LETTER

Ethane- and hydrogen-bearing carbonic fluid inclusions in a high-grade metamorphic rock

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Ethane- and hydrogen-bearing carbonic fluid inclusions are found within quartz in a leucocratic garnet granulite obtained from the Neoproterozoic Limpopo Belt in South Africa. The trapped fluids are present as secondary inclusions and show melting temperatures in the range of -60.9 to -56.9 °C, suggesting a dominantly CO₂-rich composition. The wide range of estimated CO₂ densities (0.611 – 1.020 g/cm³) indicates entrapment of the fluids at 5 kbar at 700 °C and significant subsequent density decrease due to post-peak decompression. Laser Raman analysis of the inclusions at room temperature confirmed that the trapped fluids are CO₂-rich (>95 mol%) with very minor CH₄ (2.5 – 4.6 mol%), N₂ (0.1 – 0.4 mol%), and C₂H₆ (0.01 – 0.02 mol%) constituents. A thin carbon film precipitated on the cavity wall, not visible optically, was also identified by Raman spectroscopy. We therefore infer the following carbon-forming reaction during decompression and/or cooling below 700 °C and 5 kbar: $\text{CO}_2 + \text{CH}_4 \rightarrow 2\text{C} + 2\text{H}_2\text{O}$. When the inclusions were heated to 150 °C to homogenize all the fluid phases, H₂ (0 – 0.05 mol%) and H₂O (1.7 – 0.3 mol%) were detected instead of C₂H₆. Although the processes of the formation of C₂H₆ and H₂ are not known, the presence of CH₄, C₂H₆ and H₂ in CO₂-dominant fluid is considered as a possible product of a series of reactions in the C–O–H system within the inclusion cavity during decompression/cooling.

Keywords: Carbonic fluid, Ethane, Hydrogen, Raman spectroscopy, Granulite, Limpopo Belt

INTRODUCTION

It is well known that fluids in the lower crust play an important role in the stability and transformation of mineral assemblages during high-grade metamorphism (e.g., Newton et al., 1980). For the characterization of geological fluids, fluid inclusions trapped in various minerals provide the route to obtain direct information on their chemical and physical properties. Laser Raman spectroscopy is a powerful tool for the identification and quantification of fluids trapped in minerals, and the technique has been used in a number of fluid inclusion studies (e.g., Wopenka and Pasteris, 1986; Dubessy et al., 1989). In the present study, we carried out combined microthermometric and laser Raman spectroscopic studies of fluid inclusions in granulite-facies rocks from the Limpopo Belt in South

Africa to characterize fluids related to Neoproterozoic high-grade metamorphism. Although previous fluid inclusion studies on the Limpopo Belt reported the presence of CO₂-rich fluid during high-grade metamorphism (e.g., van Reenen and Hollister, 1988; van den Berg and Huizenga, 2001; Tsunogae and van Reenen, 2007), our additional study on leucocratic gneiss from the belt identified methane, ethane, and hydrogen in the dominantly CO₂-rich fluid, which have so far not been reported for high-grade metamorphic rocks.

A leucocratic garnet gneiss sample (sample IIC1) was collected from Bandelierkop Quarry in the Southern Marginal Zone of the Limpopo Belt. Detailed petrologic and geothermobarometric studies on the locality have been carried out by Stevens and van Reenen (1992). The dominant mineral assemblage of the rock is composed of garnet, plagioclase, K-feldspar, and quartz, suggesting its partial-melting origin from pelitic granulite during prograde metamorphism. Fluid inclusions were studied in

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Figure 1. Photomicrographs and a sketch of the representative fluid inclusions in quartz obtained from the Limpopo Belt in South Africa. (a) A trail of secondary inclusions in quartz discussed in this study. (b) Enlargement of (a). (c) A sketch of secondary fluid inclusions shown in (b). Numbers indicate homogenization temperatures as discussed in the text. Q1 to Q44 are inclusion numbers for laser Raman analysis (see Table 2).

doubly polished thin (150 to 200 μm) wafers. They are present only in large quartz grains (Fig. 1a). The inclusions are ovoidal or irregular in shape, and their size varies from 2 to 20 μm . They are aligned along linear arrays that cut across the host quartz crystal and thus are secondary (Figs. 1a and 1b). No primary fluid inclusion was found.

MICROTHERMOMETRY

Microthermometric measurements were performed using a USGS heating/cooling stage at the University of Tsukuba. The detailed analytical procedure using the instrument has been summarized by Tsunogae et al. (2002). The results of the microthermometric measurements are shown in Figure 2 and are summarized in Table 1, which are available online from <http://www.jstage.jst.go.jp/browse/jmps>. Fluid densities and isochores (lines of constant volume) were calculated using the computer program “FLIN-

Figure 3. P - T trajectory of the Southern Marginal Zone of the Limpopo Belt (modified after Tsunogae et al., 2004) with isochores for carbonic fluid inclusions estimated in this study. The isochore for the highest-density inclusion (HD; Table 1) is plotted separately from the other low-density inclusions (LD).

