FINAL REPORT
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Stable-isotope probe of nano-scale mineral-fluid redox interactions

Abby Kavner, 310-206-3675, akavner@ucla.edu;
University of California, Los Angeles
Earth and Space Sciences Department
595 Charles Young Drive East
Los Angeles, CA 90095

Project Summary: Our goal is to study how stable isotopes fractionate at an aqueous/solid interface during electrochemical reduction reactions. Measurements in a wide variety of metal deposition systems including Fe, Zn, Li, Mo, and Cu, have led to observations of large isotope fractionations which strongly vary as a function of rate and temperature. For the Fe, Zn, and Li systems, our electrochemical deposition methods provide the largest single-pass fractionation factors that are observed for these systems.

Based on these and other experiments and theory showing and predicting significant and rate-dependent fractionations of isotopes at reacting interfaces, we have developed a simple statistical mechanics framework that predicts the kinetic isotope effect accompanying phase transformations in condensed systems.

In addition, we have begun to extend our studies of mineral-fluid redox interactions to high pressures and temperatures in the diamond anvil cell. We performed a series of experiments to determine solubilities of Cu and Ni at elevated pressure and temperature conditions relevant to ore-formation.

The following papers have been published based on the work supported in this grant:

J. R. Black, E. D. Young, A. Kavner, (2010) Electrochemically Controlled Iron Isotope Fractionation, Geochimica et Cosmochimica Acta, vol. 74, pp. 809-817.

J. R. Black, S. John, E.D. Young, A. Kavner, (2010) Effect of temperature and mass-transport on transition metal isotope fractionation during electroplating, *Geochim. Cosmochim. Acta*, 74 5187.

J. R. Black, J. Crawford**, S. John, and A. Kavner, (2011) Redox-driven stable isotope fractionation, in Aquatic Redox Chemistry ACS Symposium Series, Vol. 1071. Tratnyek, P.G., T. J. Grundl, and S. B. Haderlein, eds. Chapter 16, pp 345–359

J. R. Black, A. Kavner, and E. Schauble (2011) Calculation of equilibrium stable isotope partition functions for aqueous zinc complexes and metallic zinc, Geochim. Cosmochim. Acta vol 75(3) 1 February 2011, Pages 769-783 *doi:10.1016/j.gca.2010.11.019*

J. Zhang, V. Prakapenka, A. Kubo, A. Kavner, H. W. Green and L. Dobrzhinetskaya (2011) Diamond formation from amorphous carbon and graphite in presence of COH fluids: an in situ high pressure and temperature laser-heated diamond anvil cell experimental study, in Ultrahigh-Pressure Metamorphism, Dobrzhinetskaya et al., ed. Elsevier isbn 978-0-12-385144-4

J. D. Hunt, A. Kavner, E. Schauble, D. Snyder, C. E. Manning, (2011) Speciation and polymerization of aqueous silica in H_2O-KOH solutions at 25 °C, 1 bar, from Raman spectroscopy and ab initio calculations, Chem Geo, vol. 283, pp. 161-170

J. R. Black, S. G. John, A. Kavner, (2014), Coupled effects of temperature and mass transport on the isotope fractionation of zinc during electroplating, *Geochim. Cosmochim. Acta*, **124**, pp..8.

Conference presentations in 2013-2104

Kavner, A. Invited keynote speaker, Center for Electrochemistry Conference, February 2013, University of Texas, Austin

Kavner, A., S. John., J. R. Black, Predictive Framework and Experimental Tests of the Kinetic Isotope Effect at Redox-Active Interfaces, Fall Meeting American Geophysical Union, 2013.

