



Research paper

AqSo_NaCl: Computer program to calculate p-T-V-x properties in the H₂O-NaCl fluid system applied to fluid inclusion research and pore fluid calculation

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ABSTRACT

The program AqSo_NaCl has been developed to calculate pressure - molar volume - temperature - composition (p-V-T-x) properties, enthalpy, and heat capacity of the binary H₂O-NaCl system. The algorithms are designed in BASIC within the Xojo programming environment, and can be operated as stand-alone project with Macintosh-, Windows-, and Unix-based operating systems. A series of ten self-instructive interfaces (modules) are developed to calculate fluid inclusion properties and pore fluid properties. The modules may be used to calculate properties of pure NaCl, the halite-liquidus, the halite-vapourus, dew-point and bubble-point curves (liquid-vapour), critical point, and *SLV* solid-liquid-vapour curves at temperatures above 0.1 °C (with halite) and below 0.1 °C (with ice or hydrohalite). Isochores of homogeneous fluids and unmixed fluids in a closed system can be calculated and exported to a.txt file. Isochores calculated for fluid inclusions can be corrected according to the volumetric properties of quartz. Microthermometric data, i.e. dissolution temperatures and homogenization temperatures, can be used to calculate bulk fluid properties of fluid inclusions. Alternatively, in the absence of total homogenization temperature the volume fraction of the liquid phase in fluid inclusions can be used to obtain bulk properties.

1. Introduction

The water-salt fluid system occurs as the common liquid, vapour and supercritical phases in a variety of natural rocks and soils, and is described in numerous publications, which include fluid inclusion studies (e.g. Roedder, 1984). Among the large variety of types of salt, the binary H₂O-NaCl system is a good model of many natural occurring fluids. This binary fluid system can be classified thermodynamically according to its critical curve (Konynenburg and Scott, 1980): type 1, i.e. the critical curve connects the critical points of the two pure components (Fig. 1). The pressure-temperature-volume-composition properties (pTVx) of binary H₂O-NaCl solutions have been described by numerous empirical equations that usually cover only limited ranges in temperature, pressure and composition. For example, the freezing point depression of water at vapour saturation is described with a purely empirical equation that relates temperatures between 0 and -21.2 °C with compositions up to 23.6 mass% NaCl (e.g. Potter et al., 1978), whereas the pressure and molar volume are not defined. Other studies investigated the liquid-vapour immiscibility in the H₂O-NaCl system at higher temperatures and pressures and developed new smoothed data sets (e.g. Bischoff and Pitzer, 1989) and semi-empirical equations of state (e.g.

Bowers and Helgeson, 1983; Anderko and Pitzer, 1993), but again for a very limited range of temperatures and pressures. Moreover, extrapolation to conditions that exceed the range of the experimental fitting procedures may result in highly inaccurate numbers.

Driesner and Heinrich (2007) and Driesner (2007) were the first to give a semi-empirical model for the entire composition range between pure H₂O and pure NaCl, and temperature limits 0 °C to 1000 °C, and pressure limits up to 500 MPa, with reasonable extrapolation possibilities. This model is based on the unified Helmholtz energy function of Haar et al. (1984) for pure H₂O that was designed for the temperature range 0–1000 °C and pressure range up to 1500 MPa. Haar et al. (1984) claimed that their equation of state can be extrapolated up to 2227 °C and down to -13 °C, and up to pressure of 3000 MPa. Consequently, Driesner and Heinrich (2007) and Driesner (2007) were able to expand their model to these high temperature-pressure conditions by modifying the temperature parameter in the equation of state of Haar et al. (1984). Temperature is replaced by a parameter that is a function of the concentration of NaCl, temperature and pressure.

The complexity of the Driesner and Heinrich (2007) and Driesner (2007) model does not allow an easy-to-calculate method that can be performed in a simple spreadsheet. Therefore, in this study the numerous

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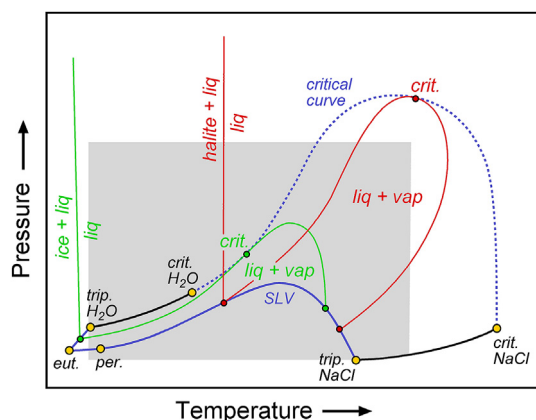


Fig. 1. Distorted schematic temperature-pressure diagram of the H_2O -NaCl system. The saturation properties (liquid + vapour) of pure H_2O and pure NaCl are illustrated between the triple and critical point with black curves. The eutectic and peritectic point are illustrated with *eut.* and *per.*, respectively. The green curve represents the liquid and vapour immiscibility of a low salinity fluid, and the red curve high salinity fluid. The liquidus of the low salinity fluid illustrates the dissolution ice in to liquid, and of the high salinity of halite in to liquid. The dashed blue curve is the critical curve, i.e. a collection of all possible critical points according to increasing salinity. The blue curve represents the halite, liquid and vapour equilibrium line (SLV) between the peritectic point and the triple point of NaCl. The shaded area represents the range of temperature and pressure that can be modelled according to Driesner and Heinrich (2007) and Driesner (2007). (modified from Bodnar and Sterner, 1987). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

calculation possibilities in the H_2O -NaCl system have been integrated within a stand-alone computer program "AqSo_NaCl", that is included in the software package "FLUIDS" (Bakker, 2003). The main objective of the present work is to make this model accessible via an "easy-to-use" interface to calculate a variety of fluid properties from microthermometric data (fluid inclusion research) and/or from specified temperature-pressure conditions within the earth. In fluid inclusion research, the new program will enable calculations of homogenization conditions, isochores of homogeneous fluids and unmixed fluids, and also the possibility to correct isochores for the volumetric properties of the host mineral of the inclusions. In addition, general property calculations may be performed of pure NaCl, the liquidus (liquid-solid), the vapourus (vapour-solid), dew-point and bubble-point curves (liquid-vapour), critical point, and the SLV-curve (solid-liquid-vapour) at temperatures above 0.1°C (with halite) and below 0.1°C (with ice or hydrohalite). The stand-alone program "AqSo_NaCl" has been developed for Macintosh, Windows and Linux, using BASIC with Xojo and RealBasic software (Xojo, Inc.). See details of availability at the end of this article.

2. Calculation procedures

Eleven windows in the program "AqSo_NaCl" have been developed to perform a variety of calculations that can be selected in the first window "Start" (Fig. 2). This window illustrates the fluid model that has been used to perform the calculations, with corresponding references, in addition to the list of specific calculation procedures to be selected.

The list of references includes the thermodynamic model that is used in this software. The main equation of state that forms the basis of all purely empirical modifications in the H_2O -NaCl system is defined for pure H_2O (Haar et al., 1984). The modifications to this equation are defined in Driesner and Heinrich (2007) and Driesner (2007), and can be applied to the entire compositional range between pure H_2O and pure NaCl, in the temperature range 0 – 1000°C , and pressure range 0 – 500 MPa. The empirical equations for saturation properties of pure H_2O , i.e. liquid-vapour curve from triple point to critical point, are obtained from Wagner and Pruss (1993). Hosieni et al. (1985) defined the

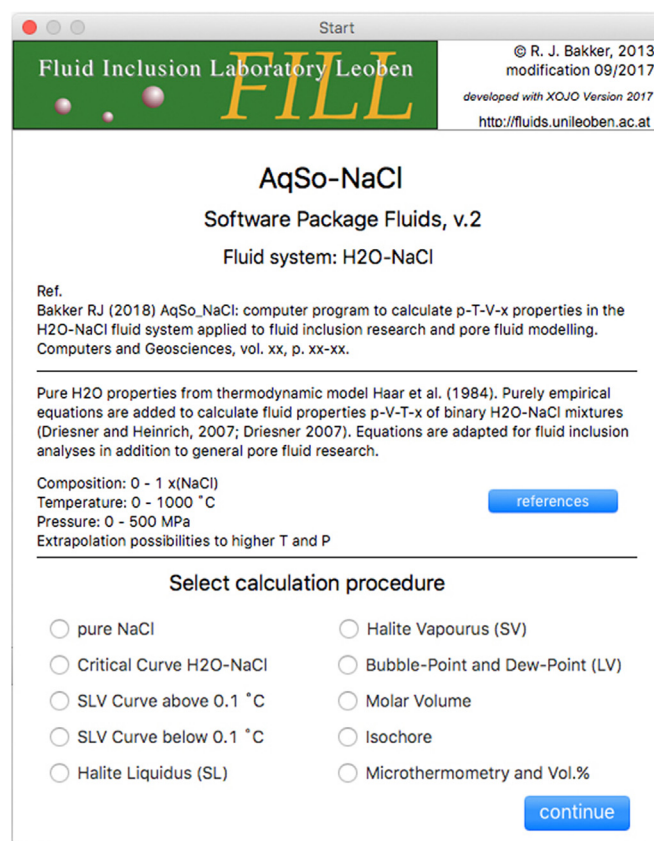


Fig. 2. First window ("Start") of the program "AqSo_NaCl". The interface is further explained in the text.

volumetric properties of α - and β -quartz, that can be used to model total volume changes of fluid inclusions in quartz. The purely empirical equations for ice and hydrohalite dissolution in the presence of vapour are defined in Potter et al. (1978), Hall et al. (1988) Sterner et al. (1988), Oakes et al. (1990), Bodnar (1993), Naden (1996), Steele-MacInnes et al. (2011), and Bakker (1999, 2012). The references include some corrections and some notifications applied to the original model from Driesner and Heinrich (2007) and Driesner (2007) that were necessary to be able to design the algorithms, and which are visualized in separate information windows. The accuracy of the results of calculations performed with the program "AqSo_NaCl" can be deduced from the work of Driesner and Heinrich (2007) and Driesner (2007).

