A revised empirical model to calculate the dynamic viscosity of H₂O-NaCl fluids at elevated temperatures and pressures (≤ 1000 °C, ≤ 500 MPa, 0-100 wt. % NaCl)

Klyukin Yu.I.¹, Lowell R.P.¹, Bodnar R.J.¹

¹. Department of Geosciences, Virginia Tech, Blacksburg, VA 24061

Abstract Examination of viscosities for the fluids in the system H₂O-NaCl predicted by the commonly-used model of Palliser and McKibbin has identified regions of pressure-temperature-salinity (*PTx*) space in which the model delivers values that are inconsistent with some experimental data and exhibits discontinuities and trends that are unexpected. Here, we describe a revised empirical model to calculate viscosity of H₂O-NaCl fluids that shows good correlation with experimental values and shows trends that are consistent with known or expected behavior outside of the region where experimental data are available. The model described here is valid over the temperature range from the H₂O solidus (~0 °C) to ~1,000 °C, from ~0.1 MPa to ≤500 MPa, and for salinities from 0-100 wt.% NaCl.

Keywords H₂O-NaCl fluid, viscosity, transport properties, numerical model

1 Introduction

The circulation of fluids in the Earth's crust plays an important role in the transport of chemical constituents (mass) and heat (energy), and is the major control on the formation of hydrothermal ore deposits (Bredehoeft and Norton, 1990). In recent decades, our understanding of the underlying principles associated with fluid circulation in response to thermal perturbations in the crust has advanced significantly through application of numerical fluid flow models. These models incorporate the transport equations that describe conservation of mass, energy and momentum of the system, and require as input the physical and thermodynamic properties of the circulating fluid. Early numerical simulations incorporated the properties of pure H₂O to simulate the natural hydrothermal fluid. For example, the properties of H₂O were used to approximate the hydrothermal fluid in systems associated with shallow continental plutons (Cathles, 1981, Norton, 1979, Norton, 1982, Norton, 1984), submarine hydrothermal systems (Fehn and Cathles, 1979, Fehn et al., 1983, Jupp and Schultz, 2000, Jupp and Schultz, 2004), and sedimentary environments (Cathles and Smith, 1983, Garven, 1985, Wood and Hewett, 1982). While most hydrothermal fluids are indeed H₂O-rich, most also contain varying amounts of salts such as NaCl, KCl, CaCl₂, FeCl₂, etc., or volatiles such as CO₂ and CH₄ (Roedder, 1972, Holloway, 1984, Bodnar et al., 2014, Yardley and Bodnar, 2014).

While the one-component system H_2O is a reasonable approximation for the composition of many low-salinity aqueous hydrothermal fluids, the fact that H_2O is a one-component system results in a phase topology that differs significantly from that of multi-component fluids. An important difference in phase topology of the one component H_2O system, compared to multi-component fluid systems, is that in a one component system liquid and vapor only coexist along the liquid-vapor equilibrium curve that terminates at a critical end point (Figure 1a; C.P.), beyond which only a single-phase (supercritical) fluid may exist. Additionally, at temperatures above the critical temperature in a one-component system such as H_2O , all physical and thermodynamic properties of the fluid vary smoothly and continuously with changing temperature and pressure, and no discontinuities in fluid properties occur. Over the past several decades, a large experimental database describing the Pressure-Volume-Temperature-Composition (PVTx) properties of aqueous electrolyte systems has been generated, especially for the system H_2O -NaCl (Sourirajan and Kennedy, 1962, Bodnar et al., 1985, Knight and Bodnar, 1989, Bischoff and Rosenbauer, 1988). A complete summary of available experimental data thorough 2008 is available in Valyashko (2008). The available experimental data have been used to develop algorithms to estimate the physical and thermodynamic properties of more complex fluids at high temperatures and pressures (Tanger and Pitzer, 1989, Anderko and Pitzer, 1993, Palliser and McKibbin, 1998c, Palliser and McKibbin, 1998b, Palliser and McKibbin, 1998a, Driesner and Heinrich, 2007, Driesner, 2007). These various algorithms have subsequently been incorporated into numerical fluid flow models (Lewis and Lowell, 2009, Weis et al., 2014) that describe the circulation of hydrothermal fluids in the crust.

One of the basic physical properties required to model fluid flow is the fluid viscosity. In most early models, the viscosity of pure H_2O was used to approximate the viscosity of the natural fluid. In the liquid region, the viscosity of pure H_2O decreases smoothly and continuously with increasing temperature at constant pressure above the critical pressure (22.064 MPa), up to approximately the PT conditions along the critical isochore (Figure 1a). With increasing temperature above the critical isochore, the viscosity shows a reversal and increases with increasing temperature at PT conditions to the low-pressure side of the critical isochore, i.e., in the vapor field (Fig. 1a). While the viscosity of pure H_2O provides a reasonable approximation for low salinity fluids and at PT conditions that are in the liquid

field for pure H₂O (i.e., at pressure greater than the pressure on the liquid-vapor curve, or greater than the pressure on the critical isochore for a given temperature), the viscosity of pure H₂O is a poor analog for the viscosity of more saline fluids, especially at *PT* conditions in the vicinity of the pure H₂O liquid-vapor curve and at *PT* conditions that would be in the vapor field for pure H₂O.

The dynamic viscosity (η – Pa·s) is included in the expression for conservation of momentum associated with fluid flow. The conservation of momentum can be defined as (Norton and Knight, 1977):

$$\vec{v} = -\frac{k\rho}{\eta}(\nabla P - \rho\vec{g}) \quad (1)$$

Where $\vec{v}$ is a vector quantity describing mass flow rate per unit area ($\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$), k is the permeability (m^2), ρ is the fluid density ($\text{kg}\cdot\text{m}^{-3}$), η is the dynamic viscosity (Pa·s), ∇P is the pressure gradient and $\vec{g}$ is the standard acceleration due to gravity ($9.81 \text{ m}\cdot\text{s}^{-2}$).

Numerical models describing the viscosity for pure H₂O were developed within the International Association for the Properties of Steam (IAPS), which in 1989 became the International Association for the Properties of Water and Steam (IAPWS). The viscosity of H₂O established in 1964 was initially presented as a set of skeleton tables, together with recommended interpolation equations by Kestin and Whitelaw (1966). Later numerical models for the viscosity of H₂O included revisions to improve the accuracy of predictions (Kestin, 1980) and to better estimate the asymptotic divergent behavior of the viscosity near the critical point of water (Watson et al., 1980) (see Figure 1a). In the latest release of the IAPWS formulation 2008, the viscosity of pure H₂O is based on Huber et al. (2009) and replaces the IAPS formulation 1985 for the Viscosity of Ordinary Water Substance issued in 2003 (Cooper and Dooley, 2008). The IAPWS 2008 formulation is based on the density of H₂O calculated by the IAPWS-95 model of water and steam properties developed by Wagner and Pruß (2002). The viscosity of pure H₂O in the IAPWS formulation 2008 has estimated uncertainties between 1 and 7 %, and is limited in its *PT* range of applicability by the solidus of H₂O at low temperature ($\sim 0.0^\circ\text{C}$), an upper temperature limit of 900°C and an upper pressure limit varying from 1000 MPa at lower

temperatures to 300 MPa at higher temperatures. The viscosity of H₂O predicted by the IAPWS formulation 2008 is shown on Figure 1a.