Watenphul, A., Scholten, L., Beermann, O., Kavner, A., Alraun, P., Falkenberg, G., Newville, M., Lanzirotti, A., Schmidt, C. Cu and Ni solubility in high-temperature aqueous fluids. Fall Meeting American Geophysical Union, 2013

Kavner Invited keynote speaker, "Isotope Electrochemistry" Gordon Conference on Electrochemistry, Jan 2014

Summary of Findings

   To examine stable isotope fractionations arising from redox-related processes, we have performed a series of laboratory electrochemistry experiments consisting of electroplating metal from an aqueous metal-salt reservoir. The general outline of these experiments is simple in concept: a small amount of metal from a variety of metal salt solutions is electroplated, and the precipitate analyzed. These experiments have been performed under a variety of different conditions and with various metals, including iron (Kavner et al., 2005; 2009; Black et al., 2010a; Black et al., 2010b;), zinc (Black et al., 2010a; Kavner et al., 2008), copper (Black et al., 2011a) and lithium (Black et al., 2009). For all of these systems, the isotope fractionation factors between the electroplated metal and the stock solution show similar and sometimes surprising trends. Below we summarize our observations and preliminary interpretations.
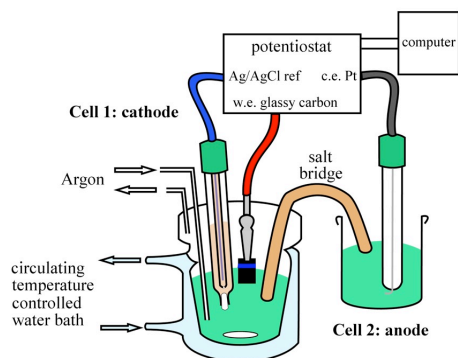

Figure 1: Schematic of electrochemical setup. Figure shows a dual cell setup separated via a salt bridge. Current and voltage are simultaneously controlled by an AutoLab Potentiostat system. The experiments are temperature controlled, and the deposition is done on a rotating disc electrode to control mass transport during the electroplating process (Gregory and Riddiford, 1952).

- *Light isotopes are preferentially electroplated.* In all cases light stable isotopes of the metals are preferentially electroplated, in a mass-dependent manner.
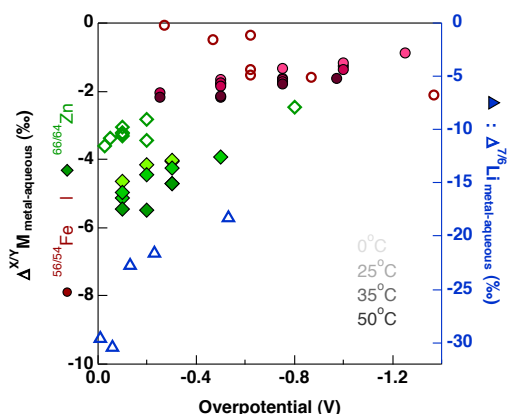

Figure 3. Summary of measured isotope fractionation as a function of overpotential for a series of electroplating experiments of iron, zinc, and lithium. Negative values indicate that in all cases, light isotopes are preferentially fractionated. Green diamonds are Zn isotopes; red circles are Fe experiments, and blue triangles are Li deposition experiments (right axis). Shading indicates temperature-dependent measurements; and open vs closed symbols indicate different solution chemistries for Zn and Fe.

- *Fractionation is dependent on rate/overpotential.* Generally, the observed fractionation decreases monotonically as the overpotential is increased, and increases with higher stir rate of the plating solution. In the experiments where a rotating disc electrode is used to control the supply of solution to the electrode, larger rotation rates generate larger fractionations.

- *Fractionation increases as temperature increases.* For experiments performed doing deposition on a planar electrode, the fractionation factor is larger at higher temperatures.

- *Fractionation is time-independent, meaning that the fractionation factor does not vary with the extent of reaction.* In most of our experiments, we have controlled the extent of reaction such that only a small amount of metal is deposited from the stock solution, thus avoiding significant evolution of the reservoir composition. In such experiments, the observed isotope fractionation is constant as a function of time (amount electroplated), as long as the electroplating rate and other factors are held constant. In the one case where we continuously electroplated zinc while monitoring the isotopic evolution of the plated material and the remaining stock solution (Kavner et al. 2008), the data could be fit within error by assuming a Rayleigh distillation of the reservoir and using a constant isotope fractionation factor equal to the isotope effect observed at low extents of reaction. In our first study of Zn electrodeposition (Kavner, 2008), we showed that the Rayleigh-style evolution reaction in which a large fraction of the reservoir of Zn ions are electroplated yields the same fractionation factor as the experiment in which only a small amount is electroplated.

