HighPGibbs, a Practical Tool for Fluid-Rock Thermodynamic Simulation in Deep Earth and Its Application on Calculating Nitrogen Speciation in Subduction Zone Fluids

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Abstract

The HighPGibbs program is designed to calculate thermodynamic equilibrium of fluid-rock minerals and solid solutions up to depths of lithospheric mantle. It uses the Gibbs free energy minimization function of the HCh package to calculate mineral-fluid equilibrium assemblages. Chemical potentials of minerals are calculated using the equations of states included in HCh; free energy of aqueous species are calculated using the Deep Earth Water model; and activity coefficients of charged species are estimated using the Davies variant of the Debye-Hückel equation. HighPGibbs was applied to calculate nitrogen speciation in eclogite-buffered fluids from 400 to 790 °C and 30 to 54 kbar, to evaluate the mobility of nitrogen in subducting oceanic crust. Regardless of whether the protolith was altered (and oxidized) or not, N(aq) or NH(aq) are the predominant form of nitrogen in the slab-fluids at sub-arc temperatures, especially in cases of moderate or hot geotherms. Given that molecular nitrogen is highly incompatible in silicate minerals, the simulation indicates that nitrogen (as NH) in silicate minerals can be liberated during metamorphic devolatilization. The majority of nitrogen in subducting crusts can be unlocked during slab devolatilization and eventually expelled to the atmosphere via degassing of arc magmas. Therefore, oceanic crusts recycled to deep earth will be depleted in nitrogen compared to the newly formed crust at spreading centers. As a result of the long-term mantle convection, large proportions of the bulk silicate earth may have suffered nitrogen extraction via subduction, and this may account for the nitrogen enrichment in the Earth's atmosphere.

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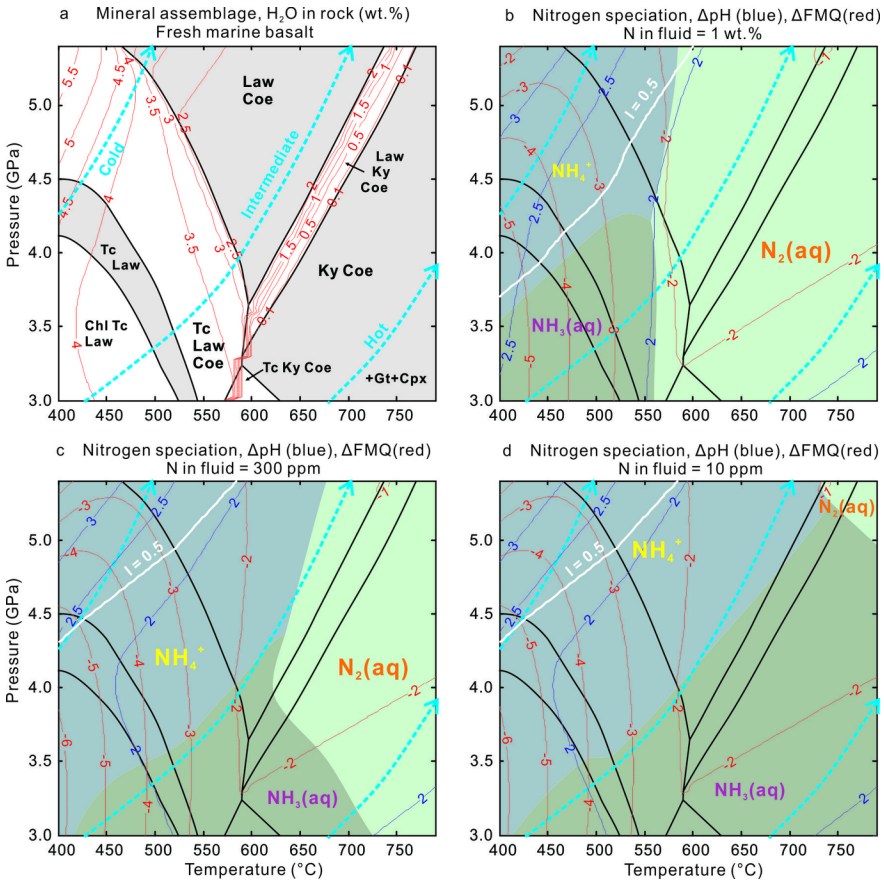

