Accurate Calculation Procedure for V-x Parameters of Hydrothermal Gold Ore Fluid Inclusions

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Abstract: Determining the V-x parameters of H_2O–NaCl–CO_2 fluid inclusions (total density of inclusions, gas content, homogenization pressure, etc.) is of great value for the exploration of hydrothermal deposits. However, previous accurate calculation methods are only applicable to H_2O–NaCl–CO_2 fluid inclusions with homogenization temperature above 300 °C and CO_2 phase homogenization temperature above the CO_2 clathrate melting temperature. In this paper, a new calculation method is proposed to accurately solve the V-x parameters of H_2O–NaCl–CO_2 fluid inclusions with complete homogenization temperature lower than 300 °C. The algorithm first determines the salinity of inclusions with respect to the melting temperature of CO_2 clathrate and the partial homogenization temperature of the CO_2 phase and then determines the internal pressure of inclusions when CO_2 clathrate is completely melted. The V-x parameters of the inclusions are then iteratively solved. The new algorithm does not require a visual estimation of the volume fraction of the CO_2 phase as an input parameter. It is possible to avoid the significant error brought about by traditional method of calculating the inclusion V-x parameters involving visual estimation of the CO_2 phase volume fraction. A computer program is developed on the basis of the new method and is applied to the analysis of fluid inclusions in medium and low temperature hydrothermal gold ore.

Keywords: H_2O–NaCl–CO_2; fluid inclusion; V-x parameter; algorithm; calculation program

1. Introduction

Geological fluid, which is involved in and has a crucial effect on numerous geological processes, is among frontiers and hotspots in geoscience [1–4]. NaCl and CO_2 are the most common solute components in various geological fluids. Many geological fluids can be approximated as H_2O–CO_2 or H_2O–NaCl–CO_2 systems, such as hydrothermal gold ore-forming fluids, intermediate-grade metamorphic fluids, etc. Therefore, determining the physical and chemical parameters, e.g., density, salinity, composition, and homogenization pressure of H_2O–NaCl–CO_2 inclusions, is one of the important foundations for studying the source and evolution of ore-forming fluids and exploring the formation mechanism of hydrothermal deposits [5–9].

Previous studies have shown that most hydrothermal gold ore-forming fluids have medium to low salinity (NaCl less than 6–10 wt %) and relatively high CO_2 content, and the complete homogenization temperature of the inclusions is between 200–400 °C [9–11]. At room temperature, the inclusions are either gas-liquid-liquid or gas-liquid, and lack halite daughter minerals. H_2S and N_2 are also very low. Therefore, a V-x parameter calculation program for the H_2O–NaCl–CO_2 inclusions is adequate for the research of hydrothermal gold ore fluid inclusion.

The thermodynamic model and calculation method are both necessary for the development of the calculation program. The determination of V-x parameters of the inclusions requires accurate calculations of the P-V-T-x and gas-liquid equilibrium composition of the H_2O–NaCl–CO_2 fluid system at 0–400 °C, 0–3000 bar. Previous state equations for H_2O–NaCl–CO_2–CH_4 system at medium-high temperature ($T > 300$ °C) or medium-low temperature equations [12–14], as well as the CO_2 solubility model could basically meet the calculation requirement [14–16]. For the latter, Song's [17] method is adequate for the calculation of H_2O–NaCl–CO_2 inclusions where the CO_2 phase homogenization temperature is higher than the CO_2 clathrate melting temperature. Mao et al. [18] proposed a method for the calculation of H_2O–NaCl–CO_2 inclusions with complete homogenization to liquid phase and homogenization pressure not higher than 1500 bar, which is based on the model of Song [17]. For the calculation of the V-x parameter of the H_2O–NaCl–CO_2 inclusions whose CO_2 phase homogenization temperature is lower than the melting temperature of the CO_2 clathrate, a valid algorithm that does not require a visual estimation of gas-liquid ratiois still absent.

