LETTER

Thermoelastic equilibrium of fluid inclusion–host mineral systems under homogenization measurement

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Microthermometric data of fluid inclusions can elucidate the physicochemical properties of lithospheric fluids, but the inclusions must satisfy several criteria to yield proper fluid information. One is the ‘constant volume criterion’: the inclusion volume must remain constant after being trapped. However, volume changes of fluid inclusions occur in nature during emplacement underground or uplifting to the surface. They can also occur during sample preparation or data collection in the laboratory. Therefore, thermoelastic deformation of the crystal lattice surrounding fluid inclusions during experiments might increase uncertainty about microthermometric data. Herein, we introduce and assess a method using the equation of state of pure CO₂ and thermoelastic equilibrium between a fluid inclusion and a host mineral to estimate fluid inclusion volume changes accurately during measurements of homogenization temperature. The estimation is valid if the inclusion and host are isotropically elastic, concentric spheres. Subsequently, we extended the equation of state to a more comprehensive Redlich and Kwong equation of state, which is applicable to more complicated fluid systems. Furthermore, for accurate treatment of the elastic effects involving an elastically anisotropic host mineral, we propose the method’s application to an anisotropic host mineral. If physical properties of the host mineral and the molar volume of the fluid inclusion at an arbitrary temperature are known, then one can use this method for accurate estimation of the molar volume at a given temperature. This microthermometric data based method can accurately elucidate characteristics of the crust and mantle–fluid activity.

Keywords: Fluid inclusion, Microthermometry, Re-equilibration, Thermoelastic equilibrium

INTRODUCTION

If a inclusion satisfies several criteria, it can provide microthermometric data that are useful to infer trapping conditions (Roedder 1984). Roedder’s rules state that fluid inclusion properties reflect the trapping conditions if (1) the inclusion has trapped a single-phase fluid (homogeneity criterion), (2) nothing has been added to or removed from the inclusion after being trapped (constant mass criterion), (3) the inclusion volume remained constant following trapping (constant volume criterion), (4) the effect of pressure is either known, negligible, or estimated independently (pressure criterion), and (5) the origin and genetic significance are known (genesis criterion). If the inclusion volume changes, or if anything is added to or lost from the inclusion following trapping, then the inclusion

must be re-equilibrated. Re-equilibration can occur during exhumation in nature or sample preparation and/or during data collection in the laboratory.

Deformation of the crystal lattice surrounding fluid inclusions will occur in response to changes in the fluid inclusion temperature and pressure, even for measurements of the homogenization temperature. Deformation occurs easily in high-temperature homogenization experiments or experiments using high-density fluid inclusions and host minerals having a large thermal expansion coefficient. Therefore, deformation of the crystal lattice surrounding fluid inclusions during measurements might increase uncertainty related to microthermometric data. For example, Lecumberri-Sanchez et al. (2012) developed a method to ascertain density, homogenization pressure, and salinity directly from the disappearance temperature of vapor phase and the dissolution temperature of halite with a high-density and high-salinity H₂O–NaCl system. Derivation of the numerical model by Lecumberri-Sanchez et al. (2012) is

based on experimentally obtained results reported by Becker et al. (2008) describing fluid inclusions in quartz. Therefore, we must devote attention to differences of physical properties of host minerals when applying their numerical model to a fluid encapsulated in host minerals of which the thermal expansion coefficient and compressibility are markedly different from those of quartz. In addition, Wang et al. (2011) and Kawakami et al. (2003) respectively investigated the temperature dependence of the Fermi splits distance of CO₂ using fluid inclusions in quartz and orthopyroxene. However, their conclusions are not mutually consistent. One cause of their mutual contradiction might be the thermoelastic equilibrium of the fluid inclusion during the experiment. Therefore, the final section of this paper presents an examination of thermoelastic effects on their experimentally obtained results.

Few studies have specifically undertaken a theoretical investigation of the mechanical re-equilibration of inclusion-host systems which have undergone changes in P - T conditions (Tait 1992; Zhang 1998). Some studies have specifically assessed viscous relaxation of host minerals (e.g., Wanamaker and Evans 1989), although we ignored the effect because of the short time-scale of the heating experiment. Studies of the thermoelastic equilibrium of a homogeneous fluid inclusion with a host phase were conducted by Tait (1992) and Zhang (1998), who gave equations for $\Delta V/V_0$ (with $\Delta V = V - V_0$, where V and V_0 respectively denote the last volume and the initial volume of a fluid inclusion) as a function of the last internal pressure, the initial internal pressure, the last external pressure, and the temperature (plus geometrical parameters and physical properties). As an application of elastic deformation correction based on the equation presented by Zhang (1998), Schiavi et al. (2016) calculated the volume changes of inclusions during the measurements of homogenization temperatures of melt inclusions. They underestimated the volume of the fluid because they assumed the fluid as an ideal gas. Generally, because some homogenization events occur at high pressure and/or low temperature conditions, one cannot ignore intermolecular forces and molecular volume. Based on work by Zhang (1998) and the equation of state (EOS) of real fluids, we propose a new method to describe the volume change of a fluid inclusion more accurately during homogenization experiments.

