

## NUMERICAL MODELING OF NaCl-H<sub>2</sub>O PHASE SEPARATION IN A MID-OCEAN RIDGE HYDROTHERMAL VENT FIELD

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### **ABSTRACT**

Mid-Ocean Ridge (MOR) hydrothermal systems host a wide array of unique metabolic strategies and play an important role in cycling of numerous elements. However, the spatial distribution of (bio-) geochemical transformations is poorly constrained, and the impact of multiphase flow on community productivity and chemical flux has not been rigorously determined. Here we report on recent efforts to incorporate an equation of state (EOS) module for the NaCl-H<sub>2</sub>O system into TOUGHREACT to study how phase separation of chloride-laden hydrothermal fluid (and pressure-temperature changes therein) impacts the chemical milieu that ultimately supports chemosynthetic hydrothermal communities in the shallow subsurface.

Phase separation of pure water in subaerial geothermal systems has long been recognized as a controlling process of heat and mass transport, but the analogous process in deep-sea hydrothermal systems, where pressures can be in excess of 400 bars, has become widely accepted only in the last few decades. The numerical treatment of phase separation in marine hydrothermal systems has been complicated by the high concentration of salt in seawater, the dominant fluid medium from which hydrothermal fluid is created by high temperature reaction with basaltic rock. The presence of salt (predominantly NaCl) in the fluid matrix adds significant complexity to the phase relations compared to pure water, and this complexity must be accurately represented in the equation of state to correctly calculate fluid transport.

To that purpose, we incorporate a NaCl-H<sub>2</sub>O EOS (Kissling, 2005) into TOUGHREACT version 1.2 (Xu et al., 2006), thereby enabling

this code to accurately model heat and mass transport in chloride-rich hydrothermal systems. The code is validated through comparison to a simulation performed with the transport code NaCl-TOUGH2, and applied to a hydrothermal upflow zone to assess the role of phase separation in this part of the system.

### **INTRODUCTION**

High temperature hydrothermal vent fields dotting mid-ocean ridges (MOR) play a significant role in heat and mass transfer from the Earth's interior to the overlying ocean. Seawater percolates downward, reacts with hot mafic rock at high temperature and pressure, and then buoyantly ascends to the surface as hydrothermal fluid, transporting the chemical cargo acquired at the base of the system to the upper reaches of ocean crust (Butterfield et al., 2003). In addition to its role as a transport medium, reducing hydrothermal fluid also serves to support a potentially vast subsurface ecosystem of chemosynthetic organisms that capitalize on steep chemical and temperature gradients within subsurface zones of mixing between seawater and hydrothermal fluid (Shock et al., 2004).

Intermingled with the chemical changes wrought by water-rock reactions are the physical changes driven by the process of phase separation, whereby a single homogeneous fluid is transformed into multiple phases, each with properties different than the parent fluid. Phase separation plays a crucial role in determining the distribution and composition of MOR hydrothermal fluids (Comou et al., 2009; Ingebritsen et al., 2010; Butterfield et al., 1994), and so must be rigorously considered in any hydrologic model that seeks to simulate MOR subsurface environments and the biological communities therein.

The TOUGH family of codes offers a well-established platform for modeling thermal-chemical-hydrologic multiphase flow in porous media at high temperatures, so it is conducive to simulating MOR hydrothermal systems. However, publicly available versions of this platform impose temperature limits that exclude important portions of ocean crust and prevent the proper accounting of salt partitioning in the vapor phase, a crucial aspect of transport in seawater-based hydrothermal systems where venting of fluids depleted in salt relative to seawater is widespread and ongoing (Butterfield et al., 1994, Lilley et al., 2003, Von Damm, 2004). A precise treatment of this phenomenon is made difficult by the fact that salt (predominantly NaCl) substantially complicates phase relations compared with pure water (Johnson and Norton, 1991, Palliser and McKibbin, 1998a, 1998b, 1998; Driesner & Heinrich, 2007; Driesner, 2007). On the other hand, because the phase relations of the NaCl-H<sub>2</sub>O system are well known for MOR pressure and temperature (PT) conditions, chloride—a nonreactive species that can be measured by existing *in situ* chloride sensors (Larson et al., 2007)—is not only a confounding factor, but also a convenient metric for diagnosing subsurface PT conditions that govern the phase separation process.

Here, we report efforts to integrate an equation of state module for the NaCl-H<sub>2</sub>O system, established for the transport-only code TOUGH2 (Kissling, 2005) and applicable for  $P < 1000$  bars and  $T = 10$ -620 °C, into TOUGHREACT. In so doing, we establish a framework for comprehensive reactive transport modeling of deep-sea MOR hydrothermal systems. We also report preliminary results for a 1D application of the platform to a generic hydrothermal discharge zone.