COR” developed by Brown (1989), based on the equation and thermodynamic data of Brown and Lamb (1989). For the isochore calculations, all the analyzed carbonic fluid inclusions are regarded as pure CO_2 since the trapped fluids contain more than 95 mol% CO_2 , as discussed in the next section.

Fluid inclusions display melting temperatures (CO_2 solid + L + V $\rightarrow$ L + V at T_m) between -60.9 and -56.9 $^{\circ}\text{C}$, with more than 90% of the T_m between -58.3 and -56.9 $^{\circ}\text{C}$, indicating that the dominant fluid trapped in quartz is CO_2 -rich and additional components are present. All the inclusions homogenized into the liquid phase. Most of them show a wide homogenization temperature (T_h) range of -4.1 to $+29.6$ $^{\circ}\text{C}$, which corresponds to CO_2 densities of 0.611 to 0.952 g/cm^3 . In contrast, rare high-density inclusions ($T_h = -10.3$ to -17.4 $^{\circ}\text{C}$, $d = 0.985$ to 1.020 g/cm^3) were also found together with the low-density inclusions (Table 1). Such wide density variation and preservation of the rare high-density inclusions in the same inclusion array (see Fig. 1c) suggest that even though all the fluid inclusions were probably trapped together, some inclusions underwent significant density decreases during decompression from a high-pressure stage (e.g., Ohyama et al., 2008; Tsunogae et al., 2008; Nishimiya et al., 2008). The highest-density inclusions were used for calculation of a specific isochore in the P - T space (Fig. 3). The estimated CO_2 isochores for the high-density inclusions intersect the clockwise P - T trajectory of the study area at around 5 kbar at 700 $^{\circ}\text{C}$ (Fig. 3), which corresponds to a retrograde decompression stage. The carbonic fluids were probably trapped along the cracks in quartz formed by post-peak rapid pressure decrease.

Figure 4. Raman spectra of representative fluid and solid inclusions discussed in this study. (a) CO₂ in inclusion Q1. (b) N₂ in inclusion Q1. (c) CH₄ and C₂H₆ in inclusion Q1. (d) Signal of C-C vibration of C₂H₆ in inclusion Q1. (e) H₂O in inclusion Q44. (f) H₂ in inclusion Q44. (g) and (h) Carbon in inclusion Q1.

LASER RAMAN ANALYSIS

The molar ratios of gas phases in individual fluid inclusions were analyzed by laser Raman spectroscopy using a @Dilor Labram type Raman spectrometer at G²R, Nancy, with an @Edge filter and a CCD detector cooled at -140 °C. The excitation radiation at 514.532 nm was provided by an Ar⁺ laser (type 2020, @Spectraphysics). The laser is focused onto the sample with a ×80 objective (∞; n.a. = 0.75; @Olympus). The minimal spatial resolution is around 1 μm on surface sample but deteriorates slightly inside the sample due to refraction. The laser power at the sample is around 60 mW. Raman data were obtained at room temperature (25 °C) and also at 150 °C after homogenizing all the fluid phases within the inclusion cavities using a Linkam heating/cooling stage for comparison. Raman spectra of CO₂, CH₄, N₂, H₂O, C₂H₆, and H₂ for representative fluid inclusions are shown in Figures 4a to 4f. C₂H₆ was identified by three Raman active vibrational Raman modes, 2955 cm⁻¹ (antisymmetric stretching), 2899 cm⁻¹ (symmetric stretching), and at 992 cm⁻¹ (C-C stretching mode), (Herzberg, 1945) (Figs. 4c and 4d). No peaks of CO, H₂S, and SO₂ were detected. Estimates of relative molar ratios of fluid species in the inclusions were determined based on peak ratios (Dubessy et al., 1989).

Temperature should a priori affect the quantification procedure since the differential scattering Raman cross-section is inversely proportional to $1 - \exp(-hc\nu_j/kT)$ (Eckhardt and Wagner, 1966; Schrötter and Klöckner, 1979) where ν_j is the wavenumber of the considered vibrational mode and h , c , k and T are the Planck constant (h), the speed of light (c), the Boltzmann constant (k) and the absolute temperature (T). Therefore, the differential Raman scattering cross-sections at temperature T is such as:

$$\frac{d\sigma_j}{d\Omega}(\nu_0, T) \propto (1 - \exp(-hc\nu_j/kT))^{-1} \quad (1),$$

where ν_0 is the wavenumber of the laser excitation. Thus, the ratio between the differential Raman scattering cross-section at temperature T and T_0 is:

$$\left[\frac{d\sigma_j}{d\Omega}(\nu_0, T) \right] / \left[\frac{d\sigma_j}{d\Omega}(\nu_0, T_0) \right] = [1 - \exp(-hc\nu_j/kT_0)] / [1 - \exp(-hc\nu_j/kT)] \quad (2).$$

