



# Extension of the IAPWS-95 formulation and an improved calculation approach for saturated properties

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## ABSTRACT

The IAPWS-95 formulation explicit in Helmholtz free energy proposed by Wagner and Pruß (The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use, *Journal of Physical and Chemical Reference Data* 2002 31(2), 387–535) is extended to calculate the volumetric property of the fluid water from 1 GPa and 273 K to 20 GPa and 4273 K. Comparison with large experimental and molecular dynamic simulation data above 1 GPa shows that the equation of state can reproduce the volume of the fluid water with an average absolute deviation of 0.52%. Thus the original IAPWS-95 formulation together with the extended part can be used in a much larger temperature–pressure region: 273–4273 K and 0–20 GPa. In addition, this paper also reports a reliable and highly efficient method to calculate the saturated properties of water so that the equation of state can be conveniently applied in the study of fluid inclusion: calculating homogenization pressures, homogenization densities (or molar volumes) and isochores. Computer code of the model can be obtained from the first author.

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## 1. Introduction

Water covers more than two thirds of the Earth's surface and can be encountered everywhere from the crust to the mantle. As one of the most important natural fluids, it plays an essential part in many processes, e.g., mineral deposits, volcanic eruptions, magmatic activities, metamorphism, hydrothermal venting, geothermal evolution, petroleum and natural gas formation and migration, and waste disposal. Therefore, understanding thermodynamic properties of water is very important for the interpretation of these physical and chemical processes in the Earth's crust and mantle. Equation of state (EOS) developed based on thermodynamic theory and reliable experimental data is a powerful tool for quantitative interpretation of every kind of thermodynamic properties of water, such as phase equilibrium, fugacity, enthalpy, and volumetric properties.

Over the last several decades, there are a lot of equations of state proposed for water (Abramson and Brown, 2004; Brodholt and Wood, 1993; Duan et al., 1992; Haar et al., 1984; Hill, 1990; Holland and Powell, 1991; Kerrick and Jacobs, 1981; Pitzer and Sterner, 1994, 1995; Saul and Wagner, 1989; Sun and Dubessy,

2010; Wagner et al., 2000; Wagner and Pruß, 2002; Zhang and Duan, 2005). Among these equations of state, the best one is the IAPWS-95 formulation explicit in Helmholtz free energy developed by Wagner and Pruß (2002). The IAPWS-95 formulation can reproduce all thermodynamic properties of water from 273.16 to 1273 K and from 0 to 1 GPa, with or close to experimental accuracy. However, when the EOS is extrapolated to higher temperatures and pressures, deviations increase with temperature when compared with the molecular dynamics simulation data. Hence, it is necessary to fit new parameters so that the EOS can be applied in a much larger temperature–pressure region.

In this work, first, the IAPWS-95 formulation is extended to predict PVT properties of water from 273 K and 1 GPa to 4273 K and 20 GPa from which other thermodynamic properties can be derived. Then, a reliable and highly efficient method is proposed to calculate the saturated properties of water. Thus, the EOS can be conveniently applied in the study of fluid inclusion: calculating homogenization pressures, homogenization densities or molar volumes, and isochores.

## 2. The IAPWS-95 formulation

The IAPWS-95 formulation of the fluid water is in terms of dimensionless Helmholtz free energy  $\phi(\delta, \tau) = f(\rho, T)/RT$ , and is sep-

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arated into two parts, an ideal-gas part  $\phi^0(\delta, \tau)$  and a residual part  $\phi^r(\delta, \tau)$ , so that:

$$\frac{f(\rho, T)}{RT} = \phi(\delta, \tau) = \phi^0(\delta, \tau) + \phi^r(\delta, \tau) \quad (1)$$

where  $f$  is specific Helmholtz free energy,  $\rho$  is density,  $T$  denotes temperature,  $\delta$  and  $\tau$  are reduced parameters which are defined as  $\delta = \rho/\rho_c$  and  $\tau = T_c/T$  with critical density  $\rho_c = 322 \text{ kg m}^{-3}$ , critical temperature  $T_c = 647.096 \text{ K}$ , and specific gas constant  $R = 0.46151805 \text{ kJ kg}^{-1} \text{ K}^{-1}$ . The ideal-gas part  $\phi^0(\delta, \tau)$  can be written as:

$$\phi^0(\delta, \tau) = \ln \delta + n_1^0 + n_2^0 + n_3^0 \ln \tau + \sum_{i=4}^8 n_i^0 \ln[1 - e^{-\gamma_i^0 \tau}] \quad (2)$$

where  $n_i^0$  and  $\gamma_i^0$  are parameters of the ideal-gas part (Table A1). The residual part  $\phi^r(\delta, \tau)$  is given by:

$$\begin{aligned} \phi^r(\delta, \tau) = & \sum_{i=1}^7 n_i \delta^{d_i} \tau^{t_i} + \sum_{i=8}^{51} n_i \delta^{d_i} \tau^{t_i} e^{-\delta^{c_i}} \\ & + \sum_{i=52}^{54} n_i \delta^{d_i} \tau^{t_i} e^{-\alpha_i(\delta - \varepsilon_i)^2 - \beta_i(\tau - \gamma_i)^2} + \sum_{i=55}^{56} n_i \Delta^b \delta \psi \end{aligned} \quad (3)$$

where  $\Delta = \theta^2 + B_i[(\delta - 1)^2]^{q_i}$ ,  $\theta = (1 - \tau) + A_i[(\delta - 1)^2]^{1/(2\beta_i)}$ ,  $\psi = e^{-C_i(\delta - 1)^2 - D_i(\tau - 1)^2}$ , parameters  $n_i$ ,  $d_i$ ,  $t_i$ ,  $c_i$ ,  $\alpha_i$ ,  $\beta_i$ ,  $\gamma_i$ ,  $\varepsilon_i$ ,  $C_i$ ,  $D_i$  and  $A_i$  are given in Table A2. All thermodynamic properties can be derived from the above equations. More details can be found in Tables 6.3–6.5 of the reference of Wagner and Pruß (2002).