DESCRIPTION OF NEW METHOD

Fundamental equation of elastic equilibrium between inclusion and the host mineral

As the sample temperature rises, the fluid density changes in response to the physical properties of a host mineral

and its inclusions. Therefore, it is necessary to correct the elastic deformation to interpret microthermometric data more accurately. Based on the formulation presented by Zhang (1998), change in the fluid inclusion volume (ΔV) can be expressed as presented below.

$$\frac{\Delta V}{V_0} \approx \frac{P_0 - P_{\text{out}}}{K_h} + \left\{ \exp \left[\int_{T_0}^T \alpha_h(T) dT \right] - 1 \right\} + \frac{P_{\text{in}} - P_{\text{out}}}{1-x} \left(\frac{x}{K_h} + \frac{3}{4G_h} \right) \quad (1)$$

In that equation, T_0 , T , V_0 , P_0 , P_{in} , and P_{out} respectively stand for the initial temperature (K), final temperature (K), initial inclusion volume, confining pressure (GPa) at T_0 , internal pressure (GPa) of the inclusion at T , and the confining pressure (GPa) at T . In addition, K_h , G_h , α_h , $K_h(P)$, and x respectively denote the bulk and shear moduli (GPa) at T , the thermal expansion coefficient of the host mineral (K⁻¹) at P_0 , the bulk modulus (GPa) as a function of the confining pressure, and the volumetric ratio of the inclusion to the host mineral grain. The method proposed herein to ascertain the molar volume comprises the combined calculation of Equation 1 and the equation of state of a fluid. This equation is valid if the inclusion and host are isotropically elastic, concentric spheres. Burnley and Davis (2004) reported that oblate shapes with high aspect ratios are especially likely to show marked deviations from results that might be predicted using a spherical model. However, for fluid inclusions having low aspect ratios (e.g., 2:1 oblate ellipsoid), the volume change can be explained well by spherical approximation. Additionally, they described the presence or absence of corners. The sharpness of internal corners affects the volume change, but to a lesser degree. Therefore, based on their results, for fluid inclusions with aspect ratios that do not exceed 2:1, the volume change can be approximated well on the assumption that they are concentric spheres, even if they have a negative crystal shape. The first term of Equation 1 expresses the volume change caused by isothermal decompression. Generally, the confining pressure under measurements of homogenization temperature is atmospheric pressure ($P_0 = P_{\text{out}} = 0.1$ MPa); the first term is approximately zero. The second term expresses the volume change caused by isobaric heating. The third term represents the volume change caused by the internal pressure of the fluid inclusion.

Case 1: Thermoelastic equilibrium of a unary system of CO₂

Fluid inclusions in mantle xenoliths are generally com-

posed of nearly pure CO₂, which in many cases homogenizes to liquid by diminishing the vapor bubble at temperatures between −56.6 and 31.1 °C. In addition, quantifying a trace amount of H₂O concentration requires heating of a sample to about 300 °C. Because the fluid inclusion volume is expected to change during such a change in temperature, correction must be made for the effect of the volume change on fluid properties such as the molar volume of the fluid. Therefore, the thermoelastic equilibrium might affect the microthermometric data. Recently, the elastic-plastic equilibrium of fluid inclusion – host mineral systems has been studied (e.g., Campione 2018) mainly for tracking volcanic plumbing systems (Levresse et al. 2016; Oglialoro et al. 2017) and for ascertaining the depth provenance of mantle xenolith (Yamamoto et al. 2007, 2012, 2014) using the internal pressure of fluid inclusions. Consequently, it is important to consider the thermoelastic equilibrium in a pure CO₂–host mineral system. First, we present an equation as an example of a unary system.