This study aims to solve the above problems by developing a computer program that can accurately calculate the V-x parameters of H_2O–NaCl–CO_2 inclusions. Two major contributions are included in this study, as described below:

1. A new iterative algorithm is proposed to solve the V-x parameters of H_2O–NaCl–CO_2 inclusions with a CO_2 phase homogenization temperature lower than the CO_2 clathrate melting temperature and to develop a calculation program. This new algorithm only takes the temperature measurement data as the input parameter and does not need to visually measure the volume fraction of the CO_2 phase.

2. A new application is developed that can accurately calculate the V-x parameters of H_2O–NaCl–CO_2 inclusions, which is based on the algorithms of Song et al. [17] and this paper. The thermodynamic properties of the H_2O–NaCl–CO_2 system with temperatures above 300 °C and temperatures below 300 °C were calculated using the equations established by Duan et al. [12], Sun and Dubessy [13]. The application is valid at a full homogenization temperature range of 200–450 °C, and is suitable for both situations in which CO_2 phase homogenization temperature is either higher or lower than CO_2 clathrate melting temperature, with no halite daughter minerals present.

2. Calculation Method

2.1. Salinity Calculation of H_2O–NaCl–CO_2 Fluid Inclusions

For H_2O–NaCl–CO_2 inclusions, salinity is generally expressed in mass fraction or mass percentage S, representing the mass fraction of NaCl in H_2O–NaCl solution. At room temperature, the H_2O–NaCl–CO_2 inclusions generally appear in two or three phases. The corresponding salinity calculation method will be introduced below with respect to these two different situations.

2.1.1. Salinity Calculation of Three-Phase H_2O–NaCl–CO_2Inclusions at Room Temperature

At room temperature, three-phase H_2O–NaCl–CO_2 inclusions (aqueous phase + CO_2 liquid phase + CO_2 gas phase) cool down to form CO_2 clathrate. After re-heating, the melting temperature of the CO_2 clathrate will be lower than the homogenization temperature of the CO_2 phase. Therefore, CO_2clathrate in the inclusion disappeared by heating so that the salinity of the inclusion could be determined with respect to the temperature. During the heating, the CO_2 clathrate disappears and the system is in four-phase equilibrium. According to the Gibbs phase rule:

$$F = C - \varphi + 2 \tag{1}$$

the number of components $C = 3$, the number of phases $\varphi = 4$, the four-phase degree of freedom $F = 1$, the salinity then has a one-to-one correspondence to the melting temperature of the clathrate, and the NaCl content of the aqueous phase is also determined when melting temperature is determined. In addition, in the case of lower temperature, the content of NaCl and water vapor in the CO_2 gas phase (bubble) and CO_2 liquid phase is negligible, and the NaCl content in the aqueous phase could

be used to calculate the salinity of the entire inclusion. Salinity could be calculated by the equation below [19,20]:

$$S \text{ (wt \%)} = 0.00098241 \times (10 - T) \times (T^2 + 45.385T + 1588.75) \tag{2}$$

where T is the melting temperature of CO_2 hydrate (−10–10 °C). This equation is valid in the NaCl salinity range of 0–24.2 wt %.

2.1.2. Salinity Calculation of Two-Phase H_2O–NaCl–CO_2 Inclusions at Room Temperature

The method above is not valid for the determination of salinity for H_2O–NaCl–CO_2 fluid inclusions exhibiting two phases at room temperature (aqueous phase + CO_2 liquid phase or CO_2 gas phase). When the inclusions cool down, CO_2 hydrate will also form. When the system is heated, the hydrate will disappear at a certain temperature. At this time, the inclusion system is on the three-phase equilibrium interface. Since the number of components is $C = 3$, the number of phases is $\varphi = 4$, and the degree of freedom of the system is $F = 2$, which means that the salinity changes not only with temperature but also with pressure. Then the aforementioned method for determining the salinity of three-phase H_2O–NaCl–CO_2 inclusions is no longer applicable.

