

Hydrogen in silicate melt inclusions in quartz from granite detected with Raman spectroscopy

Jiankang Li^{a*} and I-Ming Chou^b

By using Raman spectroscopy, hydrogen was detected, together with CH₄, N₂, H₂O, disordered graphite, and possibly a (CH₄)_n (H₂)_m compound, in silicate melt inclusions (SMIs) in quartz from Jiajika granite in China. The occurrences of H₂ in fluid or melt inclusions are rarely reported because they are not commonly expected, and also the spectral window above 4000 cm⁻¹ wavenumbers, where the dominant signals of H₂ located, is rarely covered in routine Raman analyses due to limited information of geological interest available in that spectral range. The mechanisms for the occurrence of H₂ in these SMIs are unknown. However, the retention of H₂ in these SMIs was most likely resulted from the low diffusion rate of H₂ in quartz at low temperatures and also the low H₂ gradient between SMIs and their environments surrounding the host minerals. More studies are needed to determine whether the occurrences of H₂ in inclusions in minerals are common in similar or other rock types, to formulate the mechanisms for its entrapment, and to investigate the associated geological processes. Copyright © 2015 John Wiley & Sons, Ltd.

Keywords: hydrogen; Raman spectroscopy; granite; quartz; silicate melt inclusion

Introduction

Many geological processes are affected by the redox state of the system, such as the stability of minerals, the solubility of minerals in hydrothermal fluids, the speciation of metal complexes in hydrothermal fluids, and the transportation and precipitation of metals for the formation of ores. The redox state of the system can be inferred by the presence of certain redox-related minerals or elements (e.g. hematite, magnetite, wüstite, iron, etc.) or gases (e.g. CH₄, CO, CO₂, H₂, etc.). Although the rare occurrences of H₂ in melt or fluid inclusions have been reported previously,^[1–4] some remain controversial.^[5] This is mainly because some of the measured H₂ could come from contamination or mineral reactions with water during sample treatment and/or mass spectrometric analysis of the inclusions.^[5] On the other hand, the main reasons for the rare reports on the occurrence of H₂ in melt or fluid inclusions are that H₂ was not expected because: (1) it was commonly believed that H₂ could easily diffuse out of the inclusions, and (2) the laser Raman microspectrometry (LRMS) is currently the only reliable tool for identifying H₂ in fluid inclusions,^[1,5] but the major and easily identified Raman signals for H₂ are in the spectral range beyond 4000 cm⁻¹, where geologically important information was not expected to be revealed, and therefore not commonly explored in routine analyses. In this study, H₂ was positively identified with LRMS in silicate melt inclusions (SMIs) in quartz from granite of Jiajika granitic pegmatite deposit in China. This finding reveals the needs of our future research on formulating possible mechanisms for the entrapment and retention of H₂ in these inclusions and also understanding the related geological processes.

Geological features of Jiajika granitic pegmatite deposit, China

The Jiajika granitic pegmatite rare-metal deposit in western Sichuan, China is the largest lithium deposit in Asia, where pegmatite dikes surround the granite body in both horizontal and vertical

directions.^[6] The granite is fine-grained and contains muscovite, biotite, quartz, feldspar, and tourmaline without showing obvious alteration or metasomatic effects.^[7] The studied SMIs are hosted in quartz in negative-crystal shape or irregular shape with convex and concave sides; they are mainly composed of daughter minerals, aqueous, and vapor phases (Fig. 1). The proportions between solid and fluid phases are similar in the SMIs formed in the same geological event, indicating that these SMIs were entrapped in a homogeneous fluid state.

Methods

The different phases within unopened SMIs in quartz were identified by using a JY Horiba LabRam HR800 confocal-Raman system in Horiba (China) Trading Co., Ltd. Beijing Branch. The excitation beam of 514 nm wavelength was used, and the laser was focused on the sample surface through a 100× Olympus objective lens (N.A. = 0.905). The power of laser on the sample was about 5.5 mW, and the spectral accuracy was ±0.2 cm⁻¹.

