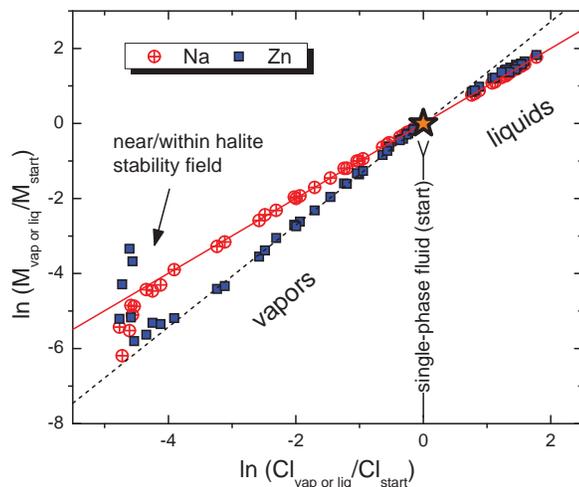


Experimental vapor-liquid partitioning of transition metals in NaCl dominated fluids

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Multi-phase fluid flow is a common occurrence in magmatic hydrothermal systems, and extensive modeling efforts using empirically derived PVTx properties of the NaCl-H₂O system are frequently conducted. We have performed hydrothermal flow experiments in the near-critical and two-phase region (410-465 °C, 250-400 bars) to derive sufficiently resolute partition coefficients for some important accessory metals. NaCl solutions (3-6 wt%) containing variable amounts (1-20 mmolal) of alkaline earth and transition metal chlorides were pumped through a Ti alloy reactor with an outlet control valve capable of maintaining set pressure within ± 0.5 bars. Flow rates were optimized to obtain the equilibrium vapor phase and the coexisting liquid was then simultaneously sampled. The included figure shows Zn data as a representative example of the metals studied (shown normalized to starting composition of the single phase fluid). Na dominates phase behavior in the system, where all metal cations must be charge balanced



by Cl. The Zn/Na ratio decreases with chlorinity in the vapor phase until conditions approach halite saturation where the trend abruptly reverses with a concomitant decrease in pH (possibly due to hydrolysis). Such volatility may play an important role in concentrating transition metals in magmatic hydrothermal systems. Uniform slopes for each metal in the vapor phase equate to relative partition coefficients (Na = 1) of the order: Cu(I) \leq Na < Fe(II) < Zn < Mg \leq Ni(II) \leq Mn(II) \leq Co(II) < Ca < Sr < Ba. While the absolute concentration of such elements in natural fluids is controlled to a first order by temperature dependant mineral solubility, phase separation can be decoupled from fluid-mineral equilibria depending on flow rate/residence time. Thus, such partition coefficients can be used to aid in both geochemical modeling and reconstruction of P-T history for multiple hydrothermal fluid samples or inclusions.

Nucleation: concentration fluctuations and polymorph selection

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Nucleation is the stochastic process that creates the first stable embryo of a new phase to initiate a phase transition. The mechanism is poorly understood because rare events processes like nucleation present special challenges to both experiments and simulations. The difficulties are particularly acute for multi-component condensed phase nucleation processes where most applications lie. I outline recent advances toward understanding nucleation mechanisms. First, I show how the free energy landscape and dynamics for development of competing polymorphs can be understood using simulations.[1,2] Then I present a new droplet theory of nucleation that couples local concentration fluctuations to nucleus size evolution.[3] The new theory may explain why recent simulations with very different solutes show similar two-step nucleation mechanisms.

[1] Peters (2009) *J. Chem. Phys.* **131**, 224103. [2] Duff, Peters (2011) *J. Chem. Phys.* **135**, 134101. [3] Peters (2011) *J. Chem. Phys.* **135**, 044107 (2011).