The following two calculation methods are mainly used for this occasion. The first method was proposed by Diamond [21], which determines the salinity in combination with the hydrate melting temperature and the partial homogenization temperature of the CO_2 measured in the metastable state. When the CO_2 gas phase and the liquid phase are homogeneous to the gas phase, the salinity is calculated as follow:

$$S \text{ (wt \%)} = 15.6151 - 0.03627x + 0.00164x^2 - 0.949y - 0.00287xy - 0.02464y^2 - 0.00107xy^2 - 0.00222y^3 \tag{3}$$

x is the partial homogenization temperature of the CO_2 phase, and the range of application is between −20 °C to 10 °C. y is the melting temperature of the hydrate and is valid between −5 °C to 13 °C. The range of salinity S is 0–21 wt % NaCl (relative to the binary H_2O–NaCl subsystem without CO_2). When the CO_2 gas phase and the liquid phase are homogeneous to the liquid phase, the salinity is calculated as follow:

$$S \text{ (wt \%)} = 15.6151 - 0.065705x + 0.00778x^2 - 1.05135y - 0.02687xy - 0.04717y^2 - 0.00138xy^2 - 0.00411y^3 \tag{4}$$

The valid range of x and S is the same as the previous equation while y is valid between −8 °C to 10 °C.

The second method, which is proposed by Fall et al. [22], determines the CO_2 phase pressure according to the carbon dioxide Fermi peak displacement method, and also determines the NaCl content according to the gas hydrate three-phase equilibrium model by Bakker [23], Duan and Sun [15]. It brings smaller salinity error for H_2O–NaCl–CO_2 two-phase inclusion in which CO_2 is a liquid phase (0.3 wt %) and much more significant error for those in which CO_2 exhibits gas phase (~3.2 wt %)

2.2. Calculation Method of V-x Parameters of H_2O–NaCl–CO_2 Inclusions

For single-component fluid inclusions, the microthermometry measurement data can be substituted into the formula to calculate the total density of inclusions and homogenization pressure. For ternary system fluid inclusions, the total density, composition, homogenization pressure and other parameters need to be determined by means of more complex thermodynamic calculation models or diagrams.

The V-x parameter depends on the thermodynamic properties of the fluid system under different temperature and pressure conditions. A few of them can be calculated by simple formulas, while for the rest, an accurate solution can only be provided by thermodynamic models with sound theoretical basis. Due to the non-ideality of the system, there are few equations that can accurately describe the thermodynamic properties of H_2O–NaCl–CO_2 systems. Parameters and the corresponding models include (1) Gas-liquid phase equilibrium composition and density of H_2O–NaCl–CO_2 ternary system

at the homogenization temperature are calculated by equation established by Duan et al. [12,14], Sun and Dubessy [13]. (2) Solubility of CO_2 in aqueous sodium chloride solution at room temperature is described by the concentration of CO_2 in aqueous NaCl solution, which could be provided by the CO_2 solubility model established and improved by Duan and collaborators [14–16,24], and the density of aqueous solutions described by the Pitzer's [25] activity coefficient model. (3) Triple-phase equilibrium pressure of CO_2 clathrate is determined by the equilibrium model established by Duan and Sun [15].

2.2.1. Traditional Algorithm for V-x Parameters of H_2O–NaCl–CO_2 Fluid Inclusions

As mentioned above, the salinity of the H_2O–NaCl–CO_2 fluid inclusions can be determined by the melting temperature of the CO_2 clathrate, but there is no simple calculation method for the CO_2 content of the inclusions. It is generally necessary to visually estimate the volume ratio of the CO_2 phase to the aqueous phase, and then the homogenization pressure and isometrics of H_2O–NaCl–CO_2 inclusions can be obtained by using the appropriate equation of state on the basis of density, composition and the estimated homogenization temperature. Nonetheless, the visual volume fraction inevitably produces large errors, giving rise to inaccurate calculation results of parameters [26,27].

Combined with theoretical calculations, Schwarz [28] plotted the V-x diagram of H_2O–CO_2 inclusions without NaCl and H_2O–NaCl–CO_2 inclusions with a salinity of 6 wt %. Bakker and Diamond [29,30] also mapped the V-x of H_2O–CO_2 inclusions based on experimental data published by Sterner and Bodnar [31]. Although the using of these diagrams does not need a visual estimation of the volume fraction of the CO_2 phase, the accuracy is poor in the low temperature region, and the applicable range of salinity is small.