The most commonly used model to calculate the viscosity of H₂O-NaCl at elevated *PT* conditions is that of Palliser and McKibbin (1998c). During our earlier studies to investigate fluid flow in submarine hydrothermal systems (Steele-MacInnis et al., 2012; Han et al., 2013), we observed unexpected behavior that could be traced back to viscosities predicted by the Palliser and McKibbin (1998c) model. This motivated us to investigate further, leading to the development of a revised model for viscosity of H₂O-NaCl at elevated *PT* conditions. Here, we compare viscosities of H₂O-NaCl determined experimentally with those predicted by the Palliser and McKibbin (1998c) model (referred to hereafter as P&M model), examine trends in viscosity predicted by the P&M model outside of the range of experimental data, and propose a revised empirical model that more faithfully reproduces the experimental data and displays smooth and expected extrapolation to *PT_x* conditions outside of the range of experimental data. We emphasize at the start that our goal is simply to develop an empirical numerical model that adequately describes variations of viscosity in temperature, pressure and composition space, and which can be incorporated into existing fluid flow models that describe flow behavior in natural systems. Developing a theoretical and experimental understanding of the mechanisms and molecular-scale interactions that lead to the observed viscosity variations deserves attention, but such efforts are well beyond the scope of this study and are not considered here. As mentioned by Abdulagatov et al. (2006), we note that the results presented here will be of interest to those involved in research related to steam-power generation, high temperature seawater desalination, geothermal energy production, oil recovery, and various industrial processes.

2 Experimental and Modeling Studies of the Viscosity of H₂O-NaCl at Elevated *PT* Conditions

Experimental characterization of the viscosity of binary H₂O-NaCl solutions is limited to relatively low temperature (<350 °C) and low salinity (<27 wt. % NaCl) conditions, except for data for the viscosity of molten NaCl at ≥800 °C. A summary of experimental studies that measured the viscosity of H₂O-NaCl solutions, including the *PT_x* range of the

experiments, experimental method used and number of data points, is provided in Table 1. Numerical models to estimate the viscosity of H₂O-NaCl solutions are thus best constrained within the *PT* range of the experimental data shown in Table 1, i.e., to approximately 300-350 °C and salinity less than 27 wt. % NaCl.

In addition to the P&M model, other models developed for the viscosity of aqueous solutions are those of Lencka et al. (1998), the TTG (Tammann-Tait-Gibson) model of Leyendekkers (1979), the model of Phillips et al. (1981) and that of Mao and Duan (2009) [hereafter referred to as M&D]. The TTG and Lencka et al. (1998) models are designed to estimate the viscosity of complex multicomponent electrolyte solutions. Thus, both models include the H₂O-NaCl system as a sub-system of the H₂O + electrolytes system, but these models are generally not used in hydrothermal fluid flow simulations for various reasons. In the case of the model of Lencka et al. (1998), the EOS is limited to ≤300 °C and concentrations up to 30 m (i.e. for H₂O-NaCl, ~64 wt. % NaCl). The TTG model is not recommended to predict viscosities of H₂O-NaCl solutions because Kestin and Shankland (1984) showed that this model tends to underestimate viscosity at high pressure and low temperature conditions (compared to experimental data).

The models by Phillips et al. (1981) and Mao and Duan (2009) are based on the same experimental data that are listed in Table 1. These models are designed to estimate viscosity of any H₂O-electrolyte solution. For H₂O-NaCl solutions, both models are limited to temperatures ≤350 °C, and salinities up to 22.6 and 26 wt. % NaCl (5 and 6 mol kg⁻¹ H₂O), and pressures up to 50 and 100 MPa, respectively. Mao and Duan (2009) report that their model agrees with experimental values to ≤1%, whereas Phillips et al. (1981) report that their model reproduces experimental data to ≤2%.

An EOS that predicts the viscosity of H₂O-NaCl over the widest range of temperature and pressure for all salinities (0-100 % NaCl) is that of Palliser and McKibbin (1998c). This model has no stated *PT* limits over which the model is valid, but based on the manner in which the P&M model was developed, it follows that the pressure and temperature limits are defined by the EOS chosen to predict the viscosity of pure H₂O, which is then used in the P&M model to calculate viscosity of H₂O-NaCl. The P&M viscosity model for brines is composed of two separate equations, one designed to calculate the viscosity in the temperature range from 0 to 800 °C, and the other to calculate the viscosity at temperature

≥ 800 °C. For temperatures above 800 °C, viscosity is a linear function of NaCl mass fraction, temperature, and the viscosity of pure H₂O at the same pressure and temperature. The viscosity at temperatures below 800 °C is described by a ninth order polynomial as a function of temperature:

$$\eta_b(P, T, x) = \frac{\eta_{H_2O}(T, P) \cdot (1+3x) \cdot \left(\frac{800-T}{800}\right)^9}{\left(\frac{800-T}{800}\right)^9 + \left(\frac{T}{800}\right)^9} + \frac{(\eta_{H_2O}(T, P) \cdot (1-x) + \mu_{NaCl}^{800} \cdot x) \cdot \left(\frac{T}{800}\right)^9}{\left(\frac{800-T}{800}\right)^9 + \left(\frac{T}{800}\right)^9} \quad (2)$$

where η_b is the dynamic viscosity of H₂O-NaCl fluid in kg m⁻¹ s; η_{H_2O} is viscosity of pure water at given PT ; μ_{NaCl}^{800} is a constant corresponding to the viscosity of molten NaCl at 800 °C calculated by eq. 5.2 from P&M, T is temperature in °C, P is pressure in bars, and x is NaCl weight fraction.

Viscosities of H₂O-NaCl fluids calculated using the P&M model for pressures of 22, 50 and 200 MPa are shown as a function of salinity and temperature on Figure 2, with several iso-viscosity lines plotted for reference. In some portions of PTx space the P&M model predicts viscosities that are unexpected, and these trends are a function of the nature of the algorithm used to calculate the viscosity. At pressures that are less than those on the pure H₂O liquid-vapor curve, or less than the pressure on the pure H₂O critical isochore, and higher than the pressure on the liquid + vapor + halite coexistence curve in the H₂O-NaCl system (hatched region in Figure 1b), most compositions in the H₂O-NaCl system are in the liquid field. However, the P&M model uses the viscosity of H₂O at the temperature and pressure of interest as a reference viscosity to calculate the viscosity of the H₂O-NaCl solution, and at PT conditions within the hatched area shown on Figure 1b pure H₂O is in the vapor field. Thus, because the model uses the viscosity of pure H₂O at the P and T of interest as the reference viscosity, and because the reference viscosity is for a “vapor” whereas the H₂O-NaCl fluid is a liquid, the viscosity is under-estimated in this PT region by the P&M model.