The user can select one out of ten possible calculation procedures that include: 1. the pure NaCl system; 2. the critical curve of H_2O -NaCl mixtures; 3. the three-phase curve SLV (halite + liquid + vapour) above 0.1°C ; 4. the three-phase curve SLV (ice or hydrohalite + liquid + vapour) below 0.1°C ; 5. the halite liquidus (SL); 6. the halite vapourus (SV); 7. bubble-point curve and dew-point curve of H_2O -NaCl mixture; 8. the molar volume; 9. isochores; and 10. microthermometric data, dissolution temperatures (T_m) and homogenization temperatures (T_h) or volume fractions at room temperatures. The "continue" button opens a new window with the specific selected calculation procedure (Appendix A).

The temperature can be defined in $^\circ\text{C}$ or Kelvin in each module. A fractional number must be introduced with a decimal point (dot) in each interface, for example, a temperature of 246.6°C must be defined as "246.6". The properties of each individual phase are revealed in tables within each module with temperature, pressure, mole fraction NaCl, mass fraction NaCl, modified temperature for calculation of the molar volume (Driesner, 2007), molar volume, density, a specific equation from Driesner (2007) that was used to calculate the molar volume, modified temperature for calculation of the enthalpy (Driesner, 2007), specific enthalpy, heat capacity and specific heat capacity. The number of digits

in the fractional part of the calculated properties is not related to the accuracy or precision of that property, but reflects a standard value defined in development tool XOJO and RealBasic.

2.1. Pure NaCl

The p - T - v properties of pure NaCl can be calculated in a divariant univariant system (Fig. A1, Appendix A). The triple point (invariant point) is defined at 800.7 °C, 0.00005 MPa, and molar volumes of 37.434 cm³/mol for the liquid phase and 30.566 cm³/mol for the solid phase. Volumetric properties, enthalpy and heat capacity of the vapour phase are not defined. The selection of a phase assemblage and parameters automatically illustrates the limits of the values of temperature, pressure and molar volume, which are mainly defined by the location of the triple point, the solid-liquid curve, the liquid-vapour curve, and the solid-vapour curve. The properties of the NaCl phases (liquid and solid), including temperature, pressure, molar volume, enthalpy and heat capacity are calculated by using the pushbutton “calculation”. The reference state of the enthalpy of solid NaCl is defined by the formation of the elements at 25 °C and 0.1 MPa (Robie et al., 1979).

A divariant system is obtained by selecting one phase in the assemblage (either “solid”, “liquid” or “vapour” in Fig. A1). Subsequently, two parameters have to be selected from the choices “Temperature”, “Pressure”, and “Molar Volume” to be able to calculate all the properties of pure NaCl. The example in Fig. A1 illustrates the calculation of the properties of liquid NaCl at 1000 °C and 10 MPa. The molar volume of liquid NaCl in this example is 40.28438 cm³/mol. The properties of the solid NaCl phase are also normally provided in this window, but remain undefined in the example because the selected temperature and pressure are within the stability field of the liquid phase. A univariant system is obtained by specifying two phases in the assemblage and one intensive parameter. These systems correspond to the liquid-vapour curve between triple point and critical point (saturation curve), liquid-solid curve (melting curve), and solid-vapour curve (sublimation curve).

2.2. Critical curve

The critical point of pure H₂O has the properties 373.976 °C, 22.054915 MPa, and 55.966 cm³/mol (Haar et al., 1984). This invariant point shifts to higher temperatures and pressures and to lower molar volumes by adding NaCl to the system. The properties of this shift can be calculated in the window “Critical Curve H₂O-NaCl” (Fig. A2, Appendix A), by selecting either “Temperature”, “Pressure”, or “Composition”. The maximum temperature of the critical point correspond to 1000 °C, at 216.167 MPa, and a composition of $x(\text{NaCl}) = 0.1345445$ (indicated in the window with the pushbutton “limits”, Fig. A2). Calculations can be extrapolated up to 2000 °C, at a pressure of 459.0487 MPa and a composition of $x(\text{NaCl}) = 0.3325705$.

The example in Fig. A2 illustrates the calculation of the critical point at 400 °C. This point corresponds to a pressure of 28.10489 MPa and a composition of $x(\text{NaCl}) = 0.0068321$ (2.182937 mass% NaCl). The molar volume at this critical point is 42.30097 cm³/mol. The enthalpy is calculated to be 38280.8 J/mol, with a reference state value of 0 J/mol at the triple point of pure H₂O. The heat capacity at this critical point is 523.5081 J/mol K. At temperatures below the critical point of pure H₂O, the program calculates the pressure from a hypothetical extrapolation, which is used in modelling the bubble-point and dew-point curve (Driesner and Heinrich, 2007).

2.3. SLV curve above 0.1 °C

The SLV curve of the binary H₂O-NaCl system above 0.1 °C represents the line in a temperature-pressure diagram where 3 phases, i.e. solid (halite), liquid (brine), and vapour coexist. The properties of this curve can be calculated by selecting one parameter, either “Temperature”, “Pressure”, “Composition Liquid”, or “Composition Vapour” (Fig. A3, Appendix

A). The limits of this curve are between the peritectic point at 0.1 °C of a binary H₂O-NaCl mixture and the triple point of pure NaCl at 800.7 °C. The limits can be illustrated by using the pushbutton “limits” (Fig. A3). Multiple solutions may exist if the parameter “Pressure” or “Composition Vapour” is selected. These solutions are illustrated after using the pushbutton “calculation SLV”. The example in Fig. A3 illustrates the calculation for a selected composition of the vapour phase of $x(\text{NaCl}) = 1.0 \cdot 10^{-4}$. This composition results in three possible temperatures: 438.471 °C, 683.3515 °C and 799.1757 °C. Selection of the first temperature corresponds to a pressure of 23.35359 MPa. The properties of the three coexisting phases solid, liquid and vapour are revealed in a table according to the selected solution. All three solutions are correct, because the specified vapour composition does not define one unique solution, and may occur at a variety of temperature-pressure conditions at the SLV curve above 0.1 °C.

2.4. SLV curve below 0.1 °C

The solid phase on the SLV curve below the peritectic point (0.1 °C) is either hydrohalite or ice, depending on the bulk salinity of the system. This curve partly represents the freezing-point depression of pure ice in an H₂O-NaCl system with low to moderate salinities. The lowest dissolution temperature of both solid phases is the eutectic point at −21.2 °C. The modification according to Driesner and Heinrich (2007) and Driesner (2007) cannot be applied in this module because the equation of state of Haar et al. (1984) for liquid H₂O is not designed for temperatures below the triple point of pure H₂O. Therefore, a variety of purely empirical equations are presented to calculate salinity from known dissolution temperatures and vice versa (Fig. A4, Appendix A). The salinity is expressed in mass% and mole% (i.e. amount of substance %). The maximum salinity is defined at the peritectic point at 26.3 mass% NaCl. The example in Fig. A4 illustrates the calculation of the salinity for ice dissolution at −15 °C. The resulting mass% NaCl values vary between 18.53 and 18.79 according to the variety of various publications. This difference is not significant considering the normally attainable precision of 0.1° in temperature measurement. The variation in calculated salinities from hydrohalite dissolution is larger, due to poorly defined models based on only few data, and due to adding a second salt in the purely empirical models, which reduces the accuracy in the binary H₂O-NaCl system (e.g. Naden, 1996; Steele-MacInnes et al., 2011).

The calculated properties of the peritectic point (vapour, liquid, halite, and hydrohalite) at 0.1 °C and 464 Pa correspond to a vapour phase composition of $4.67 \cdot 10^{-23}$ mass% NaCl and a molar volume of $4.89 \cdot 10^6$ cm³ mol^{−1}, whereas the liquid phase has 26.28 mass% NaCl and 18.22 cm³ mol^{−1} (corresponding to a density of 1.21 g cm^{−3}). The halite crystal has a molar volume of 26.93 cm³ mol^{−1}. The vapour phase contains about one molecule of NaCl in one mole of H₂O, and, therefore, can be thermodynamically modelled according to a pure H₂O system. The vapour at the eutectic point of the H₂O-NaCl system must contain even less NaCl than the peritectic point.

2.5. Liquidus (SL)

Final dissolution temperatures of halite crystals in an aqueous liquid solution in absence of the vapour phase are defined at the *liquidus* in the H₂O-NaCl system. The lower pressure limit of the liquidus is the SLV curve, where a vapour phase appears. The liquidus is a slightly curved line in a temperature-pressure diagram at a specific composition, which is only weakly dependent on pressure, and which can only vary within a limited temperature range. A pair of parameters has to be selected to calculate the liquidus properties: 1. temperature and pressure; 2. pressure and composition; or 3. composition and temperature (Fig. A5, Appendix A). The example in Fig. A5 illustrates the liquidus calculation at 300 °C and 50 MPa, that results in a salinity of $x(\text{NaCl}) = 0.1578954$. The pushbutton “limits” can be used to calculate the boundary values of the selected parameters, and reveals the lower pressure limit at the SLV curve for the selected temperature, or temperature and pressure limits at a

selected composition. The change in slope of the liquidus between $x(\text{NaCl}) = 0.1669$ and 0.2251 causes a double solution at specific temperatures. The user can select one of these solutions to calculate the liquid and solid phase properties of this system.

2.6. Vapourus (SV)

Final dissolution temperatures of halite crystals in an aqueous vapour solution in absence of the liquid phase are defined at the *vapourus* in the H_2O -NaCl system. The vapourus occurs at low pressures, below the SLV curve. Similarly to the liquidus calculation, a pair of parameters has to be selected: 1. temperature and pressure; or 2. composition and temperature (Fig. A6, Appendix A). Due to the complex shape of the vapourus and the intersections with the SLV curve, double solutions may exist at low salinities, i.e. $x(\text{NaCl}) < 1.7628 \cdot 10^{-5}$, and temperatures below 800°C . At salinities $x(\text{NaCl}) > 2.8189 \cdot 10^{-4}$ the vapourus is defined by a single solution at extremely low pressures, i.e. lower than the triple point of pure NaCl. A temperature of 500°C and a composition of $x(\text{NaCl}) = 1.0 \cdot 10^{-6}$ is selected in the example in Fig. A6, resulting in a double solution at 0.0026545 MPa and 13.09679 MPa . It must be noted that these extremely low salinities cannot be detected by measuring the freezing point depression of ice. The limits of the selected parameters can be visualized with the pushbutton 'limits', and correspond to a maximum temperature of 660.548°C for the selected composition. The user can select one of the solutions to calculate the vapour and solid phase properties of this system.