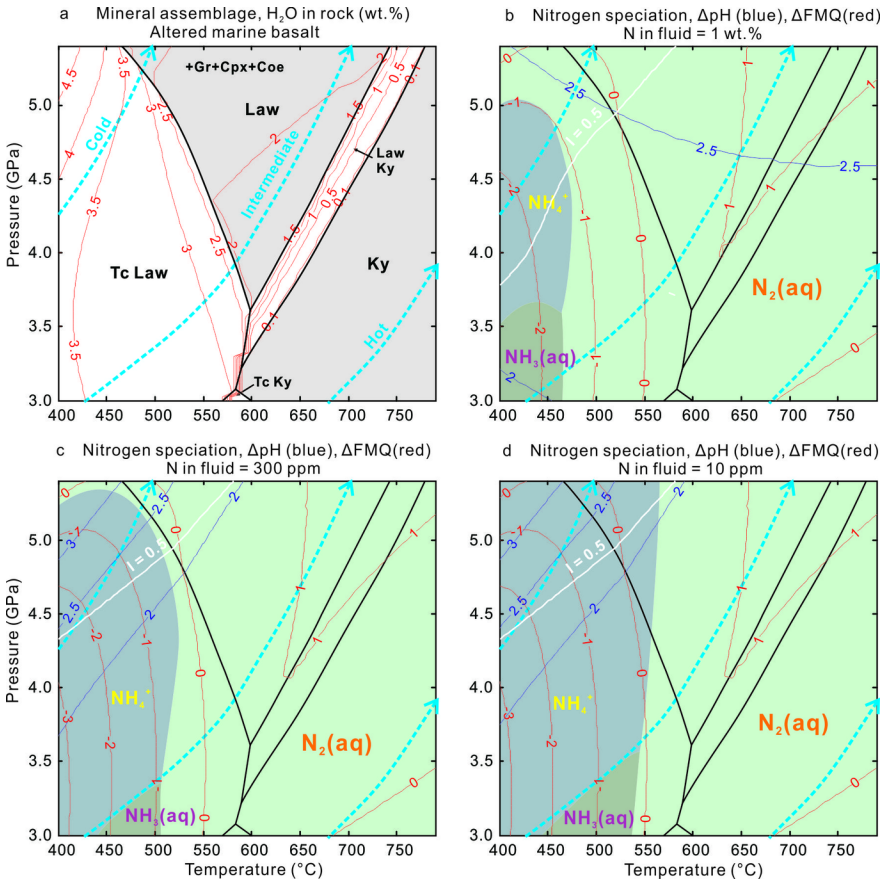

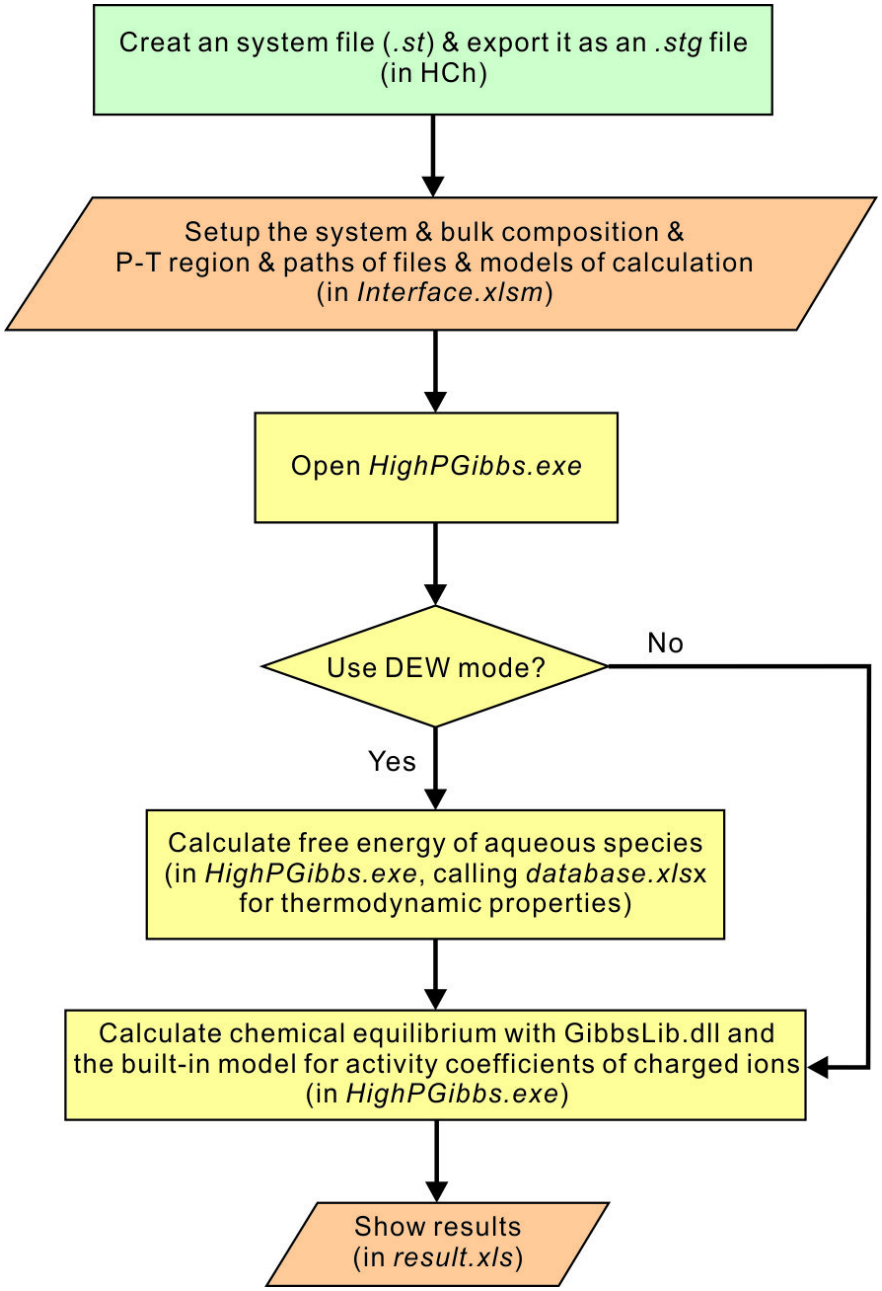

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Key Points:

- We present a thermodynamic tool that can simulate fluid-rock interaction at mantle depths.
- Most nitrogen in subducting slabs can be liberated via slab devolatilization and eventually expelled to the atmosphere.

Abstract

The HighPGibbs program is designed to calculate thermodynamic equilibrium of fluid-rock minerals and solid solutions up to depths of lithospheric mantle. It uses the Gibbs free energy minimization function of the HCh package to calculate mineral-fluid equilibrium assemblages. Chemical potentials of minerals are calculated using the equations of states included in HCh; free energy of aqueous species are calculated using the Deep Earth Water model; and activity coefficients of charged species are estimated using the Davies variant of the Debye-Hückel equation. HighPGibbs was applied to calculate nitrogen speciation in eclogite-buffered fluids from 400 to 790 °C and 30 to 54 kbar, to evaluate the mobility of nitrogen in subducting oceanic crust. Regardless of whether the protolith was altered (and oxidized) or not, N_2(aq) or NH_3(aq) are the predominant form of nitrogen in the slab-fluids at sub-arc temperatures, especially in cases of moderate or hot geotherms. Given that molecular nitrogen is highly incompatible in silicate minerals, the simulation indicates that nitrogen (as NH_4^+) in silicate minerals can be liberated during metamorphic devolatilization. The majority of nitrogen in subducting crusts can be unlocked during slab devolatilization and eventually expelled to the atmosphere via degassing of arc magmas. Therefore, oceanic crusts recycled to deep earth will be depleted in nitrogen compared to the newly formed crust at spreading centers. As a result of the long-term mantle convection, large proportions of the bulk silicate earth may have suffered nitrogen extraction via subduction, and this may account for the nitrogen enrichment in the Earth's atmosphere.

Plain Language Summary

Thermodynamic simulations are a powerful tool for investigating the geochemistry of fluid-rock systems. Such simulations are difficult to perform when pressures are higher than 5 kbar. We present a practical tool, HighPGibbs, that can calculate chemical equilibrium at pressures up to ~55 kbar, and can be used to predict the behavior of mantle fluids. It was applied to calculate the speciation of nitrogen in subduction zone fluids. The simulations show that molecular nitrogen, which is incompatible in crustal rocks, is the predominant specie in most subduction zones fluids. Therefore, most nitrogen in the subducting crusts can be unlocked by the fluids and eventually released to the atmosphere via degassing of arc magmas.

