New activity coefficients & standard state properties for CO$_2$ in aqueous fluids in the Extended Deep Earth Water (DEW) model

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$$\log \gamma_{CO2,Hm}(\text{calc.}) =$$
$$(2.80)(1/\varepsilon_{mix} - 1/\varepsilon_{H2O}) - 1.79[m_{CO2}/(55.51 + m_{CO2})] - \Gamma_\gamma$$

Decades of study of COH-bearing metamorphic and deep Earth fluids have demonstrated strong non-ideality of aqueous CO2 supported by a wealth of experimental and theoretical studies [1]. However, aqueous geochemical modeling has generally assumed ideality of aqueous CO2 owing to an extreme paucity of information about non-ideality in traditional geochemical models. The fundamental difference between the two approaches arises from the adoption of two different standard states for aqueous CO2. The COH fluid model uses a Raoultian, pure CO2 fluid standard state, but geochemical models most commonly use the Henryian, hypothetical 1.0 m standard state. The latter is adequate at low CO2 molalities. But at upper mantle conditions, where high solubilities of graphite occur [2], the assumption of ideality for CO2 is inadequate.

Here we show how a key experimental study of Raoultian non-ideality in the CO2-H2O system [3] can be translated into the aqueous geochemical standard state. The activity coefficients were used to calibrate a new equation of state inspired by the theoretical treatment of neutral aqueous species [4]. The new equation takes account of the solvation dependence of CO2 by H2O ([5], [6]) in terms of the inverses of the dielectric constants of the mixed solvent and pure water, as well as CO2-H2O interactions, enabling description of activity coefficients on a molality scale up to almost pure CO2 in geochemical models (Fig. 1). Together with a revised equation of state for the standard state free energy of aqueous CO2, the solubilities of graphite and diamond can be predicted much more accurately than previously.

The above results have been incorporated into a revised version of the aqueous speciation-solubility code EQ3 termed pyDEW (Matthews et al., this conference) enabling modeling of fluid-rock equilibria with CO2-bearing fluids in the deep Earth.

[1] Zhang and Duan (2009). *Geochimica et Cosmochimica Acta* 73, 2089-2102.

[2] Tumiati et al. (2017). *Nature commun*ications 8, 616.

[3] Aranovich and Newton (1999). *American Mineralogist* 84, 1319-1332.

[4] Helgeson et al. (1981). *American Journal of Science* 281, 1241-1516.

[5] Dandurand and Schott (1987). *Journal of Solution Chemistry* 16, 237-256.

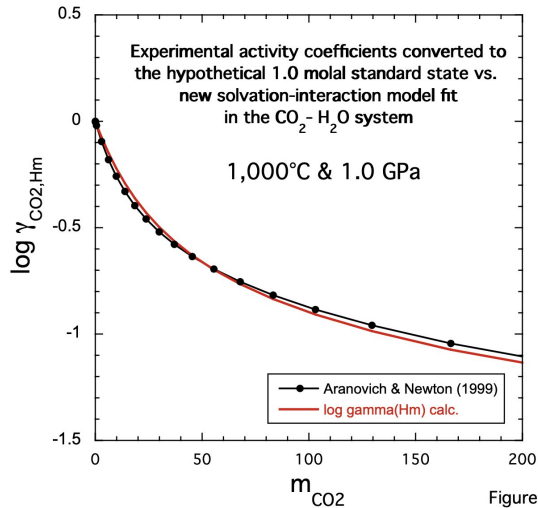[6] Walther and Schott (1988). *Nature* 332, 635-638.