For the band of CO₂ at 1388 cm⁻¹, and for $T_0 = 293$ K, and $T = 423$ K, the value of this ratio is 1.0083. Same approach can be done for the Raman scattering cross-section of the symmetric stretching band of water vapour at 3657 cm⁻¹. At 423 K, the ratio is even smaller: 1.000003975. The effect of temperature is therefore negligible for this temperature interval range. The calibration of the analysis of CO₂/H₂O ratio in CO₂-rich fluid is in progress, but we did not take into account the effect of temperature as the aim of this paper is to get an estimation of the water content. The Raman scattering cross-section of ethane was taken from data of Lapp and Penney (1977) and that of vapour water from Schrötter and Klöckner (1979).

Raman analyses of the inclusions (Tables 2, and 3; Table 3 is available online from <http://www.jstage.jst.go.jp/browse/jmps>) indicate that the fluids are composed dominantly of CO₂ (95–97 mol%; Fig. 4a) with minor amounts of N₂ (0.1–0.4 mol%; Fig. 4b), CH₄ (2.5–4.6 mol%; Fig. 4c), and C₂H₆ (0.01–0.02 mol%; Figs. 4c and 4d) at 25 °C. If the inclusions were heated at 150 °C, H₂O (1.7–0.3 mol%; Fig. 4e) and H₂ (0–0.05 mol%; Fig. 4f) were also detected as minor components, but the Raman peak of C₂H₆ disappeared at this temperature. Identification of H₂O at 150 °C results from bulk homogenization of the inclusion which contained an invisible film of water wetting the inclusion wall. Thin films of carbon between the trapped fluid and the inclusion wall from three inclu-

Table 2. Molar abundance of fluids trapped in individual fluid inclusions in sample IIC1

No.	T (°C)*	CO ₂ (mol%)	CH ₄ (mol%)	N ₂ (mol%)	C ₂ H ₆ (mol%)	H ₂ (mol%)	H ₂ O (mol%)	Carbon
Q1	25	97	2.5	0.1	0.02	n.d.	n.d.	yes
Q37	25	95	4.6	0.4	0.01	n.d.	n.d.	yes
Q39	150	99	1.1	n.d.	n.d.	n.d.	0.3	no
Q44	150	96	1.9	n.d.	n.d.	0.05	1.7	yes

Occurrences of carbon in the inclusions are also described in the Table.

* Temperature at the Raman analysis.

n.d., not detected.

sions (Figs. 4g, 4h, and Table 2) were only identified by Raman spectroscopy but were not visible under optical microscope, indicating probably less than 30 graphene layers are present. This suggests that carbon probably precipitated from the CO₂-rich fluid after entrapment.

DISCUSSION

Secondary CO₂-rich fluids trapped in quartz grains were identified in leucocratic garnet gneiss from the Limpopo Belt in South Africa. Microthermometric measurements and the secondary nature of the fluid inclusions indicate these CO₂-rich fluids were trapped during the post-peak decompression stage, approximately 700 °C at 5 kbar. Although such CO₂-rich fluids have been regarded as a peak metamorphic fluid in granulite-facies rocks worldwide (e.g., Touret, 1971), we could not find any peak metamorphic fluids in the examined sample, possibly because the peak metamorphism was fluid-absent or the trapped fluids are no more in the inclusion cavity. The CO₂-rich secondary fluids contain minor fluid components: CH₄ (2.5–4.6

mol%), C₂H₆ (0.01–0.02 mol%), and H₂ (0–0.05 mol%). The occurrence of such ethane-bearing carbonic fluids is extremely rare in middle to lower crustal rocks, and has been reported only from a few localities, such as alkaline granites and associated hydrothermal veins in Greenland (Konnerup-Madsen et al., 1985). They reported CO₂–CH₄ gaseous inclusions with 0.6–0.1 mol% C₂H₆ within quartz in alkali granite and granite veins. Both C₂H₆ (2.1 mol%) and H₂ (3.2 mol%) were detected only in CH₄-rich inclusions within chkalovite in a hydrothermal vein. Our study therefore represents the first report of C₂H₆- and H₂-bearing reduced fluid inclusions trapped in high-grade metamorphic rocks, as well as the first trace of C₂H₆ and H₂ in CO₂-rich fluid inclusions.