As stated in the introduction, the IAPWS-95 formulation is the best EOS of fluid water up to now. Although it has good extrapolation ability, the extrapolation is still limited. For instance, when temperature and pressure increase to 4273 K and 20 GPa where water is still in molecular state (Cavazzoni et al., 1999; Hamann, 1981; Schwegler et al., 2001), volumetric deviation will increase to 5.53%, which can be seen in later discussions. Therefore, if the formulation keeps unchanged in form, its parameters must be refitted at temperatures above 1273 K or pressures above 1 GPa. Above 1273 K or 1 GPa, there are several sets of experimental and molecular simulation PVT data (Abramson and Brown, 2004; Bridgman, 1942; Brodholt and Wood, 1994; Frost and Wood, 1997; Larrieu and Ayers, 1997; Wiryana et al., 1998; Withers et al., 2000; Zhang and Duan, 2005) in literature. Most of these data are used in the parameterization, except for those of Brodholt and Wood (1994), because they have obvious deviations (about 3%) from the original IAPWS-95 formulation at  $P < 1 \text{ GPa}$  and  $T < 1273 \text{ K}$ .

Numerous tries demonstrate that nine parameters of the residual part are enough for a satisfactory fitting of the data available. The nine parameters are  $n_i$  ( $i = 1, 9$ ) of Eq. (3) and the other 47 parameters of Eq. (3) can be set as zero. The parameter values are obtained by non-linear regression to the volumetric data mentioned above with the same weight. Regressed parameters  $n_i$  ( $i = 1, 9$ ) are listed

**Table 1**

Parameters of Eq. (3) at temperatures up to 4273 K with pressures between 1 and 20 GPa.

Parameter ( $n_i$ )	Value
$n_1$	0.81716378D-01
$n_2$	0.34878201D+01
$n_3$	-0.42402332D+01
$n_4$	0.45283988D+00
$n_5$	-0.43145525D+00
$n_6$	-0.25288211D-02
$n_7$	0.82906020D-02
$n_8$	-0.56101024D+00
$n_9$	0.54697978D-01

Note:  $n_i = 0$  for  $i = 10-56$ .

in Table 1. The molar volume or density of water under a given  $P$ - $T$  condition can be calculated from Eq. (4) with a Newton iteration method. If the water is in vapor state or supercritical state, we can set the initial value of density equal to that of ideal gas. If the water is in liquid state, the saturated liquid density of water can be set as initial density.

$$P = \rho RT \left[ 1 + \delta \left( \frac{\partial \phi^r}{\partial \delta} \right)_{\tau} \right] \quad (4)$$

With these parameters, the molar volume (or density) of the water can be calculated. Table 2 shows the average and maximum absolute deviations of the EOS from each set of data beyond the valid temperature–pressure region of the original IAPWS-95 formulation. The average absolute deviation from experimental volumetric data in Table 2 is 0.52%, which is within experimental uncertainties. Figs. 1 and 2 show the comparisons between the representative PVT data and the extended EOS, and the other equations of water (Abramson and Brown, 2004; Brodholt and Wood, 1993; Pitzer and Sterner, 1994). As seen in Fig. 1, the extended EOS can reproduce the molecular dynamics simulation data (Zhang and Duan, 2005) with a high accuracy, which is better than the original IAPWS-95 formulation and the equations of Abramson and Brown (2004) and Pitzer and Sterner (1994). The Brodholt and Wood (1993) EOS can also reproduce the high temperature–pressure data (Zhang and Duan, 2005) with a high accuracy, but deviate largely from the data (Abramson and Brown, 2004; Wiryana et al., 1998) in the region of low temperatures and high pressures (Fig. 2) as the Pitzer and Sterner (1994) EOS does. Therefore, the extended EOS, the original IAPWS-95 formulation and the Abramson and Brown (2004) EOS can be used to predict the molar volume of water at  $T < 1273 \text{ K}$  and  $P > 1 \text{ GPa}$  with similar accuracy. The extended EOS and the Brodholt and Wood (1993) EOS are better choices for calculating the molar volume of water in the  $T$ - $P$  region: 1273–4273 K and 1–20 GPa. Calculated molar volumes ( $\text{cm}^3 \text{ mol}^{-1}$ ) and fugacity coefficients of water from 1273 to 4273 K and from 1 to 20 GPa are listed in Tables 3 and 4, respectively. Fig. 3 shows the calculated equilibrium curves for the reactions: (a) talc = enstatite + quartz +  $\text{H}_2\text{O}$ , and (b) diaspore = corundum +  $\text{H}_2\text{O}$ ,