The P&M model also predicts viscosity trends that are unexpected in the temperature range from ~400 to 800 °C. The algorithm used to calculate viscosity in the P&M model and shown in equation (2) above can be broken down into two components, referred to here as the first term and second term on the right-hand side of Eq. (2). As shown in Figure

3, at temperatures less ~ 400 °C the viscosity is dominated by the first term of Eq. (2), whereas for temperatures between 400 and 800 °C the viscosity is dominated by the second term of Eq. (2). Moreover, owing to the form of the equation, between 400 and 800 °C the viscosity reaches a plateau and remains nearly constant with increasing temperature in this range (Figure 2, 3). Additionally, above 800 °C, a different form of relationship is used to calculate the viscosity in the P&M model, resulting in a significant and abrupt change in slope of iso-viscosity lines at 800 °C (Figure 2). Therefore, because viscosities of H₂O-NaCl fluids predicted by the P&M model show unexpected and, likely, incorrect trends in some regions of *PTx* space in which important hydrothermal processes in the crust occur, a new formulation to predict viscosities of H₂O-NaCl fluids was developed.

3 Model Development

The main criteria invoked to develop our model for the viscosity of H₂O-NaCl fluids over a wide range of *PTx* conditions relevant to crustal hydrothermal systems are (1) the model must accurately reproduce the viscosity of pure H₂O over the complete *PT* range, (2) the model must faithfully reproduce available experimental data for viscosities of H₂O-NaCl fluids, (3) the model should predict smooth variations in viscosity with changing *PTx* conditions, and with no discontinuities or abrupt changes in trend (slope) in *PTx* space, and (4) the *PTx* region in which the model predicts viscosities that are consistent with a liquid (higher density), and the *PTx* region in which the model predicts viscosities that are consistent with a vapor (lower density) must be consistent with phase topology in the H₂O-NaCl system that defines *PTx* regions in which liquid and vapor exist. The viscosity of pure H₂O calculated using the IAPWS-2008 Formulation (Huber et al., 2009) (Fig. 4a) as well as experimentally determined viscosities of various H₂O-NaCl mixtures (Fig. 4 b,c) (Kestin and Shankland, 1984, Pepinov et al., 1978, Semenyuk et al., 1977) are plotted on Figure 4 as a function of the fluid density. These, and additional experimental data listed in Table 1, have been used to develop and to test the degree to which the revised empirical model reproduces experimental data.

Figure 4a shows the viscosity of pure H₂O as a function of density along several isobars ranging from 0.1 MPa to 150 MPa. The viscosity shows a smooth and consistent variation as a function of density along individual isobars, with a consistent offset towards

higher density with increasing pressure. When NaCl is added to H₂O, the viscosity again varies in a smooth and expected manner as a function of density. Thus, the viscosity versus density trend for an H₂O-NaCl fluid with a salinity of 5 wt. % NaCl at a pressure of 10 MPa is offset to higher densities compared to the trend for pure H₂O at this same pressure (Fig. 4b). Moreover, the viscosity versus density trend for an H₂O-NaCl fluid with a salinity of 5 wt. % NaCl migrates to higher density with increasing pressure, analogous to the manner in which the trend for pure H₂O shown in Figure 4a migrates to higher densities. Finally, at a fixed pressure, the viscosity versus density trend migrates in a smooth and consistent manner to higher density with increasing salinity (Fig. 4c). The consistent manner in which the viscosity of H₂O-NaCl fluids varies with density as a function of changing salinity and pressure provides a basis for development of an algorithm to predict the viscosity of H₂O-NaCl fluids over a range of *PTx* conditions appropriate for crustal hydrothermal systems.

As shown on Figures 4b and 4c, the viscosity of an H₂O-NaCl fluid at a given pressure, temperature, and salinity (*PTx*) can be estimated from the viscosity of pure H₂O by determining the temperature at which pure H₂O has the same viscosity as that of the H₂O-NaCl fluid at the same pressure. Thus, the difference in density ($\Delta\rho$) between that of the H₂O-NaCl fluid at some pressure and that of pure H₂O having the same viscosity at that same pressure is converted into a temperature difference (ΔT). For example, Figure 5a shows the relationship between viscosity and density for pure H₂O and for an H₂O-NaCl fluid of some fixed salinity, both at the same pressure. At the conditions of interest (pressure and salinity of the H₂O-NaCl fluid), the viscosity of the H₂O-NaCl fluid is equal to the viscosity of pure H₂O having a density that is different from that of the H₂O-NaCl fluid. The density difference for these conditions is shown by ($\Delta\rho$). At the pressure of interest, the temperature at which H₂O will have the density estimated from $\Delta\rho$ may be calculated from the EOS. Then, the data shown in Figure 5a may be plotted in density-temperature space (Fig. 5b) to determine the temperature difference (ΔT) corresponding to the density difference ($\Delta\rho$). Thus, the viscosity of the H₂O-NaCl brine at some *PTx* condition is equal to the viscosity of pure H₂O at that same pressure and equivalent temperature $T^* = T + \Delta T$ according to:

$$\eta_{H_2O}(T^*, P) = \eta_b(x, T, P) \quad (3)$$

where η_{H_2O} is the dynamic viscosity of pure H₂O according to the IAPWS-2008 Formulation (Huber et al., 2009), η_{brine} is the viscosity of the H₂O-NaCl binary mixture of composition (x ; mass fraction of NaCl) at the pressure (P ; MPa) and temperature (T ; °C) of interest. The equivalent temperature T^* at which pure H₂O has the same viscosity as that of the H₂O-NaCl fluid at the same pressure is described by the relationship:

$$T^* = e_1 + e_2 \cdot T \quad (4)$$

The temperature increment, ΔT , shows a nearly linear dependence with temperature (Fig. 5c), and is independent of pressure (Fig. 6).

Developing an empirical relationship describing the value of some fluid parameter for a multi-component fluid using the value of that same parameter for pure H₂O as a reference is a common approach that has been used successfully by other workers. For example, Haas (1976) proposed a logarithmic dependence between T and T^* in his numerical model to estimate volumetric properties of the system H₂O-NaCl up to 325 °C, while Driesner (2007) used a linear dependence between T and T^* to describe volumetric properties of H₂O-NaCl up to 1,000 °C. In the present study, we found that the relationship between T and T^* to calculate viscosity is best described by fitting the coefficients e_1 and e_2 described by polynomial functions as shown below:

$$e_1 = a_1 \cdot x^{a_2} \quad (5)$$

$$e_2 = 1 - b_1 \cdot T^{b_2} - b_3 \cdot x^{a_2} \cdot T^{b_2} \quad (6)$$

where x is the weight fraction of NaCl, T is temperature in °C, and fitting coefficients a and b are listed in Table 2. For pure H₂O, T^* calculated according to Eqs. 4-6 is equal to T , i.e., $\Delta T = 0$.