2.2.2. Iterative Calculation Method for V-x Parameters of H_2O–NaCl–CO_2 Fluid Inclusions at Room Temperature

The phase volume of a H_2O–NaCl–CO_2 fluid inclusion is limited by the density, complete homogenization temperature and homogenization of the CO_2 phase due to that the inclusion is a closed system with constant volume. Parry [32] proposed an iterative calculation method to solve the CO_2 content and total density of the three-phase inclusions of H_2O–NaCl–CO_2 system. This method used the Bowers-Helgeson [33] equation to calculate the fluid thermodynamic parameters (gas-liquid phase equilibrium composition, gas phase, and aqueous phase density, etc.) required during the iterative process. Parry's method does not need to visually measure the volume or phase proportion of the inclusions, and density and X_{CO2} could be calculated using iterative method with the measurement of $T_{h,CO2}$, S, and T_h. Due to the Bowers-Helgeson equation, Parry's iterative algorithm can be used to calculate the V-x parameters of H_2O–NaCl–CO_2 fluid inclusions with a homogenization temperature above 300 °C. However, Parry's method ignores the solubility of CO_2 in NaCl aqueous solution, so the mathematical function of X_{CO2} constructed and the calculated X_{CO2} is not sufficiently accurate, and then the pressure error calculated by iterative calculation is ineligible. Furthermore, Parry's method cannot be applied for the H_2O–NaCl–CO_2 system at 0–300 °C, due to the lack of validated fluid thermodynamic functions over this temperature range.

Liu and Shen [6], and Song [17] take into account the solubility of CO_2 in aqueous sodium chloride solution at room temperature and improved the calculation accuracy of the Parry method. Song et al. [17] also used the more accurate H_2O–NaCl–CO_2 system state equation (DMW95 equation) established by Duan et al. [12] instead of the Bowers-Helgeson [17] equation. DMW95 is a state equation capable of accurately predicating P-V-T-X, phase equilibria, solubility, and activity of the H_2O–NaCl–CO_2 system. Since the DMW95 equation is only applicable to high temperature ($T > 300$ °C) H_2O–NaCl–CO_2 system, this improved calculation method is still not valid at complete homogenization temperature below 300 °C.

On the basis of Song's method, Xi et al. [34]. proposed that the dissolved amount of CO_2 in aqueous solution M_{CO2} can be calculated by the solubility model proposed by Duan and Sun [14,35]. This method can only be applied to H_2O–NaCl–CO_2 inclusions in which the CO_2 partial homogenization

temperature is higher than the melting temperature of the clathrate, and the halite daughter minerals are absent. The inclusion should also be completely homogeneous to aqueous solutions. Xi et al. [34] also suggested that for H_2O–NaCl–CO_2 inclusions with complete homogenization temperature below 300 °C and salinity below 4%, the ternary system can be approximated as a H_2O–CO_2 binary system, which expands the applicable range of temperature and pressure of the method.

Xu et al. [36] combined the improved algorithms of Song with the state equation established by Mao et al. [37] and developed an application capable of calculating V-x parameters of CO_2–H_2O fluid inclusions with a complete homogenization temperature below 350 °C, homogenization pressure below 100 MPa, which are completely homogenized to liquid phase.

Mao et al. [18] proposed a new algorithm for calculating the V-x parameters of H_2O–NaCl–CO_2 inclusions. The method uses the improved CO_2 solubility model of them in combination with the previously established aqueous solution density model to calculate the relevant thermodynamic properties of the H_2O–NaCl–CO_2 system. A calculation program is also developed based on this new algorithm, which applies to a maximum homogenization temperature of 723 K, but only for H_2O–NaCl–CO_2 inclusions that are completely homogeneous to the liquid phase [18].