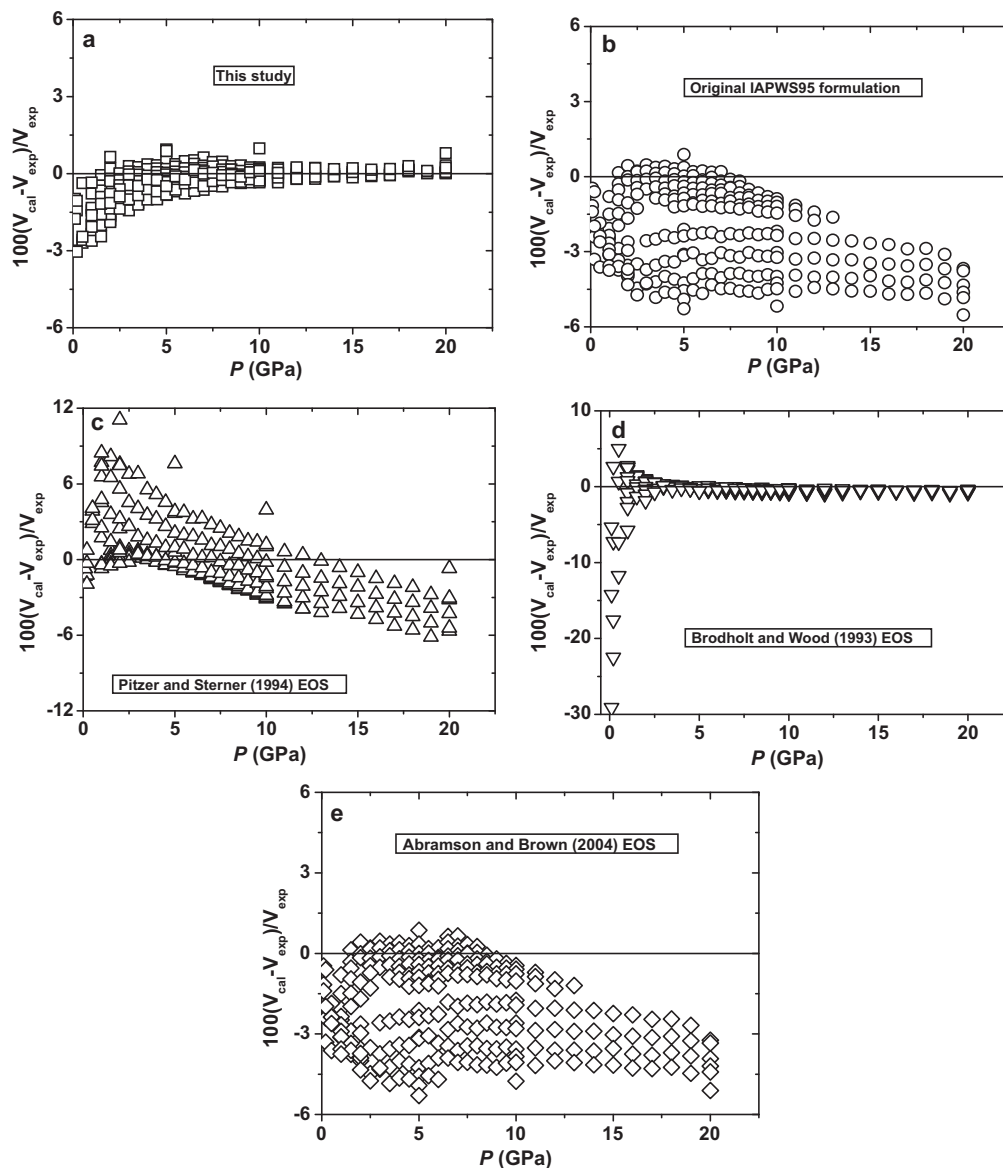
**Table 2**

Calculated volume deviations from experimental data.

Reference	$T$ (K)	$P$ (GPa)	Nd	AAD (%)	MAD (%)
Bridgman (1942)	298.15–448.15	0.49–3.58	21	0.36	0.59
Brodholt and Wood (1994) <sup>a</sup>	1203.15–1873.15	0.95–2.5	9	3.26	5.29
Frost and Wood (1997)	1273.15–1673.15	1.45	5	2.72	3.48
Larrieu and Ayers (1997)	1073.15–1173.15	1.5–2	3	1.94	2.07
Wiryana et al. (1998)	353.15–473.15	1–3.5	30	0.13	0.23
Withers et al. (2000)	983.15–1373.15	1.4–3.5	12	1.49	2.72
Abramson and Brown (2004)	373.15–673.15	1–6	131	0.24	0.93
Zhang and Duan (2005)	523.15–4273.15	0.1–20	257	0.52	3.04

AAD, average absolute deviations calculated from this model; MAD, maximal absolute deviations calculated from this model; Nd, number of data points.

<sup>a</sup> Not used in the fitting.



**Fig. 1.** Volumetric deviations from the molecular dynamics simulation data of Zhang and Duan (2005);  $V_{\text{cal}}$  and  $V_{\text{exp}}$  refer to the calculated and molecular dynamics simulation molar volume, respectively.

where thermodynamic data of minerals and water are taken from Holland and Powell (1998). Apparently, the extended EOS agrees with experimental phase equilibrium data (Aranovich and Newton, 1999; Bose and Ganguly, 1995; Chernosky et al., 1985; Grevel et al., 1994; Haas, 1972). These results suggest that the former IAPWS-95 formulation together with the extended part can be applied in a much larger temperature–pressure region (273–4273 K and 0–20 GPa), which can meet the demands of water–mineral interactions at ultra-high temperatures and pressures.

### 3. Calculation method for saturated properties

From the IAPWS-95 formulation, all thermodynamic properties can be obtained including saturated properties, e.g., saturated pressure  $P_s$ , saturated liquid density  $\rho'$  and saturated vapor density  $\rho''$ . In the studies of water fluid inclusion, these saturated properties correspond to homogenization pressure, homogenization liquid density and homogenization vapor density, respectively. However, these saturated properties are uneasy to calculate, especially when temperature approaches critical temperature of water. Under these

conditions, the iterative method has to be used to obtain these saturated properties of water, which involves two aspects: one is how to choose initial values of variables; another is how to choose iterative functions. Two kinds of methods have been used to calculate the saturated properties of water in the past. One kind of method (Ito et al., 2008; Lemmon et al., 2007; Span, 2000) is to select values of ancillary equations of  $P_s$ ,  $\rho'$  and  $\rho''$  as initial values, and  $P_s$  as iterative functions. Flaw of the method is that initial value of  $P_s$  has to be modified when approaching critical temperature because Maxwell loop is almost flat in the near-critical region. Another kind of method proposed recently by Akasaka (2008) is to choose density function as an iterative function, where the saturated density of triple point is used as initial density at temperatures between 273.16 and 606 K, and the saturated density of water at 606 K is used as the initial density at temperatures between 606 and 647.096 K. Flaws of the method lie in two aspects: one is that the iterative times increase rapidly; another is that the iterative function does not convergence from 647.09 to 647.096 K, as will be discussed later.