The temperature range over which this model for the viscosity of H₂O-NaCl is valid is limited by the temperature ranges over which (1) the IAPWS 2008 Formulation for the

viscosity of pure H₂O and (2) the model of Driesner (2007) for the *PVT_x* properties of H₂O-NaCl fluid are valid. Thus, this revised model for the viscosity of H₂O-NaCl is valid from the temperature of the H₂O solidus (0.01 °C at $P = 0.01$ MPa) to ~1,000 °C, assuming that $T^* \leq 900$ °C. The temperature limit $T^* \leq 900$ °C applies because this is the upper temperature limit for the IAPWS 2008 Formulation. The upper temperature limit of the model (1,000 °C) is constrained by the upper temperature limit of the Driesner (2007) model. The upper pressure limit for the revised viscosity model ranges from 500 MPa when the equivalent temperature T^* is between 0-160 °C, 350 MPa when T^* is between 160-600 °C, and 300 MPa when T^* is between 600-900 °C. These upper pressure limits stem from constraints placed by the Driesner (2007) model for H₂O-NaCl and the IAPWS 2008 Formulation.

Figure 7 highlights the temperature-salinity (*T_x*) region in which the revised viscosity model is valid. The solid gray area in the upper left ($T > 900$ °C and low salinity) of Figure 7a (also shown enlarged in Fig. 7b) depicts the region in which $T^* > 900$ °C and, therefore, the model is not valid. The gray area shown along the bottom and right side of Figure 7a (low to moderate temperatures and all salinities) represents the *T_x* region in which $T^* < 0.01$ °C, and the model is also invalid in this region. The hatched region shown at moderate to high temperatures and salinities in Figure 7a (and along the right side of Fig. 7c) represents the liquid + halite (L+H) field. For $T^* \leq 160$ °C the pressure limit for the model is 500 MPa, for $T^* \leq 600$ °C the pressure limit is 350 MPa, and above 600 °C the pressure limit is 300 MPa. Insets show enlargements of regions (grey color) in which $T^* \leq 0$ °C (Fig. 7b) or > 900 °C (Fig. 7c).

4 Comparison of Revised Model with the Model of Palliser and McKibbin

The viscosity of H₂O-NaCl solutions predicted by the revised model, and by the earlier P&M model, were compared with experimental data from the studies listed in Table 1 (experimental data and results of calculations are listed in Appendix 1). Figure 8 shows the differences between the experimental viscosity and viscosity calculated by the revised model (Fig. 8a), and by the P&M (Fig. 8b) and M&D models (Fig. 8c). The scatter plots show that most calculated values show good agreement with experimental values and fall close to the 1:1 line. The hatched region indicates the area in which deviation from the 1:1

line is in the range $\pm 5\%$. The histograms shown by insets in Figure 8 show the percent difference (D) between the calculated and experimentally measured viscosity, calculated according to:

$$D = (\eta_{ref} - \eta_{calc}) / \eta_{ref} \cdot 100\% \quad (7)$$

where η_{ref} is the experimentally measured viscosity and η_{calc} is the viscosity of H₂O-NaCl calculated using either the current model or those of P&M or M&D. Viscosities predicted by the revised model agree with experimental values mostly within $\pm 10\%$, whereas differences between experimental values and those predicted by the P&M model extend to -40% and to $>20\%$ (Fig. 8B), especially for higher salinity fluids. Most viscosities predicted by the M&D model reproduce experimental data to $\pm 5\%$, with a few points up to $>80\%$ for PTx conditions at which pure H₂O is a vapor but the H₂O-NaCl fluid is a liquid (Fig. 8C).

Both the P&M and M&D models significantly under-estimate viscosities for some data, especially for PT conditions that are within the hatched area shown in Figure 1b. In this case large differences result because the P&M and M&D models both use the viscosity of H₂O at the temperature and pressure of interest as the reference viscosity. However, at pressures higher than those along the vapor + liquid + halite (P_{VLH}) coexistence curve and lower than the pressure on the H₂O liquid-vapor curve (P^L_S), the reference viscosity of H₂O that is used by P&M and M&D corresponds to that of a low density H₂O vapor phase, while at the same PT conditions the H₂O-NaCl phase is a high density liquid. Thus, these models underestimate the viscosity of the liquid phase at PT conditions close to the vapor + liquid + halite (P_{VLH}) coexistence curve for compositions such that H₂O-NaCl is in the one phase field.

The revised viscosity model reported here and the P&M model are valid at any salinity and thus can be used to estimate viscosity along the vapor-saturated halite liquidus. These two models were used to estimate viscosity at PTx conditions along the vapor + liquid + halite (VLH) coexistence curve. The compositions of the vapor and liquid phases in equilibrium with halite along the VLH coexistence curve are shown on Figure 9a. Note that, except for temperatures very close to the NaCl triple point (800.7 °C), the salinity of

the vapor phase is $\ll 1$ wt% NaCl, whereas the salinity of the liquid phase in equilibrium with vapor and halite varies from about 28 wt% NaCl at 100 °C to 100 wt% NaCl at 800.7 °C. Viscosities of the liquid and vapor phases along the vapor + liquid + halite (P_{VLH}) coexistence curve predicted by the P&M model and by the revised model are shown in Figure 9b. Viscosities predicted for the vapor phase by both models are nearly identical as expected, because the concentration of NaCl in the vapor phase is very low (except very near the NaCl triple point temperature of 800.7 °C) and thus the viscosity of the vapor phase is nearly identical to that of pure H₂O. Conversely, viscosities of the liquid phase predicted by the two models show different behavior. The P&M model underestimates the viscosity of the liquid phase and predicts a viscosity similar to that of the vapor at temperatures below ~300 °C because PT conditions along the vapor + liquid + halite coexistence curve in this region are in the vapor field for pure H₂O and the P&M model uses the viscosity of H₂O vapor as the reference viscosity for the calculations. The increase in viscosity of the liquid phase predicted by the P&M model at about 400 °C (Figure 9b) is related to the form of Eq. 2, as discussed above. The viscosity of a liquid is expected to decrease with increasing temperature in concert with decreasing density as temperature increases. Conversely, the viscosity of a liquid is expected to increase as the salinity increases and approaches the viscosity of the molten (H₂O-free) salt. These two competing effects for the liquid phase along the vapor + liquid + halite coexistence curve result in an initial decrease in viscosity with increasing temperature (and increasing salinity of the liquid), until the effect of increasing salinity overcomes the temperature effect at ~400 °C (corresponding to a salinity of ~45 wt.% NaCl). Thus, the viscosity of the liquid phase along the vapor + liquid + halite coexistence curve predicted by the present model is consistent with the known (or expected) relationship between viscosity, temperature and salinity, and shows a decrease in the viscosity with increasing temperature, followed by an increase in the viscosity at higher temperatures, reflecting the effect of increasing NaCl concentration.

