



Invited review article

Combined thermodynamic–geochemical modeling in metamorphic geology: Boron as tracer of fluid–rock interaction



Matthias Konrad-Schmolke*, Ralf Halama

Institute of Earth and Environmental Science, University of Potsdam, Karl-Liebknecht-Str. 24-25, 14476 Potsdam, Germany

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ABSTRACT

Quantitative geochemical modeling is today applied in a variety of geological environments from the petrogenesis of igneous rocks to radioactive waste disposal. In addition, the development of thermodynamic databases and computer programs to calculate equilibrium phase diagrams has greatly advanced our ability to model geodynamic processes. Combined with experimental data on elemental partitioning and isotopic fractionation, thermodynamic forward modeling unfolds enormous capacities that are far from exhausted.

In metamorphic petrology the combination of thermodynamic and trace element forward modeling can be used to study and to quantify processes at spatial scales from μm to km. The thermodynamic forward models utilize Gibbs energy minimization to quantify mineralogical changes along a reaction path of a chemically open fluid/rock system. These results are combined with mass balanced trace element calculations to determine the trace element distribution between rock and melt/fluid during the metamorphic evolution. Thus, effects of mineral reactions, fluid–rock interaction and element transport in metamorphic rocks on the trace element and isotopic composition of minerals, rocks and percolating fluids or melts can be predicted.

Here we illustrate the capacities of combined thermodynamic–geochemical modeling based on two examples relevant to mass transfer during metamorphism. The first example focuses on fluid–rock interaction in and around a blueschist-facies shear zone in felsic gneisses, where fluid-induced mineral reactions and their effects on boron (B) concentrations and isotopic compositions in white mica are modeled. In the second example, fluid release from a subducted slab, the associated transport of B as well as variations in B concentrations and isotopic compositions in liberated fluids and residual rocks are modeled. We compare the modeled results of both examples to geochemical data of natural minerals and rocks and demonstrate that the combination of thermodynamic and geochemical models enables quantification of metamorphic processes and insights into element cycling that would have been unattainable if only one model approach was chosen.

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* Corresponding author at: University of Potsdam, Institute of Earth and Environmental Science, Karl-Liebknecht-Str. 24-25, 14476 Potsdam, Germany. Tel.: +49 331 977 5854; fax: +49 331 977 5700.

E-mail address: mkonrad@geo.uni-potsdam.de (M. Konrad-Schmolke).

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1. Introduction

In geosciences, field-based observations are fundamental for our interpretations of geological processes. Quantitative models, which should be based on these observations, are essential to predict the evolution of geological systems and the outcome of geological processes (Albarède, 1995). As many disciplines in geosciences are faced with the fact that their study target, such as processes in the deep Earth, is either completely inaccessible, or that spatial or temporal scales at which the processes of interest operate do not allow direct observation, numerical and analogue models have become an indispensable tool to study, quantify and predict processes in Earth and environmental sciences. The development of high resolution–high precision analytical techniques to determine chemical and isotopic compositions of rocks and minerals, an increasing number of experimental data and advances in computational resources enhance our ability to simulate Earth processes and to test the results of these models against field-based observations. As demonstrated by Goldschmidt (1954), physicochemical principles determine systematic compositional changes in rocks and minerals and are hence the key to understand geological processes. The combination of thermodynamic and geochemical forward modeling (e.g., Hebert et al., 2009; Kimura et al., 2009, 2010; Konrad-Schmolke et al., 2008b; Nagel et al., 2012) allows a more precise quantification of key geochemical parameters leading to an improved understanding of geodynamic mechanisms and enables to study and predict rates and kinematics of solid/fluid reactions.