2.7. The dew-point curve and bubble-point curve (LV)

The liquid-vapour envelope (immiscibility) of the H_2O -NaCl system is defined by the bubble-point curve, critical point, and dew-point curve, and separates a homogeneous fluid phase field (super-critical fluid) from an unmixed NaCl-enriched liquid and an H_2O -enriched vapour phase. The bubble point curve defines densities that are higher than the critical density, whereas the dew-point curve represents lower densities. The properties in the H_2O -NaCl system along these curves can be calculated by selecting a pair of parameters: 1. temperature and pressure; 2. temperature and composition of the liquid phase; 3. pressure and composition of the liquid phase; and 4. temperature and composition of the vapour phase (Fig. A7, Appendix A). The pairs 2, 3, and 4 correspond to calculation of homogenization conditions in fluid inclusions, with a known composition and homogenization temperature or pressure. The example in Fig. A7 illustrates a system with a homogenization temperature of 1100°C and a composition of $x(\text{NaCl}) = 0.2$, resulting in a homogenization pressure of 243.9119 MPa and a molar volume of $34.38885\text{ cm}^3/\text{mol}$. The pushbutton 'limits' gives the limiting values of the selected parameters, corresponding to limits in composition and pressure at the selected temperature, and limits in temperatures for a given composition. Bubble-point curve solutions are always unique (solution 1 in Fig. A7), i.e. a selected temperature and composition correspond to one intersection with the bubble-point curve. At low salinities $x(\text{NaCl}) < 2.8189 \cdot 10^{-4}$ and relative low temperatures ($< 381.4^\circ\text{C}$), the dew-point intersections may include up to three solutions at selected temperatures. At higher salinities, the temperatures of the dew-point curve always exceed those of the bubble-point curve. In other words, homogenization into the vapour phase occurs always at temperatures that are higher than homogenization into the liquid phase. At temperatures above 800.7°C , the dew-point curve has two solutions at a selected temperature: one at relative high pressures and one at relatively low pressures. The user can select one of these solutions to calculate the liquid and vapour phase properties of this system.

2.8. Molar volume

The molar volume of a phase, i.e. vapour, liquid, and solid, or a phase assemblage can be calculated at any temperature and pressure conditions

within the limits of the model (Fig. A8, Appendix A). The calculations are performed at a selected bulk composition, temperature and pressure. In the example in Fig. A8, the molar volume is calculated for a fluid system at $x(\text{NaCl}) = 0.3$, 80 MPa and 700°C . This module defines the corresponding phase assemblage, represented by a "stability field", which is either the homogeneous fluid phase, the liquid and vapour field, the liquid and solid (halite) field, or the vapour and solid (halite) field. At the selected conditions, the fluid system of the example is within the envelope of the bubble-point and dew-point curve composed of a liquid and vapour phase (Fig. A8). The calculated bulk molar volume is $34.54573\text{ cm}^3/\text{mol}$, whereas the liquid phase has a molar volume of $30.18368\text{ cm}^3/\text{mol}$ and the vapour phase $79.35735\text{ cm}^3/\text{mol}$. The properties of each individual phase are revealed in a table with volume fractions (0.7962151 for the liquid phase, Fig. A8), and molar fractions (i.e. the relative amount of H_2O and NaCl components in a specific phase).

2.9. Isochores

The temperature-pressure conditions of a constant molar volume (isochoric) for a specific bulk composition are calculated in the module "Isochores" (Fig. A9, Appendix A). Isochores are in general calculated for a homogeneous fluid, therefore, the lowest temperature and pressure conditions of a specific density are defined at the bubble-point curve, the dew-point curve, the liquidus and the vapourus. The homogenization conditions corresponding to the selected composition and molar volume are calculated with the pushbutton "hom. cond.". These conditions are the intersection of an isochore of a homogeneous fluid with the bubble-point curve, dew-point curve, liquidus or vapourus. In Fig. A9, a homogenization temperature of 679.2994 K (406.1494°C) at the bubble-point curve is calculated for a molar volume of $40\text{ cm}^3/\text{mol}$ and a composition of $x(\text{NaCl}) = 0.01$. LVSL.

At conditions below homogenization, a homogeneous fluid phase may evolve into a liquid and vapour phase, whose properties and relative proportions are restricted by the bulk properties. The isochore of the bulk homogeneous fluid can be extended within the liquid and vapour field by calculating specific temperature and pressure conditions where the properties of coexisting liquid and vapour phase correspond to these considerations. It must be noted that this multiphase isochore does not represent the metastable extension of the one-phase isochore. In addition, the homogeneous fluid phase may also evolve into a liquid and solid (halite) phase at the liquidus. The module is also able to extend the isochore calculations within this field.

The multiphase isochores within the two-phase stability field, i.e. liquid and vapour, liquid and solid, or vapour and solid, may intersect the SLV curve at lower temperatures, lower pressures and salinities of $x(\text{NaCl}) > 0.0989956$, which correspond to the formation of a halite crystal or vapour bubble, respectively. These conditions can be calculated by using the pushbutton "SLV intersection" (Fig. A9). Isochores of low salinity fluids, with $x(\text{NaCl}) < 0.0989956$, do not intersect with the SLV curve above 0.1°C , because they do not contain a solid halite crystal at any temperature. The multiphase isochores at the SLV curve calculates the relative proportions of liquid, vapour and solid according to the defined bulk molar volume and bulk composition. The phase changes that can be observed in fluid inclusions are schematically illustrated in the module.

The pushbutton "limits molar volume" (Fig. A9) calculates specific values of molar volumes at invariant points in a temperature-pressure diagram for the selected composition, to illustrate limiting values. These invariant points are 1. the bubble point at 0.1°C for low salinities, or the SLV curve at a selected higher salinities of the liquid phase; 2. the critical point or the bubble point at 1200°C if critical point exceeds 1000°C ; 3. the SLV curve at a selected composition of the vapour phase (up to three values); 4. dew points at 1200°C (up to two values).

Isochores of fluids enclosed within fluid inclusions in quartz can be corrected for the expansivity and compressibility of α - and β -quartz (Fig. A9). The constant total volume assumption of fluid inclusions can be adjusted according to modifications of quartz volume at specific

temperatures and pressures. The reference conditions of correction can be selected at homogenization conditions or at the intersection with the SLV curve, which is illustrated as the “starting point” to correct the fluid density.

The module offers the possibility to calculate the isochore in a range of temperatures, defined by a lower, and upper temperature, with a specified temperature interval (Fig. A9). The results of these calculations are given in table, and can be exported in a file (.txt), which is automatically assigned a name according to the defined molar volume.

2.10. Microthermometry

Microthermometry is a method of major importance to fluid inclusion research. Dissolution temperatures of halite, and homogenization temperatures of fluid phases are often observed in fluid inclusion studies upon progressive heating. Both temperatures can be used directly to calculate the bulk fluid properties of these inclusions in the binary H_2O -NaCl system. The module (Fig. A10, Appendix A) distinguishes between the phase reduction “three-to-two”, i.e. 1. dissolution of ice, hydrohalite or halite in the presence of liquid and vapour; 2. dissolution of vapour in the presence of halite and liquid; and 3. dissolution of liquid in the presence of halite and vapour, and the phase reduction “two-to-one”, i.e. homogenization into the liquid or vapour phase. In addition, the volume fraction of the remaining liquid phase at the SLV curve can be selected in absence of a total homogenization temperature.

The example in Fig. A10 illustrates a fluid inclusion that reveals final dissolution of a halite crystal at 350°C in the presence of liquid and vapour. The module illustrates schematically the change in phase assemblages in the fluid inclusion. The example in Fig. A10 also illustrates a total homogenization temperature from liquid and vapour into the liquid phase at 400°C . The two temperatures that reduce the number of phases within fluid inclusion, i.e. total homogenization and final dissolution temperatures cannot vary independently. The pushbutton “limits Th” (Fig. A10) calculates for a range of volume fractions of the remaining liquid phase at the SLV curve (after dissolution) the critical point and the bulk composition. The critical temperature marks the boundary temperature between homogenization into the liquid phase and into the vapour phase. In absence of a total homogenization temperature, the volume fraction of the remaining liquid after dissolution on the SLV curve can be selected to calculate bulk V-x properties of the fluid inclusion. This volume fraction can be estimated according to the method of Bakker and Diamond (2006).

The expansivity and compressibility of α - and β -quartz may result in a slightly variable total volume of fluid inclusion. Therefore, the bulk molar volume of the fluid at dissolution temperatures may differ from that at total homogenization temperatures. The module offers the possibility to correct the fluid molar volume calculation according to this effect (Fig. A10). The reference conditions of correction are defined at the total homogenization conditions.

The pushbutton “calculate” calculates the bulk composition and molar volume of the fluid inclusion according to the selected temperatures. The example in Fig. A10 illustrates that the bulk properties of the fluid inclusion are $x(\text{NaCl})$ 0.181462 and $24.49475\text{ cm}^3/\text{mol}$ at homogenization conditions. In addition, the volume fraction of the liquid phase at the SLV curve and the homogenization pressure is estimated, 94.61472% and 19.13069 MPa, respectively. These are only calculated if a total homogenization temperature is selected. Homogenization conditions are not calculated if the volume fraction is selected to calculate bulk fluid properties.

3. Example calculated phase diagrams

Temperature-pressure phase diagrams for a low salinity and high salinity fluid system have been constructed to illustrate the calculation possibilities of the program “AqSoNaCl” (Figs. 3 and 4, respectively). All the features illustrated in Figs. 3 and 4 are calculated with the software “AqSoNaCl”.