3. Calculation Program Description

3.1. A New Algorithm for V-x Parameters of H_2O–NaCl–CO_2 Two-Phase Inclusions at Room Temperature

As mentioned above, the iterative method initiated by Parry [32] and further improved by Song et al. [17] is only applicable to H_2O–NaCl–CO_2 three-phase inclusions without halite daughter minerals, and is not suitable for the two-phase inclusion of H_2O–NaCl–CO_2, in which the homogenization temperature of the CO_2 phase is lower than the melting temperature of the CO_2 clathrate.

This study proposes a new iterative algorithm to accurately calculate the V-x parameters of the H_2O–NaCl–CO_2 two-phase inclusion. The algorithm first uses the method of Diamond [21] to determine the salinity of H_2O–NaCl–CO_2 two-phase inclusions with respect to the melting temperature of CO_2 clathrate and the partial homogenization temperature of CO_2 phase measured under metastable state, and uses the three-phase equilibrium calculation model of CO_2 hydrate established by Duan and Sun [15] to determine the internal pressure of inclusions when CO_2 clathrate is completely melted. Then, the V-x parameters of the inclusions are iteratively solved by the relationship between the phase change and the volume change when the CO_2 clathrate is melted and the inclusions are completely homogenized. The new algorithm also does not require a visual estimation of the volume fraction of the CO_2 phase as an input parameter. Tables 1 and 2 provide a brief description of the input and output parameters of the method and program

Table 1. Input parameter of the program for H_2O–NaC–CO_2 inclusion.

Parameter Symbol	Description	Allowed Input Range
$T_{h, CO2}$	Partial homogenization temperature of CO_2 phase	253–304.2 K
$T_{m, cla}$	Melting temperature of CO_2 clathrate	264–283.2 K
T_h	Complete homogenization temperature of the inclusion	473–723 K

Table 2. Output parameters of the program for H_2O–NaCl–CO_2 inclusions.

Parameter Symbol	Description
V_m	Molecular volume of inclusion, cm^3/mol
X_{CO2}	Total CO_2 content of the inclusions, expressed in mole fraction
X_{H2O}	Total water content of the inclusion, expressed in mole fraction
X_{NaCl}	Total NaCl content of the inclusion, expressed in mole fraction
T_h	Complete homogenization temperature of the inclusion, K
P_{hom}	Homogenization pressure of the inclusion, bar
Φ_{CO2}	Volume fraction of CO_2 gas phase in inclusions after CO_2 clathrate melting

The specific iterative steps of the algorithm, as shown in Figure 1, are described as follows:
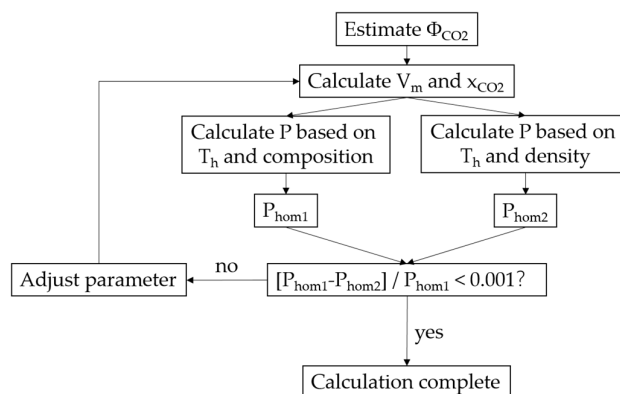

Figure 1. Flowchart for the calculation of V-x properties of two-phase CO_2–H_2O–NaCl fluid inclusions.

1. After determining the salinity of the inclusions, the internal pressure of the inclusions after the carbon dioxide hydrate is completely melted is determined according to the gas hydrate three-phase equilibrium model, and then the density of the CO_2 phase and the aqueous phase at this temperature are calculated using a proper thermodynamic model.

2. Calculating the total density (or molar volume) and CO_2 concentration X_{CO2} of the inclusion based on an initial estimation of $\varPhi_{CO2}$.

3. Determining the pressure P_{homl} at which the inclusions are at homogenization temperature T_h, which refers to the minimum pressure at which the solution or gas phase is saturated at T_h.

4. Calculating the pressure P_{homl2} at which the inclusions with certain composition and total density exhibit a single phase at the homogenization temperature.