## **METHODS**

The NaCl-H<sub>2</sub>O equation of state module of Kissling (2005) (below referred to as EOS12) is built on mathematical formulations for NaCl-H<sub>2</sub>O phase relations and fluid properties that have been studied and refined extensively (e.g., Bischoff and Pitzer, 1989; Palliser and McKibbin 1998a; Driesner & Heinrich, 2007). The module, described in detail in Kissling

(2005) and Kissling (2004), considers 6 different system states and the transitions between them using the relations of Palliser and McKibbin (1998a, 1998b, 1998c) and the primary variables pressure, temperature, chloride mass fraction and phase saturation. Compared to the version applicable to transport-only TOUGH2, some important modifications were required for both EOS12 and TOUGHREACT. They can be grouped into the following four types:

1. Adjustment of variable definitions in EOS12 to match TOUGHREACT conventions.
2. Expansion of EOS12 to accommodate TOUGHREACT-specific requirements.
3. Identification and replacement or removal of code fragments containing equations of state in TOUGHREACT not valid at higher temperature.
4. Addition of supporting code in TOUGHREACT subroutines that handle time stepping, mass and flux computation, and post-convergence variable updates.

The result of these changes, a beta version of NaCl-TOUGHREACT, was tested with a benchmark example (Kissling, 2004) to assess the veracity of its implementation in TOUGHREACT before using the platform to simulate a 1D vertical flow scenario.

## **RESULTS AND DISCUSSION**

### **Benchmark: Test of phase transitions**

A simple box model, described in detail in Kissling (2004), was set up to assess NaCl-TOUGHREACT's ability to handle phase transitions between 4 of the 6 states. Mass was withdrawn at a constant rate of 1 kg/s from a 10<sup>9</sup> m<sup>3</sup> grid block with a porosity of 0.1, a heat capacity of 1000 J/kg/K, a density of 2650 kg/m<sup>3</sup>, and an initial temperature of 350°C. Figure 1 shows the evolution of the phase distribution in the box as mass is withdrawn and pressure and temperature drop. The results from the modified code are in good agreement with results from NaCl-TOUGH2 (also shown in Figure 1), indicating that the necessary modifications are correctly implemented.

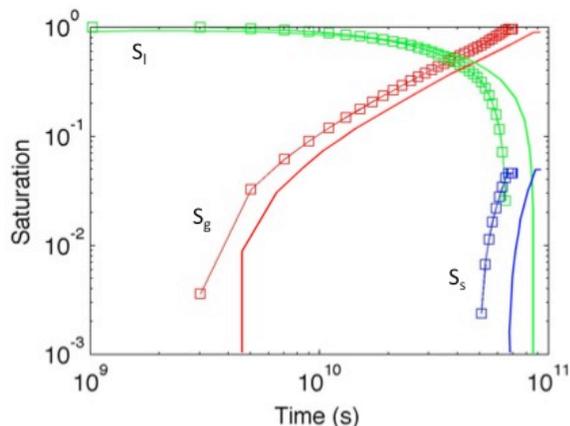


Figure 1. Benchmark example results of phase saturation as a function time. Red, green, and blue are saturation of gas, liquid and solid, respectively. Solid lines with no markers are reprinted with permission from Kissling (2004) Model A. Solid lines with open square markers represent output for the same model from NaCl-TOUGHREACT. As the pressure is decreased at 350°C, the fluid changes from pure liquid to two-phase (liquid + gas) to three-phase (liquid + gas + solid), and finally to two-phase (gas + solid). Results of NaCl-TOUGHREACT are in reasonably good agreement with results from NaCl-TOUGH2.

#### **Application: 1D Vertical Flow Scenario**

Subsurface brines in hydrothermal systems have long been postulated (Bischoff and Rosenbauer, 1989), and more recently models of brine movement and storage have been published (Fontaine and Wilcock, 2006; Fontaine et al., 2007). Moreover, brine venting has been observed at multiple sites (Fox, 1990; Von Damm, 1997). To better understand how brines (and their conjugate vapors) apportion during ascent to the surface, our current beta version of NaCl-TOUGHREACT was used to simulate the rising fluid in a hydrothermal vent system (Figure 2). In this simple 1D vertical flow scenario hot brine is injected at the base of a 1500 m column until a steady state is reached in which the modeled vent temperature matches the

upper end of observed black-smoker temperatures (Von Damm, 2004).

