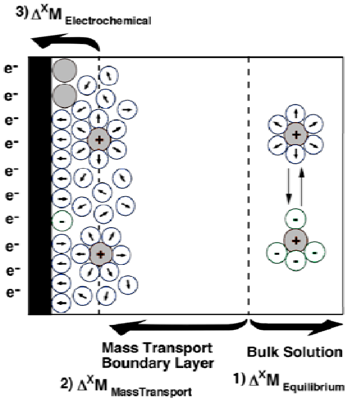
Transition metal stable isotope fractionation at a redox interface

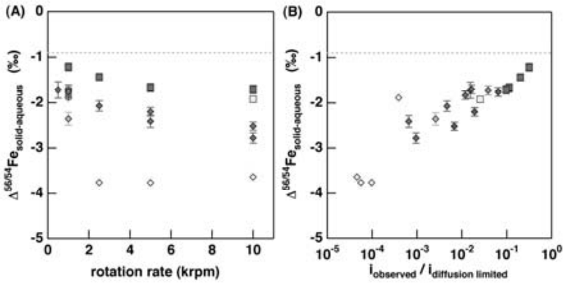
A. KAVNER, J. BLACK AND E. YOUNG

Earth & Space Science Dept. and Institute for Geophysics and Planetary Physics, UCLA, Los Angeles, CA 90095
(*correspondence: akavner@ucla.edu)

Stable isotopes are important markers for oxidation-reduction (redox) electrochemical reactions in natural systems [1]. Since redox often occurs at a solid/aqueous boundary, stable isotope fractionation may be sensitive markers for processes that occur at interfaces, such as mass transport, chemical speciation changes, and redox processes (Fig. 1). Here, we use observations of iron isotope fractionation at an electrode under controlled-kinetic conditions using a rotating disc electrode to interrogate how stable isotopes provide information about reactions at a solid/liquid interface.



High-resolution analysis of the stable isotopes of electrodeposited iron shows that light isotopes are preferentially electroplated, with increasing fractionation as a function of rotation rate (Fig 1). Our results are interpreted in terms of competing processes at the electrode: a small fractionation due to mass transport, and a larger fractionation due to electron transfer [2].



[1] Anbar (2007) *Ann. Rev. EPS* **35**, 717. [2] Kavner *et al.* (2005) *GCA* **69**, 2971

Supersaturated molecular hydrogen in coastal surface water at Otsuchi Bay, Japan

SHINSUKE KAWAGUCCI, TAKU NARITA, HAJIME OBATA, HIDEKI FUKUDA AND TOSHITAKA GAMO

Ocean Research Institute, the University of Tokyo
(kawagucci@ori.u-tokyo.ac.jp)

Molecular hydrogen (H_2) in the atmosphere is recoganized as an indirect green house gas because of its influence for the concentrations of tropospheric methane and stratospheric water vapor. Atmospheric budget has been globally estimated [1], but the role of the ocean on the H_2 budget remains poorly understood. To better understand H_2 behavior in seawater, we investigated dissolved H_2 concentrations in coastal water at Otsuchi Bay, north-eastern Japan.

Surface water sampligs and several vertical casts with a CTD-Niskin sampler were carried out at Otsuchi Bay in May and October 2008. Additionally, incubation experiments were also conducted to estimate consumption rate constants in seawater. H_2 concentrations were determined within 5% error by a newly developed head space method with a gas chromatograph and a mercuric oxide reduction detector.

H_2 concentrations in surface water were higher than atmospheric equilibrium value (supersaturated) throughout the Otsuchi Bay. Noteworthy several samples obtained from estuary region showed higher H_2 concentrations than 20 nM which are the highest values so far observed in seawater [2]. On the other hand, H_2 in deep seawaters were undersaturated. These results imply strong H_2 sources to surface water, especially near estuary. Supplied H_2 in seawater was probablly consumed microbially within the water column. The H_2 consumption rate constants were estimated by the incubation experiments using the collected seawater samples. The consumption rate constants obtained in this study ranged within those previously determined in other regions [3]. The dataset indicates possibl larger fluxes of molcular hydrogen from the coastal seawater to the atmosphere than those estimated at the present.

[1] Novelli *et al.* (1999), *JGR*, **104**, 30427-30444. [2] Sester *et al.* (1982), *DSR*, **29**, 1203-1215.[3] Punshon *et al.* (2007), *Mar. Chem.*, **105**, 129-139.