- *Fractionation does not depend on electrode composition.* In cases where experiments were performed on different electrodes (i.e. gold vs. platinum vs. glassy carbon) but under similar chemistry and potentials, variables, isotope signature of the plated material were unchanged.

- *Maximum observed fractionations occur at the lowest applied overpotentials, and yet are generally higher than predicted equilibrium fractionations.* Our observed fractionation factors vary depending on experimental conditions as listed above, but the fractionation factors that arise from the slowest kinetic conditions are the largest, larger than the predicted equilibrium fractionation factors for all elements with the exception of Li where the maximum fractionation is approximately equal to the predicted equilibrium value (Black et al., 2009).
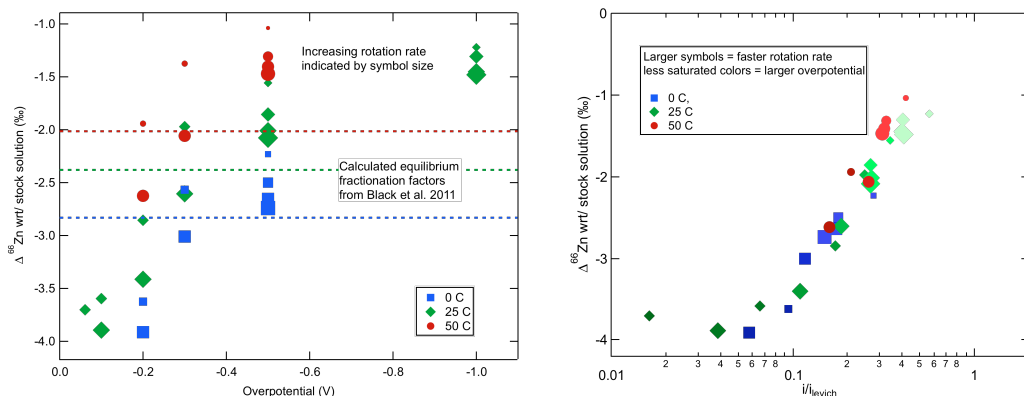
Figure 4 left: Measured $D^{66/64}Zn$ of metallic zinc, with respect to the stock solution, as a function of overpotential, rotation rate (increasing symbol size with increasing rotation rate), and temperature. Horizontal dashed lines show calculated equilibrium fractionation factors from Black et al. 2011b. Figure 5 right: Zn fractionation plotted as a function of experimental current normalized to mass-transport limited current.

Taken together, these observations suggest that there is a large kinetic isotope effect corresponding to the electro-reduction process. In addition, at least two competing processes determine the overall observed isotope fractionation of metals during electroplating. In Black et al. (2010a) and in our paper in review on Zn deposition, a competition between mass-transport and electrochemical kinetics is invoked to explain the observed fractionation that increases with temperature. Thus, our observed large isotope fractionations and their dependence on electrochemical rate is interpreted as a competition between at least two kinetic processes with different effective activation energies: a mass-transport-limited (diffusion driven) kinetics with a large activation energy and therefore temperature dependence, and which creates small fractionations close to the predicted diffusive fractionation; and electrochemical deposition kinetics, with a smaller effective activation energy, which results in very large fractionations at low deposition rates and high hydrodynamic fluxes of solute to the electrode.

Our previously supported work was successful in its two primary goals: we established that electrochemical processes create anomalously large isotope fractionations, and proved that mass transport not only is not the cause of the observed fractionations, but actually attenuates the electrochemical isotope effect. Our results strongly suggest that the observed large isotope fractionations arise from one or more processes that are occurring very close to the reacting interface. The implications are that stable isotopes are especially sensitive to the kinetic details of an electrochemically active interface. The broad goals of this research program are to continue the development of an isotope-sensitive indicator of surface reactions, using electrochemistry as a testbed. In this proposal, we build on our existing results and theoretical framework to develop an isotope-microscope sensitive to reacting electrochemical interfaces. In fact, a new derivation of isotope behavior for simple redox processes suggests that a general kinetic isotope effect can be predicted from a simple kinetic framework. Measuring the kinetic isotope effect for different reacting systems therefore provides a window into the chemical potentials of the reactants and products in a reacting system, and also a microscopic view of the reaction kinetics at the interface.