1. Introduction

Thermodynamic modeling provides a powerful tool to understand the nature and evolution of hydrothermal systems in the earth. The revised Helgeson–Kirkham–Flowers equation of state (HKF EoS; Tanger and Helgeson, 1988) is widely used for equilibrium calculations of hydrothermal systems, since it provides a self-consistent method to extrapolate the Gibbs free energies of aqueous species at elevated pressures and temperatures (P-T), even for species where high P-T experimental data are lacking. The validity of the original HKF EoS was limited to pressures lower than 5 kbar due to limits in the equation of state of water, and therefore fluid processes could only be simulated t the depths of middle crust or shallower. More recently, a significant improvement of the HKF EoS, known as the Deep Earth Water (DEW) Model, was proposed by Sverjensky et al. (2014). With the assistance of high-pressure water density (Zhang and Duan, 2005) and dielectric constants (Pan et al. 2013) calculated by molecular dynamic simulations, the DEW model extended the pressure range of the HKF EoS to up to 60 kbar,

equivalent to the depth of upper mantle. Moreover, a new method of extrapolating the stability of aqueous species from ambient conditions to high pressures was proposed with the DEW model, based mainly on the standard partial molar volume at room temperature. The model was coded as an Excel spreadsheet along with a revised thermodynamic database of aqueous species (available from Sverjensky et al., 2014). The spreadsheet calculates the standard partial molal Gibbs free energies of aqueous species as well as changes in Gibbs free energy of reactions among aqueous species, pure minerals, and gases at a given P-T, and was used to provide important insights in the nature of mantle fluids, such as their ability to carry carbon (Sverjensky et al., 2014b, Tumiati et al., 2017) and nitrogen (Mikhail and Sverjensky, 2014; Mikhail et al. 2017).

Hydrothermal activity at mantle depths, such as slab devolatilization and mantle metasomatism, is characterized by high rock/fluid ratios and thus largely buffered by rock mineralogy. Pioneering researches have investigated the geochemistry of rock-buffered fluids, and provided important insights such as the redox and pH of deep fluids and their ability to migrate rock-building lithophile elements (e.g., Galvez et al., 2015, 2016; Debret and Sverjensky, 2017). However, integrating the DEW model in complex fluid-rock systems calculation, especially those with solid solutions, remains challenging.

In this study, we introduce a practical and easy-to-use thermodynamic tool, HighPGibbs, that solves geochemical equilibrium of complex fluid-rock systems including aqueous solution, pure minerals and solid solutions at mantle pressures. HighPGibbs takes advantage of the Gibbs energy minimization solver provided by the HCh software package (Shvarov and Bastrakov, 1999) to calculate chemical equilibrium of multiphase fluid-rock systems. Previous studies have shown that the free energy minimization algorithm of HCh can well reproduce the geochemistry of complex fluid-rock systems at low pressures (e.g., Zhong et al., 2015; Xing et al., 2019). To

extend simulation to mantle depths, the DEW (Sverjensky et al., 2014) was coded in HighPGibbs, together with the Davie variant of the Debye-Hückel equation for calculation of activities of charged species in the electrolyte phase (Davies, 1962). The software calculates the distribution of elements amongst the minerals and aqueous species included in the linked, fully editable thermodynamic databases using an efficient implementation of the free energy minimization algorithm. This enables geochemical calculations of fluid-rock systems, and the software makes it easy to calculate element solubility and speciation over a P-T grid. A case study on the speciation of aqueous nitrogen in subduction zone fluids carried out using HighPGibbs is detailed in Section 3.

2. The HighPGibbs program

2.1 General description

The HighPGibbs program was developed based on HCh (Shvarov, 1999, 2008), and it reads settings from, and outputs calculated results to, Excel spreadsheets. To use HighPGibbs, it is necessary to install and register HCh and Microsoft Excel.

The HCh software package provides an ActiveX component, *GibbsLib.dll*, that calls the core functions of HCh in the Visual Basic (VB) environment. This function allows replacement of the free energies and activity coefficients of species with user-defined values, and then calculates chemical equilibrium using a Gibbs energy minimization algorithm with these given values. The VB-based software HighPGibbs takes advantage of this function; i.e., it calculates the high P-T Gibbs free energies of formation for aqueous species using the DEW model (Sverjensky et al., 2014), and then transfer these values to the free energy minimization solver of HCh.

After installation of HighPGibbs, a Microsoft Excel file (*database.xlsx*) and a HCh Unitherm folder (*HighPUnitherm*) can be found in the root fold as the default database files (see

Supporting Information for details). For all minerals and aqueous species, the apparent standard molal Gibbs free energy of formation is defined as the difference between the Gibbs free energy of the mineral at a given P-T and those of the constituent elements at reference temperature (298.15 K) and pressure (1 bar). The thermodynamic properties of aqueous species are calculated using the built-in dataset of DEW, which were reevaluated and suitable for thermodynamic calculation at elevated pressures (Sverjensky et al., 2014). For pure minerals and solid solutions, the built-in HCh database, *Unitherm*, is used. The *Unitherm* database was updated with properties of key metamorphic minerals from Holland and Powell (1998) for thermodynamic modeling of fluid-rock systems.

Following the approach used by Galvez et al. (2015) to calculate activity coefficients of aqueous species at mantle pressures, the Davies variant of the Debye-Hückel law (Davies, 1962) was implemented to calculate the activity coefficients of charged ions (accurate to a ionic strength of ~0.5 molal; Bethke (2008)), and those of neutral species and water solvent are assumed to be unit. According to the Davies equation, the activity coefficient of j_{th} solute (γ_j) is:

$$\log_{10}\gamma_j = \frac{-AZ_j^2\sqrt{I}}{1+\sqrt{I}} + 0.2AZ_j^2 I \quad (1)$$

where I is the ionic strength of the solution and Zj is the charge of j_{th} ion. A in Eq. 1 denotes the Debye-Hückel term that relates to the density ($\rho(P,T)$) and dielectric constant ($\varepsilon(P,T)$) of pure water at elevated P-T:

$$A = 1.82483 \cdot 10^6 \rho(P,T)^{0.5} (\varepsilon(P,T) \cdot T)^{1.5} \quad (2)$$

where T is temperature in K, and I is the ionic strength,

(3)

The activity coefficients depend on the ionic strength (I), which itself depends on the molality of each solute in the solution (m_j in mol/kg H_2O). In HighPGibbs, the chemical equilibrium is obtained by the following approach: (i) As a starting guess, the activity coefficients of all aqueous species are given as the values that were optimized for the previous P-T nodule, or assumed to be unit (for the first P-T nodule). The chemical equilibrium is then calculated accordingly using the free energy minimization solver of HCh, yielding a calculated composition and ionic strength (I) of the fluid. (ii) The activity coefficients of charged species are calculated based on I, and the chemical equilibrium was re-calculated, yielding an updated ionic strength (I'). (iii) Repeat (i) and (ii), until the result converges. In HighPGibbs, the circulation stops when $(\frac{I-I'}{I'})^2 < 0.01$.