Results

Raman spectroscopic analyses of the solid phases in SMIs showed that muscovite was the most common daughter mineral, and only

* Correspondence to: Jiankang Li, MLR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing 100037, China.
E-mail: Li9968@126.com

a MLR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing 100037, China

b Sanya Institute of Deep-sea Science and Engineering, Chinese Academy of Sciences, Sanya, Hainan, 572000, China



Figure 1. Photos of H_2 -bearing silicate melt inclusions in quartz in granite from Jiajika pegmatite deposit, China. V—vapor phase, Mus—muscovite, and Gls—silicate glass. The length of the scale bar is 10 μm .

a few SMLs contained quartz or silicate glass. The vapor phase commonly contained H_2O , N_2 , and CH_4 with the major CH_4 ν_1 peak between 2916.1 and 2918.0 cm^{-1} (Fig. 2). As shown in spectra d and h in Fig. 2, the vapor phase within some of the SMLs also contained H_2 showing the characteristic Raman peaks at 356, 588, 816, 1037, 4126, 4144, 4156, and 4161 cm^{-1} , and these Raman signals for H_2 matched very well with those in the reference spectra (spectra a and c in Fig. 2). In several SMLs, graphite was identified coexisting with CH_4 , H_2 , and an unknown solid species, which is possibly a $(\text{CH}_4)_n(\text{H}_2)_m$ compound with a Raman peak near 4292 cm^{-1} (spectrum e in Fig. 2).^[8] The collected Raman spectra of graphite showed that the peak intensity ratio for 1355 cm^{-1} /1585 cm^{-1} was about

0.67, corresponding to the disordered graphite with crystallite size of about 30 nm.^[9] At room temperature, the differences between the Raman shifts of pure CH_4 with pressure near 0.1 MPa and that of CH_4 in SMLs were between 0.2 and 2.2 cm^{-1} , indicating that the partial pressures of CH_4 within SMLs were less than 10 MPa, based on the calibrated equation of ref. 10.

In order to monitor the possible diffusion of H_2 out of SMLs sample wafers, several hydrogen-bearing SMLs were analyzed several times in the time interval of 166 days by using LRMS. No obvious changes were observed for the intensity ratios among N_2 , CH_4 , and H_2 (Fig. 3), indicating no detectable H_2 leak from the SMLs.

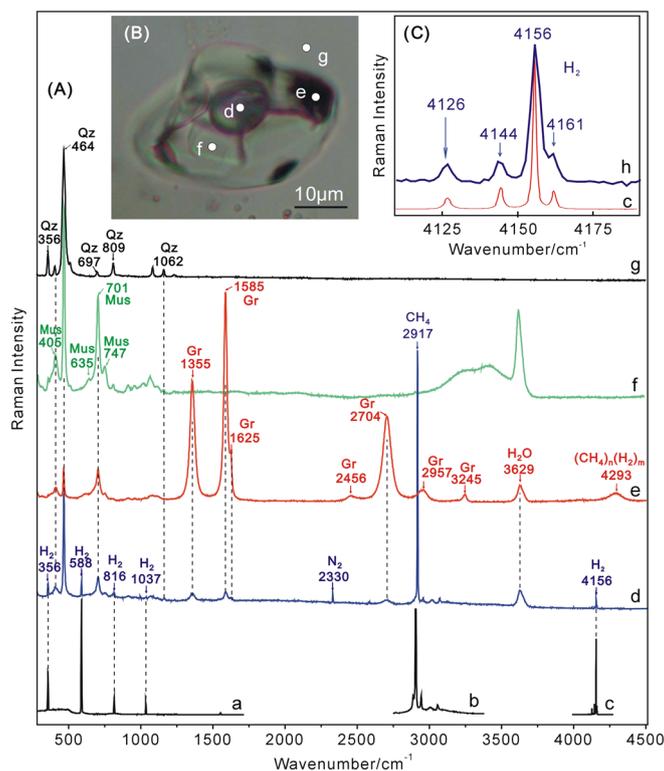


Figure 2. (A) The laser Raman spectra of solid and fluid phases in SMLs in quartz (Qz) in granite from Jiajika pegmatite deposit in China, which were collected in 120 s with two accumulations. Spectra a and c are the reference spectra of H_2 at the low and high wavenumber regions, respectively. Spectrum b is the reference spectrum of CH_4 at pressure of about 40 MPa at room temperature. Spectra d, e, f, and g were collected from the spots d, e, f, and g, respectively, in a single SML shown in (B). Spectrum e shows the presence of disordered graphite (Gr), H_2O , and possibly a $(\text{CH}_4)_n(\text{H}_2)_m$ compound. (B) Photo of a SML in quartz, showing the spots where Raman spectra were collected. Spots d, e, and f are vapor, disordered graphite, and muscovite (Mus) phases, respectively, and spot g is the host quartz. (C) Spectra h and c are, respectively, the enlarged spectra d and c in (A), showing the major Raman signals of H_2 .