C. Project summary—Cu and Ni solubility at high pressures and temperatures (Dr. A. Watenphul, A. Kavner et al. MS in preparation)

During the last year of this funding, a postdoctoral fellow Anke Watenphul was supported to determine in-situ solubilities of Cu and Ni sulfides at high pressure, temperatures, and fluid compositions relevant for Cu-Ni hydrothermal mobilization and ore deposit formation. Copper and nickel sulfide ore deposits are the most important primary sources for these metals. They are geochemically similar elements and are often associated in various geological settings. However, whereas there are huge porphyry-type hydrothermal Cu deposits, no Ni deposits of this type exist in nature. Experiments on the solubility behavior of Cu and Ni will hel to understand the differences, which have to take place at the fluid-solid interface, where the aqueous complexes are formed.

Different sets of hydrothermal diamond-anvil cell experiments at 500 and 600 °C, pressures up to 900 MPa, and aqueous NaCl solutions of various concentration and pH were carried out at the Advanced Photon Source at Argonne National Laboratory and at Petra II at DESY. The dissolved Cu and Ni concentrations were determined by confocal μ-X-ray fluorescence spectroscopy.
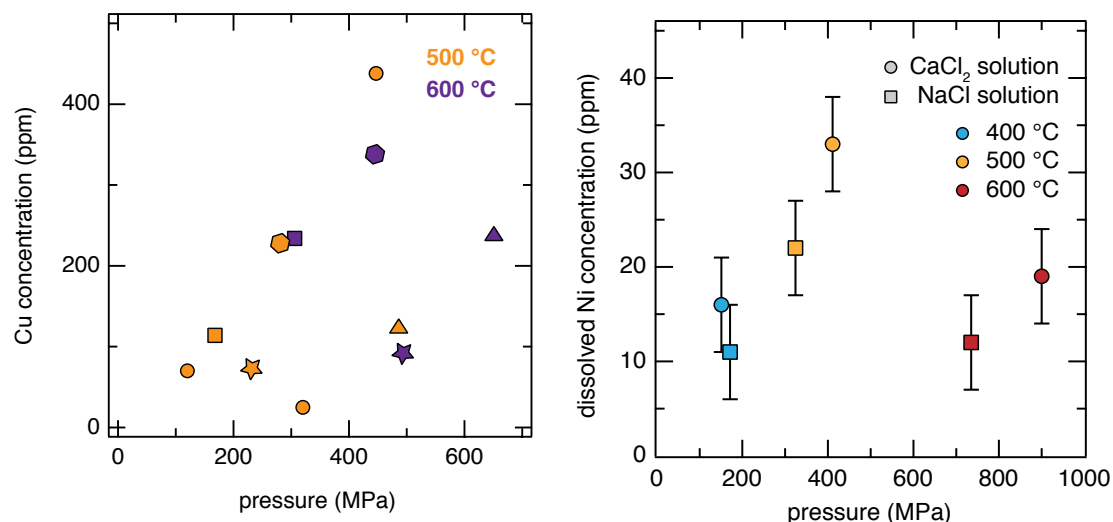

Figure 2 Left: *Dissolved Cu concentration as a function of pressure. Temperature is given by the symbol color. Same symbols refer to isochoric experiments.* ***Right****: Dissolved Ni concentration as a function of pressure. Temperature is given by the symbol color. Circles refer to CaCl$_2$ solutions as solvent, squares to NaCl solutions.*

Figure 1 and 2 summarized the data obtained so far. Very clear trends can be observed for the Cu solubility. The dissolved Cu concentration increases with increasing temperature and decreases with increasing pressure. The influence of the solvent composition, i.e. the pH of the solvent, needs further investigation. The Ni solubility has a solubility maximum around temperature with solubility increasing up to that temperature and at higher values decreasing again. At constant temperature, an increase with pressure can be observed. The composition of the solvent plays an important role on Ni solubility. So far, 2 compositions, aqueous NaCl and CaCl$_2$ solutions, were used. Significantly higher dissolved Ni concentrations were observed within the CaCl$_2$ solution pointing to the importance of the Cl$^-$ concentration of the fluid and possibly to metal–chlorine as major aqueous species.