In the calculation of saturated properties, we found that a reliable and highly efficient method is the Newton iteration method:

**Table 3**  
Calculated molar volume  $V$  ( $\text{cm}^3 \text{mol}^{-1}$ ) of water from 1273 to 4273 K and from 1 to 20 GPa.

T (K)	P (GPa)								
	1	2.5	5	7.5	10	12.5	15	17.5	20
1273	22.26	16.71	13.94	12.64	11.81	11.23	10.77	10.41	10.11
1373	23.24	17.12	14.17	12.80	11.95	11.34	10.87	10.49	10.18
1473	24.21	17.53	14.39	12.96	12.08	11.45	10.97	10.58	10.26
1573	25.19	17.94	14.62	13.13	12.21	11.56	11.06	10.66	10.34
1673	26.17	18.34	14.84	13.29	12.33	11.66	11.15	10.75	10.41
1773	27.16	18.76	15.07	13.45	12.46	11.77	11.25	10.83	10.49
1873	28.15	19.17	15.29	13.61	12.59	11.88	11.34	10.91	10.56
1973	29.14	19.58	15.52	13.77	12.71	11.98	11.43	10.99	10.63
2073	30.12	19.99	15.74	13.93	12.84	12.09	11.52	11.07	10.71
2173	31.11	20.40	15.96	14.08	12.97	12.19	11.61	11.15	10.78
2273	32.08	20.81	16.18	14.24	13.09	12.30	11.70	11.23	10.85
2373	33.06	21.23	16.41	14.40	13.21	12.40	11.79	11.31	10.92
2473	34.03	21.64	16.63	14.56	13.34	12.50	11.88	11.39	10.99
2573	35.00	22.05	16.85	14.72	13.46	12.61	11.97	11.47	11.07
2673	35.96	22.46	17.07	14.87	13.59	12.71	12.06	11.55	11.14
2773	36.92	22.87	17.29	15.03	13.71	12.81	12.15	11.63	11.21
2873	37.88	23.28	17.52	15.19	13.83	12.92	12.24	11.71	11.28
2973	38.83	23.69	17.74	15.34	13.96	13.02	12.33	11.79	11.35
3073	39.78	24.09	17.96	15.50	14.08	13.12	12.41	11.86	11.42
3173	40.73	24.50	18.18	15.65	14.20	13.22	12.50	11.94	11.49
3273	41.67	24.91	18.40	15.81	14.32	13.32	12.59	12.02	11.56
3373	42.61	25.31	18.62	15.96	14.44	13.43	12.68	12.10	11.63
3473	43.54	25.72	18.84	16.12	14.57	13.53	12.76	12.17	11.70
3573	44.48	26.12	19.06	16.28	14.69	13.63	12.85	12.25	11.77
3673	45.41	26.52	19.28	16.43	14.81	13.73	12.94	12.33	11.83
3773	46.34	26.93	19.50	16.59	14.93	13.83	13.03	12.40	11.90
3873	47.27	27.33	19.72	16.74	15.05	13.93	13.11	12.48	11.97
3973	48.19	27.73	19.93	16.90	15.18	14.03	13.20	12.56	12.04
4073	49.12	28.13	20.15	17.05	15.30	14.13	13.29	12.63	12.11
4173	50.04	28.53	20.37	17.20	15.42	14.23	13.37	12.71	12.18
4273	50.96	28.93	20.59	17.36	15.54	14.34	13.46	12.79	12.25