5. If P_{homl} and P_{homl2} are significantly different, change $\varPhi_{CO2}$ and re-calculate the total density (or molar volume) and X_{CO2} until the calculated relative difference of P_{homl} and P_{homl2} is less than 0.1%. At this time, the final total density, X_{CO2}, and $\varPhi_{CO2}$ are obtained.

The above step 3 needs to calculate the gas-liquid equilibrium composition of the H_2O–NaCl–CO_2 system on the basis of a suitable equation of state, and step 4 requires the calculation of the P-V-T-x of the H_2O–NaCl–CO_2 system. The DMW95 equation is used when $T_h > 573$ K, while the equation of state for the medium-low temperature H_2O–NaCl–CO_2 system established by Sun and Dubessy [13] is applicable when $T_h \leq 573$ K.

3.2. H_2O–NaCl–CO_2 Inclusion Parameter Calculation Program Description

Combining the iterative algorithm for calculating the V-x parameters of H_2O–NaCl–CO_2 inclusions with the related thermodynamic model introduced above, a computer program for the accurate calculation of V-x parameters of H_2O–NaCl–CO_2 inclusions is written in FORTRAN90 language, which only takes microthermometry measurement data as input parameters with no gas phase volume fraction required. Some calculation examples were also given below.

3.2.1. Program Function

An important feature of the calculation program developed in this study is that the input parameters are all microthermometry measurement data without visually measuring the CO_2 phase volume fraction. The Raman peak displacement of CO_2 is also not required as an input parameter to determine the internal pressure and composition of the inclusion. In this study, the improved algorithm of Song et al. [17] was used to calculate the V-x parameters of H_2O–NaCl–CO_2 inclusions in which the partial homogenization temperature of the CO_2 phase is higher than the melting temperature of CO_2 clathrate. For the V-x parameters of the H_2O–NaCl–CO_2 inclusions where the CO_2 phase partial homogenization temperature is lower than the CO_2 clathrate melting temperature, the new algorithm

proposed in this study is applied, which is not only suitable for three-phase H_2O–$NaCl$–CO_2 inclusions but also for two-phase H_2O–$NaCl$–CO_2 inclusions at room temperature.

The calculation program developed in this paper is based on the state equation of a wide temperature and pressure range and high precision, thus it is more applicable than any existing calculation procedures in terms of temperature and pressure condition. The program is suitable for inclusions that are either completely homogeneous to the liquid phase or completely homogeneous to gas phase. Due to the inherent defects of the thermodynamic model, the program has a large V-x parameters calculation error for critically homogeneous and near-critically homogeneous inclusions, which requires further improvement.

3.2.2. Steps for Usage

The program is provided as Supplementary File S1. The procedure for calculating the V-x value of H_2O–$NaCl$–CO_2 inclusions is as follows:

1. Enter the microthermometry measurement parameters required for the calculation, including the partial homogenization temperature of the CO_2 phase, the melting temperature of the CO_2clathrates, and the complete homogenization temperature of the inclusions.

2. Select the CO_2 phase partial homogenization mode and the inclusion completely homogenization mode, and run the Fortran executive program.

3. The calculation outputs all the seven parameters as shown in Table 2.

3.3. Calculation Example

Tables 3 and 4 provide calculation results.

Table 3. Samples for V-x parameters of H_2O–$NaCl$–CO_2 inclusions (liquid CO_2 + vapor CO_2 homogenized to vapor phase).