For further comparison of viscosities for H₂O-NaCl predicted by the P&M model and those predicted by the revised model described here, the viscosity at 50 MPa was calculated using both models over the range 100 - 1000 °C and salinity from 0-100 wt. % NaCl. At these conditions, the P&M model shows reversals in the magnitude of viscosity

at ~400 °C that are not expected based on variations in density (or other fluid properties) at these conditions (Fig. 10a). Moreover, the P&M model shows discontinuities in iso-viscosity lines at 800 °C for high salinity fluids that are related to the form of the functions used to calculate viscosity above and below this temperature (Figs. 2; 10a). The model described here shows a systematic and expected decrease in viscosity with increasing temperature at any salinity and does not show any unexpected reversals or discontinuities in viscosity (Fig. 10b). Viscosities predicted by the two models are compared on Figure 10c, where the percent difference in viscosity is contoured in T-x space. The difference is calculated according to Eq. (7), where η_{ref} is the viscosity predicted by the P&M model and η_{calc} is the viscosity predicted by the revised model. Differences between the two models are small (between -4 to 10 %) for salinities less than about 20-30 wt. % NaCl and temperatures less than about 350 °C (Fig. 10c). At temperatures above 400 °C the difference in viscosity predicted by the two models for liquid H₂O-NaCl solutions varies between 55-85 %. For example, at a salinity of 50 wt. % NaCl and 500 °C and 50 MPa, the viscosity estimated by the P&M model is 765 μ Pa s and that predicted by the revised model is 145 μ Pa s (Fig. 10a, b). As discussed above and shown on Figure 1b, in the *PT* range in which the H₂O-NaCl solution is a high-density liquid but pure H₂O is a low-density vapor, the P&M model predicts a viscosity that is lower than that predicted by the revised model. Conversely, in the *PT* range in which both the H₂O-NaCl solution and pure H₂O have liquid-like densities, the P&M model predicts viscosities that are significantly higher than those predicted by the revised model. The temperature at which the P&M model transitions from under-estimating the viscosity of H₂O-NaCl to over-estimating the viscosity is about 400 °C (see Figs. 9b and 10). We note that the T-x range in which the largest differences are observed corresponds to the temperature and salinity conditions observed in many magmatic-hydrothermal ore deposits, such as the porphyry copper deposits, and in the sub-seafloor portion of hydrothermal systems associated with magma emplacement at mid-ocean ridges.

Viscosities calculated with the current model for H₂O-NaCl fluids having salinities of 3.2 (seawater), 5, 10, 25, 50 and 75 wt. % NaCl and temperatures and pressures ranging between 100-1000 °C and 0-300 MPa, respectively, are shown in Figure 11. Note that

viscosities have only been calculated for PTx conditions within the single-phase (liquid or vapor) fields.

As an example of the application of the revised model and potential implications for numerical modeling of fluid flow in hydrothermal systems, we have calculated the viscosities of hydrothermal fluids circulating through a submarine hydrothermal system using both the revised model and the P&M model. We have taken the temperature, pressure, fluid composition and density data along a sub-seafloor flow path from Steele-MacInnis et al. (2012) and show the viscosities calculated from the two models in Figure 12. The temperature distribution in the sub-seafloor after the system has been active for 80 years is shown in Figure 12 a. The salinity(ies) and temperatures of the fluid(s) along the fluid flow path A-B-C-D-E shown in Figure 12 are shown in Figures 12b, c. Calculated viscosities at the temperatures, pressures and salinities along the flow path are shown on Figure 12d. Along the portion of the flow path where the fluid is in the one phase field (A-C), viscosities predicted by the two models are similar. However, when the fluid undergoes immiscibility to produce a high salinity liquid in equilibrium with a low salinity vapor (C-D), the two models predict similar viscosities for the vapor phase, but the P&M model predicts a viscosity for the brine (liquid) that is $\sim 2\times$ greater than that predicted by the revised model. Along the flow path from the sub-seafloor to the seafloor (D-E) the fluid is once again in the one-phase field and viscosities predicted by the two models are again similar. This example documents differences between the two models and potential implications for modeling hydrothermal systems, especially if high salinity fluids are involved and/or the PT conditions are in the region where the H_2O -NaCl fluid is a liquid and the pure H_2O reference state would be a vapor. In the example shown, the higher viscosities estimated by the P&M model for the brine (liquid) phase in the two-phase region would predict that more of the brine would remain at depth in the system, compared to the revised model in which the brine phase has a lower viscosity and would be more likely to be transported upwards towards the seafloor during hydrothermal circulation.

5 Summary and Discussion

This study compares viscosities of H_2O -NaCl fluids predicted by the model of Palliser and McKibbin (1998c) (P&M model) with a revised empirical model for viscosity

developed here. The revised model incorporates an equivalent temperature, T^* , at which the viscosity of pure H_2O has the same viscosity as that of an H_2O -NaCl fluid at the same pressure. This revised viscosity model shows better overall agreement with experimental data compared to the P&M model, and does not show unexpected trends in viscosity versus temperature or salinity that characterize the P&M model. The revised model can be used to simulate fluid flow in various geological environments over the range 0-1000 °C, ≤ 500 MPa and 0-100 wt.% NaCl. The revised model shows good agreement with the limited amount of experimental data available for H_2O -NaCl at elevated PTx conditions. As expected based on available data and our understanding of how the viscosity of aqueous fluids should change as temperature and pressure (density) change, an increase in temperature at constant Px (decrease in density) results in a decrease in viscosity, while an increase in salinity at constant PT or an increase in pressure at constant Tx both lead to an increase in density and a concomitant increase in viscosity.

While the properties that affect fluid viscosity are, in general, understood, theoretical models describing temperature, pressure and composition effects on fluid viscosity have not been developed. Indeed, Viswanath et al. (2007) note that “*There has been no comprehensive theory on the viscosity of liquids so far because of its complex nature.*” And that “*In contrast, semi-empirical and empirical methods provide reasonable results but lack generality of approach.*” Here, we offer a few general observations and interpretations that are consistent with the variations in viscosity of H_2O and H_2O -NaCl solutions as a function of temperature, pressure and composition that are consistent with our incomplete understanding of viscosity variations in PTx space.

As shown on Figure 1a, along any isobar greater than the critical pressure of H_2O (22.064 MPa), the viscosity of H_2O decreases with increasing temperature up to about 375-500°C (depending on pressure), and then increases with further increase in temperature. The viscosity of a fluid depends on the nature of the molecular interactions in the fluid. As the temperature of liquid H_2O increases, the H_2O molecules move faster and, as such, the amount of time each H_2O molecule spends interacting with neighboring H_2O molecules decreases with increasing temperature. This, in turn, decreases the average intermolecular force in the fluid. The observed decrease in viscosity of H_2O in the liquid region is consistent with this interpretation. As temperature continues to increase, and the fluid density decreases to become more gas-like,

the molecules move faster and the frequency of molecular collisions increases. As such, a larger portion of the H₂O molecules are “in contact” with another molecule and the average intermolecular force between all molecules in the volume increases, thus increasing the viscosity as temperature continues to increase. This reversal in trend of viscosity with temperature occurs approximately along the critical isochore (Figure 1a) where H₂O changes from being “liquid-like” to “gas-like”.