In this way, HighPGibbs can calculate the full distribution of species for a fluid-rock system (with given bulk compositions) up to 60 kbar. The flow chart for calculating chemical equilibrium using HighPGibbs is shown in Figure 1, and details on running the program are proved in the Supporting Information. The install file and a tutorial can be found at http://47.93.192.148/download/Tutorial%20forHighPGibbs/Download.html and Zenodo (https://zenodo.org/record/3660833#.XkEUwGgzZPY).

2.2 Limitations

HighPGibbs uses the HCh built-in models to calculate the free energy of pure minerals and solid solutions at elevated P-T. Compared with petrologic tools such as THERMOCALC, the mineral models of HCh is less complex, lacking parameters to describe the thermal expansion and compressibility of minerals, i.e., assuming the molar volumes of solids to be independent of pressure and temperature. These yield differences between the mineral assemblages predicted using HighPGibbs and those using THERMOCALC. Taking the breakdowns of two important

eclogite facies hydrous minerals (namely lawsonite and talc) for example, pseudosection of marine basalt calculated using THERMOCALC yields a lawsonite-out temperature of ~770 °C at 4 GPa (Wei and Tian, 2014), whereas that predicted by HighPGibbs is ~730 °C at the same pressure, using the same bulk composition. The talc-out temperature is calculated at ~620 °C at 4 GPa using THERMOCALC, and that is ~590 °C using HighPGibbs. Hence, HighPGibbs is not suitable for barometry or thermometry. However, in calculating mineral solubilities at high temperature, the properties of aqueous species are poorly known compared to those of minerals; hence, the errors introduced by the simplification of mineral thermodynamics are acceptable.

The program typically fails to calculate chemical equilibrium under extreme P-T conditions. In the case of calculating nitrogen speciation in eclogite-buffered fluids (see below), it solves the fluid-rock equilibrium up to ~800 °C and ~55 kbar. Practically, fluids generated from subducting basalts, greywackes or pelites behaves as supercritical fluids at pressures beyond that value, i.e., showing chemical continuum with silicate melts (Schmidt and Poli, 2014).

Finally, the Davies (1962) approach can well describe the activity coefficient of aqueous species at ionic strength ⩽0.5 molal. and the unit activity coefficient assumption for neutral species and water solvent cannot be established for concentrated solutions. Therefore, cautions should be paid when the calculated ionic strength is high.

3. Application: speciation of aqueous nitrogen in subduction zone fluids

3.1 Geological background and method

The speciation of aqueous nitrogen in the deep earth has control on the evolution of the Earth's atmosphere. More specifically, if nitrogen exists predominantly as NH_4^+, which is moderately compatible in silicate minerals, it will be partly locked in the solid earth. In contrast, it will be readily to be released into the atmosphere via degassing processes if it is mainly in the

form of N_2(aq) or NH_3(aq) (Mikhail and Sverjensky, 2014). A thermodynamic study of aqueous speciation of nitrogen using the DEW model (Mikhail and Sverjensky, 2014) showed that in a suprasubduction mantle wedge, which is more oxidized than upper mantle elsewhere, provides a suitable environment to stabilize N_2(aq). The authors suggested that this accounts for the enrichment of N_2 in the Earth's atmosphere.

Apart from mantle wedge redox, another factor that may influence the Earth's global budget of nitrogen circulation is whether nitrogen in subducting slabs can be recycled into the Earth's interior or released by slab fluids. To address this issue, Mikhail et al. (2017) calculated the speciation of nitrogen in eclogite-buffered fluids at four individual P-T conditions (10 and 50 kbar, 600 and 1000 °C), showing that the subducting crust provides suitable pH and redox to stabilize the mineralogically incompatible nitrogen species N_2(aq) or NH_3(aq), thus favoring nitrogen liberation during devolatilization. These results demonstrated the importance of the lithology of subducting rock, which buffers fluid pH and fO_2(g), in controlling the speciation of aqueous nitrogen.

In this study, to better understand the nitrogen flux in subduction zones with varying thermal structures, nitrogen speciation in basaltic eclogite-buffered fluids was calculated over a P-T grid of 400 to 790 °C and 30 to 54 kbar (at increments of 10 °C and 0.25 kbar, respectively) in the Fe-Mg-Na-Ca-Al-Si-O-H-N system. In subduction zones, thermal structure greatly influences the amounts and depths of volatile liberation (e.g., Van Keken et al., 2011). Aside from the timing and amounts of water solvent liberation, temperature has a first-order control in chemical equilibrium, and thus the P-T conditions can significantly influence the speciation of volatiles.

To evaluate the influence of the rock's redox condition, two bulk compositions were used for thermodynamic modeling, a fresh basalt at the ridge of the Pacific Ocean (sample PC CV 04

of Bézos and Humler, 2004) and the average of altered marine basalts at Pito Deep (Barker, 2010; Table 1). The calculations were carried out in the *Two-step Mode* of HighPGibbs (see Supporting Information for details), in which the equilibrium calculation at each P-T point was carried out as two steps: (i) The equilibrium of a solute-free system was calculated using the bulk composition of 100 kg of basaltic rocks (Table 1) with excess amounts of water, to obtain the water content that can stabilize the hydrous minerals in the metamorphic rock. (ii) Minor amounts of free water with dissolved nitrogen (1 kg of water with 10^{-5}, 3×10^{-4} or 10^{-2} kg of dissolved nitrogen) were added to the bulk composition of metamorphic rock obtained from step 1, to obtain the speciation of aqueous nitrogen in eclogite-buffered fluids. Three different bulk fluids compositions (with 10 ppm, 3000 ppm and 1 wt.% of dissolved nitrogen) were used to evaluate the influence of bulk nitrogen concentration on nitrogen speciation (Mikhail et al., 2017). Although the nitrogen concentrations in slab-fluids are poorly known, the broad range of selected concentrations (from 10 ppm to 1 wt.%) is likely to cover those of natural slab-fluids (Mikhail et al., 2017). A relatively low fluid/rock ratio (~0.01) was used for the calculation, to simulate the rock-buffered nature of slab-fluids in subduction zones (Connolly and Galvez, 2018). In this approach, the speciation of nitrogen in slab-fluids is evaluated as a function of slab P-T and the concentration of total fluid-borne nitrogen. The simulation reveals the compatibility of nitrogen in subducting crusts with varying geotherms and thus whether it will be liberated via devolatilization or recycled to deep earth.