A fluid composition of $x(\text{NaCl}) = 1.0 \cdot 10^{-6}$ correspond approximately

to adding a grain of salt (sediment size: medium sand, 0.25–0.5 mm) in a glass of water. This composition illustrates how the properties of a pure H_2O fluid evolves into the binary H_2O -NaCl system (Fig. 3). The saturation curve of pure water splits to make a small p-T field of liquid and vapour immiscibility between the bubble-point curve, dew-point curve and SLV curve. The minimum temperature of the dew-point curve has shifted to 298.9°C (cf. 0.01°C for pure water). Consequently, homogenization into the vapour phase can only occur at temperatures between 298.9°C and the 374.2°C (i.e. critical temperature). The solid and vapour curve of pure water (sublimation or deposition) is located at temperatures below 0.01°C . Adding this one grain of salt creates a large immiscibility field of halite (solid) and steam (vapour) up to 660.6°C and pressures up to 13.19 MPa. Fig. 3 illustrates seven isochores in the homogeneous fluid field. The isochores 18.5 , 20 , and $23\text{ cm}^3\text{ mol}^{-1}$ intersect the bubble-point curve at relatively low temperatures, which represents total homogenization into the liquid phase upon heating. The critical density isochore $56.16\text{ cm}^3\text{ mol}^{-1}$ intersects at the critical point and separates a homogenous liquid-like fluid field from a homogeneous vapour-like fluid field that is often named a super-critical fluid. The isochores 200 and $400\text{ cm}^3\text{ mol}^{-1}$ intersect the dew-point curve, whereas the isochore $1000\text{ cm}^3\text{ mol}^{-1}$ intersect the sublimation curve, all at relatively high temperatures. These intersections correspond to homogenization into the vapour phase upon heating. The locations of these isochores do not significantly differ from the isochores of pure water, but the intersections with the bubble-point curve, dew-point curve and sublimation curve are highly distinct from the saturation curve of pure water.

Fig. 4 illustrates a phase diagram for an $x(\text{NaCl}) = 0.15$ aqueous solution. This example corresponds approximately to a glass of water, which is filled with 20 vol% NaCl. The phase boundaries have significantly shifted to higher temperatures and pressures, compared to the low salinity example in Fig. 3. The liquid and vapour immiscibility field extends to high metamorphic conditions at relative low pressures (up to low pressure granulite facies), and exceeds the limits of the thermodynamic model. The liquidus intersects the SLV curve at 281.7°C and due to its negative slope, at slightly lower temperatures at higher pressures. The bubble point curve extends up to high temperatures and the critical point is located at 1339.6°C and 309.6 MPa. These calculated conditions are extrapolated from the properties of the critical curve, which have been experimentally defined only below 1000°C . The dew-point curve would start at the critical point and be located at higher temperatures and pressure, but is not illustrated in Fig. 4 because these conditions are far outside the limits of the model. The low-pressure part of the dew-point curve appears at extreme low pressures and ends very close to the

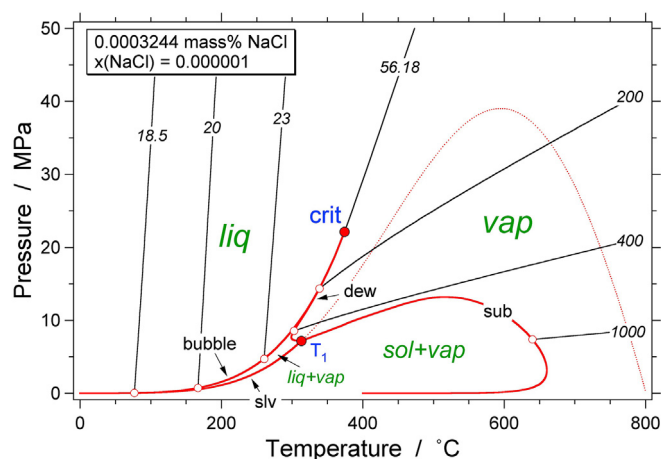


Fig. 3. Temperature-pressure diagram for a composition of $x(\text{NaCl}) = 1.10^{-6}$ calculated with the program AqSoNaCl. See text for further details. The dashed red line is projection of the SLV curve. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

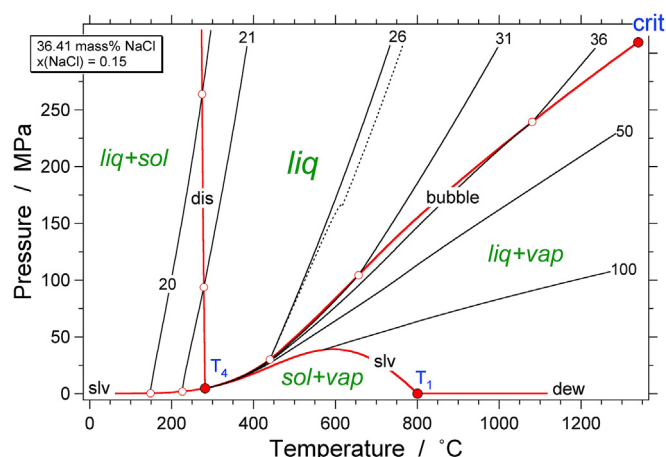


Fig. 4. Temperature-pressure diagram for a composition of $x(\text{NaCl}) = 0.15$ calculated with the program AqSo_NaCl. See text for further details.

triple point of pure NaCl at 800.7 °C. The field of a homogenous fluid phase is reduced to a liquid-like fluid at relatively high pressures, above the bubble-point curve. Fig. 4 illustrates seven isochores that are partly located in the homogeneous fluid field and partly in the heterogeneous fluid field. The isochores 20 and 21 $\text{cm}^3 \text{mol}^{-1}$ intersect the SLV curve at low pressure and cross the liquidus at higher pressures. The first intersection corresponds to disappearance of the vapour bubble, i.e. the reduction of a three phase (SLV) to a two phase (SL) assemblage within a fluid inclusion upon heating. The intersection with the liquidus is the total homogenization of fluid inclusions into the liquid phase by complete halite dissolution. There is a small change in the slope of these isochores upon crossing the liquidus. The isochores 26, 31, and 36 $\text{cm}^3 \text{mol}^{-1}$ are mainly located within the homogeneous fluid field (liquid-like) and intersect the bubble-point curves at different temperatures. Below these homogenization temperatures the isochores proceed within the immiscibility field of liquid and vapour, and cross the SLV curve near the liquidus intersection. The deviation from this intersection increases with decreasing density (or increasing molar volumes). This intersection is located at 289.4 °C for the 36 $\text{cm}^3 \text{mol}^{-1}$ isochore (c.f. 281.7 °C). The correction of the 26 $\text{cm}^3 \text{mol}^{-1}$ isochore according to the volumetric properties of quartz is illustrated in Fig. 4 with a dashed line. The kink corresponds to the α - β phase transition of quartz. The isochores 50 and 100 $\text{cm}^3 \text{mol}^{-1}$ are located within the liquid-vapour immiscibility

field, and intersect the SLV curve at 299.0 °C and 569.7 °C, respectively. The phase assemblage of the 50 $\text{cm}^3 \text{mol}^{-1}$ isochore at this temperature consists of a liquid phase, $x(\text{NaCl}) = 0.1569$ and $V_m = 22.21 \text{ cm}^3 \text{mol}^{-1}$, and a vapour phase, $x(\text{NaCl}) = 5.46 \cdot 10^{-7}$ and $V_m = 653.5 \text{ cm}^3 \text{mol}^{-1}$. The 100 $\text{cm}^3 \text{mol}^{-1}$ isochore has multiple intersections with the SLV curve, implying that halite should sublime and reappear several times upon heating a fluid inclusion with this bulk density.

Acknowledgement

I would like to thank Larry W. Diamond and an anonymous reviewer for their constructive reviews to improve the quality of this paper.

Appendix B. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.cageo.2018.03.003>.

Computer code availability

Name: AqSo_NaCl

Developer: Ronald J. Bakker, Montanuniversität Leoben, Peter-Tunner-Str. 5, Leoben, Austria telephone number: +43-4238-4026211

email: bakker@unileoben.ac.at

year first available: 2017

software required: none

program language: Basic

program size (all programs are copies of the same software that can be used for different computer operation systems)

programs developed with RealBasic

- AqSo_NaCl-Linux 8.4 MB
 - AqSo_NaCl-Mac OS (Mach-O i386) 9 MB
 - AqSo_NaCl-Mac OS (Mach-O Power PC) 8.2 MB
 - AqSo_NaCl-Mac OS (Universal) 15.9 MB
 - AqSo_NaCl.exe 8.5 MB
- programs developed with XOJO
- AqSoNaCl 18.1 MB
 - AqSo_NaCl.exe 6.3 MB

Appendix A

Series of interfaces with all possible calculation procedures.

Pure NaCl

T-P-V properties pure NaCl

☐ Solid
☒ Liquid
☐ Vapour
Liquid field

Select parameter(s)
 Check two parameters
☒ Temperature
☒ Pressure
☐ Molar Volume

Temperature SL curve = 800.7 to 1048 °C; LV curve = 800.7 to 2000 °C
 Pressure SL curve = 0.00005 to 1000 MPa; LV curve = 0.00002 to 2.12 MPa
 Molar Volume SL curve = 34.32336 to 37.43407 cm^3/mol ; LV curve = 37.43407 - 53.06931 cm^3/mol

clear all
 Temp. Unit
☐ Kelvin
☒ °Celsius

Triple point: $T = 800.7 \text{ °C}$
 $P = 0.00005 \text{ MPa}$
 $V_m (\text{liq}) = 37.434 \text{ cm}^3/\text{mol}$
 $V_m (\text{sol}) = 30.566 \text{ cm}^3/\text{mol}$

Temperature °Celsius
 Pressure MPa
 calculation

Temperature	1000	°Celsius
Pressure	10	MPa
Molar Volume (liq)	40.28438	cm^3/mol
density = 1450.761 kg/m^3		
Molar Volume (sol)	---	cm^3/mol
Enthalpy* (sol)	---	J/mol
* reference state at 298.15 K and 0.1 MPa		
Heat Capacity (sol)	---	J/mol K

Fig. A1. Interface with calculation setup and results of the properties of pure NaCl. Information in red illustrates limits and warnings of the thermodynamic model, that appear automatically on the selected setting.