**Table 4**  
Calculated fugacity coefficients  $f_c$  of water from 1273 to 4273 K and from 1 to 20 GPa.

T (K)	P (GPa)								
	1	2.5	5	7.5	10	12.5	15	17.5	20
1273	0.1839D+01	0.1061D+02	0.1876D+03	0.2845D+04	0.3807D+05	0.4613D+06	0.5155D+07	0.5383D+08	0.5306D+09
1373	0.1870D+01	0.9605D+01	0.1399D+03	0.1763D+04	0.1975D+05	0.2016D+06	0.1907D+07	0.1693D+08	0.1425D+09
1473	0.1888D+01	0.8777D+01	0.1081D+03	0.1159D+04	0.1113D+05	0.9795D+05	0.8024D+06	0.6193D+07	0.4542D+08
1573	0.1895D+01	0.8078D+01	0.8585D+02	0.8006D+03	0.6720D+04	0.5192D+05	0.3750D+06	0.2560D+07	0.1666D+08
1673	0.1893D+01	0.7482D+01	0.6986D+02	0.5756D+03	0.4292D+04	0.2957D+05	0.1911D+06	0.1171D+07	0.6855D+07
1773	0.1886D+01	0.6969D+01	0.5802D+02	0.4283D+03	0.2874D+04	0.1789D+05	0.1048D+06	0.5830D+06	0.3107D+07
1873	0.1874D+01	0.6524D+01	0.4902D+02	0.3280D+03	0.2003D+04	0.1138D+05	0.6104D+05	0.3117D+06	0.1527D+07
1973	0.1860D+01	0.6136D+01	0.4204D+02	0.2575D+03	0.1445D+04	0.7566D+04	0.3747D+05	0.1771D+06	0.8048D+06
2073	0.1843D+01	0.5794D+01	0.3652D+02	0.2065D+03	0.1073D+04	0.5220D+04	0.2406D+05	0.1061D+06	0.4501D+06
2173	0.1826D+01	0.5492D+01	0.3210D+02	0.1688D+03	0.8181D+03	0.3720D+04	0.1607D+05	0.6645D+05	0.2650D+06
2273	0.1808D+01	0.5222D+01	0.2849D+02	0.1402D+03	0.6377D+03	0.2727D+04	0.1110D+05	0.4331D+05	0.1632D+06
2373	0.1789D+01	0.4982D+01	0.2551D+02	0.1182D+03	0.5070D+03	0.2050D+04	0.7896D+04	0.2923D+05	0.1045D+06
2473	0.1771D+01	0.4766D+01	0.2302D+02	0.1009D+03	0.4102D+03	0.1575D+04	0.5769D+04	0.2033D+05	0.6934D+05
2573	0.1753D+01	0.4570D+01	0.2093D+02	0.8708D+02	0.3370D+03	0.1233D+04	0.4314D+04	0.1453D+05	0.4742D+05
2673	0.1735D+01	0.4394D+01	0.1914D+02	0.7594D+02	0.2808D+03	0.9831D+03	0.3294D+04	0.1064D+05	0.3334D+05
2773	0.1718D+01	0.4233D+01	0.1761D+02	0.6684D+02	0.2368D+03	0.7959D+03	0.2563D+04	0.7965D+04	0.2402D+05
2873	0.1701D+01	0.4086D+01	0.1629D+02	0.5931D+02	0.2020D+03	0.6534D+03	0.2027D+04	0.6077D+04	0.1769D+05
2973	0.1685D+01	0.3951D+01	0.1513D+02	0.5303D+02	0.1741D+03	0.5432D+03	0.1628D+04	0.4719D+04	0.1329D+05
3073	0.1669D+01	0.3828D+01	0.1412D+02	0.4773D+02	0.1513D+03	0.4568D+03	0.1326D+04	0.3723D+04	0.1017D+05
3173	0.1654D+01	0.3714D+01	0.1322D+02	0.4322D+02	0.1327D+03	0.3882D+03	0.1093D+04	0.2979D+04	0.7905D+04
3273	0.1639D+01	0.3609D+01	0.1243D+02	0.3937D+02	0.1172D+03	0.3330D+03	0.9111D+03	0.2416D+04	0.6239D+04
3373	0.1625D+01	0.3511D+01	0.1172D+02	0.3604D+02	0.1043D+03	0.2882D+03	0.7675D+03	0.1983D+04	0.4991D+04
3473	0.1612D+01	0.3421D+01	0.1109D+02	0.3315D+02	0.9337D+02	0.2514D+03	0.6528D+03	0.1645D+04	0.4043D+04
3573	0.1599D+01	0.3337D+01	0.1052D+02	0.3062D+02	0.8409D+02	0.2209D+03	0.5600D+03	0.1379D+04	0.3312D+04
3673	0.1586D+01	0.3258D+01	0.1001D+02	0.2840D+02	0.7613D+02	0.1954D+03	0.4843D+03	0.1167D+04	0.2742D+04
3773	0.1574D+01	0.3185D+01	0.9543D+01	0.2644D+02	0.6928D+02	0.1739D+03	0.4220D+03	0.9954D+03	0.2293D+04
3873	0.1563D+01	0.3117D+01	0.9118D+01	0.2470D+02	0.6333D+02	0.1557D+03	0.3702D+03	0.8561D+03	0.1934D+04
3973	0.1552D+01	0.3052D+01	0.8731D+01	0.2315D+02	0.5815D+02	0.1401D+03	0.3268D+03	0.7417D+03	0.1645D+04
4073	0.1541D+01	0.2992D+01	0.8377D+01	0.2176D+02	0.5360D+02	0.1267D+03	0.2902D+03	0.6470D+03	0.1410D+04
4173	0.1531D+01	0.2935D+01	0.8051D+01	0.2051D+02	0.4959D+02	0.1152D+03	0.2591D+03	0.5679D+03	0.1217D+04
4273	0.1521D+01	0.2881D+01	0.7751D+01	0.1939D+02	0.4604D+02	0.1051D+03	0.2326D+03	0.5015D+03	0.1058D+04

$\ln(f_c) = Z - 1 - \ln(Z) + \phi'$ , where  $Z$  is the compressibility factor and  $\phi'$  is the residual part of dimensionless Helmholtz free energy.

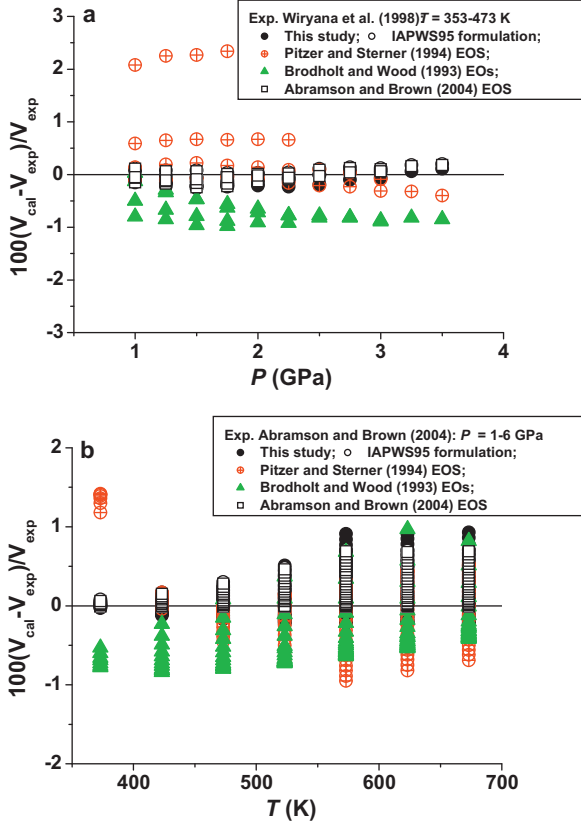


Fig. 2. Volumetric deviations from experimental data:  $V_{\text{cal}}$  and  $V_{\text{exp}}$  refer to calculated and experimental molar volume, respectively.