The column is divided into 60 gridblocks, each 25 m high with a cross sectional area of 100 m<sup>2</sup>. We use a 9% NaCl solution, which is in the range of brine chloride concentrations from other studies (Fontaine and Wilcock, 2006; Larson et al., 2009), and assign an enthalpy of 2×10<sup>6</sup> J/kg to achieve an injection fluid temperature >400 °C, which is comparable to root zone conditions derived from a chloride-adjusted silica geobarometer (Foustoukos and Seyfried, 2007). The injection rate was adjusted to achieve a pressure at the bottom of the column that was both within the pressure limits of EOS12 and consistent with inferred hydrothermal reaction zone pressures. Following the example of Fontaine et al. (2007), the flow domain was split into a 400 m ‘extrusive’ layer with permeability set to an order of magnitude higher (10x) than the lower 1100 m ‘intrusive’ layer.

Results from this simulation are shown in Figure 3. The modeled temperature in the uppermost block of the flow domain is ~396°C, which is very close to temperatures observed at 9°N latitude on the East Pacific Rise (Von Damm, 2004). Modeled chloride mass fraction of the gas phase (thought to be the dominant constituent in black smoker fluids) is 1×10<sup>-3</sup> at the surface, about 1/10<sup>th</sup> the typical chloride observed at most black smokers, though transient chloride values in this range have been observed (Lilley, 2003; Von Damm et al., 1997). Also, this simulation does not address the potential for lateral inputs in the shallow subsurface, which may elevate chloride concentrations prior to venting. The phase saturation profile suggests two-phase conditions from ~700 m depth to the surface. This is consistent with measurements reported in Von Damm, (2004) showing the venting of fluids with lower-than-seawater chloride over many years, which suggests two-phase conditions in the upper crust are ubiquitous and long-lived.

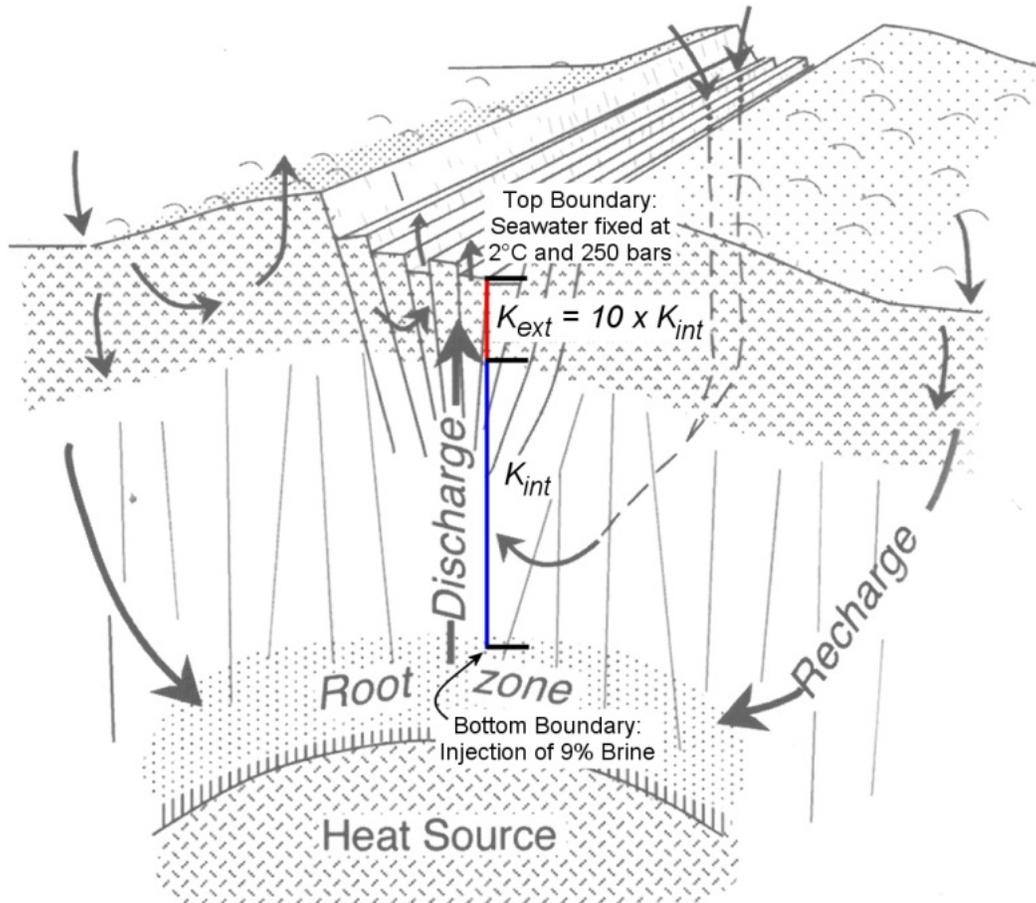


Figure 2. Cross-sectional schematic of convection cell oriented perpendicular to the spreading axis, modified from Alt (1995). The 1D example herein approximates the discharge zone, shown here in blue and red for the lower permeability intrusive layer and higher permeability extrusive layer respectively. Upper and lower boundary conditions are shown on the schematic at the top and bottom of the flow domain.

