Improved thermodynamic model calibration with Bayesian methods

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Computational thermodynamics (CT) underlies many models used to interrogate equilibria in the deep Earth. Ideally, users should be able to create custom CT models within an internally consistent framework [1]. In the shorter term, development of 'base' models, like xMELTS [2], needs a flexible calibration scheme that accommodates new data as they become available, automatically assesses measurement quality, and handles interlaboratory calibration differences. In [3] we used a Bayesian approach to develop a molar volume model for $(Ca,Fe,Mg,Mn)_3(Al,Cr,Fe^{3+})_2Si_3O_{12}$ cubic garnets. Here we add three majorite-related end members, and extend the calibration scheme to use robust fitting.

The volume model calibration is broken into two main stages: (1) estimation of end-member thermodynamic properties from volumes, heat capacities, ultrasonic sound speeds, *ab initio* equations of state and/or cation size systematics; (2) fitting of standard state volumes (V_o) and excess volume parameters (W_{ij}) to binary and mixed composition volume data. Observational uncertainties are determined empirically using intrinsic scatter in the data, which removes dependence on reported uncertainties (and provides preliminary estimates for the V_o and W_{ij}), or data weights are adjusted based on factors like starting material type and compositional analysis method. The fitting cost function incorporates weighted model residuals, allowance for outliers, and model parameter priors. Uncertainties and correlations are propagated through each calibration step.

Best-fit W_{ij} are generally small and similar to published values. A few of the W_{ij} are large and positive, but well constrained. The model compares well with an earlier version obtained by singular value analysis and manual filtering of the data ([4] and unpubl. work). The new scheme reduces the overhead for creating physically reasonable solution models from mixed data sources, provides realistic model uncertainty estimates, and allows for rapid assimilation of new data or constraints, including experimental phase equilibria.

[1] Ghiorso (2014), V21C-02, AGU FM14 [2] Ghiorso *et al*. (2007), V31C-0608, AGU FM07 [3] Antoshechkina *et al*. (2013), V13A-2584, AGU FM13. [4] Hamecher *et al*. (2012), V53A-2795, AGU FM12