$T_{h, CO2}$	$T_{m, cla}$	T_h	V_m	m_{CO2}	Wt % NaCl	P_{hom}	Φ_{CO2}
298.2	280.2	473	20.92	1.948	5.678	518.2	0.1370
298.2	278.2	473	20.74	1.757	9.004	579.7	0.1291
298.2	273.2	473	20.46	1.437	15.47	674.8	0.1147
293.2	280.2	473	20.94	1.846	5.678	469.9	0.1364
293.2	278.2	473	20.77	1.660	9.004	519.5	0.1295
288.2	280.2	473	20.94	1.814	5.678	455.5	0.1352
298.2	280.2	523	22.74	2.564	5.678	468.0	0.2144
298.2	278.2	523	22.34	2.302	9.004	533.3	0.1991
298.2	273.2	523	21.69	1.864	15.47	653.5	0.1710
293.2	280.2	523	21.28	2.348	5.678	417.3	0.2128
293.2	278.2	523	22.40	2.111	9.004	470.7	0.1992
293.2	273.2	523	21.79	1.720	15.47	569.1	0.1736
288.2	280.2	523	22.78	2.231	5.678	390.9	0.2160
288.2	278.2	523	22.43	2.000	9.004	436.4	0.1983
288.2	273.2	523	21.84	1.620	15.47	518.6	0.1748
283.2	280.2	523	22.78	2.147	5.678	372.7	0.2087
283.2	278.2	523	22.45	1.917	9.004	412.0	0.1917
283.2	273.2	523	21.88	1.530	15.47	480.6	0.1756
278.2	280.2	523	22.78	2.108	5.753	366.3	0.2027
278.2	273.2	523	21.90	1.478	15.47	456.6	0.1759
273.2	280.2	523	22.91	1.991	4.333	310.7	0.2102
273.2	278.2	523	22.52	1.797	8.483	364.2	0.1978
298.2	280.2	573	25.51	3.525	5.678	487.2	0.3109
298.2	278.2	573	24.52	3.061	9.004	562.5	0.2795
298.2	273.2	573	23.00	2.322	15.47	706.9	0.2240
293.2	280.2	573	25.60	3.142	5.678	438.6	0.3092
293.2	278.2	573	24.71	2.759	9.004	503.6	0.2817

Table 3. *Cont.*

$T_{h, CO2}$	$T_{m, cla}$	T_h	V_m	m_{CO2}	Wt % NaCl	P_{hom}	Φ_{CO2}
293.2	273.2	573	23.28	2.132	15.47	629.8	0.2319
288.2	280.2	573	25.64	2.891	5.678	407.4	0.3065
288.2	278.2	573	24.81	2.552	9.004	465.1	0.2819
288.2	273.2	573	23.45	1.988	15.47	576.1	0.2362
283.2	280.2	573	25.65	2.700	5.678	384.0	0.3038
283.2	278.2	573	24.87	2.387	9.004	435.4	0.2814
283.2	273.2	573	23.58	1.864	15.47	533.2	0.2393
278.2	280.2	573	25.65	2.603	5.753	374.1	0.3018
278.2	273.2	573	23.66	1.769	15.47	501.8	0.2409
273.2	280.2	573	25.49	2.422	4.333	32.24	0.3077
273.2	278.2	573	25.06	2.168	8.483	383.2	0.2838
298.2	280.2	623	36.71	7.756	5.678	453.4	0.5529
298.2	278.2	623	34.05	6.616	9.004	453.8	0.5105
298.2	273.2	623	27.12	3.822	15.47	573.2	0.3588
293.2	280.2	623	35.64	6.135	5.678	404.3	0.5276
293.2	278.2	623	32.66	5.109	9.004	409.4	0.4776
293.2	273.2	623	26.56	3.092	15.47	524.5	0.3381
288.2	280.2	623	34.65	5.072	5.678	373.1	0.5051
288.2	278.2	623	31.52	4.165	9.004	383.2	0.4499
288.2	273.2	623	26.31	2.674	15.47	484.9	0.3275
283.2	280.2	623	33.82	4.331	5.678	351.1	0.4861
283.2	278.2	623	30.68	3.541	9.004	364.6	0.4286
283.2	273.2	623	26.14	2.376	15.47	452.7	0.3201
278.2	280.2	623	33.32	3.970	5.753	340.8	0.4747
278.2	273.2	623	26.03	2.165	15.47	428.4	0.3146
273.2	280.2	623	33.83	3.575	4.333	316.5	0.4793
273.2	278.2	623	30.17	2.926	8.483	335.8	0.4125

Table 4. Samples for V-x parameters of H_2O–NaCl–CO_2 inclusions (liquid CO_2 + vapor CO_2 homogenized to liquid phase).

