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Electrolytic fluid speciation by Gibbs energy minimization and implications for subduction zone mass transfer

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ABSTRACT

The number of solute species required to describe the thermodynamic behavior of electrolytic fluids is a hindrance to the incorporation of aqueous geochemistry in petrological Gibbs energy minimization procedures. An algorithm is developed to overcome this problem. Beginning from the solute-free limit, chemical potentials, and phase stability are determined by minimization, the solute speciation and bulk fluid properties consistent with these chemical potentials are then computed and the procedure repeated until the chemical potentials converge. Application of the algorithm to a model for metamorphism of subducted sediment shows that accounting for solute chemistry does not change the conclusion based on molecular fluid models that a pervasive water flux from the subjacent mantle is required to explain island-arc carbon emissions by fluid-mediated slab decarbonation. This putative flux would deplete the sediment in potassium, limiting the capacity of the slab to transport water to greater depth and rendering it refractory to melting.

1. Introduction

Gibbs energy minimization is applied to a broad spectrum of geochemical and petrological problems (Leal et al., 2017). In geochemistry the focus of these applications is usually reactive transport (Wolery, 1992; Bethke, 1996), whereas in petrology the focus is predicting phase stability (DeCapitani and Brown, 1987; Connolly, 2009). This disparity has led to a situation in which many geochemical codes account for complex fluid chemistry, but seek only a local equilibrium solution, whereas petrologic codes seek a costly global solution that limits their ability to treat the complex fluid chemistry. As a means of bridging this gap Galvez et al. (2015, 2016) use phase equilibria computed by Gibbs energy minimization assuming a solute-free fluid to back-calculate solute chemistry. This method accurately estimates solute chemistry provided the solute mass is small compared to the total mass of the system, but is not well suited for reactive transport problems because the phase proportions and bulk fluid chemistry are not rigorously determined. The present work improves on this method by incorporating back-calculated fluid chemistry in an iterative Gibbs energy minimization procedure referred to here as lagged speciation. It should be remarked that there are completely robust geochemical codes (Harvie et al., 1987; Karpov et al., 2001), which, at least in principle, are capable of treating petrological models.

The utility of the lagged speciation algorithm is demonstrated by a model for devolatilization of subduction zone sediments. This problem has been made tractable by the Deep Earth Water (DEW) model for electrolytic fluids (Sverjensky et al., 2014), which extends the Helgeson–Kirkham–Flowers (HKF) formulation (Shock et al., 1992) for aqueous species to high pressure conditions. Although a number of studies have considered the implications of the DEW model for fluid-dominated subduction zone chemistry (Facq et al., 2014; Sverjensky and Huang, 2015; Tumiati et al., 2017), the present focus is the rock-dominated limit appropriate in systems where the fluid is generated by devolatilization. This limit was investigated by Galvez et al. (2015) using a variant of the DEW model. The distinction between the DEW model and the Galvez et al. (2015) variant, is that in the DEW model the solvent is H_2O and molecular volatiles are treated as solute species, whereas in Galvez et al. (2015) the solvent is a mixture of molecular volatiles. Both approaches are compared.

Subduction zone devolatilization is topical because of its potential role in various global element cycles. The observation, based on simple sub-solidus phase equilibrium models (Kerrick and Connolly, 2001a, 2001b) that carbonates persist within subducted slabs beyond sub-arc depth has motivated alternative hypotheses to explain extensive slab decarbonation. These hypotheses include:

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infiltration-driven decarbonation (Connolly, 2005; Gorman et al., 2006); C transfer by entrainment or diapirism (Dasgupta et al., 2004; Behn et al., 2011); slab-melting (Poli, 2015; Skora et al., 2015); or near-surface provenance of volcanic CO_2 (Mason et al., 2017). With the exception of the latter, all of these mechanisms are viable but unsatisfying in that they require a coincidence of processes or extreme temperatures. Evidence of sub-solidus carbonate dissolution (Frezzotti et al., 2011; Ague and Nicolescu, 2014) has prompted the suggestion that, by neglecting the solubility of non-volatile elements, early models underestimated the efficacy of simple decarbonation processes. Previous work (Kelemen and Manning, 2015) indicates dissolution may cause a two-fold increase in the carbon-content of subduction zone fluids, but does not address fluid production. The models here extend that work by tracking fluid evolution from the surface to beyond sub-arc depths.

This paper begins with a generalization of the back-calculation method (Galvez et al., 2015). The lagged speciation algorithm by which back-calculated results may be integrated into a Gibbs energy minimization procedure is then outlined and the limitations of the algorithm are explained. The final major section uses the subduction zone model to illustrate some technicalities of the method and to explore the consequences of solute chemistry on closed, open, and infiltration-driven devolatilization scenarios.

