Electronic structures of transition metal oxides and sulfides: Applications to the physics and chemistry of the Earth

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A variety of geochemical and geophysical processes result from electronic transitions in minerals and aqueous complexes. In aquatic environments, photochemical excitations on mineral surfaces release dissolved micronutrients and may have played a role in prebiotic synthesis. In the deep Earth, pressure-induced electronic transitions such as spin-pairing, metallization and changes in the band gap/Fermi energies of phases affect the density, transport properties and element partitioning in the core and mantle.

Density functional theory, using approximate exchange-correlation functionals, has enabled us to accurately predict structures and vibrational energies of minerals and aqueous complexes. We can now predict the thermodynamics, phase transitions and seismic properties of minerals in the deep earth and even the thermodynamics of metal complexation in hydrothermal solutions. However, exchange-correlation functionals such as the generalized gradient approximation (GGA) are still based on the local density approximation. Consequently, these functionals still contain an error associated with incorrectly including the electron self-interaction. The self-interaction error yields incorrect electronic structures and band gaps and precludes accurate predictions of electronic transition energies. For the case of a material like FeO, standard GGA functionals incorrectly yield a metallic ground state that becomes Pauli-paramagnetic (rather than a diamagnetic low-spin state) with pressure. Charge-transfer band gaps in Fe_2O_3 are too low. Physicists have addressed this problem using the "Hubbard U" correction to the local density approximation. However the U parameter is an empirical correction. Chemists, however, have recognized that the Hartree-Fock formalism exactly includes the self-interaction correction. A variety of "hybrid" exchange functionals have been developed (e.g., B3LYP) that empirically mix Hartree-Fock exchange with the GGA exchange-correlation functional. Here, I will present several examples to illustrate the application of these functionals to transition metal oxides and sulfides and show how the hybrid functionals predict electronic transitions of importance in geochemistry and geophysics.

Reduced gas flux from Precambrian cratons – Implications for subsurface microbiology

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Quantification of global H_2 flux has to date been based primarily on thermodynamic and geochemical modelling, or on H_2 measurements at a number of marine systems such as the Rainbow and Logatchev hydrothermal vents, the off-axis Lost City field, and more recently, at diffuse vents. H_2 sources from continental systems are significantly less well constrained. Recent exploration of saline fracture waters more than a km below the Earth's surface in Precambrian continental crust however has identified environments equally as H_2-rich as the hydrothermal vents and spreading centers, and sustaining microbial communities of H_2-utilizing methanogens and sulfate reducers [1]. Here we report on results from > 30 sites and > 250 samples and boreholes in continental Precambrian sites worldwide. Fracture waters accessed via mines and underground research laboratories contain mM concentrations of reduced gases (H_2, CH_4, ethane, propane, butane) as well as high concentrations of noble gases.

First identified in Ne isotope results from the Witwatersrand basin in South Africa [2], novel radiogenic isotope signatures have now been shown to be a consistent feature of these deep waters [3]. Integration of the noble gas signatures with compositional and isotopic information for the reduced gases provide constraints on the residence time of the fracture waters, the degree of interconnectivity of different groundwater systems, and an estimate of the amount of time these waters have been isolated from the surface. This presentation will address the distribution of ancient fluids at selected key reference sites; and the controls of this deep hydrosphere on the biodiversity and distribution of the subsurface microbial biosphere and carbon cycle.

[1] Lin *et al*. (2006) *Science* **314**, 479-482. [2] Lippmann-Pipke *et al*. (2011) *Chem. Geol.* **283**, 287-296. [3] Holland *et al*., (2013) *Nature*, *in press*.

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