The aqueous species involved in the simulation are listed in Table S1, and the sources of their thermodynamic properties can be found in *database.xlsx* of the software package (see Supporting Information for details), which includes the thermodynamic properties revised with high-pressure experiment results by Sverjensky et al. (2014). The rock-building silicates and

oxides used in this simulation are from the database of Holland and Powell (1998), and the involved minerals and the mixing models of solid solutions are listed in Table S2. In this simulation, the metamorphic rock buffers the redox and acidity of the slab-fluid, and thus influences the speciation and mobility of aqueous nitrogen.

It is noted that nitrogen-bearing mineral end members are not included in the solid solutions, and thus the nitrogen exchanges between minerals and aqueous species are neglected. Natural eclogites host ppm-levels of nitrogen as substitution for K^+ in minerals such as phengite and clinopyroxene (Mikhail et al., 2017). Given the high solubility of nitrogen in the form of N_2(aq) or NH_3(aq), the incompatible nitrogen can easily be leached by aqueous fluids (e.g., Duan et al., 2000). As long as molecular nitrogen predominates, the efficiency of nitrogen liberation is likely to be controlled mainly by the kinetics of the fluid-rock interaction (i.e., how effectively the K-bearing minerals communicate with the metamorphic fluid) rather than the equilibrium between mineralogically bound and aqueous nitrogen.

3.2 Results and discussions

The simulations show that dehydration of marine basalt at eclogite facies is controlled mainly by breakdown of lawsonite and, to a lesser extent, talc and chlorite (Figs. 2a and 3a). Two factors influencing the aqueous speciation of nitrogen, pH and fO_2(g), are also shown as the difference from neutral pH (defined as $\Delta pH = pH - pH_n$, where pH and pH_n denote the pH values of the fluid and pure water, respectively) and the fayalite-magnetite-quartz buffer (ΔFMQ), respectively (Figs. 2 and 3). The alkaline nature (ΔpH = 1.5 to 3) of the eclogite-buffered fluid is consistent with previous modeling results (Galvez et al., 2016). The reliability of the modeling results can be evaluated by the simulated ionic strength of the fluid. Under most P-T conditions, the simulated ionic strengths are between 0.1 and 0.3, well within the applicability of the Davies

equation ($I \leqslant 0.5$). The contourd of I = 0.5 are also shown in Figures 2 and 3, and the simulation results with higher pressures and lower temperatures than the contour (at the upper left corner of the P-T diagrams) yield ionic strength >0.5 and thus may not be accurate.

Consistent with previous modeling results (Mikhail and Sverjensky, 2014; Mikhail et al., 2017), this study shows that the speciation of aqueous nitrogen is controlled mainly by the redox and total nitrogen content of the slab-fluids. In altered marine basalts (Figs. 2b-d), which are more oxidized than their unaltered precursors, N_2(aq) predominates over reduced nitrogen species (NH_3(aq) and NH_4^+) in a broader P-T regime than that in fresh basalts (Figs. 3b-d). On the other hand, in both altered and fresh basalts-buffered fluids, the predominant fields of N_2(aq) shrinks with decreasing total nitrogen contents (Figs, 2 and 3).

In addition, temperature significantly controls the speciation of aqueous nitrogen speciation. In general, higher temperature favors the stabilization of N_2(aq) whereas as NH_3(aq) or NH_4^+ predominate at lower temperatures (Figs. 2 and 3). For altered marine basalts, large amounts of mineralogically bound water remained in the rock (~2.5-3.5 wt.%, mainly as lawsonite, Figs. 2b-d) at temperatures where N_2(aq) predominates in the fluids (T>~480-550 °C). The result is similar for the fresh basalts-buffered fluids with moderate or high contents of dissolved nitrogen. In these scenarios, the eclogite retains of ~2.5 wt.% water in the P-T regimes of the predominant fields of N_2(aq) (T>~580-650 °C; Figs. 3b, c). In the case of nitrogen-poor fluids (10 ppm of N, Fig. 3d) buffered by fresh basalt, NH_3(aq) predominates instead of N_2(aq), when the rock contains ~2 wt.% of mineralogically bound water as lawsonite.

Both N_2(aq) and NH_3(aq) are incompatible in silicate minerals and soluble in fluids, and thus can be scavenged from the silicate minerals during subsequent dehydration of the down-going oceanic crust (mainly by breakdown of lawsonite), regardless of the redox state of the

marine basalt. Given that molecular nitrogen is highly soluble in water under the P-T conditions of interest (see Fig. 3 in Duan et al. (2000)), the majority of structurally bound nitrogen may soon be leached out via dehydration of lawsonite. Furthermore, two processes may enhance the liberation of nitrogen. First, the devolatilization reactions (e.g., lawsonite breakdown) involve interactions amongst silicate minerals and destruction/reconstruction of crystal structures, a process that facilitates nitrogen liberation from the structures of silicate crystals (Niedermeier et al., 2009). Second, shear deformation accompanying metamorphism will facilitate communication between metamorphic minerals and fluids (e.g., Tomkins et al., 2010).

Exceptions are subduction zones with cold geotherms (Figs. 2a, 3a), where a significant amount of water can be retained to large depths (van Keken et al., 2011). In cases of fluids buffered by fresh basalt (Figs. 3b-d) or with low nitrogen contents (Fig. 2d), NH_4^+ predominates along the P-T path of the cold subduction zone and nitrogen in subducting basalt can be recycled to deep earth. This may explain the observation of surface-sourced nitrogen in diamonds, which requires nitrogen surviving subduction devolatilization and transportation to depths greater than that of diamond stability (Mikhail et al., 2014), or even to lower mantle (Palot et al., 2012). We speculate that this scenario is less common than nitrogen discharging in subduction zones. First, the stability of NH_4^+ requires both unaltered protolith (except for the cases of very low contents of dissolved nitrogen) and a cold subduction zone (Fig. 2). Second, oceanic crust will be significantly enriched in nitrogen during submarine alteration (Bebout et al., 2016), and thus altered crusts should have greater contributions to the global nitrogen circulation than their unaltered precursors.