Critical Curve H₂O–NaCl

Select Parameter

☒ Temperature

☐ Pressure

☐ Composition

clear all

Critical point pure H₂O*:

373.976 °C
22.054915 MPa
55.966 cm³/mol
321.89 kg/cm³

*Haar et al. (1984)

Temperature ° Celsius

limits min. 373.976 to max. 1000 °C (847.126 to 1273.15 K),
hypothetic extension below 373.976 °C, at slightly higher
pressures than LV-curve pure H₂O

calculation critical point

Temp. Unit

☐ Kelvin

☒ ° Celsius

Pressure	28.10849	MPa
x(NaCl)	0.0068321	
	w(NaCl) = 2.182937 %	
Molar Volume	42.30097	cm ³ /mol
	432.4063 kg/m³ (eq. 7–16 in Driesner, 2007)	
Enthalpy*	38280.8	J/mol
	* reference state at triple point pure H₂O: H(liq) = 0	
Specific H	2092.852	J/g
Heat Capacity	523.5081	J/mol K
Specific Cp	28.62076	J/g K

Fig. A2. Interface with calculation setup of the critical point of H₂O–NaCl fluid mixtures

SLV Curve

SLV curve binary H₂O–NaCl system (> 0.1 °C)

Select Parameter

☐ Temperature

☐ Composition Liquid

☒ Composition Vapour

☐ Pressure

clear all

Temp. Unit

☐ Kelvin

☒ ° Celsius

x(NaCl) vapour

limits SLV curve can only be calculated above the
peritectic point at 0.1 °C for x(NaCl) vapour >
1.43867e-25

calculation SLV

Select Solution

☒ solution 1: 438.471 ° Celsius

☐ solution 2: 683.3515

☐ solution 3: 799.1757

Pressure	23.35359	MPa
Temperature	438.471	° Celsius

	liquid	vapour	solid	unit
x(NaCl)	0.2481794	0.0001	1	frac.
w(NaCl)	51.71186	0.032434	100	%
Tmod. (Vm)	311.9843	438.2833		°C
Molar Volume	25.11421	173.3064	28.55596	cm ³ /mol
Density	1.116834	0.1039722	2.046613	g/cm ³
Driesner (2007)*	Eq. 7–16	Eq. 7–16		
	* equation number from Driesner (2007) to calculate density			
Tmod. (H)	285.3591	438.3526		°C
Enthalpy*	35245.61	52830.97	-22425.21	J/mol
	* reference state at triple point pure H₂O: H(liq) = 0			
Specific H	1256.6	2931.952	-383.7107	J/g
Heat Capacity	68.78989	92.48691	57.42205	J/mol K
Specific Cp	2.452543	5.132732	0.9825309	J/g K

Fig. A3. Interface with calculation setup of the SLV curve (halite, liquid and vapour) H₂O–NaCl fluid mixtures at temperatures above 0.1 °C (peritectic temperature).

SLV low Temperature

Dissolution at SLV below 0.1 °C in the H₂O–NaCl system

Purely empirical equations, i.e. simple polynomial regression (up to the 3rd degree) were designed by a variety of authors to relate temperatures to salinities for ice and hydrohalite dissolution in the presence of vapour. The difference between ice models is smaller than the precision in temperature measurements (± 0.1 °C) or salinity estimates (± 0.1 %).

dissolving phase

☒ ice
☐ hydrohalite

select parameter

☒ temperature
☐ salinity (mass%)
☐ salinity (amount%)

Temp. Unit

☐ Kelvin
☒ °Celsius

Temperature

-15

°Celsius

phase diagram

Limits

Eutectic point: -21.2 °C and 23.2 mass% NaCl (xNaCl = 8.51%)
Peritectic point: +0.1 °C and 26.3 mass% NaCl (xNaCl = 9.90%)

calculate

	w(NaCl)	x(NaCl)		
salinity	18.79	6.66	%	Potter et al. (1978)
	18.63	6.59	%	Hall et al. (1987)
idem			%	Stern et al. (1988)
	18.64	6.60	%	Oakes et al. (1990)
	18.63	6.59	%	Bodnar (1993)
	18.53	6.55	%	Naden (1996)
idem			%	Steele-MacInnes et al. (2011)
idem			%	Bakker (2012)

Fig. A4. Interface with calculation setup of the SLV curve (ice or hydrohalite, liquid and vapour) H₂O–NaCl fluid mixtures at temperatures below 0.1 °C, between pure H₂O and peritectic composition.

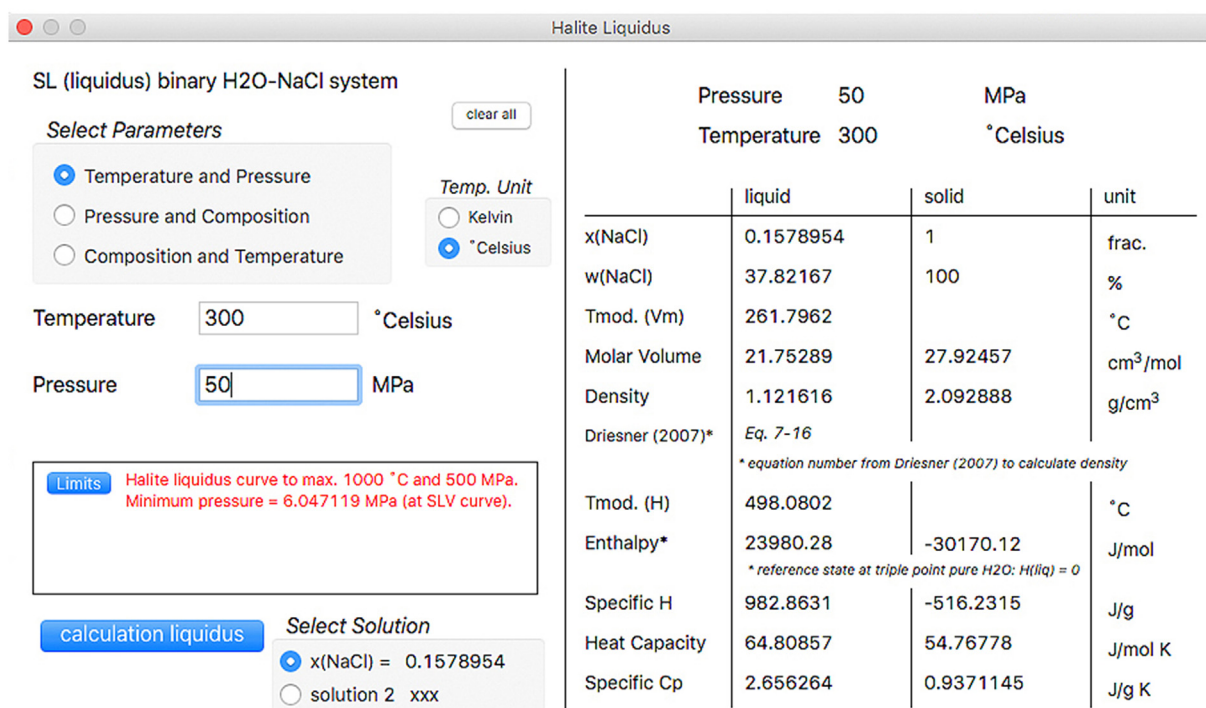


Fig. A5. Interface with calculation setup of the liquidus at temperatures exceeding 0.1 °C.

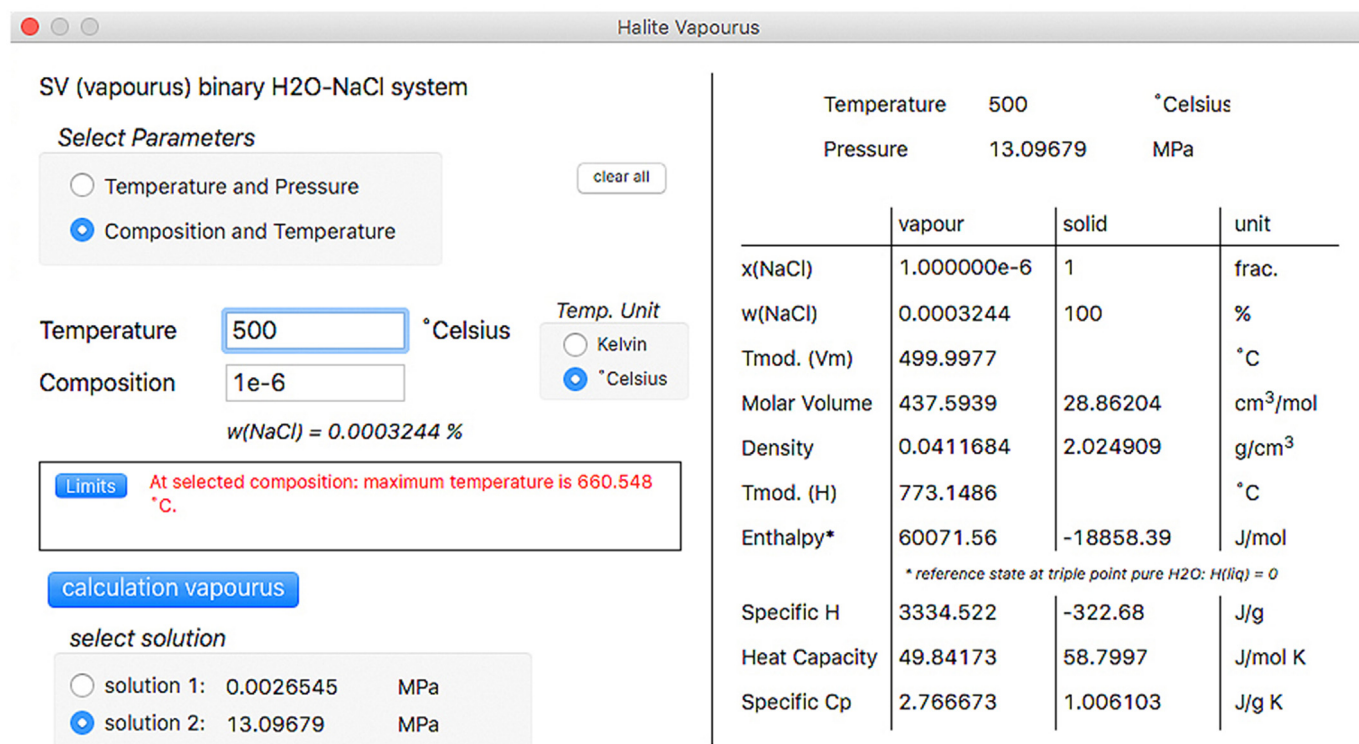


Fig. A6. Interface with calculation setup of the vapourus at temperatures exceeding 0.1 °C.