2. Back-calculated speciation

The term back-calculated speciation designates the calculation of the solute speciation of an electrolytic fluid under the assumptions of charge balance, equilibrium, known solvent composition, and specified chemical potentials (Galvez et al., 2015). The method follows by observing that the partial molar Gibbs energy of any species can be expressed

$$g^i = -n^i_{e-}\mu_{e-} + \sum_{j=1}^{c} n^i_j \mu_j \tag{1}$$

where c is the number of components, μ_j and μ_{e-} are, respectively, the chemical potential of component j and the electron, and for species i: n^i_j is the molar amount of component j, and $-n^i_{e-}$ is the molar charge, abbreviated hereafter q^i. Eq. (1) can be rearranged to express μ_{e-} in terms of the chemical potentials and the properties of charged species i

$$\mu_{e-} = \frac{1}{q^i}\left(g^i - \sum_{j=1}^{c} n^i_j \mu_j\right). \tag{2}$$

Because μ_{e-} is the same for all species at equilibrium, the partial molar Gibbs energy of any arbitrarily chosen charged species (g^i) can be related to the partial molar Gibbs energy of a charged reference species (g^k) by equating the right-hand-side of Eq. (2) for both species

$$\frac{1}{q^i}\left(g^i - \sum_{j=1}^{c} n^i_j \mu_j\right) = \frac{1}{q^k}\left(g^k - \sum_{j=1}^{c} n^k_j \mu_j\right). \tag{3}$$

Rearranging Eq. (3), the partial molar Gibbs energies of any charged species can then be expressed in terms of the reference species partial molar Gibbs energy and the chemical potentials of the system

$$g^i = \frac{q^i}{q^k}\left(g^k + \sum_{j=1}^{c} \mu_j \Delta n^i_j\right) \tag{4}$$

where $\Delta n^i_j = n^k_j - n^i_j$. In terms of a solute reference state activity model, the partial molar Gibbs energies in Eq. (4) are

$$g^i = g^{*,i} + RT\ln\left(m^i\gamma^i\right) \tag{5}$$

where $g^{*,i}$ is the solute reference state molar Gibbs energy, m^i is the molal concentration, γ^i is the activity coefficient, T is absolute temperature, and R is the universal gas constant. Applying Eq. (5) in Eq. (4) and rearranging the result

$$m^i = \frac{c^i}{\gamma^i}\left(m^k\gamma^k\right)^{q^i/q^k} \tag{6}$$

where

$$c^i = \exp\left(\frac{1}{RT}\left\{\frac{q^i}{q^k}\left[g^{*,k} + \sum_{j=1}^{c} \mu_j \Delta n^i_j\right] - g^{*,i}\right\}\right).$$

Substituting Eq. (6) into the charge balance constraint for a fluid with s charged solute species

$$\sum_{i=1}^{s} q^i\, m^i = 0 \tag{7}$$

yields

$$\sum_{i=1}^{s} \frac{q^i c^i}{\gamma^i}\left(m^k\gamma^k\right)^{q^i/q^k} = 0, \tag{8}$$

which can be solved in the ideal limit ($\gamma^i \rightarrow 1$) for m^k if the composition of the solvent, which influences $g^{*,i}$, is known. The concentrations of the remaining charged species are then obtained from Eq. (6) and those of neutral species from Eq. (5).

In the non-ideal case, additional assumptions are necessary to compute the activity coefficients in Eqs. (5), (6), and (8). Regardless of those assumptions, the method is flawed: if the solvent composition is consistent with the specified chemical potentials, as is the case when the chemical potentials and solvent composition are obtained by Gibbs energy minimization, then finite solute concentrations violate this consistency. This flaw has the consequence that, except in the limit of infinite dilution ($m^i \rightarrow 0$), there is no bulk fluid composition that simultaneously satisfies Eq. (8) and the constraint on the chemical potentials of the system, i.e., there is no thermodynamically robust relation between fluid speciation and bulk composition.

3. The lagged speciation algorithm

The limitation of simple back-calculated speciation is the absence of a relation between the calculated solute chemistry and the bulk chemistry of the fluid, which precludes evaluation of mass balance constraints. To circumvent this limitation, the present work exploits the iterative aspect of Gibbs energy minimization by successive linear programming (Connolly, 2009). The essential feature of successive linear programming is that an initial result in which the compositions of the phases are discretized at some specified resolution is iteratively refined until a desired target resolution has been achieved. The innovation here is to use a minor modification of the back-calculated speciation algorithm to estimate the Gibbs energy and composition of the stable fluid(s). In the initial optimization, the fluid may contain multiple solvent species (e.g., H_2O, CO_2, CH_4, H_2S), but is solute-free. Given the solute-free solvent composition(s) and chemical potentials obtained in this optimization, the reference state solute partial molar Gibbs energies are computed, Eq. (8) is solved for the concentration of the reference ion, and Eqs. (5) and (6) are solved for the concentrations of the remaining solute species. The solvent mole fractions are then recomputed as