$T_{h, CO2}$	$T_{m, cla}$	T_h	V_m	m_{CO2}	Wt % NaCl	P_{hom}	Φ_{CO2}
298.2	280.2	473	20.09	3.610	5.678	1998	0.1260
298.2	278.2	473	19.73	2.974	9.004	2159	0.1030
298.2	273.2	473	19.44	2.326	15.47	2217	0.08207
293.2	280.2	473	19.93	3.707	5.678	2209	0.1208
293.2	278.2	473	19.57	3.006	9.004	2384	0.09670
293.2	273.2	473	19.31	2.354	15.47	2403	0.07735
288.2	280.2	473	19.78	3.762	5.678	2432	0.1137
288.2	278.2	473	19.41	3.008	9.004	2397	0.08894
298.2	280.2	523	21.19	5.296	5.678	1403	0.1942
298.2	278.2	523	20.55	4.202	9.004	1564	0.1560
298.2	273.2	523	19.86	2.973	15.47	1770	0.1115
293.2	280.2	523	20.98	5.473	5.678	1495	0.1885
293.2	278.2	523	20.34	4.286	9.004	1660	0.1492
293.2	273.2	523	19.70	3.003	15.47	1863	0.1053
288.2	280.2	523	20.79	5.613	5.678	1574	0.1819
288.2	278.2	523	20.16	4.350	9.004	1743	0.1419
288.2	273.2	523	19.55	3.021	15.47	1947	0.09908
283.2	280.2	523	20.63	5.721	5.678	1640	0.1758
283.2	278.2	523	20.01	4.395	9.004	1812	0.1355
278.2	280.2	523	20.36	5458	6.409	1730	0.1610
278.2	273.2	523	19.31	3.030	15.47	1998	0.08831
273.2	280.2	523	20.15	5.278	6.916	1801	0.1509
273.2	278.2	523	19.70	4.141	9.904	1941	0.1182
298.2	280.2	573	22.38	7.224	5.678	1036	0.2602

Table 4. *Cont.*

$T_{h, CO2}$	$T_{m, cla}$	T_h	V_m	m_{CO2}	Wt % NaCl	P_{hom}	Φ_{CO2}
298.2	278.2	573	21.20	5.217	9.004	1157	0.1952
298.2	273.2	573	19.70	2.703	15.47	897.4	0.09942
293.2	280.2	573	22.07	7.423	5.678	1072	0.2521
293.2	278.2	573	20.91	5.260	9.004	1178	0.1851
293.2	273.2	573	19.52	2.703	15.47	897.4	0.09259
288.2	280.2	573	21.81	7.582	5.678	1103	0.2438
288.2	273.2	573	19.38	2.703	15.47	897.4	0.08610
283.2	280.2	573	21.59	7.707	5.678	1127	0.2365
283.2	278.2	573	20.45	5.260	9.004	1178	0.1656
278.2	280.2	573	21.15	7.198	6.409	1173	0.2146
278.2	273.2	573	19.15	2.703	15.47	897.4	0.07577
273.2	280.2	573	20.85	6.862	6.916	1208	0.1996

4. Conclusions

The ore-forming fluid of hydrothermal gold ore can be approximated as H_2O–$NaCl$–CO_2 system. Therefore, it is important to determine the V-x parameters of H_2O–$NaCl$–CO_2 fluid inclusions.

A new algorithm is proposed in this study for the accurate calculation of the V-x parameters of H_2O–$NaCl$–CO_2 two-phase inclusions, i.e., inclusions with a CO_2 phase homogenization temperature lower than the melting temperature of CO_2 clathrate based on microthermometry measurement data.

A calculation program is also developed for the calculation of the V-x parameters of the H_2O–$NaCl$–CO_2 inclusions. The program uses the new algorithm proposed in this study to calculate the V-x parameters of H_2O–$NaCl$–CO_2 two-phase inclusions and uses the improved Parry algorithm to calculate the V-x parameters of H_2O–$NaCl$–CO_2 three-phase inclusions, i.e., the CO_2 phase homogenization temperature is higher than the CO_2 clathrate.

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