Upon addition of salt to H₂O, the phase topology of the two-phase system changes dramatically and this, in turn, affects the topology of the viscosity variations as a function of temperature and pressure. As noted above, addition of salt to H₂O results in elimination of the critical end point and the development of a two-phase region (Figure 11). Additionally, except at very low salinities, the fluid remains “liquid-like” to much higher temperatures, compared to pure H₂O and the reversal in viscosity with increasing temperature observed for pure H₂O is absent. At a given temperature, the viscosity of H₂O-NaCl solutions increases with increasing salinity. This is explained by the fact that when NaCl is added to H₂O, the NaCl dissociates into Na⁺ and Cl⁻, and these ions interact with the polar H₂O molecule. A hydration shell forms around each ion, causing the solution structure to “collapse” and increase the density and the extent of molecular interactions. These ion-dipole interactions are stronger than the hydrogen bonding forces in pure H₂O and, combined with the increased density leads to an increase in fluid viscosity. Abdulagatov et al. (2006) note that the viscosity of H₂O-NaCl solutions increases monotonically with increasing salinity and relate the increase in salinity to various solute-solvent interactions, including ion-ion, ion-solvent and solvent-solvent interactions, as well as the size and shape of the ions. These workers also note that for some aqueous electrolyte solutions, such as H₂O-KCl, the viscosity initially decreases with increasing salinity, followed by a reversal at higher salinities.

Acknowledgments: This material is based on work supported in part by the National Science Foundation under Grant No. EAR-1019770 to RJB. We thank Robert McKibbin and Chris Palliser for useful discussions concerning their model for the viscosity of H₂O-NaCl at elevated temperatures and pressures. Kayla Lewis confirmed that the values we obtained with the Palliser and McKibbin model were consistent with values predicted by

499 that model in the FISHERS modeling code. Shreya Singh made us aware of the fact that the
500 Palliser and McKibbin model was predicting “unusual behavior” at high temperatures, and
501 this motivated us to examine the model more closely.
502

503 **6 Nomenclature**

504 $\vec{g}$ – standard acceleration due to gravity ($9.81 \text{ m}\cdot\text{s}^{-2}$)

505 k – permeability (m^2)

506 P – pressure (Pa)

507 T – temperature (°C)

508 T^* – equivalent temperature at which eq. (3)

509 x – mass fraction of NaCl

510 η – dynamic viscosity ($\text{Pa}\cdot\text{s}$)

511 η_b – dynamic viscosity of brine, H_2O -NaCl ($\text{Pa}\cdot\text{s}$)

512 $\eta_{\text{H}_2\text{O}}$ – dynamic viscosity of pure water ($\text{Pa}\cdot\text{s}$)

513 η_{NaCl}^{800} is a constant corresponding to the viscosity of molten NaCl at 800 °C calculated by eq.

514 5.2 from Palliser and McKibbin (1998c), $1500 \text{ }\mu\text{Pa s}$

515 ρ – density of the fluid ($\text{kg}\cdot\text{m}^{-3}$)

516 $\vec{u}$ – mass flow rate per unit area vector ($\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$)

517 ∇ – gradient operator, (m^{-1}) $\frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}$

518

519

Figure captions

Figure 1. (a) Viscosity of pure H₂O in the *PT* range 0-100 MPa and 100-900 °C calculated using the Huber et al. (2009) model. C.P. is the critical point (373.946 °C, 22.064 MPa), L refers to the liquid phase (density greater than the critical density), V refers to the vapor phase (density less than the critical density), and ρ_{crit} indicates the critical isochore. (b) Pressure-Temperature plot showing the liquid-vapor coexistence curve of pure water (L+V H₂O) that terminates at the critical point (C.P.) and the critical isochore for H₂O (dashed line labeled ρ_{crit}). Also shown is the vapor + liquid + halite equilibrium curve (L+V+H) for H₂O-NaCl, and the field in which an H₂O-NaCl vapor phase and halite are in equilibrium (V+H). The hatched region defined by pressures less than the H₂O liquid-vapor curve and pressure along the critical isochore, and pressures greater than the pressure on the L+V+H curve identifies the region of *PT* space in which the P&M model may predict viscosities that are too low owing to the fact that in this *PT* region H₂O is a vapor (density less than the critical density) whereas many H₂O-NaCl compositions are liquid in this *PT* region.

Figure 2. Viscosity of H₂O-NaCl fluids at 22 (a), 50 (b), and 200 (c) MPa in Temperature-Salinity (Tx) space calculated from the P&M model. The shaded regions in the lower right of the diagrams outlined by dashed lines represent the regions of Tx space in which two phases, either liquid + vapor (L+V) or liquid + halite (L+H), coexist and the model is not applicable in these regions of T-x space.

Figure 3. (top) Viscosity as a function of temperature predicted by equation (2) (P&M model) at 30 and 100 MPa for salinities of 5, 25 and 50 wt. % NaCl. (bottom) Contributions of the first (solid lines) and second (dashed lines) terms of equation 2 to the total viscosity (shown by dashed lines on the top graph) at different pressure and composition conditions. Note that the total viscosity is dominated by the contribution from the first term of equation 2 at temperatures less than about 400

°C and is dominated by the contribution from the second term of equation 2 at temperatures greater than about 400 °C.

Figure 4. (a) Dynamic viscosity of H₂O as a function of density at various pressures calculated from the Huber et al. (2009) formulation; (b) experimentally determined viscosity as a function of density for a 5 wt. % NaCl solution at various pressures (Pepinov et al., 1978, Semenyuk et al., 1977). Dashed lines are viscosities calculated by the revised model and show the expected behavior of the viscosity as a function of PT_x conditions; (c) experimentally determined viscosity at 10 MPa as a function of density for various salinities (Pepinov et al., 1978, Semenyuk et al., 1977, Kestin and Shankland, 1984). Dashed lines are viscosities calculated by the revised model and show the expected behavior of viscosity as a function of $P\rho_x$ conditions. Note that a, b and c have different viscosity (Y) scales.

Figure 5. (a) Schematic representation showing the viscosity of pure H₂O (black line) and that of an H₂O-NaCl solution (red line), both as a function of density at the same pressure. A line connecting two iso-viscosity points on the two different curves defines the difference in density, $\Delta\rho$, of the two fluids having the same viscosity; (b) Temperature as a function of density for pure H₂O (black line) and for the same H₂O-NaCl fluid (red line) as in (a), plotted along isobars. The difference in density $\Delta\rho$ defined by the viscosity-density plot in (a) is converted into a temperature difference, ΔT ; (c) The temperature increment, ΔT , plotted as a function of temperature for various salinities obtained from experimental studies. The inset shows ΔT for pure liquid NaCl.

Figure 6. Temperature increment, ΔT , for various experimental temperatures as a function of pressure using data from (Pepinov et al., 1978, Semenyuk et al., 1977). ΔT does not show a pressure dependence; thus, Equation (3) can be used to calculate viscosities of H₂O and H₂O-NaCl fluids at constant pressure for input into Equation (3).

Figure 7. (a) T^* calculated using Equations (4-6) plotted as a function of temperature and salinity. The grey shaded region indicates the region of Tx space in which T^* is outside of the range in which the model of Huber et al. (2009) is valid. The hatched region represents the field in which liquid and halite (L+H) coexist.– (b) enlargement of the low salinity, high temperature region of Tx space where $T^* > 900$ °C (grey color) and the model described here is not valid. (c) enlargement of the high salinity, high temperature region of Tx space where $T^* \leq 0.01$ °C °C (grey color) and the model described here is not valid.