Our laser Raman analysis also identified a thin film of carbon (or nano-carbon) precipitated on the walls of the inclusion cavities as inferred from the Raman spectra shown in Figures 4g and 4h. Such occurrence of carbon film have been found sometimes in methane-rich diagenetic fluid inclusions and more scarcely in H₂O–CH₄–CO₂ fluid inclusions associated with graphitic-bearing rocks but never in CO₂-rich fluid inclusions. Experimentally, nanocarbon are produced by thermal decomposition of CH₄ into H₂ in presence of catalysts (see Shah et al., 2001; Homayonifar et al., 2008, and references therein), but this explanation is not relevant to this case study. The small amount of carbon precipitated along the inclusion wall suggests that the fluid oversaturation with respect to “graphite” was small during its precipitation, contrary to the re-equilibration experiments carried out by Pasteris and Chou (1998). The low ordering of carbon suggests that precipitation occurred at rather “low temperature” since both nucleation and growth of graphite require high activation energy (Ziegenbein and Johannes, 1980).

The carbon precipitation can be explained by the C–O–H phase relation calculated at *P–T* conditions of the Limpopo rock during isochoric cooling of the inclusion as shown in Figure 5. The initial fluid is assumed to be at equilibrium with graphite and CO₂-rich with minor CH₄ as suggested from its present-day composition. Therefore, its approximate composition is plotted as spot “A” on the CO₂–CH₄ tie-line at 700 °C and 5 kbar in the diagram.

Figure 5. C–O–H diagram showing CO₂–CH₄ tie lines calculated at 700 °C, 5 kbar and 400 °C, 2.5 kbar. See text for further discussion.

During isochoric cooling down to 400 °C and 2.5 kbar, the fluid-graphite equilibrium line moves slightly away from the carbon apex of the triangle towards the O-H side. Spot "A" is then located inside the divariant field of $\text{CO}_2 + \text{CH}_4 + \text{C}$. Thus, the fluid in the inclusion is slightly oversaturated with respect to graphite making possible the precipitation of carbon via the bulk reaction:

during retrograde metamorphism. The absence of graphite in the host rock suggests that the initial fluid at its P - T conditions of trapping was not at saturation with this phase, which implies that the degree of oversaturation during cooling was even smaller, which is in favour of the low amount and low ordering state of precipitated carbon. The amount of water in the inclusion is thus partially overestimated due to carbon precipitation. However, as the amount of precipitated carbon is unknown, this overestimation remains unknown. Complete thermodynamic calculations to model fluid chemistry evolution during cooling should be done, including diffusion of H_2 inside inclusion during retrograde metamorphism (Hall and Bodnar, 1990), to know what was the main process for graphite precipitation, the extent of increase in water concentration during cooling and thus to estimate whether low temperature analysis of inclusions are representative of trapped fluids.

Another interesting feature of laser Raman analysis is the presence of ethane and hydrogen in the fluid. However, they were not identified at the same temperature condition. At room temperature, C_2H_6 was detected, but at 150 °C, we could detect H_2 and H_2O , but not C_2H_6 (Fig. 4f). H_2 is seldom identified in fluid inclusions from the C-O-H system because, during cooling, inside an inclusion considered as an isochoric and closed system, the concentration of minor species such as CO and H_2 decreases at a level usually below the detection limit of micro-Raman spectroscopy (Dubessy et al., 1989). Ethane has been included in the calculation of graphite-fluid equilibrium (Zhang and Duan, 2009). Although these calculations were carried out at higher P - T conditions, they demonstrate, as expected, that ethane concentration is significant only for CH_4 -rich fluids and reduced fluids in the redox range defined by the iron-wüstite and wüstite-magnetite buffers. Same remarks apply to the presence of molecular hydrogen. The presence of both C_2H_6 and H_2 contradicts the fact that the fluid was CO_2 -rich at a redox state nearly the upper f_{O_2} limit of graphite stability. This suggests that the fluid composition analyzed presently does not represent an equilibrium composition, even frozen at higher temperature (>400 °C). The processes of the

formation of C_2H_6 and H_2 are thus not known. The disappearance of C_2H_6 during heating at 150 °C could be tentatively interpreted as a result of cracking of ethane into methane. However, this reaction proceeds within tenths of minutes, which seems to be very fast.

To conclude, the results of this study suggest that the C_2H_6 - H_2 - H_2O -bearing carbonic fluid inclusions are a possible product of a series of reactions during post-peak decompression/cooling to room temperature. The formation of such fluids is mostly controlled by the precipitation of carbon on the inclusion wall due to overstepping of the CO_2 - CH_4 binary fluid into the stability of $\text{CO}_2 + \text{CH}_4 + \text{C}$ by rapid decompression/cooling (reaction (1)), and subsequent C-O-H reactions within the inclusion cavity during further decompression/cooling. Possible diffusion of H_2 inside inclusion is not excluded.

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DEPOSITORY MATERIALS

Tables 1, 3, and Figure 2 are available online from <http://www.jstage.jst.go.jp/browse/jmps>.

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