

Insights into Magmatic Differentiation: Energy Constrained Open-System Processes

WENDY A. BOHRSON¹ AND FRANK J. SPERA²

¹Department of Geol. Sci., Central Washington University, Ellensburg, WA. 98926 (bohrson@geology.cwu.edu)

²Institute for Crustal Studies, UCSB, Santa Barbara, CA. 93106, USA (spera@magma.geol.ucsb.edu)

The geochemistry of evolving magma bodies is governed by magma recharge, assimilation of country rock, and fractional crystallization (RAFC). The complex record of these processes is preserved in a diversity of products of differing scales, ranging from single crystals to cumulates and enclaves to cogenetic volcanic suites. A quantitative approach to understanding the consequences of RAFC, *Energy-Constrained Recharge, Assimilation, Fractional Crystallization (EC-RAFC)*, tracks the thermochemical evolution of an open-system magma body by solution of a system of coupled, non-linear ordinary differential equations that express energy, mass and species (trace elements and isotopes) conservation. EC-RAFC can be applied to magma bodies for which relevant thermal and chemical data are known; output includes mass and geochemical data for melt + crystals as the body cools to an *a priori* specified equilibration temperature. The critical aspect of EC-RAFC is that studies of the geochemistry, masses, and thermodynamics of melt + crystals can be linked, thereby providing an integrated view of the evolution of magma bodies.

EC-RAFC geochemical results are characterized by non-monotonic element-element, element-isotope trends that reflect the coupled nature of energy, mass and species constraints characteristic of natural systems. Such geochemical trends have analogues in nature but previously have been difficult to model. Using the vast geochemical data base pertinent to igneous systems, EC-RAFC can be used to investigate many problems relevant to magma dynamics, including (1) characterizing the distinctions between episodic and continuous recharge; (2) unravelling the complex geochemical history captured by crystal isotope stratigraphy studies; (3) documenting the time-dependent record of RAFC preserved in cumulates; (4) understanding the thermochemical implications implied by enclaves that form when mafic melt is added to a magma body; and (5) quantifying the conditions under which magma bodies reach chemical steady-state. Widespread application of EC-RAFC allows comparisons of the relative importance of RAFC processes in specific tectono-magmatic settings. The ability to integrate thermal and chemical results allows development of a quantitative description of the coupling of these, and this, in turn, may provide important constraints on mechanisms by which these become decoupled. Tracking masses of melts and crystals in a complex RAFC system allows predicted masses to be evaluated in light of field constraints and points to the continued necessity of placing high quality geochemical data in a field context.

Hydrolysis and precipitation of Pd(II) in 0.6 m NaCl

J.-F. BOILY AND T.M. SEWARD

Institut für Mineralogie und Petrographie, Swiss Federal Institut (ETH), Zürich, Switzerland

The hydrolysis and precipitation of aqueous solutions of 47×10^{-6} m to 10×10^{-3} m Pd(II) were investigated in 0.6 m NaCl at 298.2 K by means of potentiometry and uv-vis-spectrophotometry.

The dominant species, PdCl_4^{2-} , undergoes significant aqueous hydrolysis at $\text{pH} > 7$ but can also be accompanied by the precipitation of a brown oxide. The uv-spectra of filtered solutions of low concentrations of Pd(II) reveal bands likely to result from $\text{PdCl}_{4-x}(\text{OH})_x^{2-}$ species. Potentiometric titrations of homogeneous solutions reveal a maximum of two protons released (i.e. two hydroxyls consumed) per Pd(II) in the pH range 2-10. In addition, titrations at a wide range of concentrations of Pd(II) show no evidence for polynuclear species at equilibrium. Aqueous speciation is therefore proposed to be limited to the species PdCl_4^{2-} , $\text{PdCl}_3\text{OH}^{2-}$ and $\text{PdCl}_2(\text{OH})_2^{2-}$ with formation constants constrained both by the uv-spectra and the potentiometric titration data.

Titrations along Pd(II)-oxide precipitation edges reveal a release of 1.74 protons per precipitated Pd(II) (Figure 1), giving rise to the tentative stoichiometry $\text{PdCl}_{0.26}(\text{OH})_{1.74}$ (s), a result in accordance with the energy dispersive X-ray analyses of Byrne and Yao (2000). Moreover, X-ray diffraction patterns of a precipitate aged for 18 months at 298.2 K are characteristic of a poorly-crystallized Pd-oxide.

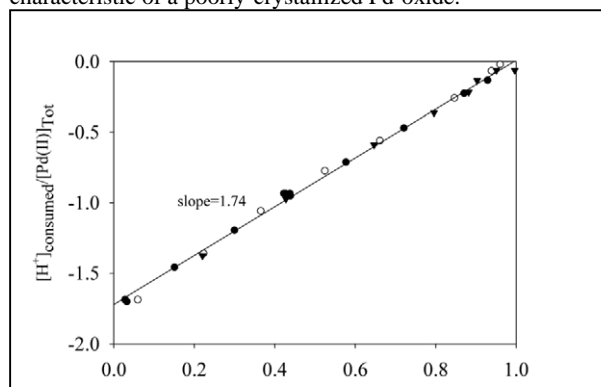


Figure 1: Normalized proton consumption as a function of the fraction of Pd(II) in solution (Equilibration time: 6 weeks) along precipitation edges ($\text{pH}=5-7$)

Reference

Byrne R.H. and Yao W., (2000), *Geochim. Cosmochim Acta* **64**, 4153-4156