selecting the values of  $\rho'$  and  $\rho''$  from auxiliary equations (Appendix A) as initial density values and the density function as iterative function, and calculating  $\delta'$  and  $\delta''$  with the following simultaneous equations:

$$\delta^{(k+1)} = \delta^{(k)} + \frac{1}{\Lambda} \{ [K(\tau, \delta'') - K(\tau, \delta')] J_{\delta}(\tau, \delta'') - [J(\tau, \delta'') - J(\tau, \delta')] K_{\delta}(\tau, \delta'') \} \quad (5)$$

$$\delta''^{(k+1)} = \delta''^{(k)} + \frac{1}{\Lambda} \{ [K(\tau, \delta'') - K(\tau, \delta')] J_{\delta}(\tau, \delta') - [J(\tau, \delta'') - J(\tau, \delta')] K_{\delta}(\tau, \delta') \} \quad (6)$$

where  $J$ ,  $K$ ,  $J_{\delta}$ ,  $K_{\delta}$ , and  $\Lambda$  are defined as:

$$J(\tau, \delta) = \delta [1 + \delta \phi_{\delta}^r(\tau, \delta)] \quad (7)$$

$$K(\tau, \delta) = \delta \phi_{\delta}^r(\tau, \delta) + \phi^r(\tau, \delta) + \ln \delta \quad (8)$$

$$J_{\delta}(\tau, \delta) = \left( \frac{\partial J}{\partial \delta} \right)_{\tau} = 1 + 2\delta \phi_{\delta}^r + \delta^2 \phi_{\delta\delta}^r \quad (9)$$

$$K_{\delta}(\tau, \delta) = \left( \frac{\partial K}{\partial \delta} \right)_{\tau} = 2\phi_{\delta}^r + \delta \phi_{\delta\delta}^r + \frac{1}{\delta} \quad (10)$$

$$\Lambda = J_{\delta}(\tau, \delta'') K_{\delta}(\tau, \delta') - J_{\delta}(\tau, \delta') K_{\delta}(\tau, \delta'') \quad (11)$$

The presented method can calculate the saturated properties of water from the temperature of the triple point (273.16 K) to that of the critical point (647.096 K). That it is better than previous two kinds of methods lies in its reliability and high efficiency. Fig. 4 shows the flow chart for the method, which is tested with the

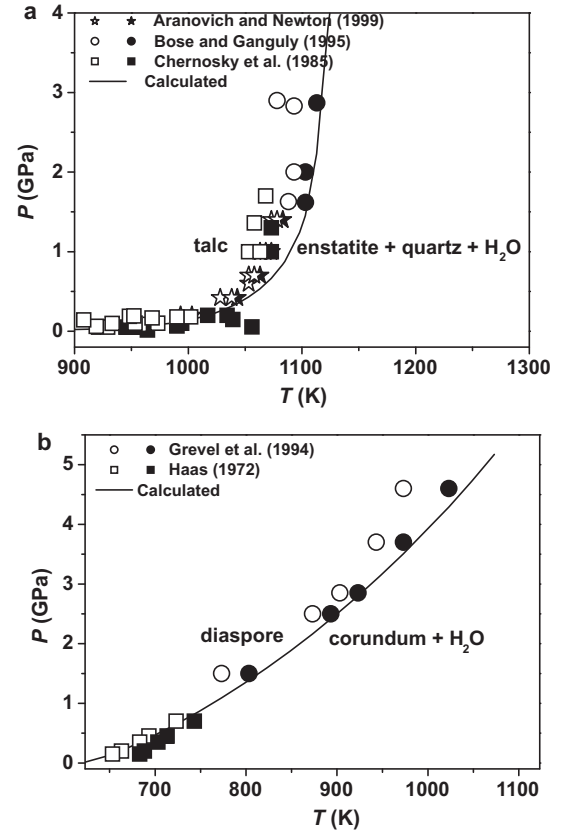


Fig. 3. Calculated  $P$ - $T$  curve for the reactions: (a) talc = enstatite + quartz +  $H_2O$  and (b) diaspore = corundum +  $H_2O$ . The  $P$ - $T$  curve below 1 GPa is from original IAPWS-95 formulation, beyond which is from the extended EOS. Thermodynamic data of minerals and water are taken from Holland and Powell (1998).

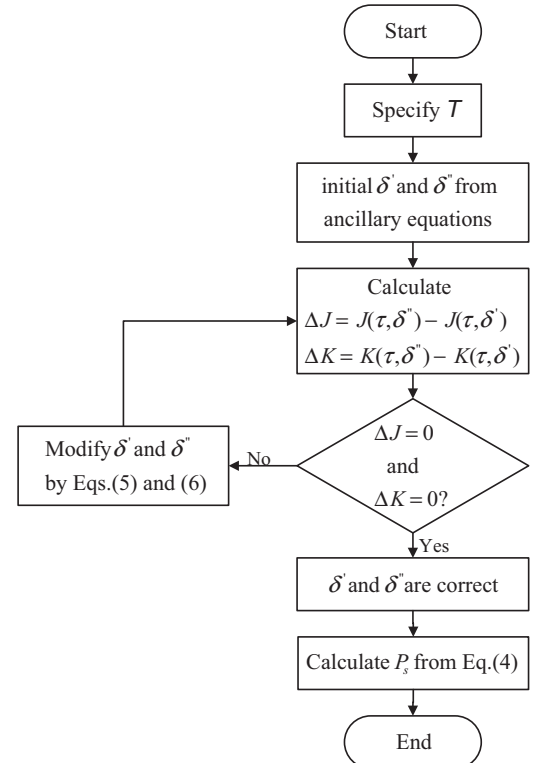


Fig. 4. Newton iteration method for the calculation of  $P_s$ ,  $\delta'$  and  $\delta''$ .