Liquid and Vapour Coexistence
clear all

LV field binary H₂O–NaCl system

dew-point and bubble-point curves

Select Parameters

☐ Temperature and Pressure

☒ Temperature and x(NaCl) liquid *

☐ Pressure and x(NaCl) liquid *

☐ Temperature and x(NaCl) vapour *

* This parameter selection corresponds to homogenization conditions in a fluid inclusion, with a known composition and homogenization temperature or pressure

Note: maximum x(NaCl) is 1 and T is 1000 °C. Extrapolation possibilities

Temperature Celsius

x(NaCl) liquid

Temp. Unit

☐ Kelvin

☒ °Celsius

Limits

At selected T: composition liquid can vary between 0.1391265 and 1, corresponding to pressure limits 244.8502 to 0.0040797 MPa

At selected x: maximum temperature is 1680.664 °C. Minimum temperature is defined by the liquidus (378.5262 °C at SLV)

calculation
Select a solution ---->

select solution

☒ solution 1: 243.9119 MPa

☐ solution 2: ---

☐ solution 3: ---

	Temperature	1100	Celsius
	Pressure	243.9119	MPa
	liquid	vapour	unit
x(NaCl)	0.2	0.0722077	frac.
w(NaCl)	44.78288	20.15855	%
Tv (mod. T)	748.5873	895.6308	°C
Molar Volume	34.38885	41.29465	cm ³ /mol
Density	0.7589844	0.5069473	g/cm
Driesner (2007)*	Eq. 7-16	Eq. 7-16	
* equation number from Driesner (2007) to calculate density			
Th (mod. T)	976.5286	1182.089	°C
Enthalpy*	79497.86	80147.56	J/mol
* reference state at triple point pure H ₂ O: H(liq) = 0			
Specific H	3045.825	3828.544	J/g
Heat Capacity	52.44037	57.09664	J/mol K
Specific Cp	2.009164	2.727432	J/g K

Fig. A7. Interface with calculation setup of the bubble-point and dew-point curve.

Molar Volume
clear all

Definition Molar Volume:

$$V_m(x, T, p) = V_m^{\text{pure H}_2\text{O}}(T^*, p)$$

Equation of state pure H₂O from Haar et al. (1984)

where $T^* = n_1 + n_2 \cdot T$

and n_1, n_2 are functions of salinity

x(NaCl)

w(NaCl) = 58.16497 %

Pressure MPa

Temperature °Celsius

Temp. Unit

☐ Kelvin

☒ °Celsius

calculate

Stability Field: liquid and vapour

Molar Volume 34.54573 * cm³/mol

*calculated according to volume fractions of phases

	liquid	vapour	solid	unit
Volume Fraction	0.7962251	0.2037749		
Molar Fraction*	0.911293	0.088707		
* distribution of amount of substance (H ₂ O + NaCl) between phases				
x(NaCl)	0.3288821	0.0032922		
w(NaCl)	61.38683	1.060187		%
Tmod. (Vm)	433.568	689.9466	---	°C
Molar Volume	30.18368	79.35735		cm ³ /mol
Density	1.03735	0.2286883		g/cm ³
Driesner (2007)*	Eq. 7-16	Eq. 7-16		
* equation number from Driesner (2007) to calculate density				
Tmod. (H)	671.177	966.8347	---	°C
Enthalpy*	56306.29	61696.55		J/mol
* reference state at triple point pure H ₂ O: H(liq) = 0				
Specific H	1798.288	3399.616		J/g
Heat Capacity	65.43406	70.38347		J/mol K
Specific Cp	2.089808	3.878284		J/g K

Fig. A8. Interface with calculation setup of the molar volume in homogenous and heterogeneous fluid stability fields.

Isochore construction H₂O-NaCl fluid mixture clear all

x(NaCl) w(NaCl) 3.172925 %
 Molar Volume cm³/mol Density 0.460482 g/cm³

Corresponding homogenisation conditions

hom. cond. **Homogenization on the bubble-point curve in the liquid phase**

Temperature 406.1494 °Celsius Temp. Unit
 Pressure 29.59592 MPa ☐ Kelvin
 Molar Volume 40 g/cm³ ☒ Celsius

SLV intersection* **Within the LV field at room temperature**

T4 --- °Celsius
 Temperature (intersect.1) --- °Celsius
 Temperature (intersect.2) --- °Celsius
 Temperature (intersect.3) --- °Celsius

* high molar volume isochores (low density) may have multiple intersections with the SLV curve

Phase changes in fluid inclusion: ☐ → ☐

limits molar volume

bubble point at 1 °C 18.04962 cm³/mol
 critical point 40.54156 cm³/mol
 SLV (vapour) ---- cm³/mol
 ---- cm³/mol
 1.755839e+6 cm³/mol
 dew points at 1200 °C 109.7201 cm³/mol
 4474.084 cm³/mol Homogenization conditions in vapour phase cannot be calculated between these two values, because it exceeds 1200 °C

Isochore correction
 Expansivity and compressibility of quartz (Hosieni et al., 1984) can be included to correct the fluid density along an isochore
☒ No
☐ Yes, starting point hom. cond.
☐ Yes, starting point SLV inter.

Temperature limits of isochore
 isochores can be constructed in both one-phase field (homogeneous) and two-phase field (heterogeneous) on either side of the homogenisation temperature

lower temperature °C
 upper temperature °C
 size temperature interval degree

calculate isochore

Temperature (°C)	Pressure (MPa)
410	31.15349
420	35.25484
430	39.42758
440	43.66064
450	47.9445
460	52.27092
470	56.63277
480	61.02391
490	65.43898
500	69.87334
510	74.32298

export data is available in: 40.txt

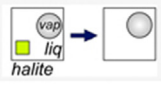
Fig. A9. Interface with calculation setup of isochores in homogenous and heterogeneous fluid stability fields.

Microthermometry

Dissolution Temperature
 reduction of a three-phase to a two-phase system

☐ Ice-LV to LV
☐ Hydrohalite-LV to LV
☒ Halite-LV to LV
☐ Halite-LV to SL
☐ Halite-LV to SV

Temperature °Celsius



Calculation of limits of homogenization temperature as a function of volume fraction of the remaining liquid at SLV curve. x(NaCl) is the bulk composition. Critical temperature (Temp. °C) defines the boundary between liquid (bubble point, temp < Tcrit) and vapour (dew point, temp > Tcrit). If critical temperature exceeds 1200 °C, homogenization can only occur in the liquid phase (liquid*).

limits Th

Vol.Frac.Liq.	x(NaCl)	Temp. °C
0.21	0.1459068	liquid*
0.2	0.1440924	liquid*
0.19	0.1421389	1178.934
0.18	0.1400295	1123.289
0.17	0.1377448	1066.344

Select second parameter

☒ Homogenization Temperature
☐ Volume Fraction Liquid at SLV %

Temp. Unit
☐ Kelvin
☒ Celsius

Homogenization Temperature
 reduction of a two-phase system to a homogeneous phase

☒ LV to L
☐ LV to V
☐ SL to L
☐ SV to V

Temperature °Celsius



Quartz Density Correction
 Expansivity and compressibility of quartz (Hosieni et al., 1984) can be included to correct the fluid density
☒ no
☐ yes

calculate*

Composition, x(NaCl)	0.181462	frac.
w(NaCl)	41.83315	%
Molar Volume	24.49475	cm ³ /mol
Density	1.034962	g/cm ³
Volume fraction liquid at SLV	94.61472	%
Pressure at homogenization	19.13069	MPa

* calculation time may take up to 10 seconds with Quad-Core Intel Xeon E5 (Mac) and up to 30 seconds with Intel (R) Core (TM) i5-6400 (Windows)

Fig. A10. Interface with calculation setup to calculated fluid bulk properties (molar volume and composition) from microthermometric data.

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Supplementary Material AqSo_NaCl

Computer program to calculate p-T-V-x properties in the H₂O-NaCl system applied to fluid inclusion research and pore fluid modelling

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Algorithms

The algorithms to calculate the properties of the H₂O-NaCl system are defined in a series of functions, (i.e. "methods" in the development tool XOJO and RealBasic) and include primary methods with the mathematical equations of the thermodynamic models, and derived methods, which use primary methods to calculate specific fluid properties. A list of symbols of all properties used in this supplementary material is given in Table 1.

symbol	physical quantity
T	temperature (Kelvin or °Celsius)
V	molar volume ($\text{cm}^3 \cdot \text{mol}^{-1}$)
p	pressure (MPa)
x	amount of substance fraction ("mole fraction")
w	mass fraction ("weight fraction")
f	fugacity (MPa)
A	Helmholtz energy ($\text{J} \cdot \text{mol}^{-1}$)
S	entropy ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)
U	internal energy ($\text{J} \cdot \text{mol}^{-1}$)
H	enthalpy ($\text{J} \cdot \text{mol}^{-1}$)
G	Gibbs energy ($\text{J} \cdot \text{mol}^{-1}$)
C_V	isochoric heat capacity ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)
C_P	isobaric heat capacity ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)
$dp/d\rho$	partial derivative of pressure to density
dp/dT	partial derivative of pressure to temperature
<i>phase</i>	solid, liquid or vapour
<i>iter.</i>	number of iterations
Subscripts	
liq	liquid phase
vap	vapour phase
bulk	bulk properties
h	homogenization
m	dissolution ("melting")
mod	modified

Table 1. List of symbols

The properties of pure H₂O (Haar et al., 1984) are the principal part of the software. The primary methods include definitions of three parts of the unified Helmholtz energy function, i.e. ideal, base, and residual Helmholtz energy ("*Haar_Base*", "*Haar_Ideal*" and "*Haar_Residual*" in Table 2). Combination of the three functions can be used to calculate a variety of thermodynamic properties. The pressure and the molar volume of the liquid and vapour phase at the saturation curve are defined by Wagner and Pruss (1993) ("*SaturationP*" and "*SaturationV*" in Table 2). In addition, the modification of the equation of state of Holloway (1977, 1981) by Bakker (1999, 2012) ("*Holloway_MolarVolume*" in Table 2) is used to calculate a first approach of the H₂O molar volume in a numerical method to calculated molar volume with the equation of Haar et al. (1984). Derived methods using these primary methods calculate isochoric and isobaric heat capacity, enthalpy, fugacity, and pressure from the unified Helmholtz energy function (Table B1). The saturation temperature (liquid and vapour) is numerically obtained from either saturation pressure or molar volume of liquid and vapour phase ("*SaturationT*").

Table 2. Primary algorithms (methods), with mathematical equations for pure H₂O, with "input" and "output" parameters. The symbols of the "input" and "output" parameters are declared in the Table 1.

<i>method name</i>	<i>input</i>	<i>output</i>
Haar_Base	T, V	*p, f, A, S, U, H, G, C _v , dp/dρ, dp/dT
Haar_Ideal	T	*A, S, U, H, G, C _v
Haar_Residual	T, V	*p, f, A, S, U, H, G, C _v , dp/dρ, dp/dT
SaturationP	T	p
SaturationV	phase, T	V
Holloway_MolarVolume	phase, T, P	V

* the total value of these properties is obtained from the sum of the three methods.