Figure 8. Relationship between experimentally determined viscosities of H₂O-NaCl and viscosity calculated by the revised model (a) the P&M model (b) and the Mao and Duan (2009) model (c). Experimental data are from the various studies listed in Table 1. Black line indicates 1:1 correlation, and the hatched region along the 1:1 line represents ± 5 % difference from the 1:1 correlation. The color scale indicates the salinity. The histograms shown in insets show the percent difference between model predicted and experimental results (calculated for n points), calculated according to equation (7). Note the different scales for both axes on the different histograms.

Figure 9. (a) Salinity of the vapor (blue line) and liquid (red line) phases in equilibrium with halite along the liquid-vapor-halite coexistence curve (L+V+H; see Figure 1b), calculated using the Driesner (2007) EOS. (b) Dynamic viscosity of the liquid and vapor phases along L+V+H curve shown in (a), calculated using the P&M model (dashed lines) and the revised model developed here (solid lines).

Figure 10. (a) Dynamic viscosity of H₂O-NaCl fluids calculated using the P&M model. (b) Dynamic viscosity of H₂O-NaCl fluids calculated with the present model. (c) Percent difference between viscosity predicted by the P&M model and the current model for various temperature and salinity conditions at 50 MPa. L+H represents the field in which liquid + halite coexist, L + V is the region in which liquid +

vapor coexist. Small open circle labeled C.P. represents the critical point corresponding to the pressure of interest (50 MPa).

Figure 11. Dynamic viscosity calculated by the current model for salinities of 3.2, 5, 10, 25, 50 and 75 wt. % NaCl at pressures between 0 and 300 MPa. The grey region indicates the region where equivalent temperature T^* is above 900 °C and the current model is not valid, L+V+H indicates the phase boundary along which liquid + vapor + halite coexist, V+H indicates the field in which vapor + halite coexist, L+V represents the region in which liquid + vapor coexist, and L + H indicates the region in which liquid + halite coexist. C.P. represents the critical point, and the line labeled ρ_{crit} that originates at the critical point represents the critical isochore.

Figure 12 (a) The temperature distribution in the sub-seafloor at 80 years after emplacement of a magma body at a mid-ocean ridge (MOR) hydrothermal system from Steele-MacInnis et al. (2012). The top of the cross section represents the seafloor and the bottom left represents the center of the heat source that is beneath the lowest level shown. The letters A-E indicate points along the flow path with immiscibility occurring in the region C-D. Variation in salinity (b) temperature (c) and viscosity (d) of a hydrothermal fluid as it flows along the PT path in the subsurface at a mid-ocean ridge hydrothermal system. Immiscibility in the region C-D produces a high salinity, high-density brine and a low salinity, low-density vapor. Viscosities of the fluids along the flow path calculated from the revised model and the P&M model are shown as solid (revised model) and dashed (P&M) lines on d.

Table captions

Table 1. Summary of experimental data for the viscosity of H₂O and H₂O-NaCl fluids

Table 2. Coefficients for Equation (4)

References

- Abdulagatov IM, Zeinalova AB & Azizov ND (2006) Viscosity of aqueous electrolyte solutions at high temperatures and high pressures. Viscosity B-coefficient. Sodium Iodide. *Journal of Chemical & Engineering Data*, **51**, 1645-1659.
- Anderko A & Pitzer KS (1993) Equation-of-state representation of phase-equilibria and volumetric properties of the system NaCl-H₂O above 573 K. *Geochimica et Cosmochimica Acta*, **57**, 1657-1680.
- Bischoff JL & Rosenbauer RJ (1988) Liquid-vapor relations in the critical region of the system NaCl-H₂O from 380 to 415 °C: A refined determination of the critical point and two-phase boundary of seawater. *Geochimica et Cosmochimica Acta*, **52**, 2121-2126.
- Bodnar R, Burnham C & Sterner S (1985) Synthetic fluid inclusions in natural quartz. III. Determination of phase equilibrium properties in the system H₂O-NaCl to 1000 °C and 1500 bars. *Geochimica et Cosmochimica Acta*, **49**, 1861-1873.
- Bodnar R, Lecumberi-Sanchez P, Moncada D & Steele-MacInnis M (2014) Fluid inclusions in hydrothermal ore deposits. In: *Treatise on Geochemistry* (ed. Scott S. D.). 2nd edn. Elsevier Ltd., Amsterdam.
- Bredehoeft JD & Norton DL (1990) Mass and Energy Transport in a Deforming Earth's Crust. In: *The Role of Fluids in Crustal Processes* (ed. N.R. Council). The National Academies Press, Washington, DC.
- Cathles LM (1981) Fluid flow and genesis of hydrothermal ore deposits. In: *Economic Geology 75th Anniversary Volume* (ed. B.J. Skinner). The Economic Geology publishing company, Lancaster.
- Cathles LM & Smith AT (1983) Thermal constraints on the formation of Mississippi Valley-Type lead-zinc deposits and their implications for episodic basin dewatering and deposit genesis. *Economic Geology*, **78**, 983-1002.
- Cooper J & Dooley R (2008) Release of the IAPWS formulation 2008 for the viscosity of ordinary water substance. Berlin, Germany: The International Association for the Properties of Water and Steam.
- Driesner T (2007) The system H₂O-NaCl. II. Correlations for molar volume, enthalpy, and isobaric heat capacity from 0 to 1000 °C, 1 to 5000 bar, and 0 to 1 X-NaCl. *Geochimica et Cosmochimica Acta*, **71**, 4902-4919.
- Driesner T & Heinrich CA (2007) The system H₂O-NaCl. I. Correlation formulae for phase relations in temperature-pressure-composition space from 0 to 1000 °C, 0 to 5000 bar, and 0 to 1 XNaCl *Geochimica et Cosmochimica Acta*, **71**, 4880-4901.
- Fehn U & Cathles LM (1979) Hydrothermal convection at slow-spreading mid-ocean ridges. *Tectonophysics*, **55**, 239-260.
- Fehn U, Green KE, Von Herzen RP & Cathles LM (1983) Numerical models for the hydrothermal field at the Galapagos Spreading Center. *Journal of Geophysical Research: Solid Earth*, **88**, 1033-1048.