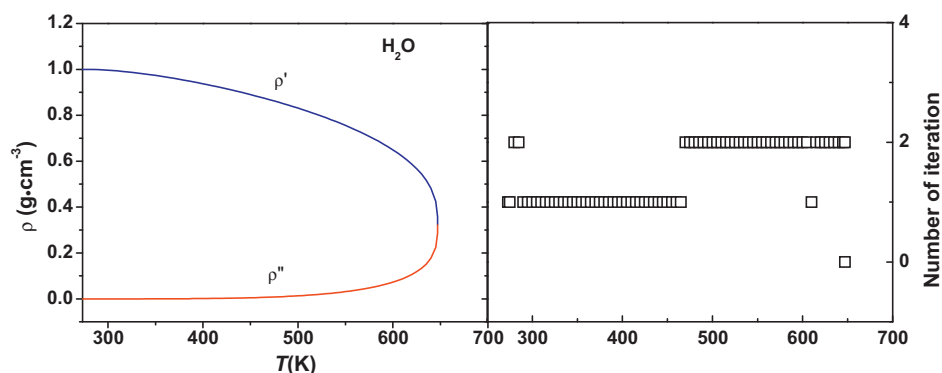


Fig. 5. Saturated liquid and vapor densities of water calculated from the IAPWS-95 formulation with an iterative method in this work.

following convergence condition:

$$|K(\tau, \delta'') - K(\tau, \delta^1)| + |J(\tau, \delta'') - J(\tau, \delta^1)| < 10^{-9} \quad (12)$$

Fig. 5 shows the calculated results by this method. Number of iterations until convergence is also plotted in the figure. It can be seen that the twice iterations are enough to meet the requirement. Fig. 6 shows the calculated results from the method used by Akasaka (2008). The average number of iteration is about 8. When temperatures are between 647.09 and 647.096 K, the method (Akasaka, 2008) cannot converge, leaving a blank region close to critical point. Calculated saturated properties of water in the near-critical region using the two kinds of methods are listed in Table 5. From Fig. 5 and Table 5, it can be seen that the method presented here is a reliable and stable algorithm in the whole liquid–vapor equilibrium region (273.16–647.096 K).

The Newton iteration method using the saturated densities from auxiliary equations as initial values and the density function as iterative function is a good choice for calculating the saturated properties of pure fluids from equations of state in form of Helmholtz free energy. We also used this kind of Newton iteration method to calculate the saturated properties of methane from equation of state (Setzmann and Wagner, 1991) and found that the calculated results are also very good from the temperature of the triple point (90.6941 K) to that of the critical point (190.564 K). For equations of state in form of Helmholtz free energy without auxiliary equations, auxiliary saturation density equations can be developed by linear regression to experimental data before using the iteration method.

Once the saturated properties of water are solved, the IAPWS-95 formulation can be easily applied to the study of fluid inclusions: to calculate homogenization pressure, homogenization density

Table 5

Comparison of calculated saturated properties in the near-critical region of water.

T (K)	$P_s$ (bar)	$\rho'$ (g cm <sup>-3</sup> )	$\rho''$ (g cm <sup>-3</sup> )	ni
This work				
647.080	220.597	0.3405	0.3034	2
647.090	220.624	0.3341	0.3097	2
647.091	220.627	0.3332	0.3107	2
647.092	220.629	0.3322	0.3118	2
647.093	220.632	0.3310	0.3130	2
647.094	220.635	0.3295	0.3144	2
647.095	220.637	0.3276	0.3163	2
647.096	220.640	0.3220	0.3220	0
Akasaka (2008)				
647.080	220.597	0.3405	0.3034	15
647.090	220.693	0.3734	0.3734	14
647.091	–	–	–	–
647.092	–	–	–	–
647.093	–	–	–	–
647.094	–	–	–	–
647.095	–	–	–	–
647.096	220.389	0.2521	0.2521	15

$P_s$ , saturated pressure;  $\rho'$ , saturated liquid density;  $\rho''$ , saturated vapor density; ni, number of iterations.

or molar volume, and isochores ( $P$ – $T$  relation) from measured homogenization temperatures. For example, a vapor–liquid water inclusion at room temperature finally homogenizes to liquid phase during heating, and homogenization temperature  $T_h = 500$  K. From these conditions, homogenization pressure  $P_h$ , homogenization density and isochores ( $P$ – $T$  relation) of water can be determined (Table 6).

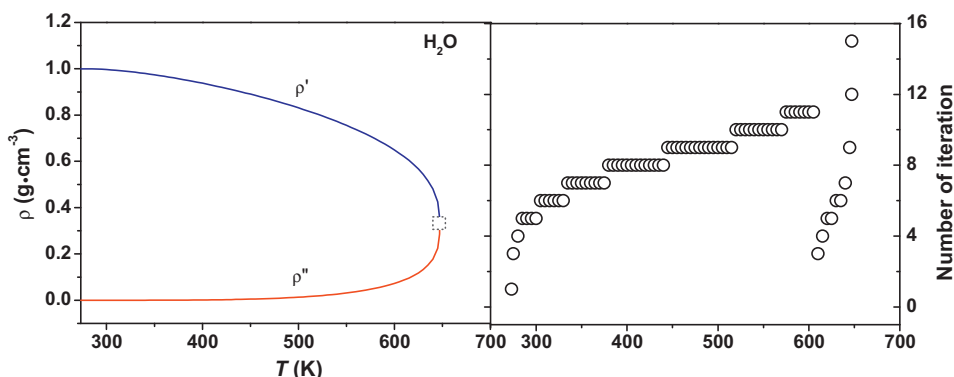


Fig. 6. Saturated liquid and vapor densities of water calculated from the IAPWS-95 formulation with the iterative method of Akasaka (2008).

**Table 6**  
Calculated results of water inclusions.

Homogenization ( $V+L \rightarrow L$ )	P–T relation			
	T (K)	P (GPa)	T (K)	P (GPa)
$T_h = 500$ K	500	0.002639	2500	2.521028
$P_h = 0.002639$ GPa	700	0.300751	2700	2.744824
$V_h = 21.67$ cm <sup>3</sup> mol <sup>-1</sup>	900	0.589937	2900	2.966888
$D_h = 0.8313$ g cm <sup>-3</sup>	1100	0.859476	3100	3.187518
	1300	1.114392	3300	3.406960
	1500	1.360024	3500	3.625421
	1700	1.599936	3700	3.843077
	1900	1.835212	3900	4.060079
	2100	2.066717	4100	4.276554
	2300	2.295139	4300	4.492615

Note:  $T_h$ ,  $P_h$ ,  $V_h$  and  $D_h$  denote homogenization temperature, pressure, molar volume and density, respectively.

