a modest degree. This result is advantageous as it allows the hydrothermal relationships to be worked out with a low degree of ambiguity. We have documented the existence of aplitic veins which grade laterally into hydrothermal veins. These hydrothermal veins bear a minimum amount of alteration, and can be seen cutting veins with greatly different strike and dip that contain calcic minerals and possess highly altered selvages. We interpret the latter veins to have formed from fluids that originated external to the orthomagmatic-hydrothermal system.

We have previously described a model in which apatite can be used to estimate magmatic volatile (F and Cl) concentrations (Trans. Royal Society Edinburgh, v. 83, p. 496; Amer. J. Science, in press) which has been applied to deeper plutonic systems. Preliminary halogen analyses have been obtained from apatites in host rocks, aplites and mafic enclaves and have been found to be unzoned within the resolution of the electron microprobe. Preliminary analyses also suggest that size and morphology of apatites do not have any correlation with halogen concentrations. Apatites from RC have lower F concentrations (2.98 wt.%) than in BL (3.14 wt.%). The Cl concentration in apatites from both plutons are similar (RC-0.03 wt.%; BL-0.05 wt.%). These values suggest that the hydroxyl component of these apatites are as follows: RC- 0.69 wt.% and BL- 0.54 wt.%. Apatites within aplites in RC have somewhat elevated F contents (3.56 wt.%) and similar Cl contents (0.03 wt.%) to the apatites contained within the host rocks into which these intrude. Similarly, apatites within aplites in BL have elevated F concentrations (3.26 wt.%) and similar Cl concentrations (0.05 wt.%) relative to those in the host rock. The calculated hydroxyl concentration of aplitic apatite is 0.09 wt.%. Based on published solubility data, model apatite saturation temperatures of 957°C and 947°C have been estimated for RC and BL, respectively, and 820°C for apatites within aplite dikes. Apatites within aplites exhibit higher Cl/OH ratios than those in host rocks as predicted (Candela, 1989, Rev. Econ. Geol. v.4); devolatilization at shallow levels does not result in depletion of a melt in Cl relative to H₂O, because of changing mass transfer systematics with decreasing pressure. These signatures are distinctly different than those of apatites from the larger volume Tuolumne Intrusive Suite which was emplaced at a deeper level in the crust.