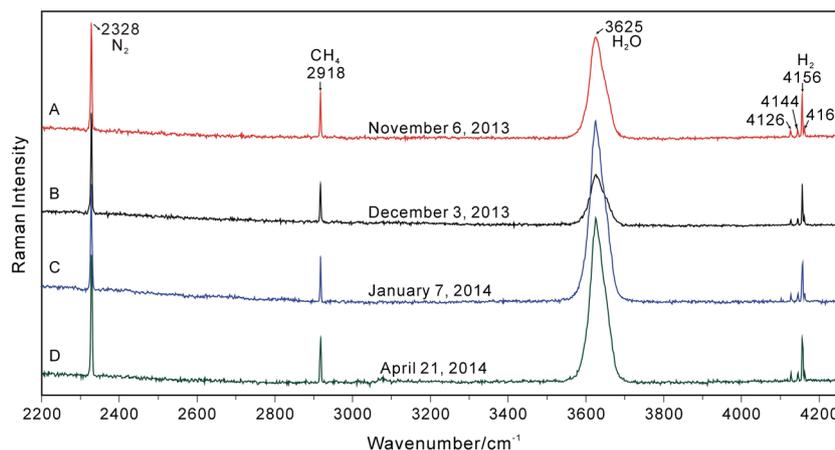


Figure 3. The laser Raman spectra of the vapor phase in a SMI in quartz in granite from the Jiajika pegmatite deposit collected in the time interval of 166 days. These spectra were collected under similar conditions (120 s with two accumulations) and normalized with the same intensity of CH₄. No obvious changes were observed for the intensity ratios among N₂, CH₄, and H₂, indicating no detectable H₂ leak from the SMIs.

Discussion

In this study, the occurrence of H₂ was positively identified with LRMS in SMIs in quartz from granite. There are several possible mechanisms for the presence of this identified H₂ in SMIs in quartz, including water radiolysis,^[3,11] H₂ diffusion from wall rocks,^[1] mineral–water reactions,^[4] and the degassing of reduced mantle, where H₂ and hydrocarbons were expected to be stable.^[12–15] Normally, pegmatitic rare-metal deposits, such as Jiajika deposit, formed at the depths of up to 15 km with a relatively sealed environment,^[16] which enhanced the entrapment and retention of H₂ in SMIs. However, the mechanisms for the origin of the detected hydrogen in these SMIs remain unknown.

Another issue needs to be discussed is the retention of H₂ in SMIs. The measurements of diffusion coefficients of H₂ in fused silica have been extended to 23 °C,^[17] but those in quartz have not been performed below 400 °C (Fig. 4, and also Fig. 6 of ref. 20 and Fig. 17 of ref. 21). All of the available data show that the diffusion

rates of H₂ in either fused silica or quartz decrease with the decrease of temperature (Fig. 4). This trend may also apply to the diffusion rates of H₂ in quartz below 400 °C. Even though measurable loss of H₂ in a fused silica capsule was reported at room temperature within 53 days,^[17] the fact that hydrogen was retained in the SMIs in quartz after the formation of granite of Jiajika pegmatite deposit about 208 Ma ago^[7] and also after the samples were cut into wafers about six years ago, indicates that the diffusion rates of H₂ in quartz were low enough at low temperatures to retain H₂ in the SMIs for a long period of time. These observations support previous predictions that H₂ mobility in quartz does not appear to be significant below 200 °C,^[22,23] and that the blocking temperature for hydrogen diffusion in quartz is apparently above 300 °C.^[24] They are also consistent with our observations of no obvious H₂ leak from a SMI within a period of 166 days at room temperature (Fig. 3). Furthermore, when compared with the experiments^[20,23] on hydrogen movement into and out of fluid inclusions in quartz, the H₂ gradient between SMIs and external environments for Jiajika pegmatite