To calculate $\Delta V/V_0$ from Equation 1, we must ascertain P_{in} using EOS of CO₂. To do so, we used the following EOS reported by Pitzer and Sterner (1995). The EOS of Pitzer and Sterner (1995) is a good choice because 1) their EOS provides wide valid isochores from 0.1 MPa and −57 °C to 10 GPa and >1700 °C and because 2), with 28 parameters, it is easier to implement in spreadsheets than the sophisticated equation reported by Span and Wagner (1996) (Hansteen and Klugel 2008). The EOS of Pitzer and Sterner (1995) is the following.

$$P_{in} \text{ (GPa)} = RT \left\{ M + c_1 M^2 - M^2 \left[\frac{(c_3 + 2c_4 M + 3c_5 M^2 + 4c_6 M^3)}{(c_2 + c_3 M + c_4 M^2 + c_5 M^3 + c_6 M^4)^2} \right] + c_7 M^2 \exp(-c_8 M) + c_9 M^2 \exp(-c_{10} M) \right\} \quad (2)$$

Therein, R ($= 8.31451 \times 10^{-3}$ GPa cm³ K^{−1} mol^{−1}), T (K) and M (mol/cm³) respectively represent the molar gas constant, temperature, and reciprocal of the molar volume, and the definition of each parameter c_1 through c_{10} , which is a function of temperature as presented by Pitzer and Sterner (1995). However, because P_{in} in the third term in Equation 1 is calculated from the ‘final’ fluid pressure, M in Equation 2 should also be calculated from the ‘final’ reciprocal of molar volume considering the effects of volume change of a fluid inclusion as in the following equation.

$$M = \rho_0 \left(1 - \frac{\Delta V}{V_0} \right) / 44.0095 \quad (3)$$

In this equation, ρ_0 (g/cm³) represents the initial density at T_0 . Actually, M is calculable from Equation 3 and is then inserted into Equation 2 to calculate P_{in} , which is then used in Equation 1. However, because $\Delta V/V_0$ is used in Equations 1 and 3 to calculate the volume change of the fluid inclusions ($\Delta V/V_0$), Equations 1–3 must be iterated until a steady numerical solution is reached. In this calculation, the initial guess of the reciprocal of the molar volume (M) was made using the reciprocal of the molar volume at room temperature. Based on Equations 1–3, we can correct the microthermometric data.

Case 2: Thermoelastic equilibrium of a multicomponent system using Redlich-Kwong EOS

Natural fluid inclusions comprise multicomponent systems. Therefore, we consider application of this method to a more comprehensive EOS. The EOS modified by Redlich and Kwong (1949), abbreviated hereinafter as MRK, became the most popular version of the van der Waals equation. The equation was extended by empirical P -dependent and T -dependent parameters, which markedly improve the ability of the equation to reproduce fluid parameters at higher temperatures and pressures.

$$P_{in} = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}(\bar{V} + b)(T)^{0.5}} \quad (4)$$

In this equation, R ($= 8.31451 \times 10^{-3}$ GPa cm³ K^{−1} mol^{−1}) is the gas constant, T (K) denotes the fluid temperature, $\bar{V}$ (cm³/mol) expresses the molar volume, and a and b are the empirically determined parameters, which generally have temperature, pressure, and composition dependence. Various adjustments of a and b parameters permit MRK to be used universally for pure fluids and their mixtures, as well as for H₂O–CO₂–NaCl fluids (Hurái et al. 2015 and references therein). If the constant mass criterion is satisfied during measurements of homogenization temperature, then the molar volume after deformation can be presented as shown below.

$$\bar{V} = \left(1 + \frac{\Delta V}{V_0} \right) \times \bar{V}_0 \quad (5)$$

In that equation, $\bar{V}_0$ represents the initial molar volume. Actually, $\Delta V/V_0$ is used in Equations 1 and 5 to calculate the fluid inclusion volume change ($\Delta V/V_0$). Equations 1, 4, and 5 must be iterated until a steady numerical solution is reached.

Case 3: extending the system to elastically anisotropic host minerals

For accurate treatment of the elastic effects involving an elastically anisotropic host, Zhang (1998) reported that anisotropy must be incorporated into the following equation.

$$\begin{aligned} \frac{\Delta V}{V_0} \approx & \frac{P_0}{K_h} + \left\{ \exp \left[\int_{T_0}^T \alpha_h(T) dT \right] - 1 \right\} \\ & + \frac{3}{(1-x')y'} \left[\frac{P_{in}x'y' - P_{out}}{(n-0.5)C_{33}+2C_{13}} \right. \\ & \left. + \frac{P_{in}y' - P_{out}}{(n+0.5)C_{33}-2C_{13}} \right] \end{aligned} \quad (6)$$

Therein, C_{ij} represents elastic constants, $n = 0.5[1 + 0.8(C_{11} + C_{12} - C_{13})/C_{33}]^{0.5}$, $x' = (R_i/R_h)^{2n}$, and $y' = (R_i/R_h)^{1.5-n}$, where R_i and R_h respectively denote the inclusion radius and the host mineral radius. Zhang (1998) argued that elastic anisotropy should be examined to reproduce -2.0% volume change of the fluid inclusions observed by HDAC experiments of Schmidt et al. (1998). When the volume change is calculated considering only compressibility and thermal expansion (1st and second terms of Equation 1), the result would be -0.7% which cannot account for the observed decrease in inclusion volume. However, the calculated variations in inclusion volume are -1.2% and -1.8% , respectively, when elastic effects are considered assuming elastic isotropy and anisotropy (Zhang 1998). They concluded that anisotropy must be incorporated for accurate treatment of the elastic effects involving an elastically anisotropic host. Therefore, if Equation 6 is used instead of Equation 1, then thermoelastic deformation can be estimated more accurately even in the case of an inclusion trapped in the elastically anisotropic host mineral.