In most cases, nitrogen in a subducting crust is mainly in the form of N_2(aq) or NH_3(aq) under sub-arc P-T conditions, and thus it will be released to the mantle wedge and expelled to the

atmosphere via arc volcanism. If the subducting slab is hot enough, large amounts of water will be released at shallower depths in fore arc regions (van Keken et al., 2011). In these cases, massive amounts of nitrogen gas may also be released via fluid venting near a trench. This is more likely to take place if the subducting crust was altered and oxidized, where N_2(aq) begins to predominate at lower temperatures (Fig. 2).

Combined with the incompatibility of nitrogen in a mantle wedge (Mikhail and Sverjensky, 2014), subduction zones provide a highway to transfer nitrogen from a subducting slab to the atmosphere, in line with the geological observation in modern convergent margins (Fischer et al., 2002). This implies not only a strong retention of nitrogen in the Earth's atmosphere, but also the mechanism that controls the long-term global nitrogen circulation. The subduction factory works as a filter that continuously intercepts nitrogen from incoming subducting crust, which was originally derived from upwelling asthenosphere at spreading centers. In the perspective of global plate tectonics, nitrogen is released to the atmosphere from not only the mantle wedge per se, but also large volumes of lithosphere fed into subduction zones.

In most cases, incompatible molecular nitrogen will predominate over NH_4^+, regardless of whether the crust underwent submarine alteration or not (Figs. 2 and 3). Therefore, elevated redox conditions are not necessary for the mobility of nitrogen during slab devolatilization, suggesting that the "nitrogen filter" may have initiated as early as the onset of plate tectonics, which may have been recycling crustal material for more than 3 billion years (e.g., Bizzarro et al., 2002). Furthermore, the hot geotherm of early Precambrian eras would also enhance the stability of N_2(aq) or NH_3(aq) (Figs. 2 and 3). As a result of the long-term mantle convection, large portions of the Earth's crust and upper mantle may have been subjected to nitrogen extraction by subduction, and this may account for the nitrogen enrichment of the Earth's

atmosphere compared to other terrestrial planets (Mikhail and Sverjensky, 2014). The simulation suggests that plate tectonics results in a net outgassing flux of nitrogen into the atmosphere, supporting the idea of increasing nitrogen in the Earth's atmosphere over geological time, a hypothesis that is still debated (Zerkle and Mikhail, 2017).

4. Conclusions

(1) The HighPGibbs software provides a practical tool to calculate chemical equilibrium of complex fluid-rock systems involving aqueous fluids, simple minerals and solid solutions at mantle depths, enabling quantitative assessment of complex fluid-rock interactions from the surface to the mantle within a self-consistent framework.

(2) In most cases, aqueous nitrogen in slab-fluids is predominated by incompatible N_2(aq) or NH_3(aq) under sub-arc P-T conditions and thus the majority of mineralogically bound nitrogen in oceanic crusts will be expelled to the atmosphere via slab subduction.

Acknowledgement

The HighPGibbs program is available at Zenodo (https://zenodo.org/record/3660833#.XkEUwGgzZPY). The data used for the thermodynamic simulation are in Tables S1 and S2 and accessible at Zenodo (https://zenodo.org/record/3660412#.XkANjaEw-QI). The comments of two anonymous reviewers provided considerable assistance in improving the software and the original submitted manuscript. This work is financially supported by the National Natural Science Foundation of China (Nos. 41872078 and 41502069), the Australian Research Council (DP190100216), the

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Figure Captions

Figure 1. The flow chart of the HighPGibb. (Black-and-white in print)

Figure 2. Results of thermodynamic simulation for fluids buffered by eclogite metamorphosed from altered marine basalt, showing P-T pseudosection showing mineral assemblage and content of lithological bound water (a) and the Predominance fields of fluid-borne nitrogen in the eclogite-buffered fluid with varying total nitrogen contents (b-d). The geotherms of hot, intermediate and cold subduction zones are for slab Moho, from van Keken et al. (2011). Also shown are the acidity (ΔpH, red lines with labels) and redox (ΔFMQ, blue) of the fluid. ΔpH is the deviation of fluid pH from neutral pH (pH_n) ($\Delta pH = pH - pH_n$), and ΔFMQ the difference in log fO_2(g) of the fluid relative to the fayalite-magnetite-quartz (FMQ) buffer ($\Delta FMQ = \log f_{O2(g),fluid} - \log f_{O2,FMQ}$). The contour of ionic strength equal to 0.5 molal (I = 0.5) is shown and P-T regime with higher pressures and lower temperatures than the contour have ionic higher than this value. Bulk rock compositions used for simulation are given in Table 1. Mineral abbreviations: Opx = orthopyroxene; Cpx = clinopyroxene; Gt = garnet; Coe = coesite; Law = lawsonite; Tc = talc; Ky = kynite; Chl = chlorite. (Color in print).

Figure 3. The same as Fig. 2, but the composition of fresh marine basalt (see Table 1) was used for the simulation. (Color in print)

Table

Table 1. Bulk rock compositions used in the modelling (in wt.%, H_2O in access)

	Altered marine basalt	**Fresh marine basalt**
SiO_2	52.03	50.12
Al_2O_3	14.33	15.41
MgO	7.80	8.81
FeO	8.99	7.85
Fe_2O_3	2.73	1.21
CaO	11.27	12.51
Na_2O	2.76	2.51

Figure 1.