The molar volume of H₂O at a selected temperature and pressure is numerically obtained with root-finding algorithms (Table B2): **a.** Brent method; and **b.** Sectant method (Press et al., 1997). At conditions close to saturation (liquid and vapour curve), the molar volume can be calculated as a liquid phase value or a vapour phase value, even at metastable conditions with the method "*Haar_Volume_Phase*" (Table B2).

The properties of the saturation curve of H₂O can also be calculated with the equation of state from Haar et al. (1984) using the theory of equal fugacities of liquid and vapour phase (Table B3, Prausnitz et al., 1980). Either a known temperature or pressure can be used to calculate equilibrium conditions.

The properties of pure NaCl are calculated with the primary methods illustrated in Table 3. Calculation of the molar volume can only be applied to a solid and a liquid phase. Temperature and pressure of the saturation line (liquid and vapour), SL line (solid and liquid) and SV line (solid and vapour) are directly calculated with these methods. Temperature of these two-phase lines can be calculated numerically from a known molar volume of the NaCl phases (Table B4). The temperature and pressure within the solid phase field and the liquid phase field are also numerically obtained from the selected parameters V-p and V-T, respectively.

The molar volume of pure α- and β-quartz at a selected temperature and pressure is calculated in the primary method "*QuartzVolume*".

Table 3. Primary methods, with mathematical equations to calculate properties of pure NaCl.

<i>method name</i>	<i>input</i>	<i>output</i>
Volume_pureNaCl	phase, T, p	V
TemperatureP_pureNaCl	line, p	T
PressureT_pureNaCl	line, T	p
Enthalpy_pureNaCl	T, p	H
Cp_pureNaCl	T, p	C _p

Calculations in the binary H₂O-NaCl system are performed with a variety of primary methods (Table 4) that include the mathematical equations from Driesner and Heinrich (2007) and Driesner (2007). These methods calculate the composition and pressure of the critical point of H₂O-NaCl mixtures, liquid phase composition of the liquidus at selected temperature and pressure, and the pressure of the SLV curve (halite, liquid and vapour) at a selected temperature. The methods "LV_LiquidBrancheX" and "LV_VapourBrancheX" calculate the composition of the liquid and vapour phase, respectively, at the dew point and bubble point curve. The methods "Temperature_Modification" and "Temperature_Enthalpy" (Table 4) calculate the parameter (T_{mod}) that replaces the true temperature in the equation of state from Haar et al. (1984), in order to calculate molar volumes and enthalpies of H₂O-NaCl mixtures, respectively.

Table 4. Primary algorithms (methods), with purely empirical mathematical equations for H₂O-NaCl mixtures.

<i>object</i>	<i>method name</i>	<i>input</i>	<i>output</i>
critical point	Critical_Composition	T	x
	Critical_Pressure	T	p
liquidus	Halite_Liquids_CompLiq	T, p	x
SLV line	SLV_Pressure	T	p
bubble point	LV_LiquidBrancheX	T, p	x
dew point	LV_VapourBrancheX	T, p	x
temperature	Temperature_Modified	T, p, x	T_{mod}
	Temperature_Enthalpy	T, p, x	T_{mod}

The primary methods in Table 4 are used in a variety of derived methods (Table B5) to calculate the critical temperature, temperature and pressure of the liquidus curve, composition and temperature of the SLV curve, temperature and pressure of the dew-point curve and bubble-point curve, molar volume correction near saturation conditions ("Volume_Correction17" and "Volume_Correction18"), and the pressure of a H₂O-NaCl mixture at a selected temperature, molar volume, and salinity.

The shapes of the dew-point curve, sublimation curve, and liquidus involve complex curvatures at specific temperature, pressure and composition conditions. Consequently, multiple pressure solutions may coexist at one specific temperature. In order to estimate the variety in solutions, the extremum of these curves are defined in the methods that are illustrated in Table 5. At low salinities, $x(\text{NaCl}) < 2.8189 \cdot 10^{-4}$, and relative low temperatures, $T < 381.4 \text{ }^{\circ}\text{C}$, the dew point curve reveals a maxima ("*Dew_maximumP*" and "*Dew_maximumT*") and a minima ("*Dew_minimumP*" and "*Dew_minimumT*"). These extremum must be taken into account in the calculation of homogenization conditions at the dew-point curve, liquidus and vapourus. At higher salinities, $x(\text{NaCl}) > 1.87 \cdot 10^{-5}$ and higher temperatures, $T > 785.2 \text{ }^{\circ}\text{C}$, the dew-point curve reveals a maxima, that is calculated with the method "*Dew_MAX*" (Table 5). This maxima is extended to the SV field at lower salinities, where it is calculated with the method "*Sub_MAX*". Multiple intersections of isochores (LV) with the SLV curve are calculated with limiting values that are calculated in "*SLV_bottom*" and "*SLV_top*". The maximum pressure of the sublimation curve at selected compositions is calculated with "*Sub_MAXPres*". The method "*SV_midvalues*" calculates the minimum molar volume of an isochore at a selected composition in the SV field that intersects twice with the SLV curve.

Table 5. Primary methods to calculate the extremum of the dew-point curve, sublimation curve, and liquidus.

<i>method name</i>	<i>input</i>	<i>output</i>
Dew_maximumP	x or T	p
Dew_maximumT	x	T
Dew_minimumP	x or T	p
Dew_minimumT	x	T
Dew_MAX	x or T	T, p or x
Sub_MAX	x or T	T, p or x
SLV_bottom	x	T or V
SLV_top	x	T or V
Sub_MAXPres	x	T, P or V
SV_midvalues	x	T or V
Liquidus_Minimum	x	T or p

The liquidus, i.e. the boundary between the homogeneous liquid field and the SL field, reveal a minimum between $x(\text{NaCl}) = 0.1669$ and 0.2251 , which can be calculated with the method "*Liquidus_Minimum*" (Table 5). The liquidus has a positive slope at higher salinities, and a negative slope at lower salinities.

Homogenization conditions (temperature and pressure) within fluid inclusions are calculated from known compositions and molar volumes with the methods illustrated in Table B6. Homogenization is the process in which two phases are transformed in to one by increasing the temperature of a system. Homogenization conditions $\text{LV} \rightarrow \text{V}$ is numerically calculated in the method "*Th_Vapour_Brent*", whereas "*Th_Liquid_Brent*" and "*Th_Liquid_Sectant*" calculate the homogenization in to the liquid phase ($\text{LV} \rightarrow \text{L}$). The extensions in the names of these methods (Brent and Sectant) refer to the type of root-finding algorithm. Homogenization at the vapourus ($\text{SV} \rightarrow \text{V}$), and at the liquidus ($\text{SL} \rightarrow \text{L}$), are numerically calculated in the methods "*Th_Vapourus_Brent*" and "*Th_Liquidus_Brent*", respectively.

The molar volumes at homogenization conditions can be corrected according to the volumetric properties of quartz at variable temperature and pressure conditions, which is causing a certain shift in homogenization temperatures and pressures. The correction can be performed at the bubble-point curve, dew-point curve, liquidus, and vapourus (the last four methods in Table B6).

Isochores of fluids trapped in fluid inclusions in quartz can be numerically calculated in the homogeneous fluid phase field, within the two-phase regions, and at the three-phase curve (SLV) "*Isochore_Correction*" in Table B7), including the LV field ("*Sub_IsochoreLV_Brent*"), the SL field ("*Sub_IsochoreSL_Brent*"), and the SV field ("*Sub_IsochoreSV_Brent*"). Isochores can be corrected according to the change in total volume of the host quartz. The output includes also the phase state of the quartz at specific isochoric conditions, either α - or β -quartz.

A combination of homogenization (two-to-one phase reduction) and dissolution temperatures (three-to-two phase reduction) can be used to calculate the bulk composition and molar volume of fluid inclusions with the method "*Th_Tm_calculationSLV*" (Table B8).

The different stability fields are defined in the method "*Fields_Definition*" (Table B9), and include the homogeneous fluid phase field, the LV field, the SL field, and the SV field. The method "*Volume_Limits*" (Table B9) calculates for a specific composition the values of molar volumes at the intersection of stability fields, and at the maximum conditions of the mathematical model.

Ice and hydrohalite dissolution conditions are calculated with a variety of primary methods according to specific publications (Table 6). These conditions correspond to the SLV curve at temperatures below 0.1 °C, in which the solid phase is either hydrohalite or ice. The methods calculate a salinity (in mass% NaCl) from selected final dissolution temperatures of either ice or hydrohalite dissolution, with relatively simple mathematical equations. The derived method "*Freezing_Point_Depression*" (Table B10) calculates a dissolution temperature of ice or hydrohalite from a selected salinity.

Table 6. Primary methods to calculate mass% NaCl from dissolution temperatures of ice and hydrohalite.

<i>method name</i>	<i>input</i>	<i>output</i>
Mass_Bakker2012	field, T, ratio	w
Mass_Bodnar93	T	w
Mass_Hall87	T, ratio	w
Mass_Naden96	field, T, ratio	w
Mass_Oakes90	T, ratio	w
Mass_Potter78	T	w
Mass_Steele2011	field, T, ratio	w
Mass_Sterner88	field, T, ratio	w

Tables with derived algorithms (methods)

Table B1. Derived methods with algorithms to calculate thermodynamic properties of pure H₂O, and a list of primary methods (see Table 2) that are included in each method. iter. is the number of iterations in the numerical approach.

<i>method name</i>	<i>input</i>	<i>output</i>	<i>included methods</i>
Haar_Cp	T, V	C _p	Haar_Base Haar_Residual
Haar_Cv	T, V	C _v	Haar_Base Haar_Residual Haar_Ideal
Haar_Enthalpy	T, V	H	Haar_Base Haar_Residual Haar_Ideal
Haar_Fugacity	T, V	f	Haar_Base Haar_Residual
Haar_Pressure	T, V	p	Haar_Base Haar_Residual
SaturationT	P or V	T, iter.	SaturationP SaturationV

Table B2. Derived methods with algorithms to calculate numerically the molar volume of pure H₂O. The solution of calculations is bracketed between a "lower" and "upper" value. iter. is the number of iterations in the numerical approach.