DISCUSSION AND IMPLICATIONS

Using the equations proposed above, one can estimate the magnitude of volume change and the main factors affecting the volume change of fluid inclusions by thermoelastic equilibrium. As explained in the **INTRODUCTION** section, although Wang et al. (2011) and Kawakami et al. (2003) respectively investigated the temperature dependence of the Fermi splits distance of CO_2 using fluid inclusions in quartz and orthopyroxene, their results were inconsistent. As a reason for the discrepancy, it is conceivable that the fluid inclusion volumes changed elastically during heating. The fluid density changes caused by thermoelastic equilibrium of fluid inclusions in quartz

Figure 1. Change in fluid densities in fluid inclusions caused by the temperature rise of host mineral grains. We assumed host mineral grains as orthopyroxene (solid lines) and quartz (dotted lines). The difference in line color (shading) represents the difference in the initial fluid density. Fluid density changes were calculated using Equations 2, 3, and 6. For comparison, density changes caused solely by thermal expansion are shown as dashed-dotted line (orthopyroxene) and dot-dot-dashed line (quartz). R_i/R_h are assumed as 0.001. Thermal expansion coefficients are inferred from work reported by Afonso et al. (2005) (orthopyroxene) and by Ackermann and Sorrell (1974) (quartz). Elastic constants are inferred from work by Jackson et al. (2007) and Webb and Jackson (1993) (orthopyroxene), and by Wang et al. (2015) and Ohno (1995) (quartz).

and orthopyroxene with various fluid densities at room temperature are expressed as a function of temperature using equations 1, 2, and 6 (Fig. 1). Overall, the tendency of the density changes of the fluid inclusion depends on the thermal expansion coefficient of the host mineral. In the case of a low-density fluid, the influence of the third term is almost negligible, but it is readily apparent that the density change amount is amplified as the initial fluid density becomes higher. Kawakami et al. (2003) and Wang et al. (2011) respectively used fluid inclusions having density of 1.176 g/cm^3 in orthopyroxene and those having a density of 0.7074 and 0.4676 g/cm^3 in quartz. As shown in Figure 1, the change in density of fluid inclusions used by Kawakami et al. (2003) and Wang et al. (2011) is almost identical in their analysis temperature range ($35\text{--}200^\circ\text{C}$). Consequently, the cause of their remarkable difference cannot be explained by a thermoelastic equilibrium. Further research must be conducted of the pressure dependence and composition dependence of the Fermi split distance.

As presented in the description of Case 3, earlier reports have described the importance of considering an anisotropic model based on microthermometric data presented by Schmidt et al. (1998) and equations demonstrated by Zhang (1998). Therefore, for elastically anisotropic host minerals, one must assess the amount of elastic deformation of the fluid inclusion using EOS of the fluids and Equations 5 and 6.

To calculate the volume change of a fluid inclusion from an arbitrary temperature to the homogenization temperature using Equations 1–6, the physical properties of the host mineral and the molar volume of the fluid at an arbitrary temperature must be used. The former can be readily referred from the literature, but the latter presents some difficulty because of elastic deformation. Several Raman-based barometers have been developed in recent years to estimate the molar volume of fluid at room temperature, which are applicable to CO₂ (Yamamoto and Kagi 2006; Hagiwara et al. 2018), CH₄ (Zhang et al. 2016), N₂ (Lamadrid et al. 2018), H₂–CH₄ (Fang et al. 2018), etc. One can calculate the molar volume accurately at the homogenizing temperature using the spectroscopically determined molar volume at room temperature, physical properties of the host mineral, and the EOS of the fluids.

Two or more homogenization temperatures must be measured to elucidate the physicochemical characteristics of a multicomponent fluid system. If those homogenization temperatures are very different, then the possibility exists that the constant volume criterion of Roedder's rules is not satisfied. To evaluate fluid properties accurately from temperatures found from the homogenization experiment, the molar volume at the homogenization temperature must be estimated. Through this study, we demonstrated this method of calculating the thermoelastic equilibrium between a fluid inclusion and a host mineral using EOS of real fluids. More detailed discussion based on fluid inclusions can be achieved using this method.

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