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Advances towards incorporating complex speciated fluids into Gibbs energy minimization calculations

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Throughout Earth's upper mantle and crust aqueous fluids are important agents of mass transfer, potentially carrying high solute loads of the rock-forming elements [1]. The Deep Earth Water (DEW) model is a thermodynamic model for speciated fluids under these conditions, and has been widely applied to understanding the chemistry of subduction zone fluids [2], the formation of diamonds [3], and (following recent model developments) the compositions of magmatic brines [4]. However, application of the DEW model is currently limited by its software implementation. The EQ3/6 software [5] is the tool used most often for DEW calculations, but running a calculation is cumbersome, the calculations generally assume open system behavior for H and O, and there is limited scope for calculating equilibrium with non-ideal solid solution phases or magmas. Many of these limitations were addressed in the lagged-speciation algorithm developed by [6]; however, this algorithm requires every component in the fluid to be present in the solid assemblage, an assumption that may be violated for dilute fluids or elements important for aqueous complexes (e.g., Cl, F, and S).

The ENKI ThermoEngine Equilibrate algorithm [7] is a generic Gibbs free energy minimisation routine, requiring only that each phase in the system has a readily evaluated Gibbs free energy surface (i.e., its value and first, second, and third order derivatives with respect to composition). In this contribution we develop a numerical approach for evaluating the Gibbs Free Energy surface of a speciated fluid (of fixed bulk composition), and thus bring the DEW model into the ENKI ecosystem as a completely generalized complex solution phase. The new developments permit mass constrained equilibrium calculations of systems containing a DEW fluid.The flexibility of the ThermoEngine framework permits rapid extension and calibration of the DEW model, as well as novel applications of fluid speciation calculations.

[1] Manning & Frezzotti (2020), Elements 16, 395-400.
[2] Debret & Sverjensky (2017), Sci. Rep. 7(1), 10351.
[3] Mikhail et al. (2021), GPL 17, 33-38.
[4] Ghiorso et al. (2023), Goldschmidt.
[5] Wolery (1992)
[6] Connolly & Galvez (2018), EPSL 501, 90-102.
[7] ENKI ThermoEngine doi:10.5281/zenodo.6527840