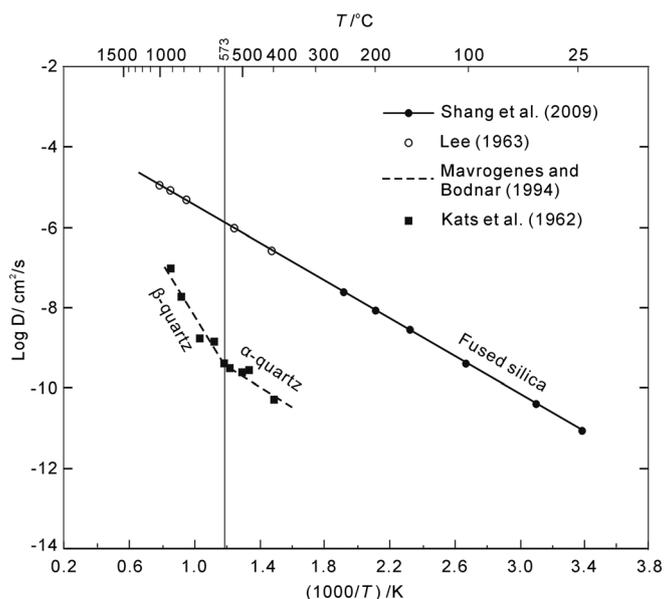


Figure 4. Comparison of the diffusion coefficients of hydrogen in fused silica (open circles from ref. 18; dots and solid line from ref. 17) with those in quartz (filled squares from ref. 19; dashed line from ref. 20).

deposit is relatively low, as indicated by the relatively weak intensities of H₂ Raman peaks, in favor of H₂ retention in SMLs in quartz. However, when our SMI samples were heated at 750 °C under 100 MPa Ar external pressure for 24 h in a cold-seal pressure vessel, the CH₄ in the inclusions was replaced by CO₂ with the disappearance of H₂, indicating significant loss of H₂ from SMLs through diffusion in quartz at high temperature. Note that the trapping temperatures of SMLs, as indicated by their total homogenization temperatures measured under external H₂O pressures in a hydrothermal diamond-anvil cell,^[25] were between 700 and 800 °C. Therefore, when the possible loss of H₂ after entrapment during cooling was considered, the amount of H₂ originally contained in this granitic magma should be higher than those currently detected in these SMLs in Jiajika pegmatite deposit. Furthermore, the reported occurrences of H₂ in natural melt or fluid inclusions should be more common if we expect and search for it.

The detection limit of H₂ in LRMS is about 1.6 atm. pressure,^[26] and the H₂ Raman signals shown in Figs 2 and 3 indicate that the H₂ pressure in the SMI is much higher than 1.6 atm. at room temperature. Therefore, the redox state in the SMLs is more reducing than the fayalite-magnetite-quartz (FMQ) buffer. However, the estimated redox states of 12 Proterozoic granite batholiths of S.W. USA, based on the annite-sanidine-magnetite oxybarometer and assuming total pressure equals water pressure, are mostly more oxidizing than the FMQ buffer between 650 and 800 °C (ref. 27; his Fig. 9). Also, the redox states of Oak Creeks batholith are more oxidizing than FMQ buffer (ref. 27 and references therein; his Fig. 10). More detailed experiments and petrographic studies are needed to determine the redox states of Jiajika granite and the related geological processes.

Conclusions

Hydrogen, coexisting with CH₄, graphite, H₂O, and a possible (CH₄)_n (H₂)_m solid compound, was identified in the SMLs in quartz from granite of Jiajika pegmatite rare-metal deposit by using Laser Raman microspectroscopy. The mechanisms for the origin of this entrapped H₂ are not known. Both the low diffusion rate of H₂ in quartz at low temperatures and the low H₂ gradient between SMLs and their environments surrounding the host mineral in granite of Jiajika pegmatite deposit favor the retention of H₂ in these SMLs. We should consider extending the Raman spectral window beyond 4000 cm⁻¹ wavenumbers in our future routine analyses of melt and/or fluid inclusions, such that we will be able to detect the presence of H₂ in these inclusions and then better understand the associated geological processes.