## CONCLUSION

We have produced a beta version of NaCl-TOUGHREACT, capable of modeling fluid transport in NaCl-H<sub>2</sub>O systems at temperatures up to 620°C and pressures up to 1000 bars. This constitutes an important step towards applying TOUGHREACT's chemical modeling capabilities to seawater-based MOR hydrothermal flow. The new platform has been benchmarked with a box model simulation that highlights the code's ability to handle phase transitions. As a first application, we simulate simple 1D vertical flow that roughly approximates an MOR hydrothermal upflow zone. The preliminary results show a steady state two-phase region in the upper 700 m of the crust, which is consistent with observations over

many years of vent fluid depleted in chloride relative to seawater.

This work provides a stepping stone to combine high temperature and pressure multiphase transport simulations in NaCl-H<sub>2</sub>O systems with the chemical modeling capabilities of TOUGHREACT. It allows an assessment of feedbacks between chemical reactions and fluid transport associated with precipitation/dissolution processes driven by compositional and thermal gradients. Additionally, the structure is in place to integrate recent improvements in the formulation of NaCl-H<sub>2</sub>O phase relations (Driesner and Heinrich, 2007; Driesner, 2007). These efforts will help establish a more comprehensive picture of the physical and chemical conditions in convection cells that drive flow at MOR vent fields.

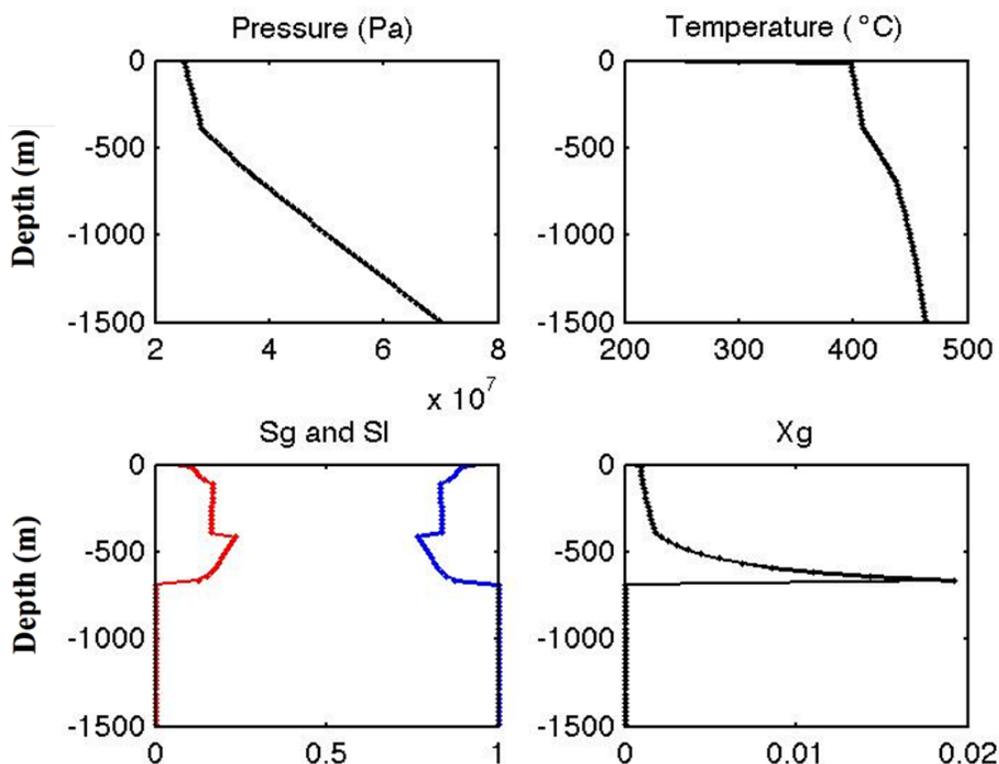


Figure 3. Results from 1D vertical flow simulation showing pressure, temperature, saturation of gas (red) and liquid (blue), and mass fraction of chloride in the vapor phase. The model results show a 700 meter long two-phase zone in the upper portion of the flow domain, which is consistent with the observed venting of chloride depleted fluids (relative to seawater) at MOR sites such as 9°N latitude on the East Pacific Rise (EPR). Temperatures at the surface in excess of 390°C are also in good agreement with EPR observations.

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