- Garven G (1985) The role of regional fluid flow in the genesis of the Pine Point Deposit, Western Canada sedimentary basin. *Economic Geology*, **80**, 307-324.
- Haas JL (1976) Physical properties of the coexisting phases and thermochemical properties of the H₂O component in boiling NaCl solutions. U. S. Geological Survey Bulletin 1421-A.
- Holloway JR (1984) Graphite-CH₄-H₂O-CO₂ equilibria at low-grade metamorphic conditions. *Geology*, **12**, 455-458.
- Huber M, Perkins R, Laesecke A, Friend D, Sengers J, Assael M, Metaxa I, Vogel E, Mareš R & Miyagawa K (2009) New international formulation for the viscosity of H₂O. *Journal of Physical and Chemical Reference Data*, **38**, 101-125.
- Jupp TE & Schultz A (2000) A thermodynamic explanation for black smoker temperatures. *Nature*, **403**, 880-883.
- Jupp TE & Schultz A (2004) Physical balances in subseafloor hydrothermal convection cells. *Journal of Geophysical Research: Solid Earth*, **109**, B05101.
- Kestin J. (Year) Published. The Transport Properties of Water Substance. Water and steam: their properties and current industrial applications: proceedings of the 9th International Conference on the Properties of Steam, 10-14 September 1979, 1980 Technische Universität München, FRG. Pergamon, 283.
- Kestin J & Shankland IR (1984) Viscosity of aqueous NaCl solutions in the temperature range 25–200 °C and in the pressure range 0.1–30 MPa. *International Journal of Thermophysics*, **5**, 241-263.
- Kestin J & Whitelaw J (1966) Sixth international conference on the properties of steam—transport properties of water substance. *Journal of Engineering for Gas Turbines and Power*, **88**, 82-104.
- Knight CL & Bodnar RJ (1989) Synthetic fluid inclusions: IX. Critical PVTX properties of NaCl-H₂O solutions. *Geochimica et Cosmochimica Acta*, **53**, 3-8.
- Lencka MM, Anderko A, Sanders SJ & Young RD (1998) Modeling viscosity of multicomponent electrolyte solutions. *International Journal of Thermophysics*, **19**, 367-378.
- Lewis KC & Lowell RP (2009) Numerical modeling of two-phase flow in the NaCl-H₂O system: Introduction of a numerical method and benchmarking. *Journal of Geophysical Research: Solid Earth*, **114**, B05202.
- Leyendekkers JV (1979) The viscosity of aqueous electrolyte solutions and the TTG model. *Journal of Solution Chemistry*, **8**, 853-869.
- Mao S & Duan Z (2009) The viscosity of aqueous alkali-chloride solutions up to 623 K, 1,000 bar, and high ionic strength. *International Journal of Thermophysics*, **30**, 1510-1523.
- Norton DL (1979) Transport phenomena in hydrothermal systems: the redistribution of chemical components around cooling magmas. *Bulletin de Mineralogie*, **102**, 471-486.
- Norton DL (1982) Fluid and heat transport phenomena typical of copper-bearing pluton environments. In: *Advances in Geology of the Porphyry Copper Deposits, Southwestern North America* (ed. S.R. Titley). University of Arizona Press, Tucson, Arizona.
- Norton DL (1984) Theory of hydrothermal systems. *Annual Review of Earth and Planetary Sciences*, **12**, 155-177.
- Norton DL & Knight JE (1977) Transport phenomena in hydrothermal systems; cooling plutons. *American Journal of Science*, **277**, 937-981.

- Palliser C & McKibbin R (1998a) A model for deep geothermal brines, I: T-p-X state-space description. *Transport in Porous Media*, **33**, 65-80.
- Palliser C & McKibbin R (1998b) A model for deep geothermal brines, II: thermodynamic properties – density. *Transport in Porous Media*, **33**, 129-154.
- Palliser C & McKibbin R (1998c) A model for deep geothermal brines, III: thermodynamic properties – enthalpy and viscosity. *Transport in Porous Media*, **33**, 155-171.
- Pepinov RI, Yusufova VD, Lobkova NV & Panakhov IA (1978) Experimental study of the viscosity of aqueous sodium chloride and sodium sulfate solutions at high temperature and pressures. *High Temperature*, **16**, 960-965.
- Phillips SL, Igbene A, Fair JA, Ozbek H & Tavana M (1981) A technical databook for geothermal energy utilization. *Lawrence Berkeley National Laboratory*.
- Roedder E (1972) *Composition of fluid inclusions*.
- Semenyuk EN, Zarembo VI & Fedorov MK (1977) Apparatus for measuring viscosities of electrolyte-solutions at temperatures of 273-673 K and pressures up to 200 MPa. *Journal of Applied Chemistry of the USSR*, **50**, 298-302.
- Sourirajan S & Kennedy GC (1962) The system H₂O-NaCl at elevated temperatures and pressures. *American Journal of Science*, **260**, 115-141.
- Steele-MacInnis M, Han L, Lowell RP, Rimstidt JD & Bodnar RJ (2012) The role of fluid phase immiscibility in quartz dissolution and precipitation in sub-seafloor hydrothermal systems. *Earth and Planetary Science Letters*, **321**, 139-151.
- Tanger JC & Pitzer KS (1989) Thermodynamics of NaCl-H₂O: A new equation of state for the near-critical region and comparisons with other equations for adjoining regions. *Geochimica et Cosmochimica Acta*, **53**, 973-987.
- Valyashko VM (2008) *Hydrothermal Properties of Materials*, Wiley.
- Viswanath DS, Ghosh TK, Prasad DHL, Dutt NVK & Rani KY (2007) *Viscosity of Liquids. Theory, Estimation, Experiment, and Data*, Dordrecht, The Netherlands, Springer.
- Wagner W & Pruß A (2002) The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. *Journal of Physical and Chemical Reference Data*, **31**, 387-535.
- Watson JTR, Basu R & Sengers JV (1980) An improved representative equation for the dynamic viscosity of water substance. *Journal of Physical and Chemical Reference Data*, **9**, 1255-1290.
- Weis P, Driesner T, Coumou D & Geiger S (2014) Hydrothermal, multiphase convection of H₂O- NaCl fluids from ambient to magmatic temperatures: a new numerical scheme and benchmarks for code comparison. *Geofluids*, **14**, 347-371.
- Wood J & Hewett T (1982) Fluid convection and mass transfer in porous sandstones - a theoretical model. *Geochimica et Cosmochimica Acta*, **46**, 1707-1713.
- Yardley BW & Bodnar RJ (2014) Fluids in the Continental Crust. *Geochemical Perspectives*. European Association of Geochemistry.

Table 1. Summary of experimental data for the viscosity of H₂O and H₂O-NaCl fluids

Salinity (wt. % NaCl)	Temperature (°C)	Pressure (bars)	Method	Uncertainty (%)	Number of data points	Reference
0.03-27.5	0-154	1-389.8	<i>n.p.</i>	<i>n.p.</i>	1161	(Ozbek et al., 1977)
0-6.8	0-300	100-1500	CAP	2	110	(Semenyuk et al., 1977)
0-24.7	10-40	1-311.6	OSD	0.3	166	(Kestin et al., 1977)
1-20	20-350	2-300	CAP	0.3	186	(Pepinov et al., 1978)
2.7-24	18-154	1-311.6	OSD	0.3	189	(Kestin et al., 1978)
0.6-6.5	5-95	1	Ub	0.02	60	(Out and Los, 1980)
5.9-26.1	24-201.5	1-321	OSD	0.2	381	(Kestin and Shankland, 1984)
0.1-26	20	1	<i>n.p.</i>	<i>n.p.</i>	23	(Haynes, 2014)
100	800-975	1	OSC	2.4	40	(Ito et al., 1989)

OSD: oscillating disc; Ub: Ubbelohde; CAP: capillary; n.p: not provided

Table 2. Fitting coefficients for equation 4

	Value
a_1	-35.9858
a_2	0.80017
b_1	1e-6
b_2	-0.05239
b_3	1.32936