Water in the deep Earth carbon, nitrogen and sulfur cycles

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Fluids such as those in subduction zones are a key component of the long-term geochemical cycles of the elements. Indeed, the long-term habitability of Earth, and possibly a deep biosphere, depends on these fluids. Yet remarkably little is known about them. Experimental and theoretical studies of mineral solubility and aqueous speciation [1] [2], and fluid inclusions in ultrahigh pressure rocks and diamonds [3], indicate that these fluids are much more complex than previously thought. Traditional models of CHON fluids [4] are completely inadequate. Real fluids in the upper mantle exist in a silicate environment and contain large amounts of dissolved silica, neutral species, ions, and metal complexes in various degrees of polymerization [2] [5]. A more comprehensive approach to fluid speciation in the upper mantle is needed.

In order to model ions, HCl must be included as a chemical component in deep fluids. This increases the variance of even a simple system such as diamond + fluid. It enables consideration of reactions involving scores of aqueous ions and metal complexes in upper mantle fluids. In turn these ionic species couple the model fluid chemistry to its silicate rock environment. Here the new Deep Earth Water (DEW) model [6] was used to calculate equilibrium constants for incorporation in data files for aqueous speciation and chemical mass transfer calculations that model fluid-rock interactions in subduction zones. Predictions include the following [7]: the disappearance of metastable equilibrium in aqueous C-species above about 3.0 GPa leading to complete chemical equilibrium between aqueous inorganic (bicarbonate and carbonate) and organic C-species (e.g. formate, acetate, and propionate); the variable speciation of N in deep fluids ensuring efficient degassing of N from subduction zones on Earth; highly variable S/C ratios as a function of temperature in subduction zone fluids leading to variation in the relative importance of these elements in the oxidation of the mantle wedges; and precipitation of diamond or graphite by pH drop at constant redox conditions.

[1] Facq et al. (2014) *GCA*, **132**, 375-390; [2] Kessel *et al.* (2005), *EPSL* **237**(**3**); 873-892; Dvir *et al.* (2011), *Contrib. Mineral Petrol.* **161**(**6**): 829-844;; [3] Frezzotti et al. (2011), *Nature Geo.*, **4**, 703-706; [4] Zhang & Duan (2009), *GCA* **73**, 2089-2102. [5] Manning et al. (2010), *EPSL* **292**, 325-336. [6] Sverjensky et al. (2014) *GCA*, **129**, 125-145; [7] Sverjensky et al., *Nature Geo.*, **4**, 703-706; Mikhail and Sverjensky, *Nature Geo.*, **7**, 816-819;