Acknowledgments

We thank Horiba (China) Trading Co., Ltd. Beijing Branch for providing JY Horiba LabRam HR800 Raman system, and assisting with the laser Raman spectroscopic analyses. This study was supported by the Chinese National Non-profit Institute Research Grant of CAGS-IMR (K1409), the National Natural Science Foundation of China (41372088), the China Geological Survey Program (1212011220805), the Knowledge Innovation Program (SIDSSE-201302), and the Hadal-trench Research Program (XDB06060100) of the Chinese Academy of Sciences.

References

- [1] T. Hrstka, J. Dubessy, J. Zachariáš, *Chem. Geol.* **2011**, *281*, 317.
- [2] G. P. Landis, A. H. Hofstra, *Econ. Geol.* **2012**, *7*, 1189.
- [3] R. J. Bakker, M. A. Elburg, *Contrib. Mineral. Petrol.* **2006**, *152*, 541.
- [4] L. E. Mayhew, E. T. Ellison, T. M. McCollom, T. P. Trainor, A. S. Templeton, *Nat. Geosci.* **2013**, *6*, 478.
- [5] K. Burlinson, *Econ. Geol.* **2013**, *108*, 1211.
- [6] J. Li, D. Wang, D. Zhang, X. Fu, *Mineralizing mechanism and continental geodynamics of typical pegmatite deposits in western Sichuan, China*, Atomic Energy Press, Beijing, **2007**.
- [7] J. Li, D. Wang, Y. Chen, *Acta Geol. Sinica* **2013**, *87*, 91.
- [8] A. Kolesnikov, V. G. Kutcherov, A. F. Goncharov, *Nat. Geosci.* **2009**, *2*, 566.
- [9] M. A. Pimenta, G. Dresselhaus, M. S. Dresselhaus, L. G. Cançado, A. Jorio, F. Saito, *Phys. Chem. Chem. Phys.* **2007**, *9*, 1276.
- [10] W. Lu, I-M. Chou, R. C. Burruss, Y. Song, *Geochim. Cosmochim. Acta* **2007**, *71*, 3969.
- [11] J. Dubessy, M. Pagel, J.-M. Beny, H. Christensen, B. Hicckel, C. Kosztolanyi, B. Poty, *Geochim. Cosmochim. Acta* **1988**, *52*, 1155.
- [12] J. R. Holloway, S. Jakobsson, *J. Geophys. Res.* **1986**, *91*, D505.
- [13] M. S. Somayazulu, L. W. Finger, R. J. Hemley, H. K. Mao, *Science*, **1996**, *271*, 1400.
- [14] H. P. Scott, R. J. Hemley, H. K. Mao, D. R. Herschbach, L. E. Fried, W. M. Howard, S. Bastea, *Proc. Natl. Acad. Sci. U. S. A.* **2004**, *101*, 14023.
- [15] E. Bali, A. Audétat, H. Keppler, *Nature* **2013**, *495*, 220.
- [16] D. London, Pegmatite, *Can. Mineral. Spec. Pub.* **10** **2008**.
- [17] L. Shang, I-M. Chou, W. Lu, R. C. Burruss, Y. Zhang, *Geochim. Cosmochim. Acta* **2009**, *73*, 5435.
- [18] R. W. Lee, *J. Chem. Phys.* **1963**, *38*, 448.
- [19] A. Kats, Y. Haven, J. M. Stevels, *Phys. Chem. Glasses* **1962**, *3*, 69.
- [20] J. A. Mavrogenes, R. J. Bodnar, *Geochim. Cosmochim. Acta* **1994**, *58*, 141.
- [21] J. Ingrin, M. Blanchard, *Rev. Mineral. Geochem.* **2006**, *62*, 291.
- [22] G. B. V. I. Morgan, I-M. Chou, J. D. Pasteris, *Geochim. Cosmochim. Acta* **1992**, *56*, 281.
- [23] G. B. V. I. Morgan, I-M. Chou, J. D. Pasteris, S. N. Olsen, *J. Metamorphic Geol.* **1993**, *57*, 155.
- [24] D. L. Hall, S. M. Sterner, *J. Metamorphic Geol.* **1995**, *13*, 345.
- [25] J. Li, S. Li, *Acta Geol. Sinica* **2014**, *88*, 854.
- [26] B. Wopenka, J. D. Pasteris, *Anal. Chem.* **1987**, *59*, 2165.
- [27] J. L. Anderson, *T. Roy. Soc. Edin-Earth* **1996**, *87*, 125.