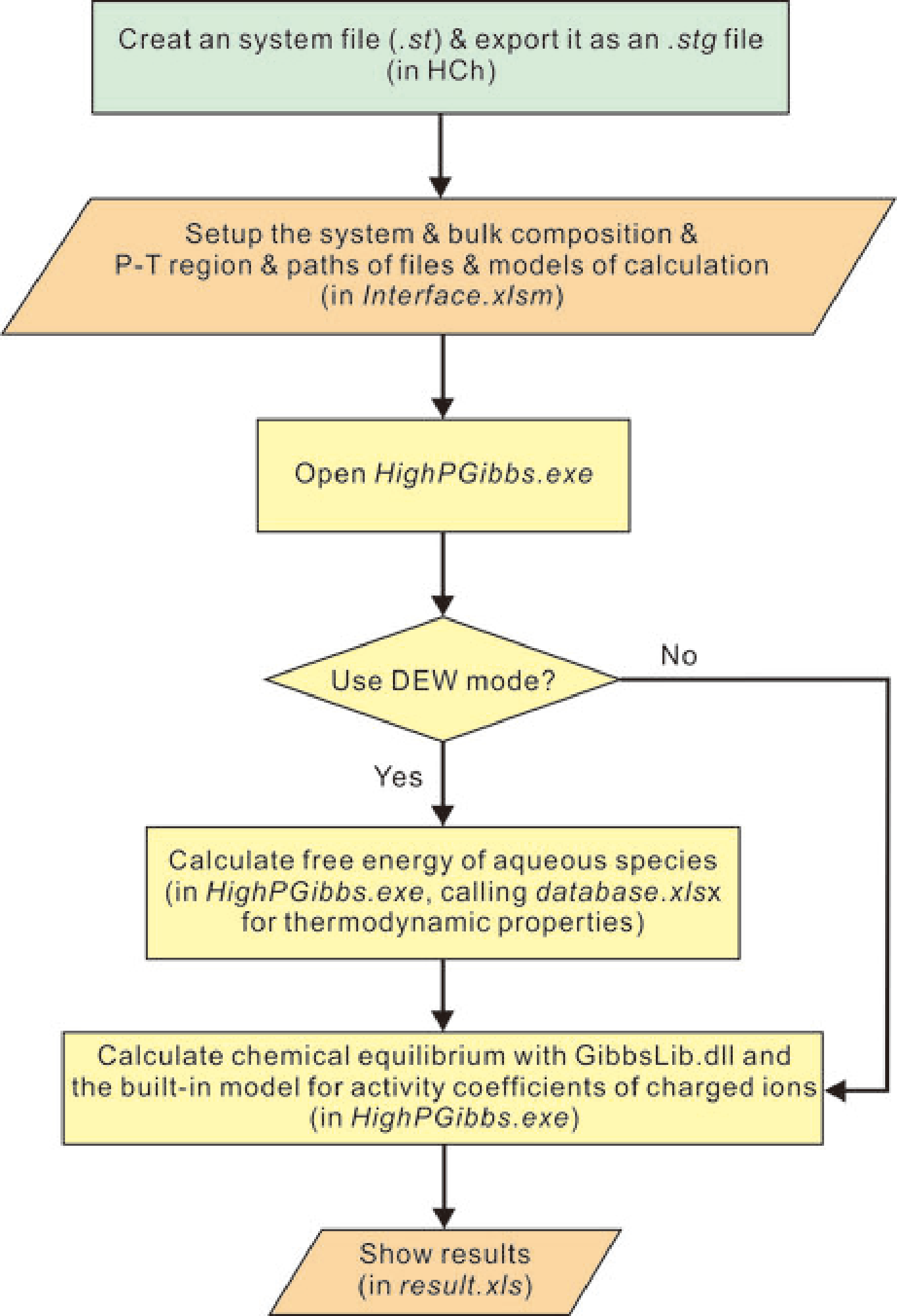

Creat an system file (.st) & export it as an .stg file (in HCh)
Setup the system & bulk composition & P-T region & paths of files & models of calculation (in Interface.xlsm)
Open HighPGibbs.exe
Use DEW mode?
No
Yes
Calculate free energy of aqueous species (in HighPGibbs.exe, calling database.xlsx for thermodynamic properties)
Calculate chemical equilibrium with GibbsLib.dll and the built-in model for activity coefficients of charged ions (in HighPGibbs.exe)
Show results (in result.xls)

Figure 2.