<i>method name</i>	<i>input</i>	<i>output</i>	<i>included methods</i>
Haar_Volume_Brent	T, p, lower, upper	V, iter.	Haar_Pressure
Haar_Volume_Sectant	T, p, lower, upper	V, iter.	Haar_Pressure
Haar_Volume_Phase	T, p, phase	V	Holloway_MolarVolume SaturationP SaturationV Haar_Pressure Haar_Volume_Brent Haar_Volume_Sectant

Table B3. Derived methods with algorithms to calculate numerically saturation condition of pure H₂O. The solution of calculations is limited between a lower and upper value. iter. is the number of iterations in the numerical approach.

<i>method name</i>	<i>input</i>	<i>output</i>	<i>include methods</i>
Equal_Fugacity_Th	P, lower, upper	T, V _{liq} , V _{vap} , f _{liq} , f _{vap} , iter.	SaturationT SaturationV Haar_Fugacity Haar_Volume_Phase
Equal_Fugacity_Ph	T, lower, upper	p, V _{liq} , V _{vap} , f _{liq} , f _{vap} , iter.	SaturationP SaturationV Haar_Fugacity Haar_Volume_Phase

Table B4. Derived methods with algorithms to calculate numerically the temperature of two-phase lines, and temperature and pressure of single-phase fields of pure NaCl.

<i>method name</i>	<i>input</i>	<i>output</i>	<i>included methods</i>
TemperatureV_pureNaCl	line, V, lower, upper	T, p, iter.	PressureT_pureNaCl Volume_pureNaCl
Pressure_pureNaCl_Field	phase, V, T, lower, upper	p, iter.	Volume_pureNaCl
Temperature_pureNaCl_Field	phase, V, p, lower, upper	T, iter.	Volume_pureNaCl

Table B5. Derived methods with algorithms to calculate numerically a variety of properties of the critical point, liquidus, SLV curve, dew-point curve, bubble point curve, molar volume corrections and pressure.

<i>method name</i>	<i>input</i>	<i>output</i>	<i>included methods</i>
Critical_Temperature	p or x	T, iter.	Critical_Composition Critical_Pressure
Halite_Liquidus_Pressure	T, x, lower, upper	p, iter.	Halite_Liquidus_Compliq
Halite_Liquidus_Temperature	p, x	T	Halite_Liquidus_Compliq
SLV_Comp	phase, T	x	LV_VapourBrancheX Halite_Liquidus_Compliq
SLV_TemperatureP	p, lower, upper	T	SLV_Pressure
SLV_TempFitting	phase, x, lower, upper	T	SLV_Comp
SLV_TemperatureX	phase, x	T	SLV_TempFitting
LV_LiquidBranche	T or p, x, lower, upper	T or p, iter.	LV_LiquidBrancheX
LV_vapourBranche	T or p, x, lower, upper	T or p, iter.	LV_VapourBrancheX
Volume_Correction17	T _{mod} , p	V	Equal_Fugacity_Th Haar_Volume_Phase
Volume_Correction18	T, P, x	V	Temperature_Modified Haar_Volume_Phase
Pressure_H2O_NaCl	T, V, x, lower, upper	p, iter.	Critical_Temperature Critical_Pressure Temperature_Modified Haar_Volume_Phase Volume_Correction17 Volume_Correction18

Table B6. Derived methods with algorithms to calculate numerically homogenization conditions.

<i>method name</i>	<i>input</i>	<i>output</i>	<i>included methods</i>
Th_Vapour_Brent	x, V, lower, upper	T, p, iter.	Dew_maximumP Critical_Pressure Dew_minimumP SLV_Pressure Dew_MAX Pressure_pureNaCl LV_VapourBranche Temperature_Modified Haar_Volume_Phase
Th_Liquid_Brent	x, V, lower, upper	T, p, iter.	SaturationP Equal_Fugacity_Ph SLV_Pressure Critical_Pressure LV_LiquidBranche Temperature_Modified Haar_Volume_Phase Volume_Correction17 Volume_Correction18
Th_Liquid_Sectant	x, V, lower, upper	T, p, iter.	LV_LiquidBranche Temperature_Modified Haar_Volume_Phase Volume_Correction17 Volume_Correction18
Th_Vapourus_Brent	x, V, lower, upper	T, p, iter.	Sub_MAX SLV_Pressure LV_VapourBranche Temperature_Modified Haar_Volume_Phase
Th_Liquidus_Brent	x, V, lower, upper	T, p, iter	Halite_Liquidus_Pressure Temperature_Modified Haar_Volume_Phase Volume_Correction17 Volume_Correction18
Homogenization_Bubble_Correction	x, V, limits, qtz	T, p, V _{mod}	Th_Liquid_Brent QuartzVolume
Homogenization_Dew_Correction	x, V, limits, qtz	T, p, V _{mod}	Th_Vapour_Brent QuartzVolume
Homogenization_Liquidus_Correction	x, V, qtz	T, p, V _{mod}	SLV_TemperatureX SLV_Pressure Temperature_Modified Haar_Volume_Phase Volume_Correction17 Volume_Correction18 Halite_Liquidus_Temperature Halite_Liquidus_Pressure Liquidus_Minimum Th_Liquidus_Brent QuartzVolume
Homogenization_Vapourus_Correction	x, V, limits, qtz	T, p, V _{mod}	Th_Vapourus_Brent QuartzVolume

Table B7. Derived methods with algorithms to calculate numerically isochores.

<i>SLV_</i>	<i>input</i>	<i>output</i>	<i>included methods</i>
Sub_IsochoreLV_Brent	$x_{\text{bulk}}, V, T,$ lower, upper	$p, x_{\text{liq}},$ $x_{\text{vap}}, \varphi_{\text{liq}},$ $V_{\text{liq}}, V_{\text{vap}}$	LV_VapourBranche LV_LiquidBranche Temperature_Modified Haar_Volume_Phase Volume_Correction17 Volume_Correction18
Sub_IsochoreSL_Brent	$x_{\text{bulk}}, V, T,$ lower, upper	$p, x_{\text{liq}},$ $x_{\text{vap}}, \varphi_{\text{liq}},$ $V_{\text{liq}}, V_{\text{vap}}$	Halite_Liquidus_Compliq Temperature_Modified Haar_Volume_Phase Volume_Correction17 Volume_Correction18 Volume_pureNaCl
Sub_IsochoreSV_Brent	$x_{\text{bulk}}, V, T,$ lower, upper	$p, x_{\text{vap}},$ $x_{\text{sol}}, \varphi_{\text{vap}},$ $V_{\text{vap}}, V_{\text{sol}}$	LV_VapourBranche Temperature_Modified Haar_Volume_Phase Volume_pureNaCl
SLV_Isochore	$T, V, x_{\text{bulk}},$ qtz	$p, x_{\text{liq}}, V_{\text{liq}},$ $\varphi_{\text{liq}}, x_{\text{vap}},$ $V_{\text{vap}}, \varphi_{\text{vap}},$ $V_{\text{sol}}, \varphi_{\text{sol}},$	SLV_Pressure SLV_Comp QuartzVolume Temperature_Modified Haar_Volume_Phase Volume_Correction17 Volume_Correction18 Volume_pureNaCl
SLV_Intersection_Brent	$x_{\text{bulk}}, V,$ lower, upper, qtz	$T, P, \varphi, x,$ V	SLV_Pressure SLV_Comp QuartzVolume Temperature_Modified Haar_Volume_Phase Volume_Correction17 Volume_Correction18 Volume_pureNaCl
Isochore_Correction	$T, x_{\text{bulk}}, V,$ $p_{\text{first}}, \text{qtz}$	$p, x_{\text{liq}}, V_{\text{liq}},$ $\varphi_{\text{liq}}, x_{\text{vap}},$ $V_{\text{vap}}, \varphi_{\text{vap}},$ $V_{\text{sol}}, \varphi_{\text{sol}},$ qtz-phase	Critical_Temperature Critical_Pressure Temperature_Modified Haar_Volume_Phase SLV_Pressure Pressure_H2O_NaCl Pressure_pureNaCl Dew_MAX LV_VapourBranche LV_LiquidBranche Sub_IsochoreLV_Brent Sub_IsochoreSL_Brent QuartzVolume

Table B8. Derived methods with algorithms to calculate V-x properties of fluid inclusions.

<i>method name</i>	<i>input</i>	<i>output</i>	<i>included methods</i>
Th_Tm_calculationSLV	$T_h, T_m, x_{liq},$ $x_{vap}, V_{liq},$ V_{vap}, qtz	$x, V, \varphi_{liq},$ p	Critical_Composition Critical_Pressure Temperature_Modified Haar_Volume_Phase Dew_MAX LV_VapourBranche Halite_Liquidus_CompLiq Volume_Limits Homogenization_Bubble_Correction Homogenization_Dew_Correction Homogenization_Liquidus_Correction

Table B9. Derived methods with algorithms to calculate the stability fields and limiting values of molar volumes of liquid, vapour and solid.

<i>method name</i>	<i>input</i>	<i>output</i>	<i>included methods</i>
Field_Definition	T, p, x	field	SLV_TemperatureX SLV_Pressure Critical_Temperature Critical_Pressure Temperature_Modified Haar_Volume_Phase Pressure_H2O_NaCl Equal_Fugacity_Ph LV_LiquidBranche Dew_maximumT Dew_minimumT Dew_MAX Dew_maximumP Dew_minimumP Pressure_pureNaCl LV_VapourBranche Sub_MAX Halite_Liquidus_Pressure
Volume_Limits	x	V	SLV_TemperatureX SLV_Pressure Temperature_Modified Haar_Volume_Phase Volume_Correction17 Volume_Correction18 SaturationP Equal_Fugacity_Ph LV_LiquidBranche Critical_Temperature Critical_Pressure Critical_Composition Pressure_pureNaCl Dew_maximumT Dew_maximumP Dew_minimumT Dew_minimumP Dew_MAX LV_VapourBranche Sub_MAX

Table B10. Derived method with algorithms to calculate numerically dissolution temperature for salinities $x(\text{NaCl}) < 0.0990$. "Cubic_Equation" is a algorithm to calculate analytically the solutions of cubic equations".

method name	input	output	included methods
Freezing_Point_Depression	eos, field, w	T	Cubic_Equation Mass_Sterner88 Mass_Oakes90 Mass_Naden96 Mass_Steele2011 Mass_Bakker2012