1.1. Thermodynamic equilibrium forward modeling in geosciences

Predicting phase and chemical equilibria extremely important in many industrial applications, such as gas distillation, cement production and the development of functional materials. Therefore, methods of calculation of phase diagrams (CALPHAD) have been successfully developed and constantly improved. Thermodynamic modeling is nowadays more frequently applied to geoscientific problems, although its application is far more complex than most approaches in material sciences. Challenges in geosciences arise from the fact that most geoscientific questions involve thermodynamic treatment of complex solid solution phases in multiphase systems, interaction of liquid and solid phases and consideration of open system behavior. The application of thermodynamic calculations to geoscientific problems became viable with the compilation of extensive datasets for thermodynamic standard state properties (e.g. Berman, 1988; Gottschalk, 1997; Helgeson et al., 1978; Holland and Powell, 1998; Robie and Hemingway, 1995), reliable equations of state for geologically relevant phases and conditions (e.g., Berman, 1988; Holland and Powell, 2011; Kerrick and Jacobs, 1981; Stixrude and Lithgow-Bertelloni, 2005) and solid solution formulations for phases of geoscientific interest (e.g., Berman, 1990; Holland and Blundy, 1994; Holland and Powell, 2003; Margules, 1895; van Laar, 1910). Regarding the interpretation of thermodynamic calculations it is noteworthy that although many of the data incorporated in the available databases are based on experiments or have been numerically determined and are internally consistent, raw experimental data on standard state thermodynamic phase properties are still sparse and incomplete. The limited amount of experimental data together with an inappropriate use of thermodynamic variables (e.g., $\mu_{\text{H}_2\text{O}}$ (chemical potential of water) vs. $n_{\text{H}_2\text{O}}$ (amount of water)) can result in significant

misinterpretations of modeled thermodynamic equilibria in geosciences (Essene, 1989; Powell et al., 2005). Therefore, it is of utmost importance that the formulation of the problem to be solved using thermodynamic modeling complies with limitations induced by the uncertainties implicit in the thermodynamic data and that the thermodynamic variables used to extract information from such models are carefully chosen.

In general, two different thermodynamic calculation approaches can be used to determine thermodynamic equilibria ($\Delta G_{\text{R}} = 0$) among fluid and solid phase assemblages:

1) Solving the equilibrium constant (K)

$$0 = \Delta\mu_0 + RT \ln K$$

where R = gas constant (in $\text{J K}^{-1} \text{mol}^{-1}$), T = temperature (in K) and $\Delta\mu_0 = \sum_{i=1}^m v_i \mu_i^0$ = free energy change for the reaction for the species in the standard state with μ_i^0 = standard state molar chemical potential of species i and v_i = stoichiometric coefficient of species i in the reaction. The equilibrium constant is defined as

$$K = \prod_{i=1}^m (a_i^{v_i})$$

where a_i = activity of species i .

2) Global Gibbs energy minimization

$$\text{minimize } G = \sum_{i=1}^m n_i \mu_i$$

where n_i = molar amount of component i and μ_i = molar chemical potential of the i th component.

Both approaches require knowledge about the Gibbs free energy of pure phases and a mathematical formulation of the relation between composition and activity/chemical potential in solution phases. Consequently, they both rely on thermodynamic data sets, which contain the standard state thermodynamic parameters and equations of state (EOS) for minerals, fluids and gases together with solution model formulations. The approach of solving the equilibrium constant furthermore requires that the phases among which the thermodynamic equilibria are calculated are pre-defined. This approach is widely utilized in aquatic geochemistry because the equilibrium constants of many aqueous reactions can be readily obtained from experiments (see Oelkers et al., 2009, and references therein). Several commercial and open source computer programs, such as PHREEQC (Parkhurst and Appelo, 1999), SUPCRT92 (Johnson et al., 1992) and THERMOCALC (Powell and Holland, 1988), are available for this purpose.

In metamorphic petrology, element fractionation processes, e.g. fractional crystallization (e.g., Konrad-Schmolke et al., 2007, 2008a; Marmo et al., 2002; Spear, 1988), water liberation (e.g., Dragovic et al., 2012; Hacker, 2008) and reactive fluid flow (e.g., Beinlich et al., 2010; Ferry and Gerdes, 1998) require thermodynamic modeling of chemically open systems (e.g., Korzhinskii, 1965). In such open systems, coexisting phases cannot be predicted a priori – a prerequisite of the equilibrium constant approach – because they are a function of the pressure (P), temperature (T) and chemical (X) evolution of the rock. Therefore, the approach of global Gibbs energy minimization is preferable

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