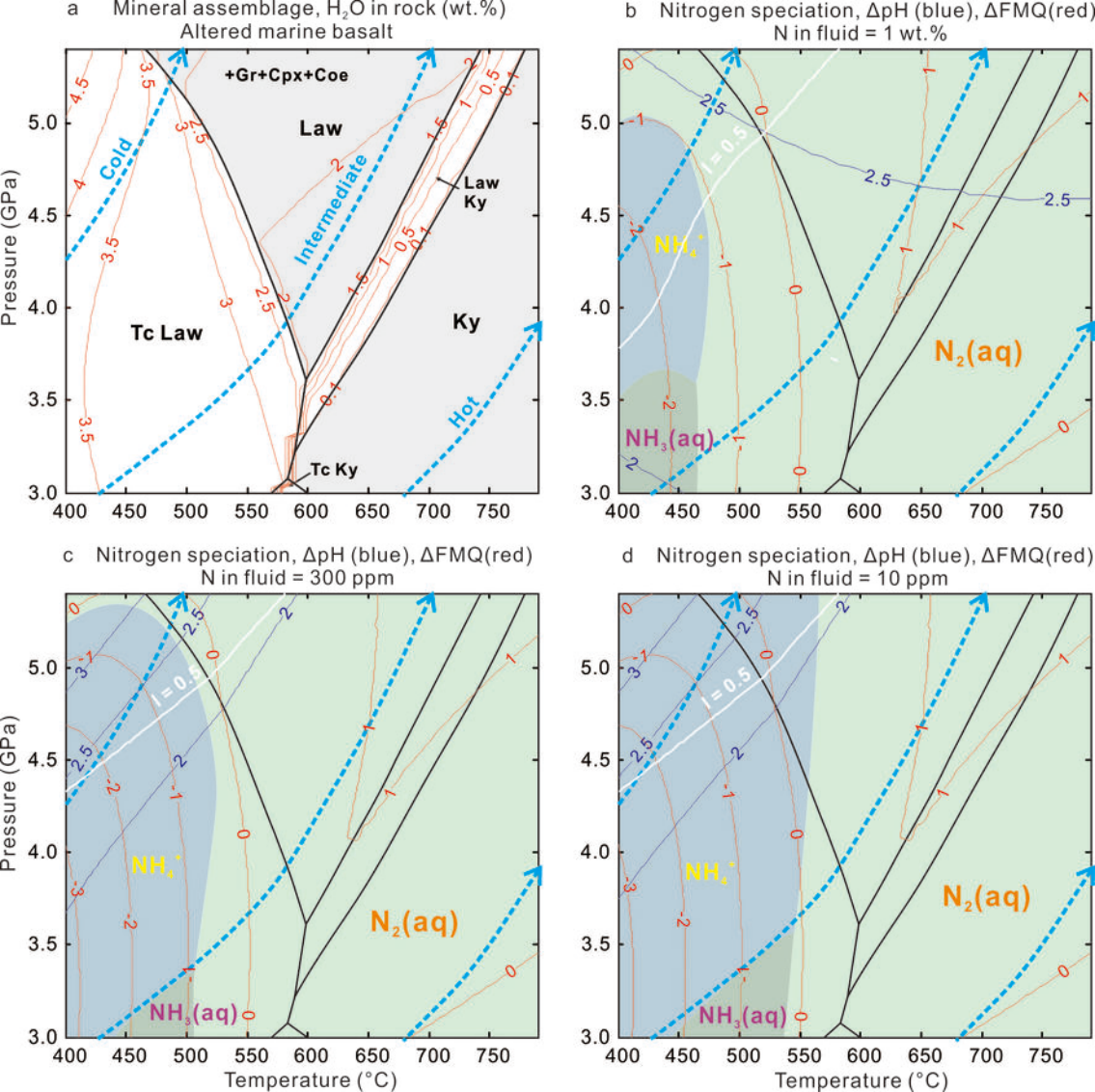
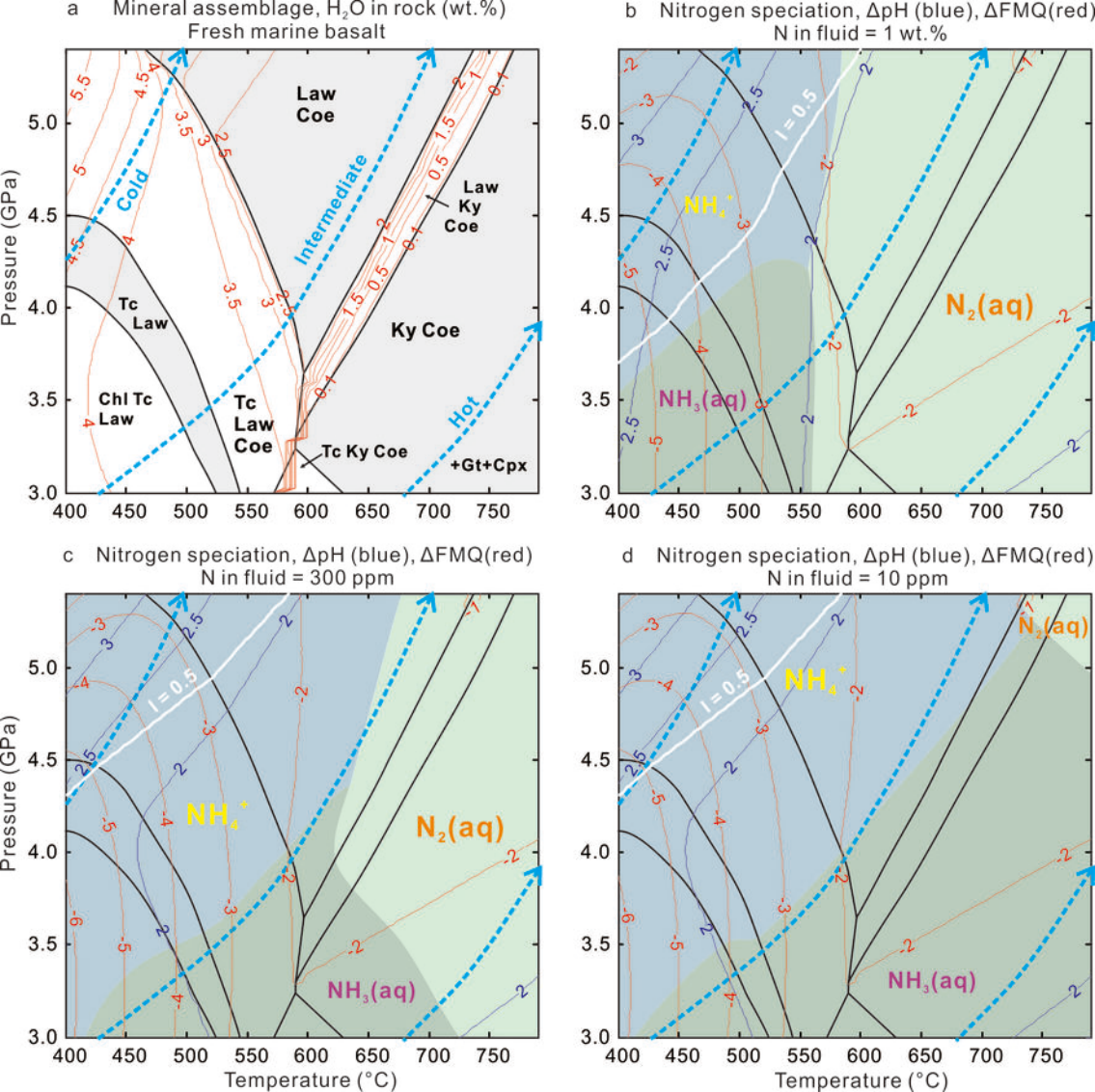

a
Mineral assemblage, H2O in rock (wt.%)
Altered marine basalt
+Gr+Cpx+Coe
Law
Cold
Intermediate
Law
Ky
Tc Law
Ky
Hot
Tc Ky
b
Nitrogen speciation, ΔpH (blue), ΔFMQ(red)
N in fluid = 1 wt.%
NH4+
N2(aq)
NH3(aq)
c
Nitrogen speciation, ΔpH (blue), ΔFMQ(red)
N in fluid = 300 ppm
NH4+
N2(aq)
NH3(aq)
d
Nitrogen speciation, ΔpH (blue), ΔFMQ(red)
N in fluid = 10 ppm
NH4+
N2(aq)
NH3(aq)
Pressure (GPa)
Temperature (°C)

Figure 3.


a Mineral assemblage, H_2O in rock (wt.%)
Fresh marine basalt
Law Coe
Cold
Intermediate
Law Ky Coe
Tc Law
Ky Coe
Chl Tc Law
Tc Law Coe
Tc Ky Coe
Hot
+Gt+Cpx
b Nitrogen speciation, ΔpH (blue), ΔFMQ(red)
N in fluid = 1 wt.%
I = 0.5
NH_4^+
N_2(aq)
NH_3(aq)
c Nitrogen speciation, ΔpH (blue), ΔFMQ(red)
N in fluid = 300 ppm
d Nitrogen speciation, ΔpH (blue), ΔFMQ(red)
N in fluid = 10 ppm
Pressure (GPa)
Temperature (°C)