**4. Conclusion**

By using nine parameters in the residual part of the IAPWS-95 formulation, the original IAPWS-95 formulation is extended to predict the PVT properties of fluid water from 1 to 20 GPa and from 273 to 4273 K, within or close to experimental uncertainties. Meanwhile, a reliable and highly efficient method is presented to calculate the saturated properties of water from the IAPWS-95 formulation so that the EOS covering a large temperature–pressure region can be conveniently applied in the study of fluid inclusion and water–mineral phase equilibria at ultra-high temperatures and pressures.

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**Appendix A. Parameters of the former IAPWS-9 formulation and ancillary equations**

In this study, the parameters of Eqs. (2) and (3) of the original IAPWS-95 formulation are listed in Tables A1 and A2, respectively. Two auxiliary equations from the reference of Wagner and Pruß (2002) are used for calculating the saturated properties of water:

$$\frac{\rho'}{\rho_c} = 1 + b_1 \vartheta^{1/3} + b_2 \vartheta^{2/3} + b_3 \vartheta^{5/3} + b_4 \vartheta^{16/3} + b_5 \vartheta^{43/3} + b_6 \vartheta^{110/3} \quad (A1)$$

$$\ln \left( \frac{\rho''}{\rho_c} \right) = c_1 \vartheta^{2/6} + c_2 \vartheta^{4/6} + c_3 \vartheta^{8/6} + c_4 \vartheta^{18/6} + c_5 \vartheta^{37/6} + c_6 \vartheta^{71/6} \quad (A2)$$

where Eq. (A1) is for the saturated liquid density, and Eq. (A2) for the saturated vapor density equation,  $\vartheta = 1 - T/T_c$ , and parameters  $b_1 - b_6$  and  $c_1 - c_6$  are listed in Table A3.

**Table A1**  
Parameters of Eq. (2).

$i$	$n_i^0$	$\gamma_i^0$	$i$	$n_i^0$	$\gamma_i^0$
1	-8.32044648201	-	5	0.97315	3.53734222
2	6.6832105268	-	6	1.27950	7.74073708
3	3.00632	-	7	0.96956	9.24437796
4	0.012436	1.28728967	8	0.24873	27.5075105

**Table A2**  
Parameters of Eq. (3).

$i$	$c_i$	$d_i$	$t_i$	$n_i$
1	-	1	-0.5	0.12533547935523D-1
2	-	1	0.875	0.78957634722828D1
3	-	1	1	-0.8780320330303561D1
4	-	2	0.5	0.31802509345418
5	-	2	0.75	-0.26145533859358
6	-	3	0.375	-0.78199751687981D-2
7	-	4	1	0.88089493102134D-2
8	1	1	4	-0.66856572307965
9	1	1	6	0.20433810950965
10	1	1	12	-0.66212605039687D-4
11	1	2	1	-0.19232721156002
12	1	2	5	-0.25709043003438
13	1	3	4	0.16074868486251
14	1	4	2	-0.40092828925807D-1
15	1	4	13	0.39343422603254D-6
16	1	5	9	-0.75941377088144D-5
17	1	7	3	0.56250979351888D-3
18	1	9	4	-0.15608652257135D-4
19	1	10	11	0.11537996422951D-8
20	1	11	4	0.36582165144204D-6
21	1	13	13	-0.13251180074668D-11
22	1	15	1	-0.62639586912454D-9
23	2	1	7	-0.10793600908932
24	2	2	1	0.17611491008752D-1
25	2	2	9	0.22132295167546
26	2	2	10	-0.40247669763528
27	2	3	10	0.58083399985759
28	2	4	3	0.49969146990806D-2
29	2	4	7	-0.31358700712549D-1
30	2	4	10	-0.74315929710341
31	2	5	10	0.47807329915480
32	2	6	6	0.20527940895948D-1
33	2	6	10	-0.13636435110343
34	2	7	10	0.14180634400617D-1
35	2	9	1	0.83326504880713D-2
36	2	9	2	-0.29052336009585D-1
37	2	9	3	0.38615085574206D-1
38	2	9	4	-0.20393486513704D-1
39	2	9	8	-0.16554050063734D-2
40	2	10	6	0.19955571979541D-2
41	2	10	9	0.15870308324157D-3
42	2	12	8	-0.16388568342530D-4
43	3	3	16	0.43613615723811D-1
44	3	4	22	0.34994005463765D-1
45	3	4	23	-0.76788197844621D-1
46	3	5	23	0.22446277332006D-1
47	4	14	10	-0.62689710414685D-4
48	6	3	50	-0.55711118565645D-9
49	6	6	44	-0.19905718354408
50	6	6	46	0.31777497330738
51	6	6	50	-0.11841182425981
52	-	3	0	-0.31306260323435D2
53	-	3	1	0.31546140237781D2
54	-	3	4	-0.25213154341695D4

$i$	$a_i$	$b_i$	$B_i$	$n_i$
55	3.5	0.85	0.2	-0.14874640856724
56	3.5	0.95	0.2	0.31806110878444

$i$	$\alpha_i$	$\beta_i$	$\gamma_i$	$\varepsilon_i$
52	20	150	1.21	1
53	20	150	1.21	1
54	20	250	1.25	1

$i$	$C_i$	$D_i$	$A_i$	$\beta_i$
55	28	700	0.32	0.3
56	32	800	0.32	0.3

**Table A3**  
Parameters of auxiliary Eqs. (A1)–(A2).

Parameter	Value	Parameter	Value
$b_1$	1.99274064	$c_1$	−2.03150240
$b_2$	1.09965342	$c_2$	−2.68302940
$b_3$	−5.10839303D−1	$c_3$	−5.38626492
$b_4$	−1.75493479	$c_4$	−17.2991605
$b_5$	−45.5170352	$c_5$	−44.7586581
$b_6$	−6.74694450D+5	$c_6$	−63.9201063

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